

Modelling dilution using exchange equations in Chemsimul

by P. Bouniol, CEA, Saclay

Sometimes, the kinetic evolution within the solution is accompanied by a volume change of this solution. Neutralization of an alkaline solution by the progressive addition of an acidic solution is a typical example. When the addition rate corresponds to a well defined speed, exchange equations can be used in order to describe the new concentrations of the different species.

For example, let us consider a simple case illustrating the progressive dilution of a saturated lime solution in pure water. The initial hypothesis are the following :

V_0 is the initial volume of pure water (dm^3)

v is the introduction rate of lime solution in pure water (dm^3/s)

$V = v \times t$ is the cumulated volume of lime solution introduced in pure water at the time t (dm^3)

After each dilution, the new concentration of a given species (does not take into account acido-basic modifications) is :

$$[\text{Sp}] = [\text{Sp}]_0 \times \frac{V_0}{V_0 + V} = [\text{Sp}]_0 \times \frac{V_0}{V_0 + v t} \quad (1)$$

Then, the dilution rate can be expressed by :

$$\frac{\partial[\text{Sp}]}{\partial t} = -[\text{Sp}]_0 \times \frac{v V_0}{(V_0 + v t)^2} \quad (2)$$

Combination of equations (1) and (2) give finally :

$$\frac{\partial[\text{Sp}]}{\partial t} = -[\text{Sp}] \times \frac{v}{V_0 + v t} \quad (3)$$

Such an expression in the exchange equation block allows *CHEMSIMUL* to re-actualize the concentration of "Sp" by numerical integration with the other components of the differential system.

In order to describe simultaneously the matter brought (initially, lime is not present in the liquid volume) and the matter dilution, the data file must list the two contributions. Note that derivatives are positive for added species, and negative for diluted species. Note also that in the case of a simple dilution in pure water, the lists of added species and diluted species are identical :

\$ SYMBOLIC CONSTANTS

* Initial volume of pure water (dm^3)

$V_0=0.5$

\$ REFRESHABLE PARAMETERS

* Introduction rate of saturated $\text{Ca}(\text{OH})_2$ solution (dm^3/s)

< $v=0.015\text{E-}3$

* Volume of introduced $\text{Ca}(\text{OH})_2$ solution (dm^3)

< $V=v*\text{TIME}$

\$ EXCHANGE

* CONTINUOUS ADDITION OF SATURATED Ca(OH)₂ SOLUTION AT 25 °C

$$\begin{aligned}d(\text{H}_2\text{O})/dt &= 55.34969072364277 \cdot v / (V_0 + V) \\d(\text{H}_3\text{O}^{+})/dt &= 4.2702434486846523 \text{E-}13 \cdot v / (V_0 + V) \\d(\text{OH}^{-})/dt &= 0.0348741532459836 \cdot v / (V_0 + V) \\d(\text{Ca}^{++})/dt &= 0.01563645668245261 \cdot v / (V_0 + V) \\d(\text{CaOH}^{+})/dt &= 0.0036012398806513687 \cdot v / (V_0 + V) \\d(\text{CaOHOH}[0])/dt &= 0.0009943255002117697 \cdot v / (V_0 + V)\end{aligned}$$

* DILUTION OF THE SPECIES

$$\begin{aligned}d(\text{H}_2\text{O})/dt &= -\text{H}_2\text{O} \cdot v / (V_0 + V) \\d(\text{OH}^{-})/dt &= -\text{OH}^{-} \cdot v / (V_0 + V) \\d(\text{H}_3\text{O}^{+})/dt &= -\text{H}_3\text{O}^{+} \cdot v / (V_0 + V) \\d(\text{Ca}^{++})/dt &= -\text{Ca}^{++} \cdot v / (V_0 + V) \\d(\text{CaOH}^{+})/dt &= -\text{CaOH}^{+} \cdot v / (V_0 + V) \\d(\text{CaOHOH}[0])/dt &= -\text{CaOHOH}[0] \cdot v / (V_0 + V)\end{aligned}$$

The run of the complete data file comprising acido-basic equilibria and ionic strength calculations allows to obtain the new speciation of the calcium during the dilution and also the pH evolution of the solution.

Figure 1 : Evolution of pH during the addition of a saturated Ca(OH)₂ solution in 0.5 dm³ of pure water (25°C).

