CO2SYS originally by Lewis and Wallace 1998

- Converted to MATLAB by Denis Pierrot at CIMAS, University of Miami, Miami, Florida (van Heuven et al., 2011)
- Vectorization, internal refinements and speed improvements by Steven van Heuven, University of Groningen, The Netherlands. Questions, bug reports et cetera: svheuven@gmail.com (van Heuven et al., 2011)
- Modifications for error propagation by JM Epitalon (Orr et al., 2018)
- Extension to include input of CO2, HCO3, CO3, NH4, and H2S by Jonathan Sharp, University of South Florida (Sharp et al., 2023)
- Modification to set pH values that do not converge to NaN, separate KHSO4 and TB, and to add the KHF of Perez & Fraga by Denis Pierrot, implemented in this version by Jonathan Sharp, University of Washington (Sharp et al., 2023)
- Bug fixes by Matthew Humphreys, NIOZ Texel, the Netherlands (Humphreys et al., 2022)
- Additional modifications for consistency with PyCO2SYS and other added options and input/output arguments by Jonathan Sharp, University of Washington (Sharp et al., 2023)

Notes at the top of CO2SYSv3

**** Changes since 3.1 by JD Sharp.
- rigorous validation performed against PyCO2SYS (https://github.com/mvdh7/PyCO2SYS)
- initial pH estimates obtained via the approach of Munhoven (2013)
- correction to solution for free scale pH within iterative pH solvers
- correction to uncertainty calculation for parameters at output conditions
- consistency implemented for [CO2(aq)] calculations
- substrate-inhibitor ratio (SIR; Bach, 2015) included as an output argument
- input uncertainty in [CO2], [HCO3], and [CO3] should now be in mol/kg
- option added for pressure corrections to K0 and fugacity factor

**** Changes since 3.0 by JD Sharp.
- added KSO4 of Waters and Millero (2013)
- added K1 and K2 of Sulpis et al. (2020)
- added K1 and K2 of Schockman and Byrne (2021)

**** Changes since 3.0 by JD Sharp based on code from D Pierrot.
- changed code to set pH values that don't converge to NaN. All

subsequent calculated values also set to NaN.
- modified input function to separate KHSO4 and TB choices
- added KHF of Perez & Fraga as choice for HF dissociation constant
- modified output to reflect all changes mentioned above

**** Changes since 3.0 by MP Humphreys.
- include Peng correction for Icase 16 and 17.
- fix Icase typo for CO2-HCO3 input pair.
- make corrections to (F) indexing in a few places.

**** Changes since 2.1 (uploaded to GitHub Jul 2019) by JD Sharp
- now allows for input of NH4+ and H2S concentrations

**** Additional changes since 2.0 by JD Sharp
- now allows for HCO3, CO3, and CO2 as input parameters for calculation and for error propagation

**** Changes since 2.0
- slight changes to allow error propagation
- new option to choose K1 & K2 from Waters et al. (2014): fixes inconsistencies with Millero (2010) identified by Orr et al. (2015)

**** Changes since 1.01 (uploaded to CDIAC at June 11th, 2009):
- Function cleans up its global variables when done (if you lose variables, this may be the cause -- see around line 570)
- Added the outputting of K values
- Implementation of constants of Cai and Wang, 1998
- Implementation of constants of Lueker et al., 2000
- Implementation of constants of Mojica-Prieto and Millero, 2002
- Implementation of constants of Millero et al., 2002 (only their eqs. 19, 20, no TCO2 dependency)
- Implementation of constants of Millero et al., 2006
- Implementation of constants of Millero et al., 2010
- Properly listed Sal and Temp limits for the available constants
- added switch for using the new Lee et al., (2010) formulation of Total Borate
- Minor corrections to the GEOSECS constants (gave NaN for some output in earlier version)
- Fixed decimal point error on [H+] (did not get converted to umol/kgSW from mol/kgSW).
- Changed 'Hfreein' to 'Hfreeout' in the 'NICEHEADERS'-output (typo)

**** Changes since 1.00 (uploaded to CDIAC at May 29th, 2009):
- added a note explaining that all known bugs were removed before release of 1.00

References in the code: (see 'Works Cited.pdf' for full APA style citations)

- K1K2 formulations
  - 1 = Roy et al 1993
    - Roy et al, Marine Chemistry, 44:249-267, 1993
    - See also: Erratum, Marine Chemistry 45:337, 1994 and Erratum, Marine Chemistry 52:183, 1996
    - Typo: In the abstract on p. 249, in the eq. for lnK1* the last term should have S raised to the power 1.5
    - lnK1 = eq. 29 on p. 254 and what they use in their abstract
    - lnK2 = eq. 30 on p. 254 and what they use in their abstract
  - 2 = Goyet and Poisson, 1989
    - Goyet and Poisson, Deep-Sea Research, 36(11):1635-1654, 1989
    - pK1 = in Table 5 on p. 1652 and what they use in the abstract
    - pK2 = in Table 5 on p. 1652 and what they use in the abstract
  - 3 = Hansson refit by Dickson and Millero
    - Hansson (1973) refit by Dickson and Millero 1987 (DM)
    - Dickson and Millero, Deep-Sea Research, 34(10):1733-1743, 1987
      - See also Corrigenda, Deep-Sea Research 36:983, 1989
    - Refit data of Hansson, Deep-Sea Research, 20:461-478, 1973 and Hansson, Acta Chemica Scandanavia, 27:931-944, 1973
    - Typo in DM on p. 1739 in Table 4: the equation for pK2* for Hansson should have a 0.000132 *S^2 instead of a 0.000116 *S^2
  - 4 = Mehrbach refit by Dickson and Millero
    - Mehrbach (1973) refit by Dickson and Millero (1987)
    - Dickson and Millero, Deep-Sea Research, 34(10):1733-1743, 1987
      - See also Corrigenda, Deep-Sea Research , 36:983, 1989
    - Refit data of Mehrbach et al., Limn Oc, 18(6):897-907, 1973
  - 5 = Hansson and Mehrbach refit by Dickson and Millero
    - Hansson (1973) and Mehrbach (1973) refit by Dickson and Millero (1987)
    - Typo in DM on p. 1740 in Table 5: the second equation should be pK2* = not pK1* =
  - 6 = GEOSECS (i.e., original Mehrbach) (Takahashi et al., 1982)

        - GEOSECS and Peng et al use K1, K2 from Mehrbach et al., Limnology and Oceanography, 18(6):897-907, 1973
            - i.e. these are the original Mehrbach dissociation constants
    - 7 = Peng (i.e., Mehrbach modified)
        - GEOSECS and Peng et al 1987 use K1, K2 from Mehrbach et al., Limnology and Oceanography, 18(6):897-907, 1973
            - i.e. these are the original Mehrbach dissociation constants
    - 8 = Millero 1979 (pure water)
        - Millero, F. J., Geochimica et Cosmochemica Acta 43:1651-1661, 1979
        - K1 from refit data from Harned and Davis, J American Chemical Society, 65:2030,2037, 1943
        - K2 from refit data from Harned and Scholes, J American Chemical Society, 43:1706-1709, 1941
    - 9 = Cai and Wang 1998
        - Cai and Wang, 1998, for estuarine use
        - Data used in this work is from:
            - K1: Mehrbach (1973) for S>15, for S<15 Mook and Keone (1975)
            - K2: Mehrbach (1973) for S>20, for S<20: Edmond and Gieskes (1970)
    - 10 = Lueker et al 2000
        - Lueker, Dickson, and Keeling, Mar. Chem. 70:105-119, 2000
        - This is Mehrbach's data refit after conversion to the total scale, for comparison with their equilibrator work
    - 11 = Mojica Prieto and Millero, 2002
        - Mojica Prieto and Millero 2002. Geochim. Et Cosmochim. Acta. 66(14):2529-2540
    - 12 = Millero et al 2002
        - Millero et al., 2002. Deep-Sea Res. I(49):1705-1723
        - Calculated from overdetermined WOCE-era field measurements
    - 13 = Millero et al 2006
        - Millero, Grahan, Huand, Bustos-Serrano, Pierrot. Mar. Chem. 100:80-94, 2006
        - From Millero 2006 work on pK1 and pK2 from titrations in Gulf Stream seawater
    - 14 = Millero 2010
        - Millero, 2010 for estuarine use

        - Marine and Freshwater Research, v.61 p.139-142
        - Fits through compilation of real seawater titration results: Mehrbach et al. (1973), Mojica-Prieto & Millero (2002), Millero et al. (2006)
    - 15 = Waters, Millero and Woosley 2014
        - Waters, Millero, and Woosley. Mar. Chem., 165, 66-67, 2014
        - Corrigendum to "The free proton concentration scale for seawater pH"
        - Effectively, this is an update of Millero (2010) formulation
    - 16 = Sulpis et al 2020
        - Sulpis, Lauvset, Hagens. Ocean Science, 16:847-862, 2020
        - This study uses overdeterminations of the carbonate system to iteratively fir K1 and K2
    - 17 = Schockman and Byrne 2021
        - Schockman and Byrne. Geochimica et Cosmochimica Acta, 300:231-245, 2021
        - This study uses spectrophotometric pH measurements to determine K1*K2 and presents a new parameterization for K2 based on these determinations
        - K1 is taken from Waters, Millero, Woosley, 2014
- KSO4 formulations
    - 1 = Dickson 1990a
        - Dickson, A. G., J. Chemical Thermodynamics, 22:113-127, 1990
        - TYPO on p.121: the constant e9 should be e8, this is from eqs 22 and 23 on p. 123, and Table 4 p. 121
    - 2 = Khoo et al., 1977
        - Khoo et al, Analytical Chemistry, 49(1):29-34, 1977
        - They find log(beta) = CO2SYS's pKS
        - Eq 20 on p. 33
    - 3 = Waters and Millero, 2013
        - Waters and Millero, Marine Chemistry, 149:8-22, 2013 with corrections from Waters et al, Marine Chemistry 165:66-67, 2014 (addendum)
- KF formulations
    - 1 = Dickson and Riley 1979
        - Dickson, A. G. and Riley, J. P., Marine Chemistry 7:89-99, 1979
    - 2 = Perez and Frage 1987
        - Perez and Frage 1987
- TB formulations
    - 1 = Uppstrom, 1979

        - Uppstrom, L. Deep-Sea Research 21:161-162, 1974
    - 2 = Lee et al 2010
        - Lee, Kim, Byrne, Millero, Feely, Yong-Ming Liu, 2010. Geochimica et Cosmochimica Acta 74 (6): 1801-1811
    - For GEOSECS cases:
        - Culkin, F., in Chemical Oceanography, ed. Riley and Skirrow, 1965
        - This is 1% lower than Uppstrom's value
- Gas Constant = 83.14462618 ml bar-1 K-1 mol-1
    - Recommended by NIST
    - https://physics.nist.gov/cgi-bin/cuu/Value?r
- Calculate TCa (Total Calcium)
    - Riley, J. P. and Tongudui, M., Chemical Geology 2:263-269, 1967
    - For GEOSECS cases (6 & 7):
        - Culkin, F. in Chemical Oceanography, ed. Riley and Skirrow, 1965
        - Quoted in Takahashi et al, GEOSECS Pacific Expedition v. 3, 1982
- Calculate TF (Total Fluoride)
    - Riley, J. P., Deep-Sea Research 12:219-220, 1965
- Calculate TS (Total Sulfide)
    - Morris, A. W., and Riley, J. P., Deep-Sea Research 13:699-705, 1966
- Calculate K0
    - Weiss, R. F., Marine Chemistry 2:203-215, 1974
    - Partial molal volume of CO2 (cm^3/mol) = 32.3, from Weiss 1974 Appendix, paragraph 3
- Calculate IonS
    - From the DOE handbook, Chapter 5, p. 13/22, eq. 7.2.4, 1994
- Calculate fH
    - Takahashi et al, Chapter 3 in GEOSECS Pacific Expedition, v. 3, 1982 (p. 80)
    - GEOSECS case (7):
        - Peng et al, Tellus 39B:439-458, 1987
        - They reference the GEOSECS report, but round the value given there off so that it is about 0.08 (1%) lower. It doesn't agree with the check value they give on p. 456.
- Calculate KB
    - Dickson, A. G., Deep-Sea Research 37:755-766, 1990 (aka Dickson 1990b)
    - GEOSECS cases (6 & 7):
        - Lyman, John, UCLA Thesis, 1957
        - Fit by Li et al, JGR 74:5507-5525, 1969
        - This is for GEOSECS and Peng et al.

- Calculate KW
  - Millero, Geochimica et Cosmochemica Acta 59:661-677, 1995
    - His check value of 1.6 umol/kg-SW should be 6.2
  - GEOSECS cases (6 & 7):
    - Millero, Geochemica et Comochemica Acta 43:1651-1661, 1979
  - Freshwater case (8):
    - Millero, Geochimica et Cosmochemica Acta 43: 1651-1661, 1979
- Calculate KP1, KP2, KP3 and KSi
  - Yao and Millero, Aquatic Geochemistry 1:53-88, 1995
    - KP1, KP2, KP3 are on the SWS pH scale in mol/kg-sw
    - KSi was given on the SWS scale in molal units
  - GEOSECS case (7):
    - KP1 = 0.02; Peng et al don't include the contribution from this term, but it is so small it doesn't contribute. It needs to be kept to that the routinces work ok.
    - KP2, KP3 from Kester, D. R., and Pytkowicz, R. M., Limnology and Oceanography 12:243-252, 1967
- Calculate KNH
  - Ammonia dissociation constant from Clegg and Whitfield (1995)
- Calculate KNH4
  - First hydrogen sulfide dissociation constant from Millero et a. (1988)
- Correct K1 K2 for pressure
  - From Millero, 1995. They are the same as Millero 1979 and Millero, 1992. They are from data of Culberson and Pytkowicz, 1968.
  - Millero, F. J., Geochemica et Cosmochemica Acta 59: 661-677, 1995.
    - Typo: a factor of 10^3 was left out of the definition of Kappa
    - Typo: the value of R given is incorrect with the wrong units
    - Typo: the values of the a's for H2S and H20 are from the 1983 values for fresh water
    - Typo: the value of a1 for B(OH)3 should be +0.1622
    - Table 9 on p. 675 has no values for Si.
    - There are a variety of other typos in Table 9 on p. 675
    - There are other typos in the paper, and most of the check values given don't check.
  - Millero, F. J., Geochemica et Cosmochemica Acta 43:1651-1661, 1979.
    - See Table 5 and eqs. 7, 7a, 7b on pp. 1656-1657
  - Millero, F. J., Sohn, Mary l., Chemical Oceanography, CRC Press, 1992. See Chapter 6.

        - Typo: this chapter has numerous typos (eqs. 36, 52, 56, 65, 72, 79, and 96 have typos).
    - Culberson, C. H., and Pytkowicz, R. M., Limnology and Oceanography 13:403-417, 1968
    - GEOSECS cases (6 & 7):
        - Takahashi et al., GEOSECS Pacific Expedition v.3, 1982 quotes Culberson and Pytkowicz, 1968, but the fits are the same as those in Edmond and Gieskes, GCA, 34:1261-1291, 1970 who in turn quote Li, personal communication
        - Edmond, John M. and Gieskes, J. M. T. M., Geochemica et Cosmochemica Acta, 34:1261-1291, 1970
- Correct KW for pressure
    - Millero, Chapter 43 in Chemical Oceanography, Academic Press, 1983.
    - Note the temperature dependence of KappaK1 and KappaKW for fresh water in Millero, 1983 are the same
    - GEOSECS case (6 & 7):
        - GEOSECS doesn't include OH term, so this doesn't matter. Peng et al didn't include pressure, but here we assume that the KW correction is the same as for the other seawater cases.
        - from Millero, 1983 and his programs CO2ROY(T).BAS
- Correct KF and KS for pressure
    - From Millero, 1995, which is the same as Millero, 1983
- Correct KP1, KP2, KP3, KSi for pressure
    - From Millero, 1995, which are the same as Millero, 1983
    - The only mention of this is Millero, 1995 where it is stated that the values have been estimated from the values of boric acid. However, there is no listing of the values in the table
    - Use the values for KB from above.
- Fugacity constants
    - In previous versions of CO2SYS, the fugacity factor was calculated assuming pressure at one atmosphere, or close to it. Starting with v3.2.1, an option to use in situ pressure is provided
    - Weiss, R. F., Marine Chemistry 2:203-315, 1974
        - They fit the data of Goff and Gratch (1946) with the vapor pressure lowering by sea salt as given by Robinson (1954)
        - This fits the more complicated Goff and Gratch, and Robinson equations from 273 to 313 deg K and 0 to 40 Sali with a standard error of 0.015%, about 5 uatm over this range

        - Goff, J. A., and Gratch, S., Trans. Am. Soc. Heating and Ventilating Engineers 52:95-122, 1946
        - Robinson, J. Marine Bio Assoc. of the U.K. 33:449-455, 1954
            - Eq. 10 on p. 350, this is in atmospheres
    - GEOSECS and Peng (6 & 7) assume pCO2 = fCO2, or FugFac = 1 (called 'p2f' in QUODcarb)