CHBE 552 PROBLEM SET 4 Assigned: March 1, 2024 Total marks: 15

Part A: 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 Algebraic models. 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.

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): Catalytic De-hydrogenation of sec-butyl Alcohol. Data for the initial reaction rate for the catalytic dehydrogenation of *sec*-butyl alcohol to methyl ethyl ketone are available. The following two models were considered for the initial rate

Model-A

$$r_{Ai} = R - \sqrt{R^2 - k_H^2}$$

where

$$R = k_H + \frac{k_H^2}{2k_R}\frac{(1+K_A p_A)^2}{K_A p_A}$$

Model-B

$$r_{Ai} = \left[(k_H)^{\lambda} + \left(\frac{k_R K_A p_A}{(1+K_A p_A)^2} \right)^{\lambda} \right]^{1/\lambda}$$

where λ=-0.7, K_A is the adsorption equilibrium constant for *sec*-butyl alcohol, k_H is the rate coefficient for the rate of hydrogen desorption controlling, k_R is the rate coefficient for surface reaction controlling, p_A is the partial pressure of *sec*-butyl alcohol.

It is noted that the parameter estimates that have been reported in the literature are given in Tables 1 and 2 below. Use the initial rate data given in Table 3 for the estimation of the parameters (k_R, k_H, and K_A for model-A and model-B) and their 95 % confidence intervals.

Table 1 Parameter Estimates for Model A

Temperature (^oF)	$k_H \times 10^2$ (lbmoles alcohol/(hr lb catalyst)	$k_R \times 10^2$ (lbmoles alcohol/(hr lb catalyst)	$K_A \times 10^2$ (atm^{-1})
575	7.65	23.5	44.4
600	7.89	81.7	53.5

Table 2 Parameter Estimates for Model B

Temperature (^oF)	$k_H \times 10^2$ (lbmoles alcohol/(hr lb catalyst)	$k_R \times 10^2$ (lbmoles alcohol/(hr lb catalyst)	$K_A \times 10^2$ (atm^{-1})
575	11.5	20.2	40.7
600	9.50	62.8	51.5

Table 3 Data for the Catalytic De-hydrogenation of sec-butyl Alcohol

Temperature (^oF)	Pressure (atm)	Feed Rate (lb-moles/hr)	r_{Ai} , Initial Rate lb-moles of alcohol/(hr)(lb-catalyst)
600	1.0	0.01359	0.0392
600	7.0	0.01366	0.0416
600	4.0	0.01394	0.0416
600	10.0	0.01367	0.0326
600	14.6	0.01398	0.0247
600	5.5	0.01389	0.0415
600	8.5	0.01384	0.0376
600	3.0	0.01392	0.0420
600	0.22	0.01362	0.0295
600	1.0	0.01390	0.0410
575	1.0	0.01411	0.0227
575	3.0	0.01400	0.0277
575	5.0	0.01401	0.0255
575	7.0	0.01374	0.0217
575	9.6	0.01342	0.0183

Problem (2): Oxidation of Propylene. The following data given in Table 1 on the oxidation of propylene over bismuth molybdate catalyst were obtained at 350 ^{o}C

Table 1 Data for the Oxidation of Propylene at 350 ^{o}C.

C_p	C_o	n	r_p
3.05	3.07	0.658	2.73
1.37	3.18	0.439	2.86
3.17	1.24	0.452	3.00
3.02	3.85	0.695	2.64
4.31	3.15	0.635	2.60
2.78	3.89	0.670	2.73
3.11	6.48	0.760	2.56
2.96	3.13	0.642	2.69
2.84	3.14	0.665	2.77
1.46	7.93	0.525	2.91
1.38	7.79	0.483	2.87
1.42	8.03	0.522	2.97
1.49	7.78	0.530	2.93
3.01	3.03	0.635	2.75
1.35	8.00	0.480	2.90
1.52	8.22	0.544	2.94
5.95	6.13	0.893	2.38
1.46	8.41	0.517	2.89
5.68	7.75	0.996	2.41
1.36	3.10	0.416	2.81
1.42	1.25	0.367	2.86
3.18	7.89	0.835	2.59
2.87	3.06	0.609	2.76

One model proposed for the rate of propylene disappearance, r_p, as a function of the oxygen concentration, C_o, the propylene concentration, C_p, and the stoichiometric number, n, is

$$r_p = \frac{k_o k_p c_o^{0.5} c_p}{k_o c_o^{0.5} + n k_p c_p}$$

where k_o and k_p are the rate parameters. Determine the parameters and their their 95 % confidence intervals by the Gauss-Newton method. It is noted that the following parameter estimates at 350 ^{o}C were reported: k_o=1,334 (0.081) [(mmol L)$^{0.5}$/(g s)], k_p=0.611(0.055) [(L/g s)]. The numbers in parenthesis are the corresponding standard errors. HINT. Test your program/method against the two numerical examples we discussed in the lecture.

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 Algebraic systems. You will then use that general purpose program to solve the three 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 Gauss Newton.