

Chapter 11. Seawater and CO₂ equilibria

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11.1 Introduction

Seawater isn't simply a reservoir of different dissolved salts, like sodium chloride, magnesium sulphate and so on; it has the capability to react in different ways, one being with carbon dioxide in the atmosphere, modifying its concentration and buffering its anthropogenic increase.

Oceans cover about 71% of the earth's surface, so even slight variations of critical parameters, like pH, salinity and so on have a huge effect on global climate, and therefore on our way of life.

The reactions involved, however, cannot be mathematically treated with the usual chemistry textbook solutions. Seawater has a high salt content (or ionic strength), and the potency of its ionic charge density totally alters the equilibrium constants, rendering such solutions (which are based on pure water) of little use. The calculation parameters are further affected by high pressures to be found in the dark abysses.

By employing Octave programming language (very similar to Matlab), the appropriate algorithms for chemical equilibria in seawater are proposed in a plain and simple scripts, ready for use, or even modification, by the reader. There is no need for advanced math or programming expertise. An introduction to basic chemistry calculations in solutions can be found elsewhere in this web-site, user friendly for experts and amateur enthusiasts alike.

Breathe in, breathe out. Let us deal now with the main gas exchange in earth oceans; like a giant lung, oceans absorb vast amounts of carbon dioxide (CO₂) from the atmosphere, and release it once again as cold water currents reach warmer areas of the globe. Indeed, CO₂ solubility varies with temperature, together with other factors such as salinity and pressure. Chemically speaking, why does seawater so readily absorb carbon dioxide, thereby buffering the anthropogenic emission of this gas?

The oceans cover about 71% of the earth's surface and gaseous exchange occurs through the ocean's surface. But the answer to this question lies deeper, in what is a widely underestimated fact: the pH (acidity level) of seawater is substantially alkaline, ranging from 8.0 to 8.7. This means that the balance of positive and negative ions is reached through a higher concentration of hydroxide ions (OH⁻) compared to hydrogen ions (H⁺).

Having a pH value greater than 7 enables seawater to react with and dissolve huge amounts of CO₂, absorbing atmospheric excess and thus affecting its concentration. However, there is a reason behind the alkalinity of seawater, its current chemical composition. While different salts are present in seawater, the primary one is sodium chloride. As with any salt, when it dissolves in water, positive charges (cations) and negative charges (anions) are generated.

11.2 Chemical Composition and Imbalance

Let's explore the mean composition of seawater in greater detail: summing up all the positive charges (Na⁺, K⁺, Mg²⁺, Ca²⁺, Sr²⁺) one obtains 605.85 mmol/Kg of solution. Carrying out the same operation for negative charges (Cl⁻, Br⁻, F⁻, SO₄²⁻) the result is slightly less: 603.25; 2.50 millimoles are clearly missing! As with all ionic solutions, seawater must obey the law of electro neutrality, so evidently some negative charges (anions) have been ruled out: they are indeed HCO₃⁻, to a minor extent OH⁻ and finally, to a far lesser extent, CO₃²⁻. The last three ions all react with atmospheric CO₂, and are therefore designated as reactive. On the contrary, the former cations and anions are classified as spectator ions (see table 1). Reactive ions have an active role in chemical equilibria, as shown in the same table.

The presence of OH⁻ (hydroxide ions) is the reason for a pH>7. Their concentration (due to the logarithmic nature of pH scale) is at pH = 8.0 equal to 0.001 mmol/L (in pure water). Under the same conditions, the H⁺ ion concentration is 100 times less. OH⁻ ions alone are insufficient to fill the gap: other negative ions are required; these are mainly HCO₃⁻ ions and also some CO₃²⁻.

This has enormous repercussions on the equilibrium of CO₂ between the atmosphere and oceans. Compared to the atmosphere, which contains around 850 Gt (gigatons) of carbon (in the form of CO₂), the oceans hold 38,000 Gt of carbon. That's nearly 45 times more.

So when we talk about CO₂ ppm in the atmosphere that is only the "top of the iceberg"! CO₂ dissolves in seawater like O₂ and N₂. However, being a reactive gas, there is an almost immediate reaction with the water itself (N₂ and O₂ do not) yielding HCO₃⁻ and CO₃²⁻. After completion of these reactions, yet a third slowly takes place (one which is nearly always disregarded): the formation of solid calcium carbonate, CaCO₃.

Spectator Ions					
Cation	mol·kg ⁻¹	g·kg ⁻¹	Anion	mol·kg ⁻¹	g·kg ⁻¹
Na ⁺	0.46906	10.7836	Cl ⁻	0.54586	19.3524
Mg ²⁺	0.05282	1.2837	SO ₄ ²⁻	0.02824	2.7123
Ca ²⁺	0.01028	0.4121	Br ⁻	0.00084	0.0673
K ⁺	0.01021	0.3991	F ⁻	0.00007	0.0013
Sr ²⁺	0.00009	0.0079			
Σ+	0.60565	12.8864	Σ-	0.60325	22.1333
			Δcharge = 0.00240+		
			Σ g·kg ⁻¹ = 35.0197		
Reactive Ions and Molecules					
H ₂ CO ₃	↔	HCO ₃ ⁻	↔	CO ₃ ²⁻	
B(OH) ₃	↔	B(OH) ₄ ⁻			
2·H ₂ O	↔	H ₃ O ⁺	↔	OH ⁻	

Table 11.1 Seawater composition: spectator ions and reactive species

In chemistry, this is known as precipitation. CaCO₃ usually has a calcite structure; aragonite, the other polymorphic structure, is slightly more soluble. Seawater is oversaturated, both in terms of calcite and aragonite, due to its relatively high Ca⁺⁺ ion concentration (10.28 mmol/Kg-solution). However, this reaction requires nucleation and the growth of crystal nuclei, and is usually sluggish (it may speed up in the cells of calcifying organisms like invertebrates). In other words, it is a heterogeneous reaction between a liquid phase and a solid one.

The destiny of this salt is to eventually sedimentate on the ocean floor (if very deep, it may fail to reach the bottom, dissociating again into ions due to the extremely high pressure, and recycle). In any case, CO₂ removed from the atmosphere will eventually form limestone.

11.3 Methods and Techniques for Dealing with the Chemistry of Seawater

Every year there are hundreds of publications and articles on this topic: some fearing ocean 'acidification' (a lowering of pH values, remaining in the alkaline range) and the consequence on calcifying organisms, and some stressing a possible increase in the ocean's ability to uptake anthropogenic CO₂. Indeed, several groups of scientists have employed computer-

aided modelling and complex models to simulate the chemical/physical behaviour of ocean water and predict the effects of man-made activities such as fossil burning.

These models cover a host of variables, and in the absence of deep insight into the structure of the complex codes used, one has no choice but to take the results at face value. Obviously, the effects of temperature, salinity and pressure on seawater are accounted for, but the codes are far from user-friendly, and even other scientists are unable to draw clear conclusions regarding the behaviour of seawater and related chemical equations.

In this context, simple Octave routines are clearly described for solving the various chemical equilibria in seawater, nothing concealed and everything accurately referenced. Anyone with a little chemical knowledge will be able to follow them. The routines and codes, can be downloaded and modified. The aim is to examine the chemical reactions that occur in seawater, using a simple and intuitive computer approach. Despite quite frequent discussion and examination in scientific papers and the press of the relationship between ocean chemistry and environmental issues (such as CO₂ uptake, ocean acidification and carbonate sediment), the basic underlying chemistry is poorly understood.

On the other hand, with Octave codes just a few ten lines long, basic chemistry can offer a variety of simple and extremely interesting results for anybody curious about reactions in seawater. Well, let's not oversimplify! Seawater solution has a high ionic strength (high density of oppositely charged ions), a fact that hinders the direct usage of equilibrium constants taken from standard thermodynamic databases. For the same reason, the temperature, pressure and salinity dependence of the above constants is not at all straightforward and must be carefully modelled. Consequently, simple chemical equilibrium constants are of limited use in the numerical solution of equilibria. On the contrary, employing the parametrisation taken from literature, and using codes for the resolution of simultaneous reactions, results can be obtained in a matter of seconds.

11.4 The fundamental equilibrium relationships

In order to tackle one or more interconnected chemical reactions, the first step is to establish a set of thermodynamic equilibrium constants and mathematically find one or more concentrations that are able to satisfy them. The picture we obtain is an equilibrium one, and at this stage no information is given on how long it takes to the system to reach that chemical equilibrium. In particular heterogeneous reactions (like calcite/aragonite formation from dissolved Ca⁺⁺ and CO₃⁻⁻ ions) may require long times, like years or decades, to be completed. On the contrary CO₂ dissolution in surface seawater requires shorter time intervals to reach equilibrium with all dissolved species (H₂CO₃, HCO₃⁻, CO₃⁻⁻) deriving from its dissolution. In the following are resumed the available expressions for all the equilibrium constants so far (2021) reported in literature. The reader will see that they all empirical relationships, which however are deducted from experimental accurate measurement. Up to day indeed no reliable theoretical treatment for so concentrate salt solutions equilibria is available.

The goal of the procedure is to compute an equilibrium constant by mean of empirical expressions, which account for temperature, hydrostatic pressure, salinity.

The first step is to obtain for a given temperature and salinity, the logarithm (e base) of the equilibrium constant K_c. In a second step this is modified by the hydrostatic pressure in a

new logarithmic value. Finally, in a third step, the from this logarithmic value the true Kc is calculated. In some case the empirical expression, taken from [literature](#), contains base-10 logarithms , which requires a transformation, or temperatures in celsius. Therefor in all the expressions T indicates temperature in K, and Tc in °C.

11.5 CO2 Partial Pressure and Fugacity

Before dealing with chemical equations in seawater, we should first focus on the compound in air that starts a series of reactions when dissolved, namely carbon dioxide. Its partial pressure is continuously monitored, by different stations around the world, the most famous one being the Mauna Loa Observatory (Hawaii).

The partial pressure of a gas in a mixture of gases is simply the total pressure multiplied by its mole fraction. However, the activity of CO2 is not exactly equal to its partial pressure. For accurate calculations, the fugacity of CO2, fCO2, may be used instead of its partial pressure. The fugacity of CO2 is numerically very similar to CO2 partial pressure in atm, and therefore corresponds to CO2 ppm in dry air by the Dalton law. The fugacity can be calculated from its partial pressure (Koerzinger,1999 Zeebe,2001), requiring two virial coefficients B and δ , which are defined as (Weiss,1974) :

$$B = (-1636.75 + 12.0408 \cdot T - 3.27957 \cdot 10^{-2} \cdot T^2 + 3.16528 \cdot 10^{-5} \cdot T^3) \cdot 10^{-6}$$

$$\delta = (57.7 - 0.118 \cdot T) \cdot 10^{-6}$$

$T [K], \quad B [m^3 mol^{-1}]$

$$f(CO_2) = p(CO_2) \cdot \exp\left(P_{tot} \frac{B+2\delta}{RT}\right) \quad P_{tot} [Pa] \quad f(CO_2), p(CO_2) [\mu atm] \quad T [K] \quad R = 8.314 [JK^{-1}]$$

$$fCO2 = ppmCO2 * \exp(101325 * ((-1636.75 + 12.0408 * T - 3.27957e-2 * T^2 + 3.16528e-5 * T^3) * 1e-6 + 2 * (57.7 - 0.118 * T) * 1e-6) / R / T);$$

f(CO2) shall be corrected by accounting for water partial pressure (pH2O) . Indeed it refers to dry air, so it must be slightly adjusted for vapor pressure of water at temperature T. This in turn depends on relative humidity (rH) and saturated water pressure, calculated according to the algorithm proposed by Weiss and Price,1980. This is calculated as a first step :

$$p(H_2O) = \exp\left\{24.4543 - \frac{6745.09}{T} - 4.8489 * \log\left(\frac{T}{100}\right) - 0.000544 * S\right\}$$

$$T [K], \quad S [(g-salt)/(kg-soln)] \quad p(H_2O) [atm], \quad \log = \log_e$$

Then f(CO2) is corrected introducing rH, although this value is usually left to 100 in the simulation (air is saturated over ocean surface).

$$f(CO_2)_{corr} = f(CO_2) \cdot \left[1 - p(H_2O) \cdot \frac{rH}{100}\right] \quad f(CO_2) [\mu atm] \quad 0 \leq rH \leq 100$$

$$Ln pH2O = 24.4543 - 6745.09 / T - 4.8489 * \log(T / 100) - 0.000544 * S;$$

$$fCO2 = fCO2 * (1 - \exp(Ln pH2O) * pH2O / 100);$$

where pH2O indicates the saturation percent at sea level. If not indicated , this value defaults to 100%, as the air layer above sea surface is likely 100% saturated in water vapor.

11.6 Ionic Strength and Ionic Activity

In seawater single ions are not dissolved in pure water, but seawater itself contains high concentrations of ions. The parameter used to characterize aqueous solutions with different amounts of oppositely charged electric charges (ions) is ionic strength, I . It is defined as half the summation of the concentrations multiplied by the respective squared ionic charge (z).

$$I = \frac{1}{2} \sum c_i \cdot z_i^2$$

The sum encompasses all ions present in the medium so that, for a NaCl solution, we have

$$I = \frac{1}{2} ([Na^+] + [Cl^-])$$

Although NaCl is the salt most responsible for the salinity of water, the properties of seawater and a pure NaCl solution with the same concentration are different. For the standard seawater composition used here the ionic strength is approximately 0.7, which corresponds to a salinity of around 35 (grams of salts per kg of water) :

Cl	= 0.54586	' Cl-	Mol/kg(solution)
Na	= 0.46906	' Na+	Mol/kg(solution)
Mg	= 0.05282	' Mg++	Mol/kg(solution)
Ca	= 0.01028	' Ca++	Mol/kg(solution)
SO4	= 0.02824	' SO4--	Mol/kg(solution)
K	= 0.01021	' K+	Mol/kg(solution)
Br	= 0.00084	' Br-	Mol/kg(solution)
Sr	= 0.00009	' Sr++	Mol/kg(solution)
F	= 0.00007	' F-	Mol/kg(solution)
B	= 0.00042	' B(OH)3 + B(OH)4-	Mol/kg(solution)

The ionic strength of seawater may be calculated from salinity (DOE, 1994)

$$I = \frac{19.924}{1000 - 1.005 \cdot S}$$

The behaviour of an ion dissolved in water depends on the electrical interaction with the other ions present in solution. Therefore the chemical 'activity' of an ion dissolved in fresh water and in seawater is quite different.

The activity of a chemical species, denoted by $\{A\}$, is strictly related to its concentration by the activity coefficient $\gamma(A)$:

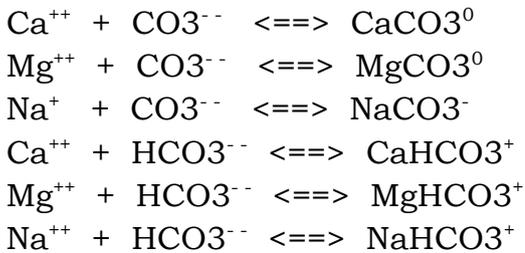
$$\{A\} = \gamma(A) \cdot [A]$$

For infinite dilution, the activity coefficient is 1, but it decreases as the solution becomes more concentrated. If you consider a simple electrolyte, deviation from ideal behaviour can be described through the effect of (relatively) long-range electrostatic interactions. For those interactions, approximations can be derived to describe the dependence of activity coefficients $\gamma(i)$ on ionic strength I .

Seawater has however a higher ionic strength which is, in turn, due to the presence of different electrolyte charges: the combination of these two facts leads to the formation of 'ion pairing' and complex formation in the electrolyte mixture.

As an example, bivalent charged carbonate ions may associate to positively charged Mg^{++} or Na^+ ions forming aliovalent ion pairs such as $NaCO_3^-$ or $MgCO_3^0$

According to Skirrow (1975), the most important ion pairing equilibria in seawater are:



Therefore electrostatic interaction of the CO_3^{--} ions with opposite charges in solution isn't the only factor that decreases the activity of the ion. The ion pairing greatly impairs the same activity, as the carbonate ion in seawater is not 'free', being combined in neutral or lower charged (aliovalent) species in solution.

If no ion-pairing would occur, the free activity coefficient γ of an ion in simple electrolyte solutions varies with ionic strength I according to the Debye-Hückel limiting law

$$\log(\gamma) = -Az^2\sqrt{I} \quad \text{valid for } I < 0.005$$

or to the Davies equation

$$\log(\gamma) = -Az^2\left(\frac{\sqrt{I}}{\sqrt{I}+1} - 0.2 \cdot I\right) \quad \text{valid for } I < 0.5$$

with $A = 1.82 \cdot 10^{-6} \cdot (\epsilon T)^{-1.5}$, where $\epsilon \approx 79$ is the dielectric constant of water, and T is the absolute temperature in K. At 25°, A is about 0.5 for water; z indicates the charge of the ion and I the ionic strength of the solution.

As the ionic strength of seawater is approximately 0.7, which is only slightly higher than the limit of the Davies equation, it should be used in a reasonable way. However, this equation and the Debye-Hückel limiting law no longer apply since they only hold for dilute solutions and simple electrolytes (as opposed to concentrated solutions and electrolyte mixtures of unlike charges) (Zeebe 2001).

The problem will be tackled by using empirical formulas for the equilibrium constants, which employ concentrations, and without the need to calculate activities. The same approach will be used for the temperature, pressure and salinity dependence of these constants.

The fitting of experimental data has been carried out by DOE 1994, Millero 1995, Weiss 1974 et al. A comprehensive review of such data can be found in Zeebe 2001, Appendix A.

11.7 Hydration of carbon dioxide $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$ (K_0)

$$K_0 = \frac{[\text{H}_2\text{CO}_3^*]}{f(\text{CO}_2)}$$

$$\text{Ln}K_0 = 9345.17/T - 60.2409 + 23.3585 \cdot \log(T/100) + S \cdot (0.023517 - 0.00023656 \cdot T + 0.0047036 \cdot (T/100)^2);$$

$$K_0 = \exp(\text{Ln}K_0)$$

$$T [K] \quad S [g/kg - \text{soln}], \quad \log = \log_e$$

As the hydration of carbon dioxide occurs in the surface layer of seawater, to this equilibrium is not assigned a pressure dependent constant.

$H_2CO_3^*$ is the sum of the true acid form H_2CO_3 and the hydrated CO_2 , indicated by $CO_2(aq)$. From now on asterisk is omitted, so that $[H_2CO_3]$ indicates the sum of acid form and hydrated CO_2 . The algorithm is taken from [Zeebe,2001](#)

$f(CO_2)$ is the fugacity of CO_2 , which is numerically very similar to CO_2 partial pressure in μatm or ppmv (parts per million in volume), if total pressure is 1 atm. by the Dalton law. For sake of simplicity in some of the script proposed here, the CO_2 fugacity is approximated by its ppmv concentration, which in turn corresponds to its partial pressure in μatm for an total pressure of 1 atm..

11.8 'Ionic water product', i.e. the equilibrium constant for the reaction



Water itself is a weak electrolyte whose dissociation must be carefully taken into account. In seawater the following expression is used to represent its dependence on temperature and salinity. As is the case for the following expressions, it should not be extrapolated to zero or near zero salinity, as it results from experiments with salinity from 25 to 45 (grams-of-salts/Kg-of-solution) (Zeebe,2001).

The equilibrium constant is first calculated as log(e) in the variable LnKw, as a function of two parameters, temperature T(K) and salinity S(grams of salt/kg of solution).

In a second program line the effect of hydrostatic pressure is accounted for, thus obtaining the LnKwP variable, eventually transformed in Kw, as listed below. The concentration of H^+ ions and consequently the pH scale refer to the 'total scale', as discussed in section 11.18.

```
LnKw = 148.9802 - 13847.26/T - 23.6521*log(T) + (118.67/T - 5.977 +
1.0495*log(T))*S^0.5 - 0.01615*S;
LnKwP = LnKw + (25.6 - 0.2324*Tc + 3.6246e-3*Tc^2)/R1/T*P + 0.5*(-5.13e-3 +
0.0794e-3*Tc)/R1/T*P^2;
Kw = exp(LnKwP);
```

$$[H^+] = \text{Total scale}, \quad pH = pH_{SWS}$$

11.9 First dissociation of carbonic acid $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ (K_1)

$$K_1 = \frac{[HCO_3^-] \cdot [H^+]}{[H_2CO_3]}$$

The computing procedure follows the three steps indicated in the preceding session. The concentration of H^+ ions and consequently the pH scale refer to the 'free scale', as discussed in section 11.18.

```
LnK1 = -log(10)*(6320.813/T + 19.568224*log(T) -126.34048 + 5.592953*S^0.5
+ 0.028845*S - (6.388e-5)*S^2 + (-225.7489*S^0.5 - 4.761*S)/T -
0.8715109*S^0.5*log(T));
```

```
LnK1P = LnK1 + (25.5 - 0.1271*Tc)/R1/T*P + 0.5*(-3.08e-3 +
0.0877e-3*Tc)/R1/T*P^2;
K1 = exp(LnK1P);
```

(Waters,2014) T[K] S[g/kg-soln] log=log_e, pH=Free Scale

11.10 Second dissociation of carbonic acid $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{--}$ (K_2)

$$K_2 = \frac{[\text{CO}_3^{--}] \cdot [\text{H}^+]}{[\text{HCO}_3^-]}$$

The computing procedure follows the three steps indicated in the preceding session. The concentration of H⁺ ions and consequently the pH scale refer to the 'free scale', as discussed in section 11.18.

```
LnK2 = -log(10)*(5143.692/T + 14.613358*log(T) - 90.18333 + 13.396949*S^0.5
+ 0.12193009*S - (3.8362e-4)*S^2 + (-472.8633*S^0.5 - 19.03634*S)/T -
2.1563270*S^0.5*log(T));
LnK2P = LnK2 + (15.82 + 0.0219*Tc)/R1/T*P + 0.5*(1.13e-3 -
0.1475e-3*Tc)/R1/T*P^2;
K2 = exp(LnK2P);
```

(Waters,2014) T[K], log=log_e, pH=Free Scale

11.11 Solubility of [calcite](#) (K_{sp}) $\text{CaCO}_3 \rightleftharpoons \text{Ca}^+ + \text{CO}_3^{--}$

$$K_{sp}(\text{cal}) = [\text{Ca}^{++}] \cdot [\text{CO}_3^{--}] \quad [] = \text{conc. in mol/(kg-solution)}$$

The solubility product, which equals the equilibrium constant, is first calculated as log(10) in the variable LogKspCal, then transformed into log(e) in the variable LnKspCal. The two parameters are temperature T(K) and salinity S(grams of salt/kg of solution).

In a third program line the effect of hydrostatic pressure is accounted for, thus obtaining the LnKspCalP variable, eventually transformed in Ksp1, as listed below.

```
LogKspCal = -171.9065 - 0.077993*T + 2839.319/T + 71.595*log10(T) +
(-0.77712 + 0.0028426*T + 178.34/T)*S^0.5 - 0.07711*S + 0.0041249*S^1.5;
LnKspCal = LogKspCal*log(10);
LnKspCalP = LnKspCal + (48.76 - 0.5304*Tc)/R1/T*P + 0.5*(-11.76e-3 +
0.3692e-3*Tc)/R1/T*P^2;
Ksp1 = exp(LnKspCalP)
```

(Zeebe,2001) T[K], log=log₁₀, S[g/kg-soln]

11.12 Solubility of aragonite (K_{sp}) $\text{CaCO}_3 \rightleftharpoons \text{Ca}^+ + \text{CO}_3^{--}$

The procedure is similar to that for calcite (11.10). Aragonite is a second crystallographic form of calcium carbonate.

$$K_{sp}(\text{ara}) = [\text{Ca}^{++}] \cdot [\text{CO}_3^{--}] \quad [] = \text{conc. in mol}/(\text{kg-solution})$$

$$\begin{aligned} \text{LogKspAra} &= -171.945 - 0.077993 \cdot T + 2903.293/T + 71.595 \cdot \log_{10}(T) + (-0.068393 + 0.0017276 \cdot T + 88.135/T) \cdot S^{0.5} - 0.10018 \cdot S + 0.0059415 \cdot S^{1.5}; \\ \text{LnKspAra} &= \text{LogKspAra} \cdot \log(10); \\ \text{LnKspAraP} &= \text{LnKspAra} + (46 - 0.5304 \cdot T_c) / R1 / T \cdot P + 0.5 \cdot (-11.76e-3 + 0.3692e-3 \cdot T_c) / R1 / T \cdot P^2; \\ \text{Ksp2} &= \exp(\text{LnKspAraP}); \end{aligned}$$

$$K_{sp}(\text{ara}) = 10^{[-171.945 - 0.077993 \cdot T + \frac{2903.293}{T} + 71.595 \cdot \log_{10}(T) + (-0.068393 + 0.0017276 \cdot T + \frac{88.135}{T}) \cdot S^{0.5} - 0.10018 \cdot S + 0.0059415 \cdot S^{1.5}]}$$

(Zeebe, 2001) T [K], $\log = \log_{10}$, S [g/kg-soln]

11.13 Dissociation of boric acid $\text{B(OH)}_3 + \text{H}_2\text{O} \rightleftharpoons \text{B(OH)}_4^- + \text{H}^+$

$$K_B = \frac{[\text{H}^+] \cdot [\text{B(OH)}_4^-]}{[\text{B(OH)}_3]}$$

$$\begin{aligned} \text{LnKB} &= (-8966.9 - 2890.53 \cdot S^{0.5} - 77.942 \cdot S + 1.728 \cdot S^{1.5} - 0.0996 \cdot S^2) / T + 148.0248 + 137.1942 \cdot S^{0.5} + 1.62142 \cdot S - (24.4344 + 25.085 \cdot S^{0.5} + 0.2474 \cdot S) \cdot \log(T) + 0.053105 \cdot S^{0.5} \cdot T; \end{aligned}$$

Then LnKB is modified by the hydrostatic pressure P

$$\text{LnKBP} = \text{LnKB} + (29.48 - 0.1622 \cdot T_c - 2.608e-3 \cdot T_c^2) / R1 / T \cdot P + 0.5 \cdot (-2.84e-3) / R1 / T \cdot P^2;$$

Finally the value of equilibrium constant is calculated as

$$\text{KB} = \exp(\text{LnKBP})$$

Ref. Zeebe, 2001 T (K), pH = Free Scale, P (atm)

11.14 Second dissociation of sulfuric acid $\text{HSO}_4^- \rightleftharpoons \text{SO}_4^{--} + \text{H}^+$

$$K_S = \frac{[\text{H}^+] \cdot [\text{SO}_4^{--}]}{[\text{HSO}_4^-]}$$

I = Ionic strength, necessary for K_S and K_F calculations, is calculated from salinity S by means of an empirical expression (Zeebe 2001)

$$I = 19.924 \cdot S / (1000 - 1.005 \cdot S);$$

$$\begin{aligned} \text{LnKS} &= -4276.1/T + 141.328 - 23.039*\log(T) + (-13856/T + 324.57 - \\ &47.986*\log(T))*I^{0.5} + (35474/T - 771.54 + 114.723*\log(T))*I - 2698/T*I^{1.5} \\ &+ 1766/T*I^2 + \log(1-0.001005*S); \\ \text{LnKSP} &= \text{LnKS} + (18.03 - 0.0466*Tc - 0.3160e-3*Tc^2)/R1/T*P + 0.5*(-4.53e-3 \\ &+ 0.09e-3*Tc)/R1/T*P^2; \\ \text{KS} &= \exp(\text{LnKSP}); \end{aligned}$$

(Zeebe,2001) $T[K]$, $pH=Free\ Scale$

11.15 Dissociation of hydrofluoric acid $HF \rightleftharpoons H^+ + F^-$

$$K_F = \frac{[H^+][F^-]}{[HF]}$$

$$\begin{aligned} I &= 19.924*S/(1000 - 1.005*S); \\ \text{LnKF} &= 1590.2/T - 12.641 + 1.525*I^{0.5} + \log(1-0.001005*S); \\ \text{LnKFP} &= \text{LnKF} + (9.78 + 0.009*Tc + 0.942e-3*Tc^2)/R1/T*P + 0.5*(-3.91e-3 + \\ &0.054*Tc)/R1/T*P^2; \\ \text{KF} &= \exp(\text{LnKFP}); \end{aligned}$$

(Zeebe,2001) $T[K]$, $pH=Free\ Scale(*)$, $I=ionic\ strenght$, $\log=\log_e$.

(*) Differently from Zeebe,2001 K_F value has NOT been converted to pH Total Scale, so pH Free Scale is used. See 11.18 for a description of the different pH scales used in seawater chemistry.

11.16 The three dissociations of phosphoric acid H_3PO_4

For the three dissociation reactions of phosphoric acid in seawater and the following of silicic acid in seawater, the formulae for empiric constants are reported, but these are not used at the present for the calculation in the 'SeaWaterCalc' code. The concentration of the two acids is very low in seawater and locally variable. They could easily be implemented by inserting them in the code.

$$\begin{aligned} K_{1P} &= \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} & H_3PO_4 &\rightleftharpoons H^+ + H_2PO_4^- \\ K_{1P} &= \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} & H_2PO_4^- &\rightleftharpoons H^+ + HPO_4^{2-} \\ K_{1P} &= \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} & HPO_4^{2-} &\rightleftharpoons H^+ + PO_4^{3-} \end{aligned}$$

$$\begin{aligned} \text{LnKa1} &= -4576.752/T + 115.525 - 18.453*\log(T) + (-106.736/T+0.69171)*S^{0.5} \\ &+ (-0.65643/T-0.01844)*S; \quad \% \text{ 1st dissociation constant} \\ \text{LnKa2} &= -8814.715/T + 172.0883 - 27.927*\log(T) + (-160.34/T+1.3566)*S^{0.5} \\ &+ (0.37335/T-0.05778)*S; \quad \% \text{ 2nd dissociation constant} \end{aligned}$$

$$\text{LnKa3} = -3070.75/T - 18.141 + (17.27039/T + 2.81197) * S^{0.5} + (-44.99486/T - 0.09984) * S; \text{ \% 3rd dissociation constant}$$

$$\text{Ka1} = \exp(\text{LnKa1}); \text{Ka2} = \exp(\text{LnKa2}); \text{Ka3} = \exp(\text{LnKa3});$$

$$\text{(Zeebe,2001)} \quad T[K], \quad pH = \text{Total Scale (see 11.18)}, \quad S[g/kg - \text{soln}]$$

11.17 Dissociation of orthosilicic acid $\text{Si(OH)}_4 \rightleftharpoons \text{H}^+ + \text{H}_3\text{SiO}_4^-$

$$K_{\text{Si}} = \frac{[\text{H}^+] \cdot [\text{H}_3\text{SiO}_4^-]}{[\text{H}_4\text{SiO}_4]}$$

$$I = 19.924 * S / (1000 - 1.005 * S); \text{ \% ionic strength}$$

$$\text{LnKSi} = -8904.2/T + 117.385 - 19.334 * \log(T) + (-458.79/T + 3.5913) * I^{0.5} + (188.74/T - 1.5998) * I + (0.07871 - 12.1652/T) * I^2 + \log(1 - 0.001005 * S);$$

$$\text{KSi} = \exp(\text{LnKSi});$$

$$\text{(Zeebe,2001)} \quad T[K], \quad [\text{H}^+] = \text{Total Scale (see 11.18)},$$

11.18 Effect of pressure on the equilibrium reactions

The effect of pressure on equilibrium constants is of paramount importance; sinking down into the depths of the oceans, pressure increases by 1 atm with every 10 meters. As the intermolecular distances between water molecules decrease slightly, the density of liquid water increases accordingly. Therefore, interionic interaction and equilibrium constants become progressively altered in relation to the pressure itself. The effects become noticeable when pressure reaches hundreds of bars; pH and solubility of calcium carbonate alter to such an extent that aragonite oversaturation, and calcite at greater depths, disappear and, if formed, these salt readily re-dissolve.

As discussed in Section 4.4 on water density, we recall that water pressure is measured in 'bars' (1 atm = 1.01325 bar; 1 bar = 0.1 Mpa), and that the surface pressure of the sea is assumed to be zero.

The effect of pressure on equilibrium constants can be calculated (Millero 1995) according to a second order polynomial expression of the natural logarithm of the ratio between $K_{i,P}$ (the value of i-esimal constant at pressure P) and $K_{i,0}$ (the value of i-esimal constant at reference zero pressure P)

$$\log\left(\frac{K_{i(P)}}{K_1}\right) = -\frac{\Delta V_i}{R^* T} P + \frac{\Delta K_i}{2 \cdot R^* T} P^2 \quad \log = \log_e \quad T[K] \quad P = \text{bar}$$

The constant value R^* is given by $R^* = 83.14472 \text{ cm}^3 \text{ bar mol}^{-1} \text{ K}^{-1}$ (corrected from the original value of 83.131, reported in Zeebe,2001 slightly biased) whereas ΔV_i is the molal volume change, and ΔK_i the compressibility change. They are in turn deconvoluted in terms of a second order polynomial which, strictly speaking, is only valid for Salinity = 35, but can be acceptable in a wider range, say 20-50.

$$\Delta V_i = a_0 + a_1 T_c + a_2 T_c^2 \quad T = [^{\circ}C]$$

$$\Delta K_i = b_0 + b_1 T_c \quad T = [^{\circ}C]$$

The values for the a_i and b_i parameters are taken from Zeebe, 2001 and are reported here for each of the reactions, where T_c indicates the temperature in $^{\circ}C$, P the pressure in bar, and T the absolute temperature ($T = T_c + 273.15$) and finally $R^* = 83.14472$.

	a0	a1	a2	b0	b1
K1 (P)	-25.50	0.1271	0.0	-0.00308	0.0000877
K2 (P)	-15.82	-0.0219	0.0	0.00113	-0.0001475
KB (P)	-29.48	0.1622	0.002608	-0.00284	0.0
KW (P)	-25.60	0.2324	-0.0036246	-0.00513	0.0000794
KS (P)	-18.03	0.0466	0.0003160	-0.00453	0.00009
KF (P)	-9.780	-0.0090	-0.000942	-0.00391	0.000054
KSP, cal (P)	-48.76	0.5304	0.0	-0.01176	0.0003692
KSP, ara (P)	-46.00	0.5304	0.0	-0.01176	0.0003692

The effect of pressure alters the values for every equilibrium constant, and must therefore be properly accounted for in the program flow. Greater detail on this can be found by inspecting the program script.

11.19 Oversaturation of $CaCO_3$

Generally speaking, in heterogeneous reactions, reactants are in different phases, like solids, liquid solutions or gaseous mixtures. One of the most relevant of such reactions is the formation or dissolution of calcium carbonate (solid/solution), according to its oversaturation value, indicated by Ω and discussed elsewhere.

Once formed biologically by calcifying organisms or by inorganic route, and with a density greater than 1, it eventually sinks into the dark abyss. Due to increasingly high pressure, solid $CaCO_3$ begins to dissolve below a certain depth, referred to as the saturation horizon where Ω is exactly equal to 1. Dissolution of the solid is not instantaneous, and the downward flux continues to a depth where the solid particles of calcium carbonate are completely dissolved. This depth is called the carbonate compensation depth. If the sea bottom does not reach such a depth, it becomes undissolved carbonate sediment. The two crystallographic forms of $CaCO_3$, calcite and aragonite, have different solubility products, the former being less soluble. Therefore, the saturation horizon and the compensation depth for aragonite are at a higher level compared to calcite. Most calcifying organisms (e.g. Coccolithophores) produce calcite, whilst coral reefs are made of aragonite.

Solving the equilibria involved in $CaCO_3$ formation with the algorithm described the oversaturation profiles at different depths can be calculated. Some of the results can be seen in the graph in Figure . The curious reader, intent on modifying input parameters and looking for new results (in a “see what happens” procedure) is re-directed to the script.

In Fig. 1 oversaturation Ω , is plotted against pressure being temperature fixed at 4°C, which is the overall temperature for the ocean's depths below the thermocline (about 300 meters). Below $\Omega=1$ (light blue area) carbonates begin their dissolution process.

One topic frequently debated today is the potential hazard for coralline reefs of the rising concentrations of CO₂, through the reduction of ocean pH and carbonate ion concentration. The effect of this, is however compensated for by an increase in oversaturation in warmer areas of oceans, where calcifying organisms and coral reefs prosper. Global warming, estimated at about 1°C from the beginning of the twentieth century to the present day, also favours oversaturation and thereby counteracts the effects of increasing CO₂ content by anthropogenic emissions. Therefore the two data should be considered together to gain a complete picture.

11.20 Dissolved Inorganic Carbon (DIC)

In ocean chemistry it is a conventional term used to indicate the sum of the concentration of seawater-dissolved CO₂, carbonic acid, bicarbonate and carbonate anions. It is measured in millimol/kg-of-solution. This value depends on different factors, the main being temperature, salinity and CO₂ concentration in the atmosphere

$$DIC[\text{mmol/kg-soln}] = [H_2CO_3]^* + [HCO_3^-] + [CO_3^{2-}] \quad \text{where} \quad [H_2CO_3]^* = [CO_2]_{aq} + [H_2CO_3]$$

Salinity can be varied by user, the default value being 35 g/kg-soln. The imbalance (difference between cations and anions, not accounting for H⁺ and OH⁻) depends linearly on salinity, according to :

$$\text{Imb} = 0.00218 \cdot 35 / S \quad (S = \text{salinity in g/kg-soln})$$

The program calculates the equilibrium values of DIC as a function of temperature and CO₂ concentration for a given salinity. It should be considered that seawater reaches the thermodynamic equilibrium with a delay of some months.

The simple script is listed here below.

```
clear;clc;format shortE;format compact;
global K1 K2 Kw H2CO3 HCO3 CO3 OH H Imb

function y = neut(pH) % ==> pH free scale, i.e. chemical true scale, always used if not
otherwise stated !!
    global K1 K2 Kw H2CO3 HCO3 CO3 OH H Imb
    H = 10^(-pH);
    HCO3 = K1*H2CO3/H;
    CO3 = K2*HCO3/H;
    OH = Kw/H;
    y = Imb + H - OH - HCO3 - 2*CO3;
endfunction

R = 8.314;
i = 0;S = 35; % salinity, in grams of salts in 1 kg of solution , this can be varied
for Tc = 0:2:30 % temperature in Celsius (°C)
    ++i;j = 0;
    T = Tc + 273.15;Imb = 0.00218;
    Imb = Imb*35/S;
    % H2CO3 <==> H+ + HCO3- (Waters,2014)
    LnK1 = -log(10)*(6320.813/T + 19.568224*log(T) -126.34048 + 5.592953*S^0.5 + 0.028845*S -
(6.388e-5)*S^2 + (-225.7489*S^0.5 - 4.761*S)/T -0.8715109*S^0.5*log(T));
    % HCO3- <==> H+ + CO3-- (Waters,2014)
```

```

LnK2 = -log(10)*(5143.692/T + 14.613358*log(T) - 90.18333 + 13.396949*S^0.5 +
0.12193009*S - (3.8362e-4)*S^2 + (-472.8633*S^0.5 - 19.03634*S)/T -
2.1563270*S^0.5*log(T));
% CO2 + H2O <==> H2CO3 (Zeebe,2001)
LnK0 = 9345.17/T - 60.2409 + 23.3585*log(T/100) + S*(0.023517 - 0.00023656*T +
0.0047036*(T/100)^2);
% H2O <==> H+ + OH- (DOE 1994) (Zeebe,2001) pH = pH(SWS) considered = pH free !
LnKw = 148.9802 - 13847.26/T - 23.6521*log(T) + (118.67/T - 5.977 + 1.0495*log(T))*S^0.5
- 0.01615*S;
K1 = exp(LnK1);K2 = exp(LnK2);K0 = exp(LnK0);Kw = exp(LnKw);
for ppmCO2 = 300:10:500 % parts per million (in volume) of CO2 in the atmosphere
    H2CO3 = K0*ppmCO2*1e-6;+j;
    [pH,fval,info] = fzero(@neut,[0,14]); % call to fzero
    DIC(i,j) = H2CO3 + HCO3 + CO3;
    temp(i,j) = Tc;ppm(i,j) = ppmCO2;
endfor
endfor
plot(temp(:,11),DIC(:,11)*1000,'r','LineWidth',2);grid on;grid minor on;xlabel('temperature
°C');ylabel('DIC [mmol/kg]')
title('DIC versus temperature @ 400 ppm CO2');
figure;
plot(ppm(11,:),DIC(11,)*1000,'r','LineWidth',2);grid on;grid minor on;xlabel('ppm CO2 in
dry air');ylabel('DIC [mmol/kg]')
title('DIC versus ppmCO2 @ 20 °C');
figure;
surf(temp,ppm,DIC);colorbar;title('DIC vs. temperature and ppmCO2');
xlabel('temperature °C');ylabel('ppm CO2 in dry air');zlabel('DIC');

```

Two nested loops are evident, the innermost being for ppmCO2 and the outermost for temperature. The CO2 concentration (parts per million) varies from 300 to 500 (step 10) and temperature varies from 0 to 30°C (step 2°C). For each pair of ppmCO2 and temperature the statement *fzero* is invoked for the *'neut(pH)'* function. This function finds the electric charge imbalance of the solution. By varying the pH scale between 0 and 14, *fzero* tries to find the y value as close as possible to zero

$$y = \text{Imb} + \text{H} - \text{OH} - \text{HCO}_3 - 2 \cdot \text{CO}_3;$$

```
[pH,fval,info] = fzero(@neut,[0,14]);
```

Once pH satisfying the above condition is determined, the concentrations of H2CO3, HCO3-,CO3--,OH- follow as a consequence, and hence DIC is calculated

The script produces three figures, for a given salinity value. The first two are bidimensional plots, the third is a tridimensional one

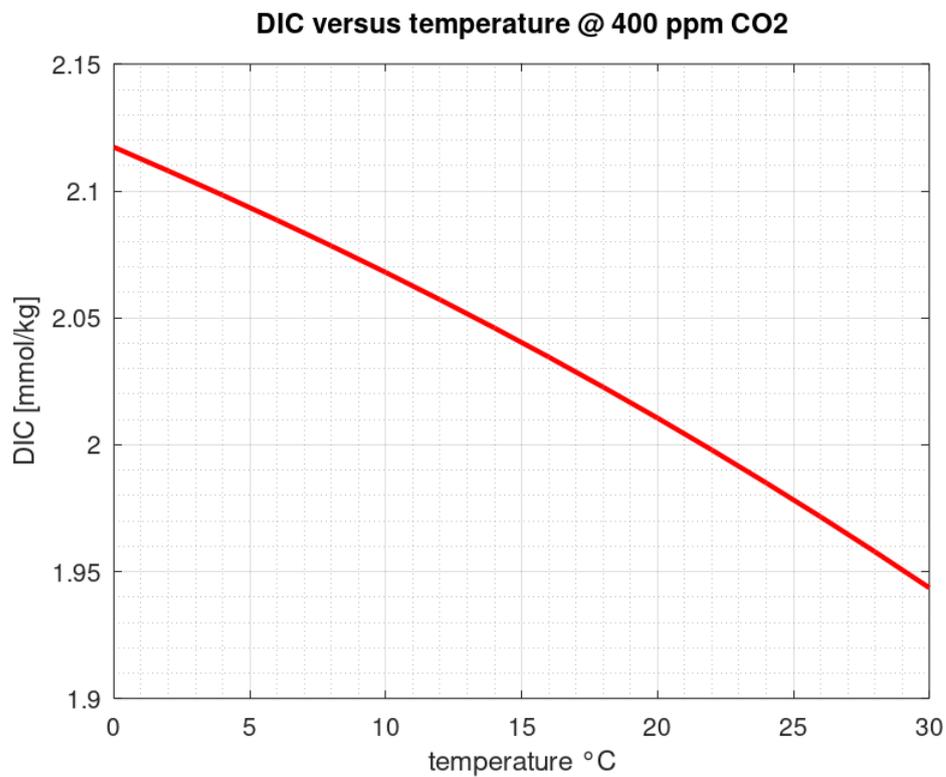


Fig 11.1 DIC as a function of temperature (S = 35; ppmCO₂ = 400)

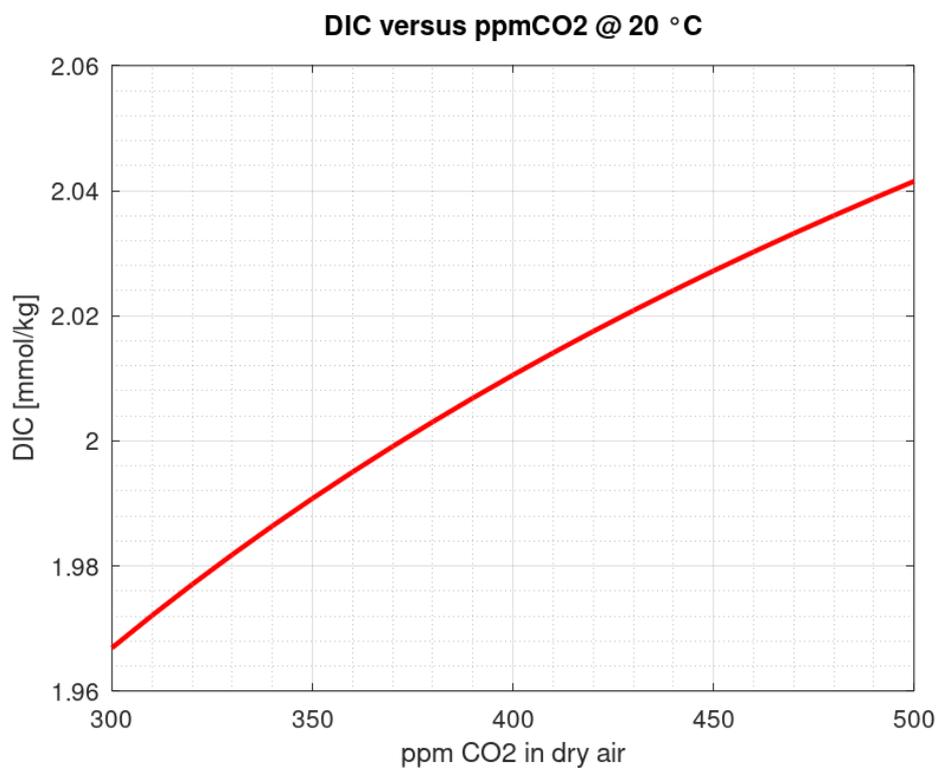


Fig 11.2 DIC as a function of ppmCO₂ (S = 35; temperature = 20°C)

DIC vs. temperature and ppmCO2

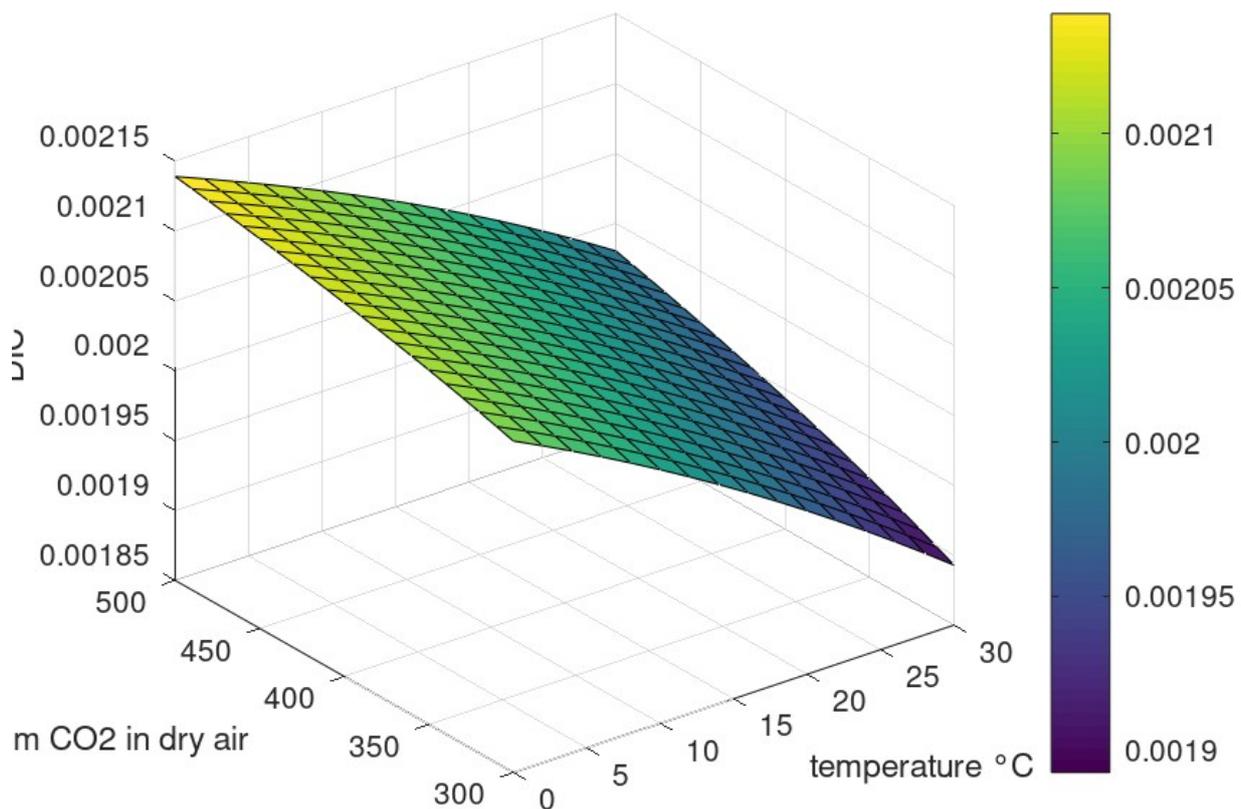


Fig 11.3 DIC as a function of both temperature and ppmCO2 (S = 35)

11.21 Different pH scales in Seawater Chemistry

In chemical oceanography, three main different pH scales are currently used; free, total and seawater. This point is not to be neglected; when dealing with acidity constants of hydrogen ion transfer reactions (as is the case of H₂CO₃) the use of a consistent pH scale is mandatory. The values of different pH scales in seawater differ by up to 0.12 units (Zeebe 2001).

The pH value is in theory defined as the negative logarithm of the activity (in braces) of hydrogen ions

$$pH = \log_{10} \{ H^+ \}$$

Unfortunately, individual ion activities cannot be determined experimentally. Indeed, the concentration of one single ion cannot be varied independently, because electroneutrality is required. Therefore the 'free' pH scale for seawater has been proposed:

$$pH_F = \log_{10} [H^+]_F$$

where $[H^+]_F$ stands for the free hydrogen ion concentration, including hydrated forms, like H₃O⁺ and H₉O₄⁺ (Dickson 1984)

Indeed, free protons do not exist in any significant amount in aqueous solutions. Rather, the proton is bonded to a water molecule thus forming H₃O⁺. This in turn is hydrogen bonded to three other water molecules to form an H₉O₄⁺ ion (Dickson 1984, p.2299).

To be noted that, as usual in ocean chemistry, the concentrations in square brackets are expressed in mol/Kg (water) and not in mol/L as is more usual in general chemistry.

In 1973, Hanson defined a total scale for pH so as to include the effect of sulphate ions in its definition.

$$pH_T = \log_{10} [H^+]_T \quad \text{where} \quad [H^+]_T = [H^+] + [HSO_4^-]$$

The bisulphate ion (HSO_4^-) is a rather weak acid ($K_{a1} \approx 2.1 \cdot 10^{-2}$) so it is not completely dissociated in H^+ and SO_4^{2-} ions. Once the K_a is known, a relationship between the two scales can be inferred. This in turn requires an accurate value of K_a in seawater, which would be difficult to obtain. But by using Hanson's total pH scale in seawater, the calculation of K_a for bisulphate ion can be avoided.

This total scale will be used in the empirical expressions for the various acidity constants, including the ionic water product. This choice seems to conflict with the usual free pH scale as used in general chemistry, but is necessary due the use of the total scale in the experimental determination of the various constants. Therefore, in the code shown below, this total scale will be employed.

The third scale is the so-called seawater scale, which only slightly differs from the preceding one.

The need to introduce this scale is due to the presence of fluoride ions (F^-) in seawater. Consequently, we have to account for the protonation of F^- ions according to the equilibrium:



Indeed, hydrofluoric acid is a weak acid. In standard seawater however, the concentration of fluoride ions is $7.0 \cdot 10^{-5}$ Mol/Kg of water, about 400 times lower than the concentration of sulphate ions, $2.8 \cdot 10^{-2}$ Mol/Kg, therefore the seawater scale differs by no more than 0.01 pH units from the total scale. In the following table the transformation between the three pH scales are shown, both in terms of concentrations and pH units.

$$[H^+]_T = [H^+]_F \cdot \left(1 + \frac{[SO_4^{2-}]}{K_{a1}}\right)$$

$$[H^+]_{SW} = [H^+]_F \cdot \left(1 + \frac{[SO_4^{2-}]}{K_{a1}} + \frac{[F^-]}{K_{a2}}\right)$$

$$[H^+]_{SW} = [H^+]_T \cdot \left(1 + \frac{[F^-]}{K_{a2}}\right)$$

$$pH_T = pH_F - \log_{10} \left(1 + \frac{[SO_4^{2-}]}{K_{a1}}\right)$$

$$pH_{SW} = pH_F - \log_{10} \left(1 + \frac{[SO_4^{2-}]}{K_{a1}} + \frac{[F^-]}{K_{a2}}\right)$$

$$pH_{SW} = pH_T - \log_{10} \left(1 + \frac{[F^-]}{K_{a2}}\right)$$

If $K_{a1} \approx 2.1 \cdot 10^{-2}$ and $[SO_4^{2-}] = 2.8 \cdot 10^{-2}$ then the difference between pH_T and pH_F scale would be ≈ 0.37 pH unit, but this would be valid only in pure water.

Under the same conditions (pure water) then the difference between pH_{SW} and pH_T scale would be ≈ 0.37 pH unit.

11.22 Complete equilibria solved at hydrostatic pressure greater than zero

The following script employs the equations 11.5 throughout 11.15, therefore dissociation of phosphoric acid and orthosilicic acid are not considered. Indeed their concentrations are locally widely variable in seawater, so as they are considered apart, in a dedicated script. The script looks complex, however only apparently.

The function $y=neut(pH)$ computes imbalance of ionic charges as a function of pH. Solubility of $CaCO_3$ (calcite form) is also taken into account inside the function. In the function the various equilibria are solved, namely first and second dissociation of carbonic acid, dissociation of fluoridric acid, second dissociation of sulfuric acid (the first is considered to be complete), reaction of boric acid. The [hydrolysis](#) of calcium and magnesium [aqua ions](#) (solvated ions) schematically written as:



although occurring to some minor extent, is not considered in here. The contribution of such reactions can be neglected, as demonstrated in some previous calculations.

The pH scale used is the (true) free scale, except in some instances where the sws scale is required (second dissociation of sulfuric acid) (see section 11.19).

Six parameters can be varied in the main for...endfor cycle. They are listed here, together with their default values. However, only one parameter at a time can be varied, by inserting its value and range in the proper script line (in red).

Tc = 15;	temperature in Celsius (°C)
ppmCO2 = 410;	parts per million (in volume) of CO2 in the atmosphere
P = 0;	hydrostatic pressure in atm. P=0 means sea surface.
S = 35;	salinity, in grams of salts in 1 kg of solution
pptF = 0.001;	fraction of CaCO3 which actually precipitates
pH2O = 100;	H2O vapour pressure in % of saturation at sea level

The program output is both numerical and graphic. In the following are reported an output text example, in which the hydrostatic pressure is varied and the corresponding graphics. The complete script is listed in [appendix](#) together with some different output text tables as examples.

Output example in command window:

```
Temp = temperature in degree Celsius (°C)
CO2 = ppmv, parts per million in volume of CO2 in dry air
pptF = fraction of CaCO3(calcite) which precipitates, ratio to complete precipitation(when omega=1)
Pres = pressure in atm x 100
Saln = salinity in grams of dissolved salts per kg of solution
pHfr. pHtot pHsws = different pH scales, free, total and seawater
pOH = -log10[OH-]
H2CO3 HCO3 CO3 = concentrations in millimol/kg-solution
DIC = Dissolved Inorganic Carbon in mmol/kg-soln
Alk = alkalinity in mmol/kg-soln Alk = 2*CO3+HCO3+OH+BOH4-H
Ca++ CaCO3 = concentrations in mmol/kg-soln
sovr1 sovr2 = Calcite and aragonite overasaturation (omega)
pH2O = water vapour pressure above sea level
Cout = mmol/kg-soln of carbon absorbed(-) or outgassed (+) from the first iteration
+-----+
|Temp|CO2|pptF|Pres|Saln|pHfr.|pHtot|pHsws| pOH |H2CO3 |HCO3-|CO3-- | DIC | Ca++ | Alk |CaCO3|over1|over2| pH2O | Cout
+-----+
|15.0|410|0.00|0.00|35.0|8.142|8.084|8.075|5.542|0.0151|1.969|0.1665|2.151|10.272|2.385|0.008|3.965|2.546|0.0165|0.00
```

15.0	410	0.00	0.20	35.0	8.134	8.076	8.067	5.541	0.0151	1.971	0.1658	2.152	10.272	2.385	0.008	3.814	2.455	0.0165	-0.00
15.0	410	0.00	0.40	35.0	8.126	8.069	8.060	5.540	0.0151	1.972	0.1650	2.152	10.273	2.385	0.007	3.670	2.368	0.0165	-0.00
15.0	410	0.00	0.60	35.0	8.118	8.062	8.053	5.539	0.0151	1.974	0.1642	2.153	10.273	2.385	0.007	3.531	2.283	0.0165	-0.00
15.0	410	0.00	0.80	35.0	8.110	8.054	8.046	5.538	0.0151	1.975	0.1634	2.154	10.273	2.385	0.007	3.398	2.202	0.0165	-0.00
15.0	410	0.00	1.00	35.0	8.101	8.047	8.039	5.537	0.0151	1.977	0.1627	2.154	10.273	2.386	0.007	3.270	2.125	0.0165	-0.00
15.0	410	0.00	1.20	35.0	8.093	8.039	8.032	5.535	0.0151	1.978	0.1619	2.155	10.273	2.386	0.007	3.148	2.050	0.0165	-0.00
15.0	410	0.00	1.40	35.0	8.085	8.032	8.025	5.534	0.0151	1.979	0.1611	2.156	10.273	2.386	0.007	3.030	1.978	0.0165	-0.00
15.0	410	0.00	1.60	35.0	8.077	8.024	8.019	5.533	0.0151	1.981	0.1604	2.156	10.273	2.386	0.007	2.917	1.909	0.0165	-0.00
15.0	410	0.00	1.80	35.0	8.069	8.017	8.012	5.531	0.0151	1.982	0.1596	2.157	10.273	2.387	0.007	2.809	1.842	0.0165	-0.01
15.0	410	0.00	2.00	35.0	8.061	8.009	8.005	5.530	0.0151	1.984	0.1589	2.158	10.274	2.387	0.006	2.705	1.778	0.0165	-0.01
15.0	410	0.00	2.20	35.0	8.053	8.002	7.998	5.529	0.0151	1.985	0.1582	2.159	10.274	2.387	0.006	2.605	1.716	0.0165	-0.01
15.0	410	0.00	2.40	35.0	8.044	7.995	7.991	5.528	0.0151	1.987	0.1574	2.159	10.274	2.388	0.006	2.510	1.657	0.0165	-0.01
15.0	410	0.00	2.60	35.0	8.036	7.987	7.984	5.527	0.0151	1.988	0.1567	2.160	10.274	2.388	0.006	2.418	1.600	0.0165	-0.01
15.0	410	0.00	2.80	35.0	8.028	7.980	7.977	5.526	0.0151	1.990	0.1560	2.161	10.274	2.388	0.006	2.329	1.545	0.0165	-0.01
15.0	410	0.00	3.00	35.0	8.020	7.972	7.970	5.525	0.0151	1.991	0.1553	2.161	10.274	2.389	0.006	2.244	1.492	0.0165	-0.01
15.0	410	0.00	3.20	35.0	8.012	7.965	7.963	5.524	0.0151	1.993	0.1546	2.162	10.274	2.389	0.006	2.163	1.441	0.0165	-0.01
15.0	410	0.00	3.40	35.0	8.004	7.957	7.956	5.523	0.0151	1.994	0.1539	2.163	10.275	2.389	0.005	2.084	1.392	0.0165	-0.01
15.0	410	0.00	3.60	35.0	7.996	7.950	7.949	5.523	0.0151	1.996	0.1532	2.164	10.275	2.390	0.005	2.009	1.345	0.0165	-0.01
15.0	410	0.00	3.80	35.0	7.988	7.943	7.942	5.522	0.0151	1.997	0.1525	2.165	10.275	2.390	0.005	1.937	1.300	0.0165	-0.01
15.0	410	0.00	4.00	35.0	7.980	7.935	7.935	5.522	0.0151	1.999	0.1518	2.165	10.275	2.390	0.005	1.867	1.256	0.0165	-0.01

