



Getting started with the MARCHEMSPEC Marine Chemical Speciation Models

Supplement: Using the Models Within **MATLAB**

Version 1.1

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The Marine Chemical Speciation Model (MARCHEMSPEC) was created by SCOR Working Group 145 (2015 – 2022), and it is being further developed under the auspices of the Joint Committee on the Properties of Seawater. The members of SCOR Working Group 145 were as follows:

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This document describes the use, within MATLAB, of the MARCHEMSPEC speciation models for the following systems: (i) natural waters containing the ions of seawater, optionally including trace metals; (ii) artificial seawater and artificial seawater acidified with HCl; (iii) Tris buffers in artificial seawater.

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It is available from marchemspec.org.

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version 1.1 (02/24)

David R. Turner and Simon L. Clegg

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1. Introduction

This Supplement to the document of Clegg and Turner (2023) describes the use of the MARCHEMSPEC models within MATLAB, using a single function that calls the appropriate model for a single problem at a time. The types of natural water or solution that can be modelled are as follows:

- Seawater (of a specified practical salinity and temperature) that, optionally, can be adjusted to a user-defined alkalinity.
- A natural water containing the ions of seawater at a specified temperature, but with concentrations of individual solutes specified by the user, and which can also be adjusted for alkalinity.
- The same as both options above, but including the following trace metals so that their complexation by inorganic ions can be calculated: Al^{3+} , Cd^{2+} , Co^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} . Phosphate and silicate $\text{Si}(\text{OH})_4$, and calculations of their acid-base speciation, can also be included.
- Artificial seawater, of the type using in the calibration of the seawater total pH scale, of a specified nominal practical salinity and temperature. This may, optionally, be acidified by adding HCl.
- Artificial seawater at a specified temperature, to which can be added HCl and Tris to create buffer solutions.
- Solutions containing the ions of artificial seawater, H^+ , and Tris at a specified temperature, but with concentrations of individual solutes specified by the user.

The outputs of the model, to MATLAB arrays, are: (i) concentrations and activity coefficients of all species at equilibrium, and seawater state parameters and trace metal complexation (according to the model called). The seawater state parameters are: pH (on three scales), $f\text{CO}_2$, $p\text{CO}_2$, total alkalinity, total dissolved inorganic carbon, the carbonate, borate, bisulphate, HF, and water dissociation constants K_1 , K_2 , K_B , K_S , K_F , and K_W . For definitions of these quantities, see Table 1 of Chapter 2 in Dickson et al. (2007). The calcium carbonate concentration product is also output by the model. Concentrations and seawater state parameters are presented on both a molality and mole fraction basis. The names used for these output state parameters are given in **Table 1** of this Supplement.

See the References section later for the source papers describing the MARCHEMSPEC models.

In this release of the model some aspects of the activity coefficient treatment of $\text{Fe}[\text{III}] \text{OH}^-$ complexes have been revised, and the MarChemSpec MATLAB function is now able to equilibrate solutions to single values or pairs of seawater state variables for argument *iCalc* values of 4 and 5 only. This additional capability is described in a separate supplement *Calculations for Natural Waters of Defined Alkalinity, Total Dissolved Inorganic Carbon, pH, and Partial Pressure or Fugacity of CO_2 Using MATLAB*.

1.1 Concentration scales

The following scales are used by MARCHEMSPEC, and will be referred to in this document:

- Moles per kg of pure water (**molality**)

- Moles per kg of solution (**amount content**)

The common practice in oceanography is to express compositions on a moles per kg of solution basis (for which the recommended term is **amount content**). In solution chemistry and particularly solution thermodynamics – the calculation of activity coefficients and speciation – moles per kg of pure water solvent (**molality**) is used. The convenience of the latter scale becomes clear when considering changes of natural water composition from seawater stoichiometry. For example, in a seawater in which there is a more Mg^{2+} and less Na^+ than normal only the molalities of these two species are different from their values in standard seawater. However, when expressed on an amount content basis, *all* concentrations are changed.

The MarChemSpec function will accept input compositions on *both* scales, and always outputs results on both scales. The two are used and referred to throughout this document.

This MARCHEMSPEC software for MATLAB uses same underlying code as the standalone versions of the models, and the references cited below can be read in conjunction with this Supplement for more information.

Other relevant MARCHEMSPEC documents

Copies of these documents are available from the authors, or from marchemspec.org.

S. L. Clegg and D. R. Turner (2023) *Getting Started with the MARCHEMSPEC Marine Chemical Speciation Models*, SCOR/IAPSO WG 145.

S. L. Clegg and D. R. Turner (2023) *Getting Started with the MARCHEMSPEC Marine Chemical Speciation Models*. Supplement: *Calculating the Inorganic Complexation of Trace Metals*, SCOR/IAPSO WG 145.

D. R. Turner and S. L. Clegg (2023) *Getting Started with the MARCHEMSPEC Marine Chemical Speciation Models*. Supplement: *Calculations for Natural Waters of Defined Alkalinity, Total Dissolved Inorganic Carbon, and Borate*, SCOR/IAPSO WG 145.

2. Installing MARCHEMSPEC for MATLAB

Separate versions of the MarChemSpec MEX function, and associated files, are available to run on computers with the following operating systems:

- Windows (version 7 and higher), 64 bit
- Linux

The programs and associated files and directories are provided as a zip file (Windows), and as a zipped tar file (Linux). We expect to be able to produce versions of the models to run on Apple machines in the future.

“Installation” of MARCHEMSPEC involves simply extracting the contents of the zip file or other archive to your computer. Before doing this, decide what your main working directory will be, and create it. This is the one that will hold the MATLAB function, the library and related files containing the model, and a number subdirectories. For this illustration, we assume that the main working directory is **c:\marchemspec_mb**. After extracting your files to this directory (or your chosen equivalent), you should have a structure like this:

c:\marchemspec_mb - contains MEX file, program library file, and text files Pitzer.par, Pitzer.rcn, and DO_NOT_DELETE.txt.

c:\marchemspec_mb\docs - documentation, including this manual.

c:\marchemspec_mb\examples - contains example scripts for different types of calculation.

c:\marchemspec_mb\seawater - contains Uncert.mst (for seawater solutions).

c:\marchemspec_mb\seawater\{BC, CCA, AAC, NCA, _lnKeql} - files of variances.

c:\marchemspec_mb\ASWbuffer - contains Uncert.mst (for artificial seawater and buffer solutions).

c:\marchemspec_mb\ASWbuffer\{BC, CCA, AAC, NCA, _lnKeql} - files of variances.

The above example is how the directories would look on a Windows computer. The structures would be analogous on Linux, for example ‘/home/usr/marchemspec_mb’ instead of ‘c:\marchemspec_mb’.

Important: if you also install one or more of the standalone Fortran MARCHEMSPEC programs, or other MARCHEMSPEC functions and libraries (such as that for Python), make sure they are all in separate directories, otherwise files that have the same names (but different contents according to the model) may be copied over each other.

3. Using the MarChemSpec Function

Seven different types of calculation can be carried out, corresponding to those summarised in the Introduction. The required one is specified by a constant, **iCalc**, which is the first argument of the MarChemSpec function. The meanings of the different values of iCalc are listed in the table below.

Group	iCalc	Calculation type
A	1	HCl in artificial seawater of specified nominal salinity.
	2	Tris buffer in artificial seawater of specified nominal salinity.
	3	Solutions containing the ions of artificial seawater, H^+ , and Tris buffer, with user-specified molalities of all solutes.
B	4	Reference seawater of specified salinity, which may have its alkalinity altered by the addition of H^+ or OH^- .
	5	Solutions containing the ions of standard seawater, with user-specified molalities of all solutes.
C	6	Reference seawater of specified salinity, which may have its alkalinity altered by the addition of H^+ or OH^- , and including trace metals Al^{3+} , Cd^{2+} , Co^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} .
	7	Solutions containing the ions of standard seawater, with user-specified molalities of all solutes including PO_4^{3-} , $Si(OH)_4$, and the metal ions Al^{3+} , Cd^{2+} , Co^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} .

Notes: The recipe for artificial seawater and for Tris buffer solutions containing artificial seawater, relevant to iCalc 1-3 above, is that of DelValls and Dickson (1998). Reference seawater has composition given by Millero et al. (2008), see their Table 4.

The group identifiers A-C above are important: MATLAB should either be closed and then reopened if changing between groups A, B and C (in any order) for successive calculations, or the MATLAB “clear all” command used instead.

3.1 Telling MATLAB where the MARCHEMSPEC files are

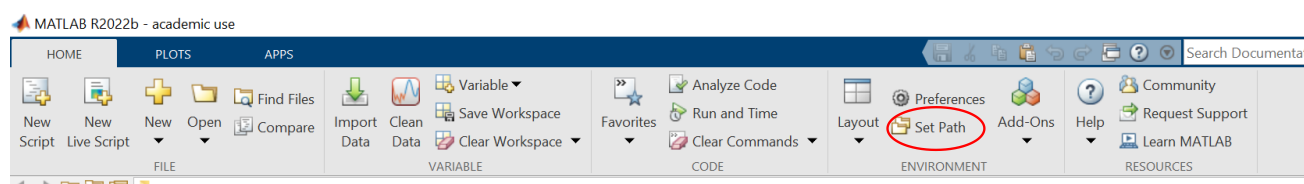
It is necessary to specify to MATLAB the location of the MEX file containing the MATLAB MarChemSpec function, and the library file containing the model itself. Slightly different procedures are required for Windows and Linux systems. These are described below:

3.1.1 Steps for Windows

First, the MATLAB MEX file, and the program library file MarChemSpec.dll, should be kept in the same directory (as supplied in the zip file). MATLAB expects them either to be in the same location, or for the dll file to be in the system path. It is simpler to keep them both together.

Next, we tell MATLAB where the MEX file is by adding the directory name to the MATLAB path. This can be done in more than one way:

One method is to do it interactively. Within the MATLAB application click on “Set path” in the HOME menu:



Then click on “Add Folder...” and in the window “Add folder to path” select c:\marchemspec_mb (or other working directory that has been chosen in the installation).

Alternatively, the path can be specified using the `addpath()` command before calling the MarChemSpec function. This can be added to the example scripts that have been provided, if necessary. Using the example working directory from section 2, such a command would be:

```
addpath('c:\marchemspec_mb\')
```

Notice that we include the terminating ‘\’. This example is for Windows. On Linux and Apple machines the directory separator is ‘/’.

If you previously downloaded an earlier version of MarChemSpec, and you added the folder containing the earlier version(s) to the MATLAB path, then it is essential that either the old folder is removed from the path or that you overwrite the old MarChemSpec dll file or shared object library with the new copy in this distribution. Otherwise you may find that you are running an older version of the model despite the new download.

We also communicate two directory locations to the MarChemSpec function, as the text string arguments **strFilesDirectory** and **strCovmxDirectory**. The first of these strings must specify the directory containing the files Pitzer.par and Pitzer.rcn which will be read by the function. In our example, this is directory c:\marchemspec_mb, and so this assignment is made within each example script before the first call of MarChemSpec:

```
strFilesDirectory = 'c:\marchemspec_mb\'
```

The second text string argument must specify the directory where the two subdirectories **seawater** and **ASWbuffer** are located. (This directory must also contain the file DO_NOT_DELETE.txt.) In the zip file or other archive that you have downloaded both of these subdirectories are also present in c:\marchemspec_mb. Therefore the assignment is the same as that above:

```
strCovmxDirectory = 'c:\marchemspec_mb\'
```

This assignment must be made before the first call of the MATLAB MarChemSpec function. If you choose to move subdirectories seawater and ASWbuffer elsewhere, make sure that: (i) they are kept together (ie, both subdirectories of the same parent directory); (ii) the parent directory contains the file DO_NOT_DELETE.txt. The model code searches for this file in the location specified by strCovmxDirectory. If the file isn’t found, the function will terminate with an error message.

3.1.2 Steps for Linux

We will assume that the MATLAB MEX file, and the program library file libMarChemSpec.so, are kept in the same directory (as supplied in the zipped tar file) for simplicity. On Linux systems we must first tell the operating system where to find the library file libMarChemSpec.so. This is done at a command prompt, *before* starting MATLAB, by issuing two commands. If the location of the library file is /home/usr/marchemspec_mb/ then these commands are:

```
export LD_PRELOAD=/home/usr/marchemspec_mb/libMarChemSpec.so
export LD_LIBRARY_PATH=/home/usr/marchemspec_mb:$LD_LIBRARY_PATH
```

Note that the first command is essential, otherwise some function names in libMarChemSpec.so will clash with those in other libraries used by MATLAB.

After MATLAB has been started, the addPath() command shown in the previous section can be used to specify the location of the MEX file (here '/home/usr/marchemspec_mb/').

The locations of the Pitzer.par and Pitzer.rcn files, and of the directories holding the files of variances, are communicated to the MarChemSpec function using the arguments strFilesDirectory and strCovmxDirectory in exactly the same way as described in the previous section.

3.2 What happens if I make a mistake?

We have tried to trap two kinds of errors:

1. The MarChemSpec function is called incorrectly, for example with an array argument of the wrong size or shape, or with an argument missing. If this happens, the function will display an explanatory error message (and will not call the underlying model).
2. The call of the MarChemSpec function is correct, but some of the data being passed to the model are wrong. This could be anything from an invalid value of iCalc, to a negative species molality or amount content, or an input solution composition for which the ions are not charge balanced. In such cases the function will return, and display an error message that has been generated by the MARCHEMSPEC model. You should correct the error and try again.

Important: we have made every effort to trap invalid input data (case 2 above), and return error messages. However, should an error be detected by the model *after* it has begun a calculation then it is likely that it will write a message to a text file with the extension .err and then **stop**. Because the model is running within MATLAB this 'stop' will also close down MATLAB. If this happens then look at the error file (most likely called MCS.err) for the description of the problem, correct it, and try again after reloading MATLAB. If there is no such file, contact the program authors.

3.3 The diagnostic MarChemSpec argument iFail

For all calculations the MarChemSpec function returns a value of the diagnostic variable **iFail**. If your call of the function fails, then checking the value of iFail may help you work out why. The meanings of different values are as follows:

iFail	Meaning	Comment
-10	The value of iFail on input (which currently must be 0 or 1) has not been recognised.	Not used with MATLAB.
-6	Debug output was requested (iFail = 1) but, although the log file was opened successfully, attempts to write to it (just some header info in a format statement) failed.	Not used with MATLAB.
-5	Debug output was requested (iFail = 1) but the log file could not be opened in either strFilesDirectory or the present working directory.	Not used with MATLAB.
-1	Argument ErrorMessage has a LEN or SIZE too small to be of use. No calculations will be done.	Not relevant to the MarChemSpec MATLAB function.
0	Success. Values of the MARCHEMSPEC internal iFail and nObjFun variables can be found in optional function argument iUser.	This is a normal result, after a successful call of the function and underlying model. The internal iFail and other numbers are unlikely to be of interest under most circumstances.
10	An error has been detected (e.g., a change of model) that probably requires the user to exit MATLAB and start again from scratch.	This is a result of a change of calculation type (iCalc) that is also a change of group (A-C). See explanation in text.
100	An error has been detected: the user should correct this and call the wrapper again.	This is the result of the model detecting invalid data, which is likely to be explained in an error message.

3.4 What do I do next?

Now you are ready to begin using the MarChemSpec MATLAB function. Just double click on the .m example script that you want to run to start MATLAB, or navigate to the script within MATLAB. If the directory containing the script is not on the MATLAB path then you will as usual be asked to “Change folder” or “Add to path” to fix this. One example script is provided for each of the seven types of calculation listed in the table at the beginning of section 3.

An alternative approach would be to open MATLAB, making sure you carry out the appropriate path assignments described in section 3.1, and also open one of the example scripts in a text editor. There is useful explanatory information in these scripts. Commands can be cut and pasted into MATLAB as needed.

In the next part of this document we show examples of each of the types of calculation (iCalc). These examples contain lists of inputs and outputs, and their meanings, and provide sufficient information for you to be able to do calculations for your own problems.

4. Examples of Different MARCHEMSPEC Calculations

In this section we present examples of the seven types of calculation ($iCalc = 1 - 7$). We begin with the seawater and trace metal calculations ($iCalc = 4 - 7$). These are followed by the artificial seawater and buffer examples ($iCalc = 1 - 3$). Note that there is a separate document that describes how to do calculations for fixed values of seawater state parameters (alkalinity, dissolved inorganic carbon, and others). These involve the use of arguments *iFix* and *ValuesFixed*. See also the version history at the end of this document.

4.1 Reference seawater ($iCalc = 4$)

The seawater composition is Reference Seawater as defined in the TEOS-10 system (www.teos-10.org). Full details of the Reference Seawater composition can be found in (Millero et al., 2008). For this calculation the MATLAB call has the form:

[*Outputs*, *NamesOutputs*, *cSpecies_out*, *mSpecies_out*, *ActCoeffs*, *NamesSpecies*, *iFail*] = ...

MarChemSpec(*iCalc*, *tC*, *S*, *P*, *mH*, *nSpecies*, *iFix*, *ValuesFixed*, *nOut*, *strFilesDirectory*, *strCovmxDirectory*);

Input arguments

Argument	Value	Meaning
<i>iCalc</i>	4 (fixed)	
<i>tC</i>	-5 <= <i>tC</i> <= 45 ^a	Temperature (°C)
<i>S</i>	0 < <i>S</i> <= 45 ^a	Practical salinity
<i>P</i>	1 (fixed)	Pressure (atm) (this version of MarChemSpec is coded only for 1 atmosphere pressure).
<i>mH</i>		The alkalinity (amount content) of the reference seawater is decreased by <i>mH</i> mol kg ⁻¹ (<i>mH</i> can be positive or negative).
<i>nSpecies</i>	9 (fixed)	The row lengths of <i>cSpecies_out</i> , <i>mSpecies_out</i> , <i>ActCoeffs</i> , and <i>NamesSpecies</i>
<i>iFix</i>	0 (fixed)	Reserved for future development.
<i>ValuesFixed</i>	2x2 array [0 0;0 0] (fixed)	Reserved for future development.
<i>nOut</i>	54 (fixed)	The number of state variables and stoichiometric equilibrium constants to be returned in the array <i>Outputs</i> .
<i>strFilesDirectory</i>	c:\marchemspec_mb\ ^b	Folder containing the text files (Pitzer.par, Pitzer.rcn) read by the model.
<i>strCovmxDirectory</i>	c:\marchemspec_mb\ ^b	Folder containing directories seawater and ASWbuffer.

Notes:

^a If these ranges are exceeded, the calculation will fail, returning a value of *iFail* = 100 and an explanatory message.

^b These are the standard folder locations, but must be set to wherever the model files have been installed.

The input argument *mH* has different meanings according to the value of *iCalc*. For these *iCalc* = 4 calculations, it is used to make changes to alkalinity. The reference seawater, at salinity 35, has a defined alkalinity of 2.304×10^{-3} mol per kg (amount content). The alkalinity varies with salinity, and you can easily determine the value by calling MARCHEMSPEC for the desired salinity and temperature, with *mH* set to zero. If you want to *decrease* the alkalinity of a solution by *x* mol per kg (amount content) then set *mH* to +*x* (i.e., *x* is positive because we are *adding* H⁺ to the solution, and substituting it for Na⁺). Conversely, if you want to *increase* alkalinity by *x* mol per kg, then set *mH* to -*x* (it is negative, and we are adding OH⁻ to the solution as NaOH).

This simple approach to adjusting alkalinity can still be used, and the MARCHEMSPEC document *Calculations for Natural Waters of Defined Alkalinity, Total Dissolved Inorganic Carbon, and Borate* should be consulted for details. However, this method has been superseded and the model is now able to equilibrate solutions to assigned values of pairs or single values of pH (total or free), DIC, alkalinity, and *pCO*₂ or *fCO*₂. For further information, and examples for *iCalc* equal to 4 and 5, please see the MATLAB supplement referred to in the Introduction.

4.1.1 Outputs for *iCalc* = 4

The calculated quantities include the chemical speciation, solute activity coefficients, osmotic coefficient, and a number of seawater state variables. These are described below.

Individual chemical species

The names are given in the $3 \times nSpecies$ cell *NamesSpecies* where the three rows refer to cations, anions and neutral species respectively. The contents of *NamesSpecies* are:

H	Na	Mg	Ca	K	MgOH	Sr	MgF	CaF
Cl	SO4	HSO4	OH	Br	HCO3	CO3	B(OH)4	F
B(OH)3	CO2	HF	MgCO3	CaCO3	SrCO3			

The arrays *cSpecies_out*, *mSpecies_out* and *ActCoeffs* contain the individual chemical species' amount contents, molalities and activity coefficients respectively. These arrays are arranged in the same way as *NamesSpecies*, so that for example *mSpecies_out*(1,2) is the molality of Na⁺.

State variables, including stoichiometric equilibrium constants

These results are given in the $nOut \times 2$ array *Outputs*. The first column contains values of the quantities, and the second column their uncertainties. The missing value code is 99. The meaning of each element is given in abbreviated form in the cell *NamesOutputs*. In the full descriptions below, the concentration basis is either molality (*m*) or amount content (*a.c.*), and the pH scale is either total (T), seawater (SW), or free (F).

Row(i)	NamesOutputs(i)	Conc. basis	pH scale	Full description
1	Osm. coeff.	<i>m</i>	-	Osmotic coefficient
2	ln(aW)		-	ln (activity of water)
3	pH(T)(m)	<i>m</i>	T	pH on the total scale ('T')
4	pH(SW)(m)	<i>m</i>	SW	pH on the seawater scale ('SW')
5	pH(F)(m)	<i>m</i>	F	pH on the free scale ('F')
6	pCO ₂	-	-	CO ₂ partial pressure
7	fCO ₂	-	-	CO ₂ fugacity
8	Tot.Alk.(m)	<i>m</i>	-	Total alkalinity
9	DIC(m)	<i>m</i>	-	Total dissolved inorganic carbon
				<i>Below: stoichiometric dissociation constants K*</i>
10	K*(CO ₂)(T,m)	<i>m</i>	T	CO ₂
11	K*(HCO ₃)(T,m)	<i>m</i>	T	HCO ₃
12	K*(B(OH) ₃)(T,m)	<i>m</i>	T	B(OH) ₃
13	K*(H ₂ O)(T,m)	<i>m</i>	T	Water ion product
14	K*(HF)(T,m)	<i>m</i>	T	HF
15	K*(HSO ₄)(T,m)	<i>m</i>	T	HSO ₄
16	K*(CO ₂)(SW,m)	<i>m</i>	SW	CO ₂
17	K*(HCO ₃)(SW,m)	<i>m</i>	SW	HCO ₃
18	K*(B(OH) ₃)(SW,m)	<i>m</i>	SW	B(OH) ₃
19	K*(H ₂ O)(SW,m)	<i>m</i>	SW	water
20	K*(HF)(SW,m)	<i>m</i>	SW	HF
21	K*(HSO ₄)(SW,m)	<i>m</i>	SW	HSO ₄
22	K*(CO ₂)(F,m)	<i>m</i>	F	CO ₂
23	K*(HCO ₃)(F,m)	<i>m</i>	F	HCO ₃
24	K*(B(OH) ₃)(F,m)	<i>m</i>	F	B(OH) ₃
25	K*(H ₂ O)(F,m)	<i>m</i>	F	Water ion product
26	K*(HF)(F,m)	<i>m</i>	F	HF
27	K*(HSO ₄)(F,m)	<i>m</i>	F	HSO ₄
28	Ca.CO ₃ (m)	<i>m</i>	-	Ca x CO ₃ concentration product
29	pH(T)	<i>a.c.</i>	T	pH on the total scale
30	pH(SW)	<i>a.c.</i>	SW	pH on the seawater scale
31	pH(F)	<i>a.c.</i>	F	pH on the free scale
32	pCO ₂	-	-	CO ₂ partial pressure
33	fCO ₂	-	-	CO ₂ fugacity
34	Tot.Alk.	<i>a.c.</i>	-	Total alkalinity
35	DIC	<i>a.c.</i>	-	Total dissolved inorganic carbon
				<i>Below: stoichiometric dissociation constants K*, all given as pK* (-log₁₀(K*))</i>

36	pK*(CO2)(T)	a.c.	T	CO ₂
37	pK*(HCO3)(T)	a.c.	T	HCO ₃
38	pK*(B(OH)3)(T)	a.c.	T	B(OH) ₃
39	pK*(H2O)(T)	a.c.	T	Water ion product
40	pK*(HF)(T)	a.c.	T	HF
41	pK*(HSO4)(T)	a.c.	T	HSO ₄
42	pK*(CO2)(SW)	a.c.	SW	CO ₂
43	pK*(HCO3)(SW)	a.c.	SW	HCO ₃
44	pK*(B(OH)3)(SW)	a.c.	SW	B(OH) ₃
45	pK*(H2O)(SW)	a.c.	SW	Water ion product
46	pK*(HF)(SW)	a.c.	SW	HF
47	pK*(HSO4)(SW)	a.c.	SW	HSO ₄
48	pK*(CO2)(F)	a.c.	F	CO ₂
49	pK*(HCO3)(F)	a.c.	F	HCO ₃
50	pK*(B(OH)3)(F)	a.c.	F	B(OH) ₃
51	pK*(H2O)(F)	a.c.	F	water
52	pK*(HF)(F)	a.c.	F	HF
53	pK*(HSO4)(F)	a.c.	F	HSO ₄
54	p[Ca.CO3]	a.c.	-	Ca x CO3 concentration product

4.2 Solutions containing the ions of seawater (user-defined composition) (iCalc = 5)

This calculation is essentially the same as for iCalc = 4, except that the composition of the natural water (the input solution) can be varied from that of reference seawater. In order to do this the composition is specified in terms of individual species molalities or amount contents.

For this calculation the MATLAB call has the form:

[Outputs, NamesOutputs, cSpecies_out, mSpecies_out, ActCoeffs, NamesSpecies, iFail] = ...

MarChemSpec(iCalc, tC, P, iConc, Species_in, iFix, ValuesFixed, nOut, strFilesDirectory, strCovmxDirectory);

Input Arguments

Argument	Value	Meaning
<i>iCalc</i>	5 (fixed)	
<i>tC</i>	-5 <= <i>tC</i> <= 45 ^a	Temperature (°C)
<i>P</i>	1 (fixed)	Pressure (atm) (this version of MarChemSpec is only for a pressure of 1 atmosphere).
<i>iConc</i>	1 or 2	1 - <i>Species_in</i> are molalities, 2 - <i>Species_in</i> are amount contents.

<i>Species_in</i>	3x9 array ^b	The molalities or amount contents of the solution components, see the following table for the species and their order.
<i>iFix</i>	0 (fixed)	Reserved for future development.
<i>ValuesFixed</i>	2x2 array [0 0;0 0] (fixed)	Reserved for future development.
<i>nOut</i>	54 (fixed)	The number of state variables and stoichiometric equilibrium constants to be returned in the array <i>Outputs</i> .
<i>strFilesDirectory</i>	c:\marchemspec_mb\ ^c	Folder containing the text files (Pitzer.par, Pitzer.rcn) read by the model.
<i>strCovmxDirectory</i>	c:\marchemspec_mb\ ^c	Folder containing directories seawater and ASWbuffer.

^a If this range is exceeded, the calculation will fail, returning a value of *iFail* = 100 and an explanatory message.

^b The molalities or amount contents (according to the value of *iConc*) of the principal species are placed in this array. See below for the list of species, which is *not* the same as that for the output arrays.

^c These are the standard folder locations, but must be set to wherever the model has been installed.

Although the *Species_in* array must have 9 columns (and 3 rows), only the positions below – the first 8 columns in the case of the anions – are used to input molalities or amount contents. The other elements of the array can be set to zero.

The *Species_in* composition array

	1	2	3	4	5	6	7	8	9
1	H	Na	Mg	Ca	K	Sr			
2	Cl	SO4	OH	Br	HCO3	CO3	B(OH)4	F	
3	B(OH)3	CO2	HF						

You can see above that HSO₄⁻, and several ion pairs, are omitted. Their concentrations will still be calculated by the model, but the inputs are most easily specified by using total amounts.

The input concentrations must be charge balanced, to at least 1 part in 10⁵.

There is no restriction in the ways that species that take part in acid-base reactions can be entered. For example, a molality or amount content of CO₂ could be entered in *Species_in* as the species CO₂, as H⁺ and HCO₃⁻, as 2H⁺ and CO₃²⁻, or as any combination of the three forms.

For typical oceanographic applications, the above inputs can be written in a slightly different way, to correspond more closely to seawater compositions as commonly expressed:

The *Species_in* composition array (alternative):

	1	2	3	4	5	6	7	8	9
--	---	---	---	---	---	---	---	---	---

1	0.0	Na	Mg	Ca	K	Sr			
2	Cl	SO4	OH (Alk.)	Br	0.0	0.0	0.0	F	
3	B	C	0.0						

In the above table **B**, **C**, and **F** are total boron, dissolved inorganic carbon (DIC), and fluoride, respectively. These definitions require that the inputs for HCO_3^- , CO_3^{2-} , B(OH)_4^- , and HF are set to zero. If the H^+ input is also set to zero then **OH** is the alkalinity of the solution. This provides a convenient method of specifying a seawater of a given alkalinity. The amount contents for salinity 35 reference seawater, expressed in this way, are:

***Species_in* composition array, values for salinity 35 reference seawater**

	1	2	3	4	5	6	7	8
1	0.0	0.46896739	0.052817091	0.010282053	0.010207664	9.0694486E-5		
2	0.54586956	0.028235220	0.0023044118	8.4210795E-4	0.	0.	0.	6.8310315E-05
3	4.1516848E-4	1.9663336E-3	0.					

The amount contents above can be used as a starting point for creating seawater compositions of differing DIC, total borate, total fluoride, and alkalinity. Remember that alkalinity is not affected by changes in the first three of these variables.

Important: Any changes made to the defined alkalinity of 0.0023044118 (this is for salinity 35 seawater, the value will be different for other salinities) **must** be matched by a corresponding change in the amount contents of one or more major ions (Ca^{2+} and/or Na^+ are natural choices for this) so that charge balance is retained. For examples of how to change the alkalinity, and tables of the alkalinity of reference seawater of various salinities, see the MARCHEMSPEC document *Calculations for Natural Waters of Defined Alkalinity, Total Dissolved Inorganic Carbon, and Borate*. We note that, in the same way as for iCalc equal to 4, the model is now able to equilibrate solutions to assigned values of pairs or single values of pH (total or free), DIC, alkalinity, and $p\text{CO}_2$ or $f\text{CO}_2$ in a simpler way than described above. For further information, and examples for iCalc equal to 4 and 5, please see the MATLAB supplement referred to in the Introduction.

4.2.1 Outputs for iCalc = 5

All of the outputs are identical to those for the iCalc = 4 case described above. That is to say, the following arrays have the same types, sizes, and contents:

Outputs, *NamesOutputs* - seawater state variables, stoichiometric dissociation constants and their uncertainties; the names of all the quantities.

cSpecies_out, *mSpecies_out*, *ActCoeffs*, *NamesSpecies* – amount contents, molalities, and activity coefficients of all solute species; the names of all the species.

4.3 Reference seawater including GEOTRACES core elements (iCalc = 6)

The inputs for this problem are the same as those for $iCalc = 4$. However, in this case very small amounts of trace metals are added to the seawater, within the program, so that the degree of complexation by inorganic anions can be calculated. The trace metals are: Al^{3+} , Cd^{2+} , Co^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} . Outputs are the fractions of the trace metals that are free, and also complexed by each of the inorganic anions of reference seawater. For this calculation the MATLAB call has the form:

[*Outputs*, *NamesOutputs*, *cSpecies_out*, *mSpecies_out*, *ActCoeffs*, *NamesSpecies*, *iFail*] = ...

MarChemSpec(*iCalc*, *tC*, *S*, *P*, *mH*, *nSpecies*, *iFix*, *ValuesFixed*, *nOut*, *strFilesDirectory*, *strCovmxDirectory*);

Input arguments

Argument	Value	Meaning
<i>iCalc</i>	6 (fixed)	
<i>tC</i>	$-5 \leq tC \leq 45^a$	Temperature ($^{\circ}C$)
<i>S</i>	$0 < S \leq 45^a$	Practical salinity
<i>P</i>	1 (fixed)	Pressure (atm) (this version of MarChemSpec is coded only for 1 atmosphere pressure).
<i>mH</i>		The alkalinity (amount content) of the reference seawater is decreased by mH mol kg^{-1} (mH can be positive, negative, or zero).
<i>nSpecies</i>	39 (fixed)	The row lengths of <i>cSpecies_out</i> , <i>mSpecies_out</i> , <i>ActCoeffs</i> , and <i>NamesSpecies</i>
<i>iFix</i>	0 (fixed)	Reserved for future development.
<i>ValuesFixed</i>	2x2 array [0 0; 0 0] (fixed)	Reserved for future development.
<i>nOut</i>	40 (fixed)	The number values of fractional complexation (of each metal, with each ligand) to be returned in the array <i>Outputs</i> .
<i>strFilesDirectory</i>	c:\marchemspec_mb\ ^b	Folder containing the text files (Pitzer.par, Pitzer.rcn) read by the model.
<i>strCovmxDirectory</i>	c:\marchemspec_mb\ ^b	Folder containing directories seawater and ASWbuffer.

^a If these ranges are exceeded, the calculation will fail, returning a value of *iFail* = 100 and an explanatory message.

^b These are the standard folder locations, but must be set to wherever the files have been installed.

The alkalinity of the seawater can be varied by using the input argument *mH*. This is explained in the section of this document for $iCalc = 4$.

4.3.1 Outputs for $iCalc = 6$

The calculated quantities include the chemical speciation and solute activity coefficients, in this case for a very large number of species (most of which are the inorganic complexes of trace metals).

Individual chemical species

The names of the species are given in the $3 \times nSpecies$ cell *NamesSpecies* where the three rows refer to cations, anions and neutral species respectively. The contents of *NamesSpecies* are:

Columns 1-8

	1	2	3	4	5	6	7	8
1	H	Na	Mg	Ca	K	MgOH	Sr	MgF
2	Cl	SO ₄	HSO ₄	OH	Br	HCO ₃	CO ₃	B(OH) ₄
3	B(OH) ₃	CO ₂	HF	MgCO ₃	CaCO ₃	SrCO ₃	H ₃ PO ₄	Si(OH) ₄

Columns 9-16

	9	10	11	12	13	14	15	16
1	CaF	Al	Cd	Co	Cu[2]	Fe[2]	Fe[3]	Mn
2	F	PO ₄	HPO ₄	H ₂ PO ₄	SiO(OH) ₃	AlF ₄	AlF ₅	AlF ₆
3	AlF ₃	Al(OH) ₃	CaHPO ₄	CdCO ₃	Cd(OH) ₂	CoCO ₃	Co(OH) ₂	Cu[2]CO ₃

Columns 17-24

	17	18	19	20	21	22	23	24
1	Ni	Pb	Zn	AlF	AlF ₂	AlOH	AlOH ₂	CdOH
2	AlOH ₄	CaPO ₄	CdCO ₃ ₂	Co(OH) ₃	Cu[2](CO ₃) ₂	Fe[2](OH) ₃	Fe[3](OH) ₄	MgPO ₄
3	Cu[2](OH) ₂	Fe[2]CO ₃	Fe[2]OH ₂	Fe[3]F ₃	Fe[3](OH) ₃	MgHPO ₄	MnCO ₃	NiCO ₃

Columns 25-32

	25	26	27	28	29	30	31	32
1	CoOH	Cu[2]HCO ₃	Cu[2]OH	Fe[2]OH	Fe[3]F	Fe[3]F ₂	Fe[3]OH	Fe[3](OH) ₂
2	Ni(OH) ₃	Pb(CO ₃) ₂	PbCl ₃	Pb(OH) ₃	Zn(OH) ₃	Zn(OH) ₄		
3	Ni(OH) ₂	PbCO ₃	PbCl ₂	Pb(OH) ₂	PbSO ₄	ZnCO ₃	Zn(OH) ₂	

Columns 33-39

	33	34	35	36	37	38	39	
1	MnOH	NiOH	PbCl	PbHCO ₃	PbOH	ZnHCO ₃	ZnOH	
2								
3								

The arrays *cSpecies_out*, *mSpecies_out* and *ActCoeffs* contain the individual chemical species' amount contents, molalities and activity coefficients respectively. These arrays are arranged in the same way as *NamesSpecies*, so that for example *mSpecies_out*(1,2) is the molality of Na⁺.

Fractional speciation

These values are given in the $2 \times nOut$ array *Outputs*. The first column gives the fractional speciation and the second column is reserved for uncertainties (these are not yet included in the model). The meaning of each element is given in abbreviated form in the cell *NamesOutputs*: full descriptions are given below:

Outputs for iCalc = 6

Row(i)	NamesOutputs(i)	Metal	Fractions of the total metal (1 st column of Outputs)
1	AL (free)	Al ³⁺	As free Al ³⁺
2	AL (as OH)		Bound to OH ⁻
3	AL (as F)		Bound to F ⁻
4	CD (free)	Cd ²⁺	As free Cd ²⁺
5	CD (as CO3)		Bound to CO ₃ ²⁻
6	CD (as OH)		Bound to OH ⁻
7	CO (free)	Co ²⁺	As free Co ²⁺
8	CO (as CO3)		Bound to CO ₃ ²⁻
9	CO (as OH)		Bound to OH ⁻
10	CU[2] (free)	Cu ²⁺	As free Cu ²⁺
11	CU[2] (as HCO3)		Bound to HCO ₃ ⁻
12	CU[2] (as CO3)		Bound to CO ₃ ²⁻
13	CU[2] (as OH)		Bound to OH ⁻
14	FE[2] (free)	Fe ²⁺	As free Fe ²⁺
15	FE[2] (as CO3)		Bound to CO ₃ ²⁻
16	FE[2] (as OH)		Bound to OH ⁻
17	FE[3] (free)	Fe ³⁺	As free Fe ³⁺
18	FE[3] (as OH)		Bound to OH ⁻
19	FE[3] (as F)		Bound to F ⁻
20	MN (free)	Mn ²⁺	As free Co ²⁺
21	MN (as CO3)		Bound to CO ₃ ²⁻
22	MN (as OH)		Bound to OH ⁻
23	NI (free)	Ni ²⁺	As free Ni ²⁺
24	NI (as CO3)		Bound to CO ₃ ²⁻
25	NI (as OH)		Bound to OH ⁻
26	PB (free)	Pb ²⁺	As free Pb ²⁺
27	PB (as CL)		Bound to Cl ⁻
28	PB (as SO4)		Bound to SO ₄ ²⁻
29	PB (as HCO3)		Bound to HCO ₃ ⁻
30	PB (as CO3)		Bound to CO ₃ ²⁻
31	PB (as OH)		Bound to OH ⁻
32	ZN (free)	Zn ²⁺	As free Zn ²⁺
33	ZN (as HCO3)		Bound to HCO ₃ ⁻
34	ZN (as CO3)		Bound to CO ₃ ²⁻
35	ZN (as OH)		Bound to OH ⁻

4.4 Solutions containing the ions of seawater, and including the GEOTRACES core elements (user-defined composition) (iCalc = 7)

This calculation is essentially the same as for iCalc = 6, except that the composition of the natural water (the input solution) can be varied from that of reference seawater. The trace metal, silicate and phosphate concentrations can also be varied. The solution composition is therefore specified in terms of individual species molalities or amount contents.

For this calculation the MATLAB call has the form:

[*Outputs*, *NamesOutputs*, *cSpecies_out*, *mSpecies_out*, *ActCoeffs*, *NamesSpecies*, *iFail*] = ...

MarChemSpec(*iCalc*, *tC*, *P*, *iConc*, *Species_in*, *iFix*, *ValuesFixed*, *nOut*, *strFilesDirectory*, *strCovmxDirectory*);

Input arguments

Argument	Value	Meaning
<i>iCalc</i>	7 (fixed)	
<i>tC</i>	-5 <= <i>tC</i> <= 45 ^a	Temperature (°C)
<i>P</i>	1 (fixed)	Pressure (atm) (this version of MarChemSpec is coded only for 1 atmosphere pressure).
<i>iConc</i>	1 or 2	1 - <i>Species_in</i> are molalities; 2 - <i>Species_in</i> are amount contents
<i>Species_in</i>	3x39 array ^b	The total molalities or amount contents of the solution components.
<i>iFix</i>	0 (fixed)	Reserved for future development.
<i>ValuesFixed</i>	2x2 array [0 0;0 0] (fixed)	Reserved for future development.
<i>nOut</i>	40 (fixed)	The number values of fractional complexation (of each metal, with each ligand) to be returned in the array <i>Outputs</i> .
<i>strFilesDirectory</i>	c:\marchemspec_mb\ ^c	Folder containing the text files (Pitzer.par, Pitzer.rcn) read by the model.
<i>strCovmxDirectory</i>	c:\marchemspec_mb\ ^c	Folder containing directories seawater and ASWbuffer.

^a If this range are exceeded, the calculation will fail, returning a value of *iFail* = 100 and an explanatory message.

^b See the next table for the order in which the values must be entered.

^c These are the standard folder locations, but must be set to wherever the files have been installed.

Although the *Species_in* array must have 39 columns (and 3 rows), only the positions below – the first 16 columns in the case of the cations – are used to input molalities or amount contents. The other elements of the array can be set to zero.

Elements of *Species_in* composition array

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	H	Na	Mg	Ca	K	Sr	Al	Cd	Co	Cu	Fe(II)	Fe(III)	Mn	Ni	Pb	Zn
2	Cl	SO ₄	OH	Br	HCO ₃	CO ₃	B(OH) ₄	F	H ₂ PO ₄							
3	B(OH) ₃	CO ₂	HF	Si(OH) ₄												

In the same way as for the *iCalc* = 5 case, in which individual species concentrations are input, *Species_in* can be viewed as containing the following components:

Elements of *Species_in* composition array (equivalent alternative):

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	0.0	Na	Mg	Ca	K	Sr	Al	Cd	Co	Cu	Fe(II)	Fe(III)	Mn	Ni	Pb	Zn
2	Cl	SO ₄	OH (Alk.)	Br	0.0	0.0	0.0	F	P							
3	B	C	0.0	Si												

In the above table **B**, **C**, and **F** are total boron, dissolved inorganic carbon (DIC), and fluoride, respectively. These definitions require that the inputs for HCO₃⁻, CO₃²⁻, B(OH)₄⁻, and HF are set to zero. Total phosphate (**P**) is entered as H₂PO₄⁻ (which does not affect the alkalinity), and total silicate as Si(OH)₄ (which also does not affect the alkalinity). If the H⁺ input is to zero then **OH** is the alkalinity of the solution. This provides a convenient method of specifying a seawater of a given alkalinity.

The composition of salinity 35 seawater, expressed using the totals in the above table, can be found in the section for *iCalc* = 5. See also the MARCHEMSPEC document *Calculations for Natural Waters of Defined Alkalinity, Total Dissolved Inorganic Carbon, and Borate*. Remember that any trace metal concentrations entered in *Species_in* must be charge balanced with the same number of equivalents of an anion (Cl⁻ for example). The total phosphate, H₂PO₄⁻, could be entered as equal amounts of Na⁺ and H₂PO₄⁻.

4.4.1 Outputs for *iCalc* = 7

The calculated quantities include the chemical speciation and solute activity coefficients, in this case for a very large number of species (most of which are the inorganic complexes of trace metals).

Individual chemical species

The names of the species are given in the 3 × *nSpecies* cell *NamesSpecies* where the three rows refer to cations, anions and neutral species respectively.

The arrays *cSpecies_out*, *mSpecies_out* and *ActCoeffs* contain the individual chemical species' amount contents, molalities and activity coefficients respectively. These arrays are arranged in the same way as *NamesSpecies*, so that for example *mSpecies_out*(1,2) is the molality of Na⁺.

The contents of both all arrays are the same as for the *iCalc* = 5 case, and the description for that case should be referred to.

Fractional speciation

These values are given in the $nOut \times 2$ array *Outputs*. The first column gives the fractional speciation and the second column is reserved for uncertainties (these are not yet included in the model). The meaning of each element is given in abbreviated form in the cell *NamesOutputs*. The table describing the output of fractional speciation for *iCalc* = 6 should be consulted for details. Note that, if phosphate is included in the solution then its complexes with cations will be included in the output arrays.

There will be entries in the *Outputs* array only for those trace metals present in the solution.

4.5 HCl in artificial seawater (*iCalc* = 1)

Solutions such as this are relevant to the calibration of the total pH scale, and speciation model development. The artificial seawater (ASW) recipe is that of Dickson (1990).

For this calculation the MATLAB call has the form:

[*Outputs*, *NamesOutputs*, *cSpecies_out*, *mSpecies_out*, *ActCoeffs*, *NamesSpecies*, *iFail*] = ...

MarChemSpec(*iCalc*, *tC*, *S*, *P*, *mH*, *nSpecies*, *nOut*, *strFilesDirectory*, *strCovmxDirectory*)

Input arguments

Argument	Value	Meaning
<i>iCalc</i>	1 (fixed)	
<i>tC</i>	-5 <= <i>tC</i> <= 45 ^a	Temperature (°C)
<i>S</i>	0 < <i>S</i> <= 45 ^a	Nominal practical salinity
<i>P</i>	1 (fixed)	Pressure (atm) (this version of MarChemSpec is coded only for 1 atmosphere pressure).
<i>mH</i>	0 <= <i>mH</i> <= 0.1 ^b	Molality of HCl that is substituted for the same molality of NaCl in artificial seawater.

<i>nSpecies</i>	7 (fixed)	The number of columns of output arrays <i>cSpecies_out</i> , <i>mSpecies_out</i> , <i>ActCoeffs</i> , and <i>NamesSpecies</i>
<i>nOut</i>	8 (fixed)	The number of state variables and thermodynamic quantities to be returned in the array <i>Outputs</i> .
<i>strFilesDirectory</i>	c:\marchemspec_mb\ ^c	Folder containing the text files (Pitzer.par, Pitzer.rcn) read by the model.
<i>strCovmxDirectory</i>	c:\marchemspec_mb\ ^c	Folder containing directories seawater and ASWbuffer.

^a If these ranges are exceeded, the calculation will fail, returning a value of *iFail* = 100 and an explanatory message

^b *mH* must be less than equal to the Na⁺ molality, otherwise the calculation will fail, returning a value of *iFail* = 100 and an explanatory message.

^c These are the standard folder locations, but must be set to wherever the model has been installed.

4.5.1 Outputs for *iCalc* = 1

The calculated quantities include the chemical speciation, solute activity coefficients, the osmotic coefficient, and a number of other thermodynamic quantities. These are described below.

Individual chemical species

The names of the species are given in the $3 \times nSpecies$ cell *NamesSpecies* where the three rows refer to cations, anions and neutral species respectively. The contents of *NamesSpecies* are:

H	Na	Mg	Ca	K	MgOH	(TrisH)
Cl	SO4	HSO4	OH			
(Tris)						

The arrays *cSpecies_out*, *mSpecies_out* and *ActCoeffs* contain the individual chemical species' amount contents, molalities and activity coefficients respectively. These arrays are arranged in the same way as *NamesSpecies*, so that for example *mSpecies_out*(1,2) is the molality of Na⁺. Note that this system does not include Tris, so the elements (1,7) (TrisH⁺) and (3,1) (Tris) in the three species arrays are not used.

State variables and thermodynamic quantities

These are given in the $nOut \times 2$ array *Outputs*. The first column gives values and the second column their calculated uncertainties. All of these results are on a molality basis (m). The missing value code is 99. The meaning of each element is given in abbreviated form in the cell *NamesOutputs*: full descriptions are given below:

Row i	NamesOutputs(i)	Full description
1	Osm. coeff.	Osmotic coefficient
2	ln(aW)	ln (activity of water)
3	ln(K*(H2O))(m)	ln (stoichiometric ion product of water)
4	-log10(mH)	pH on the free scale
5	-log10(mH+mHSO4)	Note that in acidic solutions thermodynamic total this is not equivalent to the pH on the total scale, pH _T .
6	E-E0	Harned cell potential (V) expressed as an offset from the standard potential E ⁰ .
7 ^a	ln(K*(TrisH))(m)	ln (stoichiometric dissociation constant of TrisH ⁺)
8	ln(K*(HSO4))(m)	ln (stoichiometric dissociation constant of HSO ₄ ⁻)

^a This quantity is not output for this value of iCalc (because no Tris or TrisH⁺ are present).

4.6 Tris buffers in artificial seawater (iCalc = 2)

In these calculations both HCl and Tris can be added to solutions of artificial seawater, to create buffer solutions containing Tris and TrisH⁺. These additions to the solution are made in such a way that TrisH⁺ is substituted for Na⁺, and follows the approach of DelValls and Dickson (1998). This model is a draft, and is for 25 °C only (because interactions of Tris and TrisH⁺ with other ions are only known at this temperature.)

For this calculation the MATLAB call has the form:

[Outputs, NamesOutputs, cSpecies_out, mSpecies_out, ActCoeffs, NamesSpecies, iFail] = ...

MarChemSpec(iCalc, tC, S, P, mH, mTris, nSpecies, nOut, strFilesDirectory, strCovmxDirectory)

Input Arguments

Argument	Value	Meaning
<i>iCalc</i>	2 (fixed)	
<i>tC</i>	25 (fixed)	Temperature (°C)
<i>S</i>	0 < S ≤ 45 ^a	Nominal practical salinity
<i>P</i>	1 (fixed)	Pressure (atm) (this version of MarChemSpec is coded only for 1 atmosphere pressure).
<i>mH</i>	0 ≤ <i>mH</i> ≤ 0.1 ^b	Effectively, this is the molality of TrisHCl that is substituted for NaCl in the artificial

		seawater. To obtain an equimolal Tris buffer enter mH equal to $mTris / 2$.
$mTris$	$0 < mTris < 0.1$ ^a	Total molality of Tris, i.e. the sum of Tris and $TrisH^+$ molalities.
$nSpecies$	7 (fixed)	The row lengths of $cSpecies_out$, $mSpecies_out$, $ActCoeffs$, and $NamesSpecies$.
$nOut$	8 (fixed)	The number of state variables and stoichiometric equilibrium constants to be returned in the array $Outputs$.
$strFilesDirectory$	c:\marchemspec_mb\ ^c	Folder containing the text files (Pitzer.par, Pitzer.rcn) read by the model.
$strCovmxDirectory$	c:\marchemspec_mb\ ^c	Folder containing directories seawater and ASWbuffer.

^a If this range is exceeded, the calculation will fail, returning a value of $iFail = 100$ and an explanatory message.

^b Note that mH must be less than equal to the Na^+ molality in solution otherwise the calculation will fail, returning a value of $iFail = 100$ and an explanatory message.

^c These are the standard folder locations, but must be redefined if the files are installed elsewhere.

4.6.1 Outputs for $iCalc = 2$

The calculated quantities include the chemical speciation, solute activity coefficients, osmotic coefficient, and a number of seawater state variables. These are described below.

Individual chemical species

The names of the species are given in the $3 \times nSpecies$ cell $NamesSpecies$ where the three rows refer to cations, anions and neutral species respectively. The contents of $NamesSpecies$ are:

H	Na	Mg	Ca	K	MgOH	TrisH
Cl	SO4	HSO4	OH			
Tris						

The arrays $cSpecies_out$, $mSpecies_out$ and $ActCoeffs$ contain the individual chemical species' amount contents, molalities and activity coefficients respectively. These arrays are arranged in the same way as $NamesSpecies$, so that for example $mSpecies_out(1,2)$ is the molality of Na^+ .

State variables and thermodynamic quantities

These are given in the $nOut \times 2$ array $Outputs$. The first column gives values and the second column their calculated uncertainties. The missing value code is 99. All of these results are on a molality basis (m). The meaning of each element is given in abbreviated form in the cell $NamesOutputs$: full descriptions are given below:

Row i	NamesOutputs(i)	Full description
1	Osm. coeff.	Osmotic coefficient
2	ln(aW)	ln (activity of water)
3	ln(K*(H2O))(m)	ln (stoichiometric ion product of water)
4	-log10(mH)	pH on the free scale
5	-log10(mH+mHSO4)	Note that in acidic solutions thermodynamic total this is not equivalent to the pH on the total scale, pH _T .
6	E-E0	Harned cell potential (V) expressed as an offset from the standard potential E ⁰ .
7	ln(K*(TrisH))(m)	ln (stoichiometric dissociation constant of TrisH ⁺)
8	ln(K*(HSO4))(m)	ln (stoichiometric dissociation constant of HSO ₄ ⁻)

4.7 Tris buffer and HCl in solutions containing the ions of artificial seawater (user-defined composition) (iCalc = 3)

The calculations are for solutions containing the ions of artificial seawater, and including H⁺ and Tris molalities as inputs. The properties of Tris buffers in media that differ from seawater stoichiometry can therefore be calculated. **However, for solutions containing Tris the model is a draft and is valid for 25 °C only.**

For this calculation the MATLAB call has the form:

[*Outputs*, *NamesOutputs*, *cSpecies_out*, *mSpecies_out*, *ActCoeffs*, *NamesSpecies*, *iFail*] = ...

MarChemSpec(*iCalc*, *tC*, *P*, *iConc*, *Species_in*, *nOut*, *strFilesDirectory*, *strCovmxDirectory*)

Input arguments

Argument	Value	Meaning
<i>iCalc</i>	3 (fixed)	
<i>tC</i>	-5 ≤ <i>tC</i> ≤ 45 ^a	Temperature (°C)
<i>P</i>	1 (fixed)	Pressure (atm) (this version of MarChemSpec is coded only for a pressure of 1 atmosphere)
<i>iConc</i>	1 (fixed)	<i>Species_in</i> must be molalities.
<i>Species_in</i>	3 x 7 array	Composition of the solution, including H ⁺ and Tris as needed.
<i>nOut</i>	8 (fixed)	The number of state variables and stoichiometric equilibrium constants to be returned in the array <i>Outputs</i> .

<i>strFilesDirectory</i>	c:\marchemspec_mb\ ^b	Folder containing the text files (Pitzer.par, Pitzer.rcn) read by the model.
<i>strCovmxDirectory</i>	c:\marchemspec_mb\ ^b	Folder containing directories seawater and ASWbuffer.

^a If this range is exceeded, the calculation will fail, returning a value of *iFail* = 100 and an explanatory message.

^b These are the standard folder locations, but must be set to wherever the model files have been installed.

Although the *Species_in* array must have 7 columns (and 3 rows), only the positions below – the first 5 columns in the case of the cations – are used to input total molalities of the various species. The other elements of the array can be set to zero.

H	Na	Mg	Ca	K
Cl	SO4			
Tris				

4.7.1 Outputs for *iCalc* = 3

All of the outputs are the same as for the *iCalc* = 2 case:

- The names of the chemical species are given in the $3 \times nSpecies$ cell *NamesSpecies* where the three rows refer to cations, anions and neutral species respectively. The contents of *NamesSpecies*.
- The arrays *cSpecies_out*, *mSpecies_out* and *ActCoeffs* contain the individual chemical species' amount contents, molalities and activity coefficients respectively. These arrays are arranged in the same way as *NamesSpecies*, so that for example *mSpecies_out*(1,2) is the molality of Na⁺.
- State variables and thermodynamic quantities are listed in the $nOut \times 2$ array *Outputs*. The first column gives values and the second column their calculated uncertainties. The missing value code is 99. All of these results are on a molality basis (*m*). The meaning of each element is given in abbreviated form in the cell *NamesOutputs*.

Tables

This section contains the tables referred to earlier in the document.

Table 1. Definitions of the seawater-related quantities (seawater state parameters, including equilibrium constants) presented in Outputs array for iCalc equal to 4 and 5. See Dickson et al. (2007) for the equations for the equilibrium constants.

Quantity	Definition	Quantity	Definition
pH (T)	pH _T , pH on the total scale	pH (SW)	pH _{sw} , pH on the seawater scale
pH (F)	pH _F , pH on the free scale	pCO ₂	<i>p</i> CO ₂ , the equilibrium partial pressure of CO ₂ (atm).
fCO ₂	<i>f</i> CO ₂ , the equilibrium fugacity of CO ₂ (atm.)	DIC	C _T , total dissolved inorganic carbon
Tot. Alk.	A _T , total alkalinity		
Total pH basis (indicated by suffix ‘(T)’)			
K* (CO ₂)	<i>K</i> ₁ , the stoichiometric dissoc. constant of CO ₂ *.	K* (HCO ₃)	<i>K</i> ₂ , the stoichiometric dissoc. constant of HCO ₃ ⁻ .
K* (B (OH) ₃)	<i>K</i> _B , the stoichiometric dissoc. constant of B(OH) ₃ .	K* (H ₂ O)	<i>K</i> _w , the ion product of water.
K* (HF)	<i>K</i> _F , the stoichiometric dissoc. constant of HF.		
SW pH basis (seawater scale) (indicated by suffix ‘(SW)’)			
K* (CO ₂)	These definitions are the same as those above, but with the concentration of H ⁺ expressed on the seawater scale.	K* (HCO ₃)	These definitions are the same as those above, but with the concentration of H ⁺ expressed on the seawater scale.
K* (B (OH) ₃)		K* (H ₂ O)	
Free pH basis (indicated by suffix ‘(F)’)			
K* (CO ₂)	These definitions are the same as those above, but with the concentration of H ⁺ expressed on the free scale.	K* (HCO ₃)	These definitions are the same as above, but on the free pH scale.
K* (B (OH) ₃)		K* (H ₂ O)	
K* (HF)			K* (HSO ₄)
Other properties			
Ca . CO ₃	The product of the concentrations (on a molality or amount content basis) of total dissolved Ca ²⁺ and total dissolved CO ₃ ²⁻ .		

References

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Version History

1.00 – The initial release, prepared for the Launch and Tutorial sessions at Woods Hole Oceanographic Institution (15-16 June, 2023).

1.01 (July, 2023) Revisions to the underlying MarChemSpec code to correct the treatment of Cu^{2+} interactions with Cl^- ions, which previously gave erroneous activity coefficients and complexation of this metal ion at temperatures other than 25 °C. Revisions to the underlying MarChemSpec code to correct the reading of a directory path from file Uncert.mst (this does not affect the use of the currently released versions of the code, because this path entry is left blank).

1.1 (February, 2024) The MarChemSpec treatment of the activity coefficients and formation of Fe[III] hydrolysis products has been revised (and some other improvements made), and the model is now able to equilibrate input aqueous solutions to fixed values of either one or two seawater state variables. This involves the MarChemSpec function arguments *iFix* and *ValuesFixed*, and is described in a separate document *Calculations for Natural Waters of Defined Alkalinity, Total Dissolved Inorganic Carbon, pH, and Partial Pressure or Fugacity of CO₂ Using MATLAB*. This new capability is, at present, only enabled for the seawater model (*iCalc* equal to 4 and 5).

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