

## Numerical methods

### Amount of the substance

Huge differences between valid concentration values leads to numerical instability of substance accumulation.

$$der(n) = q \quad (1) \text{ Accumulated molar flow of the substance with tolerance based on } n$$

The same mathematical expression of the equation (1) can be designed with substitution of "ln = log(n)":

$$\begin{aligned} der(\ln) &= \frac{q}{n} & (2) \text{ Accumulated molar flow of the substance} \\ n &= e^{\ln} & \text{with tolerance based on } \ln=\log(n) \end{aligned}$$

Expressions (1) and (2) are mathematically the same, but numerically different. Especially, very small concentrations of substances need to have numerical tolerance based on logarithm (2), otherwise ratio between computed value by (1) and correct result can grow up to multiple orders of magnitude. The situations where concentration (mass or amount of substance) fall below typical values of numerical tolerances are in chemistry very common e.g., hormones or equilibria where almost all substrates are converted into products.

Even accumulation in different quantities could lead to the same tolerance. E.g. mass accumulation  $der(m) = q_m$ , where  $m = MM \cdot n$  and MM is molar mass of the substance.

$$\begin{aligned} der(\ln) &= \frac{q_m}{m} = \frac{MM \cdot q}{MM \cdot n} = \frac{q}{n} & (3) \text{ Accumulated mass flow of the substance} \\ m &= MM \cdot e^{\ln} & \text{with the same tolerance based on } \ln=\log(n) \end{aligned}$$

### Chemical inertia of directional flow

As amount of substance also the flows can reach very huge and also very small values.

$$der(q) \cdot L = \Delta r \quad (4) \text{ Chemical inertial acceleration with tolerance based on } q$$

The same mathematical expression of the equation (4) can be designed with substitution  $lq=\log(q)$

$$\begin{aligned} der(lq) &= \frac{\Delta r}{L \cdot q} & (5) \text{ Chemical inertial acceleration with} \\ q &= e^{lq} & \text{tolerance based on } \log(q) \end{aligned}$$

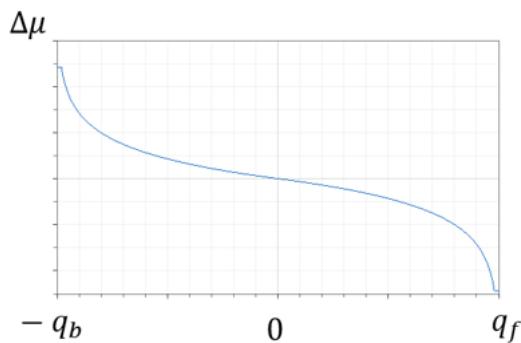
However, the flow must be non-zero and positive. So, the user must define these components as directional allowing flow only in forward direction. As initial value we can't set zero, but a number very close to zero. Default initial  $lq=\log(\text{Modelica.Constants.small})/2$  caused the flow small enough to be unimportant for chemical processes and be still representable until value  $\log(\text{Modelica.Constants.small})$  (e.g. if  $lq = \log(1e-60)/2 = -69$  then  $q = 1e-30 \text{ mol/s}$  with representable limits of  $lq=-138, q=1e-60 \text{ mol/s}$  and  $lq=138, q=1e60 \text{ mol/s}$ ).

Please note that one mole of substance contains  $6.02214076e23$  particles (Avogadro's constant). Having positive flow less than  $1e-30 \text{ mol/s}$  means lower flow than 1 particle per two weeks. And this flow is still representable, significant and inside tolerances of numerical calculation.

### Traditional chemical kinetics limits

If we propose process rate  $q$  as forward rate  $q_f$  minus backward rate  $q_b$ , then the limiting values for molar flow rate are straightforward: from minus backward to plus forward rate. However, reaching (or crossing) one of these limits goes to singularity (or undefined results) of electro-chemical potential gradient if we want to still fulfil kinetics equations. So, we need thresholds, ideally independent of order of magnitude of molar flow. For this reason we define parameter  $C_q$ , where limits will be  $-(1-C_q)q_b$  and  $(1-C_q)q_f$ . Behind this limits the gradient remains constant.

$$\Delta\mu = \begin{cases} -R \cdot T \cdot \ln(C_q), & q < (C_q - 1)q_b \\ -R \cdot T \cdot \ln\left(1 + \frac{q}{q_b}\right), & (C_q - 1)q_b \leq q \leq 0 \\ R \cdot T \cdot \ln\left(1 - \frac{q}{q_f}\right), & 0 \leq q \leq (1 - C_q)q_f \\ R \cdot T \cdot \ln(C_q), & (1 - C_q)q_f < q \end{cases} \quad (6) \text{ Thresholds of electro-chemical potential loss}$$



### Turning the flow in boundaries

The idea of inertial connector is designed for directional flows e.g., between source A and sink B. Inertial potential of A is zero and inertial potential of B is the difference between potential of B and kinetic potential of incoming substance. However, if the flow is near zero then numerical regulation is necessary. To allow different orders of magnitudes for different substances we need also here some scaling. So, the threshold molar flow for this regulation is selected as product of a parameter  $C_n$  with amount of the substance in boundary(source/sink). This does not start to turn even very small molar flows if they are still reasonable in contrast with current amount of the substance. And in the other hand, it also remains reasonable high regulation interval for regular substances in the same simulation.