Package 'EqSolvR'

July 25, 2018

Title Chemical Equilibrium Solver

Version 1.2.5

Date 2018-07-13

Description Package for solving chemical equilibria for a given set of reactants and products. The motivation for this program was to enable the calculation of pH and speciation given a simple mix of salts. Normally temperatures range between 300°C and 400°C at 0.5 kb. This package has been writting in such a manner that an advanced user can easily set their own reactants, products and temperature in the generic version (chemsolve_generic). chemsolve_generic is the workhorse for chemsolve. Equations are solved numerically using the multiroot function from rootSolve package.

Depends R (>= 2.12)

Imports rootSolve

BugReports https://github.com/shearwavesplitter/EqSolvR/issues

License GPL (>= 3)

Encoding UTF-8

LazyData true

RoxygenNote 6.0.1.9000

R topics documented:

chemsolve *Mass balance and charge solver*

Description

Mass balance and charge balance solver for chemical equilibria at 0.5 kb. This is a wrapper function for chemsolve_generic and prods.

Usage

```
chemsolve(Tc = 400, Nat = 0.4, Kt = 0.2, Clt = 0.6, SO4t = 0.2,
  Cat = 0.1, Mgt = 0.1, start = c(1e-06, 1e-05, 0.3, 0.1, 0.3, 0.01,
  0.001, 0.02), maxitr = 100, exprod = NULL, exconstit = NULL,
  exnumz = NULL, excharges = NULL, exa = NULL, exK = NULL, bal = "Cl")
```

Arguments

Tc	Temperature (degrees C - between 300 and 400)
Nat	Sodium concentration (mol/kg); total
Kt	Potassium (mol/kg); total
Clt	Chloride (mol/kg); total
SO4t	Sulphate (mol/kg); total
Cat	Calcium (mol/kg); total
Mgt	Magnesium (mol/kg); total
start	Initial guess for the calculated equilbrium concentrations of the basis species (in the order of H+, OH-, Na+, K+, Cl-, SO42+, Ca2+, Mg2+).
maxitr	Maximum number of iterations
exprod	A vector of the names of the additional complex(es)
exconstit	A vector of the chemical symbol names of the the basis species that are constitute each of the the additional complexes
exnumz	A vector of the stiochiometry given by the equilibrium reaction for each of the additional complexes
excharges	A vector of the charge of the additional complex species
exa	A vector of the ion size parameters for the complexes of the additional complex species
exK	A vector of the log K of the dissociation constants of the additional complex species
bal	Species to balance against (Defaults to Cl, can also be set to NULL for none)

Details

A wrapper for the chemsolve_generic function that allow easy addition of product species. Use the generic function (chemsolve_generic) if new basis species need to be added or if the log K/temperature range is extended (up or down).
Normally total moles anions = total moles cations. The charge balance (without any speciation) is adjusted to zero by balancing against Cl- (default) as otherwise the calculation is too sensitive to H+. The balancing species can be easily changed to any of the other basis species (or none).
Choose reasonable starting values; for H+, OH- and equilibrium concentrations of the basis species. If negative concentrations are calculated, choose better initial starting values.
To exclude a basis value set the basis concentration to zero and the concentrations of this and the derived species will be vanishing small and can be ignored. In the generic version of the program the basis species are simply left out.
The basis species are: Na+, K+, Mg2+, Ca2+, Cl-, SO42-. The default complexes are: NaCl°, KCl°, HCl°, KOH°, NaOH°, KSO4-, NaSO4-,HSO4-,CaSO4°,MgSO4°, MgCl+,CaCl+,CaCl2°,MgOH+,CaOH+.
Additional complexes based on the existing basis species can easily be added (see example below).
To set up a problem in chemsolve or chemsolve_generic it is relatively trivial to set up and manipulate a sequence of commands in Excel and cut and past into R. Complex dissociation constants (log K) are from SupCrt 92 slop98.dat http://geopig.asu.edu/?q=tools
The Debye_Hückel parameters (A, B) equations are polynomial fits to data at 0.5 kb from tables in Helgeson & Kirkham (1974).
Note Bdot is not used.
Helgeson H. C. and Kirkham D. H. (1974) Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: II. Debye-Hückel parameters for activity coefficients and relative partial molar properties American Journal of Science 274, 1199-1261.

Value

A list containing the concentrations, activity coefficients, and pH at equilibrium

---

`chemsolve_generic` *Mass balance and charge solver for general cases*

Description

Mass balance and charge balance solver for chemical equilibria. This is the workhorse for chemsolve and requires the prods function

Usage

```
chemsolve_generic(solvent = c("H", "OH"), solvcharge = c("1", "-1"),
  solva = c("9", "4"), Ksoln = -11.356, species, conc, a, charges, prod, A,
  B, Bdot = 0, start, maxitr = 100, bal = "Cl")
```

Arguments

solvent	Symbols for solvent species (should not be changed for water)
solvcharge	Charges for solvent species (should not be changed for water)
solva	Ion size parameters (should not be changed for water)
Ksoln	log K of the solvent
species	Chemical symbols of the basis species
conc	Total concentrations of the basis species (mol/kg)
a	Ion size parameters for the basis species
prod	Dataframe detailing the derived species (Output from prods function)
A	A value
B	B value
Bdot	Bdot value is zero by default
start	Initial guess for the calculated equilibrium concentration of the basis species (in the same order as the solvent and then the species vectors)
maxitr	Maximum number of iterations
bal	The species to charge balance against (e.g. the default of "Cl") or NULL for none

Details

A generic function to add any basis species, product species or if the log K/temperature range need to be extended. Requires all parameters (e.g. log K at the given temperature). The temperature is indirectly set through the log K, A, B & Bdot values. These parameters need to be reinitialised each time, together with reactants and products, if a calculation across a range of temperatures is required. A useful upgrade would be to carry over defaults and use a lookup table and interpolation to initialise the parameters across a range of temperatures. This is similar to the wrapper function except that there the defaults are built in and cannot be changed by the casual user.

Value

A list containing the concentrations, gamma values, and pH at equilibrium

Examples

```
## Define all the product species including KHSO4° FeSO4° and FeCl+
## which are not included as default species in chemsolve
## LogK are at 400°C and 0.5kb. Firsly parameters for the products are defined
prd=c("NaSO4","HSO4","KSO4","NaCl","KCl","HCl","KOH","NaOH","CaSO4",
"MgSO4","MgCl","CaCl","CaCl2","MgOH","CaOH","FeCl","FeSO4","KHSO4")
prdnms=c(2,2,2,2,2,2,2,2,2,2,2,2,3,2,2,2,2,3)
prdconstit=c("Na","SO4","H","SO4","K",
"SO4","Na","Cl","K","Cl","H","Cl","K","OH","Na","OH","Ca","SO4","Mg","SO4","Mg","Cl",
"Ca","Cl","Ca","Cl","Cl","Mg","OH","Ca","OH","Fe","Cl","Fe","SO4","K","H","SO4")
prdK=c(-3.549,-7.444,-3.899,-1.737,-1.236,-2.689,-1.446,-1.164,-6.173,-6.014,-3.18,
-3.692,-4.783,-6.149,-5.635,-5.745,-3.814, -8.701)
prda=c(4,4,4,0,0,0,0,0,0,0,8,6,0,8,6,6,0,0)
```

```
## product input is created with the prods function
products <- prods(names=prd,number=prdnms,species=prdconstit,K=prdK,a=prda)

## Starting species are defined for chemsolve
chspec=c("Na", "K", "Cl","SO4", "Ca", "Mg","Fe")
chconc=c(0.4, 0.2, 0.8, 0.2, 0.1, 0.1,0.1)
cha=c(4, 3,3.5, 4, 6, 8,6)
chc=c(1, 1, -1, -2, 2, 2,2)

## chemsolve is now run with the previously defined products
## Defaults include water as the solvent and a charge balance against Cl
## A & B are at 400°C and 0.5kb
chemsolve_generic(species = chspec, conc = chconc, a = cha, charges = chc, A = 1.8789,B = 0.423, Bdot = 0,
start = c(1e-06, 1e-05, 0.3, 0.1, 0.3,0.01, 0.001, 0.02,1e-8),  prod = products)
```

`ktable` *Table of K constants*

Description

Table of K constants

Usage

```
ktable
```

Format

A data frame containing K values at given temperatures

`prods` *Create prod dataframe*

Description

Creates the dataframe of the derived species for use in chemsolve_generic

Usage

```
prods(names, number, species, K, a)
```

Arguments

names	A vector of names of the species which react to form the basis species
number	A vector of the number of basis consituents for each of the product species given by the equilibrium equation
species	A vector of the chemical symbols of the product species in terms of the basis species
K	A vector of log K values for the product species
a	A vector of ion size parameters for the product species

Index