

## Modelica Library of Chemical Processes

(Chemical 2.0)

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### Chemical solution

There are two base components, which should be included in almost all chemical models. The chemical solution and the chemical substance. Chemical solution joins 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 “dQ” and mechanical power of the solution “dW” 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).

$$U = \int (dQ - dW) \quad (3) \text{ Free Internal energy}$$

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

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

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

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

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 “dW” is part of the change of free internal energy of the solution as mentioned in equation (3).

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

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

$$ds = dV/A \quad (10) \text{ Displacement-Volume change relation}$$

Having these equations for solution it is defined through all solution's substances the relation between added heat "dQ" 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 "φ" and electrical current "i". The non-zero electric potential "φ" 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<sub>j</sub>" is the molar amount of j-th substance base molecules, "z<sub>j</sub>" is the charge number of the j-th substance (e.g. -1 for electron, +2 for Ca<sup>2+</sup>), and "F" is the Faraday's constant.

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

Having internal relation between electric potential "φ" 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 redefines 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 makes 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	$dH = \sum dH_j$	$T$ – temperature
$dV_j$ – volumetric flow ; change of volume	$dV = \sum dV_j$	$p$ – pressure
$i_j$ – electric current ; change of charge	$i = \sum i_j$	$\varphi$ - electric potential
$n_j$ – amount of substance particles	$n = \sum n_j$	$n$ – amount of solution
$m_j$ – mass of substance	$m = \sum m_j$	$m$ – mass
$V_j$ – volume of substance	$V = \sum V_j$	$V$ – volume
$G_j$ – free Gibbs energy of substance	$G = \sum G_j$	$G$ – free Gibbs energy
$Q_j$ – electric charge of substance	$Q = \sum Q_j$	$Q$ – electric charge
$I_j$ – mole-fraction based ionic strength of substance	$I = \sum I_j$	$I$ – mole fraction based ionic strength

The properties of the substance as molar mass “MM”, charge number of ion “z”, molar volume “V<sub>m</sub>” or molar enthalpy “H<sub>m</sub>” 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 “dN<sub>j</sub>” into the amount of base molecules of the substance “N<sub>j</sub>” using equation (12). Having the amount of particles of the substance “n<sub>j</sub>” and the amount of solution “n” there is possible to present the mole fraction of the substance in solution “x<sub>j</sub>” as equation (16), which is typically the same as activity of the substance “a<sub>j</sub>” defined by equation (21). However there exist some special cases, when the activity is different. This can be corrected by activity coefficient “γ<sub>j</sub>” different as 1.

$$N_j = \int dN_j \quad (12) \text{ Amount of the substance base molecules}$$

$$m_j = MM \cdot N_j \quad (13) \text{ Mass of the substance}$$

$$n_j \quad (14) \text{ Amount of substance particles}$$

$$n_j \quad (15) \text{ Amount of substance free base molecule}$$

$$x_j = n_j/n \quad (16) \text{ Mole fraction of the substance}$$

$$c_j = n_j/V \quad (17) \text{ Concentration of the substance}$$

$$b_j = n_j/m \quad (18) \text{ Molality of the substance}$$

$$M_j = m_j/V \quad (19) \text{ Mass concentration of the substance}$$

$$X_j = m_j/m \quad (20) \text{ Mass fraction of the substance}$$

$$a_j = \gamma_j \cdot x_j \quad (21) \text{ Activity of the substance}$$

If all molecules of the substance remain in solution alone = unbound in their free separated form, then  $N_j = n_j = n_j$ . However, for some substances the bonds between base molecules are known and affects the composition such as  $N_j > n_j > n_j$ . E.g. water – see ref. Mateják, Marek, and Jiří Kofránek. 2020. “Molar Amount of Water.” Medsoft32 (1): 59.

The main equation of the substance is the definition of electrochemical potential as the fundamental equation of physical chemistry – equation (22), where “μ<sup>o</sup>” is the chemical potential of the pure substance (a<sub>j</sub>=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 (φ=0).

$$\mu_j = \mu_j^o + R \cdot T \cdot \ln(a_j) + F \cdot z_j \cdot \varphi \quad (22) \text{ Electrochemical potential of the substance in the solution}$$

$$\mu_j^o + R \cdot T \cdot \ln(a_j) \quad (23) \text{ Chemical potential of the substance in the solution}$$

$$\mu_j^o \quad (24) \text{ Chemical potential of the pure substance}$$

The chemical potential of the pure substance “μ<sup>o</sup>” 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 “μ” 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	μ – 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 (25), where “ $v_j$ ” is stoichiometry number 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  $v_1=-3$ ,  $v_2=2$ ,  $v_3=4$ ).

$$0 = \sum (v_j \cdot \mu_j) \quad (25) \text{ Chemical equilibrium}$$

$$dn_j = v_j \cdot dn_p \quad (26) \text{ Molar change of the substance}$$

Where at equilibrium each molar flow of the substance “ $dn_j$ ” and molar flow of the process “ $dn_p$ ” is zero.

Each chemical reaction in solution without electric potential ( $\phi=0$ ) reaches the standard equilibrium coefficient “ $K$ ” as equation (27), 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 (27) is mathematically expressed from (22) and (25) at zero electric potential ( $\phi=0$ ).

$$K = \prod a_j^{v_j} = e^{-\left(\frac{\sum (v_j \cdot \mu_j^0)}{R \cdot T}\right)} \quad (27) \text{ Equilibrium (dissociation) coefficient of the chemical reaction}$$

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 (28) derived from the equilibrium (25).

$$\Pi = \frac{\mu_{out}^0 - \mu_{in}^0}{V_m} = \frac{R \cdot T}{V_m} \ln \left( \frac{a_{out}}{a_{in}} \right) \quad (28) \text{ Osmotic pressure}$$

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 (25), 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  $\mu^\circ$ , 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 (29) derived from the equilibrium (25).

$$\varphi = \varphi_{out} - \varphi_{in} = \frac{R \cdot T}{F \cdot z_j} \ln \left( \frac{a_{out}}{a_{in}} \right) \quad (29) \text{ Membrane potential}$$

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 (25) is derived the relation between the tabulated Henry's coefficients as equation (30),  $\mu_g^\circ$  as chemical potential of the pure gaseous substance and  $\mu_d^\circ$  as extrapolated chemical potential of the pure dissolved substance. The same principle is the vaporization of the solvent called Raoult's law (31), where the fraction between liquid dissolved activity  $a_d$  and gaseous form  $a_g = p_{vap}/p_{air}$  is also determined by  $\mu_d^\circ$  of pure liquid and  $\mu_g^\circ$  of pure vapor of the substance. The last relation from gas dissolution series is dissolution in solid substances called as Sievert's law (32), which is equilibrating a little longer, but the situation at equilibrium is similar.

$$k_H = \frac{a_d}{a_g} = e^{\frac{\mu_g^\circ - \mu_d^\circ}{R \cdot T}} \quad (30) \text{ Henry's coefficient}$$

$$p_{vap} = p_{air} \cdot e^{-\left(\frac{\mu_g^\circ - \mu_d^\circ}{R \cdot T}\right)} \cdot a_d \quad (31) \text{ Raoult's vapor pressure}$$

$$k_S = \frac{a_d}{a_g} = e^{\frac{\mu_g^\circ - \mu_d^\circ}{R \cdot T}} \quad (32) \text{ Sieverts' coefficient}$$

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  $p_{air} = 100 \text{ kPa}$  and  $a_d=1$  as equation (31).

## Chemical substance and process definition

Let start with empirical tabulated curve for heat capacity at constant atmospheric pressure dependent on temperature  $T$ :

$$c_p = R \sum_{i=1}^7 a_i T^{i-3} \quad (33) \text{ Molar heat capacity function}$$

(For setting substance to constant heat capacity just set  $a_3 = c_p/R$ ).

Molar heat capacity as function of temperature can be integrated:

$$\int c_p dT \triangleq R \left( -\frac{a_1}{T} + a_2 \ln(T) + \sum_{i=3}^7 a_i \frac{T^{i-2}}{i-2} \right) \quad (34) \text{ Integration of } c_p$$

$$\int \frac{c_p}{T} dT \triangleq R \left( -\frac{a_1}{2T^2} - \frac{a_2}{T} + a_3 \ln(T) + \sum_{i=4}^7 a_i \frac{T^{i-3}}{i-3} \right) \quad (35) \text{ Integration of } c_p/T$$

Now we use relation between molar heat capacity and molar enthalpy or molar entropy at unchanged pressure and unchanged amount of substance:

$$c_p = \left( \frac{\partial H}{\partial T} \right)_{p,n} = T \left( \frac{\partial S}{\partial T} \right)_{p,n} \quad (36) \text{ Relations between molar heat capacity, molar enthalpy and molar entropy}$$

As a result of integration using these relations we can define formation enthalpy, standard entropy and formation entropy of the substance at reference pressure p (Ref: McBride B.J., Zehe M.J., and Gordon S. (2002): NASA Glenn Coefficients for Calculating Thermodynamic Properties of Individual Species. NASA report TP-2002-211556):

$$\Delta_f H = \int c_p dT + F \cdot z_j \cdot \varphi + R \cdot b_1 \quad (37) \text{ Enthalpy of formation}$$

$$S^o = \int \frac{c_p}{T} dT + R \cdot b_2 \quad (38) \text{ Standard entropy}$$

$$\Delta_f S = \int \frac{c_p}{T} dT + c_1 \ln \frac{p}{p_0} + c_2 \frac{p - p_0}{R \cdot T} \cdot V_{m,pure} + R \cdot b_3 \quad (39) \text{ Entropy of formation}$$

Using these definitions, each substance can be defined by 7 coefficients  $a_1 \dots a_7$  and 3 coefficients  $b_1 \dots b_3$ . Coefficients  $a_1 \dots a_7$  are fitting its heat capacity curve. Coefficient  $b_1$  is fitting together with  $a_1 \dots a_7$  enthalpy of formation at defined temperature and pressure. Coefficient  $b_2$  is fitting together with  $a_1 \dots a_7$  standard entropy at defined temperature and pressure. And  $b_3$  is fitting together with  $a_1 \dots a_7$  Gibbs energy of formation at defined temperature and pressure using equation (40). Combination of coefficients  $c_1$  and  $c_2$  reflects entropy-pressure dependence such as phase of the substance. E.g. ideal gases has  $(c_1, c_2) = (1, 0)$  and incompressible substances has  $(c_1, c_2) = (0, 1)$ .

$$\Delta_f S^o = \frac{\Delta_f H^o - \Delta_f G^o}{T_0} \quad (40) \text{ Free molar entropy of formation at } T_0=298.15\text{K and } p_0=100\text{kPa}$$

To allow variable pressure p or variable electrochemical potential  $\varphi$  the substance model must be extended.

$$\mu_{pure} = \Delta_f G = \Delta_f H - T \cdot \Delta_f S \quad (41) \text{ Electro-chemical potential of pure substance}$$

If we look at the relation (28) 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 incompressible substance as in equation (39).

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 using equation (39) at 25°C and 0V as following algebraic operation expressed by equation (40).

$$\mu_{pureIG} = \Delta_f G^o + T \cdot R \cdot \ln\left(\frac{p}{p_0}\right) + R \cdot T \cdot \ln\left(\frac{p_j}{p}\right) = \Delta_f G^o + R \cdot T \cdot \ln\left(\frac{p_j}{p_0}\right) \quad (42) \text{ Chemical potential of ideal gas}$$

If there is a need to set activity coefficient other than 1 then it should be written as exponent of ratio between molar volume excess and molar volume base by following relations:

$$\ln(\gamma) = \frac{V_{m,Excess}}{V_{m,Base}} \quad (43) \text{ Logarithm of activity coefficient}$$

$$V_m = V_{m,Base} + V_{m,Excess} \quad (44) \text{ Molar volume}$$

Where molar volume is molar mass MM per density:

$$\rho = \frac{MM}{V_m} \quad (45) \text{ Density}$$

Having these parameters, we can write substance and process definition as vectors.

$$\mathbb{S} = (a_1, \dots, a_7, b_1, b_2, b_3, c_1, c_2, MM, z, V_{m,Base}, V_{m,Excess}) \quad (46) \text{ Substance definition}$$

$$\mathbb{P} = (\Delta a_1, \dots, \Delta a_7, \Delta b_1, \Delta b_2, \Delta b_3, \Delta c_1, \Delta c_2, \Delta MM, \Delta z, \Delta V_{m,Base}, \Delta V_{m,Excess}) \quad (47) \text{ Process definition}$$

Let assume chemical a reaction example.

$$\mathbb{A} \xleftrightarrow{\mathbb{P}} \mathbb{B} \quad (48) \text{ Chemical reaction example}$$

Then the definition vectors reach following equation:

$$\mathbb{A} + \mathbb{P} = \mathbb{B} \quad (49) \text{ Relation between definitions of example (48)}$$

These definitions can handle also reaction  $\mathbb{P}$  with stoichiometry vector  $v$  (positive for product, negative for reactants) with multiple substrates and reactants as  $\mathbb{S}$  (vector of vectors).

$$\mathbb{P} = \sum_{j=1}^n (v_j \cdot \mathbb{S}_j) \quad (50) \text{ General electro-chemical process between multiple substances}$$

To achieve mass balance of chemical process the process molar mass change  $\Delta MM$  should be zero.

To achieve electric charge balance of chemical process the charge change  $\Delta z$  should be zero.

By definition are these vectors operation linear with additivity and homogeneity properties. Even more the curves (33), (37), (38) and (39) remains smooth and differentiable on temperature. If we know process, we can even evaluate the substrate definition such as (51) from equation (50).

$$\mathbb{S}_1 = \frac{1}{v_1} \left( \mathbb{P} - \sum_{j=2}^n (v_j \cdot \mathbb{S}_j) \right) \quad (51) \text{ Substances definition from process}$$

## Chemical kinetics

Chemical kinetics is using forward rate coefficient  $k_f$  and backward rate coefficient  $k_b$ . Rate of reaction is difference between forward rate and backward rate:

$$q = q_f - q_b \quad (52) \text{ Rate of process}$$

Forward and backward rate definition:

$$q_f = k_f \cdot a_s \quad (53) \text{ Forward rate of process is based on substrates' activity}$$

$$q_b = k_b \cdot a_p \quad (54) \text{ Backward rate of process is based on products' activity}$$

Relation between forward and backward rate coefficient and dissociation constant K:

$$K = \frac{k_f}{k_b} = e^{-\sum_j \left( v_j \cdot \frac{\mu_j^0}{RT} \right)} \quad (55) \text{ Dissociation coefficient of process}$$

$$a_s = \prod_{j \in S} a_j^{-v_j} = e^{\sum_{j \in S} \left( -v_j \cdot \frac{\mu_j - \mu_j^0}{RT} \right)} \quad (56) \text{ Substrates' activity}$$

$$a_p = \prod_{j \in P} a_j^{v_j} = e^{\sum_{j \in P} \left( v_j \cdot \frac{\mu_j - \mu_j^0}{RT} \right)} \quad (57) \text{ Products' activity}$$

The rate of chemical process is algebraically expressed from equations above:

$$q = q_f \cdot \left( 1 - e^{\frac{\Delta\mu}{R \cdot T}} \right) = q_b \cdot \left( e^{\frac{\Delta\mu}{R \cdot T}} - 1 \right) \quad (58) \text{ Rate of process}$$

$$\Delta\mu = \mathbf{v} \cdot \boldsymbol{\mu} \quad (59) \text{ Free molar Gibbs energy of the reaction}$$

Where R is gas constant,  $k_f$  is molar-fraction based forward rate coefficient, T is temperature,  $v_s$  is stoichiometric number of s-th substrate,  $\mu_s^0$  is formation Gibbs energy of s-th substrate plus electric part of electrochemical potential,  $\mu_s$  is electrochemical potential of s-th substrate.

Molar flow of j-th substrate/product is expressed based on its stoichiometry:

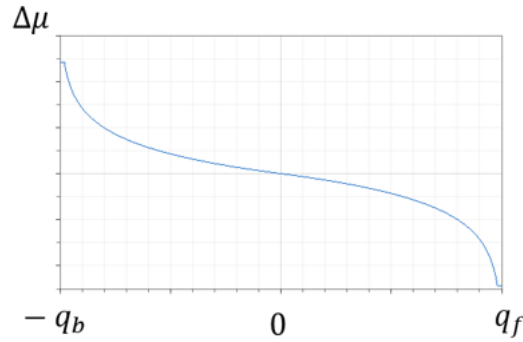
$$q_j = v_j \cdot q \quad (60) \text{ Molar flows of process' substances}$$

Electro-chemical potential loss (Kinetic free molar Gibbs energy of the reaction) as an inverse function from molar flow can be expressed as follows:



$$\Delta\mu = \begin{cases} -R \cdot T \cdot \ln\left(1 + \frac{q}{q_b}\right), & q < 0 \\ R \cdot T \cdot \ln\left(1 - \frac{q}{q_f}\right), & 0 \leq q \end{cases} \quad (61) \text{ Electro-chemical potential loss as inverse process rate function (58)}$$

The process flow  $q$  must be higher than negative backward rate  $-q_b$  and lower than forward rate  $q_f$ . If it is not some limit values of minimal and maximal  $\Delta\mu$  must be set.



Temperature dependence of chemical kinetics can be written using Arrhenius equation using activation energy  $E_a$  and pre-exponential factor  $A$  as parameters:

$$k_f = A \cdot e^{-E_a/(R \cdot T)} \quad (62) \text{ Arrhenius equation}$$

Just for output (e.g. fitting experimental data): Elasticity  $\varepsilon$  of the  $j$ -th substance in process at rate  $q$  and substance activity  $a_j$  is a function of  $q$  and  $a_j$  during constant activities of other substances and constant state of solution.

$$\varepsilon_j = \frac{\partial q}{\partial a_j} \cdot \frac{a_j}{q} = \frac{\partial \ln q}{\partial \ln a_j} \quad (63) \text{ Elasticity of } j\text{-th substance in chemical process with rate } q$$

$$\varepsilon_S = \frac{\partial q}{\partial a_S} \cdot \frac{a_S}{q} = \frac{q_f}{q} = \frac{\partial \ln q}{\partial \ln a_S} \quad (64) \text{ Elasticity of substrates' activity}$$

$$\varepsilon_P = \frac{\partial q}{\partial a_P} \cdot \frac{a_P}{q} = -\frac{q_b}{q} = \frac{\partial \ln q}{\partial \ln a_P} \quad (65) \text{ Elasticity of products' activity}$$

## Chemical inertia

Definition: **Speed of particle**  $v$  [m/s] is as change of position  $ds$  [m] per change of time  $dt$  [s]:

$$v = \frac{ds}{dt} \quad (66) \text{ Speed of particle}$$

$$dv = \frac{\partial v}{\partial s} \cdot ds + \frac{\partial v}{\partial t} \cdot dt \quad (67) \text{ Total derivative of speed}$$

Definition: **Acceleration of the particle**  $a$  [m/s<sup>2</sup>]:

$$a = \frac{dv}{dt} = \frac{\partial v}{\partial s} \cdot v + \frac{\partial v}{\partial t} \quad (68) \text{ Acceleration of the particle}$$

Definition: **Force**  $F$  [N] needed to accelerate particle is a change of its energy  $dG$  [J] per change of its position  $ds$  [m]:

$$F = \frac{dG}{ds} = m \cdot a \quad (69) \text{ Force to accelerate particle}$$

So, we can write it as change of electro-chemical potential  $d\mu$  [J/mol] using molar mass  $MM$  [kg/mol], because it shifts the amount of particles from 1 particle to 1 mol of particles:

$$\frac{d\mu}{ds} = MM \cdot \frac{\partial v}{\partial s} \cdot v + MM \cdot \frac{\partial v}{\partial t} \quad (70) \text{ Molar force to accelerate particle}$$

Definition: **Molar flow**  $q$  [mol/s] in direction of velocity  $v$  [m/s], where  $A_s$  [m<sup>2</sup>] is a cross-section area through which the flow happens and  $V_m$  [m<sup>3</sup>/mol] is a molar volume of the substance:

$$q = v \cdot \frac{A_s}{V_m} \quad (71) \text{ Molar flow}$$

Definition: **Chemical inertia**  $L$  [kg.m<sup>2</sup>/mol<sup>2</sup>]:

$$L = \frac{MM \cdot V_m}{A} \cdot \Delta s \quad (72) \text{ Inertia coefficient}$$

Definition: **Kinetic electro-chemical potential change**  $\Delta\hat{\mu}$  [J/mol] on change of velocity from  $v_2$  to  $v_1$  [m/s].

$$\Delta\hat{\mu} = MM \cdot \frac{v_2^2 - v_1^2}{2} \quad (73) \text{ Kinetic electro-chemical potential change}$$

The equation (70) can be integrated through interval of displacement  $\Delta s$  [m] during unchanged area  $A$ , unchanged molar volume  $V_m$  and fixed flow acceleration  $\overline{\partial q / \partial t}$  [mol/s<sup>2</sup>] on step  $\Delta s$  as:

$$\begin{aligned} \Delta\mu &= \Delta\hat{\mu} + L \cdot \frac{\overline{\partial q}}{\partial t} \\ \frac{\overline{\partial q}}{\partial t} \cdot \Delta s &= \int_{s_1}^{s_2} \frac{\partial q}{\partial t} ds \end{aligned} \quad (74) \text{ from (70)}$$

Definition: **Inertial electro-chemical potential**  $r$  [J/mol]:

$$\Delta r = r_2 - r_1 = L \cdot \frac{\overline{\partial q}}{\partial t} \quad (75) \text{ Inertial electro-chemical potential}$$

So, the equation (74) can be written as:

$$\Delta\mu = \Delta\hat{\mu} + \Delta r \quad (76) \text{ The same as (74)}$$

And this equation is the base of inertial connectors, where values of kinetic potential  $\Delta\hat{\mu}$  [J/mol] are taken as stream inputs and values of inertial potential  $r$  [J/mol] are equal between connected components as effort to change the molar flow in each step of numerical integration.

Definition: **Kinetic molar enthalpy**  $\hat{H}$  and **kinetic molar entropy**  $\hat{S}$ :

$$\hat{H} = \hat{\mu} + T \cdot \hat{S}, \quad (H = \mu + T \cdot S) \quad (77) \text{ Kinetic molar enthalpy}$$

$$\hat{S} = -\frac{\partial \hat{\mu}}{\partial T}, \quad \left( S = -\frac{\partial \mu}{\partial T} \right) \quad (78) \text{ Kinetic molar entropy from (36) and (77)}$$

$$S = \hat{S} - \frac{\partial r}{\partial T} \quad (79) \text{ Relation of kinetic molar entropy from (76) and (78)}$$

$$H = \hat{H} + r - T \cdot \frac{\partial r}{\partial T} \quad (80) \text{ Relation of kinetic molar enthalpy from (77) and (79)}$$

Energy conservation laws at  $k$  nodes connected together:

$$\sum (q_k \cdot \mu_k) = 0, \quad \sum (q_k \cdot H_k) = 0, \quad \sum (q_k \cdot S_k) = 0 \quad (81) \text{ Energy conservation laws}$$

$$\sum (q_k \cdot \hat{\mu}_k) = 0, \quad \sum (q_k \cdot \hat{H}_k) = 0, \quad \sum (q_k \cdot \hat{S}_k) = 0$$

$$\sum (q_k \cdot r_k) = 0, \quad \sum \left( q_k \cdot \frac{\partial r_k}{\partial T} \right) = 0 \quad (82) \text{ Comes from (81)}$$

Mixing flows at k nodes connected nodes together:

$$\begin{aligned} \forall k: \quad L \cdot \text{der}(q_k) &= r_k - r_{k,int} \\ \forall k: \quad \widehat{\mu}_k + r_{k,int} &= \widehat{\mu}_{mix} + r_{mix} \end{aligned} \quad (83) \text{ Inertial connections}$$

$$\widehat{\mu}_{mix} = \frac{\sum(\widehat{\mu}_{in} \cdot q_{in})}{\sum(q_{in})}$$

$$\widehat{H}_{mix} = \frac{\sum(\widehat{H}_{in} \cdot q_{in})}{\sum(q_{in})}$$

$$\widehat{S}_{mix} = \frac{\sum(\widehat{S}_{in} \cdot q_{in})}{\sum(q_{in})}$$

where mixed kinetic electro-chemical potential, enthalpy and entropy is calculated only from inflows. Outflowing connectors are set to  $\widehat{\mu}_{mix}$ ,  $\widehat{H}_{mix}$ ,  $\widehat{S}_{mix}$  and  $r_{mix}$ .

Having defined connectors with flow q and non-flow r and input  $\hat{\mu}$  also each inertial process with stoichiometric numbers  $\nu$  with kinetics function  $\Delta\mu(q, \dots)$  can be described as follows, where k is the substance index:

$$\begin{aligned} \forall k: \quad L \cdot \text{der}(\nu_k \cdot q) &= r_k - r_{k,int} \\ \forall k: \quad \widehat{\mu}_k + r_{k,int} &= \mu_k \end{aligned} \quad (84) \text{ Inertial process with chemical kinetics}$$

$$\nu \cdot \mu = \Delta\mu(q, \quad q_f(\widehat{\mu}_s), \quad q_b(\widehat{\mu}_p), \quad q_{ref})$$