# Package 'EqSolvR'

July 30, 2018

**Title** Chemical Equilibrium Solver

**Version** 1.2.5

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**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:

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| chemsolve | *Mass balance and charge solver* |

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### 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

## Examples

```
## Add KHSO4° as an additional complex given the existing list of basis species and
## calculate the equilibrium concentrations and pH at 400°C.
chemsolve(exprod =  c("KHSO4"), exconstit = c("K", "H", "SO4"),
exnumz =  c(3), excharges =  c(0), exa =  c(0),  exK =  c(-8.701), bal = "Cl")
## Determine the equilibria at a range of temperatures.
## Additional complexes can be added per the previous example.
temps <- seq(300,400,10) #A vector of temperatures repeating every 10 degrees from 300 to 400
## Na concentration is changed slightly from the default. Further parameters can be added.
r <- lapply(temps,chemsolve,Nat=0.45) #Creates a list of the results
r[[1]] #Display results from first temperature
r[[10]] #Display the results of the 10th temperature
```

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chemsolve_generic *Mass balance and charge solver for general cases*

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**Description**

Mass balance and charge balance solver for chemical equilibria. This is the workhorse for chem-solve 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)
```

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| ktable | *Table of K constants* |
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**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 |

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