Program Developed for CO$_2$ System Calculations

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CO$_2$ SYSTEM CALCULATIONS

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PREFACE

Investigators interested in studying the ocean carbonate system are not in complete agreement on how to calculate inorganic carbon speciation in seawater. Over the years there have been many determinations and reviews of the constants used to describe the dissociation of carbon dioxide (CO_2) in the ocean, but no universally accepted set of constants exists. Several subtly different pH scales remain in common use, as do variations in the definition of total alkalinity and arguments over the relative merits of reporting the partial pressure vs the fugacity of CO_2. As ocean CO_2 measurements become steadily more accurate and investigators seek to evaluate very small changes in concentrations, these issues grow in importance.

We recently released a computer program that we hope will be of general use and perhaps help to clear up some of the confusion. Given any two of the four measurable carbonate system parameters, this program calculates the other two, together with the inorganic carbon speciation and the saturation of calcite and aragonite. The program also allows the user to select from four different pH scales and several sets of dissociation constants widely cited in the literature.

Run in "single input" mode, the program reports calculated results together with the sensitivity of the calculated parameters to uncertainties in input parameters, constants, and the like. Run in "batch input" mode, the program can be used to process large data sets, such as cruise data derived from spreadsheets. In writing the code we spent considerable time cross-checking the relevant literature and checking units and scales. We are reasonably confident that the program itself does not introduce any errors and is consistent with the primary literature.

The program is written in compiled MICROSOFT QuickBASIC and runs under DOS on almost any personal computer processor. As a result, the user interface is functional but not flashy. The program includes on-line documentation, as well as a listing of typographical errors and inconsistencies culled from the literature. We may develop a MICROSOFT Visual Basic for Applications version if the demand for it is sufficient.

More information on this program is available from Ernie Lewis at Brookhaven National Laboratory (see Sect. 16 for contact information). This work was supported by the U.S. Department of Energy, Office of Biological and Environmental Research, under Contract No. DE-ACO2-76CH00016.

1. INTRODUCTION

The program CO2SYS performs calculations relating parameters of the carbon dioxide (CO_2) system in seawater and freshwater. The program uses two of the four measurable parameters of the CO_2 system [total alkalinity (TA), total inorganic CO_2 (TCO_2), pH, and either fugacity (fCO_2) or partial pressure of CO_2 (pCO_2)] to calculate the other two parameters at a set of input conditions (temperature and pressure) and a set of output conditions chosen by the user. It replaces and extends the programs CO2SYSTM.EXE, FCO2TCO2.EXE, PHTCO2.EXE, and CO2BTCH.EXE, which were released in May 1995. It may be run in single-input mode or batch-input mode and has a variety of options for the various constants and parameters used. An on-screen information section is available that includes documentation on various topics relevant to the program. This program may be run on any 80 x 86 computer equipped with the DOS operating system by simply typing CO2SYS at the prompt after loading the executable file CO2SYS.EXE.

2. CO_2 SYSTEM IN SEAWATER

The CO_2 system in seawater is characterized by four measurable parameters: TA, TCO_2 (i.e., the sum of the dissolved CO_2, the carbonate, and the bicarbonate), pH, and either fCO_2 or pCO_2. pCO_2 is the partial pressure of CO_2 in wet (100% water-saturated) air which is in equilibrium with the sample. Both fCO_2 and pCO_2 are proportional to the dissolved CO_2. The fugacity is about 0.3% to 0.4% lower than the partial pressure over the range of interest, due to the nonideality of CO_2. TA and TCO_2 are independent of temperature and pressure; fCO_2, pCO_2, and pH are not. The knowledge of any two of these parameters, along with the temperature, salinity, pressure, abundances of other constituents of seawater, and the relevant equilibrium constants, allows the determination of the other two parameters.

Unfortunately, this is not as easy as it sounds. The two definitions of alkalinity in current usage differ in how minor species are treated. Four different pH scales [total, seawater, free, and NBS (National Bureau of Standards, now the National Institute of Standards and Technology)] are in current usage (it is even more complicated in the literature, where the distinction between the total scale and the seawater scale has not always been made). The situation with the equilibrium constants is potentially more confusing: There are several different formulations of K_1 and K_2 (the first and second dissociation constants of carbonic acid in seawater) and also several formulations for the other dissociation constants of interest, on various pH and concentration scales.

Many of these differences are slight, but their importance is in direct proportion to the desired precision of the calculated values. The correction for the nonideality of CO_2, for instance, is only around 0.3% under most conditions, but this correction is near the precision of some measurements systems. The difference in the definitions of alkalinity consists mainly in the treatment of phosphate. This difference may seem minor, but a modest phosphate concentration, such as 3 micro-moles per kilogram of seawater ($\mu mol/kg$-SW), can result in a difference in fCO_2 (or pCO_2) of 20 micro-atmospheres (μatm) or more, when calculated from TA and TCO_2, depending on the definition of alkalinity. This difference, therefore, is quite significant.

We evaluated several other programs that performed calculations relating the seawater CO_2 system parameters. These programs differed in the values of the constants used and in what contributions to the alkalinity were considered. To get an idea of the differences, we ran three programs with the following inputs: TA = 2300 μmol/kg-SW; TCO_2 = 2000 μmol/kg-SW; no phosphate or silicate (two of the programs did not have an option to include these); and temperature (°C), salinity [on the Practical Salinity Scale (PSS)], and pressure (in dbar) equal to 20, 35, and 0, respectively. The results were as follows:

Program	pCO_2 (μatm)	pH	pH scale	HCO_3^- (μmol/kg)	CO_3^{2-} (μmol/kg)
1	336	8.229	Free	1767	223
2	351	8.088	Seawater	1772	216
3	330	8.247	NBS	1782	208

As can be seen, the pH values are on different pH scales and thus are difficult to compare. The values for pCO_2, though, should be the same regardless of pH scale, as should the values for the concentrations of HCO_3^- and CO_3^{2-}.

Closer inspection (this means looking at the codes) reveals some of the reasons for the differences. Program 1 did not include the contribution of OH to the alkalinity (which would be about 5 μmol/kg-SW), nor did it include the contributions of phosphate and silicate. It used the K_1 and K_2 values from Goyet and Poisson (1989) and the value of K_{SO_4} from the data of Khoo et al. (1977), but refit by other investigators. It did not include a correction for the nonideality of CO_2, but did include pressure corrections. Program 2 did not include the contributions of phosphate and silicate, but did include pressure corrections and a correction for the nonideality of CO_2. The values of K_1 and K_2 were those of Roy et al. (1993), and the value of K_{SO_4} was that of Dickson (1990a). Program 3 did include the contributions of phosphate and silicate, but had no corrections for the nonideality of CO_2 or for pressure. The values of K_1 and K_2 used were from Mehrbach et al. (1973). Each of the programs used a different value for K_B, the dissociation constant for boric acid.

It can thus be seen how different programs, with no coding errors, can yield very different results. Because of this, we decided to provide a single program that encompassed a wide variety of choices for CO_2 system constants, pH scales, etc., in order to facilitate the assessment of the CO_2 system calculations to such choices.

3. PROGRAM CO2SYS INFORMATION

The program CO2SYS is designed for either single-input mode or batch-input mode, and allows for a variety of options, including the choice of various formulations for K_1 and K_2, two distinct formulations for K_{SO_4} (Dickson 1990a; Khoo et al. 1977), the choice of four pH scales (free, total, NBS, or seawater), and the use of either fCO_2 or pCO_2.

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Any two CO_2 system parameters (TA, TCO_2, fCO_2 or pCO_2, and pH) may be chosen as the inputs from which the other two parameters will be calculated. Contributions to the alkalinity from phosphate, silicate, and OH are included, as are the effects of pressure and the nonideality of CO_2. An on-screen information section is available that includes discussions of the various options and provides references for the values used and for other topics that are relevant to the program. Every effort has been made to make this program as correct, complete, and user-friendly as possible. However, the program is not fail-safe, and some familiarity with the CO_2 system in seawater is assumed. Most of the fits to the constants are valid only over a restricted range of salinities (mostly 20 to 40). Values outside of this range should not be expected to yield correct results.

The units used for the variables in this program are micro-moles per kilogram of seawater (μmol/kg-SW) for concentrations of TA, TCO_2, etc.; micro-atmospheres (μatm) for pCO_2 and fCO_2; and parts per million (ppm) for the mole ratio of CO_2 in dry air. All temperatures are in °C, all salinities are on the PSS, and all pressures are in dbar. Depth in meters may be used instead of pressure; these parameters differ by only 3% at 10,000 dbar and less at lower pressures, well within the uncertainties of the pressure effects on the equilibrium constants. In this documentation, units for the concentration of [H^+], necessary to clearly define the pH scale, are mol/kg-SW for the total, seawater, and free pH scales (note that the original definition in the literature for the free pH scale was in molal units), and mol/kg-H_2O (molal) for the NBS scale (by definition).

Because the equilibrium constants given in the literature are on various pH scales and in various concentration units (molar, molal, or mol/kg-SW), it is imperative that they be converted correctly to the desired scale. In developing this program, much work was done to ensure that these conversions were made correctly. Data are sparse for many of the constants. Those values used in this program were those we chose to be the best from the available data. Many errors and inconsistencies were found in the literature. In writing this program, a list of these typographical errors was compiled. This list is included as an Appendix to this report because it may be of interest to those involved in calculations for the carbonate system. Although most of the errors are very minor, it is hoped that the use of this list will save time and effort for anyone wishing to delve further into the topic.

Occasionally, for certain inputs of TCO_2 and fCO_2 or pCO_2, the system has no solution for the given input conditions. If this situation arises in single-input mode, the user is notified and the parameters may be re-entered. If this occurs in batch-input mode, −999 is printed for TA, pH, and the other calculated parameters for that sample.

4. VERSION HISTORY

The programs CO2SYSTM.EXE, FCO2TCO2.EXE, PHTCO2.EXE, and CO2BTCH.EXE were released in May 1995. To the best of our knowledge, no serious errors have been found in these programs. One possible problem is that the fits for the constants are not valid for extrapolation to salinity 0.

Program CO2SYS replaces and extends the four programs listed above.

Version 0.00, from February 1997, was only preliminary and should not be used for calculations. The pressure corrections to the carbonate solubilities were incorrect.

Version 1.02 was released in March 1997. The pressure corrections to the pH scale conversions were done incorrectly. These errors had a very minor effect in most cases.

Version 1.03 was released in May 1997. It is believed to be accurate.

Version 1.04 was released later in May 1997. It differs from version 1.03 only cosmetically (typographical errors were corrected, etc.). No differences should exist between calculations performed using this version and version 1.03.

Version 1.05 was released in October 1997. It differs from version 1.04 cosmetically (e.g., typographical errors were corrected) and in that some different code was used for better efficiency (no code errors were found). No differences should exist between calculations performed using this version and versions 1.03 and 1.04.

5. SINGLE-INPUT MODE

In single-input mode, after selection of the various options for the values of the constants, etc., the user is prompted for the following:

- salinity,
- concentrations of phosphate and silicate,
- input temperature and pressure (or depth),
- output temperature and pressure (or depth), and
- two known CO_2 system parameters at the input conditions.

The input temperature and pressure, at which the values of the two known CO_2 system parameters are given, may be those at which measurements were performed in the laboratory, for example, while the output conditions may refer to *in situ* conditions. The program will use "default" values for a variable (i.e., the last value occurring for that particular variable, given in parentheses) when the user hits the "enter" key. These default values may be useful for comparing the effects that various formulations of the constants have on the calculated parameters.

The program will then calculate the other two CO_2 system parameters at the input conditions. TA and TCO_2, which do not vary with temperature and pressure, are used to calculate the pH and fCO_2 or pCO_2 at the output conditions. Also calculated for both the input and the output conditions are

- the sensitivity of the output results to small variations of the inputs;
- the contributions to the alkalinity and carbon speciation;
- fCO_2 and pCO_2 in wet (100% saturated) air;
- xCO_2 (the mole fraction of CO_2 in dry air assuming 1 atm total pressure);
- Omega (the degree of saturation) for calcite and for aragonite;
- the Revelle factor (homogeneous buffer factor);

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- pH values on all four pH scales (total, seawater, free, and NBS); and
- the values of pK_1, pK_2, pK_W, and pK_B on the chosen pH scale.

The user may scroll forward or backward through the various screens. Information is available on-screen for the various options and can be accessed while running the program.

The program lists the estimated accuracy of K_0 and the 2S (two standard deviation) precision of the constants K_1 and K_2 to allow an estimate to be made of the uncertainty of the final answer caused by the uncertainty in the equilibrium constants.

6. BATCH-INPUT MODE

6.1 Inputs

Batch-input mode is designed to be used with large data sets, such as files created by MICROSOFT EXCEL or other spreadsheet programs. In this mode, data are read from an input file and results are calculated and printed to an output file. After the various options are chosen, the user is prompted for:

- the name of the input file,
- the name of the output file,
- the number of header lines in the input file,
- the number of ID fields preceding the data for each sample,
- a numeric value to denote missing data, and
- an option to flag samples containing missing data.

Each line in the input file must contain the following fields for one sample:

- the ID fields (the number of which is selected by the user),
- salinity (on the PSS),
- total phosphate (in μmol/kg-SW),
- total silicate (in μmol/kg-SW),
- temperature (°C) of the input CO_2 system parameters,
- pressure (dbar) of the input CO_2 system parameters,
- temperature (°C) for output conditions,
- pressure (dbar) for output conditions,
- the first known CO_2 system parameter, and
- the other known CO_2 system parameter.

It is VERY IMPORTANT that the input data be in the correct format and that the correct order of the CO_2 system parameters be followed:

- TA will always come first if used;
- TCO_2 (if used) will precede any parameter except TA;
- pH (if used) is next;
- fCO_2 (or pCO_2) will always be last if used.

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Units used are μmol/kg-SW and μatm. Six example data files, CASE1.INP–CASE6.INP, are included with the program; there is one data file for each of the choices of CO_2 system input parameters. Following is the sample data file CASE1.INP:

> **This is CASE1.INP, a test program for CO2SYS. It works for case 1.**
> **line1, 35., 3., 55., 20., 0, 5, 1000, 2400., 2200.**
> **line2, 35., 0, 0, 20, 0, 5, 1000, 2400., 2300.**
> **line3, 33., 2., 122., 15, 0, 5, 0, 2300., 2200.**
> **line4, 35., 0, 0, 20, 0, 15, 0, 2300., 2100.**
> **line5, 33., 3., 2., 25, 0, 10, 100, 2200., 2100.**

In this example, the input data are comma-separated (this is recommended), but they may also be space-separated. For space-separated data, the ID fields MUST be within double quotes; for comma-separated data, this is not required. (Note that MICROSOFT EXCEL puts double quotes around each double quote when importing a CSV file.) It can occur that for certain inputs of TCO_2 and fCO_2 (or pCO_2), the system has no solution for the given input conditions. If this occurs, -999 is printed for the TA, pH, and the other calculated parameters.

6.2 Missing Values

Because a data set may contain values that are missing or unknown, the user may define a numeric value to be the missing-value designator (MVD). If an MVD is not defined by the user, the default value -9 will be used. IT IS IMPERATIVE THAT A VALUE BE PROVIDED IN EACH OF THE INPUT DATA FIELDS; therefore, unknown values should always be set equal to the MVD.

If the MVD is input for one of the CO_2 system parameters, no calculations will be made and each output variable will be given the value of the MVD. If the MVD is input for one of the non-CO_2 system parameters, a default value will be used in calculations and that sample will be flagged (if that option has been chosen). HOWEVER, the MVD will be printed in the output file for that variable. OBVIOUSLY, CAUTION SHOULD BE USED IN INTERPRETING THE RESULTS WHEN THERE ARE MISSING VALUES IN THE INPUT FILE.

The defaults used are

- salinity: 35;
- total phosphate: 0 μmol/kg-SW;
- total silicate: 0 μmol/kg-SW;
- input temperature: 20°C;
- input pressure: 0 dbar;
- output temperature: the value of the input temperature; and
- output pressure: the value of the input pressure.

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6.3 Output

The output file will contain header lines with the following:

- the input file name and the date;
- the choice of constants, K_{SO_4}, and pH scale;
- any other header lines input by the user; and
- labels for the output fields.

The output data are comma-separated with one line per sample. Each line will contain the same fields as the input data plus the following calculated values:

- the other two CO_2 system parameters at the input conditions,
- pH and fCO_2 (or pCO_2) at the output conditions,
- Omegas for calcite and aragonite at the input conditions,
- $[HCO_3^-]$ and $[CO_3^{2-}]$ at the input conditions,
- Omegas for calcite and aragonite at the output conditions, and
- $[HCO_3^-]$ and $[CO_3^{2-}]$ at the output conditions.

If the user chooses to flag missing data, an extra field will be appended. This field will contain the MVD value if there are missing data or a zero if there are no missing data. The pH values are reported on the scale chosen by the user. To load the output file into MICROSOFT EXCEL, simply open it as comma-separated with the extension "CSV".

7. CHOICES FOR CONSTANTS IN THIS PROGRAM

A large number of values are needed in the calculations. These include the following:

- the various dissociation constants:
  - K_1 and K_2 for carbonic acid,
  - K_B for boric acid,
  - K_W for water,
  - K_{SO_4} for the bisulfate ion,
  - K_F for hydrogen fluoride,
  - K_{P1}, K_{P2}, and K_{P3} for phosphoric acid, and
  - K_{si} for silicic acid;
- K_{sp}(calcite) and K_{sp}(aragonite), the saturation solubility products for calcite and aragonite;
- the pressure dependence of the dissociation constants and the solubility products;
- the concentrations of the various species assumed to be proportional to the salinity (the concentrations of phosphate and silicate may vary and are input by the user):
  - TB for total boron,
  - TS for total sulfate,
  - TF for total fluoride, and
  - TCa for total calcium;
- K_0, the solubility of CO_2 in seawater;
- the vapor pressure of water above seawater;
- the virial coefficients of CO_2 and CO_2-air; and

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- f_H, the activity coefficient of the hydrogen ion.

These values have been determined by many different investigators in many ways. Most assume values of temperature and salinity within ranges typically found in the oceans, so the use of values outside these ranges may result in fits being extrapolated beyond the region where data were collected.

There are eight choices for the constants used in this program. They differ mostly in the formulation of K_1 and K_2, but there are other slight differences as well, which are described below. These eight choices are

1. Roy et al. (1993);
2. Goyet and Poisson (1989);
3. Hansson (1973a,b), refit by Dickson and Millero (1987);
4. Mehrbach et al. (1973), refit by Dickson and Millero (1987);
5. Dickson and Millero's fit of the combined Hansson/Mehrbach data;
6. GEOSECS Choice (Takahashi et al. 1982);
7. Peng Choice (Peng et al. 1987); and
8. Freshwater Choice.

Constants are converted to the appropriate pH and concentration scales, if necessary, before calculations are made.

In all cases, K_0, the solubility of CO_2 in seawater, is from Weiss (1974), who combined the measurements of Murray and Riley (1971) with some of his own and fit the resulting data. Estimates of the accuracy of K_0 vary from 0.2% (Weiss 1974) to 0.5% (Dickson and Riley 1978). The virial coefficients of CO_2 and CO_2-air are from Weiss (1974). The vapor pressure of H_2O above seawater is from Weiss and Price (1980). The concentrations of sulfate and fluoride are from Morris and Riley (1966) and Riley (1965), respectively. The value of K_{SO_4} is from either Khoo et al. (1977) or Dickson (1990a) (this is a choice the user makes). Both of these are given in units of mol/kg-H_2O and both are (inherently) on the free pH scale. K_F is from Dickson and Riley (1979). It is also (inherently) on the free pH scale and is given in units of mol/kg-H_2O. Sulfate and fluoride contribute almost nothing to the alkalinity under most circumstances, but their concentrations and dissociation constants are important in converting between the various pH scales. The value used for f_H, the activity coefficient of the hydrogen ion (also necessary in converting between pH scales) is from the fit given in Takahashi et al. (1982), except for the Peng Choice, in which case the fit given in Peng et al. (1987) is used.

The relevant equilibrium constants that define the speciation of CO_2 in seawater, K_1 and K_2, have been determined for various temperatures and salinities by several different investigators. Four sets of measurements remain worthy of consideration. These measurements were made by Roy et al. (1993) on the total pH scale in units of mol/kg-H_2O, Goyet and Poisson (1989) on the seawater pH scale in units of mol/kg-SW, Hansson (1973a,b) on the total pH scale in units of mol/kg-SW, and Mehrbach et al. (1973) on the NBS pH scale in units of mol/kg-SW. The data of Hansson (1973a,b) and Mehrbach et al. (1973), both separately and together, have been refit by Dickson and Millero (1987) on the seawater scale in units of mol/kg-SW. Both

GEOSECS (Takahashi et al. 1982) and Peng et al. (1987) used the fit given in Mehrbach et al. (1973).

The following are approximate 2S precisions of the fits of the data: (Remember that **precision** and **accuracy** are NOT the same!):

Source	K_1	K_2
Roy et al. (1993)	2%	1.5%
Goyet and Poisson (1989)	2.5%	4.5%
Hansson (1973a,b), refit by Dickson and Millero (1987)	3%	4%
Mehrbach et al. (1973), refit by Dickson and Millero (1987)	2.5%	4.5%
Dickson and Millero (1987), combined fit	4%	6%
Mehrbach et al. (1973)	1.2%	2%
Freshwater Choice	0.5%	0.7%

7.1 Constant Choices 1 to 5

Constant Choices 1 to 5 differ only in the values of K_1 and K_2 and are therefore discussed together. The value of K_B is from Dickson (1990b) and TB is from Uppstrom (1974). The calcium concentration used is from Riley and Tongudai (1967). The values of K_{sp} for calcite and aragonite are from Mucci (1983). The effects of pressure on K_1 and K_2 are from Millero (1995). The effects of pressure on K_B are from Millero (1979) (but without the salinity dependence). Note that typographical errors in Millero (1995) include a factor of 1000 left out of the definition of Kappa and an incorrect value and incorrect units for the gas constant R (see Appendix A). The pressure correction for K_{sp} for calcite is from Ingle (1975) and that for aragonite from Millero (1979).

The definition of alkalinity used is that of Dickson (1981):

$$TA = [HCO_3] + 2[CO_3] + [B(OH)_4] + [OH] + [HPO_4] + 2[PO_4] + [SiO(OH)_3] + [HS] + 2[S] + [NH_3] - [H] - [HSO_4] - [HF] - [H_3PO_4] ,$$

except that the contributions from HS, S, and NH_3 are not included.

Values for K_W, K_{P1}, K_{P2}, K_{P3}, and K_{Si} are from Millero (1995), where they are given on the seawater scale.

7.2 GEOSECS Choice

The GEOSECS option was designed to replicate the calculations performed in the GEOSECS atlases by Takahashi et al. (1982). These calculations were made on the NBS pH scale using the values of K_1 and K_2 from Mehrbach et al. (1973) and the value of K_B from Lyman (1957) as fit by Li et al. (1969).

The definition of alkalinity used was

$$TA = [HCO_3] + 2[CO_3] + [H_2BO_3] \, ,$$

which did not include effects of OH, phosphate, or silicate. No correction was applied for the nonideality of CO_2 (thus implying fCO_2 and pCO_2 are the same). The boron concentration was from Culkin (1965) and is about 1% lower than that used for Constant Choices 1 to 5. A fit for f_H was given for salinities of 20 to 40.

Some typographical errors in the GEOSECS report were noted and corrected: in the pressure dependence of K_2, the given value 26.4 should be 16.4, and in the equation for $\ln K_W$, the expression $C/\ln T$ should be $C*\ln T$. One can verify these corrections by checking the original references for Takahashi et al. (1982). The ratio K_{sp}(aragonite) / K_{sp}(calcite) is given as 1.48 in the original reference (Berner 1976), but the value of 1.45 given in the GEOSECS report was used both in that work and in this program for the GEOSECS Choice. The GEOSECS report also contains a discussion on the effects of OH, phosphate, and silicate (see pp. 79–82, especially Table 1 on p. 81, of Takahashi et al. 1982). From this discussion, it can be seen how important the effects of these species can be, especially for the calculated value of fCO_2 (or pCO_2). The GEOSECS table also has a typographical error: 17.8 for A_w in Pacific Surface Water should be 7.8.

7.3 Peng Choice

This choice replicates the calculation scheme used by Peng et al. (1987), which is similar to that of GEOSECS (Takahashi et al. 1982). This scheme has been used extensively by modelers. Peng et al. (1987) worked on the NBS pH scale and included effects of phosphate, silicate, and OH, but did not distinguish between fCO_2 and pCO_2. The values of K_1 and K_2 used were from Mehrbach et al. (1973) as given in that paper, and the value of K_B was from Lyman (1957) as fit by Li et al. (1969). The boron concentration was from Culkin (1965) and is about 1% lower than that used for Constant Choices 1 to 5. The value of f_H given in their paper was NOT the same as that given in the GEOSECS report as claimed; rather, it had been rounded off and was therefore about 1% higher, corresponding to a change of 0.004 in pH. Note that the check value given in Peng et al. (1987) does not match either fit.

Peng et al. (1987) did not treat calcite and aragonite solubility or pressure effects. However, these effects are included in the program CO2SYS for the Peng Choice by using values for solubility and pressure dependence of K_1, K_2, and K_B from GEOSECS and values for the pressure dependence of OH and phosphate and silicate dissociation as are used in Constant Choices 1 to 5.

Peng et al. (1987) used K_{P2} and K_{P3} from Kester and Pytkowicz (1967), K_{Si} from Sillen et al. (1964, p. 751), and K_W from Millero (1979).

The definition of alkalinity used by Peng et al. (1987) is

$$TA = [HCO_3] + 2[CO_3] + [H_2BO_3] + [H_3SiO_4] + [H_2PO_4] + 2[HPO_4] + 3[PO_4] + [OH] \, .$$

This equation differs from the equation for TA of Dickson (1981) which is used in Constant

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Choices 1 to 5 mainly in that it is greater by an amount equal to the total phosphate:

$$TP = [PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4] \, .$$

This difference seems insignificant, but under certain conditions it can affect the calculated fCO_2 appreciably.

7.4 Freshwater Choice

The definition of alkalinity used in this case is

$$TA = [HCO_3] + 2[CO_3] + [OH] - [H] \, .$$

K_1, K_2, and K_w are from Millero (1979): K_w is a refit of data from Harned and Owen (1958); K_1 is a refit of the data of Harned and Davis (1943); and K_2 is a refit of the data of Harned and Scholes (1941). Pressure effects on these constants are from Millero (1983).

The activity coefficient of H^+, f_H, does NOT equal 1 at salinity 0 due to liquid junction effects (included in its definition). It has also been found to be electrode dependent. Thus, even though the values of pH on the free, total, and seawater scales will coincide at salinity 0, the value on the NBS scale will differ. For these reasons, for this choice only, a pH value is given without reference to a pH scale.

Only one set of measurements of K_1 and K_2 have been made in seawater at salinity <10. Although the values can be extrapolated to salinity 0, they change by a considerable amount over this interval: between salinities 0 and 5, K_1 varies by a factor of 2 and K_2 varies by a factor of 6.5 to 9.2, depending on temperature; for comparison, between salinities 5 and 35, K_1 varies by a factor of less than 1.5 and K_2 varies by a factor of less than 3. Thus, a fit of K_1 and K_2 for values of salinity in this range would be prone to large uncertainty. For this reason, only values of K_1 and K_2 valid at salinity 0 (freshwater) are used.

8. ALKALINITY

The definition of alkalinity (TA) used in this program for Constant Choices 1 to 5 is the same as that of Dickson (1981):

$$TA = [HCO_3] + 2[CO_3] + [B(OH)_4] + [OH] + [HPO_4] + 2[PO_4] + [SiO(OH)_3] + [HS]$$
$$+ 2[S] + [NH_3] - [H] - [HSO_4] - [HF] - [H_3PO_4] \, ,$$

except that the contributions of HS, S, and NH_3 are not included.

For the Peng Choice, the definition of Peng et al. (1987) is used. The main difference is that it is greater by an amount equal to the total phosphate:

$$TP = [PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4] \, .$$

Though this seems small, it can have a large effect on the calculated fCO_2. For instance, when

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fCO_2 (or pCO_2) is calculated from TA and TCO_2, a modest phosphate concentration such as 3 $\mu mol/kg$-SW, can result in a difference of 20 μatm or more, depending on which definition of alkalinity is used.

The definition used for the GEOSECS Choice is from Takahashi et al. (1982):

$$TA = [HCO_3] + 2[CO_3] + [H_2BO_3] ,$$

and for the Freshwater Choice is

$$TA = [HCO_3] + 2[CO_3] + [OH] - [H] .$$

In this program values of alkalinities are given in micromoles per kilogram of seawater ($\mu mol/kg$-SW).

9. K_{SO_4} CHOICES

K_{SO_4} is defined to be the dissociation constant for the reaction

$$HSO_4^- = H^+ + SO4^{2-} ;$$

thus,

$$K_{SO_4} = [H] * [SO_4] / [HSO_4] .$$

There are two equations for KSO_4 that are still in current usage: Khoo et al. (1977) and Dickson (1990a). Although many older papers used values of Khoo et al. (1977), the values of Dickson (1990a) are now recommended. The values of Khoo et al. (1977) are between 15 to 45% lower than those of Dickson, depending primarily on temperature. The main effect of this difference will occur when converting from one pH scale to another, or when working on a scale for which equilibrium constants must be converted (e.g., most constants were determined on either the total scale or the seawater scale). The use of the Dickson values when converting from the total pH scale to the free pH scale will result in pH values that are 0.015 to 0.03 units lower than those obtained using values of Khoo et al. (1977).

10. fCO_2 AND pCO_2

The fugacity of CO_2 (fCO_2) in water is defined to be the fugacity of CO_2 in air which is in equilibrium with the water. The partial pressure of CO_2 in wet (100% water-saturated) air (pCO_2) is defined to be the product of the mole fraction of CO_2 in wet air and the total pressure. This is the same as the product of the mole fraction of CO_2 in dry air [$xCO_2(dry)$] and ($p_{tot} - p_{H_2O}$), where p_{H_2O} is the vapor pressure of water above seawater. At pressures of the order of 1 atm, fCO_2 in air is about 0.3% lower than the pCO_2 due to the nonideality of CO_2 (Weiss 1974). This program assumes a pressure near 1 atm (where most equilibrators function) for the conversion between partial pressure and fugacity.

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fCO_2 is related to TCO_2 and pH by the following equation:

$$fCO_2 = \frac{[CO_2^*]}{K_0} = \frac{TCO_2}{K_0} * \frac{H*H}{H*H + K_1*H + K_1*K_2},$$

where $[CO_2^*]$ is the concentration of dissolved CO_2, K_0 is the solubility coefficient of CO_2 in seawater, and K_1 and K_2 are the first and second dissociation constants for carbonic acid in seawater.

Units for fCO_2 and pCO_2 in this program are μatm. The value of xCO_2(dry) given in this program assumes p_{tot} = 1 atm. GEOSECS (Takahashi et al. 1982) and Peng et al. (1987) did not distinguish between fCO_2 and pCO_2, nor did some other programs that we have evaluated.

11. REVELLE FACTOR

The Revelle, or homogeneous buffer, factor is the percentage change in fCO_2 (or pCO_2) caused by a 1% change in TCO_2 at constant alkalinity. It depends on temperature, salinity, and the total alkalinity and TCO_2 (or any combination of two of the CO_2 system parameters) of the sample. It is calculated at both the input and output conditions using the following:

Revelle factor = $(dfCO_2/dTCO_2) / (fCO_2/TCO_2)$

at constant TA.

Normal seawater values are between 8 and 20.

12. CALCIUM SOLUBILITY

The solubility product (K_{sp}) is calculated for both calcite and aragonite, and the saturation states are given in terms of the solubility ratio, Omega, which is defined as

Omega = $[CO_3^{2-}]*[Ca^{2+}] / K_{sp}$.

Thus, values of Omega <1 represent conditions of undersaturation, and values of Omega >1 represent conditions of oversaturation.

The concentration of calcium, $[Ca^{2+}]$, is assumed to be proportional to the salinity, and the carbonate concentration, $[CO_3^{2-}]$, is calculated from TCO_2, pH, and the values of K_1 and K_2 for carbonic acid. For Constant Choices 1 to 5, the calcium concentration used is from Riley and Tongudai (1967). The values of K_{sp} for calcite and aragonite are from Mucci (1983). The pressure correction for K_{sp} for calcite is from Ingle (1975) and that for aragonite is from Millero (1979).

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For the GEOSECS Choice and the Peng Choice, the concentration of calcium is from Culkin (1965). The value of K_{sp} for calcite is from Ingle (1975). [GEOSECS had referenced Ingle et al. (1973), but this is incorrect.] The value of K_{sp} for aragonite is from Berner (1976). (Berner stated that K_{sp} for aragonite is 1.48 times K_{sp} for calcite; GEOSECS gave and used the value 1.45 instead of 1.48. The program CO2SYS also uses 1.45.) The pressure corrections to these constants are from Takahashi et al. (1982). [The original reference given for the pressure corrections is not valid, and the fit used appears to be new to Takahashi et al. (1982).]

13. PRESSURE EFFECTS

The equilibrium constants depend on pressure as well as on temperature and salinity. Data are scarce on the effects of pressure on these constants in seawater, and most values are estimated from molal volume data. Few measurements have been made for K_1 and K_2 (of carbonic acid) and K_B (of boric acid) at only a few combinations of temperature, salinity, and pressure in seawater (mostly in artificial seawater). All work assumed that f_H, the activity coefficient of H^+ (including liquid junction effects), is independent of pressure. Some of the pH scale conversions do depend on pressure, however. Values of the constants should be (1) converted initially to the seawater or NBS pH scale WITHOUT pressure-corrected pH scale conversions, (2) then corrected for pressure, and (3) then converted to the desired pH scale WITH pressure-corrected pH scale conversions. Measurements have also been made for the effects of pressure on the solubility of calcite and aragonite in seawater.

Depth in meters and pressure in decibars are used interchangeably in this program. They differ by only 3% at 10,000 dbar and less at lower pressures—well within the uncertainties of the pressure effects on the constants. No salinity dependence of the pressure corrections is used in this program.

For the Freshwater Choice, the effects of pressure on K_1, K_2, and K_W are from Millero (1983).

Peng et al. (1987) did not consider the effects of pressure, but they are included in the program CO2SYS for the Peng Choice. For Constant Choices 1 through 5 and the Peng Choice, the effects of pressure on the values of K_{P1}, K_{P2}, and K_{P3} are from Millero (1995). The only mention of K_{Si} was in Millero (1995), where it is stated that the values have been estimated from the values of boric acid, but they are not listed in the table. In the program CO2SYS, the values used are the same as those for the pressure effects on K_B given in Millero (1995). For the effects of pressure on K_W, the fit given in Millero (1983) is used. GEOSECS did not include the effects of OH, phosphate, or silicate, so these are irrelevant for that choice.

For the GEOSECS Choice and the Peng Choice, the effects of pressure on K_1, K_2, and K_B are those given in the GEOSECS report (Takahashi et al. 1982). The reference given there is Culberson and Pytkowicz (1968), but the fits are actually those from Edmond and Gieskes (1970) who, in turn, quote Li (personal communication). In the fit for the correction for K_2 due to pressure, the GEOSECS report had the value 26.4, but the value 16.4 was used, which was consistent with their calculations, as well as with the fit given in Edmond and Gieskes (1970). The effects of pressure on the solubility of calcite and aragonite are also those from Takahashi et al. (1982). [The original reference given in that work for the pressure corrections

is not valid, and the fit used appears to be new to Takahashi et al. (1982).]

For the Constant Choices 1 to 5, the effects of pressure on K_1 and K_2 are from Millero (1995), and those for K_B are from Millero (1979), but without the salinity dependence. These fits are from the data of Culberson and Pytkowicz (1968). The effects of pressure on K_{SO_4} and K_F are from Millero (1995). Note that typographical errors in Millero (1995) include a factor of 1000 left out of the definition of Kappa and an incorrect value and incorrect units for the gas constant R. The pressure correction for K_{sp} for calcite is from Ingle (1975) and that for aragonite is from Millero (1979).

14. pH SCALES

The various pH scales are interrelated by the following equations:

$$a_H = 10^{(-pH_{NBS})} = f_H * H_{sws}$$

and

$$H_{free} = H_{tot}/(1 + TS/K_{SO_4}) = H_{sws}/(1 + TS/K_{SO_4} + TF/K_F),$$

where
a_H is the activity and f_H is the activity coefficient of the H^+ ion (this includes liquid junction effects),
TS and TF are the concentrations of SO_4^{2-} and fluoride, and
K_{SO_4} and K_F are the dissociation constants of HSO_4^- and HF in seawater.

The conversions depend on temperature, salinity, and pressure. At 20°C, salinity 35, and 1 atm, pH values on the total scale are approximately

- 0.09 units lower than those on the free scale,
- 0.01 units higher than those on the seawater scale, and
- 0.13 units lower than those on the NBS scale.

The concentration units for a_H on the NBS scale are mol/kg-H_2O. The concentration units used in the program CO2SYS for [H^+] on the other scales are mol/kg-SW (note that the free scale was originally defined in units of mol/kg-H_2O). The difference between mol/kg-SW and mol/kg-H_2O is about 0.015 pH units at salinity 35 (the difference is nearly proportional to salinity). The seawater scale was formerly referred to as the total scale, and each scale is still sometimes referred to as the other in the literature.

The fit of f_H used in this program is valid from salinities 20 through 40. f_H has been found to be electrode-dependent, and does NOT equal 1 at salinity 0 due to the liquid junction potential.

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Values on the NBS pH scale are only accurate to 0.005 (at best).

All work on pressure effects on pH has assumed that f_H is independent of pressure.

For discussions of the various pH scales see Dickson (1984, 1993), Millero et al. (1993), Butler (1992), or Culberson (1981). Attention is required because in some of these references the distinction between the total and the seawater pH scales was not made.

15. ON-SCREEN INFORMATION

An information section that may be accessed from several places in the program provides on-screen help for the following topics:

1. General information (Introduction)
2. pH Scales
3. fCO_2 and pCO_2
4. K_{SO_4} Choices
5. Batch-Input Mode
6. GEOSECS Choice
7. Peng Choice
8. Freshwater Choice
9. Pressure Effects
10. Calcium Carbonate Solubility (Omega values)
11. Alkalinity
12. Revelle Factor
13. Constants Used

16. ADDITIONAL INFORMATION

For questions, comments, or to report any problems, please contact:

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A very useful reference for all aspects of the CO_2 system in seawater is the *Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water* (DOE 1994). The web site for information on this reference is

http://www-mpl.ucsd.edu/people/adickson/CO2_QC/ .

A listing of the errata in this handbook is also available at this site.

A copy of the printed report may be obtained from the Carbon Dioxide Information Analysis Center at no charge while supplies last. Requests should be addressed to:

Address: Carbon Dioxide Information Analysis Center
Oak Ridge National Laboratory
Post Office Box 2008
Oak Ridge, Tennessee 37831-6335, U.S.A.

Telephone: 423-574-0390 or 423-574-3645 (Voice)
423-574-2232 (Fax)

Electronic Mail: Internet: cdiac@ornl.gov

Other particularly useful references are Park (1969), Skirrow (1975), Butler (1991), Millero and Sohn (1992), and Millero (1995) (see Appendix A for a listing of some of the errata in this paper).

Appendix A lists some typographical errors found in the references for this report as well as in other papers on this topic.

17. ACKNOWLEDGMENTS

18. REFERENCES

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Culkin, F. 1965. The major constituents of sea water. pp. 121–61. In J. P. Riley and G. Skirrow (eds.), *Chemical Oceanography*. Academic Press, New York.

Dickson, A. G. 1981. An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. *Deep-Sea Research* 28A:609–23.

Dickson, A. G. 1984. pH scales and proton-transfer reactions in saline media such as sea water. *Geochemica et Cosmochemica Acta* 48:2299–2308.

Dickson, A. G. 1990a. Standard potential of the reaction: $AgCl(s) + \frac{1}{2}H_2(g) = Ag(s) + HCl(aq)$, and the standard acidity constant of the ion HSO_4^- in synthetic seawater from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics* 22:113–27.

Dickson, A. G. 1990b. Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K. *Deep-Sea Research* 37:755–66.

Dickson, A. G. 1993. pH buffers for sea water media based on the total hydrogen concentration scale. *Deep-Sea Research* 40:107–18.

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Dickson, A. G., and J. P. Riley. 1978. The effect of analytical error on the evaluation of the components of the aquatic carbon-dioxide system. *Marine Chemistry* 6:77–85.

Dickson, A. G., and J. P. Riley. 1979. The estimation of acid dissociation constants in seawater media from potentiometric titrations with strong base. I. The ionic product of water—K_w. *Marine Chemistry* 7:89–99.

DOE (U.S. Department of Energy). 1994. *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water. Version 2.* ORNL/CDIAC-74. A. G. Dickson and C. Goyet (eds.), Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn.

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Hansson, I. 1973b. The determination of dissociation constants of carbonic acid in synthetic sea water in the salinity range of 20–40‰ and temperature range of 5–30°C. *Acta Chemica Scandanavia* 27:931–44.

Harned, H. S., and R. Davis, Jr. 1943. The ionization constant of carbonic acid in water and the solubility of carbon dioxide in water and aqueous salt solutions from 0 to 50°. *Journal of the American Chemical Society* 65:2030–37.

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Harned, H. S., and S. R. Scholes, Jr. 1941. The ionization constant of HCO_3^- from 0 to 50°. *Journal of the American Chemical Society* 43:1706–09.

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—. 1994. Erratum. *Marine Chemistry* 45:337.
—. 1996. Erratum. *Marine Chemistry* 52:183.

Sillen, L. G., A. E. Martell, and J. Bjerrum. 1964. Stability constants of metal-ion complexes, 2nd ed. Special Publication No. 17. Chemical Society (Great Britain), London. [Referenced in Takahashi et al. 1982 as Sillen and Martel (1964).]

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Weiss, R. F. 1974. Carbon dioxide in water and seawater: The solubility of a non-ideal gas. *Marine Chemistry* 2:203–15.

Weiss, R. F., and B. A. Price. 1980. Nitrous oxide solubility in water and seawater. *Marine Chemistry* 8:347–59.

APPENDIX A:

TYPOGRAPHICAL ERRORS
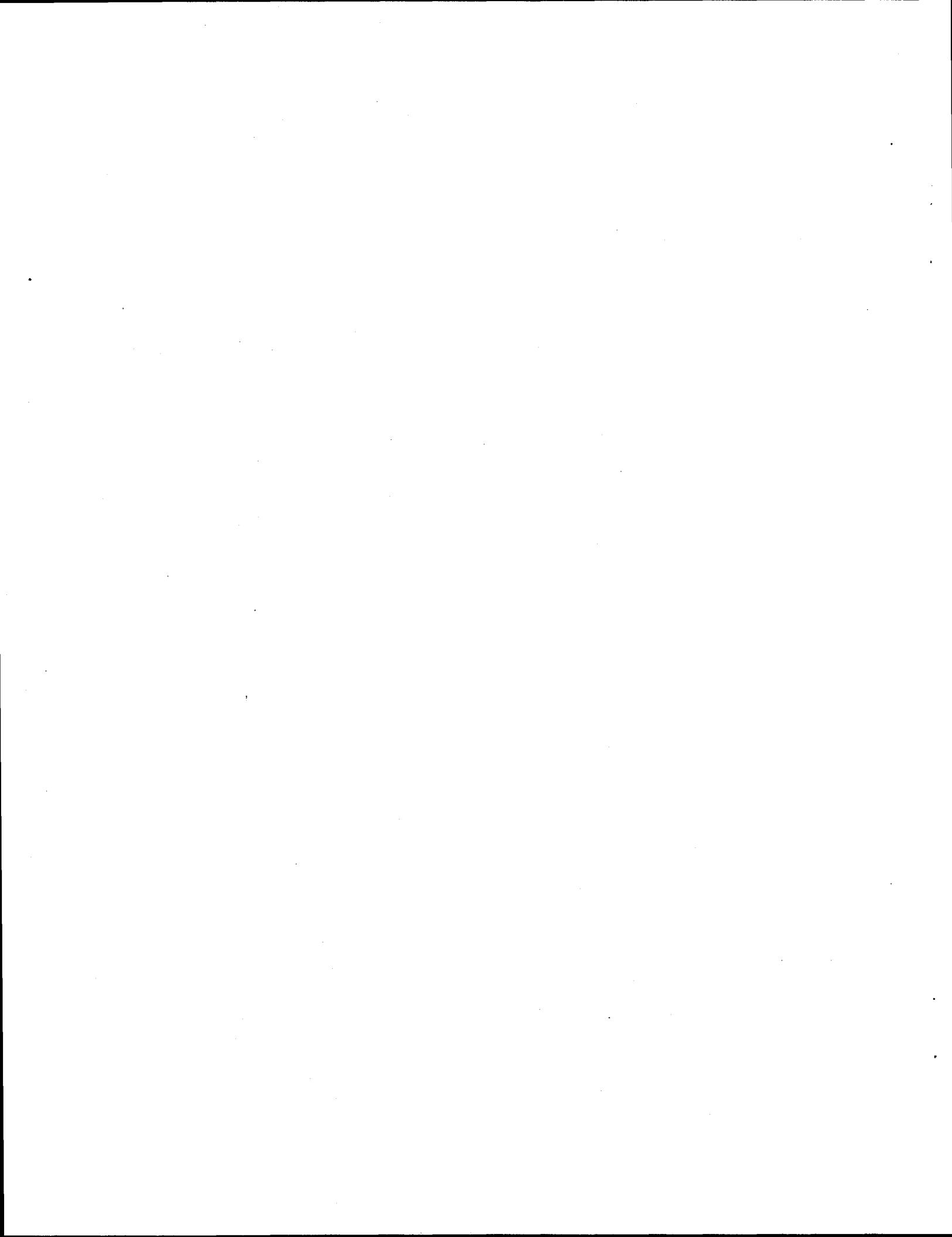
APPENDIX A: TYPOGRAPHICAL ERRORS

This Appendix lists errors that have been found in references for the program documentation as well as in other papers related to this topic; however, the listing is not meant to be comprehensive. Although many corrections are extremely minor, it is hoped that this compilation will save both time and effort for those who use it. Last revision version 1.08, 10-13-97.

Campbell, D. M., F. J. Millero, R. Roy, L. Roy, M. Lawson, K. M. Vogel, and C. Porter-Moore. 1993. The standard potential for the hydrogen-silver, silver chloride electrode in synthetic seawater. *Marine Chemistry* 44:221–33.

- On p. 230 in Eq. 37: The expression "$\ln K_{HSO_4}$" should be "$\log_{10} (K_{HSO_4})$."

Chen, H., R. Wanninkhof, R. A. Feely, and D. Greeley. 1995. Measurement of fugacity of carbon dioxide in seawater: an evaluation of a method based on infrared analysis. NOAA Technical Memorandum ERL AOML-85. Atlantic Oceanographic and Meteorological Laboratory, Miami.

- On p. 15: Table 2 states, "1. In our work (expressed in terms of the seawater hydrogen scale):...."; however, the formula for K_B given is on the total scale, and the formulae for K_{P2}, K_{P3}, and K_{Si} are on the NBS scale. It is unclear whether these formulae were converted.
- On pp. 15 and 16: The formulae for Total Borate (TB) are incorrect. They should read: "Total Borate (TB) = 0.00001188 * S" for cases 1 and 3, and "Total Borate (TB) = 0.00001173 * S" for case 2.
- On p. 24, two lines under Table 3: The expression "$dXCO_2/dT$" should be "$d(\ln XCO_2)/dT$."

Clayton, T. D., and R. H. Byrne. 1993. Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. *Deep-Sea Research* 40: 2115–29.

- On p. 2119 in Eq. 12b: The second "−47.986" should be "+114.723."

Clayton, T. D., R. H. Byrne, J. A. Breland, R. A. Feely, F. J. Millero, D. M. Campbell, P. P. Murphy, and M. F. Lamb. 1995. The role of pH measurements in modern oceanic CO_2-system characterization: Precision and thermodynamic consistency. *Deep-Sea Research II* 42:411–29.

- In Table 2 on p. 419: In the equation for pK_{1M}, the value "9.794" should be "9.7944."
- In Table 2 on p. 419: K_F as given is expressed in units mol/kg-H_2O.
- On p. 427: The reference for Johnson et al. (1992) should be "*Analytical Chemistry* 64:...."

Dickson, A. G. 1990a. Standard potential of the reaction: AgCl(s) + ½H_2(g) = Ag(s) + HCl(aq), and the standard acidity constant of the ion HSO_4^- in synthetic seawater from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics* 22:113–27.

- The title has two consecutive "ands."
- On p. 121 in Table 4: The term "e9" should be "e8."

Dickson, A. G. 1990b. Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K. *Deep-Sea Research* 37:755–66.

- On p. 756 after Table 1: The expression "$m_s = m_{35}*I_{35}/I_s$" should be "$m_s = m_{35}*I_s/I_{35}$."
- On p. 762 in Eq. 18: The term "α_2" should be "α_3."

Dickson, A. G., and F. J. Millero. 1987. A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Research* 34:1733–43.

- On p. 1738: The expression "2(A−1)" in the second equation should be "(2A−1)."
- Corrigenda. 1989. *Deep-Sea Research* 36:983.
  - This corrects a typographic error in p. 1739 in Table 4: In the equation for pK_2^* for Hansson, the value "$0.000116 *S^2$" should be "$0.000132 *S^2$."
  - Also, on p. 1740 in Table 5: The second equation should read "pK_2^*," not "pK_1^*."
  - Also, in the third equation in Table 5 (p. 1740): The term "0.00668 S" should be "0.0068 S."

Dickson, A. G., and J. P. Riley. 1979a. The estimation of acid dissociation constants in seawater media from potentiometric titrations with strong base. I. The ionic product of water—K_W. *Marine Chemistry* 7:89–99.

- On p. 97 in Equation 7: The value "0.9415" should be "0.09415."

Dickson, A. G., and J. P. Riley. 1979b. The estimation of acid dissociation constants in seawater media from potentiometric titrations with strong base. II. The dissociation of phosphoric acid. *Marine Chemistry* 7:101–109.

- (From A. Dickson, personal communication) In the equation for pK_{2P} in the abstract and in Table II on p. 109: The number "4.176" should be "4.196."
- On p. 109 in Table II: Units should be "mol/kg-soln," not "mol/kg-H_2O."

Goyet, C., and E. Peltzer. 1994. Comparison of the August-September 1991 and 1979 surface partial pressure of CO_2 distribution in the Equatorial Pacific Ocean near 150° W. *Marine Chemistry* 45:257–66.

- On p. 261: The term "0.098T" should be "0.0098T."
- Also, the reference given (UNESCO. 1987. Thermodynamics of the carbon dioxide system in seawater. UNESCO Technical Papers in Marine Science 51.) does not discuss this equation or the one above it.

Goyet, C., and A. Poisson. 1989. New determination of carbonic acid dissociation constants in seawater as a function of temperature and salinity. *Deep-Sea Research* 36:1635–54.

- In the Abstract and Tables 4 and 5: The symbol "T" represents both °C and K.

- On p. 1645 in Table 4: The fits which allow "extrapolation to S = 0" contain a constant term and thus do not match the "S = 0" values.

Hansson, I. 1973a. A new set of acidity constants for carbonic acid and boric acid in seawater. *Deep-Sea Research* 20:461–78.

- On p. 467, line 17: The phrase "four temperatures" should read "four salinities."
- On p. 470 in Table 3: The term "moles" should be "millimoles."

Lee, K., and F. J. Millero. 1995. Thermodynamic studies of the carbonate system in seawater. *Deep-Sea Research* 42:2035–61.

- On p. 2037 after Eq. 3: The value for the concentrations of SO_4 should be proportional to "S/35," not "35/S."
- On p. 2038 after Eq. 5: The concentrations of SO_4 and F should be proportional to "S/35," not "35/S."
- On p. 2056, two lines up: The statement "The calculated values of pK_2 (S = 35)..." should NOT have the expression "(S = 35)," as the fit has a salinity dependence.
- On p. 2058: The actual title for the reference of Clayton and Byrne is "Spectrophotometric seawater pH measurements: Total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results."
- On p. 2061 in the equation for $\ln K_B$: The expression "log $\{[H^+]_{SWS}/[H^+]_T\}$" should be "ln $\{[H^+]_{SWS}/[H^+]_T\}$."
- On p. 2061 in the equation for $\ln K_{HSO_4}$: The value "114.273" should be "114.723" and the expression "2968/T" should be "2698/T."
- On p. 2061: The values for the concentrations of SO_4, F, and B should be proportional to "S/35," not "35/S."

Mehrbach, C., C. H. Culberson, J. E. Hawley, and R. M. Pytkowicz. 1973. Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnology and Oceanography* 18:897–907.

- On p. 898 in Table 1: The "F_1" term in Eq. 5 is negative the "F_1" in Eq. 6.

Millero, F. 1979. The thermodynamics of the carbonate system in seawater. *Geochemica et Cosmochemica Acta* 43:1651–1661.

- On p. 1651, in Eq. 4: The expression "C/T" should be "C*T."

Millero, F. J. 1983. Influence of pressure on chemical processes in the sea. Chapter 43. In J. P. Riley and R. Chester (eds.), *Chemical Oceanography.* Academic Press, New York.

- On p. 51, for Table 43.29 to be correct:
  o in Eq. 94: The value "–26.69" should be "–25.59."
  o in Eq. 95: The term "0.1700t" should be "0.0800t."

Millero, F. J. 1995. Thermodynamics of the carbon dioxide system in the oceans. *Geochemica et Cosmochemica Acta* 59:661–77.

- On p. 664: Equation 32 uses Khoo's value of K_{HSO_4} (Khoo et al. 1977), but on p. 667 it is stated that Khoo's value is unreliable and should not be used. This is unclear.

- On p. 667: In the first full paragraph it is stated that the values of K_{HSO_4} were determined from Eq. 30 after Roy's constants were converted to the SWS pH scale. The value of K_{HSO_4} is needed to convert pH scales and cannot be found from Eq. 30.

- On p. 668: It is stated that the total pH scale should be used; however, in the next paragraph, Roy's constants are converted to the seawater scale, and this scale is used for most of the rest of the paper.

- On p. 669, in the title for Fig. 10: The equations are misnumbered. Equations 46 and 47 should be Eqs. 48 and 49, and Eqs. 48 and 49 should be Eqs. 50 and 51.

- On p. 669, Eq. 52: The constant K_B is on the total pH scale (this was not stated but can be determined from the reference).

- On p. 670, Eq. 63: The constant K_W is on the seawater pH scale (this wasn't stated but is consistent with programs of Millero).

- On p. 670: The given check value after Eq. 64 of "1.6 μmol/kg" should be "6.2 μmol/kg." There is no easy way to see how 1.6 was obtained.

- On p. 670, Eqs. 65, 66, and 67: These are on the seawater pH scale (this was not stated, but can be determined from the DOE Handbook).

- On p. 671, after Eq. 71: The check values "0.792" and "0.204" should be "0.852" and "0.140." If pH = 8.2 is used, or if K_{P3} is increased by a factor of 1.55, the given check values are close.

- On p. 671, Eq. 72: The constant K_{Si} is on the seawater pH scale (this was not stated but can be determined from the DOE Handbook).

- On p. 671, after Eq. 73: For the given values "I = 0.7" and "t = 25°C," the value of pK_{Si} is given as "9.47." (molality). However, when these two values are used, the actual resultant value of pK_{Si} is "9.365" (molality) which corresponds to "9.380" in mol/kg-soln. Two scenarios would explain the discrepancy: (1) either "t" is incorrect (plugging in the value t = 20°C would give the value of pK_{Si} as 9.47), or (2) the pH scale is incorrect (the value for pK_{Si} of 9.38 on the total pH scale = 9.47 on the seawater scale in the same concentration units).

- On p. 671, after Eq. 73: Using the values given for pK_{Si} of "9.47" and for pH of "7.5" yields "0.0106 $[Si]_T$," rather than "0.0127 $[Si]_T$."

- On p. 671, Eq. 74: The pH scale on which K_{1S} is given is not stated. From the original reference, it was determined in artificial seawater without F, so it must be on the total pH scale.

- On p. 671, after Eq. 75: The value for pK_{1S} at t = 25°C and S = 35, is incorrectly given as "6.98" and should be "6.51." The value "6.98" can be obtained, however, by plugging in t = 25°C and S = 0.

- On p. 671, after Eq. 75: The value of "0.768" is consistent with the value for pK_{1S} of "6.98" (which is incorrect). The correct value should be "0.9071."

- On p. 671, Eq. 76: The pH scale on which K_{NH_4} is given isn't stated. From the original reference it is on the seawater scale.

- On p. 671, after Eq. 77: The value for pK_{NH_4} of "9.19" is incorrect and should be "9.26." It is not clear how the incorrect value was obtained.

- On p. 671, after Eq. 77: The value "0.020" is consistent with "9.19" (which is incorrect). It should be "0.017."

- On p. 672, column 2: A parameter is defined as "X = TA/TCO$_2$." Note that Goyet et al. (1993) in a paper on a similar topic (Goyet, C., F. J. Millero, A. Poisson, and

D. Shafer. 1993. Temperature dependence of CO_2 fugacity in seawater. *Marine Chemistry* 44:205–219) define a parameter as "$X = TCO_2/TA$." This difference in definitions could cause confusion.

- On p. 673, Eq. 86: If fCO_2 at 20°C AND X are known, then fCO_2 at ANY temperature can be calculated exactly! The only way to know X is to know TA AND TCO_2, and either one of these and fCO_2 at 20°C is also sufficient to find fCO_2 at any temperature.
- On p. 675, after Eq. 90: The value and the units for R are incorrect. The true value is "$R = 83.145$ bar-cm^3/(mol-K)."
- On p. 675, column 1: The reference to Millero (1989) should probably be Millero (1983b).
- On p. 675, Eq. 92: There are no values of b_2 in Table 9. Probably they are equal to 0; this would be consistent with previous work.
- On p. 675: The left-hand side of Eq. 92 should be $(1000)*\Delta K$, or the last two columns in Table 9 should be $1000*b_1$ and $1000*b_2$ in order to be correct.
- On p. 675 in Table 9: The values of a_0, a_1, and a_2 for H_2O and H_2S are the FRESHWATER values given in Millero (1983).
- On p. 675 in Table 9: There are no a and b values for $Si(OH)_3$. Before the heading "Conclusions" on the same page it is stated that they are "estimated" from those of boric acid. It is unclear whether or not it is meant that they are assumed to be equal to those for boric acid.
- On p. 675 in Table 9: The value of a_1 for $B(OH)_3$ should be "+0.1622" to agree with Millero (1979).
- On p. 675 in Table 9: The values of a_1 for calcite and aragonite should be "+0.5304" to agree with Millero (1979).
- On p. 675 in Table 9: The value of $-a_0$ for aragonite should be "–46.0" (or "–45.96") to agree with Millero (1979).
- On p. 675 in Table 9: The value of b_1 for calcite should be "+0.3692" to agree with Millero (1979).
- On p. 677, in column 2: There is a problem with the reference "Millero, F. J. (1982). The thermodynamics of seawater at one atmosphere. *Ocean Sci. Eng.* 7: 403–60." It should probably read:
  - Millero, F. J. (1976). The thermodynamics of seawater at one atmosphere. *American Journal of Science* 276:1035–77.
  - Millero, F. J. (1982). Thermodynamics of seawater: the PVT properties. *Ocean Sci. Eng.* 7: 403–60.

Millero, F. J., T. Plese, and M. Fernandez. 1988. The dissociation of hydrogen sulfide in seawater. *Limnology and Oceanography* 33:269–74.

- On p. 271 just before Eq. 7: It is stated that the NBS and the total pH scales are related by "$a_H' = f_H * [H^+]_T$," but this does not include fluoride. The relation usually used is "$a_H' = f_H * [H^+]_{SWS}$," which does include fluoride. This means that the f_H used in this equation is the activity coefficient for seawater containing no fluoride.
- On p. 273: The fit for f_H combines data which were taken in seawater (artificial and actual) containing fluoride with values that were taken in artificial seawater without fluoride.

Millero, F. J., and M. L. Sohn. 1992. The carbonate system. pp. 267–319. In F. J. Millero and M. L. Sohn, *Chemical Oceanography*. CRC Press, Boca Raton, Fla.

- On p. 275: There is ambiguity and inconsistency in the definitions and distinctions between the total and the seawater pH scales.
- On p. 276: Equation 31 should read "A = −1226.966...."
- On p. 276: Equation 36 is incorrect in several places: the denominator in the first expression should be squared, and the terms CH and COH should not be in the numerator but rather by themselves. This expression also makes the approximation that $K_1^* \gg K_2^*$.
- On p. 279: The right-hand side of Eq. 52 should read:
  "pK_1 + (−840.39/T + 19.894 −3.0189 ln T) * $S^{\frac{1}{2}}$ + 0.0068 S."
- On p. 280: The last term in Eq. 56 should be "0.0217 S," not "1.0217 S."
- On p. 281: The last term in Eq. 65 should be "0.01767 S," not "1.01767 S."
- On p. 281: The second equals sign in Eq. 72 should be a minus sign.
- On p. 282 in Eq. 79: The term "63.9806" should be "63.806."
- On p. 286: Equation 96 has brackets and parentheses missing in several places.

- Fits for the constants are from the following sources:
  - p. 273: The fit for K_W is from Millero (1979) from data of Hansson (1973 a,b).
  - p. 273: The equations for ΔV and ΔK for K_W are from Millero (1983).
  - p. 276: The fit for β_{HSO_4} is from Millero (1986).
  - pp. 279 and 280: The equations for K_1 and K_2 are from Dickson and Millero (1987) from the combined data of Hansson (1973 a,b) and Mehrbach et al. (1973).
  - p. 280: The equations for ΔV and ΔK for the constants K_1 and K_2 are from Millero (1979).
  - p. 281: The fit for K_B is from Millero (1979) from data of Hansson (1973a,b).
  - p. 281: The equations for ΔV and ΔK for K_B are from Millero (1979).
  - p. 281: The fits for K_{sp} for calcite and aragonite are from Millero (1979).
  - pp. 281 and 282: The equations for ΔV and ΔK for calcite are from Ingle (1975).
  - p. 282: The equations for ΔV and ΔK for aragonite are from Millero (1979).
  - p. 282: The pH variation with T and P is from Millero (1979).

- These are the source references:
  - Millero, F. J. 1979. *Geochemica et Cosmochemica Acta* 43:1651–61.
  - Dickson, A. G., and F. J. Millero. 1987. *Deep-Sea Research* 34:1733–43; see also Dickson, A. G., and F. J. Millero. 1989. *Deep-Sea Research* 36:983.
  - Millero, F. J. 1983. Influence of pressure on chemical processes in the sea. Chapter 43. In J. P. Riley and R. Chester (eds.), *Chemical Oceanography*. Academic Press, New York.
  - Millero, F. J. 1986. *Limnology and Oceanography* 31:839–47.
  - Ingle, S. E. 1975. *Marine Chemistry* 3:301–19.

Millero, F. J., J. Z. Zhang, S. Fiol, S. Sotolongo, R. N. Roy, K. Lee, and S. Mane. 1993. The use of buffers to measure the pH of seawater. *Marine Chemistry* 44:143–52.

- On p. 149, Eq. 23, and on p. 150, Eqs. 25 and 27: The multiplication sign (×) should be a division sign (/).

Millero, F. J., J. Z. Zhang, K. Lee, and D. M. Campbell. 1993. Titration alkalinity of seawater. *Marine Chemistry* 44:153–66.

- On p. 156, column 2, about 10 lines down: The expression "14±1 mM" should be "14 ± 1 μM."

Peng, T. H., T. Takahashi, W. S. Broecker, and J. Olafsson. 1987. Seasonal variability of carbon dioxide, nutrients and oxygen in the North Atlantic surface water: Observations and a model. *Tellus* 39B:439–58.

- On p. 455: The fit of f_H is NOT the same as the one in GEOSECS, as claimed, but rather is rounded off. It is about 1% higher (this results in a change of 0.004 in pH).
- On p. 456: The given check value for f_H does not match the fit given in that paper or the GEOSECS fit.
- NOTE: On p. 455, Eq. A3: This definition of TA is different from that of Dickson; it is higher by an amount equal to the total phosphate.

Roy, R. N., L. N. Roy, K. M. Vogel, C. Porter-Moore, T. Pearson, C. E. Good, F. J. Millero, and D. M. Campbell. 1993. The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45°C. *Marine Chemistry* 44:249–67.

- On p. 254 in the label for Fig. 2: The expression "$3m(CO_3^{2-})$" should be "$2m(CO_3^{2-})$."
- On pp. 254 and 258: The authors claim 2S precisions of "0.004" in pK_1 and "0.006" in pK_2. From Andrew Dickson (personal communication, 1997), these should be "0.008" in pK_1 and "0.006" in pK_2.
- On p. 257: The authors use Khoo's value for K_{SO_4}, not Dickson's, but reference Dickson earlier (p. 252).
- Erratum. 1994. *Marine Chemistry* 45:337. This replaces Tables 3 and 4.
- Erratum. 1996. *Marine Chemistry* 52:183. This fixes a typographic error in the Abstract on p. 249: In the equation for ln K_1^*: The last term should have S raised to the power 1.5. It also fixes a typographic error in Eq. 34 on p. 256: The value "310.48919" should be "2310.48919."

Takahashi, T., R. T. Williams, and D. L. Bos. 1982. Carbonate chemistry. pp. 77–83. In W. S. Broecker, D. W. Spencer, and H. Craig, *GEOSECS Pacific Expedition, Volume 3, Hydrographic Data 1973–1974*. National Science Foundation, Washington, D.C.

- On p. 79 in No. 5 in list of constants: In the equation for $K_2'(P)$, the value "26.4" should be "16.4."
- On p. 79: The reference in No. 6. in the list of constants should actually be Ingle, S. E. 1975. *Marine Chemistry* 3:301–19. Reference [21] is not correct.
- On p. 79 in the equation for K_{sp}'(aragonite): The value "1.45" should be "1.48" [this is what Berner uses on p. 722 of Berner (1976)].
- On p. 79 in No. 8 in the list of constants: Reference [20] is not correct; that Culberson reference is only indirectly related to the topic under discussion.
- On p. 79 in the equation for K_{sp}'(calcite,P): The plus sign should be an equals sign.

- On p. 80 in the equation for ln K_w': The expression "C/lnT" should be "C*lnT."
- On p. 81 in Table 1: The value "17.8" for Pacific Surface Water should be "7.8."

UNESCO. 1987. Thermodynamics of the carbon dioxide system in seawater. UNESCO Technical Papers in Marine Science 51.

- On p. 50: The term ".00116" in the equation for pK_2^* should be "0.000132."

Weiss, R. F., and B. A. Price. 1980. Nitrous oxide solubility in water and seawater. *Marine Chemistry* 8:347–59.

—. Errata. 1980. *Marine Chemistry* 9:221.

- On p. 355, Table III, row 5, column 2: The value "4.245" should be "5.245."
- On p. 355: Line 3 below Table III should read: "...1.1% and 1.5%, respectively, below our results."

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