Numerical methods

Amount of the substance

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

$$der(n) = q$$

(1) 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)":

$$der(ln) = \frac{q}{n}$$
$$n = e^{ln}$$

(2) Accumulated molar flow of the substance with tolerance based on ln=log(n)

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.

$$der(ln) = \frac{q_m}{m} = \frac{MM \cdot q}{MM \cdot n} = \frac{q}{n}$$
$$m = MM \cdot e^{ln}$$

(3) Accumulated mass flow of the substance with the same tolerance based on ln=log(n)

Chemical inertia

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

$$der(q) \cdot L = \Delta r$$

(4) Chemical inertial acceleration with tolerance based on q

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

$$der(lq) = \begin{cases} \dfrac{\Delta r}{L \cdot q}, & |q| > 0 \\ 0, & otherwise \end{cases}$$

(5) Chemical inertial acceleration with tolerance based on log(|q|)

However, direction of the flow must be solved because in contrast with amount of substance it can be also negative. The condition is selected to allow zero crossing at specific cases, if the ratio between flow and its acceleration fall below chosen limit factor (which means huge derivation of lq in direction towards zero flow).

$$q = \begin{cases} e^{lq}, & Q \wedge D \vee Q \wedge C \vee \neg Q \wedge D \wedge \neg C \\ -e^{lq}, & \neg Q \wedge \neg D \vee \neg Q \wedge C \vee Q \wedge I \wedge \neg C \\ 0, & otherwise \end{cases}$$ (6) Accelerated flow

$$Q \equiv (pre(q) \geq 0)$$
$$D \equiv (\Delta r > 0)$$
$$I \equiv (\Delta r < 0)$$
$$C \equiv (|L \cdot pre(q)| > \varepsilon \cdot |\Delta r|)$$
(7) Parts of flow direction condition

Tolerance constant ε must be higher than zero. Setting ε too high increase sensitivity and allows zero crossing even if it is not necessary. The meaning of $1/\varepsilon$ can be described as maximum of $der(lq)$ towards zero flow. E.g. if $\varepsilon = 1e - 5$ then maximum of $der(lq)$ is $1e5$, what means that zero crossing happens if q>=0 and der(q)<=-1e5*q or q<0 and der(q)>=1e5*(-q). Please note, that there is not fixed limit for flow or flow acceleration.