CHBE 552 PROBLEM SET 5 Assigned: March 1, 2024 Total marks: 15

Prepare a General Purpose Program using the programming language and/or software of your choice in order to implement the Gauss-Newton Method with Marquardt's modification for ODE systems. Marquardt's modification will enable your program to avoid potential convergence problems. You will then use that general purpose program to solve the two problems given below. Solve the third problem using the program you developed for Algebraic systems

Part A: For each problem, report clearly the following:

1. Cast the problem into according to our notation for the relevan vectors and matrices e.g. parameter vector **k**, output vector **y** etc.
2. Give the equations for the elements of the sensitivity (G) matrix.
3. Prepare tables with the following columns (iteration number, value of the objective function, parameter values starting from the initial guess). NOTE: If your program does not converge or it converges with more than 30 iterations then report only the first 30 iterations and the last five that you have recorded (in the non-convergence case).
4. Report the 95 % confidence intervals of the parameters or the standard errors of the parameters
5. Plot calculated versus experimental quantities for each one of the elements of the output vector **y** i.e if you measure two quantities give two plots of these measurements versus their corresponding calculated values based on the optimal parameter estimates.
6. Give a **brief comment** about the performance of your program in each case (problem) e.g. did it converge with zero Marquardt or not? Is the uncertainty of the parameters large or not?

Problem 1. Toluene Hydrogenation. Consider the following reaction scheme

$$A \underset{r_{-1}}{\overset{r_1}{\longleftrightarrow}} B \xrightarrow{r_2} C$$

where A is toluene, B is 1-methyl-cyclohexane, C is methyl-cyclohexane, r_1 is the hydrogenation rate (forward reaction) and r_{-1} the disproportionation rate (backward reaction). Data are available from Belohlav et al. *Can J. Chem. Eng.* 75, 735-742, 1997).

The proposed kinetic model describing the above system is given next (Belohlav et al. 1997):

$$\frac{dC_A}{dt} = -r_1 + r_{-1} \quad ; \quad C_A(0) = 1 \qquad (16.33a)$$

$$\frac{dC_B}{dt} = r_1 - r_{-1} - r_2 \quad ; \quad C_B(0) = 0 \qquad (16.33b)$$

$$\frac{dC_C}{dt} = r_2 \quad ; \quad C_C(0) = 0 \qquad (16.33c)$$

The rate equations are as follows

$$r_1 = \frac{k_H K_A^{rel} C_A}{K_A^{rel} C_A + C_B + K_C^{rel} C_C} \qquad (16.34a)$$

$$r_{-1} = \frac{k_D K_B^{rel} C_B}{K_A^{rel} C_A + C_B + K_C^{rel} C_C} \qquad (16.34b)$$

$$r_2 = \frac{k_2 K_B^{rel} C_B}{K_A^{rel} C_A + C_B + K_C^{rel} C_C} \qquad (16.34c)$$

where C_i (i=A, B, C) are the reactant concentrations and K^{rel} the relative adsorption coefficients. $K_B^{rel} = 1$

The hydrogenation of toluene was performed at ambient temperature and pressure in a semi-batch isothermal stirred reactor with commercial 5% Ru-act catalyst. Hydrogen was automatically added to the system at the same rate at which it was consumed. Particle size of the catalyst used and efficiency of stirring were sufficient for carrying out the reaction in the kinetic regime. Under the experimental conditions validity of Henry's law was assumed.

The data are given below in Table 16.25. You are asked to use the Gauss-Newton method and determine the parameters k_H, k_D, k_2, $K_{A\text{-}rel}$, and $K_{C\text{-}rel}$ as well as their 95% confidence intervals.

For comparison purposes, it is noted that Belohlav et al. (1997) reported the following parameter estimates: k_H=0.023 *min*$^{-1}$, k_D=0.005 *min*$^{-1}$, k_2=0.011 *min*$^{-1}$, $K_{A\text{-}rel}$=1.9, and $K_{C\text{-}rel}$=1.8.

Table 16.25 Data for the Hydrogenation of Toluene

τ (min)	C_A	C_B	C_C
0	1.000	0.000	0.000
15	0.695	0.312	0.001
30	0.492	0.430	0.080
45	0.276	0.575	0.151
60	0.225	0.570	0.195
75	0.163	0.575	0.224
90	0.134	0.533	0.330
120	0.064	0.462	0.471
180	0.056	0.362	0.580
240	0.041	0.211	0.747
320	0.031	0.146	0.822
360	0.022	0.080	0.898
380	0.021	0.070	0.909
400	0.019	0.073	0.908

Problem #2. **Methylester Hydrogenation.** Consider the following reaction scheme

$$A \xrightarrow{r_1} B \xrightarrow{r_2} C \xrightarrow{r_3} D$$

where A, B, C and D are the methyl esters of linolenic, linoleic, oleic and stearic acids and r_1, r_2 and r_3 are the hydrogenation rates. The proposed kinetic model describing the above system is given next (Belohlav et al. 1997).

$$\frac{dC_A}{dt} = -r_1 \quad ; \quad C_A(0) = 0.101 \qquad (16.35a)$$

$$\frac{dC_B}{dt} = r_1 - r_2 \; ; \quad C_B(0) = 0.221 \qquad (16.35b)$$

$$\frac{dC_C}{dt} = r_2 - r_3 \; ; \quad C_C(0) = 0.657 \qquad (16.35c)$$

$$\frac{dC_D}{dt} = r_3 \quad ; \quad C_D(0) = 0.0208 \qquad (16.35d)$$

The rate equations are as follows

$$r_1 = \frac{k_1 K_A^{rel} C_A}{C_A + K_B^{rel} C_B + K_C^{rel} C_C + K_D^{rel} C_D} \qquad (16.36a)$$

$$r_2 = \frac{k_2 K_B^{rel} C_B}{C_A + K_B^{rel} C_B + K_C^{rel} C_C + K_D^{rel} C_D} \qquad (16.36b)$$

$$r_3 = \frac{k_3 K_C^{rel} C_C}{C_A + K_B^{rel} C_B + K_C^{rel} C_C + K_D^{rel} C_D} \qquad (16.36c)$$

Table 16.26 Data for the Hydrogenation of Methylesters

τ (min)	C_A	C_B	C_C	C_D
0	0.1012	0.2210	0.6570	0.0208
10	0.0150	0.1064	0.6941	0.1977
14	0.0044	0.0488	0.6386	0.3058
19	0.0028	0.0242	0.5361	0.4444
24	0.0029	0.0015	0.3956	0.6055
34	0.0017	0.0005	0.2188	0.7808
69	0.0003	0.0004	0.0299	0.9680
124	0.0001	0.0002	0.0001	0.9982

where C_i (i=A, B, C, D) are the reactant concentrations and K_{rel} the relative adsorption coefficients. $K_A^{rel} = 1$. The experiments were performed in an autoclave at elevated pressure and temperature. The Ni catalyst DM2 was used. The data are given in Table 16.26. The objective is to determine the parameters k_1, k_2, k_3, $K_{A\text{-}rel}$, $K_{B\text{-}rel}$, $K_{C\text{-}rel}$, $K_{D\text{-}rel}$ as well as their standard errors. It is noted that $K_{A\text{-}rel}$=1.

Belohlav et al. (1997) reported the following parameter estimates: k_1=1.44 min^{-1}, k_2=0.03 min^{-1}, k_3=0.09 min^{-1}, $K_{B\text{-}rel}$=28.0, $K_{C\text{-}rel}$=1.8 and $K_{D\text{-}rel}$=2.9.

Part B. Prepare a General Purpose Program using the programming language and/or software of your choice in order to implement the Luus-Jaakola Method for ODE systems. You will then use that general purpose program to solve the two problems given above. For each problem you should present and discuss your results and comment about the ability of the method and how it compares with GN.