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Chemical Akzo Nobel Problem; Mathematical Description and Its SolutionVia Model Maker Software

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Abstract

Akzo Nobel problem describes a chemical process, in which two species, FLB and ZHU, are mixed, while carbon dioxide is continuously added. The resulting species of importance is ZLA. The reaction equations are given by Akzo Nobel as an Initial Value Problem (IVP). This IVP is a stiff system of six non-linear Differential Algebric Equations (DAEs) of index one. In this paper mathematical description of the problem is presented and the results of solving this problem via Model Maker software is illustrated.

1. Introduction

Mathematical modeling play a prominent role in a range of application areas, including biology, chemistry, engineering, epidemiology, microelectronics, economics, and finance [1]. Chemical Akzo Nobel problem describes a chemical process which originates from Akzo Nobel Centeral Research in Arnhem, The Netherlands. The processreactions model is a set of of six non-linear Differential Algebric Equations (DAEs) of index onewhich will be described later.

ModelMakersoftware can be utilized to solve the set of differential equations of Chemical Akzo Nobel problem.ModelMaker software is an ideal modeling environment which is applied in all areas of modeling science: environmental science, chemistry, pharmacokinetics, mathematics and etc. its extensive range of functions allow to model any system continuous

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and discontinuous functions, stiff systems and stochastic systems. This software uses numerical methods to solve differential equations. Using ModelMaker we can solve equations that cannot be solved by analytical methods[2].Kabaei et al modelled migration of radionuclides released as fallout through the food-chain to humans using the ModelMaker software [3]. In another study, a PT(physiological toxicokinetic) model for competitive inhibition of m-xylene metabolism by ethanol in human was investigated using the ModelMaker software [4].

In this study, the Chemical Akzo Nobel problem mathematical model is implemented in ModelMaker software and graphic representation of time variation of the different species present in the system is obtained. The integration method can also be selected, in this case the fourth order Runge–Kutta method was chosen for a modeling time of 180 minutes.

2. Modelling

2.1 Origion of the Problem

Chemical Akzo Nobel problem describes a chemical process which originates from Akzo Nobel Centeral Research in Arnhem, The Netherlands. In the interest of commercial competition, the names of the chemical species are fictitious. At the beginning of the process FLB and ZHU species are present and carbon dioxide is continuously added. These species participate in 5 reactions and various products like ZLA, LB, H2O and Nitrate are produced which ZLA is the main product. These reaction equations, as given by Akzo Nobel, are given in Figure 1. The last reaction equation describes an equilibrium with known equilibrium constant.

$$2\,FLB + 0.5\,CO_2 \xrightarrow{k_1} FLBT + H_2O \qquad (1)$$

$$ZLA + FLB \underset{k_2}{\overset{\overset{k_2}{\overset{\longrightarrow}{K}}}{\longleftarrow}} FLBT + H_2O \qquad (2)$$

$$FLB + 2\,ZHU + CO_2 \xrightarrow{k_3} LB + \text{nitrate} \qquad (3)$$

$$FLB.\text{ZHU} + 0.5\,CO_2 \xrightarrow{k_4} \text{ZLA} + H_2O \qquad (4)$$

$$\text{FLB} + \text{ZHU} \underset{\leftarrow}{\overset{\rightarrow}{}} \text{FLB.ZHU} \qquad (5)$$

Figure 1. Reaction scheme for Chemical Akzo Nobel problem.

The value of$K_s = \frac{[FLB.ZHU]}{[FLB].[ZHU]}$ plays a role in parameter estimation. The other equations describe reactions with ratesgiven by equations 1-5

$$r_1 = k_1.[FLB]^4.[CO_2]^{\frac{1}{2}} \quad (1)$$

$$r_2 = k_2.[FLBT].[ZHU] \quad (2)$$

$$r_3 = \frac{k_2}{K}.[FLB].[ZLA] \quad (3)$$

$$r_4 = k_3.[FLB].[ZHU]^2 \quad (4)$$

$$r_5 = k_4.[FLB.ZHU]^2.[CO_2]^{\frac{1}{2}} \quad (5)$$

respectively. Here the square brackets "[ ]"denote concentrations.The inflow of carbon dioxide per volume unit is denoted by F_{in}, and satisfies

$$F_{in} = klA.\left(\frac{p(CO_2)}{H} - [CO_2]\right) \quad (6)$$

where klA is the mass transfer coeficient, H is the Henry constant and $p(CO_2)$is the partial carbondioxide pressure. $p(CO_2)$is assumed to be independent of $[CO_2]$. The parameters $k_1, k_2, k_3, k_4, K,\ klA, p(CO_2)$, H and $p(CO_2)$are given constants[1].

The process is started by mixing 0.444 mol/liter FLB with 0.007 mol/liter ZHU. The concentrationof carbon dioxide at the beginning is 0.00123 mol/liter. Initially, no other species are present. Thesimulation is performed on the time interval $[0, 180\ minutes]$.Identifying the concentrations [FLB], [CO2], [FLBT], [ZHU], [ZLA], [FLB.ZHU] with $y_1, \dots, y_6$respectively, one easily arrives at the mathematical formulation of the preceding section.

2.2 Mathemathical Description of the Problem

The problem is of the form **[1]**

$$M\frac{dy}{dt} = f(y), y(0) = y_0, y \in \mathbb{R}^6, \qquad 0 \le t \le 180$$

The matrix M is of rank 5 and given by

$$M = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

The function f is defined by

$$f(y) = \begin{bmatrix} -2r_1 + r_2 - r_3 - r_4 \\ -0.5r_1 - r_4 - 0.5r_5 + F_{in} \\ +r_1 - r_2 + r_3 \\ -r_2 + r_3 - 2r_4 \\ +r_2 + r_3 + r_5 \\ K_s.y_1.y_4 - y_6 \end{bmatrix}$$

where the $r_i$and F_{in} are auxiliary variables, given by

$$r_1 = k_1.y_1^4.y_2^{\frac{1}{2}} \quad (7)$$

$$r_2 = k_2.y_3.y_4 \quad (8)$$

$$r_3 = \frac{k_2}{K}.y_1.y_5 \quad (9)$$

$$r_4 = k_3.y_1.y_4^2 \quad (10)$$

$$r_5 = k_4.y_6^2.y_2^{\frac{1}{2}} \quad (11)$$

$$F_{in} = klA.\left(\frac{p(CO_2)}{H} - y_2\right) \quad (12)$$

The values of the parameters $k_1,\ k_2,\ k_3,\ k_4,\ K,\ klA,\ p(CO_2)$ and $H$are

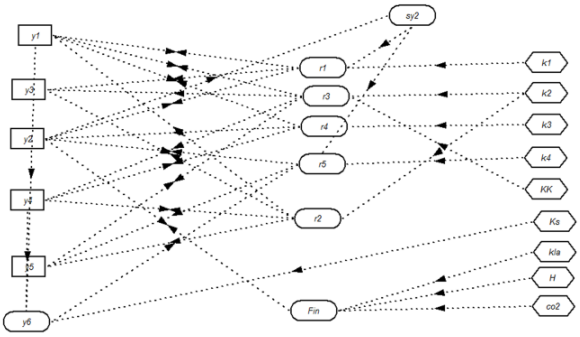
k_1=18.7, k_2=0.58, k_3=0.09, k_4=0.42,

K=34.4,klA=3.3, $p(CO_2)$=0.9, H=737

Finally, the initial vector $y_0$is given by

$$y_0 = (0.437 \quad 0.00123 \quad 0 \quad 0 \quad 0 \quad 0.367)^T.$$

2.3 implementation in ModelMaker softwre



3. Results and Discussion

Figures 2-6 present the behavior of the solution over the integration interval [0, 180 minutes] using ModelMaker software.

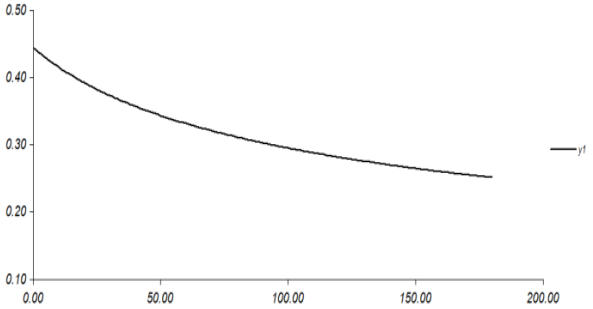


Figure 2. Changes in FLB over the integration interval.

As FLB is a reactant in reations 1-3 and also participates in reaction 5 with relatively high equilibrium constant, its reduction with time could be predicted.

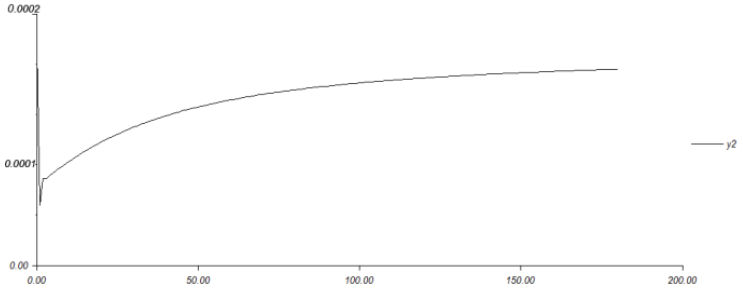


Figure 3. Changes in CO_2 over the integration interval.

CO_2 concentration change is affected by two phenemona, its transfer from gas form with continious inflow of F_i and its consumption in reactions 1, 3 and 5. The term $\frac{d[CO_2]}{dt}$ is expressed as $(-0.5r_1-r_4-0.5r_5+F_{in})$and strongly depends on the concentrations of[FLB], [CO_2], [ZHU], and [FLB.ZHU] which are reducing with time soconsumption rate of CO_2 is decreasing while mass transfer of CO_2 is increasing.

CO_2 concentration play an important role in the amount of mass transfer of CO_2 into liquide phase from its gasous form. the Henry constant and the partial carbondioxide pressure are assumed to be constant parameters.

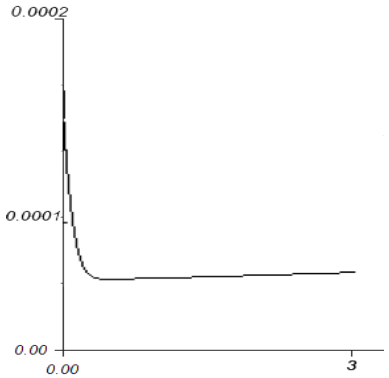


Figure 4. Changes in CO_2over [0-3] minute.

Figuere 4 shows CO_2 concentration change over the [0-3] minute time interval because of its high rate of consumption. AsCO_2 concentration is affected by different mass transfer and kinetic phenomena it has anrelatively complex behavior.

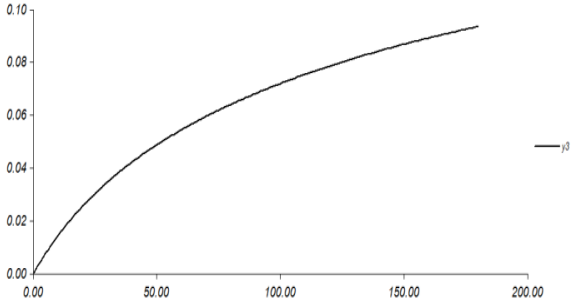


Figure 5. Changes in FLBT over the integration interval.

FLBT species is not present in the medium at first and it is produced through reaction 1. It is also in equilibrium with FLB and ZLA in reaction 2.

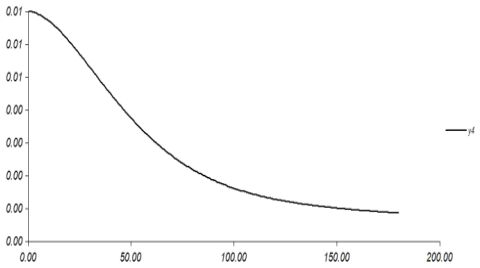


Figure 6. Changes in ZHU over the integration interval.

ZHU is present at the beginning and as shown in figuere 6 it is consumed almost completely in the set of reactions.

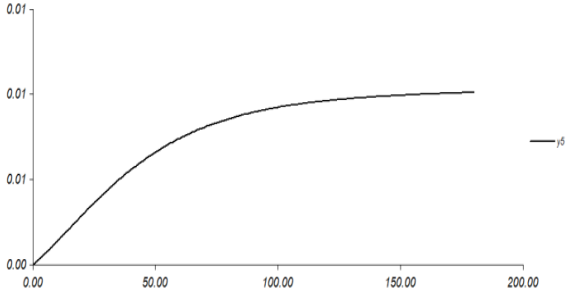


Figure 7. Changes in ZLA over the integration interval.

As noted already, ZLA is the resulting species of importance. Figuere 7 represents that ZLA increases until reaches its steady state value.Therefor there is anegligible change in its concentration after 180 minute and there is no gain in continuing the system.

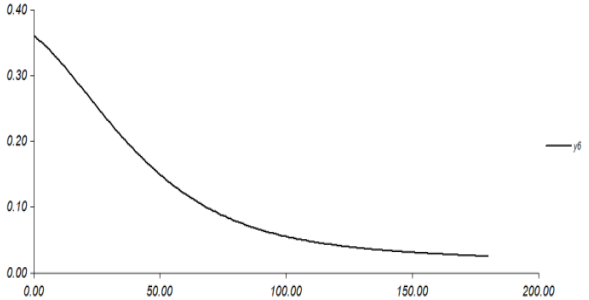


Figure 8. Changes in FLB.ZHU over the integration interval.

FLB.ZHU is in equilibrium with FLB and ZHU. Its concentration decreases according toLe Chatelier's principle while FLB and ZHU are continuously consuming in reactions. Le Chatelier's principle states thatchanging the concentration of an ingredient will shift the equilibrium to the side that would reduce that change in concentration. The chemical system will attempt to partially oppose the change affected to the original state of equilibrium [5].

According to the numerical solution of the chemical Akzo Nobel problem the behavoiur of different species can be predicted. As discussed before, the set of of six non-linear Differential Algebric Equations (DAEs) which describes the process of chemical Akzo Nobel problem is implemented in ModelMaker software and the changes in species concentration

over integration time has been obtained. It must be noted that all of the species in the system reach nearly steady state in 180 minute.

Using ModelMaker software, chemical akzonobel problem can be solved in other cases such as different partial carbondioxide pressure or reactant concentrations and the results can be used in order to find optimum conditions for this process.

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