

# PhreeqcI

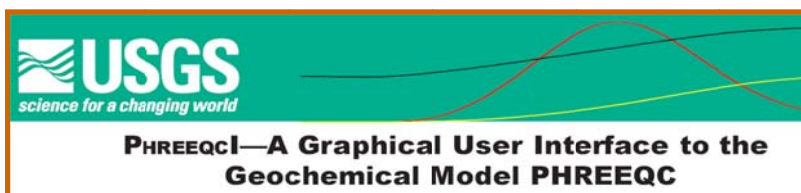
## Introductory Course

(Exercises booklet, chapters 4 and 5)

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[http://wwwbrr.cr.usgs.gov/projects/GWC\\_coupled/phreeqci/](http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqci/)

Many of the examples and concepts used in this booklet can be found further developed in:

- Appelo, C. A. J., Postma, D., 2005. Geochemistry, groundwater and pollution (2nd edition). A. A. Balkema Publishers, Leiden, 649 pp.
- Parkhurst, D. L., Appelo, C. A. J., 1999. User's guide to PHREEQC (Version 2) – A computer program for speciation, batch-reaction, one-dimensional transport and inverse geochemical calculations. U. S. Geological Survey Water Resources Investigations Report 99-4259. U. S. Geological Survey, Denver, 312 pp.
- Parkhurst, D.L., and Appelo, C.A.J., 2013, Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497 p., available only at <http://pubs.usgs.gov/tm/06/a43/>.

# 4 Carbonates and CO<sub>2</sub>

## Remarks:

The **EQUILIBRIUM-PHASES** tool can be used not only to equilibrate water with solid phases, but also with gas phases. This is particularly important in the reactions that occur on the Earth surface. At present the concentration of CO<sub>2</sub> in the atmosphere is ≈380 ppm (in volume), which is equivalent to a partial pressure  $PCO_2 = 380 \times 10^{-6}$  atm. At 25 °C and low pressure, gases behave ideally and their activity is equivalent to the dimensionless value of their partial pressure expressed in atm. In the case of CO<sub>2</sub>:

$$[CO_{2(g)}] = PCO_2 = 3.8 \times 10^{-4} \quad (4.1)$$

where *g* stands for gas phase. The CO<sub>2(aq)</sub> saturation index of an aqueous solution open to interchange with atmosphere (e.g., a rain drop) is given by:

$$SI = \log(PCO_2) = \log(3.8 \times 10^{-4}) = -3.4202 \quad (4.2)$$

**EQUILIBRIUM-PHASES** can be adjusted to a saturation index different from zero, which is particularly useful to equilibrate aqueous solutions with the ambient CO<sub>2</sub> partial pressure.

Note that to facilitate calculations the species H<sub>2</sub>CO<sub>3(aq)</sub> and CO<sub>2(aq)</sub> are usually summed up as H<sub>2</sub>CO<sub>3<sup>0</sup>(aq)</sub>. Phreeqc uses the label CO<sub>2</sub> to represent H<sub>2</sub>CO<sub>3(aq)</sub> + CO<sub>2(aq)</sub>.

**Simulation 4.1.** Calculate pH and carbonate species distribution in rainwater. Do not consider oxygen in a first approach. (File name: Rainwater) (Use Table 4.1)

**Table 4.1**

Simulation	$\Sigma C(+4) = TIC$ (mol/kgw)	$m(H_2CO_3^0)$	$m(HCO_3^-)$	$m(CO_3^{2-})$	pH
4.1					

**Simulation 4.2.** Calculate pH and carbonate species distribution of an aqueous solution in equilibrium with calcite but isolated from the atmosphere. (File name: Calcite\_closed) (Use Table 4.2)

**Simulation 4.3.** Calculate pH and carbonate species distribution of an aqueous solution in equilibrium with calcite and at ambient partial pressure of CO<sub>2</sub>. (File name: Calcite\_open) (Use Table 4.2)

**Table 4.2**

Simulation	$TIC$ (mol/kgw)	$m(H_2CO_3^0)$	$m(HCO_3^-)$	$m(CO_3^{2-})$	$\Sigma Ca$	$m(Ca^{2+})$	pH
4.2							
4.3							

### Questions:

Compare the results of simulations 4.2 and 4.3.

Which one of the two solutions has dissolved more calcite?

What are the differences in pH and carbonate species distribution?

Are solutions 4.2 and 4.3 supersaturated or undersaturated for aragonite? What does this mean?

### Remarks:

Occasionally, it could be convenient to define a pseudo-phase to perform some particular calculations. This can be done using the **PHASES** keyword.

A typical example is when we need to adjust pH to fixed values in batch-reaction simulations. This can be done by means of an artificial phase named, e.g., pH\_FIX defined with the identity reaction  $H^+ = H^+$  and  $\log K = 0$ . Thus, the saturation index with respect to this phase is:

$$SI_{pH-FIX} = \log[H^+] = -pH \quad (4.3)$$

and the pH can be fixed by specifying a given saturation index for pH\_FIX. To attain the specified pH an acid or a base must be chosen to be added to the aqueous solution. This can be done by including a formula in the column [Alt. Formula] of the table in the **EQUILIBRIUM\_PHASES** window. By default, the mineral or phase defined by phase name dissolves or precipitates to attain the target saturation index. However, if an alternative formula is entered, the stoichiometry of the **alternative formula** is added or removed from the aqueous solution to attain the target saturation index.

(Note: If an acid is specified and, in fact, a base is needed to attain a target pH, the program will fail to find a solution)

**Simulation 4.4.** Calculate the carbonate species distribution of an aqueous solution isolated from the atmosphere) with a total C(+4) concentration  $TIC = 1$  mmol/kg water. Use HCl for  $pH < 7$  and NaOH for  $pH > 7$  as alternative formulas. (File name: pH\_FIX) (Use Table 4.3)

**Table 4.3**

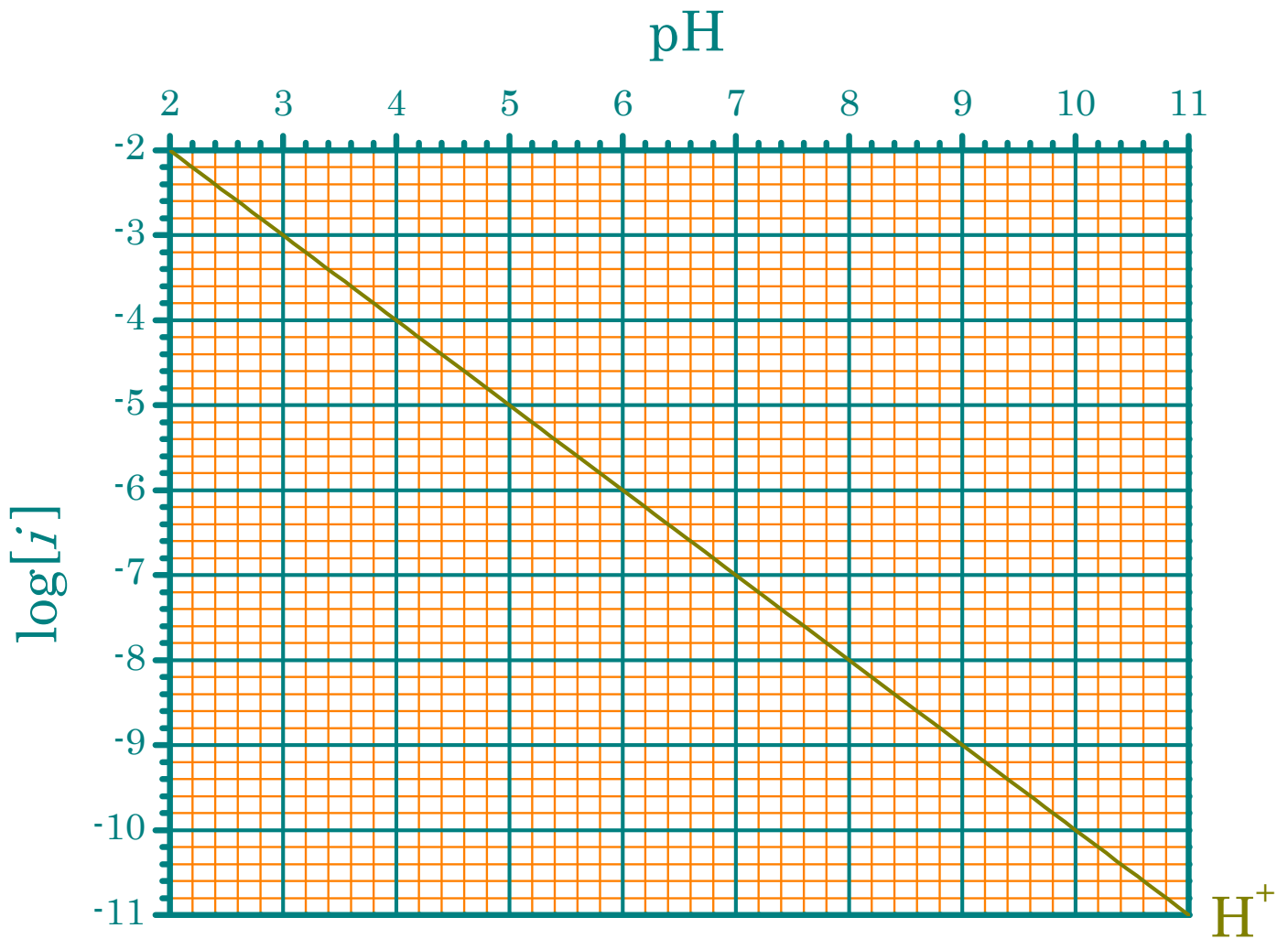
pH	$TIC$ (mol/kgw)	$m(H_2CO_3^0)$	$\log [H_2CO_3^0]$	$m(HCO_3^-)$	$\log [HCO_3^-]$	$m(CO_3^{2-})$	$\log [CO_3^{2-}]$
2							
3							
4							
4.5							
5							
6.352							
7.0							
7.5							
8							
9							
10.329							
11							

**Questions:**

Represent the values of  $\log[\text{H}_2\text{CO}_3^*]$ ,  $\log[\text{HCO}_3^-]$ , and  $\log[\text{CO}_3^{2-}]$  obtained at different pH on Figure 4.1.

What general conclusions can be drawn from Table 4.3 and Figure 4.1?

What happen at  $\text{pH} = 6.352$  and  $10.329$ ? Why?



**Figure 4.1.** Logarithm of the activity of the aqueous species  $i$ .

### Remarks:

For most waters, the alkalinity equals  $m(\text{OH}^-) + m(\text{HCO}_3^-) + 2m(\text{CO}_3^{2-})$ , but Phreeqc considers also all the other species that consume protons and provides an alkalinity value calculated from the alkalinity contribution (see Chapter 2 in this booklet) of the involved species. Measured alkalinity can also be specified in the input file, since **Alkalinity** is defined as a **SOLUTION\_MASTER\_SPECIES** in the Phreeqc database. Normally only the carbonate ions are of quantitative importance for the measured alkalinity. If the alkalinity is specified in the input, the mole-balance equation for alkalinity is included to calculate the total molality of C(+4), which is the element associated with alkalinity in Phreeqc.dat. If both the alkalinity and the total molality of C(+4) are specified in the input, the pH will be calculated in the speciation calculation and will not be equal to the input pH.

In usual practice one of the following pairs of variables are analyzed: pH and alkalinity, *TIC* and alkalinity, *PCO<sub>2</sub>* and alkalinity, or *PCO<sub>2</sub>* and pH. The determination of any two of these variables fixes the ones remaining in the aqueous carbonate system.

**Simulation 4.5.** Calculate the carbonate species distribution of an aqueous solution with Alkalinity = 2.814 meq/kgw and pH = 7.43 (File name: Alkalinity1) (Use Table 4.4)

**Simulation 4.6.** Calculate the carbonate species distribution of an aqueous solution with Alkalinity = 2.814 meq/kgw and *TIC* = 3.035 mmol/kgw. Start from the default pH. (File name: Alkalinity2) (Use Table 4.4)

**Simulation 4.7.** Calculate the carbonate species distribution of an aqueous solution with Alkalinity = 2.814 meq/L and  $\log(\text{PCO}_2) = -2.18$ . Adjust solution pH to equilibrium with  $\text{PCO}_2 = 10^{-2.18}$ . (File name: Alkalinity3) (Use Table 4.4)

**Simulation 4.8.** Calculate the carbonate species distribution of an aqueous solution with pH = 7.43 and  $\log(\text{PCO}_2) = -2.18$ . Adjust C(+4) to equilibrium with  $\text{PCO}_2 = 10^{-2.18}$ . (File name: Alkalinity4) (Use Table 4.4)

**Table 4.4**

Simulation	pH	<i>Alk</i> (eq/kgw)	<i>TIC</i> (mol/kgw)	$\text{CO}_2(g)$ <i>SI</i> = $\log(\text{PCO}_2)$
4.5				
4.6				
4.7				
4.8				

### Questions:

Compare the results of simulations 4.5, 4.6, 4.7, and 4.8.

### Remarks:

As previously shown, the **SOLUTION\_MASTER\_SPECIES** block of Phreeqc.dat is used to define the correspondence between element names and aqueous primary and secondary master species and include the formula or gram formula weight (**gfw**) used to convert grams into moles when the concentrations are entered in mg/L or ppm. In the case of Alkalinity, the **gfw\_formula** compiled in Phreeqc.dat is  $\text{Ca}_{0.5}(\text{CO}_3)_{0.5}$  (gfw = 50.05). This is so because alkalinity is frequently reported as calcium carbonate in mg/L and  $\text{CaCO}_3$  has an equivalent weight of 50.5. However, when in a given analysis alkalinity is reported as  $\text{HCO}_3^-$  mg/L, this fact has to be considered in introducing the input data with the **SOLUTION** keyword. This can be done by writing the chemical formula (from which the gfw will be calculated) in the column labelled [As formula/GFW] in the input table.

**Simulation 4.9.** Calculate the carbonate species distribution corresponding to the analyses in Table 4.5. (File name: Alpujarras) (Use Table 4.6)

**Table 4..5.** Units are mg/L. Alkalinity is reported as  $\text{HCO}_3^-$  in mg/L.<sup>1</sup>

T °C	pH	Na <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	Alk	SO <sub>4</sub> <sup>2-</sup>
18.3	7.23	9	20	63	16	269	24

**Table 4..6.**

<i>TIC</i> (mol/kgw)	Log( <i>PCO</i> <sub>2</sub> )	Log[CO <sub>3</sub> <sup>2-</sup> ]	Log[Ca <sup>2+</sup> ]	<i>SI calcite</i>

### Remarks:

As previously shown, in order to simulate fixed partial pressures of gas components (the case of a finite aqueous solution in contact with the atmosphere or with an infinite gas reservoir) the keyword **EQUILIBRIUM\_PHASES** can be used. In such a case, the partial pressure of the gas component in the reservoir does not change, regardless of the extent of the reactions. Moreover, the keyword **GAS\_PHASE** can be used to define the composition of a **fixed-total-pressure** or a **fixed-volume** multicomponent gas phase. This gas phase may be subsequently equilibrated with aqueous solutions and solid phases to simulate reactions. If the gas reservoir is finite and the pressure on the gas phase is constant, then a fixed-pressure gas phase is appropriate (e.g., a fixed pressure bubble that will vary in volume with the reaction extent). If the gas reservoir is finite and the volume that the gas phase fills is constant, then a fixed-volume gas phase is appropriate (the pressure in the gas volume will vary with the reaction extent. The identifier **-pressure** is not used for a fixed-volume gas phase.

### Keywords:

**GAS\_PHASE**



<sup>1</sup> Groundwater analysis of the Triassic Alpujarras aquifer. Compiled by Appelo and Postma (2005)

**Simulation 4.10.** Calculate the speciation of an aqueous solution which is in equilibrium with calcite and open to the atmospheric CO<sub>2</sub>. Use  $P_{CO_2} = 3.8 \times 10^{-4}$  atm. The amount of dissolved calcite is displayed in the Phase assemblage output block (Initial-Final-Delta). (File name: Calcite\_open) (Use Table 4.7)

**Simulation 4.11.** Calculate the speciation of an aqueous solution initially open to atmospheric CO<sub>2</sub>, which is then isolated from the atmosphere and put in equilibrium with calcite. Use  $P_{CO_2} = 3.8 \times 10^{-4}$  atm. The amount of dissolved calcite is displayed in the Phase assemblage output block (Initial-Final-Delta). (File name: Calcite\_closed1) (Use Table 4.7)

**Simulation 4.12.** Calculate the speciation of an aqueous solution isolated from the atmosphere and in equilibrium with calcite. The amount of dissolved calcite is displayed in the Phase assemblage output block (Initial-Final-Delta). (File name: Calcite\_closed2) (Use Table 4.7)

**Simulation 4.13.** Calculate the speciation of an aqueous solution in contact with a finite volume of gas (1 kg of solution in contact with 0.5 L of gas) and in equilibrium with calcite. Use  $P_{CO_2} = 3.8 \times 10^{-4}$  atm. The amount of dissolved calcite is displayed in the Phase assemblage output block (Initial-Final-Delta). (File name: Calcite\_gas\_finite) (Use Table 4.6)

**Table 4..7.**

Simulation	pH	<i>Alk</i> (eq/kgw)	Dissolved calcite (moles)	<i>TIC</i> (mol/kgw)	CO <sub>2</sub> (g) <i>SI</i> = log( $P_{CO_2}$ )
4.10					
4.11					
4.12					
4.13					

**Questions:**

- Compare the results of simulations 4.10, 4.11, 4.12, and 4.13.
- In which conditions is a larger amount of calcite dissolved?
- Does the partial pressure of CO<sub>2</sub> decreases or increases during the dissolution process?
- Does calcite dissolution removes CO<sub>2</sub> from the gas phase?
- Is there a relationship between *TIC* and pH?

# 5 Redox processes

## Remarks:

In dealing with redox processes Phreeqc uses the concept of  $pe$ . In analogy to pH, the parameter  $pe$  is given by:

$$pe = -\log[e^-] \quad (5.1)$$

where  $[e^-]$  is the electron activity, which should be interpreted as the tendency to release or accept electrons. High positive values of  $pe$  indicate oxidizing conditions and low negative values reducing conditions. On this basis, Phreeqc.dat compiles redox reactions using electron activities. In fact,  $e^-$  is included in **SOLUTION\_SPECIES**. Thus, for instance, in the reaction  $Fe^{2+} = Fe^{3+} + e^-$ , equilibrium is described by the expression:

$$K = \frac{[Fe^{3+}][e^-]}{[Fe^{2+}]} = 10^{-13,02} \quad (5.2)$$

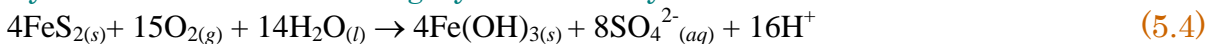
as can be observed editing the database with WordPad.

Under Earth surface conditions the main oxidizing agent is the atmospheric oxygen. The oxygen partial pressure in the atmosphere is  $PO_2 = 0.2$  atm. Therefore:

$$SI = \log(PO_2) = \log(0.2) = -0.699 \quad (5.3)$$

## Remarks:

Pyrite oxidation can be roughly described by the whole reaction:



which is a simplified reaction that involves two processes of oxidation:



Oxygen obviously is the oxidant, electron acceptor:



**Simulation 5.1.** Calculate the pH and the species distribution resulting from dissolution-oxidation of 0.002 moles of pyrite in 1 kg water which is in contact with the atmosphere. Equilibrate with hematite to precipitate the excess of dissolved  $Fe^{3+}$ . Use  $PCO_2 = 3.8 \times 10^{-4}$  atm and  $PO_2 = 0.2$  atm. (File name: Pyrite1) (Use Table 5.1)

**Simulation 5.2.** Calculate the speciation of 1 kg of aqueous solution initially open to the atmosphere, which is then isolated and make react with 0.002 moles of pyrite. Note that in this case the aqueous solution would become supersaturated with respect to pyrite and, therefore, the reaction would actually stop before complete dissolution of the 0.002 moles. Equilibrate with pyrite in a third stage to precipitate the excess. Use  $PCO_2 = 3.8 \times 10^{-4}$  atm and  $PO_2 = 0.2$  atm. (File name: Pyrite2) (Use Table 5.1)

**Simulation 5.3.** Calculate the pH and the species distribution resulting from dissolution-oxidation of 0.002 moles of pyrite in 1 kg water, which is in contact with the atmosphere and in equilibrium with calcite. Equilibrate with hematite to



precipitate the excess of dissolved  $\text{Fe}^{3+}$ . Use  $P_{\text{CO}_2} = 3.8 \times 10^{-4}$  atm and  $P_{\text{O}_2} = 0.2$  atm. (File name: Pyrite3) (Use Table 5.1)

**Table 5.2**

Simulation	$\Sigma\text{SO}_4^{2-} = \text{S}(6)$ (mol/kgw)	$\Sigma\text{S}(-2)$ (mol/kgw)	Dissolved pyrite (moles)	$SI(\text{O}_2)$	$pe$	pH
5.1						
5.2						
5.3						

**Questions:**

Compare the results of simulations 5.1, 5.2, and 5.3.

Why does pH increase in simulations 5.1 and 5.2?

What happen with the oxygen in simulation 5.2? Does pyrite dissolves completely in this case? Why?

How are the redox conditions in 5.1, 5.2, and 5.3?

**Remarks:**

In the presence of oxygen, the decomposition of organic matter can be symbolized by the carbohydrate oxidation reaction:



**Simulation 5.4.** Calculate the speciation of 1 kg of aqueous solution initially open to the atmosphere, which was then isolated and put in contact with 0.001 moles of carbohydrate to oxidize them. Use  $P_{\text{CO}_2} = 3.8 \times 10^{-4}$  atm and  $P_{\text{O}_2} = 0.2$  atm. Compare the results with the speciation of rainwater. Rainwater speciation is given after the first simulation stage in the program (water open to the atmosphere) (File name: Carbohydrate) (Use Table 5.2)

**Table 5.2**

Simulation	pH	$pe$	$SI(\text{O}_2)$	$TIC$ (mol/kgw)	$TOC^2$ (mol/kgw)
Rainwater					
$\text{CH}_2\text{O}$ oxidation					

**Questions:**

Compare the final  $TIC$  and  $TOC$  with that of rainwater.

Why does pH increase during oxidation?

What happens with the oxygen?

Which are the redox conditions at the end of the oxidation process?

<sup>2</sup> Total Organic Carbon =  $\Sigma\text{C}(-4)$

### Remarks:

Methane ( $\text{CH}_4$ ) is a common constituent of anoxic ground water that generates in the final stage of the reductive sequence. The generation of bubbles of methane from decomposition of organic matter can be simulated using the **GAS\_PHASE** tool of Phreeqc. For a fixed-pressure gas phase, when the sum of the partial pressures of the component gases exceeds the specified pressure of the gas phase, a gas bubble forms. Once the bubble forms, the volume and composition of the gas bubble vary with the extent of reactions.

**Simulation 5.5.** Calculate the evolution of a bubble of gas generated by decomposition of 20 mmoles of organic matter (carbon, hydrogen, and oxygen released with the carbohydrate –  $\text{CH}_2\text{O}$  – stoichiometry) in contact with 1 kg of aqueous solution at a depth of 10 m (assumed equivalent to a fixed pressure of 2 atm). Consider that the aqueous solution is initially equilibrated with calcite and has a partial pressure of  $\text{CO}_2$  of 0.01 atm ( $SI = -2$ ). Monitor the reaction by considering a sequence of 1 millimol  $\text{CH}_2\text{O}$  decomposition steps. Use selected\_output to represent the evolution of the gas phase (volume and moles of  $\text{CH}_4$  and  $\text{CO}_2$ ) and the saturation indices with respect to these gases. (File name: Bubble) (Selected\_output file name: Bubble.sel)

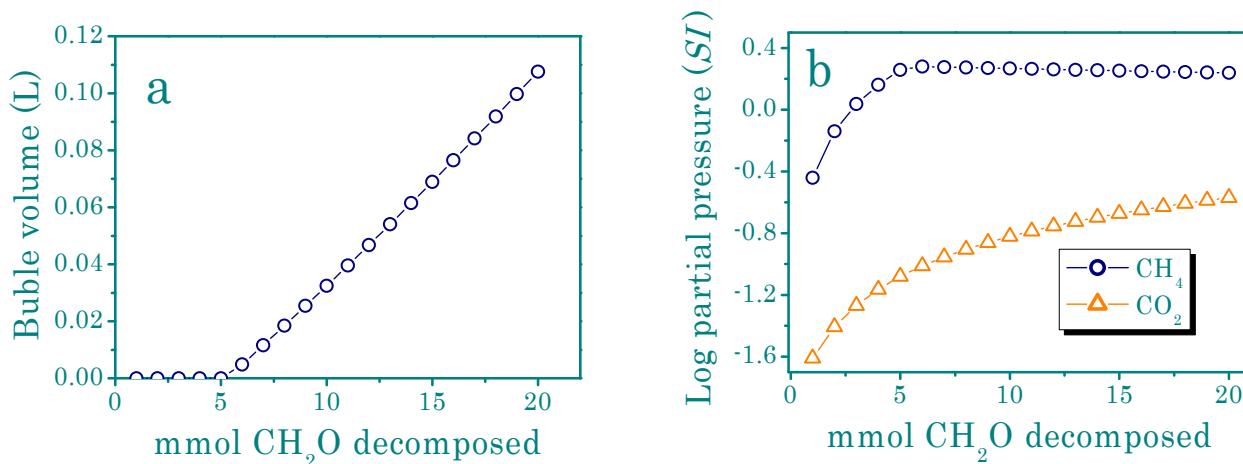
### Questions:

Open the selected\_output file with Microsoft Excel and examine the compiled results.

Plot the gas volume as a function of the decomposed organic matter to obtain a graph similar to the one shown in Figure 5.1a.

Plot the saturation indexes for  $\text{CH}_4$  and  $\text{CO}_2$  to obtain a graph similar to the one shown in Figure 5.1b.

What do Figures 5.1a and 5.1b mean?



**Figure 5.1.** Evolution of a gas bubble during the decomposition of organic matter.

### Remarks:

While Phreeqc deals with true equilibrium relationships, partial equilibrium situations (in which a multi-component, heterogeneous system is in equilibrium with respect to some processes or reactions, but out of equilibrium with respect to others) are very frequent both in nature and laboratory. For instance, at the  $P_{O_2}$  of the Earth's atmosphere,  $N_{2(g)}$  is thermodynamically unstable relative to  $NO_3^-$ , due to the redox reaction:



In Phreeqc.dat the mass action equation for this reaction is:

$$\log K = \log[NO_3^-] - 6pH - 5pe - \frac{1}{2}\log(PN_2) = -103.54 \quad (5.10)$$

However, this reaction is not feasible and should be blocked in Phreeqc in calculating the interaction of aqueous solutions with the atmosphere.

**Simulation 5.6.** Calculate the speciation of water open to the atmosphere. Do not only consider  $PCO_2 = 3.8 \times 10^{-4}$  atm and  $PO_2 = 0.2$  atm, but also  $PN_2 = 0.78$  atm. Compare the results with the previous speciation of rainwater (see previous results in Table 5.2. (File name: Nitrogen1) (Use Table 5.3)

**Table 5.3**

Simulation	pH	$pe$	Dissolved $N_2$ (mol/kgw)	$mNO_3^-$ (mol/kgw)
5.6				

### Questions:

Compare the final pH with that of rainwater.

Which is the most abundant nitrogen species in solution?

Is this scenario realistic?