CO2SYS (ver.2.3.xls)

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.

The program **CO2SYS** performs calculations relating parameters of the carbon dioxide (CO2) system in seawater and freshwater. The program uses two of the four measurable parameters of the CO2 system [total alkalinity (TA), total inorganic CO2 (TCO2), pH, and either fugacity (fCO2) or partial pressure of CO2 (pCO2)] 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.

CO2 System in Seawater

The CO2 system in seawater is characterized by four measurable parameters: TA, TCO2 (i.e., the sum of the dissolved CO2, the carbonate, and the bicarbonate), pH, and either fCO2 or pCO2. pCO2 is the partial pressure of CO2 in wet (100% water-saturated) air which is in equilibrium with the sample. Both fCO2 and pCO2 are proportional to the dissolved CO2. The fugacity is about 0.3% to 0.4% lower than the partial pressure over the range of interest, due to the nonideality of CO2. TA and TCO2 are independent of temperature and pressure; fCO2, pCO2, 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 K1 and K2 (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.

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 K1 and K2, two distinct formulations for KSO4 (Dickson 1990a; Khoo et al. 1977), the choice of four pH scales (free, total, seawater, or NBS), and the use of either fCO2 or pCO2.
Any two CO2 system parameters (TA, TCO2, fCO2 or pCO2, 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 CO2. 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 CO2 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, TCO2, etc.; micro-atmospheres (µatm) for pCO2 and fCO2; and parts per million (ppm) for the mole ratio of CO2 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 program, 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-H2O (molal) for the NBS scale (by definition).

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 CO2 system parameters at the input conditions.
The input temperature and pressure, at which the values of the two known CO2 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 CO2 system parameters at the input conditions. TA and TCO2, which do not vary with temperature and pressure, are used to calculate the pH and fCO2 or pCO2 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;
• fCO2 and pCO2 in wet (100% saturated) air;
• xCO2 (the mole fraction of CO2 in dry air assuming 1 atm total pressure);
• Omega (the degree of saturation) for calcite and for aragonite;
• the Revelle factor (homogeneous buffer factor);
• pH values on all four pH scales (total, seawater, free, and NBS); and
• the values of pK1, pK2, pKW, and pKB on the chosen pH scale.
The user may scroll forward or backwards 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 K0 and the 2S (two standard deviation) precision of the constants K1 and K2 to allow an estimate to be made of the uncertainty of the final answer due to the uncertainty in the equilibrium constants.

Choices for Constants in this Program
A large number of values are needed in the calculations. These include the following:

- the various dissociation constants:
  - K1 and K2 for carbonic acid,
  - KB for boric acid,
  - KW for water,
  - KSO4 for the bisulfate ion,
  - KF for hydrogen fluoride,
  - KP1, KP2, and KP3 for phosphoric acid, and
  - KSi for silicic acid;
- Ksp(calcite) and Ksp(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;
- K0, the solubility of CO2 in seawater;
- the vapor pressure of water above seawater;
- the virial coefficients of CO2 and CO2-air; and

*f*H, the activity coefficient of the hydrogen ion.

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 = [HCO3] + 2[CO3] + [B(OH)4] + [OH] + [HPO4] + 2[PO4] + [SiO(OH)3] + [HS] + 2[S] + [NH3] - [H] - [HSO4] - [HF] - [H3PO4],

except that the contributions of HS, S, and NH3 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 = [PO43-] + [HPO42-] + [H2PO4-] + [H3PO4].

Though this seems small, it can have a large effect on the calculated fCO2. For instance, when fCO2 (or pCO2) is calculated from TA and TCO2, a modest phosphate concentration, such as 3 µmol/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 = [HCO3] + 2[CO3] + [H2BO3] ,

and for the Freshwater Choice is:

TA = [HCO3] + 2[CO3] + [OH] - [H] .

In this program values of alkalinities are given in micro-moles per kilogram of seawater (µmol/kg-SW).

fCO2 and pCO2

The fugacity of CO2 (fCO2) in water is defined to be the fugacity of CO2 in air which is in equilibrium with the water. The partial pressure of CO2 in wet (100% water-saturated) air (pCO2) is defined to be the product of the mole fraction of CO2 in wet air and the total pressure. This is the same as the product of the mole fraction of CO2 in dry air [xCO2(dry)] and (ptot - pH2O), where pH2O is the vapor pressure of water above seawater. At pressures of the order of 1 atm, fCO2 in air is about 0.3% lower than the pCO2 due to the nonideality of CO2 (see Weiss 1974). This program assumes a pressure near 1 atm (where most equilibrators function) for the conversion between partial pressure and fugacity.

fCO2 is related to TCO2 and pH by the following equation:

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          [CO2*]       TCO2              H*H
    fCO2 = ------   =   ----    *    ------------------
           K0           K0          H*H + K1*H + K1*K2
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where [CO2*] is the concentration of dissolved CO2, K0 is the solubility coefficient of CO2 in seawater, and K1 and K2 are the first and second dissociation constants for carbonic acid in seawater.

Units for fCO2 and pCO2 in this program are µatm. The value of xCO2(dry) given in this program assumes ptot = 1 atm. GEOSECS (Takahashi et al. 1982) and Peng et al. (1987) did not distinguish between fCO2 and pCO2 nor did some other programs that we have evaluated.

Calcium Solubility
The solubility product (Ksp) 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 = [CO32-]*[Ca2+] / Ksp .
Thus, values of Omega < 1 represent conditions of undersaturation, and values of Omega > 1 represent conditions of oversaturation.
The concentration of calcium, [Ca2+], is assumed to be proportional to the salinity, and the carbonate concentration, [CO32-], is calculated from TCO2, pH, and the values of K1 and K2 for carbonic acid. For Constant Choices 1 to 5, the calcium concentration used is from Riley and Tongudai (1967). The values of Ksp for calcite and aragonite are from Mucci (1983). The pressure correction for Ksp for calcite is from Ingle (1975) and that for aragonite is from Millero (1979).

pH Scales
The various pH scales are inter-related by the following equations:
aH = 10(-pHNBS) = fH * Hsws , and
Hfree = Htot / (1 + TS/KSO4) = Hsws / (1 + TS/KSO4 + TF/KF) ,
where
aH is the activity and fH is the activity coefficient of the H+ ion (this includes liquid junction effects),
TS and TF are the concentrations of SO42- and fluoride, and
KSO4 and KF are the dissociation constants of HSO4- 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 (about)
• 0.09 units lower than those on the free scale
• 0.01 units higher than those on the seawater scale
• 0.13 units lower than those on the NBS scale
The concentration units for aH on the NBS scale are mol/kg-H2O. 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-H2O). The difference between mol/kg-SW and mol/kg-H2O 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.