



Getting started with the MARCHEMSPEC Marine Chemical Speciation Models

Version 1.1

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(See also the Supplement to this document)



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 of the MARCHEMSPEC speciation model for natural waters containing the ions of seawater. Supplements demonstrate the use of related programs for inorganic complexation of trace metals in the same types of solutions, and the calculation of the changes in seawater state parameters caused by a changes in natural water composition.

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Getting Started with the MARCHEMSPEC

Marine Chemical Speciation Models

version 1.1 (02/2024)

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1. Preamble

This document, and its Supplements, describe the executable MARCHEMSPAC programmes that run in a command prompt window on your computer (or remotely on a server). These programs are for the calculation of acid-base and inorganic complexation equilibria in the following solutions:

1. Solutions containing the species of Standard Seawater (Na^+ , Mg^{2+} , Ca^{2+} , K^+ , Sr^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , Br^- , CO_3^{2-} , B(OH)_4^- , F^- , OH^- , B(OH)_3 , CO_2^*), and H^+ , HSO_4^- , and HF .
2. Pairs of solutions containing the same species as (1) above, but in differing concentrations. The program calculates the change in various seawater state parameters caused by the composition change.
3. Solutions as in (1) above, but also containing the trace species Al^{3+} , Cd^{2+} , Co^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} , PO_4^{3-} , and Si(OH)_4 and their inorganic complexes and acid-base reaction products.
4. Solutions containing the species of artificial seawater (Na^+ , Mg^{2+} , Ca^{2+} , K^+ , Cl^- , SO_4^{2-}), and H^+ , HSO_4^- , OH^- , and (optionally) the buffer species Tris and TrisH^+ .

The programs for (1) and (2) above provide values of the following the *seawater state parameters* and estimates of their estimated uncertainties: 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 in Chapter 2 of Dickson et al. (2007). The calcium carbonate concentration product is also output. The names used for these output parameters are given in **Table 1**.

The programs for cases (1) and (2) above provide estimates of total uncertainties of the calculated seawater state parameters and their differences, and the program for case (4) can do so for a variety of different quantities (chiefly useful for applications related to the definition and calibration of the total pH scale).

The development of chemical speciation models (1,2, and 4) is described by Humphreys et al. (2022), and Clegg et al. (2022, 2023). The trace metal complexation model is described in a draft document available from the authors.

This document describes the setup and use of the program and associated files for case (1) above, which is the model for natural waters containing the species of seawater. Separate Supplements describe the use of the other programs, and the minor ways in which they differ from this one.

1.1 Current version

Version 1.1 is a release of MarChemSpec that includes the ability to automatically adjust the compositions of solutions to fixed, user-specified, pairs or single values of the seawater state parameters pH (total or free), total alkalinity, total dissolved inorganic carbon, $p\text{CO}_2$ or $f\text{CO}_2$ (fugacity). This new feature has so far been implemented for calculations if type (1) above only. Instructions for using the new feature are given in the Supplement *Calculations for Natural Waters*

of Defined Alkalinity, Total Dissolved Inorganic Carbon, pH, and Partial Pressure or Fugacity of CO₂.

The changes to this document, relative to v1.01, explain how to use MarChemSpec in the same way as for previous versions, *without* the new features. This is necessary because the input file **MCS.dat** now has some additional options that must be assigned values. Only sections 4 and 5 of this document, and Appendix 3, have been modified. At a later release this document and the Supplement will be combined into one.

References

S. L. Clegg, M. P. Humphreys, J. F. Waters, D. R. Turner, and A. G. Dickson (2022) Chemical speciation models based upon the Pitzer activity coefficient equations, including the propagation of uncertainties. II. Tris buffers in artificial seawater at 25 °C, and an assessment of the seawater 'Total' pH scale. *Mar. Chem.* 244, art. No. 104096, 24 pp.

S. L. Clegg, J. F. Waters, D. R. Turner, and A. G. Dickson (2023) Chemical speciation models based upon the Pitzer activity coefficient equations, including the propagation of uncertainties. III. Seawater from the freezing point to 45 °C, including acid-base equilibria. *Mar. Chem.* 250, art. no. 104196, 21 pp.

A.G. Dickson, C.L. Sabine, J.R. Christian (Eds.) 2007. *Guide to Best Practices for Ocean CO₂ Measurements*. North Pacific Marine Science Organisation. PICES Special Publication 3, IOCCP Report No. 8, 176 pp.

M. P. Humphreys, J. F. Waters, D. R. Turner, A. G. Dickson, and S. L. Clegg (2022) Chemical speciation models based upon the Pitzer activity coefficient equations, including the propagation of uncertainties: Artificial seawater from 0 to 45 °C. *Mar. Chem.* 244, art. no. 104095, 23 pp.

2. This MARCHEMSPEC Program

It calculates acid base speciation and seawater state parameters for natural waters containing the species of standard seawater (in arbitrary concentrations, not just standard seawater stoichiometry).

The **inputs** are the temperature, and salinity or composition of a natural water (in terms of the concentrations of species in moles per kg of seawater, or alternatively moles per kg of pure water).

The **outputs** are the equilibrium acid-base speciation and seawater state parameters noted in the previous section, together with estimates of the total uncertainty of each calculated state parameter. All outputs are presented on both an amount content (moles per kg of solution) and molality (moles per kg of pure water) basis.

All inputs and outputs are from/to plain text files. Most outputs are also written to comma separated value (.csv) files, which can be read directly into spreadsheet applications.

An important note about **concentration scales**: The common practice in oceanography is to express compositions on a moles per kg of seawater basis (known as **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 examples described in this document are generally presented and discussed in terms of molalities, although MARCHEMSPEC model results are given on *both* concentration scales. Also, all the example inputs in the MCS.dat input files are listed for both concentration scales (and either can be used by the model).

2.1 Availability

Separate versions of the programs are available to run on computers with the following operating systems:

- Windows (at least version 7 and higher), 64 bit
- Linux, and macOS (for “Apple Silicon”)

The programs and associated files and directories are provided as a zip file (Windows), and as zipped tar files (Linux and macOS).

3. How to Install MARCHEMSPEC

The executable program and its input and output files must be present in one directory. Other files, which are read by the program but do *not* need to be edited by the user, are present in various subdirectories. The contents of the zip file (Windows), or other compressed archive, should be extracted into the directory you wish to work in, i.e., where the executable program and input and output text files will be. For example, if this directory is c:\marchemspec, then the resulting structure should be:

c:\marchemspec - contains program and input/output files

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

c:\marchemspec\seawater - contains Uncert.mst

c:\marchemspec\seawater\{BC, CCA, AAC, NCA, _lnKeq1} - contain files of variances

See below for instructions specific to each operating system.

3.1 Windows

Copy the zip file to the directory you wish to work in (e.g., c:\marchemspec in the above example), and extract the contents to the same directory by right-clicking on the file in Windows File Explorer, choosing 7-Zip, and then following the prompt. (This instruction works for Windows 10, and the procedure may differ slightly on other versions. There is also more than one program that can be used to zip/unzip files.)

3.2 Linux and macOS (“Apple Silicon”)

Copy the tar file to the directory you wish to work in, and extract the contents using the command

```
tar -xzf tar_file_name.
```

There is an extra action that *may* be needed for macOS and for Linux systems before you can run the model. The executable file MCS_sea in the top level directory must have ‘execute’ permission, and this can be added using the operating system command chmod. If you find that it is needed, navigate to the directory containing MCS_sea, and issue the command:

```
chmod +x ./MCS_sea
```

You should now be able to run the program, by typing ./MCS_sea. If you are working on a macOS system, and a system error is returned (e.g., ‘permission denied’, ‘exec format error’), then check that execute permission was correctly updated in System Preferences. Open System Preferences and navigate to Privacy & Security > Developer Tools *or* Security & Privacy > General (depending on macOS version). Make sure that Terminal app has permission to execute programs downloaded from the internet.

Adding execute permission only needs to be done once, and then MCS_sea should run normally.

3.3 The MARCHEMSPEC Files

After extracting the contents of the zip file or other archive, the directory that you will be running the program in should contain the files and other directories listed and described in the document [List_of_files_sea.pdf](#). Below we describe only the files of the model (executable, and input and output).

Executable:

MCS_sea.exe (Windows), or MCS_sea (Linux and macOS)

Data input:

MCS.dat – must contain input temperatures and compositions. The supplied file includes all the compositions used in the examples in this document, expressed on both a molality (moles per kg of pure water) and amount content (moles per kg of solution) basis.

Results output:

MCS.rs1 – contains verbose output of all results.

MCS.rs2 – column output species amount contents, molalities, and activity coefficients.

MCS.rs4 – column output of calculated seawater parameters (molality-based).

MCS.rs5 – column output of calculated seawater parameters (amount content-based).

There are also three files with the extension .csv (for example, MCS.rs2.csv), which contain the same information as the files with normal column output but as comma separated values. These .csv files can be read directly into spreadsheet programs.

Entries of 99.0 in the files of column output indicate property or uncertainty values that could not be calculated. This is likely to be either because the solution does not contain the species of interest (for example $K^*(\text{BOH}_3)$ will be assigned 99.0 for solutions that do not contain any borate species), or where there is no uncertainty because the quantity is defined exactly by the input composition. In the .rs1 files containing verbose results the equivalent entry is ‘n.a.’ (meaning ‘not applicable’).

Other files (these should *not* be altered):

MCS.sen, Pitzer.mst, Pitzer.par, Pitzer.rcn

Beneath the directory containing the above files is subdirectory ‘seawater’. This contains the text file Uncert.mst (which should also not be altered) and further subdirectories which contain information used in the estimation of uncertainties.

Important: Successive runs of the model will overwrite the existing output files, so if you have results you want to save then move them to another directory.

4. Quick Start

In this section we demonstrate how to do the simplest MARCHEMSPEC calculation, and then look at the results.

First, open the text file **MCS.dat**, and go to the line that begins:

```
Problem type (enter 0-11):
```

Either type the number '0' (without quotes) after the semicolon, or leave the line after the ':' entirely blank. These actions ensure that the numbered options (1-4) below this line are not read, and the model only calculates the properties of the solution compositions that are input. Next, do the following:

1. Go to the line in **MCS.dat** that begins:

```
Enter the type of input composition (1, 2 or 3):
```

Type the number '3' (without quotes) after the semicolon. This means that the natural water compositions will be specified as practical salinities.

2. All lines that begin with a '#' in **MCS.dat** will be treated as comments and ignored. On successive non-comment lines beneath that described above, enter values of the temperature (in Kelvin) followed by practical salinity, one pair of values per line. For example, enter the following for a calculation of the properties of a salinity 35 seawater at 298.15 K:

```
298.15 35.
```

You can enter as many lines of values as you wish. The program will only stop when it either reaches the end of the file, or encounters an error of some kind.

Suggestion: if you keep multiple sets of input data in **MCS.dat**, but only want to do calculations for a small group of values, then place a string of characters such as '===' (which cannot be read as numbers) on the line after the last of the compositions of interest. This will cause the program to stop.

3. Run the program by typing 'MCS_sea.exe' (without quotes) at the Windows prompt followed by <Enter>, (or './MCS_sea' followed by <Enter> on Linux or macOS systems). The text 'MCS working..' should then appear on the screen. This means that the program is running. When it has finished, there will be another message indicating completion. Error messages will also be written to screen.

How long do the calculations take? About 5-6 seconds for 1 composition on a typical PC.

4. Now examine the results in the text files noted above. The contents are briefly summarised here, and the quantities and symbols used are explained in more detail in **Appendix 1**.

MCS.rs1 – all the results, in an easy to read form. See **Table 1** for definitions of the symbols used. The results are grouped under the following headings:

- Speciation and Activity Coefficients (note that ‘molinity’ is the amount content of the species, in moles per kg of solution).
- Seawater Related Quantities. This section contains the calculated thermodynamic pH (on the total, seawater and free scales), stoichiometric equilibrium constants of all acid-base equilibria, and the concentration product of Ca^{2+} and CO_3^{2-} . Model estimates of uncertainties are also listed. All quantities are given on both an amount content and molality basis.

MCS.rs2 (and .csv) – contains all the results shown in the Speciation and Activity Coefficients section of the .rs1 file, but in column format. Species names are capitalised (hence ‘NA’ rather than ‘Na’ for sodium), and all parentheses are omitted (hence ‘BOH3’, not ‘B(OH)3’, for boric acid). Prefixes: m – molality; g – molality based activity coefficient; k – amount content (molinity).

(MCS.rs3) – this filename is not used.

MCS.rs4 (and .csv) – contains all the molality-based results shown in the Seawater Related Quantities section of the .Rs1 file, but in column format. Acid-base equilibrium constants are expressed on the different pH bases indicated by the following suffixes: _T – total pH scale; SW – seawater scale; _F – free scale. The prefix u indicates the estimated uncertainty of the calculated quantity.

MCS.rs5 (and .csv) – contains all the amount-content based results shown in the Seawater Related Quantities section of the .Rs1 file, but in column format. Symbols have the same meanings as for the .rs4 file described above.

This completes the overview of how to do the simplest of MARCHEMSPEC calculations. In the next section we show how to enter compositions of natural waters that differ from that of seawater.

5. Different Types of MARCHEMSPEC Calculation

In the Quick Start section we showed that calculations at specified temperatures and practical salinities can be done by entering pairs of T , S in the **MCS.dat** file. For example, to calculate the seawater properties for practical salinities 35 and 5 at a temperature of 5 °C (278.15 K), the relevant lines of **MCS.dat** would look like this:

```
# END OF DESCRIPTION
#####

#
Problem type (enter 0-11): 0
#

{lines for entering four integer options, which should be ignored}

#
Enter the type of input composition (1, 2 or 3): 3
#
278.15  35.
278.15  5.
=== end of data ===
```

The lines beginning ‘#’ are all comment lines (ignored by the program). The entry of ‘0’ for the problem type tells the model that the simplest type of calculation – determining the equilibrium speciation and properties of the input solutions – is being done. The entry of ‘3’ for the type of input composition means that practical salinities will be entered in the file. Next, after a blank comment line (which is optional) the temperatures and salinities are entered, with one pair per line. There is no limit to the numbers of lines.

The list of data can be terminated by starting a new line with *any* characters that cannot be read as a number. This will cause the program to stop. In the example above, ‘=== end of data ===’ has been used.

To calculate the properties of a solution that does *not* have the composition of reference seawater it is necessary to input solute molalities or amount contents individually. These should be entered in **MCS.dat** on one line per solution (after the temperature), and in the order cations, anions, and then neutral (uncharged) solutes. The order of individual species is that shown in **Appendix 2**. The amounts of species that are involved in equilibria can be specified in whatever way is most convenient: for example, an amount content X of dissolved CO_2^* could be entered as this amount, or alternatively as X of H^+ and X of HCO_3^- , or $2X$ of H^+ and X of CO_3^{2-} . The program will determine the equilibrium.

In order to do the above enter a ‘1’ or ‘2’ in **MCS.dat** for the desired concentration unit, and then on the following lines enter the temperature (K) followed by the species concentrations. Below are molalities for a salinity 35 seawater, taken from Table 4 of Millero et al. (2008). Note: the values

have been split over several lines, for legibility, and the species names added. See the supplied **MCS.dat** for some further examples that can be used.

T	H ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	K ⁺	MgOH ⁺	Sr ²⁺	
298.15	0.0E0	4.860597E-1	5.474210E-2	1.065680E-2	1.05797E-02	0.0E0	9.40E-05	
MgF ⁺	CaF ⁺	Cl ⁻	SO ₄ ²⁻	HSO ₄ ⁻	OH ⁻	Br ⁻	HCO ₃ ⁻	
0.0E0	0.0E0	5.657647E-1	2.926430E-2	0.0E0	8.20E-6	8.7280E-4	1.78030E-3	
CO ₃ ²⁻	B(OH) ₄ ⁻	F ⁻	B(OH) ₃	CO ₂ [*]	HF	MgCO ₃ ^o	CaCO ₃ ^o	SrCO ₃ ^o
2.4770E-4	1.0450E-4	7.080E-5	3.2580E-4	1.0E-5	0.0E0	0.0E0	0.0E0	0.0E0

In the above list there are entries for the following ion pairs in the model: MgOH⁺, MgF⁺, CaF⁺, MgCO₃^o, CaCO₃^o, and SrCO₃^o. These can be set to zero for input, as has been done here. Their equilibrium concentrations will be calculated by the program, as will acid-base equilibrium (notice H⁺ is also entered as zero in this example).

The data can also be entered as comma separated values, which can be useful if the input data are prepared using a spreadsheet program. See **Appendix 3** for details.

Any alterations of compositions must be done in a way that preserves overall charge balance. If the fractional error in charge balance of the input solution exceeds a tolerance of 1/10⁵, the program will stop (and print an error message to the screen). For example, if we wanted to increase the molality of Mg²⁺ from the above 0.0547421 by adding a further 0.01 mol kg⁻¹ of Mg²⁺ then it would be necessary either to increase the molalities of one or more anions to increase the negative charge by 2×0.01, or reduce the molalities of one or more of the other cations to achieve the same effect (or some combination of the two).

The composition of seawater used in this example, and ones generated for other salinities by the addition or subtraction of water, entails an assumed alkalinity and a defined total dissolved inorganic carbon concentration. In future versions of the program it will be possible to directly equilibrate the composition of the solution to fixed values of pairs of the four quantities thermodynamic total pH (−log₁₀([H⁺] + [HSO₄⁻])), total alkalinity, dissolved organic carbon, and *p*CO₂ (partial pressure of CO₂). This has not been implemented yet. Alterations of these quantities therefore have to be made by altering the acidity of the solution directly and/or altering total carbonate or borate concentrations. There are some examples below this can be done.

We recommend that you read the MARCHEMSPEC Supplement *Calculations for Natural Waters of Defined Alkalinity, Total Dissolved Inorganic Carbon, and Borate*, which shows how the input data for seawater can be recast so that values of total dissolved inorganic carbon, borate, and alkalinity can be input directly as elements of the solution composition (in place of values for species CO₂^{*}, B(OH)₃, and OH⁻).

Example 1: change of pH

To change pH, either add H⁺ and subtract the same number of moles of Na⁺, or add OH⁻ and add the same number of moles of Na⁺. This maintains charge balance. To obtain the results in **Table 2**, we

took the seawater composition given above and added the molalities of H^+ or OH^- given in the table (and compensating molalities of Na^+ to maintain overall charge balance). The same procedure, but using amount contents, would yield very similar results. In **Table 2**, notice how the $p\text{CO}_2$ is much more sensitive to pH_T changes than is alkalinity. (The total dissolved inorganic carbon is constant, of course.)

Example 2: change of total dissolved inorganic carbon

Changes of the total dissolved inorganic carbon ($\text{CO}_2^* + \text{HCO}_3^- + \text{CO}_3^{2-}$, plus carbonate in ion pairs with the alkaline earth metal cations) can be made by these methods:

- (i) Increasing/decreasing the input molality or amount content of CO_2^* . This is equivalent to adding or removing $2\text{H}^+ + \text{CO}_3^{2-}$. Additions lower the pH_T , but the alkalinity does not change.
- (ii) Adding/subtracting NaHCO_3 from the solution (which changes both pH_T and alkalinity).
- (iii) Adding/subtracting NaCO_3 from the solution (which also affects both pH_T and alkalinity).

Some calculations of these cases are shown in **Tables 3-5**.

Try running the examples shown in the tables (the input data for these cases can be found in the supplied **MCS.dat** file), and examine the effects of changing the concentrations of the major ions such Na^+ , Mg^{2+} , Cl^- , and SO_4^{2-} .

You should also try some examples based on the seawater composition in the table on Supplement *Calculations for Natural Waters of Defined Alkalinity, Total Dissolved Inorganic Carbon, and Borate*. This table shows, side by side, the amount content composition of salinity 35 reference seawater both as individual species concentrations, and as values corresponding to DIC, alkalinity and total borate. See what happens when you adjust these values (remembering to retain charge balance if you are adjusting alkalinity).

6. Help and Further Information

For news about the models, and downloads of the latest versions, go to marchemspec.org.

For questions about the models for solutions containing the species of artificial seawater, and standard seawater, contact Simon Clegg (s.clegg@uea.ac.uk). For questions about the model of complexation of trace species (described in one of the Supplements to this document), contact David Turner (david.turner@marine.gu.se).

The papers that describe the development of the models are cited in section 1 of this document (Preamble).

Appendix 1. Description of Model Output

This appendix contains detailed descriptions of the model output in the various results text files.

A1.1 Results in file MCS.rs1

Here we explain the output in this file, starting from the top.

1. The problem number is listed, and the temperature (Kelvin). The pressure, in the current version of the model, is always 1 atm.

2. Speciation and Activity Coefficients

This is the calculated composition of the solution, involving the usual acid-base equilibria and also the formation of a number of ion pairs (e.g., CaCO_3° , MgF^+ , MgOH^+). Values are listed for the molality-based activity coefficients (Act. Coeff.) the species molalities (Molality, moles per kg of pure water), and amount content or molinity (Molinity, moles per kg of solution).

At the bottom of this section are listed the water activity, the molality-based osmotic coefficient, and ionic strength.

3. Seawater Related Quantities

This section contains values of the various measures of pH, the stoichiometric equilibrium constants for the carbonate system and other acid-base reactions, and the concentration product of calcium carbonate. The symbols used in this section are defined in **Table 1**, which also lists the corresponding symbols used by Dickson et al. (2007), and defined in their chapter 2, Table 1.

Note that this section of the .rs1 output file is divided into two parts: in the first part all values are molality based (moles per kg of pure water), and in the second part they are amount content based (i.e., moles per kg of solution). In the second part the equilibrium constants are listed as pK values ($-\log_{10}(K)$), to correspond to common usage elsewhere.

4. Tests of the Calculation of Solution Equilibria, and Solver Details

These sections display results that are only useful for checking that the program works correctly. The percentage errors in the calculation of each chemical equilibrium in the computation are first listed. The calculation of equilibrium is carried out in two parts: a simple first estimate, and then a complete calculation. Values of the integer flag 'iFail' of zero indicate success.

Reference: Dickson, A.G., Sabine, C.L., Christian, J.R. (Eds.), 2007. *Guide to Best Practices for Ocean CO₂ Measurements*. North Pacific Marine Science Organisation. PICES Special Publication 3, IOCCP Report No. 8, 176 pp.

A1.2 Results in file MCS.rs2, and MCS.rs2.csv

These files contains the same results as in section 'Speciation and Activity Coefficients' of the .rs1 file, but in column format (separated by spaces, not tabs). The comma separated value (.csv) file

contains the same information, and can be read directly into spreadsheet programs such as Excel. The column headers have the following meanings:

iCount – the problem number.

iFail – the status flag for the calculation of equilibrium. A zero indicates success.

Err – if errors are detected there will be character codes in this column.

T – temperature (Kelvin)

P – pressure (atmospheres). This value is fixed at unity.

aW – water activity.

Osm – molality-based osmotic coefficient.

prefix ‘k’ – the amount content (also called ‘molinity’) of the solute species. For example, kH is the amount content (moles per kg of solution) of the H^+ ion.

prefix ‘m’ – the molality (moles per kg of pure water) of the solute species.

prefix ‘g’ – the molality-based activity coefficient of the species.

The order of the dissolved species (cations, then anions, then uncharged species, left to right) is as follows for the seawater model

H^+ Na^+ Mg^{2+} Ca^{2+} K^+ $MgOH^+$ Sr^{2+} MgF^+ CaF^+ Cl^- SO_4^{2-} HSO_4^- OH^- Br^- HCO_3^- CO_3^{2-}
 $B(OH)_4^-$ F^- $B(OH)_3$ CO_2^* HF $MgCO_3^0$ $CaCO_3^0$ $SrCO_3^0$

This is the same order as it used for input compositions in the **MCS.dat** file. Note the omission of charges in the names of ions in the output file, the use of all capital letters in the chemical symbols, and the omission of parentheses (e.g., BOH3 instead of B(OH)3) because these can cause problems when read into other applications and used as column names.

A1.3 Results in file MCS.rs4, and MCS.rs4.csv

These files contains the molality-based results from section ‘Seawater Related Quantities’ of the .rs1 file, but in column format. The comma separated value (.csv) file can be read directly into spreadsheet programs such as Excel.

Entries of 99.0 indicate property or uncertainty values that could not be calculated, most likely because the solution does not contain the species of interest (for example $K^*(BOH3)$ will be assigned 99.0 for solutions that do not contain any borate species). Column headers have the following meanings:

iCount – the problem number.

T – temperature (Kelvin)

P – pressure (atmospheres). This value is fixed at unity.

pH_{T, SW, F} – pH on the total (T), seawater (SW) or free (F) scales

upH_{T, SW, F} – the model-estimated uncertainties of the three different forms of pH.

pCO₂, and **upCO₂** – the calculated equilibrium partial pressure of CO₂ (atm.), and its estimated uncertainty.

fCO₂, and **ufCO₂** – the calculated equilibrium fugacity of CO₂ (atm.), and its estimated uncertainty.

DIC, and **uDIC** – the total dissolved inorganic carbon content of the solution (moles per kg of pure water), and its estimated uncertainty.

TotAlk, and **uTotAlk** – the alkalinity of the solution (moles per kg of pure water), and its estimated uncertainty.

Ca_CO₃, **uCa_CO₃** – the molality product of total Ca²⁺ and total CO₃²⁻, and its uncertainty.

Acid – base equilibrium constants – these stoichiometric constants are listed in the form **K{dissociating species}_{pH scale}**. Thus the dissociation constant of HCO₃⁻ on the total pH scale is given as **KHCO₃_T**, and on the seawater scale by **KHCO₃_SW**, and on the free pH scale by **KHCO₃_F**. A prefix of ‘u’ denotes the corresponding uncertainty (hence **uKHCO₃_F** for the estimated uncertainty in **pKHCO₃_F**).

A1.4 Results in file MCS.rs5, and MCS.rs5.csv

These files contain the amount content based results from section ‘Seawater Related Quantities’ of the .rs1 file, but in column format. The comma separated value (.csv) file can be read directly into spreadsheet programs such as Excel.

Column headers have the same meanings as for the .rs4 files described above, apart from the change in concentration units to amount contents. However, equilibrium constants and amount content concentration product of Ca²⁺ and CO₃²⁻ are presented on a log₁₀ basis, as follows.

Equilibrium constants

These values, and their estimated uncertainties, are expressed as p*K* (-log₁₀(*K*)), to conform to general usage elsewhere and for ease of comparability. The headers of the columns of results are named as follows:

pK{dissociating species}_{pH scale}. Thus the p*K* of the dissociation constant of HCO₃⁻ on the total pH scale is given as **pKHCO₃_T**, on the seawater scale by **pKHCO₃_SW**, and on the free pH scale by **pKHCO₃_F**. A prefix of ‘u’ denotes the corresponding uncertainty (hence, for example, **upKHCO₃_T** for the estimated uncertainty in **pKHCO₃_T**).

The column headers for the p*K* value of the amount content product of total Ca²⁺ and total CO₃²⁻, and its uncertainty, are enclosed in [] hence: **p[Ca_CO₃]** and **up[Ca_CO₃]**.

Appendix 2. Species in the Seawater Model

Here we list the solute species that are included in the MARCHEMSPEC seawater model. The order is important: it is the same as that in which the solute species are listed in the ‘master’ file Pitzer.mst, and is the order in which species concentrations (as molalities or amount contents) must be entered in data input files such as MCS.dat. It is also the order in which the species are listed on the various output files.

The model contains the major species present in the standard seawater of Millero et al. (2008), plus a number of ion pairs that are formed from their reaction, and which have been found to be needed by various investigators to represent the measured thermodynamic properties.

Species of the seawater model

Cations			Anions			Neutral Species		
#	Full Name	Column Name	#	Full name	Column Name	#	Full Name	Column Name
1	H ⁺	H	10	Cl ⁻	CL	19	B(OH) ₃	BOH3
2	Na ⁺	NA	11	SO ₄ ²⁻	SO4	20	CO ₂ [*]	CO2
3	Mg ²⁺	MG	12	HSO ₄ ⁻	HSO4	21	HF	HF
4	Ca ²⁺	CA	13	OH ⁻	OH	22	MgCO ₃ ⁰	MGCO3
5	K ⁺	K	14	Br ⁻	BR	23	CaCO ₃ ⁰	CACO3
6	MgOH ⁺	MGOH	15	HCO ₃ ⁻	HCO3	24	SrCO ₃ ⁰	SRCO3
7	Sr ²⁺	SR	16	CO ₃ ²⁻	CO3			
8	MgF ⁺	MGF	17	B(OH) ₄ ⁻	BOH4			
9	CaF ⁺	CAF	18	F ⁻	F			

Notes: The species names listed in the “Speciation and Activity Coefficients” section of the .rs1 file are the same as for the full names listed above, but without charges (and without superscript ‘^o’ in the case of the carbonate ion pairs). The column names, which are all in capital letters, are used in the output in the .rs2 file. These names do not include parentheses. Within the MARCHEMSPEC code (and in file Pitzer.mst) this is model number 2.

Appendix 3. Input Data as Comma Separated Values

The normal layout of the **MCS.dat** file, as supplied, is as follows:

1. Information about how to enter data, with each line of this information beginning with a comment character '#' (without quotes).
2. The line: Problem type (enter 0-11): 0
The zero after the semicolon means that the equilibrium state of the input solution(s) will be calculated.
3. A series of four numbered options, which are ignored for problem type zero entered above.
4. The line: Enter the type of input composition (1, 2 or 3): 1
The number after the semi-colon indicates whether solution compositions will be entered as molalities (1), amount contents (2) or salinities (3).
5. Lines of temperatures and compositions, consisting of numbers separated by spaces.
6. The data can be interspersed with comment lines, which begin with a '#'.

The essential elements of the data file are items 2 to 5 only. So, a valid **MCS.dat** file could begin like this:

```
Problem type (enter 0-11): 0
Enter the type of input composition (1, 2 or 3): 1
298.15 0.00000E+00 6.699568E-05 7.545337E-06 1.468872E-06 (+ further values)
298.15 0.00000E+00 6.699871E-04 7.545678E-05 1.468939E-05 (+ further values)
```

where the values above are temperature (T , in Kelvin) followed by the molalities of H^+ , Na^+ , Mg^{2+} and Ca^{2+} , etc.

It is also possible to read data as comma separated values, which is useful if the input compositions are prepared using a spreadsheet program such as Excel. If seawater species molalities or amount contents were created using a spreadsheet and written to a file as comma separated values (.csv) then the file will look something like this:

```
T,mH,mNa,mMg,mCa, (+ further names)
298.15,0.00000E+00,6.699568E-05,7.545337E-06,1.468872E-06, (+ further values)
298.15,0.00000E+00,6.699871E-04,7.545678E-05,1.468939E-05, (+ further values)
```

The first row contains whatever column names you used in the spreadsheet. To edit this comma separated value file into a form that can be read by the MARCHEMSPEC program, just comment out the line of column names (with a '#'), and add the lines that specify the problem type, and the type of input composition, like this:

```
Problem type (enter 0-11): 0
Enter the type of input composition (1, 2 or 3): 1
# T,mH,mNa,mMg,mCa, (+ further names)
298.15,0.00000E+00,6.699568E-05,7.545337E-06,1.468872E-06, (+ further values)
298.15,0.00000E+00,6.699871E-04,7.545678E-05,1.468939E-05, (+ further values)
```

The additions are in **bold**.

Don't forget: the input file must still be called **MCS.dat**. The program always reads this file for its input data.

Tables

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

Table 1. Definitions of the seawater-related quantities ('seawater state parameters') tabulated in the MCS.rs1 results file (and presented in column form in files MCS.rs4 and MCS.rs5)

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	<i>C</i> _T , total dissolved inorganic carbon
Tot.Alk.	A _T , total alkalinity		
Total pH basis (indicated by suffix ‘_T’, in the files of column output)			
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’, in the files of column output)			
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’, in the files of column output)			
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⁻ .		

Table 2. Effect of adding H^+ or OH^- to change pH_T of a salinity 35 seawater at 25 °C.

Added H^+ molality	Added OH^- molality	pH_T (mol kg^{-1} seawater basis)	Total Alkalinity (10^{-3} mol kg^{-1} seawater)	pCO_2 (10^{-4} atm.)
-	1×10^{-4}	8.2433	2.4009	2.2704
-	1×10^{-5}	8.1315	2.3141	3.0420
-	1×10^{-6}	8.1192	2.3054	3.1395
-	-	8.1178	2.3044	3.1506
1×10^{-6}	-	8.1165	2.3034	3.1618
1×10^{-5}	-	8.1039	2.2948	3.2651
1×10^{-4}	-	7.9637	2.2079	4.6527

Notes: Calculated properties of standard seawater are in bold.

Table 3. Effect of adding/removing CO_2^* to or from a salinity 35 seawater at 25 °C.

Added OH^- molality	Added CO_2^* molality	Added HCO_3^- molality	pH_T (mol kg^{-1} seawater basis)	Total Alkalinity (10^{-3} mol kg^{-1} seawater)	pCO_2 (10^{-4} atm.)	DIC (10^{-3} mol kg^{-1} seawater)
0.001	-	-0.001	9.4752	2.3045	0.00194	1.0015
0.0001	-	-0.0001	8.2613	2.3044	2.0583	1.8699
0.00001	-	-0.00001	8.1331	2.3044	3.0145	1.9567
-	-	-	8.1178	2.3044	3.1506	1.9663
-	0.00001	-	8.1024	2.3044	3.2944	1.9760
-	0.0001	-	7.9499	2.3044	5.0512	2.0628
-	0.001	-	6.3953	2.3043	221.68	2.9310

Notes: Calculated properties of standard seawater are in bold. The additions or subtractions of the amounts of the three species (CO_2^* , OH^- , HCO_3^-) always sum to be equivalent to an addition or subtraction of CO_2^* . The change is expressed this way so that, after adjusting a composition of seawater in the MCS.dat file, none of the input species molalities or amount contents is below zero (which would be trapped as an error).

Table 4. Effect of adding/removing NaHCO_3 to or from a salinity 35 seawater at 25 °C.

Added H^+ molality	Added OH^- molality	Added Na^+ molality	Added HCO_3^- molality	pH_T (mol kg^{-1} seawater basis)	Total Alkalinity (10^{-3} mol kg^{-1} seawater)	$p\text{CO}_2$ (10^{-4} atm.)	DIC (10^{-3} mol kg^{-1} seawater)
-	-	-0.001	-0.001	8.3321	1.3397	0.9107	1.0016
-	-	-0.0001	-0.0001	8.1343	2.2079	2.8719	1.8699
-	-	-0.00001	-0.00001	8.1194	2.2948	3.1222	1.9567
-	-	-	-	8.1178	2.3044	3.1506	1.9663
-	-	0.00001	0.00001	8.1162	2.3141	3.1791	1.9760
-	-	0.0001	0.0001	8.1022	2.4009	3.4408	2.0628
-	-	0.001	0.001	7.9875	3.2690	6.5360	2.9309

Notes: Calculated properties of standard seawater are in bold.

Table 5. Effect of adding/removing Na_2CO_3 to or from a salinity 35 seawater at 25 °C.

Added H^+ molality	Added OH^- molality	Added Na^+ molality	Added HCO_3^- molality	pH_T (mol kg^{-1} seawater basis)	Total Alkalinity (10^{-3} mol kg^{-1} seawater)	$p\text{CO}_2$ (10^{-4} atm.)	DIC (10^{-3} mol kg^{-1} seawater)
0.001	-	-0.002	-0.001	5.6184	0.3748	218.08	1.0016
0.0001	-	-0.0002	-0.0001	7.9687	2.1115	4.2675	1.8699
0.00001	-	-0.00002	-0.00001	8.0960	2.2851	3.2358	1.9567
-	-	-	-	8.1178	2.3044	3.1506	1.9663
-	0.00001	0.00002	0.00001	8.1203	2.3237	3.0697	1.9760
-	0.0001	0.0002	0.0001	8.2167	2.4973	2.4921	2.0628
-	0.001	0.002	0.001	8.7196	4.2336	0.8652	2.9309

Notes: Calculated properties of standard seawater are in bold. The additions or subtractions of the amounts of the four species (H^+ , OH^- , Na^+ , and HCO_3^-) always sum to be equivalent to an addition or subtraction of Na_2CO_3 . The change is expressed this way so that, after adjusting a composition of seawater in the MCS.dat file, none of the species molalities or amount contents is below zero (which would be trapped as an error).

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 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) – Modification of the MarChemSpec code to automatically adjust the compositions of solutions to fixed, user-specified, pairs or single values of the seawater state parameters pH (total or free), total alkalinity, total dissolved inorganic carbon, $p\text{CO}_2$ or $f\text{CO}_2$ (fugacity). This is done using new options in the **MCS.dat** input file, which are described in the Supplement to this manual. The chemical model is unchanged from before, except for a minor correction to the calculation of the fugacity coefficient of CO_2 .

You can now determine the version number of the MarChemSpec code you are using by typing 'MCS_sea.exe V' followed by <Enter>' at the command prompt. (This is not possible for previous versions of the code.)

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