CAS 741: SRS

Aqueous Speciation Diagram Generator

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Revision History

Table 1: Revision History

Date	**Developer(s)**	**Change**
10.5.2017	S. Palmer	First revision of document

Reference Material

This section records information for easy reference.

Table of Units

Throughout this document SI (Système International d'Unités) is employed as the unit system. In addition to the basic units, several derived units are used as described below. For each unit, the symbol is given followed by a description of the unit and the SI name.

symbol	**unit**	**SI**
m	length	metre
kg	mass	kilogram
s	time	second
°C	temperature	centigrade
mol	amount of substance	mole
l	volume	litre ($\mathrm{l} = 10^{-3} \cdot \mathrm{m}^3$)
Pa	pressure	pascal ($\mathrm{Pa} = \mathrm{kg\,m^{-1}\,s^{-2}}$)
bar	pressure	bar ($\mathrm{bar} = 10^5 \cdot \mathrm{Pa}$)

Table of Symbols

The table that follows summarizes the symbols used in this document along with their units. The choice of symbols was made to be consistent with chemistry literature. The symbols are listed in alphabetical order.

symbol	**unit**	**description**
A	–	reactant species in a chemical equation
B	–	product species in a chemical equation
K	–	equilibrium constant
p	–	the total number of user supplied chemical equilibrium reactions
$\overline{RK}_{in}$	–	the input set of all pairs of reactions and associated equilibrium constants
$\overline{S}$	–	a set of aqueous solute species in a chemical system
$\overline{S}_{in}$	–	the input set of all aqueous solute species in the chemical system
$\overline{T}_{in}$	–	the input set of total concentrations of chemical elements
X	–	arbitrary chemical species
x	–	arbitrary chemical element

x_{tot}	mol/l	total concentration of an arbitrary chemical element x
$[X]$	mol/l	concentration of the arbitrary chemical species X
$\{X\}$	–	activity of the arbitrary chemical species X
z_X	–	charge number of an arbitrary aqueous solute X

Abbreviations and Acronyms

symbol	**description**
A	Assumption
DD	Data Definition
GD	General Definition
GS	Goal Statement
IM	Instance Model
LC	Likely Change
PS	Physical System Description
R	Requirement
SATP	Standard Ambient Temperature and Pressure
SRS	Software Requirements Specification
SpecGen	The Aqueous Speciation Diagram Generator program
T	Theoretical Model

Contents

1 Introduction

1.1 Purpose of Document

The purpose of this document is to describe the requirements for the Aqueous Speciation Diagram Generator program (herein referred to as SpecGen), a software product that will produce a speciation diagram given a set of chemical reactions and element totals that define a chemical system as inputs. The goals and theoretical models used in the SpecGen code are provided, with an emphasis on explicitly identifying assumptions and unambiguous definitions. This document is intended to be used as a reference to provide all information necessary to understand and verify the transformation of inputs to outputs. The SRS is abstract: the contents describe the problem being solved, but not how to solve it.

This document will be used as a starting point for subsequent development phases, including writing the design specification and the software verification and validation plan. The design document will show how the requirements are to be realized, including decisions on the numerical algorithms and programming environment. The verification and validation plan will show the steps that will be used to increase confidence in the software documentation and the implementation. Although the SRS fits in a series of documents that follow the so-called waterfall model, the actual development process is not constrained in any way. Even when the waterfall model is not followed, as Parnas and Clements point out, the most logical way to present the documentation is still to "fake" a rational design process.

1.2 Scope of Requirements

The scope of the requirements includes collecting all input parameters that describe a chemical system. Given the appropriate inputs, the code for SpecGen is intended to use the data to produce a speciation diagram in the pH range 0 to 14.

1.3 Characteristics of Intended Reader

Reviewers of this documentation should have an understanding of first year undergraduate physical chemistry. Knowledge about chemical activity is assumed.

1.4 Organization of Document

The organization of this document follows the template for an SRS for scientific computing software proposed by [1] and [2] (in Sec:Refe), with some aspects taken from [3]. The presentation follows the standard pattern of presenting goals, theories, definitions, and assumptions. For readers that would like a more bottom up approach, they can start reading the data definitions in Sec:DataDefi and trace back to find any additional information they require.

The goal statements are refined to the theoretical models, and the theoretical models to the instance models. The data definitions are used to support the definitions of the different

models.

2 General System Description

This section identifies the interfaces between the system and its environment, describes the user characteristics and lists the system constraints.

2.1 System Context

- User Responsibilities:
  - Ensure that the input data is correct.
  - Ensure that the input data is sufficient to specify a chemical system that has a unique speciation solution.
- SpecGen Responsibilities:
  - Detect data type mismatch, such as a string of characters instead of a floating point number.
  - Determine if the inputs satisfy the required physical and software constraints.
  - Solve the system of equations arising from the input data to generate the output data.
  - Generate a plot of the output data.

2.2 User Characteristics

The end user of SpecGen should have an understanding of first year undergraduate physical chemistry.

2.3 System Constraints

There are no system constraints.

3 Specific System Description

This section first presents the problem description, which gives a high-level view of the problem to be solved. This is followed by the solution characteristics specification, which presents the assumptions, theories, definitions and finally the instance models.

3.1 Problem Description

Chemical speciation refers to the stable (equilibrium) distribution of chemical species in a given chemical system. Speciation diagrams, which plot species concentrations against an independently varied parameter of the system, are useful tools for displaying speciation data in a concise and easy to use format. The production of speciation diagrams requires solving a set of non-linear equations which arise from the chemical reactions of the species present in a chemical system. As the number of reactions taking place in a system increases, producing speciation diagrams can quickly become a tedious undertaking when done manually.

SpecGen will produce a speciation diagram given a set of chemical reactions, equilibrium constants, and element totals that define a chemical system. SpecGen will be specific to speciation of ions in aqueous systems under varying pH, which is of particular importance in the fields of aqueous process engineering and hydrometallurgy. The diagram generated by SpecGen will plot speciation of all aqueous species (excluding H^+ and OH^-) across the pH range 0 to 14.

3.1.1 Terminology and Definitions

This subsection provides a list of terms that are used in the subsequent sections and their meaning, with the purpose of reducing ambiguity and making it easier to correctly understand the requirements:

Activity: the "effective concentration" of a species in a chemical system

Equilibrium: the state of a chemical system in which species concentrations are stable

SATP: standard ambient temperature pressure ($T = 25°C,\ P = 1$ bar)

3.1.2 Physical System Description

The physical system of SpecGen includes the following elements:

PS1: An unspecified volume of liquid water containing dissolved chemical species under equilibrium conditions.

3.1.3 Goal Statements

Given a set of chemical species present in an aqueous chemical system, a set of reversible reactions and associated equilibrium constants that the species are subject to, and the total concentrations of all elements present in the species set (excluding O and H), the goal statements are:

GS1: Calculate the equilibrium concentrations of all chemical species present in the system over the pH range 0 to 14.

GS2: Generate a plot of the equilibrium concentrations of all chemical species present in the system versus pH.

3.2 Solution Characteristics Specification

The instance models that govern SpecGen are presented in § 3.2.5. The information to understand the meaning of the instance models and their derivation is also presented, so that the instance models can be verified.

3.2.1 Assumptions

This section simplifies the original problem and helps in developing the theoretical model by filling in the missing information for the physical system. The numbers given in the square brackets refer to the theoretical model [T], general definition [GD], data definition [DD], instance model [IM], or likely change [LC], in which the respective assumption is used.

A1: All generated speciation diagrams are at SATP conditions.

A2: In accordance with A1, all user supplied equilibrium constants are assumed to be values measured under SATP conditions.

A3: The chemical system is assumed be a single-solvent solution, where the solvent is liquid water at SATP.

A4: The chemical species in all of the user supplied equations are assumed to be aqueous solutes.

A5: The activity of liquid water is assumed to be 1.0.

A6: The activities of all aqueous solute species are assumed to be equal to their concentration.

A7: All chemical equations supplied by the user are assumed to be reversible (finite equilibrium constant).

3.2.2 Theoretical Models

This section focuses on the general equations and laws that SpecGen is based on.

Number	T1
Label	**Equational representation of reversible chemical reactions**
Equation	$\alpha_1 A_1 + \cdots + \alpha_n A_n \rightleftharpoons \beta_1 B_1 + \cdots + \beta_m B_m$
Description	The above equation represents a reversible chemical reaction where: n is the number of reactants m is the number of products A_i is the i^{th} reactant species α_i is the stoichiometric coefficient of the i^{th} reactant B_j is the j^{th} product species β_j is the stoichiometric coefficient of the j^{th} product
Source	Wikipedia (2016)
Ref. By	GD??

Number	T2
Label	**Conservation of mass (concentration balance)**
Equation	$x_{tot} = \sum\{X : S \mid x \in X \bullet \#x\langle X\rangle \cdot [X]\}$
Description	The total dissolved concentration of an element in an aqueous solution is equal to the sum of the concentrations of all species which contain that element. This is captured in the above equation, where: x is a chemical element x_{tot} is the total dissolved concentration of x in a solution X is an aqueous species in solution S is a set of all aqueous species in a solution $\#x\langle S\rangle$ is the number of occurrences of x in X $[X]$ is the concentration of X in solution
Source	
Ref. By	GD??

Number	T3
Label	**Charge neutrality of aqueous solutions**
Equation	$\sum\{X : S \bullet z_X \cdot [X]\} = 0$
Description	Aqueous solutions must be electrically neutral, and thus the concentration of positive charge from dissolved solutes must balance with the concentration of negative charge from dissolved solutes. This is reflected in the equation above, where: X is an aqueous species in solution S is a set of all aqueous species a solution z_X is the charge number of X $[X]$ is the concentration of X
Source	
Ref. By	GD??

Number	T4
Label	**Law of mass action (forward)**
Equation	$r_+ = k_+ \prod_{i=1}^{n} \{A_i\}^{\alpha_i}$
Description	The law of mass action describes the forward and backward reaction rates for a chemical reaction. For a chemical reaction expressed in the equational form given in T1, the equation above expresses the law of mass action in the forward direction, where: r_+ is the forward reaction rate ($\mathrm{mol\,s^{-1}}$). k_+ is the forward rate constant ($\mathrm{mol\,s^{-1}}$). n is the number of reactants. A_i is the i^{th} reactant species. $\{A_i\}$ is the activity of A_i. α_i is the stoichiometric coefficient of the i^{th} reactant.
Source	**?**
Ref. By	DD3, DD??

Number	T5
Label	**Law of mass action (backward)**
Equation	$r_- = k_- \prod_{j=1}^{m} \{B_j\}^{\beta_j}$
Description	The law of mass action describes the forward and backward reaction rates for a chemical reaction. For a chemical reaction expressed in the equational form given in T1, the equation above expresses the law of mass action in the backward direction, where: r_- is the backward reaction rate ($\mathrm{mol\,s^{-1}}$). k_- is the backward rate constant ($\mathrm{mol\,s^{-1}}$). m is the number of products. B_j is the j^{th} product species. $\{B_j\}$ is the activity of B_j. β_j is the stoichiometric coefficient of the j^{th} product.
Source	**?**
Ref. By	DD3, DD**??**

Number	T6
Label	**Chemical equilibrium**
Equation	$k_+ \prod_{i=1}^{n} \{A_i\}^{\alpha_i} = k_- \prod_{j=1}^{m} \{B_j\}^{\beta_j}$
Description	When a chemical reaction is in equilibrium, the forward and reverse reaction rates are the same. Using T4 and T5, this idea is expressed in the equation above, where: k_+ is the forward rate constant ($\mathrm{mol\,s^{-1}}$). n is the number of reactants. A_i is the i^{th} reactant species. $\{A_i\}$ is the activity of A_i. α_i is the stoichiometric coefficient of the i^{th} reactant. k_- is the backward rate constant ($\mathrm{mol\,s^{-1}}$). m is the number of products. B_j is the j^{th} product species. $\{B_j\}$ is the activity of B_j. β_j is the stoichiometric coefficient of the j^{th} product.
Source	**?**
Ref. By	DD3, DD??

Number	T7
Label	**Equilibrium constant**
Equation	$K = \frac{r_+}{r_-} = \frac{\prod_{j=1}^{m}\{B_j\}^{\beta_j}}{\prod_{i=1}^{n}\{A_i\}^{\alpha_i}}$
Description	The ratio of the forward and backward rate constants for a reaction forms a new constant called the equilibrium constant. Using T6, we can relate the equilibrium constant to the activities of the products and reactants. This is shown in the equation above, where: K is the equilibrium constant. r_+ is the forward reaction rate ($\mathrm{mol\,s^{-1}}$). k_+ is the forward rate constant ($\mathrm{mol\,s^{-1}}$). n is the number of reactants. A_i is the i^{th} reactant species. $\{A_i\}$ is the activity of A_i. α_i is the stoichiometric coefficient of the i^{th} reactant. r_- is the backward reaction rate ($\mathrm{mol\,s^{-1}}$). k_- is the backward rate constant ($\mathrm{mol\,s^{-1}}$). m is the number of products. B_j is the j^{th} product species. $\{B_j\}$ is the activity of B_j. β_j is the stoichiometric coefficient of the j^{th} product.
Sources	**?**
Ref. By	IM1

3.2.3 General Definitions

This section collects the laws and equations that will be used in deriving the data definitions, which in turn are used to build the instance models. [Some projects may not have any content for this section, but the section heading should be kept. —SS] [Modify the examples below for your problem, and add additional definitions as appropriate. —SS]

Number	GD1
Label	**Water dissociation equilibrium**
SI Units	–
Equation	$K_{H_2O}: \ 10^{-14} = \{H^+\} \cdot \{OH^-\}$
Description	This is the equilibrium equation for the dissociation of water. The equation arises from T7 using the value of 10^{-14} for the equilibrium constant at SATP, where: $\{H^+\}$ is the activity of H^+ $\{OH^-\}$ is the activity of OH^-
Source	(**?**, p. 8)
Ref. By	DD3, DD**??**

3.2.4 Data Definitions

This section collects and defines all the data needed to build the instance models. The dimension of each quantity is also given. [Modify the examples below for your problem, and add additional definitions as appropriate. —SS]

Number	DD1
Label	**Set of equilibria**
Symbol	$\overline{K}$
SI Units	–
Equation	$\overline{K} = \left\{ (R, K_R) : \overline{RK}_{in} \ \bullet \ K_R = \frac{\prod_{j=1}^{m} \{B_j\}^{\beta_j}}{\prod_{i=1}^{n} \{A_i\}^{\alpha_i}} \text{ with reaction } R \right\} \cup K_{H_2O}$
Description	Uses T7
Sources	**?**
Ref. By	IM1

Number	DD2
Label	**Set of mass balance equations**
Symbol	$\overline{M}$
SI Units	–
Equation	$\overline{M} = \{x_{tot} : \overline{T}_{in} \bullet \sum\{X : \overline{S}_{in} \mid x \in X \bullet \#x\langle X\rangle \cdot [X]\} = x_{tot}\}$
Description	Uses T2
Sources	**?**
Ref. By	IM1

Number	DD3
Label	**Charge balance equation**
Symbol	C
SI Units	–
Equation	$C : \sum\{X : \overline{S}_{in} \bullet z_X \cdot [X]\} = 0$
Description	Uses T7
Sources	**?**
Ref. By	IM1

3.2.5 Instance Models

This section transforms the problem defined in § 3.1 into one which is expressed in mathematical terms. It uses concrete symbols defined in § 3.2.4 to replace the abstract symbols in the models identified in § 3.2.2 and § 3.2.3.

The goals [reference your goals —SS] are solved by [reference your instance models —SS]. [other details, with cross-references where appropriate. —SS] [Modify the examples below for your problem, and add additional models as appropriate. —SS]

Number	IM1
Label	**System of non-linear equations to find equilibrium concentrations**
Input	$\overline{K}$, $\overline{M}$, C
Output	$\{X : S \mid X \neq OH^- \wedge X \neq H^+ \bullet \{[X] \text{ for } 0 \leq pH \leq 14\}\}$, when the system of non-linear equations $\overline{K} \cup \overline{M} \cup C$ is satisfied
Description	
Sources	?
Ref. By	IM??

Derivation of ...

[May be necessary to include this subsection in some cases. —SS]

3.2.6 Data Constraints

Tables 2 and 4 show the data constraints on the input and output variables, respectively. The column for physical constraints gives the physical limitations on the range of values that can be taken by the variable. The column for software constraints restricts the range of inputs to reasonable values. The constraints are conservative, to give the user of the model the flexibility to experiment with unusual situations. The column of typical values is intended to provide a feel for a common scenario. The uncertainty column provides an estimate of the confidence with which the physical quantities can be measured. This information would be part of the input if one were performing an uncertainty quantification exercise.

The specification parameters in Table 2 are listed in Table 3.

Table 2: Input Variables

Var	Physical Constraints	Software Constraints	Typical Value	Uncertainty
x_{tot}	$L > 0$	$x_{tot_{\min}} \leq x_{tot}$	0.1 mol/l	2.5%

* The user.

** There must be an accompanying equilibrium constant for every equation supplied by the user.

3.2.7 Properties of a Correct Solution

A correct solution must satisfy the system of non-linear equations described by [FILL IN —SP].

Table 3: Specification Parameter Values

Var	Value
L_{min}	0.1 m

Table 4: Output Variables

Var	Physical Constraints
T_W	$T_{\text{init}} \leq T_W \leq T_C$ (by A**??**)

4 Requirements

This section provides the functional requirements, the business tasks that the software is expected to complete, and the nonfunctional requirements, the qualities that the software is expected to exhibit.

4.1 Functional Requirements

R1: [Requirements for the inputs that are supplied by the user. This information has to be explicit. —SS]

R2: [It isn't always required, but often echoing the inputs as part of the output is a good idea. —SS]

R3: [Calculation related requirements. —SS]

R4: [Verification related requirements. —SS]

R5: [Output related requirements. —SS]

4.2 Nonfunctional Requirements

[List your nonfunctional requirements. You may consider using a fit criterion to make them verifiable. —SS]

5 Likely Changes

LC1: [Give the likely changes, with a reference to the related assumption (aref), as appropriate. —SS]

References

Wikipedia. Reversible reaction — wikipedia, the free encyclopedia, 2016. URL https://en.wikipedia.org/w/index.php?title=Reversible_reaction&oldid=748515123. [Online; accessed 6-October-2017].

6 Appendix

[Your report may require an appendix. For instance, this is a good point to show the values of the symbolic parameters introduced in the report. —SS]

6.1 Symbolic Parameters

[The definition of the requirements will likely call for SYMBOLIC_CONSTANTS. Their values are defined in this section for easy maintenance. —SS]