Modelica Chemical Library - User’s Guide

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Abstract

New library for (electro)chemical processes is released. It is based on equilibrating the electrochemical potentials of the substances as following the modern theory of physical chemistry. As the theories behind also the library is very general. The chemical solution has full thermodynamic state with possibility to connect it with thermal, mechanical and electrical components of Modelica Standard Library 3.2.1. This paper show how to implement the three examples: lead-acid battery, the hydrogen burning engine and the chloride shift of human red cells. Even the complex processes can be composed only from a few base components such as component for chemical solution, component for chemical substance or component for chemical reaction. Behind these components are only fundamental laws of thermodynamics and physical chemistry. And all was designed to be very intuitive and easy to use.

Keywords: Modelica library, physical chemistry, thermodynamics equilibria, electrochemical potential, electrochemical cell, internal energy, semipermeable membrane

# Introduction

The Chemical library becomes from library for physiological calculations called Physiolibrary. We used the Physiolibrary to implement the biggest model of human physiology of the year 2010 called HumMod. Now we called the model Physiomodel and we are continuing the extended it in more detailed microscopic and chemical levels. The macroscopic processes and regulations of human physiology are already validated by experiments on animals and human. However the chemical processes in the models was until today a black-boxes with inputs and outputs defined more with empirical relationships than with strict physical theory. Using this empirical behavior the expectations was well formed for the elementary processes. And the new library starts to theoretically describe these processes in more details using last modern fundamental relations of thermodynamics and physical chemistry. This chemical library allows to move different substances in different direction across membrane at the same time, which was not possible using for example Modelica.Fluid package because stream constructs move the substances only in direction of the main stream.

This new chemical library solves the more detailed electrochemical environment of human cells and cellular electrochemical processes, where the Physiolibrary failed.

For example we found that the equilibrium of osmolarities (as validated and verified for macroscopic and capillary membranes) was not in good agreement with measured data of cellular membranes. The real data of human blood (Raftos et al.) have total molarity of plasma 289 mmol/L and molarity of intracellular space of erythrocytes 207 mmol/L at osmotic equilibrium. These values are definitely not the same and the explanation of these disproportions was hidden in physical chemistry. Equilibrating the electrochemical potential instead of osmolarity can describe each type of membrane and each type of substance to reach the expected values as measured in osmotic experiments for both organ and cellular membranes.

The other problem with old Physiolibrary approach was, that it does not automatically calculate the membrane equilibriums for electrically charged substances. The very specific blocks for calculating the Donnan’s equilibriums at glomerular membrane was created to reach expected concentrations of electrolytes at semipermeable membrane. However, there was not generated any membrane electric potential, which is the result of this electrolyte’s equilibrium. Now with the chemical library it can be automatically solved the Donnan’s equilibria on semipermeable membrane together with Nernst membrane potential as a consequence of the equilibrated electrochemical potentials of the permeable substances.

Connecting these electrochemical processes in cellular membrane with chemical reactions we realized that the relations are general enough to calculate phase-changes, gas solubility, electrochemical cells, and other known chemical processes. The result is a library, which allows to create any type of chemical reaction in any type of solution at any conditions. We made it in one hand with thermodynamics and physical chemistry relations behind. In Modelica it really seems that they can be only rewritten the selected base definitions from these theoretical approach. And all starts to work above our expectations.

# Chemical Substance

The Chemical in version 1.1.0 contains only tree models of chemical substances: ideal gas, incompressible substance and subunit substance. However the user can very easy (re)define their own model of substance just by inserting the right expression for pure substance activity coefficient, molar volume, molar entropy and molar enthalpy based on the current solution state (temperature, pressure, electric potential and ionic strength) and the substance data. The object-oriented design allows to define substance data as the part of the substance model. So the user can select his own substance parameters according to his substance model. Because the usage of substance data record is limited only inside its substance model package, which is redefined by user.

In our examples work only with ideal gas substances (gases) and incompressible substances (liquids or solids). The definition data are molar mass of the substance, number of charge of the substance, molar heat capacity of the substance at constant pressure, free formation enthalpy and free formation Gibbs energy. And the parameter density only for incompressible substance. All at temperature of 25°C and pressure 1 bar. Because these parameters are usually tabulated in chemical tables at this standard state. So the full definition of the substance is only to create the record of the parameters. This way was already defined more than 35 real chemical substances in example package of this chemical library. The usage of these predefined substances data are very simple. In the parameter dialog of the chemical substance it can be selected the right record with this data as shown in Figure 1.

This setting is typically the most important setting of each chemical model. All equilibrium coefficients, standard voltages, dissolution coefficients, saturated vapor pressures and so on, are automatically solved using these substance data. As a result for example the chemical reaction component need to define only the stoichiometry coefficient and from the connected substances. And it reach the equilibrium at the right equilibrium coefficient.

# Example of lead-acid battery

The lead-acid electrochemical cells are characterized with two chemical reactions:

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| PbO2 + HSO4- + 3 H+ +2 e- ↔ PbSO4 + 2 H2O | (1) |
| Pb + HSO4- ↔ PbSO4 + H+ + 2 e- | (2) |

Building of one cell of lead-acid battery (Figure 2) using the library starts with definition of three solutions. Two for lead electrodes and one for liquid acid solution. This can be done by drag and drop of the library class Components.SimpleSolution class into the diagram. The first instance we called “cathode” and the second “solution” and the last “anode”. We set the parameter ElectricalGround as “false” for all of these solutions to reach possibility of non-zero voltage of the solution. Now we can to specify the chemical substances inside the chemical solutions. We drag and drop the library class Components.Substance into the “solution” as chemical substances H2O(liquid), H+(aqueous), HSO4-(aqueous) representing the liquid

aqueous solution of sulfuric acid; into the “cathode” PbSO4(solid) and PbO2(solid) representing the elements of positive electrode; and into “anode” the substances Pb(solid) and PbSO4(solid) representing the elements of negative electrode. As was mentioned for all this substances must be selected appropriate substance data definition, e.g. Examples.Substances .Water\_liquid, .Lead\_solid, .Lead\_dioxide\_solid, .Lead\_sulfate\_solid and so on. The last, very special substance is an electron. This class is called Components.Electrone and it must be added for each electrode to translate electron flows from the chemical reaction to the electric current. Each of these substances must be connected to the appropriate solution using solution port situated in bottom of the components icons. Having all substances it is possible to implement the chemical reactions. Drag and drop of library class Components.Reaction for both chemical reactions and setting they parameters into appropriate number of reactants and products and their stoichiometry allows to connect each substance with the reaction as expressed in reaction (1) and reaction (2). This setting can be done using parameter dialog of the cathode chemical reaction (1) as there are four types of substrates (nS=4) with stoichiometric coefficients 1 for first and second reactant, 3 for third reactant and 2 for forth reactant (s={1,1,3,2}) and there are two types of products (nP=2) with stoichiometry 1 for PbSO4 and 2 for water (p={1,2}) following the chemical scheme of the first chemical reaction above. After setting the number of reactants and products there is possible to connect the substances with reaction. Each instance of reaction was an array of connectors for substrates and an array of connectors for products and the user must be very careful to connect each element of this array in the same order as defined by stoichiometric coefficients. This means that for example the water must be connected in index 2 of products of the first chemical reaction, because the second product was stoichiometry 2 as defined for H2O. The chemical reaction (2) must be set analogically as nS=2, nP=3, p={1,1,2} with connections of substance ports of Pb to substrate[1], HSO4- to substrate[2], PbSO4 to product[1], H+ to product[2] and e- to product[3] as graphically represented in Figure 2.

Now, the electrochemical cell is already implemented. However the simulation need the initial state of substances, which for the fully charged battery means that almost all elements of cathode is PbO2 and almost all elements of anode is Pb. At this state can be the sulfuric acid very concentrated, what increases the effectivity of the electrochemical cell. To set this state it is possible just double-click on PbO2 and Pb and set the amount e.g. 1mol, the same as the total amount of “cathode” and “anode” components. These total amounts of solutions must be equal or greater than sum of all substances inside. To set them the user must double click on the border of solution and using the parameter dialog rewrite the value of amountOfSolution\_start also to 1mol for both electrodes. If we went to examine also mass of volume properties of electrodes, there must be set the initial values of these physical quantities. However they in this example do not have impact to generated electric currents or electric potentials, so without we can ignore them this time without loss of generality. To set the pure concentrated sulfuric acid we can set the amount of SO4- and H+ also to 1 mol, what makes the total amount of substances in liquid “solution” 2 mol (solution1. amountOfSolution\_start=2). This fully charged ideal state is ready to simulate when it is connected the electric ground into one of the electric port of the one electron.

These battery can be connected to any electrical circuit, which is slowly discharging it. For example if we only connect the simple electric resistance of 1 Ohm as expressed in Figure 3 then the simulation of discharging process during 13 hours and 45 minutes gives the results of electric current and electric potential as in Figure 4.

# Example of hydrogen burning engine

In contrast with oxidation-reduction reactions describing processes in lead-acid electrochemical cell is the gaseous reaction of the hydrogen burning very simple:

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| 2 H2 + O2 <-> 2 H2O | (3) |

However this reaction generates big amount of energy, which can be used for mechanical or thermal purposes.

The building of this model using the chemical library is very easy. At first we drag and drop the library class Components.IdealGasSolution to the diagram of our new model. The instance is called “idealsGas” in Figure 5. For this solution we need to set the area of the piston (e.g. 1 dm2), where the pressure makes the force of the green mechanical port of the upper side. The next parameter is the initial volume of the gas inside (e.g. 1 liter). All three substance can be added using drag and drop of library class Components.Substance. Because this model uses gases, the substanceModel must be changed to some gases substance such as ideal gas substance model prepared in library as Interfaces.IdealGasSubstanceModel. The substance data must be selected to define the appropriate substance as Examples.Substances.Hydrogen\_gas, Examples.Substances.Oxygen\_gas and Examples.Substances.Water\_gas. And the initial amount of substances can be prepared for ideal solution of hydrogen and oxygen gases in ratio 2:1 to reach the chemical equation above with expectation that at the end of burning only water substance will be presented. If we want to start without any force at the beginning of the simulation we must to calculate the amount of particles using ideal gas equation, so there should be (2/3)\*p\*V/(R\*T) of H2 particles and (1/3)\*p\*V/(R\*T) of O2 particles, where p=100 000 Pa, V=0.001 m3, R=8.314 J.K-1.mol-1, T=298 K. All substances must be connected with solution using solution port of blue color situated in the bottom side of each substance and each solution. Then the chemical reaction is inserted into the diagram of this model as library class Components.Reaction and it is set to 2 substrates (nS=2) with stoichiometry s={2,1} and one product with stoichiometry 2 (p={2}). The substances are then connected using substance connectors of violet color with appropriate indexes: H2 to substates[1], O2 to substates[2] and H2O to products[1]. Now is the model prepared to simulate in condition of not connected heat port and not connected mechanical port. This simulation reach the theoretical ideal thermally isolated (zero heat flow from/to the solution) and isobaric (zero force generated on piston) conditions.

However in the real word there is always some thermal energy flow from the solution and this cooling process can be connected using the thermal connector of Modelica Standard Library 3.2.1. For example as simple thermal conductor of thermal conductance 2W/K to constant temperature environment at 25°C as expressed in Figure 5. The mechanical power of the engine can be connected to robust mechanical model. However in our example we select only very strong mechanical spring with spring constant of 1e6 N/m to stop the motion of the piston to generate the pressure, see Figure 5. The results of this experiment is shown in Figure 6.

# Example of chloride shift

Only in last century was discovered the real function of membranes in biology. Division of solutions of organism makes different conditions for different processes. For example each cell of the body is surrounded by cellular membrane composed with special very compact lipid double-layer. Any lipophobic compound (not soluble in lipids) cannot cross it without special proteins called membrane channels. So even a water molecules must have a membrane channels (called aquaporines) to cross the cellular membrane. The chloride shift (also known as Hamburger shift) is in both directions exchanging an aqueous chloride Cl- for an aqueous bicarbonate HCO3- across the cellular membrane of blood red cells using the membrane channel “Band 3”. As each passive membrane channel it allows only to equilibrate the electrochemical potentials of the specific permeable ions on both sides of membrane. The different electric potentials on each side of membrane causes their different concentrations at equilibrium. And backwards, the equilibrium of different ions compositions of the solution on both sides of the membrane causes the measurable electric membrane potential. It is not so intuitive, because even the both solution does not need to have any electric charge there can be a non-zero electric potential for permeable ions. This potential for permeable ions at equilibrium is called Nernst membrane potential and in the chemical library it is a direct mathematical result of the equality of electrochemical potential of the ion in the both solutions.

The mature red cell (erythrocyte) is the simplest cell in the body. Its primary function is transport of blood gases as oxygen O2 (from lungs to tissues) and carbon dioxide CO2 (from tissue to lungs). The chemical processes behind the gases transport is a bit complex, because the capacity of the water for only their free dissolved forms is very low. To transport sufficient amount of O2 and CO2 the gas must be chemically bound to hemoglobin as described in Matejak et al. and/or transported as different substance, which can be presented in water in much higher concentration than only free dissolved form allows. So to transport sufficient amount of CO2 it must be changed to HCO3- using chemical reaction:

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| CO2 + H2O <-> HCO3- + H+ | (4) |

This reaction takes place mainly inside the red cells, because only here is presented an enzyme called carbonic anhydrase. So the increase of total carbon dioxide content of blood in tissue and its decrease in lungs is always connected with chloride shift between blood plasma and intracellular fluid of erythrocytes as represented in Figure 7.

The intracellular solution must be set with possible nonzero electric potential (ElectricalGround=false), because as a result the membrane potential of erythrocytes is calculated as -10mV in good agreement with experimental data.

# Discussion

Nowadays there exist alternative free Modelica libraries for chemical calculations such as FCSys v0.2, FuelCellLib 1.0, Modelica\_EnergyStorage v3.2.1, BioChem v1.2 or our Physiolibrary v2.3. However, we are not satisfied with these libraries, because none of them is based on equilibrating of electrochemical potentials. So there is not so easy to implement the real equilibriums on electrochemical processes. And we feel that without realistic equilibria it is very hard to implement any kinetics.

In the Chemical library we carefully select only the fundamental definitions from physical chemistry and thermodynamics to derive other known chemical relations. For example the definitions of an electrochemical potential of each chemical substance in homogenous chemical solution is defined in physical chemistry as a composition of a relative pure substance energy (typically tabulated as free molar Gibbs energy of formation) as part of replaceable substance model, a chemical dissolution component as the chemical status of the substance in the solution (reflecting the concentration of the substance in the solution) and an electrical component as the electrical status of the substance in the solution with non-zero electrical potential. The relative energy of the pure substance must be compatible with all tabulated equilibrium coefficients. For example equilibrium coefficients of chemical reactions (as expressed from free Gibbs energy of the reaction), Henry’s coefficient for gas dissolution equilibrium, Raoult’s vapor pressure equilibrium, Nernst membrane electric potential for electrolyte equilibrium on semipermeable membrane, Donnan’s equilibrium ratios on semipermeable membrane and so on. These known relations do not need to be explicitly written in code, because they are the results of algebraic manipulation of the implemented relations as we mathematically and numerically proved during development. So the usage of the library is very simplified, because with few chemical substances is typically possible to build many type of reactions. And having a set of already defined chemical substances it is known also each equilibrium coefficient of each reaction between them. The same principle as these Gibbs energies of substances can be applied also to heat energies (enthalpies), because there is the same relation called Hess’ law between free enthalpy of chemical processes and relative (free) enthalpies of the substances (typically tabulated as free molar enthalpies of formation). So the user do not need to set even the heat consumed or released from the reaction, this heat energy is also automatically derived from the substance definitions.

The mentioned examples together with many other processed are implemented and tested in Example package of the library. They starts with definition of very simple general chemical reaction, heating of water solutions, exothermic reaction, vaporization of water, O2 and CO2 gas solubility in aqueous solutions, enzymatic reaction, Harned cell (as typical pH measurement of electrochemical cell), water self-ionization, carbon dioxide in water solution, inorganic phosphate in water solution, albumin (blood plasma protein with 218 sides for binding of H+) titration model by Figge-Fencl, allosteric models of hemoglobin oxygenation by Monod-Wyman-Changeux. All these examples illustrates the usages of only a few components such as the chemical solution, chemical substance and chemical reaction is.

During building of the Chemical library was created one mathematical trick how to reach better numerical stability of the electrochemical equilibrations. Because from physical chemistry behind there must be the molar substance flow dependent on logarithm of the substance concentration. This is very unusual for other physical domains and it is not surprise, that the numerical solvers are not prepared to this logarithmic dependences. We help to this solvers by an algebraic trick, which redefine the state variable to “*lnn*” as logarithm of the amount of substance “*n*”.

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This notation means mathematically the same as der(*n*)=*dn*. However it is more stable during equilibration phase, where the amount of substance should not reach zero and it definitely cannot reach negative values.

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