

# Modelica Library of Chemical Processes

(Chemical 1.1.0)

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## Basic definitions

There are two base components, which should be included in almost all chemical models. The chemical solution and the chemical substance. Chemical solution join together all substances inside and provide to each chemical substance the current state of temperature “T” and pressure “p”. These physical quantities are the characterization of the solution. They are the result of the fundamental relations of thermodynamics:

$$H = U + p \cdot V \quad (1) \text{ Pressure-Volume relationship}$$

$$G = H - T \cdot S \quad (2) \text{ Temperature relationship}$$

Where “U” is the free internal energy as the integration of heat energies added the solution “ $\partial Q$ ” and mechanical power of the solution “ $\partial W$ ” as equation (3); “G” is a free Gibbs energy defined as the sum of each electrochemical potential “ $\mu_j$ ” multiplied by amount of the j-th substance “ $n_j$ ” in the solution as equation (4); “H” is the enthalpy of the solution, which is also extensive property and can be calculated from molar enthalpies of the substances “ $H_{m,j}$ ” as equation (5); “V” is a volume of the solution, which is also extensive property as the sum of all molar volumes “ $V_{m,j}$ ” of the substances in the solution as equation (6); and amount of all substances “n” is the sum of amount of each substance in the solution as equation (7).

$$U = \int (\partial Q - \partial W) \quad (3) \text{ Free Internal energy}$$

$$G = \sum (n_j \cdot \mu_j) \quad (4) \text{ Free Gibbs energy}$$

$$H = \sum (n_j \cdot H_{m,j}) \quad (5) \text{ Free enthalpy}$$

$$V = \sum (n_j \cdot V_{m,j}) \quad (6) \text{ Volume}$$

$$n = \sum n_j \quad (7) \text{ Amount of solution}$$

Some mechanical aspects must be added to make a work with the solution, for example as piston in the motor with a fixed area “A” equaled to  $\pi r^2$ , where r is an internal radius of the cylinder. The solution pressure can be converted to force by equation (9) and the force can be accumulated by displacement of the piston to the work of the solution “W” using equation (8) and (10). Change of this mechanical energy becomes from internal energy of the solution, so derivation of the work “ $\partial W$ ” is part of the change of free internal energy of the solution as mentioned in equation (3).

$$W = F \cdot s \quad (8) \text{ Work of the chemical solution}$$

$$p = F/A \quad (9) \text{ Pressure-Force relation}$$

$$s = V/A \quad (10) \text{ Displacement-Volume relation}$$

Having these equations for solution it is defined through all solution’s substances the relation between added heat “ $\partial Q$ ” and temperature “T” and the relation between force “F” and the position “s”. It means that the solution has two standard additional connectors – the thermal connector of Modelica Standard Library 3.2 (MSL) as Modelica.Thermal.HeatTransfer.Interfaces.HeatPort and

mechanical connector from MSL as Modelica.Mechanics.Translational.Interfaces.Flange\_a. And Modelica compilers will handle the causality for each couple of these physical quantities.

The chemical solution can have also the electrical properties as electrical potential “ $\varphi$ ” and electrical current “ $i$ ”. The non-zero electric potential “ $\varphi$ ” has a direct impact to each substance with non-zero charge number. And the change of the charges has the meaning of electric current as in equation (11), where “ $n_j$ ” is the molar amount of j-th substance, “ $z_j$ ” is the number of charge of the j-th substance (e.g. -1 for electron, +2 for  $\text{Ca}^{2+}$ ), and “ $F$ ” is the Faraday’s constant.

$$i = \sum \partial(F \cdot n_j \cdot z_j) \quad (11) \text{ Electric current of the solution}$$

Having internal relation between electric potential “ $\varphi$ ” and electric current “ $i$ ” there is presented also standard electrical port for the solution as Modelica.Electrical.Analog.Interfaces.Pin. However typical electroneutral solution should have zero electric potential, so the typical usage of this port is to connect it in the electrical ground. Setting some non-zero voltage source can cause the electrochemical processes, which are dependent on electric potential of the solution.

Each extensive property of the chemical solution, which can be calculated from properties of the chemical substances inside, is connected to the substances of the solution via solutionPort. The solution port redefine the sums above into the Kirchhoff’s node relation for flow variables. In reality there are not physical flows. However the automatically generated sum to zero is an ideal candidate to calculate all these extensive properties of the solution. This mathematical trick is used only to simplify the usage to user, which can connect all substances into one port of the chemical solution. And in the side of the chemical solution is the total extensive property presented in connector as non-flow variable having the same value for each substance. The exception from this extension variable pattern make quantities of three additional solution ports – thermal, mechanical and electrical noted as first three rows in the next table.

flow variables on side of the j-th substance	Kirchhoff's junction rule – on solution	non-flow variable of the solution
$dH_j$ – enthalpy ; heat energy flow ; heat change	$dH + \sum dH_j = 0$	$T$ – temperature
$dV_j$ – volumetric flow ; change of volume	$dV + \sum dV_j = 0$	$p$ – pressure
$i_j$ – electric current ; change of charge	$i + \sum i_j = 0$	$\varphi$ - electric potential
$n_j$ – amount of substance	$-n + \sum n_j = 0$	$n$ – amount of solution
$m_j$ – mass of substance	$-m + \sum m_j = 0$	$m$ – mass
$V_j$ – volume of substance	$-V + \sum V_j = 0$	$V$ – volume
$G_j$ – free Gibbs energy of substance	$-G + \sum G_j = 0$	$G$ – free Gibbs energy
$Q_j$ – electric charge of substance	$-Q + \sum Q_j = 0$	$Q$ – electric charge
$I_j$ – mole-fraction based ionic strength of substance	$-I + \sum I_j = 0$	$I$ – mole fraction based ionic strength

The properties of the substance as molar mass “ $MM$ ”, charge number of ion “ $z$ ”, molar volume “ $V_m$ ” or molar enthalpy “ $H_m$ ” can be expressed in the substance definition, which will be shown at the end of this article.

The model of substance is accumulating the molar flow of the substance “ $\partial n_j$ ” into the amount of substance “ $n_j$ ” using equation (12). Having the amount of substance “ $n_j$ ” and the amount of solution “ $n$ ” there is possible to present the mole fraction of the substance in solution “ $x_j$ ” as equation (13), which is typically the same as activity of the substance “ $a_j$ ” defined by equation (15). However there exist some special cases, when the activity is different. This can be corrected by activity coefficient “ $\gamma_j$ ” different as 1.

$$n_j = \int \partial n_j \quad (12) \text{ Amount of the substance}$$

$$x_j = n_j/n \quad (13) \text{ Mole fraction of the substance}$$

$$c_j = n_j/V \quad (14) \text{ Concentration of the substance}$$

$$a_j = \gamma_j \cdot x_j \quad (15) \text{ Activity of the substance}$$

The main equation of the substance is the definition of electrochemical potential as the fundamental equation of physical chemistry – equation (16), where “ $\mu^o$ ” is the chemical potential of the pure substance ( $a_j=1$ ), and R is gas constant. The chemical potential is independent on electric potential and it is equal to the electrochemical potential at zero electric potential ( $\varphi=0$ ).

$$\mu_j = \mu_j^o + R \cdot T \cdot \ln(a_j) + F \cdot z_j \cdot \varphi \quad (16) \text{ Electrochemical potential of the substance in the solution}$$

$$\mu_j^o + R \cdot T \cdot \ln(a_j) \quad (17) \text{ Chemical potential of the substance in the solution}$$

$$\mu_j^o \quad (18) \text{ Chemical potential of the pure substance}$$

The chemical potential of the pure substance “ $\mu^o$ ” is the main property of the substance. It is temperature and pressure dependent and its derivation for ideal gas substance and for incompressible substance is in the end of this article.

Using this electrochemical potential “ $\mu$ ” together with molar flow “ $q$ ” of the substance it is defined the substance connector.

flow variable	non-flow variable
$q$ – molar flow of the substance	$\mu$ – electrochemical potential of the substance

## Chemical processes

The most, if not all, chemical processes are equilibration of the electrochemical potentials. The chemical equilibrium is state, when the chemical process stops and it does not generate any molar changes of any substance. And at this time the sum electrochemical potentials of reactants is the same as the sum of electrochemical potentials of products. Each equilibrium of electrochemical potentials is described by the equation (19), where “ $v_j$ ” is stoichiometry coefficient negative for reactants and positive for products (e.g. transport of the substance  $A_{in} \leftrightarrow A_{out}$  has stoichiometry  $v_{in}=-1$ ,  $v_{out}=1$ ; chemical reaction  $3 A_1 \leftrightarrow 2 A_2 + 4 A_3$  has stoichiometry  $v_1=-3$ ,  $v_2=2$ ,  $v_3=4$ ).

$$0 = \sum (v_j \cdot \mu_j) \quad (19) \text{ Chemical equilibrium}$$

$$\partial n_j = v_j \cdot \partial n_p \quad (20) \text{ Molar change of the substance}$$

Where at equilibrium each molar flow of the substance “ $\partial n_j$ ” and each molar flow of the process “ $\partial n_p$ ” is zero.

Each chemical reaction in solution without electric potential ( $\varphi=0$ ) reaches the standard equilibrium coefficient “K” as equation (21), which is also the direct result of molar Gibbs energy of the reaction calculated using Hess’ law from chemical potentials of pure substances as usually calculated in physical chemistry. The equation (21) is mathematically expressed from (16) and (19) at zero electric potential ( $\varphi=0$ ).

$$K = \prod a_j^{v_j} = e^{-\left(\frac{\sum (v_j \cdot \mu_j^o)}{R \cdot T}\right)} \quad (21) \text{ Equilibrium (dissociation) coefficient of the chemical reaction}$$

The equilibrium of the diffusion process of the substance ends with the same electrochemical potentials “ $\mu$ ” of the substance in each place of the solution. The same “ $\mu$ ” means the same activity “ $a$ ” of the substance and the same “ $a$ ” means the same mole fraction “ $x$ ” of the substance. So the ideal diffusion ends with homogenous mixture, where the concentration of the substance is the same at each place.

The osmosis is the diffusion of electroneutral ( $z_j=0$ ) substances through semipermeable membrane. It is a membrane, through which some substances can freely diffuse and other cannot. For example the cellular membrane in biology is very selective and even a water must have a membrane channel to be enabled the transport through it. The water cross the membrane to reach the same mole fraction on both sides if there are the same pressure on both side of the membrane. If not, and the pressures are different, then the pressure dependence at equilibrium is reaching osmotic pressure “ $\Pi$ ” of the substance with molar volume “ $V_m$ ” as in equation (22) derived from the equilibrium (19).

$$\Pi = \frac{\mu_{out}^o - \mu_{in}^o}{V_m} = \frac{R \cdot T}{V_m} \ln \left( \frac{a_{in}}{a_{out}} \right) \quad (22) \text{ Osmotic pressure}$$

The other situation is on semipermeable membrane for electrolytes ( $z_j \neq 0$ ), the substances which has an electric charge. Because at steady state the Donnan’s equilibrium is reached as expected, the concentrations of the free diffusible ion can be different on both side of the membrane during this equilibrium. However the electrochemical potentials of this ion is the same on both side of the membrane. This phenomena generate the direct relation between Donnan’s coefficient as ration of ion concentration and membrane potential as difference of electric potentials of the solutions. This equation is known as Nernst potential of the permeable ion and it is the direct result of the equilibration equation (19), where the stoichiometry of the same ion is  $v_{in}=-1$ ,  $v_{out}=1$  and electrochemical potentials of the same ion are  $\mu_{in}$  and  $\mu_{out}$  with the same  $\mu^o$ , temperature  $T$  and activity coefficient  $\gamma$  on both side of the membrane. And the membrane potential is the difference of the electric voltages of the solutions as in equation (23) derived from the equilibrium (19).

$$\varphi = \varphi_{out} - \varphi_{in} = \frac{R \cdot T}{F \cdot z_j} \ln \left( \frac{a_{in}}{a_{out}} \right) \quad (23) \text{ Membrane potential}$$

Gas dissolution in liquids equilibrates the electrochemical potentials between the gaseous and the dissolved substance. This process is called Henry’s law and the ratio between gaseous and dissolved concentration is called Henry’s coefficient “ $k_H$ ”. From the steady state equation (19) is derived the relation between the tabulated Henry’s coefficients as equation (24),  $\mu_g^o$  as chemical potential of the pure gaseous substance and  $\mu_d^o$  as extrapolated chemical potential of the pure dissolved substance.

The same principle is the vaporization of the solvent called Raoult's law (25), where the fraction between liquid dissolved activity  $a_d$  and gaseous form  $a_g = p_{\text{vap}}/p_{\text{air}}$  is also determined by  $\mu_d^0$  of pure liquid and  $\mu_g^0$  of pure vapor of the substance. The last relation from gas dissolution series is dissolution in solid substances called as Sievert's law (26), which is equilibrating a little longer, but the situation at equilibrium is similar.

$$k_H = \frac{a_d}{a_g} = e^{\frac{\mu_g^0 - \mu_d^0}{R \cdot T}} \quad (24) \text{ Henry's coefficient}$$

$$p_{\text{vap}} = p_{\text{air}} \cdot e^{-\left(\frac{\mu_g^0 - \mu_d^0}{R \cdot T}\right)} \cdot a_d \quad (25) \text{ Raoult's vapor pressure}$$

$$k_S = \frac{a_d}{a_g} = e^{\frac{\mu_g^0 - \mu_d^0}{R \cdot T}} \quad (26) \text{ Sieverts' coefficient}$$

As it is known the vaporization is highly dependent on pressure and temperature. The vaporization curve is known as the temperature relationship of vaporization pressure at  $p_{\text{air}} = 100 \text{ kPa}$  and  $a_d = 1$  as equation (25).

### Chemical substance

The most of previous processes are well described at standard temperature of  $25^\circ\text{C}$  and standard pressure of  $100 \text{ kPa}$ . In all equations of equilibrium of the chemical processes as (21), (22), (23), (24), (25) and (26) the measurable coefficients have the meaning of differences between  $\mu^0$ . This means, that only a relative values for  $\mu^0$  is needed to know of equilibriums coefficients. Typically there are selected the substances in their typical phase as reference with  $\mu^0 = 0$  and the other phases and composite substances are relatively defined to these reference substances. These relative  $\mu^0$  values are called free formation molar Gibbs energies of the substances " $\Delta_f G^0$ " and they are typically tabulated at temperature  $T_0 = 25^\circ\text{C}$  and  $p_0 = 100 \text{ kPa}$ . So it is reasonable for these standard conditions to define  $\mu_{25^\circ\text{C}, 1\text{bar}}^0 = \Delta_f G^0$  and  $H_{m, 25^\circ\text{C}, 1\text{bar}} = \Delta_f H^0$ , where " $\Delta_f H^0$ " is the free formation molar enthalpy of the substance as the amount of heat consumed by one mole of the substance during whole formation process from the reference substances. Also the molar entropy  $\Delta_f S^0$  at standard temperatures can be expressed from equation (27). This value is usually not tabulated for the substances and must be really calculated by equation (27). Man must not be confused with the standard molar entropy of the substance, which is an absolute quantity usually noted as " $S^0$ ". However the Hess' law calculation of process entropies should give the same entropy of the chemical process.

$$\Delta_f S^0 = \frac{\Delta_f H^0 - \Delta_f G^0}{T_0} \quad (27) \text{ Free molar entropy of formation at } T_0 = 298.15 \text{ K and } p_0 = 100 \text{ kPa}$$

The enthalpies and the entropies at different pressure and temperature conditions can be easily extended for idealized substances as ideal gas (molar volume  $V_m = R \cdot T/p$ ) or incompressible substance, for which the molar volume  $V_m$  is constant at each temperature and pressure.

$$H_{m,g} = \Delta_f H^0 + c_p \cdot (T - T_0) \quad (28) \text{ Molar enthalpy of the ideal gaseous substance}$$

$$H_{m,s} = \Delta_f H^0 + c_p \cdot (T - T_0) \quad (29) \text{ Molar enthalpy of the incompressible substance}$$

$$S_{m,g} = \Delta_f S^0 + c_p \cdot \ln\left(\frac{T}{T_0}\right) - R \cdot \ln\left(\frac{p}{p_0}\right) \quad (30) \text{ Molar entropy of the ideal gas substance}$$

$$S_{m,s} = \Delta_f S^0 + c_p \cdot \ln\left(\frac{T}{T_0}\right) - \frac{p - p_0}{T} \cdot V_m \quad (31) \text{ Molar entropy of the incompressible substance}$$

$$\mu_g^o = H_{m,g} - T \cdot S_{m,g}$$

(32) Chemical potential of the pure ideal gas substance

$$\mu_s^o = H_{m,s} - T \cdot S_{m,s}$$

(33) Chemical potential of the pure incompressible substance

Where  $c_p$  is molar heat capacity of the substance at constant pressure. The meaning of this substance property is the ratio of heat change per change of temperature in one mole of the substance. If the solution does not exchange any other energy with environment then the heat flow from environment is the same as change of internal energy as equation (3). The change of Gibbs energy is equal to change of temperature multiplied by entropy during isobaric heating as equation (35), which is the direct result of fundamental equation (34) at isobaric heating.

$$\partial U = \partial(G + T \cdot S - p \cdot V) = T \cdot \partial S - p \cdot \partial V$$

(34) Fundamental thermodynamic relation

$$\partial G = \partial p \cdot V - \partial T \cdot S = \partial(H - T \cdot S)$$

(35) Change of Gibbs energy and change of enthalpy as a result of fundamental equation (34)

$$\partial H = T \cdot \partial S + \partial p \cdot V$$

(36) Ideal gas isochoric heating

$$c_v = \frac{1}{n} \left( \frac{\partial U}{\partial T} \right)_{v,n} = T \left( \frac{\partial S_{m,g}}{\partial T} \right)_{v,n}$$

(Molar heat capacity of ideal gas at constant volume and amount of substance)

$$c_p = \left( \frac{\partial H_{m,g}}{\partial T} \right)_{p,n} = T \left( \frac{\partial S_{m,g}}{\partial T} \right)_{p,n}$$

(37) Molar heat capacity of ideal gas at constant pressure

$$c_v = \frac{1}{n} \left( \frac{\partial U}{\partial T} \right)_{v,n} = T \left( \frac{\partial S_{m,s}}{\partial T} \right)_{v,n}$$

(38) Incompressible substance isochoric heating (Molar heat capacity of incompressible at constant volume)

$$c_p = \left( \frac{\partial H_{m,s}}{\partial T} \right)_{p,n} = T \left( \frac{\partial S_{m,s}}{\partial T} \right)_{p,n}$$

(39) Molar heat capacity of incompressible at constant pressure

So the temperature shift of ideal gas is the solution of differential equation  $\partial H_m = \partial T^*(c_p)$  for free molar enthalpy and the differential equation  $T^* \partial S_m = \partial T^*(c_p)$  for free molar entropy. In the case of incompressible substances are the equations  $\partial H_m = \partial T^* c_p$  and  $T^* \partial S_m = \partial T^* c_p$ . These relations give the temperature shifts as presented in (28), (29), (30) and (31) for fixed pressure condition.

If we look at the relation (22) of osmotic pressure of incompressible substance then we see the pressure shift of  $(p-p_0) \cdot V_m$ . By definition this pressure-volume energy is part of the internal energy, but not a part of enthalpy, so it must be included in entropy of the substance as in equation (31).

And if we imagine that the chemical processes of the ideal gas substance are driven only by partial pressure independently of ambient pressure of the whole gaseous solution we need to add a correction shift also to molar entropy of the pure gas, which change the mole fraction of gas to meaning of partial pressure in scale of different pressures of the solutions. Mathematically it is the total pressure of solution “p” is extracted from electrochemical potential defined by equation (32) at 25°C and 0V as following algebraic operation expressed by following equation.

$$\mu_j = \Delta_f G^o + T \cdot R \cdot \ln \left( \frac{p}{p_0} \right) + R \cdot T \cdot \ln \left( \frac{p_j}{p} \right) = \Delta_f G^o + R \cdot T \cdot \ln \left( \frac{p_j}{p_0} \right) \quad (40) \text{ Ideal gas at 25°C}$$

And because the other states of matter should be also consistent with previous theory, there is an option to define any “state of matter” with new calculation of the molar enthalpy, molar entropy, free molar Gibbs energy, molar volume and other base substance properties with any possible dependences on pressure, temperature, electric potential and ionic strength of the solution.

## Chemical kinetics

The rate of chemical process (41) is designed to reach chemical equilibrium (19) ( $\partial n_p = 0$  if and only if  $\sum(v_j \cdot \mu_j) = 0$ ) with possibility of speed turnover. For this purposes are proposed two parameters of kinetics:  $k_C$  and  $k_E$ . The parameter  $k_C$  is describing the speed of the process near equilibrium. The parameter  $k_E$  is describing the shape of dependence on energetic difference from equilibrium.

$$\partial n_p = k_C \left( \sum (v_j \cdot \mu_j) \right) \cdot e^{-k_E |\sum (v_j \cdot \mu_j)|} \quad (41) \text{ Chemical kinetics}$$

The example of parametrization is possible to see in scale of mathematical expression  $u \cdot \exp(-|u|)$  as Figure 1-3, where  $u = \sum(v_j \cdot \mu_j)$  is the process energy difference, red line is "rate= $u$ " and blue line is "rate= $u \cdot \exp(-|u|)$ ".

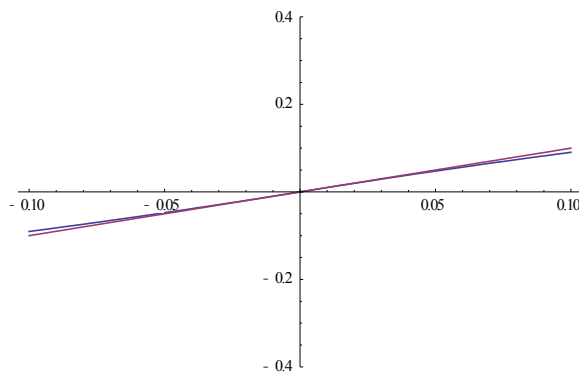


Figure 2) Linear behavior is caused with zero  $k_E$  or process energy difference  $\ll 1/k_E$ .

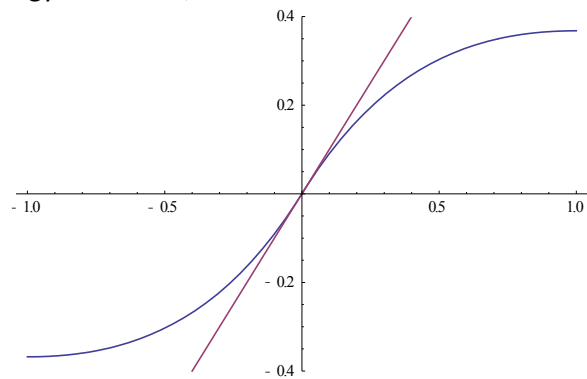


Figure 1) Chemical process has maximal rate at energy difference =  $1/k_E$ .

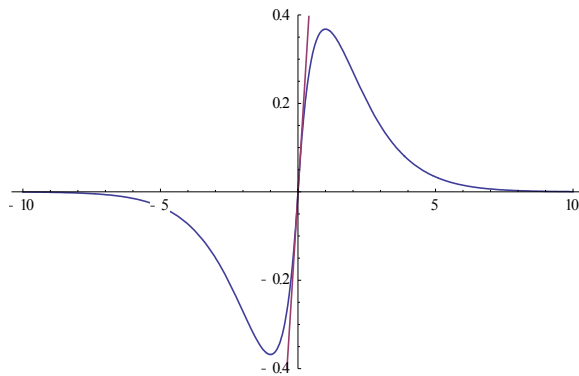


Figure 3) If actual energy difference of the process increases above  $1/k_E$  then the rate rapidly slow down.

This allows to define chemical processes, which need the energy for begin of the process. Typical example is the combustion.