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 foun elesewhere in this web-site, user friendly for experts and amateur enthusiasts alike.

Breathe in, breathe out. Let as deal now with the main gas exchange in earth oceans; like a giant lung, oceans absorb vast amounts of carbon dioxide (CO_2) from the atmosphere, and release it once again as cold water currents reach warmer areas of the globe. Indeed, CO_2 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 CO_2, 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.

2. Chemical Composition and Imbalance

Let's explore the mean composition of seawater in greater detail: summing up all the positive charges (Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}) one obtains 605.85 mmol/Kg of solution. Carrying out the same operation for negative charges (Cl^-, Br^-, F^-, SO_4^{2-}) 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 HCO_3^-, to a minor extent OH^- and finally, to a far lesser extent, CO_3^{2-}. The last three ions all react

with atmospheric CO_2, 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 HCO_3^- ions and also some CO_3^{2-}.

This has enormous repercussions on the equilibrium of CO_2 between the atmosphere and oceans. Compared to the atmosphere, which contains around 850 Gt (gigatons) of carbon (in the form of CO_2), the oceans hold 38,000 Gt of carbon. That's nearly 45 times more.

So when we talk about CO_2 ppm in the atmosphere that is only the "top of the iceberg"! CO_2 dissolves in seawater like O_2 and N_2. However, being a reactive gas, there is an almost immediate reaction with the water itself (N_2 and O_2 do not) yielding HCO_3^- and CO_3^{2-}. After completion of these reactions, yet a third slowly takes place (one which is nearly always disregarded): the formation of solid calcium carbonate, $CaCO_3$.

Spectator Ions					
Cation	$mol \cdot kg^{-1}$	$g \cdot kg^{-1}$	Anion	$mol \cdot kg^{-1}$	$g \cdot kg^{-1}$
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			
$\Sigma+$	0.60565	12.8864	$\Sigma-$	0.60325	22.1333
			$\Delta charge$ = 0.00240+		
			$\Sigma\ g \cdot kg^{-1}$ = 35.0197		
Reactive Ions and Molecules					
H_2CO_3	←→	HCO_3^-	←→	CO_3^{2-}	
$B(OH)_3$	←→	$B(OH)_4^-$			
$2 \cdot H_2O$	←→	H_3O^+	←→	OH^-	

Table 1 Seawater composition: spectator ions and reactive species

In chemistry, this is known as precipitation. $CaCO_3$ 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, CO_2 removed from the atmosphere will eventually form limestone.

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 CO_2. 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 CO_2 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.