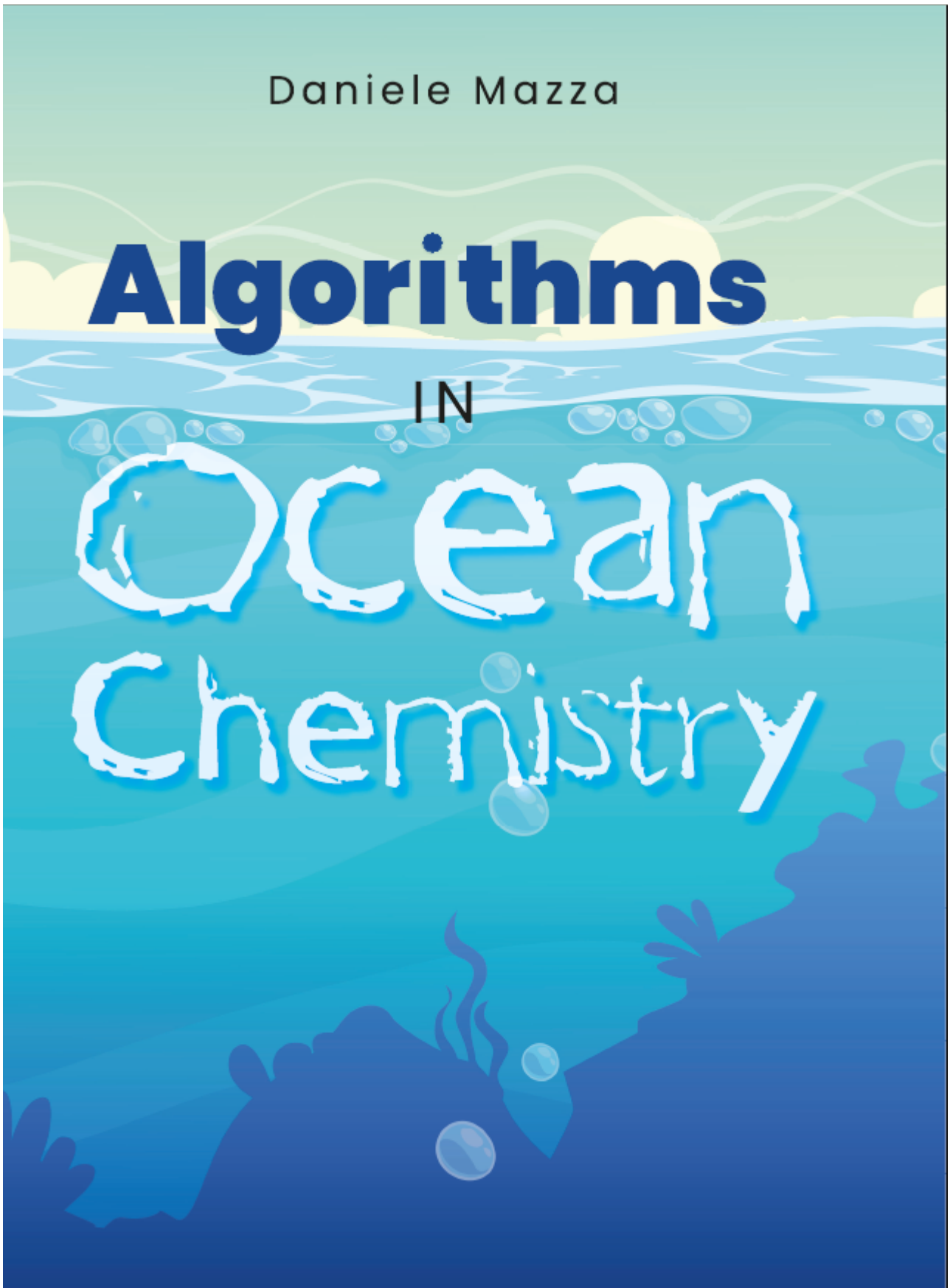


Daniele Mazza

Algorithms

IN

Ocean Chemistry



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Current research interests have shifted to environmental and climatic issues, in particular to ocean chemistry and CO₂ equilibria in seawater.

Reference web sites are:

www.oceanchemistry.info

www.molecularmodels.eu

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Daniele Mazza

Algorithms in Ocean Chemistry

The ocean as seen by a Chemist: algorithms for unlocking
the mysteries within

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Author | Daniele Mazza

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FOREWARD

For at least a decade, Chemistry has been described by the mass media as a wretched science responsible for the pollution of our planet and food, knowingly confusing the responsibilities of man with those of Science! On the contrary, Chemistry is the Science that par excellence enables man to understand life itself. What would the science of food be without well-grounded chemical bases, for example? Little more than light reading matter! In his thesis, Professor Mazza gives a demonstration of the power of Chemistry by applying it with originality to a system that is as complex as it is fundamental for the planet and human life itself. The reader is presented with an algorithm for calculating chemical equilibria that are occurring in our ocean waters as we speak, with surprising results, like for example the calculation of the anthropogenic CO₂ uptake by oceans or the effect of this on the supersaturation of calcium carbonate.

It is highly readable, enabling even the "non-specialist" to get to the end without strenuous reasoning or the need for any particular insight!

The ocean seen by a chemist proves to be a new missing piece (thus far) for unlocking the mysteries contained within.

Prof. Francesco Marino, Politecnico di Torino, former Professor of Materials Engineering

PREFACE

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.

In this book, the appropriate algorithms for chemical equilibria in seawater are proposed in a plain and simple basic language that's ready for use, or even modification, by the reader. There is no need for advanced math or programming expertise. Equilibria are solved by iterative procedures that require no differential calculus, and instructions are given on how to access executable codes from the Ocean Chemistry website (www.oceanchemistry.info). There is even an introduction to basic chemistry calculations in solutions in the first three chapters, thereby making the manual completely user friendly for experts and amateur enthusiasts alike.

CHAPTER 1 - Introduction and Methods

1.1 Introduction

Breathe in, breathe out. 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.

1.2 Chemical Composition and Reactivity

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 1.1). 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, CaCO_3 .

Spectator Ions					
Cation	$\text{mol} \cdot \text{kg}^{-1}$	$\text{g} \cdot \text{kg}^{-1}$	Anion	$\text{mol} \cdot \text{kg}^{-1}$	$\text{g} \cdot \text{kg}^{-1}$
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
			$\Delta \text{charge} = 0.00240+$		
			$\Sigma \text{ g} \cdot \text{kg}^{-1} = 35.0197$		
Reactive Ions and Molecules					
H_2CO_3	\leftrightarrow	HCO_3^-	\leftrightarrow	CO_3^{2-}	
$\text{B}(\text{OH})_3$	\leftrightarrow	$\text{B}(\text{OH})_4^-$			
$2 \cdot \text{H}_2\text{O}$	\leftrightarrow	H_3O^+	\leftrightarrow	OH^-	

Table 1.1 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.

1.3 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, this handbook offers simple routines with clearly described codes 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, which are also present on my website, can be downloaded and modified. The aim of this book 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 computer codes just a few hundred 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.

Before tackling seawater reactions, some introductory concepts need to be clarified, like how a chemical reaction evolves in time (kinetic systems) and how one or multiple simultaneous reactions can reach a state of equilibrium (equilibrium calculations). Instead of using the classical set of differential equations which describe the time-evolution of the kinetic systems, a computer aided, iterative procedure will be applied. Using the same logical approach, simultaneous equilibria will be solved by iterative procedures, rather than through a complex mathematical approach. The routines employ simple, basic language that's easy to use, whether directly or transferred into other languages. The specific basic language is JustBASIC, and it can be downloaded for free at www.justbasic.com. I am aware that much more sophisticated languages exist, but the performances of JustBASIC are perfectly aligned with the needs and difficulty level of the algorithms in this book.

CHAPTER 2 - Kinetic Systems

2.1 How a Reaction Evolves in Time

Chemical reactions are processes in which a substance or substances (known as reactants) are transformed into other products. When this change occurs directly, providing a complete description of the reaction mechanism presents few difficulties. However, complex processes in which the substances undergo a series of stepwise changes (each constituting a reaction in its own right) are much more common.

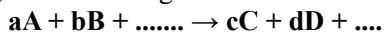
A simple case of the above is a single-step irreversible reaction, in which the products cannot be converted back to the original reactants. In this case, the rate of forward reaction decreases until all the reagents have been consumed, and the reaction terminates.

On the contrary, in a single-step reversible reaction, the apparent rate of forward reaction will decrease in line with the accumulation of reaction products until a state of dynamic equilibrium is finally established. At equilibrium, the forward and backward reactions proceed at equal rates.

Generally speaking, model reactions are set up and the appropriate differential equations recorded. The equations are then integrated so as to arrive at an expression relating well established thermodynamic parameters of the reactions (like activation energy, equilibrium constants) to concentrations that vary with time. The approach (excluding elementary simple reactions) is cumbersome and requires a good command of differential-calculus knowledge. Here, much simpler iterative procedures are used, without the need for integration.

Approximate solutions can often be found by using some simplifying assumptions. In this way, the model can be used as a basis to describe the process. Quite often, with a tiny increase in programming efforts and further refinement, and the elimination of approximation, considerable modification and improvements can be achieved.

In kinetics, the parameters of interest are the quantities of reactants and products, and their rate of change. Starting with a single irreversible reaction, expressions for reactants are given a negative sign as the reactants are used up during a reaction. Product amounts increase and their rate of change is therefore positive. As they are not constants, the rates are written as differentials. Thus, in terms of a general reaction



The reaction rates for the individual components are:

$$r1 = -1/a \cdot d[A]/dt$$

$$r2 = -1/b \cdot d[B]/dt$$

$$r3 = +1/c \cdot d[C]/dt$$

$$r4 = +1/d \cdot d[D]/dt$$

a,b,c,d are the so-called stoichiometric coefficients, necessary to balance the reactants and products. Their inverses divide the prime derivative of concentrations, so that $r1 = r2 = r3 = r4 = R$ (overall rate of the reaction)

The square brackets denote concentrations in moles per liter, symbolised M. On the contrary, in seawater calculations, concentrations are given in moles per kg, thereby avoiding variances due to increases in water pressure and a resulting decrease in volume (in the depth of the oceans).

In addition, unless otherwise indicated only closed, homogeneous systems are considered, in which there is no gain or loss of material during the reaction. Reactions are considered to proceed isothermally, so that temperature can be treated as an independent variable.

The rate (R) of a reaction at a fixed temperature is proportional to the concentration of reactants as can be seen in the following form

$$R = r_1 = r_2 = r_3 = r_4 = k([A]^\alpha \cdot [B]^\beta) \quad (2.1)$$

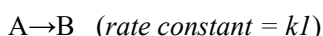
The proportionality constant k in 2.1 is called the rate constant. The k unit can be deduced on examination of the rate expression; it has dimensions of (concentration)⁽¹⁻ⁿ⁾•(time)⁻¹.

The sum of all the exponents of the concentrations, $n = \alpha + \beta + \dots$ is the overall order of reaction, while α is the order of reaction with respect to A, and β is the order of reaction with respect to B, and so on.

In the case of an irreversible reaction, the reaction order for each reacting compound should be determined experimentally since it cannot be predicted from the equations describing the reaction. The exponents may be positive integers (as is usual for simple reactions) or fractions (when a reaction occurs through different intermediate steps). Apart from simple reactions, they do not have to be equal to the stoichiometric coefficients of the reactant in the net reaction. We shall see that this does not apply to reversible reactions; when they reach equilibrium the stoichiometric coefficients are equal to the reaction order for each component.

Up to now we have considered irreversible reactions. In the following chapter we shall see that reversible reactions occur as well. In such cases, one must also consider the transformation from reactants to products.

2.2 First-Order Reactions



The rate of a first-order reaction is proportional to the first power of the concentration of only one reactant. This means that the amount $d[A]$, which undergoes chemical change in the short time interval dt , depends only on the amount of A present at that instant, assuming that there is no change in volume, temperature, or any other factors that could affect the reaction.

The rate expression which describes a first-order reaction is

$$-d[A]/dt = k_1 \cdot [A] \quad (2.2)$$

As can be seen in chemistry textbooks, the equation above can be rearranged and integrated, introducing $[A]_0$ as the initial quantity of the reacting substance A in a given volume and x as the amount which reacts in time t . It follows that $([A]_0 - x)$ is the amount of A remaining after time t . The exponential form of the integrated equation is

$$[A] = [A]_0 \cdot (1 - \exp(-k_1 \cdot t)) \quad (2.3)$$

This analytical expression is shown here merely for comparison, but all the subsequent reactions will be solved in this handbook using iterative computer procedures. The code listed below is all that is needed to solve and display the variations of concentrations during

a first-order irreversible reaction.

The iterative procedure consists of a for..next cycle in the program. This is repeated until the reaction reaches its end point. In the example, 100 cycles are sufficient. Code lines, or parts thereof beginning with the symbol (') are comments.

```
dim A(100),B(100)
A(0) = 60 ' initial concentration of A
B(0) = 0 ' initial concentration of B
k1 = 0.1 ' reaction constant
t1 = 100 ' final time
for t = 1 to t1 ' reaction takes place
  A(t) = A(t-1) - A(t-1)*k1
  B(t) = B(t-1) + A(t-1)*k1
next t
call DrawScreen
```

The 'DrawScreen' routine is used for graphical presentation of the results and is listed in the appendix. Its graphical output is shown in Fig.2.1

The initial condition of this simulation is $[A]_0 = 60 \text{ mMol/L}$, $k_1 = 0.1 \text{ sec}^{-1}$, time in seconds from 0 to 100 and a time-step of 1 second.

The concentration of A exponentially decreases to zero, whilst that of B rises to 60. All the values are stored in two matrices to be used for the plot (or other purposes).

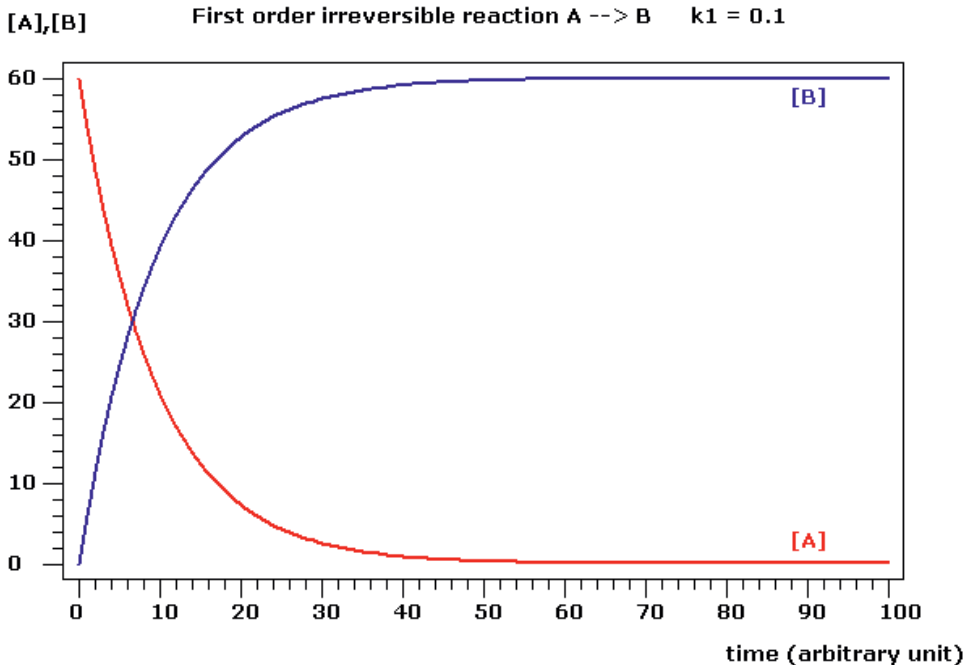


Fig.2.1 First-order irreversible reaction and plot of the A and B concentration versus time.

2.3 Second-Order Reactions

When two reactants, A and B, react in such a way that the reaction rate is proportional to the first power of the product of their respective concentrations, the compounds are said to undergo a second-order reaction.

If $[A]_0$ and $[B]_0$ designate the initial quantities of the two reacting chemicals A and B, and x is the number of moles of A or B which react in a given time interval t , then the rate of formation of product C can be described by the following mechanism

<i>time</i>	<i>A</i>	<i>B</i>	<i>C</i>
<i>0</i>	$[A]_0$	$[B]_0$	<i>0</i>
<i>t</i>	$[A]_0 - x$	$[B]_0 - x$	<i>x</i>

and by the following differential equation:

$$dx/dt = k1 \cdot ([A]_0 - x) \cdot ([B]_0 - x) \quad (2.4)$$

This differential equation can be integrated, but in this handbook it will be solved by a much simpler iterative procedure. The results in Fig.2.2 show that after a certain time the concentrations reach a stable value (or more precisely asymptotically). One of the two reactants (in our simulation B) reaches zero concentration. Consequently, the reaction can no longer evolve and comes to a halt.

```
dim A(100),B(100),C(100)
  A(0) = 60 ' initial concentration of A
  B(0) = 40 ' initial concentration of B
  C(0) = 0  ' initial concentration of C
  k1 = 0.003 ' reaction constant
  t1 = 100 ' final time
for t = 1 to t1 ' reactions take place
  A(t) = A(t-1) - A(t-1)*B(t-1)*k1
  B(t) = B(t-1) - A(t-1)*B(t-1)*k1
  C(t) = C(t-1) + A(t-1)*B(t-1)*k1
next t
call DrawScreen
```

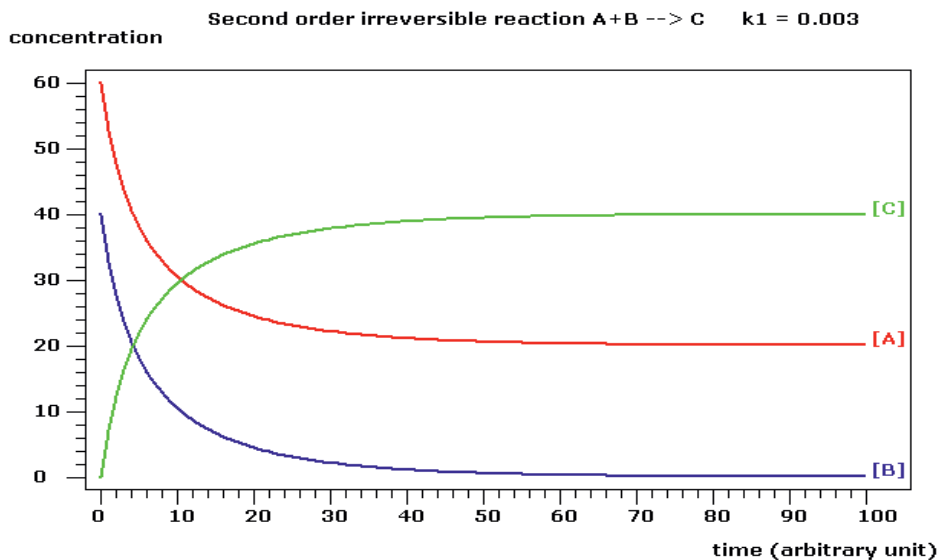


Fig.2.2 Second-order irreversible reaction.

2.4 Consecutive Irreversible Reactions



The mechanism implies a series of three, four or even more consecutive reactions, the products of the first being simultaneously the reagents of the second, and so on.

The mathematical treatment is really cumbersome, but as usual a simple iterative procedure can help us. Let's see the table first:

<i>time</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
0	$[A]_0$	$[B]_0$	$[C]_0$	$[D]_0$
<i>t</i>	$[A]_0 - x$	$[B]_0 + x - y$	$[C]_0 + y - z$	$[D]_0 + z$

where x is the amount of A transformed in B after a certain time t , y the amount of B transformed in C and z of C to D.

The corresponding differential equations are

$$\begin{aligned} - \frac{d[A]}{dt} &= k_1 \cdot [A] \\ + \frac{d[B]}{dt} &= k_1 \cdot [A] - k_2 \cdot [B] \\ + \frac{d[C]}{dt} &= k_2 \cdot [B] - k_3 \cdot [C] \\ + \frac{d[D]}{dt} &= k_3 \cdot [C] \end{aligned}$$

The code is here below

```
dim A(100),B(100),C(100),D(100)
A(0) = 50 ' initial concentration of A
B(0) = 10 ' initial concentration of B
C(0) = 0 ' initial concentration of C
D(0) = 0 ' initial concentration of C
k1 = 0.08 ' reaction constant of reaction A-->B
```

```

k2 = 0.04 ' reaction constant of reaction B-->C
k3 = 0.08 ' reaction constant of reaction C-->D
t1 = 100 ' final time
for t = 1 to t1 ' reactions take place
  A(t) = A(t-1) - A(t-1)*k1
  B(t) = B(t-1) + A(t-1)*k1 - B(t-1)*k2
  C(t) = C(t-1) + B(t-1)*k2 - C(t-1)*k3
  D(t) = D(t-1) + C(t-1)*k3
next t
call DrawScreen

```

and the corresponding plot is in Fig.2.3

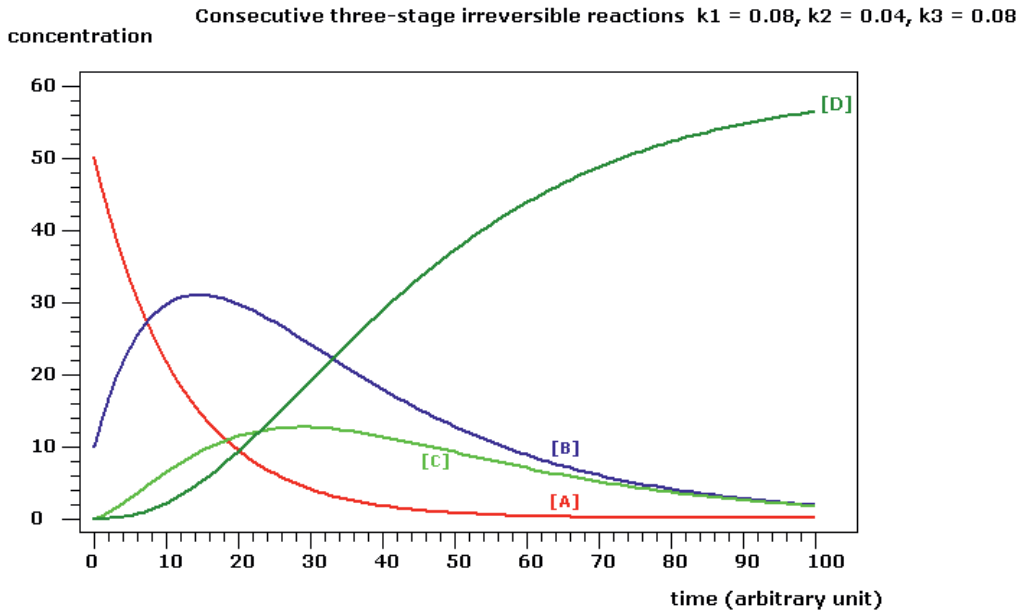


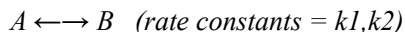
Fig.2.3 Consecutive irreversible reactions.

CHAPTER 3 - Reversible Equilibrium Reactions

3.1 From Kinetics to Equilibrium

Reversible reactions are those in which the products can be converted back to the original reactants. In a system of reversible reactions, the apparent rate of the forward reaction will decrease as the reaction products accumulate, until eventually a state of dynamic equilibrium is established. At equilibrium, the forward and backward reactions proceed at equal rates.

A first-order reversible reaction can be represented by this simple mechanism



where k_1 , k_2 rate constants refer to the direct (from left to right) and inverse reaction. The true rate of concentration change for either reactant is given by the difference in the rates in the opposite directions, each proportional to the concentration of the reacting compound. The differential equations for this mechanism are

$$-d[A]/dt = k_1 \cdot [A] - k_2 \cdot [B]$$

$$-d[B]/dt = k_2 \cdot [B] - k_1 \cdot [A]$$

Instead of finding a mathematical solution for these equations, the usual iterative procedure as described below will be used.

```
dim A(100),B(100)
A(0) = 40   ' initial concentration of A
B(0) = 10   ' initial concentration of B
k1 = 0.04  ' reaction constant of direct reaction
k2 = 0.02  ' reaction constant of inverse reaction
t1 = 100   ' final time
for t = 1 to t1 ' reactions take place
  A(t) = A(t-1) - A(t-1)*k1 + B(t-1)*k2
  B(t) = B(t-1) + A(t-1)*k1 - B(t-1)*k2
next t
call DrawScreen
```

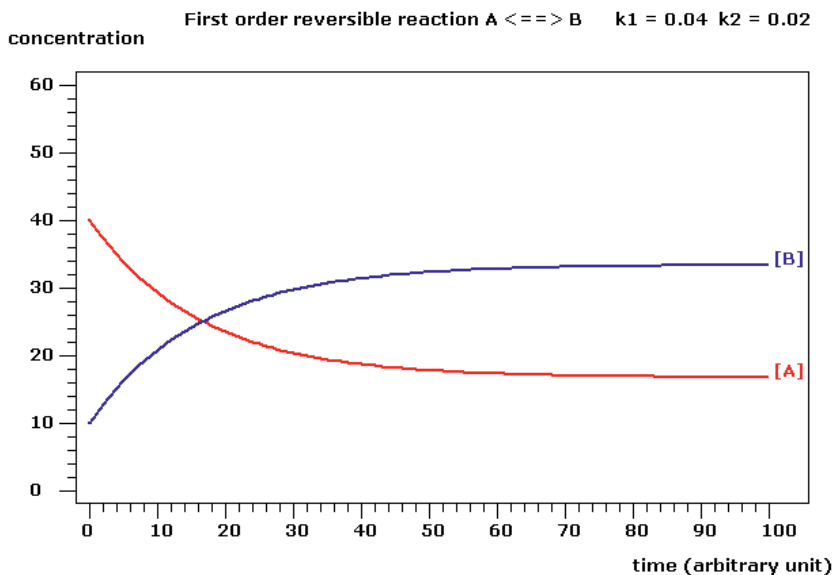


Fig.3.1 First-order irreversible reaction

When a reversible chemical reaction like the above reaches equilibrium, the rates of the forward (v_1) and reverse (v_2) reactions are exactly equal, and the net rate of reaction (V_{net}) is zero (Fig 3.1). Under these conditions $v_1 = v_2$, and seeing that $v_1 = k_1 \cdot [A]$, $v_2 = k_2 \cdot [B]$ one obtains:

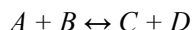
$$k_1 \cdot [A] = k_2 \cdot [B] \qquad k_1/k_2 = [B]/[A] = K_{eq} \quad (3.1)$$

If we are interested in the equilibrium concentrations, no matter how long it takes for the reaction to reach them, there is only one constant to be addressed, K_{eq} (*equilibrium constant*)

K_{eq} is the ratio between the two rate constants and, as it is independent from concentrations, only temperature affects it. By knowing the initial concentrations of reactants $[A]_0$ and $[B]_0$ and K_{eq} , we are always able to calculate the final (equilibrium) concentrations. This can be done mathematically by solving first, second or even third degree equations, or by iterative procedure, as shown in the following.

3.2 Reversible Reaction of Higher Order

Let's discuss this with a slightly more complex reversible reaction, with an order higher than one. For example, the reaction



As soon as the substances A and B start to react in the reaction vessel, they produce C and D with a rate that can be expressed as

$$r_1 = k_1 \cdot [A][B] \quad (3.2)$$

where each of the quantities in brackets is the molar concentration at a given time.

Being an equilibrium reaction, as soon as C and D are formed, they start to react together (unless removed from the reaction vessel). The rate of this inverse reaction will increase with C and D concentrations

$$r_2 = k_2 \cdot [C][D] \quad (3.3)$$

whilst the rate r_1 will decrease due to the shortage of A and B. At a certain time, the molar concentration of reactants and products will reach such a value that the rate of direct and inverse reaction will match, so we can write

$$r_1 = k_1 \cdot [A][B] = r_2 = k_2 \cdot [C][D]$$

It is a dynamic equilibrium, as it is the case overall in chemistry, during which the quantities of A and B that disappear are balanced by those obtained by C and D.

By transforming the above equation, one obtains

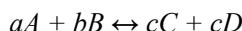
$$\frac{k_1}{k_2} = K_{eq} = \frac{[C] \cdot [D]}{[A] \cdot [B]} \quad (3.4)$$

where the constant K_{eq} is a new constant (the ratio of the forward and reverse rate constants) called the *equilibrium constant*. Each of the quantities in brackets is the *equilibrium* concentration of the substance shown. At any given temperature, the value of K_{eq} remains constant no matter whether you start with A and B, or C and D, and regardless of the proportions in which they are mixed. K_{eq} varies with temperature because k_1 , and k_2 vary with temperature, but not by exactly the same amount. This dependence on temperature is discussed at the end of this chapter.

3.3 Law of Mass Action

Equation 3.4 applies to *any* chemical reaction at equilibrium, no matter how many or how complicated the intermediate steps in going from reactants to products. It is worth stressing that as long as eq. xx-1 is valid, the concentrations therein are the equilibrium concentrations. Some reactions are very fast, so that equilibrium is reached after just a few seconds, others reach it after years or never.

If we consider the general case



where a,b,c,d indicate the stoichiometric coefficients, the equilibrium constant can be written as

$$K_{eq} = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b} \quad (3.5)$$

which is the general formulation of the law of mass action (Guldberg-Waage, 1864) that states: *in a chemical system at equilibrium and constant temperature, the ratio between the product of the concentrations of chemicals formed (each elevated to its stoichiometric coefficient) and that of the reagents is a constant value.*

It can be shown by thermodynamics that in the law of mass it is the use of coefficients that balances the reaction itself. They are not therefore to be confused with α, β coefficients of the reaction rate of an irreversible reaction.

The above 3.5 expression of the law of mass action is particularly useful in solution. However, it can also describe equilibrium between two or more phases, as will be shown in the following four cases:

3.3.1 In gaseous reactions concentrations are usually substituted by partial pressures, giving the expression

$$K_p = \frac{P(C)^c \cdot P(D)^d}{P(A)^a \cdot P(B)^b} \quad (3.6)$$

where P(A)...are the partial pressures (in atm.) of the reacting gases and it can be demonstrated that:

$$K_p = K_{eq}(RT)^{(c+d-a-b)} \quad (3.7)$$

R being the universal gas constant and T the absolute temperature.

3.3.2 In the equilibrium systems considered above, all the substances are in a homogeneous phase (liquid, gaseous). However, chemical reactions may also occur in heterogeneous systems, with two phases. Let's consider, as an example, a reaction between a solid (CaCO₃) and its decomposition products. The temperature reaction is 900°C



As an initial prediction, we can write

$$K_{p'} = \frac{P(\text{CaO}) \cdot P(\text{CO}_2)}{P(\text{CaCO}_3)} \quad (3.8)$$

but because vapour pressures of solids are very low, they can be disregarded, or more precisely, as they are constant values at a certain temperature they can be included in the equilibrium constant, thus obtaining a new K_p constant:

$$K_{p'} = a/b \cdot P(\text{CO}_2) \quad K_p = K_{p'} \cdot (b/a) = P(\text{CO}_2) \quad (3.9)$$

In summary: if heterogeneous equilibria concerns solids and gases, equilibrium expression only contains partial pressures of gases, each raised to the stoichiometric coefficients.

3.3.3 If we consider the solution of a sparingly soluble salt, for example CaCO₃, once it has formed a saturated solution, an equilibrium exists between the solid salt and its ions in solution, as in



For this heterogeneous equilibrium, the mass action law is applicable (where *sp* stands for solubility product)

$$K_{eq} = \frac{[\text{Ca}^{++}] \cdot [\text{CO}_3^{--}]}{[\text{CaCO}_3]} \quad (3.10)$$

As solids always have the same concentration, it is included in *K_{eq}*, thus obtaining

$$K_{sp} = [\text{Ca}^{++}] \cdot [\text{CO}_3^{--}]$$

For a general salt of composition M_mA_n ↔ mM^{b+} + nA^{a-} the solubility product will be expressed as

$$K_{sp} = [M^{b+}]^m \cdot [A^{a-}]^n \quad (3.11)$$

As an example, let's consider sodium phosphate $Mg_3(PO_4)_2$, which is present with a variable concentration in seawater. It has a very low solubility product, so as to be a nearly-insoluble salt:



3.3.4 Gas – liquid equilibria are also common. In ocean chemistry, one fundamental reaction is the dissolution of atmospheric carbon dioxide (CO_2) in water which, in the first instance, forms carbonic acid (H_2CO_3). The mass action law for the dissolution reaction $CO_2 + H_2O \leftrightarrow H_2CO_3$ states that

$$K_{eq} = \frac{[H_2CO_3]}{P(CO_2) \cdot [H_2O]} \quad (3.12)$$

However, molar concentration of water is constant (1000/18 in pure water) and is incorporated in K_{eq} . The partial pressure of carbon dioxide is expressed in atm in the S.I. System. The term $[H_2CO_3]$ comprises the concentration of CO_2 dissolved in water or $CO_2(aq)$ which is the first reaction product of gaseous CO_2 with water.

3.4 The Hydrogen Ion in Solution

Chemical reactions in aqueous solutions (including the chemistry of life processes) very often depend on the concentration of hydrogen ions (H^+) in the solution. As we shall see, we may deal with hydrogen ion concentrations which range from over 1 M to less than 10^{-14} M. Consequently, it is convenient to express these concentrations on a logarithmic basis; for this purpose the terms "pH" and "pOH," have been introduced. Hydrogen ion concentrations are represented by "pH" and hydroxide ion concentrations by "pOH", denoted by the relations:

$$\begin{aligned} \text{pH} &= -\log [H^+] \\ \text{pOH} &= -\log [OH^-] \end{aligned}$$

In keeping with this usage, we also use $pK_w = -\log K_w$
You may recall that $\log AB = \log A + \log B$, therefore $\text{pH} + \text{pOH} = \text{pK}_w = 14$

Water is a *weak* electrolyte, ionizing slightly and reversibly as $H_2O \leftrightarrow H^+ + OH^-$. The H^+ is hydrated, forming chiefly H_3O^+ ions. Just as we ignore the hydration of all the metal ions (for convenience in writing equations), we also often ignore the hydration of H^+ . We must always remember, however, that a bare proton (an H^+) can never exist in solution by itself.

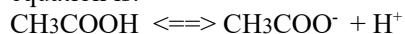
This dissociation reaction is always at equilibrium, with extremely rapid formation and recombination of H^+ and OH^- . Because it is always at equilibrium, the principles of chemical equilibrium discussed apply, and we can write the equilibrium constant expression. This equilibrium is of such importance that K bears the special subscript w. In pure water at 25.0°C, the concentration of H^+ is $1.0 \cdot 10^{-7}$ M, that is, $[H^+] = 1.0 \cdot 10^{-7}$ M. Because the dissociation provides equal numbers of H^+ and OH^- ions, it also follows that in pure water $[OH^-] = 1.0 \cdot 10^{-7}$ M. Knowing the equilibrium concentrations, we can evaluate K_w numerically: $K_w = 1.0 \cdot 10^{-7} \times 1.0 \cdot 10^{-7} = 1.0 \cdot 10^{-14}$ (mol/L)²

This constant applies to *all* water solutions. It follows that if we add acid to water, and thereby increasing the $[H^+]$, there must be a corresponding decrease in $[OH^-]$, and vice versa. HCl is a strong acid that completely dissociates in water.

This means that in a 0.10 M HCl solution $[H^+] = 0.10$ M. Because $[H^+][OH^-] = 1.0 \cdot 10^{-14}$, it follows that $[OH^-] = 1.0 \cdot 10^{-14}$ M, one millionth of the concentration in pure water. NaOH is a strong base, which is also completely dissociated in water. A 0.10 M NaOH solution will have $[OH^-] = 0.10$ M, and an associated $[H^+]$ that is $1.0 \cdot 10^{-13}$ M.

3.5 Strong and Weak Electrolytes

When we put a strong electrolyte (such as HCl) into solution, essentially all the molecules dissociate to ions; in this case, H^+ and Cl^- . But when we put a weak electrolyte into solution, such as acetic acid (CH_3COOH), only a small fraction of the molecules dissociate. The equation is:



Because this reaction is at equilibrium, we can apply the mathematical expression

$$K_{diss} = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

The equilibrium constant for the ionization of a weak electrolyte is usually designated as K_{diss} , which we call the ionization constant. Ionization constants are determined by experimental measurements of equilibrium concentrations. For example, to determine K_{diss} for acetic acid, we prepare a solution of known concentration and, by any of several methods, measure the H^+ concentration or the pH. The method most widely used today is measuring with a pH meter, which gives a direct dial reading for the pH.

However, in practical calculations on weak and very weak acids, self-dissociation of water must be considered, and we thereby obtain a system with two equations and two unknowns.

$$K_{diss} = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$K_w = [H^+][OH^-] = 1.0 \cdot 10^{-14} \text{ at } 25^\circ C$$

The corresponding iterative procedure for hydrofluoric acid (a simple monoprotic acid found in the composition of seawater) is listed and commented on in the appendix (code001.bas).

3.6 Biprotic Weak Acids

In some cases, we find two or even three hydrogen atoms in the same molecule that are able to dissociate in aqueous solution. An important example in seawater is carbonic acid, H_2CO_3 , which originates from CO_2 (aq), i.e. the dissolved form of CO_2 (gas). In this dissolved form, the water dipoles interact with the charges in the CO_2 molecule without forming new chemical bonds. The concentration of H_2CO_3 is, however, much smaller (about 0.3%) than that of CO_2 (aq). The sum of the two electrically neutral forms, true carbonic acid H_2CO_3 and aqueous carbon dioxide, which are chemically inseparable, is usually denoted as $H_2CO_3^*$ or simply H_2CO_3 .

In the computer code listed in the appendix (code 002.bas), carbonic acid is used as an example. Three equilibria (including water self-dissociation) are solved simultaneously by means of an iterative procedure. The dissociation constants K_{a1} and K_{a2} refer to pure water

at 25°C, and given that the reaction vessel is deemed as closed, it is not necessary to consider CO₂ partial pressure at this stage.

The code is self-explanatory to some extent. Moreover, the program structure can simulate the addition of a strong base, as in NaOH, the example having a concentration of 0.03 M (mol/L).

3.7 Triprotic Acids

As an example of triprotic acid we shall consider phosphoric acid, being a constituent of seawater. It dissociates according to the following (the *Keq* refers to pure water at 25°).

The three dissociation constants of phosphoric acid, $Ka1 = 7.5 \cdot 10^{-3}$ (1st dissociation constant), $Ka2 = 6.2 \cdot 10^{-3}$ (2nd dissociation constant) and $Ka3 = 4.4 \cdot 10^{-13}$ (3rd dissociation constant) and $Kw = 1 \cdot 10^{-14}$ (ionic product of water) refer to pure water and 25°C.

In the simulation, the possible addition of a strong base (NaOH) and a strong acid (HCl) is considered, both assumed to be completely dissociated and therefore regarded as ions, as can be seen in the code003.bas listed in the appendix.

3.8 Biprotic Acid with Salt/Hydroxide Precipitation

In an even more complex system of reactions we deal with a biprotic acid (carbonic acid again) which interacts with calcium ions (Ca⁺⁺) in solution giving (if the solution becomes supersaturated) a white precipitate of CaCO₃. Moreover, magnesium ions (Mg⁺⁺), whose concentration in seawater is five times greater than calcium ions, may form solid magnesium hydroxide (in this case). The latter is a hydroxide with a very low solubility ($Ksp = 8.9 \cdot 10^{-12}$). Programs can simulate the addition to the reaction vessel of many chemicals, like magnesium and calcium chloride, sodium carbonate and bicarbonate, sodium hydroxide (strong base) and chloridric acid (a strong acid).

The different equilibria are of course solved with iterative procedures, in which pH values are varied in certain ranges, each time with a smaller step (the cycle uses the 'j' variable). The reaction container is deemed closed with respect to CO₂ exchange with the surrounding atmosphere. Due to the many reactants, the code list takes up some pages, and it is listed in the appendix as code004.bas. In the example the starting composition for simulation is as follows (values in mol/liter):

```
Na2CO3 = 0.2   ' Soluble salt completely dissociated in Na+ and CO3-- ions
NaHCO3 = 0.1   ' Soluble salt completely dissociated in Na+ and HCO3- ions
CaCO3   = 0.0   ' Sparingly soluble salt. Solubility product Ksp needed
NaOH    = 0.1   ' Strong electrolyte, completely dissociated in Na+ and OH- ions
HCl     = 0.4   ' Strong electrolyte, completely dissociated in H+ and Cl- ions
CaCl2   = 0.6   ' Soluble salt completely dissociated in Ca++ and Cl- ions
MgCl2   = 0.2   ' Soluble salt completely dissociated in Mg++ and Cl- ions
H2CO3   = 0.005 ' Hydrated CO2
```

CHAPTER 4 – From Pure Water to Concentrated Salt Solutions

4.1 Ionic Strength and Ionic Activity

Up to now we have considered ions dissolved in pure water, but seawater contains quantities 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).

$$I = 0.5 * \sum c_i * z_i^2$$

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

$$I = 0.5 * ([Na^+] * 1 + [Cl^-] * 1)$$

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)

$$I = 19.924 / (1000 - 1.005 * S)$$

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 $\gamma(A)$:

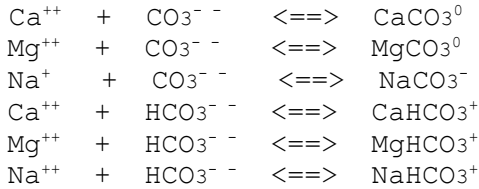
$$\{A\} = \gamma(A) * [A]$$

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 γ (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:



The 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.

Considering the effect of ion pairing on activities, it is useful to talk about 'free' and 'total' activity coefficients. If no ion pairing occurs, like in dilute solutions, free and total activity coefficients coincide. In seawater however, the total activity coefficient can be dramatically lower than the free one, as many of the bivalent carbonate ions form ion pairs.

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

$$\log(\gamma_f) = -A z^2 \sqrt{I} \quad \text{valid for } I < 0.005$$

or to the Davies equation

$$\log(\gamma_f) = -A z^2 \left(\sqrt{I}/(\sqrt{I} + 1) - 0.2 * I \right) \quad \text{valid for } I < 0.5$$

with $A = 1.82 * 10^6 (\epsilon T)^{-1.5}$, 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 in this handbook 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.

Before going any further, three topics must be clarified, pH, salinity and density.

4.2 Different pH Scales

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 H_2CO_3) 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 of hydrogen ions $\text{pH} = -\log_{(10)} a(\text{H}^+)$

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:

$$\text{pHF} = -\log_{(10)}[\text{H}^+]_{\text{F}}$$

where $[\text{H}^+]_{\text{F}}$ stands for the free hydrogen ion concentration, including hydrated forms, like H_3O^+ and H_9O_4^+ (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 H_3O^+ . This in turn is hydrogen bonded to three other water molecules to form an H_9O_4^+ 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.

$$\text{pHT} = -\log_{(10)}[\text{H}^+]_{\text{T}} \quad \text{where} \quad [\text{H}^+]_{\text{T}} = [\text{H}^+]_{\text{F}} + [\text{HSO}_4^-]$$

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^- 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.

$[H^+]_T = [H^+]_F \cdot (1 + [SO_4^{--}] / Ka_1)$
$[H^+]_{sw} = [H^+]_F \cdot (1 + [SO_4^{--}] / Ka_1 + [F^-] / Ka_2)$
$[H^+]_{sw} = [H^+]_T \cdot (1 + [F^-] / Ka_2)$
$pH_T = pH_F - \log_{10}(1 + [SO_4^{--}] / Ka_1)$
$pH_{sw} = pH_F - \log_{10}(1 + [SO_4^{--}] / Ka_1 + [F^-] / Ka_2)$
$pH_{sw} = pH_T - \log_{10}(1 + [F^-] / Ka_2)$

If $Ka_1 \approx 2.1 \cdot 10^{-2}$ and $[SO_4^{--}] = 2.8 \cdot 10^{-2}$ 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.

4.3 Salinity

Seawater composition varies widely, although the relative ratios of dissolved species are nearly constant. So in standard simulations only salinity can vary, while the relative composition of seawater remains constant. Salinity is expressed in grams of dissolved species per kg of solution. The values are taken from DOE 1994 (with borates).

[Cl-]	= 0.54586	*	S/35	mol/kg (solution)
[Na+]	= 0.46906	*	S/35	mol/kg (solution)
[Mg2+]	= 0.05282	*	S/35	mol/kg (solution)
[Ca2+]	= 0.01028	*	S/35	mol/kg (solution)
[SO4--]	= 0.02824	*	S/35	mol/kg (solution)
[K+]	= 0.01021	*	S/35	mol/kg (solution)
[Br-]	= 0.00084	*	S/35	mol/kg (solution)
[Sr2+]	= 0.00009	*	S/35	mol/kg (solution)
[F-]	= 0.00007	*	S/35	mol/kg (solution)
[Btot]	= 0.00042	*	S/35	{B(OH)3 + B(OH)4-} mol/kg (solution)

For those who enjoy modifying code, rewriting that part of the code with other compositions might work, if the composition is not too far from electrical neutrality. Indeed, the neutrality is always assured by the addition of hydrogen (H^+) or hydroxyl (OH^-) ions, which in turn changes the pH. But, if the initial salt composition is very unbalanced, the resulting pH may be outside 0-14 limits, causing the program to crash.

The standard seawater composition as listed may be supersaturated with respect to calcite or aragonite formation. Calcite is the less soluble form of calcium carbonate, so theoretically it

should be the first to precipitate. Coral reef is however made up of aragonite, a fact that should be considered.

4.4 Density

The calculation of the density of seawater requires a number of steps (Millero and Poisson, 1981; Gill, 1982; Zeebe, 2001). In the following, the density of seawater (*roSTP*) is expressed in kg m^{-3} , or g dm^{-3}) and is calculated in function of temperature (in $^{\circ}\text{C}$), pressure *p*(in bars) and salinity.

First the density of pure water (*roPw*) is calculated as a function of temperature with a fifth degree polynomial. (see code below).

As a second step, the density of seawater at 1 bar (i.e. $P = 0$) is calculated as a function of salinity starting from *roPw* and employing a second order mixed polynomial, whose first two coefficients depend on temperature according to a fourth and second degree polynomial.

As a third and final step, the density of seawater according to pressure *P* (*roSTP*) is given using the secant bulk modulus *Ksb3*, which in turn derives from *Ksb2* and *Ksb1*, as shown in the code below.

Care must be taken for two reasons. First, in ocean chemistry, the unit measure for pressure is the 'bar', which is similar but not equal to atmosphere: $1.000 \text{ atm} = 1.01325 \text{ bar}$. For those who like S.I. Units, $1 \text{ atm} = 101325 \text{ Pa}$ (pascal) and $1 \text{ bar} = 0.1 \text{ MPa}$ (megapascal). Second, the algorithms employed only assume the effect of water column pressure, so on the sea surface itself the pressure is assumed to be zero. This is unrealistic, as it neglects air pressure being nearly equal to 1 atm at sea level, but should be used as the empiric algorithms assume so. The code is listed in the appendix (code006.bas).

4.5 Concentration Units

In ocean chemistry, the use of a non-standard concentration scale is widely diffused, the so-called gravimetric unit. It is expressed by the moles (mol) of a solute per kg of solution. It differs therefore from molarity (used in most chemistry, being the number of moles per litre of solution) and from molality (number of moles per kg of solvent, here water). If not otherwise stated, the gravimetric scale will be used here.

Knowing the composition of seawater, changing from the gravimetric scale to molality involves the following steps:

- 1- Calculation of the total mass of the substances in 1 kg of solution, on the basis of their atomic weights and their concentration.
- 2- Calculation of the mass of water in 1 kg of solution, the difference being $1.000 - \Sigma \text{mass of solutes}$.
- 3- The gravimetric concentration of each ion or substance is divided by the above mass of water to give the corresponding molality.

Knowing the density of seawater, and changing from the gravimetric scale to molarity involves the following steps:

- 1- Calculation of the density of the seawater solution, according to the procedure () expressing the result in kg/liter.
- 2- The gravimetric concentration of each ion or substance is multiplied by the above density to give the corresponding molarity.

CHAPTER 5 – Effect of Temperature and Salinity on Equilibrium Constants

5.1 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, f_{CO_2} , 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), requiring two virial coefficients B and d , as explained here in the following (from Zeebe 2001)

$$f_{\text{CO}_2} = p_{\text{CO}_2} \cdot \exp\left(p \frac{B + 2d}{RT}\right)$$

where f_{CO_2} and p_{CO_2} are in μatm , the total pressure, P , is in Pa (1 atm = 101325 Pa), the first virial coefficient of CO₂, B , and the parameter d are in $\text{m}^3 \text{mol}^{-1}$, $R = 8.314 \text{ J K}^{-1}$ is the gas constant and the absolute temperature, T , in Kelvin.

B has been determined by Weiss, (1974):

$$B(\text{m}^3 \text{mol}^{-1}) = \left(-1636.75 + 12.0408 T - 3.27957 \cdot 10^{-2} T^2 + 3.16528 \cdot 10^{-5} T^3 \right) 10^{-6}.$$

The parameter d is the cross virial coefficient,

$$d (\text{m}^3 \text{mol}^{-1}) = (57.7 - 0.118 \cdot T) \cdot 10^{-6}$$

Here below is the simple code needed to calculate fugacity from ppm (parts per million) of CO₂.

```
T = 25 + 275 ' temperature in K
R = 8.314
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)
H2CO3 = K0*fCO2*1e-6
```

The last line of the code shows how the concentration of H₂CO₃^{*} (which comprises the true acid form H₂CO₃ and hydrated CO₂) can be calculated, knowing the K₀ value, as shown in the next topic.

5.2 The Hydration of Carbon Dioxide (K_0) $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$

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

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

$$\begin{aligned} \ln K_0 &= 9345.17/T - 60.2409 + 23.3585 \ln(T/100) \\ &+ S \left[0.023517 - 0.00023656 T + 0.0047036 (T/100)^2 \right] \end{aligned}$$

$f(\text{CO}_2)$ is the fugacity of CO_2 , which is numerically very similar to CO_2 partial pressure in milli atm and therefore corresponds to CO_2 ppm in dry air by the Dalton law. For further insight see Section 5.1. Because we have to calculate various combinations of equilibrium relationships, we have to use the consistent set of constants provided by DOE (1994) which is based on measurements in artificial seawater.

5.3 K_w , the Ionic Water Product due to $\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ Reaction.

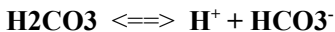
$$K_w = [\text{H}^+] \cdot [\text{OH}^-]$$

As explained in Section 3.4, 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).

$$\begin{aligned} \ln K_w &= 148.96502 - 13847.26/T - 23.6521 \ln T \\ &+ [118.67/T - 5.977 + 1.0495 \ln T] S^{1/2} - 0.01615 S \end{aligned}$$

$$\begin{aligned} \text{Ln}K_w &= 148.96502 - 13847.26/T - 23.6521 \cdot \log(T) + (118.67/T - 5.977 + \\ &1.0495 \cdot \log(T)) \cdot S^{0.5} - 0.01615 \cdot S \\ K_w &= \exp(\text{Ln}K_w) \cdot [\text{H}^+]_{\text{Total scale}} \end{aligned}$$

5.4 The First Dissociation Constant of Carbon Dioxide (K_1)



$$K_1 = [\text{HCO}_3^-] \cdot [\text{H}^+] / [\text{H}_2\text{CO}_3^*]$$

$$\begin{aligned} \ln K_1 &= 2.83655 - 2307.1266/T - 1.5529413 \ln T \\ &- (0.207608410 + 4.0484/T) \sqrt{S} \\ &+ 0.0846834 S - 0.00654208 S^{3/2} + \ln(1 - 0.001005 S) \end{aligned}$$

$$\begin{aligned} \text{Ln}K_1 &= 2.83655 - 2307.1266/T - 1.5529413 \cdot \log(T) - (4.0484/T + \\ &0.20760841) \cdot S^{0.5} + 0.0846834 \cdot S - 0.00654208 \cdot S^{1.5} + \log(1 - \\ &0.001005 \cdot S) : K_1 = \exp(\text{Ln}K_1) \cdot [\text{H}^+] = [\text{H}^+]_{\text{Total scale}} \end{aligned}$$

5.5 The Second Dissociation Constant of Carbon Dioxide (K₂) $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{--}$

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

$$\begin{aligned} \ln K_2 = & -9.226508 - 3351.6106/T - 0.2005743 \ln T \\ & -(0.106901773 + 23.9722/T) \sqrt{S} \\ & + 0.1130822 S - 0.00846934 S^{3/2} + \ln(1 - 0.001005 S) \end{aligned}$$

$$\begin{aligned} \text{LnK2} = & -9.226508 - 3351.6106/T - 0.2005743 * \log(T) - (23.9722/T + \\ & 0.106901773) * S^{0.5} + 0.1130822 * S - 0.00846934 * S^{1.5} + \log(1 - \\ & 0.001005 * S); K2 = \exp(\text{LnK2}) \quad [\text{H}^+] = [\text{H}^+]_{\text{Total}} \text{ scale} \end{aligned}$$

5.6 The solubility of calcite (K_{sp}) $\text{CaCO}_3 \rightleftharpoons \text{Ca}^{++} + \text{CO}_3^{--}$

$$K_{\text{sp}}(\text{cal}) = [\text{Ca}^{++}] \cdot [\text{CO}_3^{--}]$$

$$\begin{aligned} \log K_{\text{sp}}(\text{cal}) = & -171.9065 - 0.077993 T + 2839.319/T \\ & + 71.595 \log T \\ & + (-0.77712 + 0.0028426 T + 178.34/T) S^{1/2} \\ & - 0.07711 S + 0.0041249 S^{1.5} \end{aligned}$$

$$\begin{aligned} \text{LogKspCal} = & -171.9065 - 0.077993 * T + 2839.319/T + 71.595 * \log(T) / a1 \\ & + (-0.77712 + 0.0028426 * T + 178.34/T) * S^{0.5} - 0.07711 * S + \\ & 0.0041249 * S^{1.5}; \text{LnKspCal} = \text{LogKspCal} * \log(10) \end{aligned}$$

5.7 The Solubility of Aragonite (K_{sp}) $\text{CaCO}_3 \rightleftharpoons \text{Ca}^{++} + \text{CO}_3^{--}$

$$K_{\text{sp}}(\text{arg}) = [\text{Ca}^{++}] \cdot [\text{CO}_3^{--}]$$

$$\begin{aligned} \log K_{\text{sp}}(\text{arg}) = & -171.945 - 0.077993 T + 2903.293/T \\ & + 71.595 \log T \\ & + (-0.068393 + 0.0017276 T + 88.135/T) S^{1/2} \\ & - 0.10018 S + 0.0059415 S^{1.5} \end{aligned}$$

$$\begin{aligned} \text{LogKspAra} = & -171.945 - 0.077993 * T + 2903.293/T + 71.595 * \log(T) / a1 \\ & + (-0.068393 + 0.0017276 * T + 88.135/T) * S^{0.5} - 0.10018 * S + \\ & 0.0059415 * S^{1.5} \\ \text{LnKspAra} = & \text{LogKspAra} * \log(10) \end{aligned}$$

5.8 The Partial Hydrolysis of Ca Ions $\text{Ca}^{++} + \text{OH}^- \rightleftharpoons \text{Ca}(\text{OH})^+$

$$K_7 = \frac{[\text{Ca}(\text{OH})^+]}{[\text{Ca}^{++}] \cdot [\text{OH}^-]}$$

$$\text{deltaG} = -7576 \text{ 'Joule:} K_7 = \exp(-1 \cdot \text{deltaG} / (\text{R} \cdot \text{T}))$$

5.9 The Partial Hydrolysis of Mg Ions $\text{Mg}^{++} + \text{OH}^- \rightleftharpoons \text{Mg}(\text{OH})^+$

$$K_8 = \frac{[\text{Mg}(\text{OH})^+]}{[\text{Mg}^{++}] \cdot [\text{OH}^-]}$$

$$\text{deltaG} = -14656 \text{ 'Joule:} K_8 = \exp(-1 \cdot \text{deltaG} / (\text{R} \cdot \text{T}))$$

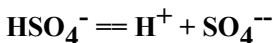
5.10 The Dissociation of Boric Acid $\text{B}(\text{OH})_3 + \text{H}_2\text{O} \rightleftharpoons \text{B}(\text{OH})_4^- + \text{H}^+$

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

$$\begin{aligned} \ln K_B = & \left(-8966.90 - 2890.53 S^{1/2} - 77.942 S + 1.728 S^{3/2} \right. \\ & \left. - 0.0996 S^2 \right) / T \\ & + 148.0248 + 137.1942 S^{1/2} + 1.62142 S \\ & - (24.4344 + 25.085 S^{1/2} + 0.2474 S) \ln T \\ & + 0.053105 S^{1/2} T \end{aligned}$$

$$\begin{aligned} \text{LnKB} = & (-8966.9 - 2890.53 \cdot S^{0.5} - 77.942 \cdot S + 1.728 \cdot S^{1.5} - \\ & 0.0996 \cdot S^2) / T + 148.0248 + 137.1942 \cdot S^{0.5} + 1.62142 \cdot S - (24.4344 + \\ & 25.085 \cdot S^{0.5} + 0.2474 \cdot S) \cdot \log(T) + 0.053105 \cdot S^{0.5} \cdot T : \text{KB} = \\ & \exp(\text{LnKB}) \text{ ' [H+]} = [\text{H+}]_{\text{Total}} \text{ scale} \end{aligned}$$

5.11 The Dissociation of Sulphuric Acid $\text{HSO}_4^- \rightleftharpoons \text{SO}_4^{--} + \text{H}^+$



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

$$\begin{aligned} \ln K_S = & -4276.1/T + 141.328 - 23.093 \ln T \\ & + (-13856/T + 324.57 - 47.986 \ln T) I^{1/2} \\ & + (35474/T - 771.54 + 114.723 \ln T) I \\ & - \frac{2698}{T} I^{3/2} + \frac{1776}{T} I^2 + \ln(1 - 0.001005 S) \end{aligned}$$

where I (ionic strength) = $19.924 \cdot S / (1000 - 1.005 \cdot S)$

Here it is imperative to use the [H⁺] free concentration, as we are dealing with acid sulphate dissociation. Therefore the [H⁺] concentration does not include the [HSO₄⁻] concentration participating to equilibrium.

5.12 The Dissociation of Hydrofluoric Acid $\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$

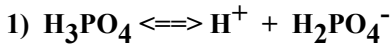
$$K_F = \frac{[\text{H}^+] \cdot [\text{F}^-]}{[\text{HF}]}$$

$$\ln K_F = \frac{1590.2}{T} - 12.641 + 1.525 T^{1/2} + \ln(1 - 0.001005 S) + \ln(1 + S_T/K_S)$$

where S_T (total concentration of sulphate) = 0.02824*S/35 : [H⁺] = [H⁺] Total scale

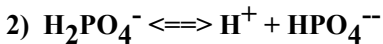
5.13 The Three Dissociations of Phosphoric Acid H_3PO_4

For the three dissociation reactions of phosphoric acid and the following of silicic acid, 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.



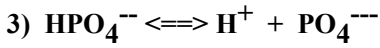
$$K_{1P} = \frac{[\text{H}^+] \cdot [\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$

$$\ln K_{1P} = \frac{-4576.752}{T} + 115.525 - 18.453 \ln T + \left(\frac{-106.736}{T} + 0.69171 \right) S^{1/2} + \left(\frac{-0.65643}{T} - 0.01844 \right) S$$



$$K_{2P} = \frac{[\text{H}^+] \cdot [\text{HPO}_4^{--}]}{[\text{H}_2\text{PO}_4^-]}$$

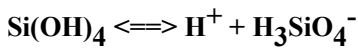
$$\ln K_{2P} = \frac{-8814.715}{T} + 172.0883 - 27.927 \ln T + \left(\frac{-160.34}{T} + 1.3566 \right) S^{1/2} + \left(\frac{0.37335}{T} - 0.05778 \right) S$$



$$K_{3P} = [\text{H}^+] \cdot [\text{PO}_4^{3-}] / [\text{HPO}_4^{2-}]$$

$$\begin{aligned} \ln K_{3P} = & \frac{-3070.75}{T} - 18.141 + \left(\frac{17.27039}{T} + 2.81197 \right) S^{1/2} \\ & + \left(\frac{-44.99486}{T} - 0.09984 \right) S \end{aligned}$$

5.14 The Dissociation of Silicic Acid Si(OH)_4



$$K_{\text{Si}} = [\text{H}^+] \cdot [\text{H}_3\text{SiO}_4^-] / [\text{Si(OH)}_4]$$

$$\begin{aligned} \ln K_{\text{Si}} = & \frac{-8904.2}{T} + 117.385 - 19.334 \ln T \\ & + \left(3.5913 - \frac{458.79}{T} \right) I^{1/2} + \left(\frac{188.74}{T} - 1.5998 \right) I \\ & + \left(0.07871 - \frac{12.1652}{T} \right) I^2 + \ln (1 - 0.001005 S) \end{aligned}$$

For all the expressions the total $[\text{H}^+]$ scale is used. I (ionic strength) = $19.924 \cdot S / (1000 - 1.005 \cdot S)$

CHAPTER 6 - The Practical Repercussions

6.1 Atmospheric CO₂ Equilibrates with Seawater.

The earth's oceans contain 99.9% of the planet's surface thermal energy, whilst its atmosphere holds only 0.07%. Primarily, this is due to the high thermal capacity of liquid water and, secondarily, the surface circulation of the first 100 meters from the ocean's surface. Thereby, huge quantities of seawater are exposed to solar heating. We can say that the oceans are a thermal reservoir for mankind.

As a consequence, while the atmospheric processes influence the weather for short periods, up to two weeks, the overall climate (months, years) is generally governed by ocean circulation. So far so good, but if oceans influence climate, what factors are responsible for ocean temperature itself? At first glance the answer looks easy. Oceans do not exhibit any internal energy sources, but merely collect most of the solar radiation striking the planet's surface and practically all the infra-red radiation (DLR or Downward Longwave Radiation) being sent back by atmospheric greenhouse gas, excluding the negligible heat from submerged volcanoes, thermal conduction through the earth's crust and cosmic rays.

In summary:

- 1- Not all of the incoming energy flux from the Sun (1367 W/m^2 on average) reaches the ocean surface. A part of this solar flux is reflected back into space (about 30%) due to the 'albedo' of the earth. The remaining 70% heats up the surface of the oceans; as this energy is in the form of visible light or near infra-red, it is absorbed into the uppermost 30-40 meters of water.
- 2- Surface water irradiates in the infra-red region (according to Planck's law) so it cools down a little.
- 3- Eventually the same surface receives a part of the infra-red radiation from the low troposphere.

All the rest being the same, the above three fluxes reach a stable (stationary) state, heating the surface layer of the oceans up to a certain temperature. It ranges from -2°C in the Arctic Ocean to 30°C in tropical waters according to the incidence angle of the Sun's radiation and therefore to the incoming energy per square meter.

Ocean seawater is in continuous circulation, the physical reason being the density variation due, in turn, to differences in salinity and temperature. These two factors have counteracting effects on density. Increased temperature reduces density by thermal dilatation of seawater, while the same increases both evaporation and salinity. Warm tropical waters with higher density submerge when they reach colder areas in the northern or southern hemisphere. However the effects are not easily foreseen.

6.2 Air-Sea Flux of CO₂

Total oceanic carbon content is about 38000 Gt (gigatons), a value that has been continuously increasing in the recent past. The total emission of carbon (as CO₂) in the atmosphere due to fossil combustion currently stands at about 10.5 GtC/y (gigatons of

carbon per year), of which 4.5 GtC/y is absorbed by the oceans. These values are continually increasing. For means of comparison, in 1990 (thirty years ago) the values were 6.4 and 2.8 GtC/y respectively.

The temperature gradient of oceanic waters and their circulation affect the air-sea flux of CO₂. In the tropics, the partial pressure of CO₂ in the surface waters exceeds the atmospheric partial pressure, driving outgassing. Conversely, at high northern latitudes, the pCO₂ in the ocean is less than that in the atmosphere, leading to an influx of CO₂. In the Southern Ocean, the uptake flux is relatively weaker than in the Northern.

The driving force for the CO₂ flux is a disequilibrium between the DIC (Dissolved Inorganic Carbon) and DIC (sat), which is the DIC when equilibrium is finally reached and DIC no longer varies. Under these circumstances, the CO₂ influx and outflux are exactly the same. For more insight see Section ... (kinetic).

According to Williams and Follows (2011), the difference between DIC and DIC (sat), called Δ DIC, lies in the range ± 0.06 mmol/L, with most values however lying at ± 0.02 for vast areas of oceans.

In order to calculate DIC (sat) we must solve all the reactions from 5.1 to 5.11 simultaneously. The procedure, although more complex, is in principle the same as the one adopted for the resolution of weak acid equilibrium in water, as in Sections 3.5, 3.6 and 3.7. the pH value is iteratively changed, equilibria are solved with that precise value of pH and electrical neutrality is calculated.

When neutrality (i.e. the summation of all positive and negative ions) reaches a minimum, the procedure stops and the 'pHstep' is reduced ten times, in order to increase precision. Then the cycle is restarted and continues, until the desired precision of the concentrations has been fulfilled (code007 in appendix).

In the code (code007.bas), CO₂ fugacity is calculated at the very beginning. The pH scale is the total (Hansson) scale, calcite (CaCO₃) precipitation is not accounted for at this stage, pressure is 1 atm. (the influence of pressure on equilibria will be discussed in the next chapter). In fig. 6.1 the results of the calculation with this procedure for three of the most relevant parameters are shown, Dissolved Inorganic Carbon (DIC, calculated at saturation), pH and calcite oversaturation for a concentration of CO₂ ranging from 300 to 500 ppm.

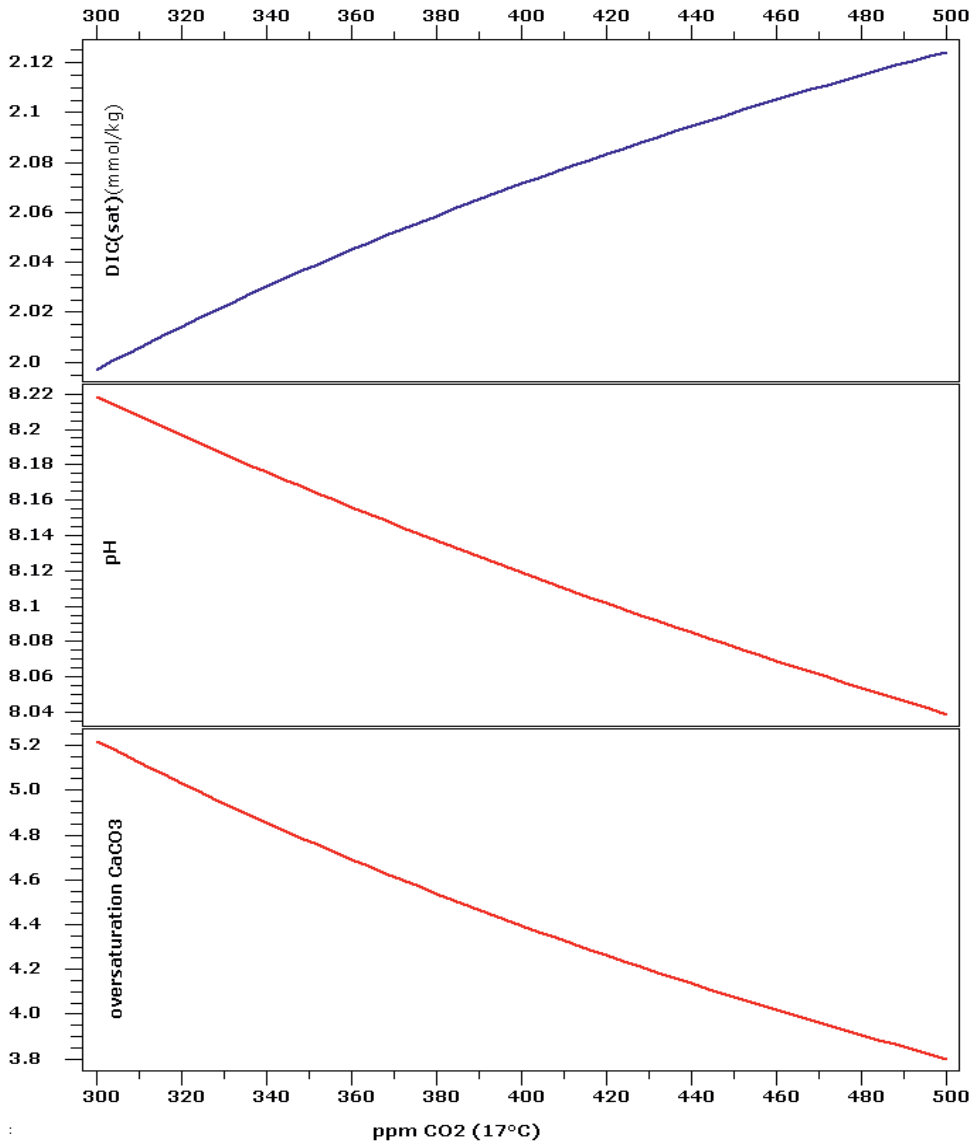


Fig. 6.1 DIC (saturation) pH and oversaturation versus different CO2 ppm at 1 atm. pressure.

6.3 Dissolved Inorganic Carbon

Carbon dioxide dissolves and reacts in seawater forming hydrated (dissolved) H_2CO_3^* , which is defined as the sum of the aqueous form of carbon dioxide, $\text{CO}_2(\text{aq})$ and true carbonic acid, H_2CO_3 . As previously discussed, carbonic acid participates in a series of equilibria which generate bicarbonate ions HCO_3^- and carbonate ions CO_3^{2-} . All these chemical species are collectively referred to as Dissolved Inorganic Carbon (or DIC in short).

$$\text{DIC} = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

where the square brackets denote concentrations in seawater defined per unit mass in

mmol/kg. Typically, 90% of DIC is made up of bicarbonate ions, about 9% carbonate ions and only a small remainder, up to 1%, of dissolved carbon dioxide. Therefore, the transfer of CO₂ into bicarbonate and carbonate ions leads to the ocean holding 50 times as much carbon as in the overlying atmosphere. This inorganic carbon in the ocean is about 40 times larger than the amount held as organic (biological) carbon. As shown in fig. its value increases from 2.00 to 2.12, a relatively small variation with an increase from 300 to 500 ppm of CO₂.

As indicated by Williams (2011) there is a timescale for air-sea equilibration and hence a time needed for DIC to reach DIC (saturation). This is mainly due to the thickness of the mixed surface layer and the time taken to reach an equilibrium with the atmosphere. For a non-reactive gas such as dissolved oxygen (O₂), on assuming a mixed-layer thickness of 100 m, the characteristic timescale for air-sea exchange is about one month ($\tau = 3 \cdot 10^6$ s). In other terms, the time constant of the phenomenon τ is to be inserted in a kinetic model like those depicted in Section 3.1 with a consequent inverse exponential law:

$$\Delta c(t) = \Delta c(t_0) \cdot \exp(-t / \tau)$$

where t is the time in seconds, $\Delta c(t)$ is the difference between the concentration of oxygen in the mixed layer at equilibrium and at the time t and $\Delta c(t_0)$ the same difference at the time = 0. It can be easily seen that when $t = \tau$, $\Delta c(t) / \Delta c(t_0) = \exp(-1) = 0.368$, meaning that 63,2% of that transformation (in this case oxygen dissolution) has already occurred.

The exchange timescale for a reactive gas, like CO₂, is much longer than that of a non-reactive gas, such as oxygen. The reason is to be found in the complex equilibria involved after CO₂ is solubilized in water. According to D.H Williams (2011), the equilibration timescale for CO₂ increases in relation to the amount of oxygen by a factor given by:

$$\tau (\text{CO}_2) = \tau(\text{O}_2) \cdot \text{DIC} / (\text{B} \cdot [\text{H}_2\text{CO}_3]) \approx \tau (\text{O}_2) \cdot 10$$

where the ratio DIC/[H₂CO₃] is on the order of 100, the buffer factor B (or Revelle factor, explained in Section 8.2) is on the order of 10, so that the time constant in this case is about 1 year ($\tau = 3 \cdot 10^7$ s). In one year, 63.2% of the reactive solubilization of CO₂ takes place in the first 100m of seawater below the surface.

6.4 pH and Seawater Acidification

In Section 3.4 the different pH scales were explained and compared.

The total (Hansson) scale here employed varies from 8.22 (300 ppm CO₂) to 8.04(500 ppm CO₂). The term 'acidification' is not applicable here because the pH remains in the alkaline range. Moreover, pH neutrality is no longer 7.00 (pure water 25°C) but 6.77, thereby expanding the range of alkalinity. Simulations with SeaWaterCalc (explained later in detail) show that with the current composition of seawater, even 5000 ppm CO₂ does not bring the pH into the acidity field.

One could argue that the pH scale is a logarithmic one: this is true, but even so, transferring to a linear scale, H⁺ concentration increases by about 58% and consequently [OH⁻] decreases by the same amount from pH 8.22 to pH 8.02.

6.5 Oversaturation

In Section 3.3.3 the solubility equilibrium of a sparingly soluble salt (CaCO₃) was

discussed. The solubility product can be defined as $K_{sp}(T,S,P) = [Ca^{++}] \cdot [CO_3^{-}]$, where concentrations are in mol/kg-solution and K_{sp} depends on temperature T, salinity S and pressure P.

Now from a point of view of equilibrium, once the solubility product is complete, the salt should begin to precipitate almost instantly. However, this happens through nucleation (aggregate formation on a nanometer scale) which, in turn, grows to form solid particles of salt. From an energetic standpoint, if the particle size is in the nanometer scale, the growth is not a favourable process due to the high ratio between the particle's surface area and its mass. Therefore, it is a common issue to find oversaturated salt solution. Seawater is a case, with respect to calcite/argonite formation.

As calcite is less soluble than $CaCO_3$, it is subject to oversaturation.

For any set of concentrations in a reaction mixture, we can set up a ratio of concentrations that have the same form as the equilibrium constant expression. This ratio is called the reaction quotient and is designated Q . For a hypothetical generalized reaction, $A + B \rightleftharpoons C + D$, the reaction quotient, first written in terms of activities, and then as concentrations assuming a concentration reference state, is

$$Q = \frac{[C] \cdot [D]}{[A] \cdot [B]}$$

If a reaction is at equilibrium, $K_{eq} = Q$, but our reaction mixture is not at equilibrium. Therefore, it is useful to define a non-dimensional value Ω given by the ratio between Q and K_{sp} or, in other words, the product of the calcium and carbonate concentrations divided by the solubility product:

$$\Omega = \frac{[Ca^{++}] \cdot [CO_3^{--}]}{K_{sp}}$$

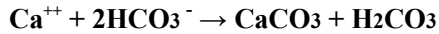
By definition, $\Omega = 1$ at equilibrium; $\Omega < 1$ reflects undersaturation favourable for the dissolution of solid calcium carbonate (if present anyway); and $\Omega > 1$ reflects supersaturation leading to $CaCO_3$ precipitation out of solution. In our oceans today, precipitation of calcium carbonate can be biologically mediated by calcifying organisms too. As can be seen in fig.6.1 by increasing CO_2 content of the atmosphere from 300 to 500 ppm, oversaturation decreases from 5.2 to 3.8 at $17^\circ C$ with standard seawater composition. The kinetics of calcium carbonate formation in supersaturated solutions follows the principles outlined in Chapter 2. Due to its relevance in seawater carbonate chemistry, the kinetics of this reaction and its effects on the CO_2 fluxes will be discussed in the next paragraph.

6.6 CO_2 Outgassing During Calcite Formation

Calcium carbonate is apparently the final sink for CO_2 . Carbonate rocks continuously form and sediment on the ocean floor. At shallower depths, the process of redissolution begins once more. On a time scale of several thousand years, the ultimate removal of atmospheric CO_2 as a result of fossil fuel combustion requires transfer of oceanic carbon to lithosphere by the formation of sediments, thereby closing the carbon cycle.

Quite often, calcite formation (the less soluble form of calcium carbonate) is written with a

simple reaction:



This reaction is chosen from among other possibilities on the basis that the most abundant ion in carbonate equilibria is the bicarbonate HCO_3^- ion. The above results in the formation of carbonic acid, and reports in popular literature or newspapers on calcium carbonate formation often speak about the 'acidification' of seawater due to the release of carbonic acid as the reaction proceeds.

According to popular literature and the press, carbonic acid could simply decompose to form CO_2 :



As a consequence, the formation of 1 mole of calcium carbonate would produce the same amount of CO_2 , rendering it useless at removing this gas from the atmosphere.

But although the above reactions are not formally wrong, the results are slightly skewed, in the same way that telling half the truth often results in a lie. A truer picture can be achieved by considering and solving this as simultaneous equilibria.

Running the SeaWaterCalc program, we can simulate a progressive precipitation of calcite by introducing a fractional value, called the precipitation factor (**pptF**), which simply instructs the code to perform a partial precipitation of CaCO_3 , with respect to the total amount that would be formed if the reaction were complete. This simulates a slow reaction, like carbonate formation, which takes place over many years. Chemically speaking, pptF is simply the fractional yield of the products obtained from a certain quantity of reagents in a given time interval.

Fig 6.2 is a graphical representation of the results of such simulations for three seawater temperatures, 10°, 17° and 24°C, standard seawater composition, salinity = 35 and pressure = 0 (sea level) A striking feature is the emission of CO_2 into the air, resulting from the precipitation reaction, continuing as long as pptF continues to increase. The carbon emitted (or more precisely outgassed as CO_2 , red line) is always much lower than the carbon transformed into solid carbonate (blue line), and nature is thereby armed with a powerful tool to mitigate (and to fully compensate for long term) the anthropogenic emission of CO_2 .

In the figure, the grey arrow indicates the net influx of CO_2 during the reaction. In tropical seas, where calcifying organisms do a better job, the temperature is around 24°C and, as seen from comparison of the three figures, the influx is higher. In other words, CO_2 is swept away more quickly. On the ordinate scale, as previously mentioned, pptF stands for precipitation factor or reaction yield (advancement). On the x-axis, as said above, the precipitation factor (pptF) can be seen, which can be considered as the reaction yield. To be noted is the overall x scale, which goes from 0 to 0.08 only, therefore the reaction proceeds only up to 8% of its total potential.

The real situation is slowly moving towards equilibrium, which will be reached in the end. How long will it take? It may take many years, but the phenomenon will move in that direction, and not the reverse. On the geological timescale, limestone will undergo subduction by tectonic plate movements, heated by magma and, in the long term,

decomposed to CO₂ and calcium silicates. CO₂ will be emitted into the air by volcanoes again after millions of years, to such an extent that all fossil fuels will be burned out!

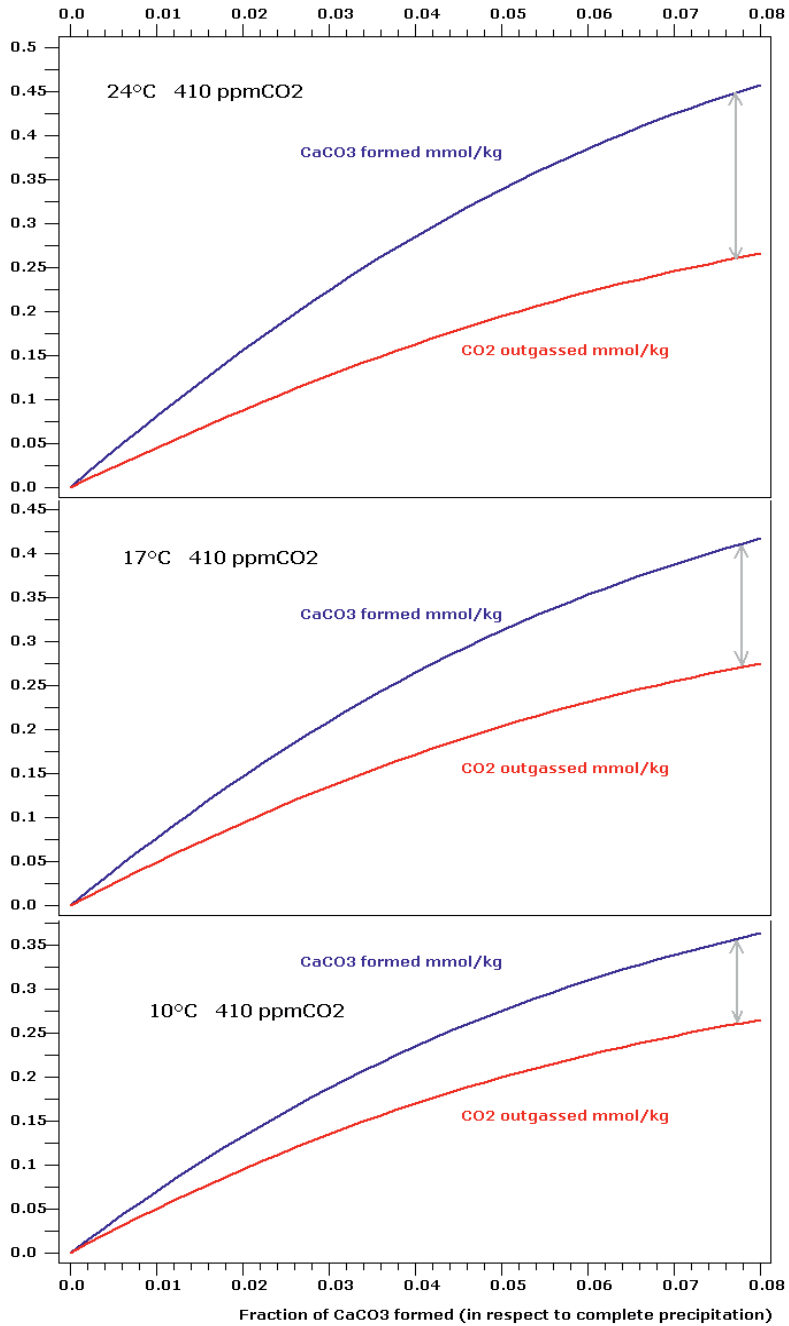


Fig. 6.2 Calcite formation and outgassing of CO₂ as a function of precipitation factor for CaCO₃

CHAPTER 7 – Pressure Effect on Equilibrium Reactions

7.1 Pressure Acting on Homogeneous Equilibria

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*)

$$\ln \left(\frac{K_{i,P}}{K_{i,0}} \right) = - \frac{\Delta V_i}{R_i T} P + 0.5 \frac{\Delta k_i}{R_i T} P^2$$

The constant value R_i is given by $R_i = 83.131 \text{ cm}^3 \text{ bar mol}^{-1} \text{ K}^{-1}$, 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.

$$\Delta V_i = a_0 + a_1 \cdot T_c + a_2 \cdot T_c^2$$

$$\Delta k_i = b_0 + b_1 \cdot T_c + b_2 \cdot T_c^2$$

The values for the *a* and *b* parameters are taken from Millero 1979 and Millero 1995 and are reported here for each of the reactions, where T_c indicates the temperature in °C, *P* the pressure in bar, and *T* the absolute temperature ($T = T_c + 273.15$) and finally $R_i = 83.131$.

In the formulas, $\ln K_{i,0}$ indicates the natural logarithm of K_i at $P=0$, while $\ln K_{i,P}$ the natural logarithm of the same equilibrium constants at pressure $P>0$ (in bars). The same applies for every equilibrium constant. Fig... resumes all the expressions used.

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 will be given in Chapter 8

$$K_1 = [\text{HCO}_3^-] \cdot [\text{H}^+] / [\text{H}_2\text{CO}_3^*]$$

$$\text{LnK1P} = \text{LnK1} + (25.5 - 0.1271 \cdot \text{Tc}) / \text{R1} / \text{T} \cdot \text{P} + 0.5 \cdot (-3.08 \text{e-}3 + 0.0877 \text{e-}3 \cdot \text{Tc} - 0.21685 \text{e-}3 \cdot \text{Tc}^2) / \text{R1} / \text{T} \cdot \text{P}^2$$

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

$$\text{LnK2P} = \text{LnK2} + (15.82 + 0.0219 \cdot \text{Tc}) / \text{R1} / \text{T} \cdot \text{P} + 0.5 \cdot (1.13 \text{e-}3 - 0.1475 \text{e-}3 \cdot \text{Tc} - 0.1562 \text{e-}3 \cdot \text{Tc}^2) / \text{R1} / \text{T} \cdot \text{P}^2$$

$$K_w = [\text{H}^+] \cdot [\text{OH}^-]$$

$$\text{LnKwP} = \text{LnKw} + (25.6 - 0.2324 \cdot \text{Tc} + 3.6246 \text{e-}3 \cdot \text{Tc}^2) / \text{R1} / \text{T} \cdot \text{P} + 0.5 \cdot (-5.13 \text{e-}3 + 0.0794 \text{e-}3 \cdot \text{Tc} - 0.2109 \text{e-}3 \cdot \text{Tc}^2) / \text{R1} / \text{T} \cdot \text{P}^2$$

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

$$\text{LnKBP} = \text{LnKB} + (29.48 - 0.1622 \cdot \text{Tc} - 2.608 \text{e-}3 \cdot \text{Tc}^2) / \text{R1} / \text{T} \cdot \text{P} + 0.5 \cdot (-2.84 \text{e-}3 - 0.2283 \text{e-}3 \cdot \text{Tc}^2) / \text{R1} / \text{T} \cdot \text{P}^2$$

$$K_{\text{sp}}(\text{cal}) = [\text{Ca}^{++}] \cdot [\text{CO}_3^{--}]$$

$$\text{LnKspCalP} = \text{LnKspCal} + (48.76 - 0.5304 \cdot \text{Tc}) / \text{R1} / \text{T} \cdot \text{P} + 0.5 \cdot (-11.76 \text{e-}3 + 0.3692 \text{e-}3 \cdot \text{Tc} - 0.3432 \text{e-}3 \cdot \text{Tc}^2) / \text{R1} / \text{T} \cdot \text{P}^2$$

$$K_{\text{sp}}(\text{arg}) = [\text{Ca}^{++}] \cdot [\text{CO}_3^{--}]$$

$$\text{LnKspAraP} = \text{LnKspAra} + (46 - 0.5304 \cdot \text{Tc}) / \text{R1} / \text{T} \cdot \text{P} + 0.5 \cdot (-11.76 \text{e-}3 + 0.3692 \text{e-}3 \cdot \text{Tc} - 0.3162 \text{e-}3 \cdot \text{Tc}^2) / \text{R1} / \text{T} \cdot \text{P}^2$$

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

$$\text{LnKSP} = \text{LnKS} + (18.03 - 0.0466 \cdot \text{Tc} - 0.3160 \text{e-}3 \cdot \text{Tc}^2) / \text{R1} / \text{T} \cdot \text{P} + 0.5 \cdot (-4.53 \text{e-}3 + 0.09 \text{e-}3 \cdot \text{Tc} - 0.1595 \text{e-}3 \cdot \text{Tc}^2) / \text{R1} / \text{T} \cdot \text{P}^2$$

$$K_F = [\text{H}^+] \cdot [\text{F}^-] / [\text{HF}]$$

$$\text{LnKFP} = \text{LnKF} + (9.78 + 0.009 \cdot \text{Tc} + 0.942 \text{e-}3 \cdot \text{Tc}^2) / \text{R1} / \text{T} \cdot \text{P} + 0.5 \cdot (-3.91 \text{e-}3 + 0.054 \cdot \text{Tc} - 0.1005 \text{e-}3 \cdot \text{Tc}^2) / \text{R1} / \text{T} \cdot \text{P}^2$$

Finally, the values of the equilibrium constants are calculated from their logarithms

$$\begin{aligned} K1 &= \exp(\text{LnK1P}) : K2 = \exp(\text{LnK2P}) : K0 = \exp(\text{LnK0}) : K_w = \exp(\text{LnKwP}) \\ Ksp1 &= \exp(\text{LnKspCalP}) : Ksp2 = \exp(\text{LnKspAraP}) : K_S = \exp(\text{LnKSP}) : K_F = \exp(\text{LnKFP}) \\ KB &= \exp(\text{LnKBP}) \end{aligned}$$

In the appendix, code 005.bas is the general routine for the complete and simultaneous set of

calculations. It can be simply downloaded from my web-site (www.oceanchemistry.info) and is ready to run. It requires a text file input (SeaWaterCalc.txt) from which all starting parameters are read, but the reader is strongly recommended to read the lines and the comments related to the pressure effects.

7.2 Pressure Acting on Heterogeneous Equilibria

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 in Section 6.5.

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 in the preceding sections of this book, (whose usage will be comprehensively described in Chapter 8) the oversaturation profiles at different depths can be calculated. Some of the results can be seen in the graph in Fig. 7.1. The curious reader, intent on modifying input parameters and looking for new results (in a “see what happens” procedure) is directed to Chapter 8.

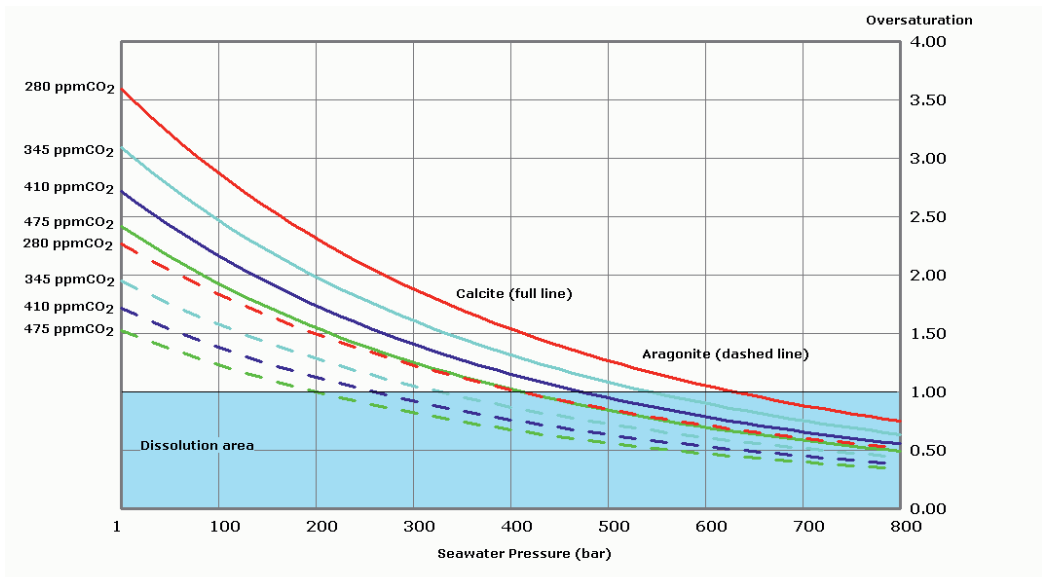


Fig. 7.1 Oversaturation for calcite at different ppmCO₂ versus pressure

In Fig. 7.1 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). The four colored curves correspond to four concentrations of CO₂ values (red = 280 pre-industrial value; cyan = 345; blue = 410 present day value; green = 475 ppm). The full line indicates calcite and the dashed line, aragonite. 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, evident from Fig.7.2. 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 figures... should be considered together to gain a complete picture.

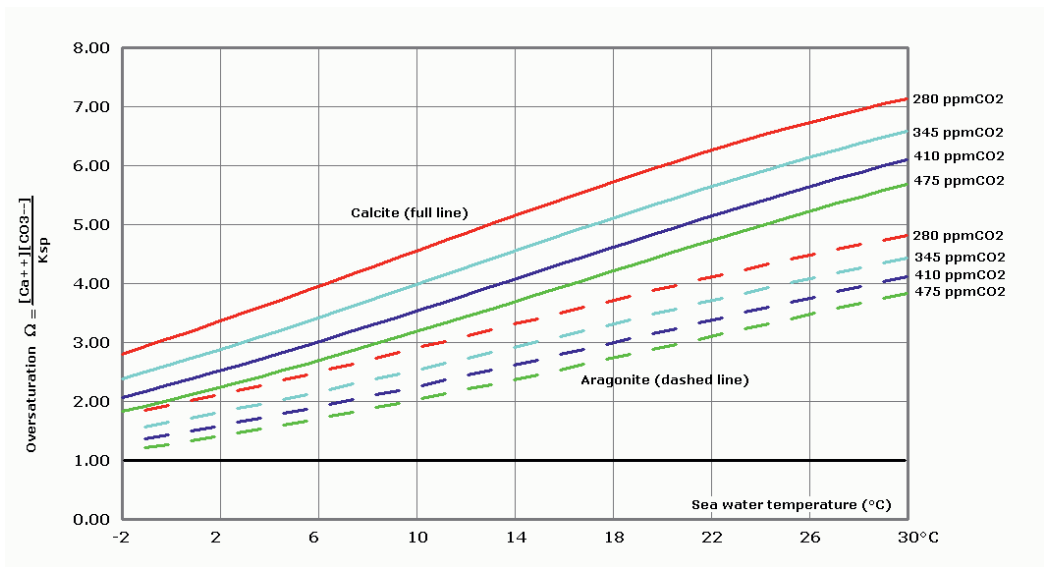


Fig. 7.2 Oversaturation for calcite at 1 atm. versus temperature of seawater

CHAPTER 8 – Examples and Applications

8.1 The Global Scenario

Transferring all these simulations for seawater equilibria to the whole ensemble of the oceans is far from straightforward. A complex pattern emerges as temperature, salinity and DIC vary from arctic waters to tropical ones. By way of example, DIC distribution on the ocean's surface is depicted in fig.8.1.

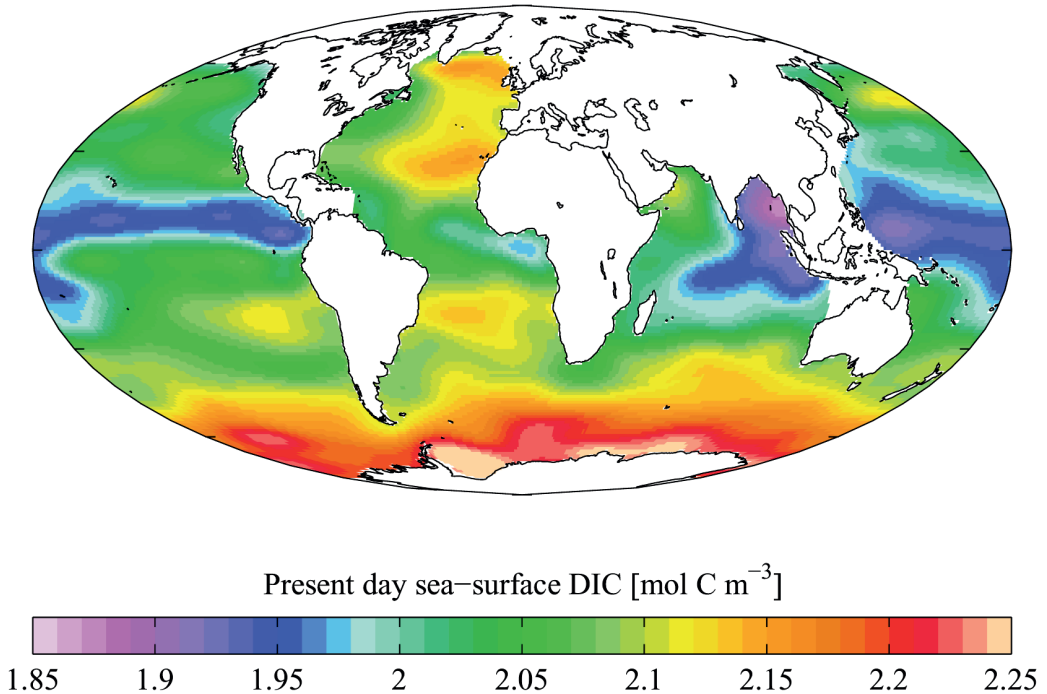


Fig 8.1. Present day surface DIC (from wikipedia/commons/d/df/WOA05_GLODAP_pd_DIC_AYool.png By Plumbago. Own work CCBY-SA 3.0)

As in the atmosphere, ocean streams (like the famous Gulf Stream) move huge masses of waters, which eventually sink (a fact known as vertical mixing). This vertical mixing in the ocean is driven by buoyancy. The two factors that determine buoyancy in the ocean are temperature and salinity. The sinking of waters from the surface to the ocean depths takes place in Polar Regions where the surface water is cold and salty, and hence heavier. This, in turn, determines a movement of tropical waters toward Polar Regions, which causes evaporation and an increase in salinity, thereby closing the cycle. In other regions, the ocean surface is warmer than the water underneath, so that any vertical mixing is suppressed. Some vertical mixing still takes place near the surface due to wind stress, resulting in an oceanic mixed layer extending up to around 100 m in depth and slowly exchanging with the deeper ocean. Dynamic variation (as discussed in Section 6.3) results in gaseous exchange with the air in the mixed layer (volume = $3.6 \cdot 10^{16}$ m³) over a time scale of around 1 year. Equilibration of the whole ocean, for example in response to a change in atmospheric CO₂, has a much longer time scale of around 120 years or more.

Therefore, in applying the algorithm to the oceans as a whole many precautions must be taken, always bearing in mind that, while CO₂ concentration is practically uniform, there are marked temperature, salinity and DIC variations across the globe. From my own experience, one can divide the simulation task into two steps: first, by assuming a fixed value for some parameters, for example the average present-day DIC taken from fig. 8.1 as 2.06.; second, by finding out how the fixed parameter(s) change according to latitude or other local geographical parameters. An example will help clarify the procedure.

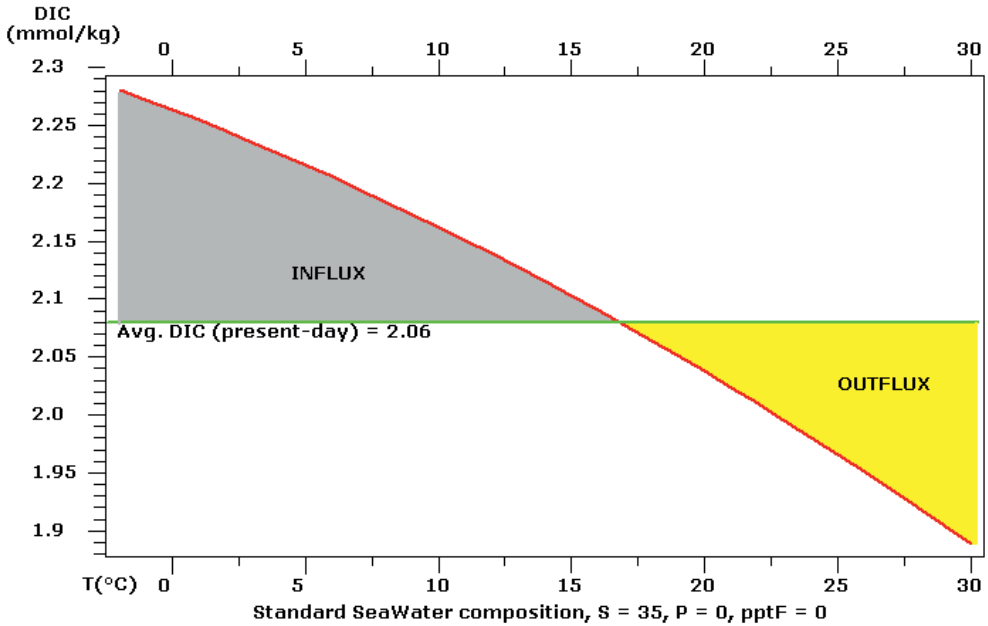


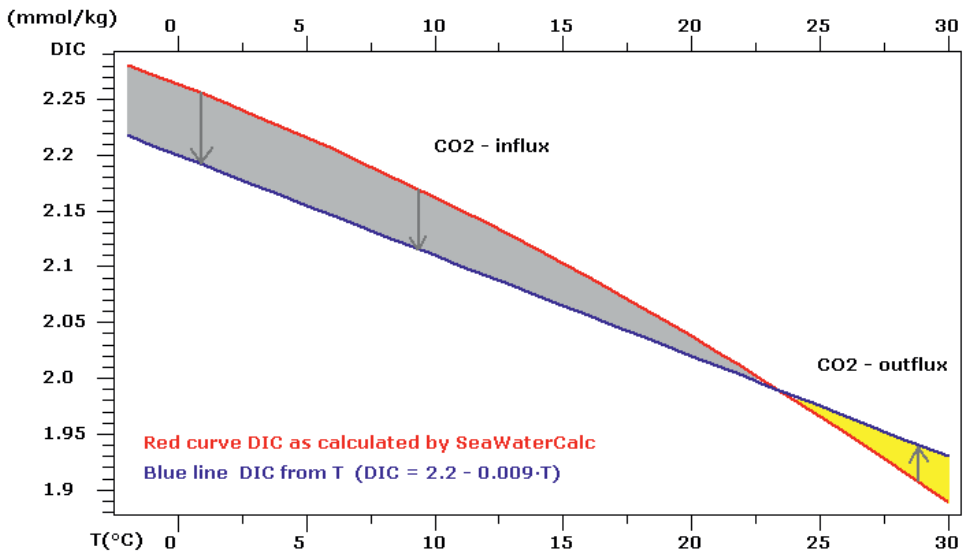
Fig. 8.2 Difference between present-day average DIC (green line) and equilibrium (saturation) DIC with 410 ppm, standard seawater composition.

As we know, there is an ocean uptake of CO₂ in colder areas (high latitudes) and an ocean outgassing in warmer ones (tropics). The red curve in Fig. 8.2 corresponds to DIC saturation, as calculated with SeaWaterCalc for standard seawater composition, in equilibrium with 410 ppm CO₂ (no precipitation of calcite) as a function of temperature from -2 to 30°C. If we compare the red curve with the horizontal line (green) corresponding to present-day average DIC (estimated at 2.06 mmol/kg), we can see how, for T < 17°C, there can be an uptake of CO₂ and an outgassing for T > 17°C. We can improve our simulation by accounting for the variation of DIC around the globe (see Fig.8.1). Comparing the picture in Fig 8.1 with a temperature map of the ocean surface, one can assume that temperature and DIC have a linear relationship, and moreover (as first approximation) that at 0°C, DIC equals 2.20, decreasing then (linearly) to 1.93 at 30°C.

On this basis, the following linear relationship could be derived:

$$\text{DIC} = 2.20 - 0.009 \cdot T(^{\circ}\text{C})$$

When using this DIC dependence from temperature, one can obtain a more realistic picture of the CO₂ flux, as shown in Fig. 8.3



DIC (red) is calculated by SeaWaterCalc with Salinity = 35, 410 ppmCO₂, zero pressure (sea surface)

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Fig. 8.3 DIC Saturation (red) and present-day DIC for variable temperatures.

An evaluation of the DIC disequilibrium associated with the plot, ($\Delta\text{DIC} = \text{DIC}_{\text{sat}} - \text{DIC}$) gives results from 0.06(0°C) to -0.05(30°C), perfectly comparable with the values given in fig 6.15(b) page 147 of Williams 2011, which range from 0.06 to -0.06 for the ocean surface overall across the globe inferred from 'an independent global climatology'.

The key point is to transform this useful information on ocean DIC disequilibrium into CO₂ in- or out-flux. This can be done using the 'famous' Takahashi plot with relative data, as diffused in literature and numerous books since 2002. It reports the air-sea CO₂ flux based on a compilation of ocean surface observations from Takahashi et al. (2002). According to personal interpolation of the data from SeaWaterCalc and literature, the approximate correspondence between ΔDIC and the consequent annual mean CO₂ flux is:

$$\text{CO}_2 \text{ flux (mol m}^{-2} \text{ y}^{-1}) \approx 100 * \Delta\text{DIC (mmol/kg-solution)}$$

This approximate equation enables us however to estimate air-sea CO₂ flux on the basis of relatively simple simulations and algorithms.

The empirical expression of DIC on the basis of temperature alone (thus disregarding the contribution of salinity), also allows us to calculate from DIC the concentration of CO₂ in atmosphere at equilibrium at a given temperature. With a reference value of 410 ppm, if the equilibrium concentration has a lower value (see Fig. 8.4), as happens up to 23 °C, then seawaters are prone to absorb CO₂. On the contrary, they will desorb it at temperatures over 23°C.

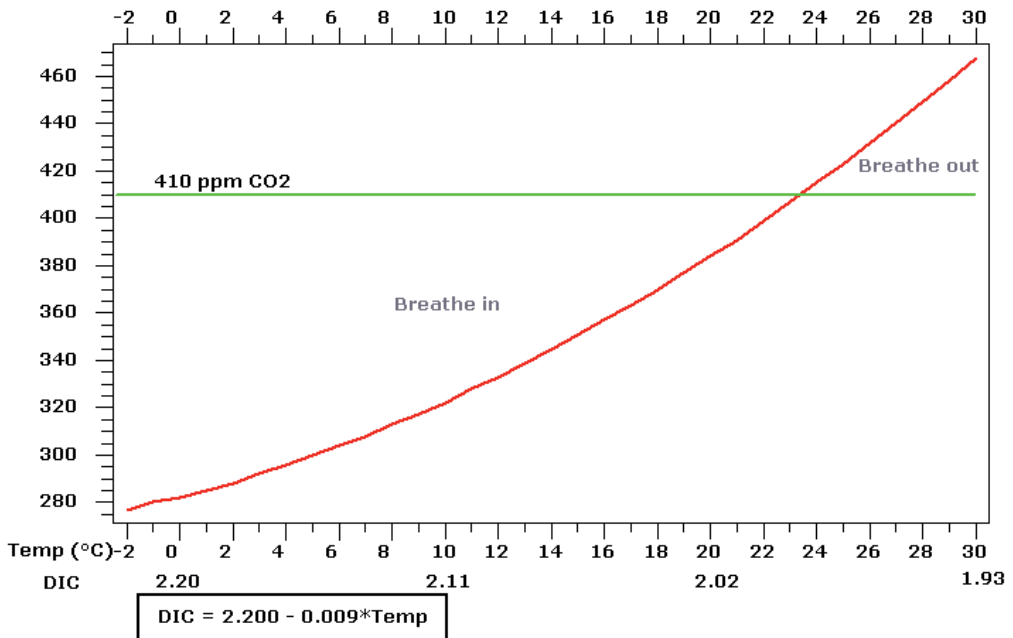


Fig. 8.4 In- and Out-flux of CO₂ as deduced by equilibrium CO₂ calculation (red line) as a function of T and DIC.

8.2 The Revelle Buffer Factor and Alkalinity

The relationship between fractional changes in pCO₂ and in DIC is formally expressed in terms of the Revelle buffer factor B, which is defined as the ratio between the relative changes in pCO₂ and DIC (Bolin-Erickson 1959),

$$B = (\delta pCO_2 / pCO_2) / (\delta DIC / DIC)$$

In other words, the Revelle buffer factor is a measure of the relationship between changes in pCO₂ and consequent variation of DIC in seawater. Being the ratio between two pure numbers, it is a pure number in its own right. In today's ocean surface, B varies from 6 in the warmest tropical waters (30°C) to 16 in high latitudes or arctic waters (-2°C). As a consequence of its relevance to the scale of DIC increase compared to the increase of anthropogenic CO₂, many attempts have been made to simulate or evaluate it using physico-chemical seawater characteristics.

Using the iterative approach and the routines described here, with some minor modification (not listed), anybody can calculate this 'B' factor. There is no need to introduce cumbersome and confusing-looking accessory concepts like alkalinity or carbonate alkalinity, so often viewed as necessary by many textbooks.

If the reader wishes to change the chemical composition of the seawater, this can be easily achieved in the input text file (SeaWaterCalc.txt) for each element or compound. Alkalinity is often cited and used because it is an experimentally measured parameter with a simple

HCl titration of seawater but, thanks to the available algorithms, it can also be deduced from composition. In particular, Total Alkalinity (TA) is defined as the concentration of all the bases that can accept H^+ when a titration is made with HCl to the carbonic end point, when all carbonate species are transformed into H_2CO_3 (around pH 3-4, titration with methyl orange). The following is an explicit version, taking into account the hydroxyl and oxonium ions:

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [H_3SiO_4^-] + [MgOH^+] + [OH^-] + [H^+]$$

It can be simply calculated from the output file of the main program (untitled.txt)

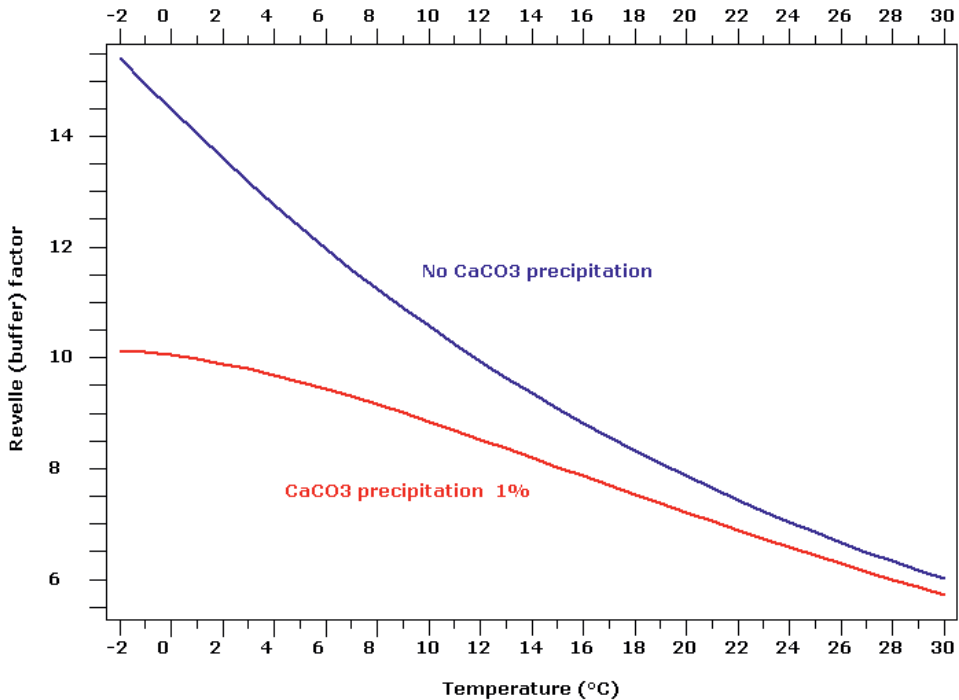


Fig. 8.5 Temperature dependence of Revelle factor with (blue) no $CaCO_3$ precipitation and with (red) a precipitation factor of 0.01 (1%). Simulations with SeaWaterCalc for 410 ppm of CO_2 .

8.3 Increasing Anthropogenic CO_2

The recent interest in the distribution of CO_2 in the oceans is related to the need to understand how the increased amount of the emissions of this gas in the atmosphere will be buffered by carbonate equilibria in seawater. The partial pressures of CO_2 in the atmosphere (pCO_2) have been studied by a number of researchers. The classical measurements of pCO_2 were first made by Keeling (Keeling-Worf 2004) at the Mauna Loa Observatory in Hawaii, back in 1958. More recent measurements have been made on the air trapped in ice cores up to 400 thousand years ago. These measurements clearly demonstrate that CO_2 is increasing in the atmosphere because of the burning of fossil fuels. However, the final amounts in the atmosphere are only $\approx 52\%$, the oceanic sink accounting for $\approx 48\%$ of the total fossil-fuel burning and cement-manufacturing (Sabinel 2004). In 2009 Khatiwala et al. derived, as they

describe it, “an observationally based reconstruction of the spatially-resolved, time dependent history of anthropogenic carbon in the ocean over the industrial era (AD 1765 to AD 2008)” based on a suite of sampled ocean tracers (Fig. 8.6).

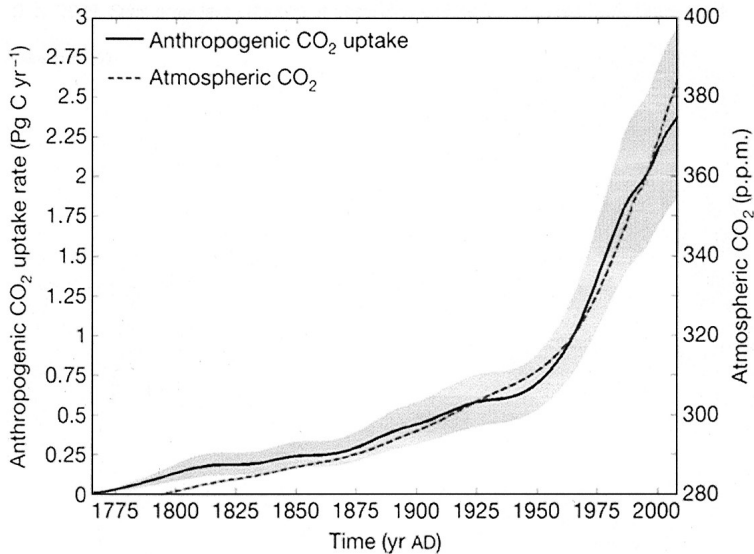


Fig. 8.6 Atmospheric CO₂ concentration and oceanic uptake rate for anthropogenic carbon (with shaded error envelope) plotted against time. Adapted from Khatiwala et al. 2009.

Interest has now evolved towards possible future trends. Using the SeaWaterCalc code, and interpolating the data of Mauna Loa with a second degree polynomial, to a certain point it is possible to foresee the future behaviour of some parameters, like in Fig 8.7, pH and pH with 1% precipitation of CaCO₃

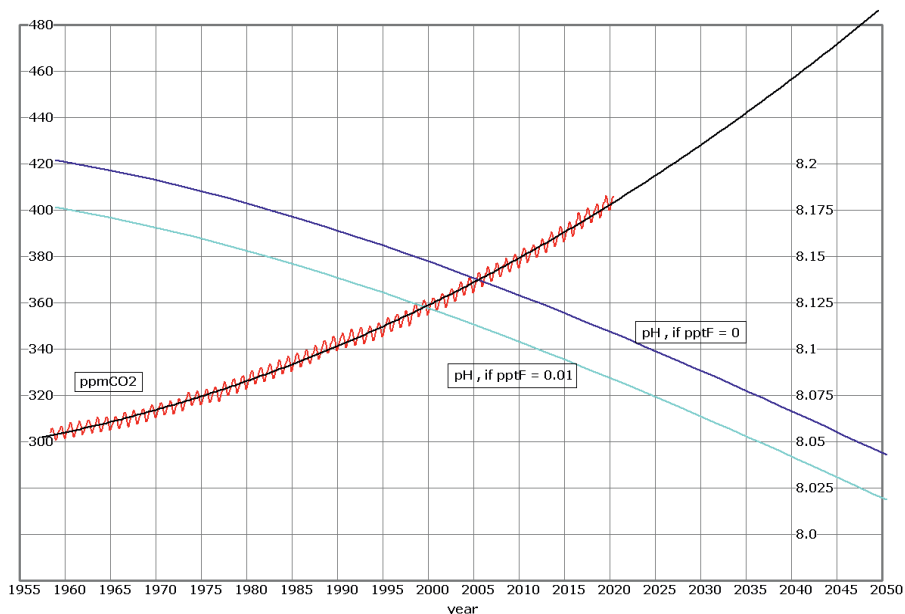


Fig. 8.7 Parabolic interpolation (black) of the Mauna Loa data (Keeling curve, red) from the start of measurements (1958) up to now. Based on the values of the interpolated black curve, the pH equilibrium values are calculated up to 2050 (blue curve without calcite precipitation, cyan line pptF = 0.01)

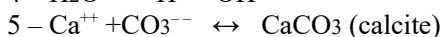
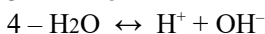
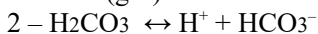
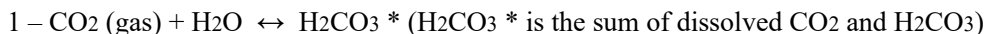
8.4 Contributions to CO₂ Absorption by Fresh Waters

Rather surprisingly, in oceanic chemistry the CO₂ absorption contribution by fresh waters is never considered. When meteoric water (rain water) flows or comes into contact with carbonate rocks (containing CaCO₃), the dissolution of calcite (or aragonite) occurs spontaneously due to the high content of CO₂ dissolved in rain water. In fact, this water has absorbed CO₂ throughout the entire course of the formation and precipitation of its rain droplets.

As to a single reaction step, quite often the expression of the dissolution of calcite by meteoric waters is written as:



It suggests that CO₂ is consumed in a stoichiometric 1:1 manner when calcite is dissolved. However, being the above reaction only one part of a series of equilibria, and not a single step reaction, it is therefore necessary to consider all the equilibria (below) in the chemical system in an attempt to find a correct quantitative resolution.



As the empirical approximations of K_{eq} described in Chapter 5 are no longer valid when salty water is substituted with fresh water, we should use another approach, referring ourselves to the appropriate Gibbs energy values from a literature database. Gibbs energy is also the chemical potential that is minimised when a system reaches equilibrium at constant pressure. As such, it is a convenient criterion of spontaneity for isobaric (constant pressure and variable volume) processes. Gibbs free energy, originally called available energy, was developed in the 1870s by the American mathematical physicist Willard Gibbs.

The change in Gibbs free energy, ΔG , in a reaction is a very useful parameter. It can be thought of as the maximum amount of work obtainable from a reaction at constant pressure (usually reactions occur at ambient pressure, 1 atm). For example, in the oxidation of glucose, the main energetic reaction in living cells, the change in Gibbs free energy is $\Delta G = 686 \text{ kcal} = 2870 \text{ kJ}$. The change in Gibbs free energy associated with a chemical reaction is a useful indicator of whether the reaction will proceed spontaneously. Since the change in free energy is equal to the maximum useful work which can be produced by the reaction then a negative ΔG indicates that the reaction can happen spontaneously. Knowing the ΔG value of a reaction, the value of its equilibrium constant can be calculated. For a generic reaction like $aA + bB = cC + dD$ it can be demonstrated (see also Section 3.3) that when equilibrium is reached:

$$K_{eq} = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b} = \exp[-\Delta G/(RT)]$$

The complete list of considered equilibria is already written above, their equilibrium constants are calculated from Gibbs energy values (data are taken mainly from NIST or other thermodynamic databases). Remember that $K_{(eq)} = \exp(-\Delta G/RT)$, R being the gas constants and T the absolute temperature. By using the thermodynamic Gibbs energy we can account for the temperature dependence of the equilibrium constants. The code needed to solve the system is in some way similar to SeaWaterCalc code in the iterative procedures, but different in the usage of numerical values of the equilibrium constants, as they are now calculated from Gibbs energy.

1- $\Delta G = -20302 - T^*(-96.25)$ (Joule/mol/K)

2- $\Delta G = 7660 - T^*(-96.2)$ (Joule/mol/K)

3- $\Delta G = 14850 - T^*(-148.1)$ (Joule/mol/K)

4- $\Delta G = 55836 - T^*(-80.66)$ (Joule/mol/K)

5- $\Delta G = -13050 - T^*(-202.9)$ (Joule/mol/K)

From the above treatment of inorganic carbon chemistry in fresh water and the simultaneous resolution of temperature-dependent equilibria, interesting results are obtained. They are presented in graphic form in figures 8.8 and 8.9, for the sake of simplicity. One striking finding is that the molar amount of CO_2 absorbed and calcium ions released in solution by calcite dissolution nearly coincide (green and blue curves). The increase in DIC is indicated by the red curve. It can reach values of up to 1.3 mmol/L at equilibrium, obviously when sufficient time is given. It is not so far from the common values for seawater (from 1.85 to 2.20), but it is likely that fresh waters are still a long way

off from equilibrium when they join oceanic waters, thereby changing their composition completely.

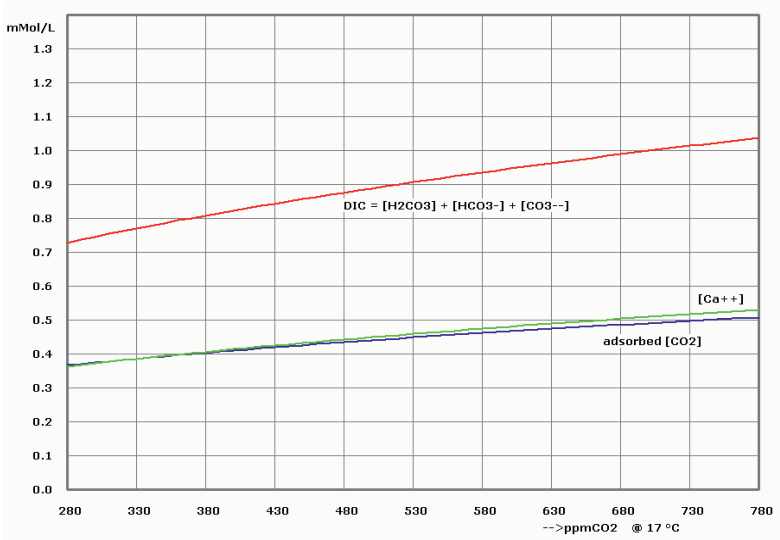


Fig. 8.8 Trend of dissolution of calcite when ppm CO2 in the atmosphere grow from 280 (pre-industrial value) to 780. Temperature is 17°C in the simulation.

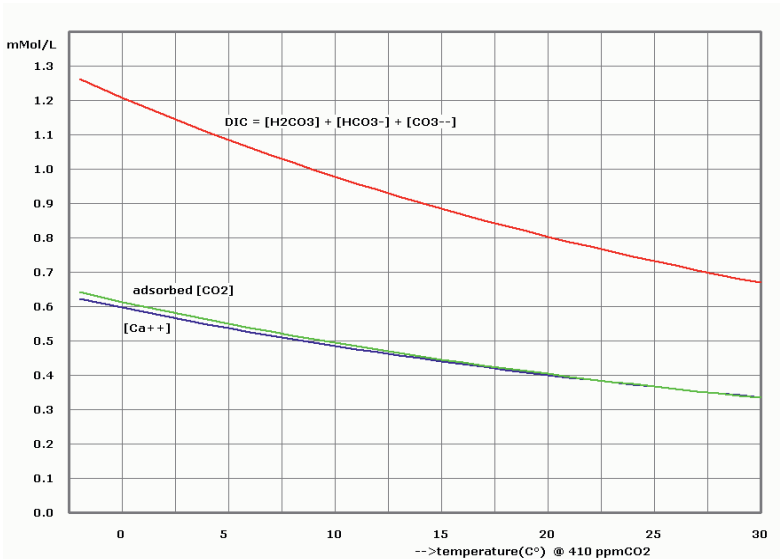


Fig. 8.9 Trend of dissolution of calcite when seawater temperatures increase from -2°C (arctic seas) to 30°C (tropical seas). CO2 ppm are 410 in the simulation.

APPENDIX 1 - Code listing

code001.bas Weak acid (HF) dissociation-----

```

' HF <=> H+ + F-
' Kal = [H+]*[F-]/[HF]
Atot = 0.08 ' [HF] initial concentration, before dissociation
Kal = 3.5e-4 ' dissociation constant of fluoridric acid
Kw = 1e-14 ' ionic water product
pH1 = 0:pH2 = 14 ' initial pH range
pHstep = 1 ' initial pH step
for j = 1 to 6 ' number of refinement
  for pH = pH1 to pH2 step pHstep
    H = 10^(-1*pH)
    OH = Kw/H
    ' here we solve (two equations, two unknowns)
    ' Kal = [H+]*[F-]/[HF]
    ' Atot = [F-]+[HF]
    F = Kal*Atot/(H + Kal)
    HF = H*F/Kal
    Neut = H - OH - F
    if Neut<0 then exit for
  next pH
  pH2 = pH
  pH1 = pH2 - pHstep
  pHstep = pHstep/10
next j
print " pH = ";pH
print " [H+] = ";H
print " [F-] = ";F
print " [HF] = ";HF
print "-----"
end

```

code002.bas Biprotic weak acid (H2CO3) dissociation-----

```

' H2CO3 <=> H+ + HCO3-
' Kal = [H+]*[HCO3-]/[H2CO3]
' HCO3- <=> H+ + CO3--
' Ka2 = [H+]*[CO3--]/[HCO3-]

Atot = 0.02 ' total concentration of H2CO3 before dissociation
Kal = 4.45e-7 ' 1st diss H2CO3
Ka2 = 4.69e-11 ' 2nd diss HCO3-
Kw = 1e-14
NaOH = 0.03 ' molar concentration of sodium hydroxide, if added
Na = NaOH ' being a strong base, it dissociates completely
pH1 = 0
pH2 = 14
pHstep = 1
for j = 1 to 8
  for pH = pH1 to pH2 step pHstep
    H = 10^(-1*pH)
    ' here we solve (3 equations, 3 unknowns)
    ' Kal = [H+]*[HCO3-]/[H2CO3]
    ' Ka2 = [H+]*[CO3--]/[HCO3-]
    ' Atot = [CO3--]+[HCO3-]+[H2CO3]
    CO3 = Kal*Ka2*Atot/(H*H + Kal*H + Kal*Ka2)
    HCO3 = H*CO3/Ka2
    H2CO3 = H*HCO3/Kal
    OH = Kw/H
    Neut = H + Na - OH - HCO3 - 2*CO3
    if Neut<0 then exit for
  next pH
  pH2 = pH
  pH1 = pH2 - pHstep
  pHstep = pHstep/10
next j
end

```

code003.bas Triprotic acid (H3PO4) dissociation-----

```

' H3PO4 <=> H+ + H2PO4-
' Kal = [H+]*[H2PO4-]/[H3PO4]
' H2PO4- <=> H+ + HPO4--
' Ka2 = [H+]*[HPO4--]/[H2PO4-]

```

```

' HPO4-- <=> H+ + PO4---
' Ka3 = [H+]*[PO4---]/[HPO4--]

Atot = 0.28 ' total amount of H3PO4 added (total P content)
Ka1 = 7.5e-3 ' 1st dissociation constant
Ka2 = 6.2e-8 ' 2nd dissociation constant
Ka3 = 4.4e-13 ' 3rd dissociation constant
Kw = 1e-14 ' ionic product of water
NaOH = 0.06 ' NaOH added (mol/L)
HCl = 0.01 ' HCl added (mol/L)

Na = NaOH ' being a strong base, it dissociates completely
Cl = HCl ' being a strong acid, it dissociates completely
print " H3PO4 added = ";Atot
print " NaOH added = ";NaOH
print " HCl added = ";HCl
print "-----"
pH1 = 0
pH2 = 14
pHstep = 1
for j = 1 to 8 ' each step of the loop pHstep decreases 10x
  for pH = pH1 to pH2 step pHstep ' loop of pH
    H = 10^(-1*pH):OH = Kw/H
    ' here we solve the system of 4 equations, 4 unknowns
    ' Ka1 = H*H2PO4/H3PO4
    ' Ka2 = H*HPO4/H2PO4
    ' Ka3 = H*PO4/HPO4
    ' Atot = H3PO4 + H2PO4 + HPO4 + PO4
    PO4 = Ka1*Ka2*Ka3*Atot/(H*H*H + Ka1*H*H + Ka1*Ka2*H + Ka1*Ka2*Ka3)
    HPO4 = H*PO4/Ka3
    H2PO4 = H*HPO4/Ka2
    H3PO4 = H*H2PO4/Ka1
    Neut = H + Na - Cl - OH - H2PO4 - HPO4*2 - PO4*3
    if Neut<0 then exit for
  next pH
  pH2 = pH
  pH1 = pH2 - pHstep
  pHstep = pHstep/10
next j

```

code004.bas -----

```

' CHEMICAL ADDED TO THE REACION VESSEL (1 LITER) ARE LISTED HERE:

Na2CO3 = 0.2 ' added moles. Soluble salt completely dissociated in Na+ and CO3-- ions
NaHCO3 = 0.1 ' added moles. Soluble salt completely dissociated in Na+ and HCO3- ions
CaCO3 = 0.0 ' added moles. Sparligly soluble salt. Solubility product Ksp needed
NaOH = 0.1 ' added moles. Strong electrolyte, completely dissociated in Na+ and OH- ions
HCl = 0.4 ' added moles. Strong electrolyte, completely dissociated in H+ and Cl- ions
CaCl2 = 0.6 ' added moles. Soluble salt completely dissociated in Ca++ and Cl- ions
MgCl2 = 0.2 ' added moles. Soluble salt completely dissociated in Mg++ and Cl- ions
H2CO3 = 0.005 ' added moles of carbonic acid, a weak acid partially dissociated

' FROM THE ABOVE WE DEFINE SOME PARAMETERS :
Ctot = Na2CO3 + NaHCO3 + CaCO3 + H2CO3 'total concentration of all forms of carbonate (CO3--) ion
Catot = CaCO3 + CaCl2 'total concentration of all forms of carbonate (Ca++) ion
Na = Na2CO3*2 + NaHCO3 + NaOH 'total concentration of sodium (Na+) ions
Cl = HCl + CaCl2*2 'total concentration of chloride (Cl-) ions
Mgtot = MgCl2 'total concentration of magnesium (Mg++) ions

' CHEMICAL EQUILIBRIUM CONSTANTS
Kw = 1e-14 ' ionic water product, kw = [H+]*[OH-]
Ka1 = 4.45e-7 ' 1st dissociation constant for H2CO3, Ka1 = [H+]*[HCO3-]/[H2CO3]
Ka2 = 4.69e-11 ' 2nd dissociation constant for H2CO3, Ka2 = [H+]*[CO3-]/[HCO3-]
Ksp = 3.8e-9 ' Solubility product of calcite at 25°C Ksp = [Ca+]*[CO3--]
Ksp2 = 8.9e-12 ' Solubility ptduct of brucite at 25°C Ksp2 = [Mg+]*[OH-]^2

pH1 = 0:pH2 = 14 ' pH range to be examined
pHstep = 1 ' initial step for the pH variation
for j = 1 to 8 ' in each of these cycles pH step will be reduced ten times
  for pH = pH1 to pH2 step pHstep
    H = 10^(-1*pH) ' [H+] is by definition 10^(-pH) or pH = log(10){H+}
    OH = Kw/H

    ' Control of precipitation of Mg(OH)2
    ' if the product Mg*OH*OH is greater than solubility product of Mg(OH)2 then it precipitates
    Mg = Ksp2/OH/OH
    if Mg<Mgtot then
      MgOH2 = Mgtot - Mg

```



```

else
  Mg = Mgtot
end if

' Csol is the total carbon in solution, in the different forms H2CO3,HCO3-,CO3--
' CaCO3 is the amount of solid precipitate of CaCO3-calcite per liter
' NOW WE SOLVE A SYSTEM OF SIX EQUATION AND SIX UNKNOWNS
' It requires some algebra and finally a 2nd order equation
' 1) Ka1 = [H+][HCO3-]/[H2CO3] or in basic form Ka1 = H*HCO3/H2CO3
' 2) Ka2 = [H+][CO3--]/[HCO3-] or in basic form Ka2 = H*CO3/HCO3
' 3) Csol = CO3 + HCO3 + H2CO3
' 4) Ksp = [Ca+][CO3--] or Ksp = Ca*CO3
' 5) CaCO3 + Csol = Ctot total amount of carbon in reaction vessel
' 6) CaCO3 + Ca = Catot total amount of calcium in the reaction vessel
' LET US JUMP TO SOLUTION, FINDING AT FIRST Csol value
a1 = Ka1*Ka2
b1 = Ka1*Ka2*(Catot - Ctot)
c1 = -1*Ksp*(H*H + Ka1*H + Ka1*Ka2)
Csol = (-1*b1 + sqr(b1*b1 - 4*a1*c1))/2/a1
if Csol>Ctot then Csol = Ctot
CO3 = Ka1*Ka2*Csol/(H*H + Ka1*H + Ka1*Ka2)
HCO3 = H*CO3/Ka2
H2CO3 = H*HCO3/Ka1
CaCO3 = Ctot - Csol
Ca = Catot - CaCO3
Neut = H + Na + Ca*2 + Mg*2 - OH - Cl - HCO3 - CO3*2
' Important point: electrolytic solution MUST be electrically neutral
if Neut<0 then exit for ' if the case we jump out of the for-->next loop
next pH
pH2 = pH
pH1 = pH2 - pHstep
pHstep = pHstep/10 ' Now pHstep id divided by ten
next j ' and we do this eight times
end

' code 005.bas -----
' This is the main,central code for SeaWaterCalc iterative procedures
' It requires gone input text file (SeaWaterCalc.txt) given as example here below
' Code005 can be downloaded as an executable file as well (SeaWaterCalc.exe) from my web site
' www.oceanchemistry.info. With this option there is no need to download justbasic environment.

' Example of input text file (SeaWaterCal.txt). Only one of the first 5 lines can contain a to ...
step..statement (in the example is the second line

Tc = 17 ' temperature in Celsius (°C)
ppmCO2 = 300 to 500 step 4 ' parts per million (in volume) of CO2 in the atmosphere
P = 0 ' pressure in atm. P=0 means ambient pressure, 1 atm.
S = 35 ' salinity, in grams of salts in 1 kg of solution
pptF = 0 ' fraction of CaCO3 which actually precipitates
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)
save .csv file = 1' (0=no 1 = yes)

' *****
' All concentrations are in mol/kg(solution) !!!! *
' *****

' ----- subroutines area, the main program has to be found on www.oceanchemistry.info -----

sub calculus
T = 273.15 + Tc
' H2CO3 <=> H+ + HCO3- (DOE 1994)
LnK1 = 2.83655 - 2307.1266/T - 1.5529413*log(T) - (4.0484/T + 0.20760841)*S^0.5 + 0.08468345*S -
0.00654208*S^1.5 + log(1 - 0.001005*S)
' HCO3- <=> H+ + CO3-- (DOE 1994)
LnK2 = -9.226508 - 3351.6106/T - 0.2005743*log(T) - (23.9722/T + 0.106901773)*S^0.5 + 0.1130822*S
- 0.00846934*S^1.5 + log(1 - 0.001005*S)
' CO2 + H2O <=> H2CO3 (Weiss 1994)

```

```

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) ' pH = pHT
LnKw = 148.96502 - 13847.26/T - 23.6521*log(T) + (118.67/T - 5.977 + 1.0495*log(T))*S^0.5 -
0.01615*S
' HSO4- <=> H+ + SO4--
I = 19.924*S/(1000 - 1.005*S) ' ionic strenght, useful for KS and KF calculations
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)
' HF <=> H+ + F-
LnKF = 1590.2/T - 12.641 + 1.525*I^0.5 + log(1 - 0.001005*S) + log(1 + SO4/exp(LnKS))
' Ca++ + OH- <=> CaOH+
deltaG = -7576
K7 = exp(-1*deltaG/(R*T))
' Mg++ + OH- <=> MgOH+
deltaG = -14656
K8 = exp(-1*deltaG/(R*T))
' CaCO3calcite <=> Ca++ + CO3--
LogKspCal = -171.9065 - 0.077993*T + 2839.319/T + 71.595*log(T)/a1 + (-0.77712 + 0.0028426*T +
178.34/T)*S^0.5 - 0.07711*S + 0.0041249*S^1.5
LnKspCal = LogKspCal*a1
' CaCO3calcite <=> Ca++ + CO3--
LogKspAra = -171.945 - 0.077993*T + 2903.293/T + 71.595*log(T)/a1 + (-0.068393 + 0.0017276*T +
88.135/T)*S^0.5 - 0.10018*S + 0.0059415*S^1.5
LnKspAra = LogKspAra*a1
' B(OH)3 + H2O <=> H+ + B(OH)4-
LnKB = (-8966.9 - 2890.53*S^0.5 - 77.942*S + 1.728*S^1.5 - 0.0996*S^2)/T + 148.0248 +
137.1942*S^0.5 + 1.62142*S - (24.4344 + 25.085*S^0.5 + 0.2474*S)*log(T) + 0.053105*S^0.5*T

' now we modify the above equilibrium constants in order to account for pressure (sealevel P=0)

LnK1P = LnK1 + (25.5 - 0.1271*Tc)/R1/T*P + 0.5*(-3.08e-3 + 0.0877e-3*Tc - 0.21685e-
3*Tc^2)/R1/T*P^2
LnK2P = LnK2 + (15.82 + 0.0219*Tc)/R1/T*P + 0.5*(1.13e-3 - 0.1475e-3*Tc - 0.1562e-3*Tc^2)/R1/T*P^2
LnKwP = LnKw + (25.6 - 0.2324*Tc + 3.6246e-3*Tc^2)/R1/T*P + 0.5*(-5.13e-3 + 0.0794e-3*Tc -
0.2109e-3*Tc^2)/R1/T*P^2
LnKBP = LnKB + (29.48 - 0.1622*Tc - 2.608e-3*Tc^2)/R1/T*P + 0.5*(-2.84e-3 - 0.2283e-
3*Tc^2)/R1/T*P^2
LnKspCalP = LnKspCal + (48.76 - 0.5304*Tc)/R1/T*P + 0.5*(-11.76e-3 + 0.3692e-3*Tc - 0.3432e-
3*Tc^2)/R1/T*P^2
LnKspAraP = LnKspAra + (46 - 0.5304*Tc)/R1/T*P + 0.5*(-11.76e-3 + 0.3692e-3*Tc - 0.3162e-
3*Tc^2)/R1/T*P^2
LnKSP = LnKS + (18.03 - 0.0466*Tc - 0.3160e-3*Tc^2)/R1/T*P + 0.5*(-4.53e-3 + 0.09e-3*Tc - 0.1595e-
3*Tc^2)/R1/T*P^2
LnKFP = LnKF + (9.78 + 0.009*Tc + 0.942e-3*Tc^2)/R1/T*P + 0.5*(-3.91e-3 + 0.054*Tc - 0.1005e-
3*Tc^2)/R1/T*P^2
' calcola i valori effettivi delle costanti dai logaritmi
K1 = exp(LnK1P):K2 = exp(LnK2P):K0 = exp(LnK0):Kw = exp(LnKwP):Ksp1 = exp(LnKspCalP):Ksp2 =
exp(LnKspAraP)
KS = exp(LnKSP):KF = exp(LnKFP):KB = exp(LnKBP)

' Now starts the iterative procedure
' We use fugacity of CO2 (Koertzingler formula)
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)
H2CO3 = K0*fCO2*1e-6
pH1 = 0: pH2 = 14:Ca = Cal
pHstep = 1
for j = 1 to 8
for pH = pH1 to pH2 step pHstep ' ==> pH free scale, i.e. chemical true scale
H = 10^(-1*pH) ' this scale is used only for bisulphate equilibrium
calculation
' HSO4- formation
HSO4 = H*SO4/(KS + H)
HT = H + HSO4 '==> pH total (Hansson) scale [HT] = [H+] + [HSO4-]
HCO3 = K1*H2CO3/HT ' this scale is used hereinafter for ALL equilibria
calculations, except solubility check
CO3 = K2*HCO3/HT
OH = Kw/HT
' HF formation
HF = HT*F/(KF + HT)
' CaOH+ formation
CaOH = K7*Cal*OH/(K7*OH + 1)
Ca = Cal - CaOH
' MgOH+ formation
MgOH = K8*Mg1*OH/(K8*OH + 1)
Mg = Mg1 - MgOH
' B(OH)3 + H2O reaction
BOH4 = KB*B1/(HT + KB)
' solubility check for CaCO3

```

```

    if (Ca*CO3)>Ksp1 then
      x1 = (Ca*CO3 - Ksp1)/CO3 ' first degree equation
      Ca = Ca - x1*pptF
    end if
    ' end of solubility check
    Neut = H - OH + 2*Ca + 2*Mg + 2*Sr + MgOH + CaOH + Na + K - 2*(SO4-HSO4) - BOH4 - HCO3 -
2*CO3 - Cl - (F-HF) - Br - HSO4
    if Neut<0 then exit for ' For..next continues until neutrality becomes negative
  next pH
  pH2 = pH ' New pH range and pH step are assigned (more strict)
  pH1 = pH2 - pHstep
  pHstep = pHstep/10
next j
end sub

```

code006.bas (density of seawater)

```

'roPw = density of pure water in kg/m3
'roST = density of seawater at 1 atm in kg/m3
'roSTP = density of seawater at salinity S, temperature Tc, pressure P

S = 35 ' salinity, g/(kg-soln)
Tc = 25 ' temperature, degree Celsius
P = 1000 ' pressure, bars

roPw = 999.842594 + 6.793952e-2*Tc - 9.095290e-3*Tc^2 + 1.001685e-4*Tc^3_
- 1.120083e-6*Tc^4 + 6.536332e-9*Tc^5
A = 8.24493e-1 - 4.0899e-3*Tc + 7.6438e-5*Tc^2 - 8.2467e-7*Tc^3_
+ 5.3875e-9*Tc^4
B = -5.72466e-3 + 1.0227e-4*Tc - 1.6546e-6*Tc^2
C = 4.8314e-4
roST = roPw + A*S + B*S^1.5 + C*S^2
Ksb1 = 19652.21 + 148.4206*Tc - 2.327105*Tc^2_
+ 1.360477e-2*Tc^3 - 5.155288e-5*Tc^4
Ksb2 = Ksb1 + S*(54.6746 - 0.603459*Tc + 1.09987e-2*Tc^2-0.1670e-5*Tc^3)_
+ S^1.5*(7.944e-2 + 1.6483e-2*Tc - 5.3009e-4*Tc^2)
Ksb3 = Ksb2 + P*(3.239908 + 1.43713e-3*Tc + 1.16092e-4*Tc^2 -
5.77905e-7*Tc^3) +
P*S*(2.2838e-3 - 1.0981e-5*Tc - 1.6078e-6*Tc^2) + 1.91075e-4*P*S^1.5_ + P^2*(8.50935e-5 - 6.12293e-
6*Tc + 5.2787e-8*Tc^2)_
+ P^2*S*(-9.9348e-7 + 2.0816e-8*Tc + 9.1697e-10*Tc^2)
roSTP = roST/(1 - P/Ksb3)
print "The density of seawater is ";roSTP;" kg/m3"
print "S = ";S;" g/cm3"
print "Tc = ";Tc;" °C"
print "P = ";P;" bars"

```

code007.bas - fugacity of CO2 -----

```

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)
H2CO3 = K0*fCO2*1e-6
pH1 = 0; pH2 = 14
pHstep = 1 ' starting pH step
for j = 1 to 8
  for pH = pH1 to pH2 step pHstep
    H = 10^(-1*pH)
    ' HSO4- formation
    HSO4 = H*SO4/(KS + H)
    HT = H + HSO4 ' pH total (Hansson) scale [HT] = [H+] + [HSO4-]
    HCO3 = K1*H2CO3/HT
    CO3 = K2*HCO3/HT
    OH = Kw/HT
    ' HF formation
    HF = HT*F/(KF + HT)
    ' CaOH+ formation
    CaOH = K7*Cal*OH/(K7*OH + 1)
    Ca = Cal - CaOH
    ' MgOH+ formation
    MgOH = K8*Mg1*OH/(K8*OH + 1)
    Mg = Mg1 - MgOH
    ' B(OH)3 + H2O reaction
    BOH4 = KB*B1/(HT + KB)
    Neut = H - OH + 2*Ca + 2*Mg + 2*Sr + MgOH + CaOH + Na + K_
- 2*(SO4-HSO4) - BOH4 - HCO3 - 2*CO3 - Cl - (F-HF) - Br - HSO4
    if Neut<0 then exit for
  next pH

```



```

' ----- sub's -----
sub calculus
T = 273.15 + Tc
Keq1 = exp(log(K1) - deltaH1/R*(1/T - 1/T0))
Keq2 = exp(log(K2) - deltaH2/R*(1/T - 1/T0))
Keq3 = exp(log(K3) - deltaH3/R*(1/T - 1/T0))
Kw = exp(log(K4) - deltaH4/R*(1/T - 1/T0))
Ksp1 = exp(log(K5) - deltaH5/R*(1/T - 1/T0))
'Ksp2 = exp(log(K6) - deltaH6/R*(1/T - 1/T0))
H2CO3 = Keq1*ppmCO2*1e-6
pH1 = 0: pH2 = 14:Ca = Cal
pHstep = 1
for j = 1 to 8
  for pH = pH1 to pH2 step pHstep
    H = 10^(-1*pH)
    HCO3 = Keq2*H2CO3/H
    CO3 = Keq3*HCO3/H
    OH = Kw/H
    'print "CO3 ini =" ;CO3
    'CaOH+ formation
    'CaOH = K7*Cal*OH/(K7*OH + 1)
    'Ca = Cal - CaOH
    'MgOH+ formation
    'MgOH = K8*Mg1*OH/(K8*OH + 1)
    'Mg = Mg1 - MgOH
    ' solubility check for CaCO3
    Ca = pptF*Ksp1/CO3
    ' end of solubility check
    Neut = H + 2*Ca - OH - HCO3 - 2*CO3
    if Neut<0 then exit for ' For..next continues until neutrality becomes negative
  next pH
  pH2 = pH ' New pH range and pH step are assigned (more strict)
  pH1 = pH2 - pHstep
  pHstep = pHstep/10
next j
print " | ";using("#",Tc);" | ";using("####",ppmCO2);" | ";using("#.###",pH);
print " | ";using("###.###",H2CO3*1000);" | ";using("###.###",HCO3*1000);
print " | ";using("#.#####",CO3*1000);" | ";using("###.###",Ca*1000);
print " | ";using("###.###",1000*(H2CO3 + HCO3 + CO3));
print " | ";using("###.###",1000*(H2CO3 + HCO3 + CO3 - Ca));" |
'stampa nel file 'dat.csv'
' print #1,ppmCO2;",";Tc;",";Ca*1000;",";1000*(H2CO3 + HCO3 + CO3);",";1000*(H2CO3 + HCO3 + CO3 -
Ca)
end sub

```

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