GAUSS-NEWTON METHOD FOR <u>ODE MODELS</u>[1]

Mathematical models are of the form

$$\frac{d\mathbf{x}(t)}{dt} = \mathbf{f}(\mathbf{x}(t), \mathbf{u}, \mathbf{k}) \quad ; \quad \mathbf{x}(t_0) = \mathbf{x}_0 \qquad (6.1)$$

$$\mathbf{y}(t) = \mathbf{C}\mathbf{x}(t) \qquad (6.2)$$

where

$\mathbf{k}=[k_1,k_2,\ldots,k_p]^T$ is a *p-dimensional* vector of parameters ;

$\mathbf{x}=[x_1,x_2,\ldots,x_n]^T$ is an *n-dimensional* vector of state variables;

$\mathbf{x}_0$ is an *n-dimensional* vector of initial conditions for state variables;

$\mathbf{u}=[u_1,u_2,\ldots,u_r]^T$ is an *r-dimensional* vector of manipulated variables;

$\mathbf{f}=[f_1,f_2,\ldots,f_n]^T$ is a *n-dimensional* vector function of known form);

$\mathbf{y}=[y_1,y_2,\ldots,y_m]^T$ is the *m-dimensional* output vector i.e., the set of variables that are measured experimentally; and

$\mathbf{C}$ is the $m\times n$ observation matrix, which indicates the state variables (or linear combinations of state variables) that are measured experimentally.

Experimental data are available as measurements of the output vector as a function of time, i.e., $[\hat{\mathbf{y}}_i, t_i]$, i=1,…,N. The <u>objective function</u> is

$$S(\mathbf{k})=\sum_{i=1}^{N}[\hat{\mathbf{y}}_i - \mathbf{y}(t_i,\mathbf{k})]^T \mathbf{Q}_i [\hat{\mathbf{y}}_i - \mathbf{y}(t_i,\mathbf{k})] \qquad (6.4)$$

$$S(\mathbf{k}) = \sum_{i=1}^{N} (e_{i1}, e_{i2}, \ldots, e_{im}) \begin{pmatrix} q_1 & & 0 \\ & q_2 \ddots & \\ 0 & & q_m \end{pmatrix} \begin{bmatrix} e_{i1} \\ e_{i2} \\ \vdots \\ e_{im} \end{bmatrix}$$

$$= \sum_{i=1}^{N} \left(q_1 e_{i1}^2 + q_2 e_{i2}^2 + \cdots + q_m \cdot e_{im}^2 \right)$$

The Gauss-Newton method is the most appropriate one for ODE models (Bard, 1970)[2].

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[1] Englezos, P. and N. Kalogerakis, "*Applied Parameter Estimation for Chemical Engineers*", Marcel-Dekker, New York, 2001

[2] Bard, Y., "Comparison of Gradient Methods for the Solution of Nonlinear Parameter Estimation Problems", *SIAM J. Numer. Anal.*, 7, 157-186 (1970).

6.2 THE GAUSS-NEWTON METHOD

An estimate $\mathbf{k}^{(j)}$ is available at the j^{th} iteration. Linearization around $\mathbf{k}^{(j)}$

$$\mathbf{y}(t_i,\mathbf{k}^{(j+1)}) = \mathbf{y}(t_i,\mathbf{k}^{(j)}) + \left(\frac{\partial \mathbf{y}^T}{\partial \mathbf{k}}\right)_i^T \Delta\mathbf{k}^{(j+1)} \quad (6.5)$$

$$\mathbf{y} = \mathbf{C}\mathbf{x} \Rightarrow \quad \mathbf{y}(t_i,\mathbf{k}^{(j+1)}) = \mathbf{C}\mathbf{x}(t_i,\mathbf{k}^{(j)}) + \mathbf{C}\left(\frac{\partial \mathbf{x}^T}{\partial \mathbf{k}}\right)_i^T \Delta\mathbf{k}^{(j+1)} \quad (6.6)$$

The sensitivity matrix $\mathbf{G}(t_i) \equiv (\partial\mathbf{x}^T/\partial\mathbf{k})^T$ is not obtained by simple differentiation. It can be obtained from eq. 6.1 by differentiating both sides with respect to $\mathbf{k}$

$$\frac{\partial}{\partial \mathbf{k}}\left(\frac{d\mathbf{x}}{dt}\right) = \frac{\partial}{\partial \mathbf{k}}\left(\mathbf{f}(\mathbf{x},\mathbf{u},\mathbf{k})\right) \qquad (6.7)$$

Reversing the order of differentiation on the LHS and performing the implicit differentiation of the RHS we obtain the following ($n \times p$) ODEs

$$\frac{d}{dt}\left[\left(\frac{\partial \mathbf{x}^T}{\partial \mathbf{k}}\right)^T\right] = \left(\frac{\partial \mathbf{f}^T}{\partial \mathbf{x}}\right)^T \left(\frac{\partial \mathbf{x}^T}{\partial \mathbf{k}}\right)^T + \left(\frac{\partial \mathbf{f}^T}{\partial \mathbf{k}}\right)^T \qquad (6.8)$$

or

$$\frac{d\mathbf{G}(t)}{dt} = \left(\frac{\partial \mathbf{f}^T}{\partial \mathbf{x}}\right)^T \mathbf{G}(t) + \left(\frac{\partial \mathbf{f}^T}{\partial \mathbf{k}}\right)^T \quad ; \quad \mathbf{G}(t_0) = \mathbf{0}. \qquad (6.9)$$

This is a *matrix differential equation* and represents a set of $n{\times}p$ ODEs. Solution of the above equations enables computation of $\mathbf{y}(t_i,\mathbf{k}^{(j+1)})$.

Substitution of the latter into the objective function and use of the stationary condition $\partial S(\mathbf{k}^{(j+1)})/\partial\mathbf{k}^{(j+1)} = \mathbf{0}$, yields a linear equation for $\Delta\mathbf{k}^{(j+1)}$

$$\mathbf{A}\,\Delta\mathbf{k}^{(j+1)} = \mathbf{b} \qquad (6.11)$$

where

$$\mathbf{A} = \sum_{i=1}^{N} \mathbf{G}^T(t_i)\mathbf{C}^T\mathbf{Q}_i\mathbf{C}\mathbf{G}(t_i) \quad \text{and } \mathbf{b} = \sum_{i=1}^{N} \mathbf{G}^T(t_i)\mathbf{C}^T\mathbf{Q}_i\,[\,\hat{\mathbf{y}}_i - \mathbf{C}\mathbf{x}(t_i,\mathbf{k}^{(j)})] \quad (6.12\text{-}13)$$

Solution of the above equation yields $\Delta\mathbf{k}^{(j+1)}$ and hence, $\mathbf{k}^{(j+1)}$ is obtained from

$$\mathbf{k}^{(j+1)} = \mathbf{k}^{(j)} + \mu\Delta\mathbf{k}^{(j+1)} \qquad (6.14)$$

where μ is a stepping parameter $(0<\mu\leq 1)$ to be determined by the bisection rule.

Thus, a sequence of parameter estimates is generated, $\mathbf{k}^{(1)}$, $\mathbf{k}^{(2)}$,… which often converges to the optimum, $\mathbf{k}^*$, if the initial guess, $\mathbf{k}^{(0)}$, is sufficiently close.

6.2.1 Gauss-Newton Algorithm for ODE Models

1. Input the initial guess for the parameters, $\mathbf{k}^{(0)}$ and NSIG.
2. For j=0,1, 2,…, repeat.
3. **Integrate state** and **sensitivity equations** to obtain $\mathbf{x}(t)$ and $\mathbf{G}(t)$. At each sampling period, t_i, i=1,…,N compute $\mathbf{y}(t_i,k^{(j)})$, and $\mathbf{G}(t_i)$ to set up matrix $\mathbf{A}$ and vector $\mathbf{b}$.
4. Solve the linear equation $\mathbf{A}\Delta\mathbf{k}^{(j+1)}=\mathbf{b}$ and obtain $\Delta\mathbf{k}^{(j+1)}$.
5. Determine μ using the bisection rule and obtain $\mathbf{k}^{(j+1)}=\mathbf{k}^{(j)}+\mu\Delta\mathbf{k}^{(j+1)}$.
6. Continue until the maximum number of iterations is reached or convergence is achieved (i.e., $\frac{1}{p}\sum_{i=1}^{p}\left|\frac{\Delta k_i^{(j+1)}}{k_i^{(j)}}\right| \leq 10^{-NSIG}$).
7. Compute statistical properties of parameter estimates

NOTE

$\mathbf{G}$(t) can be re-written as

$$\mathbf{G}(t) \equiv \left(\frac{\partial \mathbf{x}^T}{\partial \mathbf{k}}\right)^T = \left[\left(\frac{\partial \mathbf{x}}{\partial k_1}\right), \left(\frac{\partial \mathbf{x}}{\partial k_2}\right), \ldots, \left(\frac{\partial \mathbf{x}}{\partial k_p}\right)\right] = [\mathbf{g}_1, \mathbf{g}_2, \ldots, \mathbf{g}_p] \quad (6.15)$$

In this case the *n-dimensional* vector $\mathbf{g}_1$ represents the sensitivity coefficients of the state variables with respect to parameter k_1 and satisfies the following ODE,

$$\frac{d\mathbf{g}_1(t)}{dt} = \left(\frac{\partial \mathbf{f}^T}{\partial \mathbf{x}}\right)^T \mathbf{g}_1(t) + \left(\frac{\partial \mathbf{f}}{\partial k_1}\right) \; ; \quad \mathbf{g}_1(t_0)=\mathbf{0} \qquad (6.16a)$$

Similarly, the *n-dimensional* vector $\mathbf{g}_2$ represents the sensitivity coefficients of the state variables with respect to parameter k_2 and satisfies the following ODE,

$$\frac{d\mathbf{g}_2(t)}{dt} = \left(\frac{\partial \mathbf{f}^T}{\partial \mathbf{x}}\right)^T \mathbf{g}_2(t) + \left(\frac{\partial \mathbf{f}}{\partial k_2}\right) \; ; \quad \mathbf{g}_2(t_0)=\mathbf{0} \qquad (6.16b)$$

Finally for the last parameter, k_p, we have the corresponding sensitivity vector $\mathbf{g}_p$

$$\frac{d\mathbf{g}_p(t)}{dt} = \left(\frac{\partial \mathbf{f}^T}{\partial \mathbf{x}}\right)^T \mathbf{g}_p(t) + \left(\frac{\partial \mathbf{f}}{\partial k_p}\right) \; ; \quad \mathbf{g}_p(t_0)=\mathbf{0} \qquad (6.16c)$$

EXAMPLES

6.5.1 A Homogeneous Gas Phase Reaction. Estimate rate constants k_1 and k_2 for the reaction of NO with O_2: $2NO + O_2 \longleftrightarrow 2NO_2$

$$\frac{dx}{dt} = k_1(\alpha - x)(\beta - x)^2 - k_2x^2 \quad ; \quad x(0) = 0 \quad (6.45)$$

where α=126.2, β=91.9 and x is the concentration of NO_2. The concentration of NO_2 was measured experimentally as a function of time.

The model is of the form $dx/dt=f(x,k_1,k_2)$ where $f(x,k_1,k_2)=k_1(\alpha-x)(\beta-x)^2-k_2x^2$. The single state variable x is also the measured variable (i.e., y(t)=x(t)). The sensitivity matrix, **G**(t), is a *(1×2)-dimensional* matrix with elements:

$$\mathbf{G}(t) = \left[G_1(t),\ G_2(t)\right] = \left[\left(\frac{\partial x}{\partial k_1}\right), \left(\frac{\partial x}{\partial k_2}\right)\right] \quad (6.46)$$

In this case, Equation 6.16 simply becomes,

$$\frac{dG_1}{dt} = \left(\frac{\partial f}{\partial x}\right)G_1 + \left(\frac{\partial f}{\partial k_1}\right) \quad ; \quad G_1(0) = 0 \quad (6.47a)$$

and similarly for $G_2(t)$,

$$\frac{dG_2}{dt} = \left(\frac{\partial f}{\partial x}\right)G_2 + \left(\frac{\partial f}{\partial k_2}\right) \quad ; \quad G_2(0) = 0 \quad (6.47b)$$

where

$$\left(\frac{\partial f}{\partial x}\right) = -k_1(\beta-x)^2 - 2k_1(\alpha-x)(\beta-x) - 2k_2x \quad (6.48a)$$

$$\left(\frac{\partial f}{\partial k_1}\right) = (\alpha-x)(\beta-x)^2 \quad (6.48b)$$

$$\left(\frac{\partial f}{\partial k_2}\right) = -x^2 \quad (6.48c)$$

Eqns 6.47a and 6.47b should be solved simultaneously with the state equation (Eq. 6.45).

6.5.2 Pyrolytic Dehydrogenation of Benzene to Diphenyl and Triphenyl[3]

Reactions:

$$2C_6H_6 \longleftrightarrow C_{12}H_{10} + H_2$$
$$C_6H_6 + C_{12}H_{10} \longleftrightarrow C_{10}H_{14} + H_2$$

Kinetic model:

$$\frac{dx_1}{dt} = -r_1 - r_2 \quad (6.50a)$$

$$\frac{dx_2}{dt} = \frac{r_1}{2} - r_2 \quad (6.50b)$$

where

$$r_1 = k_1\left[x_1^2 - x_2(2-2x_1-x_2)/3K_1\right] \quad (6.51a)$$

$$r_2 = k_2\left[x_1x_2 - (1-x_1-2x_2)(2-2x_1-x_2)/9K_2\right] \quad (6.51b)$$

where

x_1 *lb-mole* of benzene per *lb-mole* of pure benzene feed
x_2 denotes *lb-mole* of diphenyl per *lb-mole* of pure benzene feed.

The parameters k_1 and k_2 are unknown *reaction rate constants* whereas K_1=0.242 and K_2 = 0.428 are *equilibrium constants*.

Table 6.2. Data for the Pyrolytic Dehydrogenation of Benzene

Reciprocal Space Velocity (t) × 10^4	x_1	x_2
5.63	0.828	0.0737
11.32	0.704	0.113
16.97	0.622	0.1322
22.62	0.565	0.1400
34.0	0.499	0.1468
39.7	0.482	0.1477
45.2	0.470	0.1477
169.7	0.443	0.1476

[3] Hougen, O., and K.M. Watson, *Chemical Process Principles*, Vol. 3, J. Wiley, New York, NY, 1948. Seinfeld, J.H., and G.R. Gavalas, *AIChE J.*, 16, 644-647 (1970).

As both state variables are measured, the output vector is the same with the state vector, i.e., $y_1=x_1$ and $y_2=x_2$. The feed to the reactor was pure benzene.

Using our standard notation

$$\frac{dx_1}{dt} = f_1(x_1, x_2; k_1, k_2) \qquad (6.52a)$$

$$\frac{dx_2}{dt} = f_2(x_1, x_2, k_1, k_2) \qquad (6.52b)$$

where $f_1=(-r_1-r_2)$ and $f_2=r_1/2-r_2$.

The sensitivity matrix, $\mathbf{G}(t)$, is a *(2x2)-dimensional* matrix with elements:

$$\mathbf{G}(t) = [\mathbf{g}_1(t), \mathbf{g}_2(t)] = \left[\left(\frac{\partial \mathbf{x}}{\partial k_1}\right), \left(\frac{\partial \mathbf{x}}{\partial k_2}\right)\right] =$$

$$\begin{bmatrix} G_{11}(t) & G_{12}(t) \\ G_{21}(t) & G_{22}(t) \end{bmatrix} = \begin{bmatrix} \left(\frac{\partial x_1}{\partial k_1}\right) & \left(\frac{\partial x_1}{\partial k_2}\right) \\ \left(\frac{\partial x_2}{\partial k_1}\right) & \left(\frac{\partial x_2}{\partial k_2}\right) \end{bmatrix} \qquad (6.53)$$

Equations 6.16 then become,

$$\frac{d\mathbf{g}_1(t)}{dt} = \left(\frac{\partial \mathbf{f}^T}{\partial \mathbf{x}}\right)^T \mathbf{g}_1(t) + \left(\frac{\partial \mathbf{f}}{\partial k_1}\right); \qquad \mathbf{g}_1(t_0)=\mathbf{0} \qquad (6.54a)$$

and

$$\frac{d\mathbf{g}_2(t)}{dt} = \left(\frac{\partial \mathbf{f}^T}{\partial \mathbf{x}}\right)^T \mathbf{g}_2(t) + \left(\frac{\partial \mathbf{f}}{\partial k_2}\right); \qquad \mathbf{g}_2(t_0)=\mathbf{0} \qquad (6.54b)$$

Taking into account Equation 6.53

$$\begin{bmatrix} \frac{dG_{11}}{dt} \\ \frac{dG_{21}}{dt} \end{bmatrix} = \begin{bmatrix} \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} \\ \frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} \end{bmatrix} \begin{bmatrix} G_{11} \\ G_{21} \end{bmatrix} + \begin{bmatrix} \frac{\partial f_1}{\partial k_1} \\ \frac{\partial f_2}{\partial k_1} \end{bmatrix}; \quad G_{11}(t_0)=0,\ G_{21}(t_0)=0 \qquad (6.55a)$$

and

$$\begin{bmatrix} \dfrac{dG_{12}}{dt} \\ \dfrac{dG_{22}}{dt} \end{bmatrix} = \begin{bmatrix} \dfrac{\partial f_1}{\partial x_1} & \dfrac{\partial f_1}{\partial x_2} \\ \dfrac{\partial f_2}{\partial x_1} & \dfrac{\partial f_2}{\partial x_2} \end{bmatrix} \begin{bmatrix} G_{12} \\ G_{22} \end{bmatrix} + \begin{bmatrix} \dfrac{\partial f_1}{\partial k_2} \\ \dfrac{\partial f_2}{\partial k_2} \end{bmatrix} \quad ; \quad G_{21}(t_0)=0,\ G_{22}(t_0)=0 \quad (6.55b)$$

Finally, we obtain the following equations

$$\frac{dG_{11}}{dt} = \left(\frac{\partial f_1}{\partial x_1}\right)G_{11} + \left(\frac{\partial f_1}{\partial x_2}\right)G_{21} + \frac{\partial f_1}{\partial k_1} \quad ; \quad G_{11}(0)=0 \qquad (6.56a)$$

$$\frac{dG_{21}}{dt} = \left(\frac{\partial f_2}{\partial x_1}\right)G_{11} + \left(\frac{\partial f_2}{\partial x_2}\right)G_{21} + \frac{\partial f_2}{\partial k_1} \quad ; \quad G_{21}(0)=0 \qquad (6.56b)$$

$$\frac{dG_{12}}{dt} = \left(\frac{\partial f_1}{\partial x_1}\right)G_{12} + \left(\frac{\partial f_1}{\partial x_2}\right)G_{22} + \frac{\partial f_1}{\partial k_2} \quad ; \quad G_{12}(0)=0 \qquad (6.56c)$$

$$\frac{dG_{22}}{dt} = \left(\frac{\partial f_2}{\partial x_1}\right)G_{12} + \left(\frac{\partial f_2}{\partial x_2}\right)G_{22} + \frac{\partial f_2}{\partial k_2} \quad ; \quad G_{22}(0)=0 \qquad (6.56d)$$

where

$$\left(\frac{\partial f_1}{\partial x_1}\right) = -k_1\left(2x_1 + \frac{2x_2}{3K_1}\right) - k_2\left(x_2 - \frac{1}{9K_2}(4x_1 - 4 + 5x_2)\right) \qquad (6.57a)$$

$$\left(\frac{\partial f_1}{\partial x_2}\right) = -k_1\left(\frac{1}{3K_1}(2x_2 + 2x_1 - 2)\right) - k_2\left(x_1 - \frac{1}{9K_2}(5x_1 - 5 + 4x_2)\right) \qquad (6.57b)$$

$$\left(\frac{\partial f_2}{\partial x_1}\right) = \frac{k_1}{2}\left(2x_1 + \frac{2x_2}{3K_1}\right) - k_2\left(x_2 - \frac{1}{9K_2}(4x_1 - 4 + 5x_2)\right) \qquad (6.57c)$$

$$\left(\frac{\partial f_2}{\partial x_2}\right) = \frac{k_1}{2}\left(\frac{1}{3K_1}(2x_2 + 2x_1 - 2)\right) - k_2\left(x_1 - \frac{1}{9K_2}(5x_1 + 4x_2 - 5)\right) \qquad (6.57d)$$

$$\left(\frac{\partial f_1}{\partial k_1}\right) = -\left[x_1^2 + \frac{1}{3K_1}\left(x_2^2 + 2x_1x_2 - 2x_2\right)\right] \qquad (6.57e)$$

$$\left(\frac{\partial f_2}{\partial k_1}\right) = \frac{1}{2}\left[x_1^2 + \frac{1}{3K_1}\left(x_2^2 + 2x_1x_2 - 2x_2\right)\right] \qquad (6.57f)$$

$$\left(\frac{\partial f_1}{\partial k_2}\right) = -\left[x_1x_2 - \frac{1}{9K_2}\left(2x_1^2 - 4x_1 + 5x_1x_2 - 5x_2 + 2x_2^2 + 2\right)\right] \qquad (6.57g)$$

$$\left(\frac{\partial f_2}{\partial k_2}\right) = -\left[x_1x_2 - \frac{1}{9K_2}\left(2x_1^2 - 4x_1 + 5x_1x_2 - 5x_2 + 2x_2^2 + 2\right)\right] \qquad (6.57h)$$

Solution of the two *state equations* (6.52) and the four *sensitivity equations* (Equations 6.56a-d) yields **x**(t) and **G**(t) which are used in setting up matrix **A** and vector **b** at each iteration of the Gauss-Newton method.

The ordinary differential equation that a particular element, G_{ij}, of the (*nxp*)-*dimensional* sensitivity matrix satisfies, can be written directly using the following expression,

$$\frac{dG_{ij}}{dt} \equiv \frac{d}{dt}\left(\frac{\partial x_i}{\partial k_j}\right) = \sum_{k=1}^{n}\left(\frac{\partial f_i}{\partial x_k}\right)\left(\frac{\partial x_k}{\partial k_j}\right) + \frac{\partial f_i}{\partial k_j} \equiv \sum_{k=1}^{n}\left(\frac{\partial f_i}{\partial x_k}\right)G_{kj} + \frac{\partial f_i}{\partial k_j} \qquad (6.58)$$

NOTE: USE THIS SENSITIVITY EQUATION INSTEAD OF 6.16

6.5.3 Catalytic Hydrogenation of 3-Hydroxypropanal (HPA) to 1,3-Propanediol (PD)[4]

Model:
$$\frac{dC_{HPA}}{dt} = -[r_1 + r_2]C_k - [r_3 + r_4 - r_{-3}] \qquad (6.59a)$$

$$\frac{dC_{PD}}{dt} = [r_1 - r_2]C_k \qquad (6.59b)$$

$$\frac{dC_{Ac}}{dt} = r_3 - r_4 - r_{-3} \qquad (6.59c)$$

where C_k is the concentration of the catalyst (10 *g/L*) and the reaction rates are

$$r_1 = \frac{k_1 P C_{HPA}}{H\left[1 + \left(\frac{K_1 P}{H}\right)^{0.5} + K_2 C_{HPA}\right]^3} \qquad (6.60a)$$

$$r_2 = \frac{k_2 C_{PD} C_{HPA}}{1 + \left(\frac{K_1 P}{H}\right)^{0.5} + K_2 C_{HPA}} \qquad (6.60b)$$

$$r_3 = k_3 C_{HPA} \qquad (6.60c)$$

$$r_{-3} = k_{-3} C_{Ac} \qquad (6.60d)$$

$$r_4 = k_4 C_{Ac} C_{HPA} \qquad (6.60e)$$

where

k_j (j=1, 2, 3, -3, 4) are rate constants *(L/(mol min g)*
K_1 and K_2 are the adsorption equilibrium constants *(L/mol)* for H_2 and HPA respectively
P is the hydrogen pressure *(MPa)* in the reactor
H is the Henry's law constant = 1379 *(L bar/mol)* at 298 *K*.

These are the seven model parameters (k_1, k_2, k_3, k_{-3}, k_4, K_1 and K_2) to be determined from the measured concentrations of HPA and PD.

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[4] Zhu, X. D., G. Valerius, and H. Hofmann, , *Ind. Eng. Chem. Res*, 36, 3897-2902 (1997).

Table 6.3Data for the Catalytic Hydrogenation of 3-Hydroxypropanal (HPA) to 1,3-Propanediol (PD) at 5.15 MPa and 45℃

t (*min*)	C_{HPA} (*mol/L*)	C_{PD} (*mol/L*)
0.0	1.34953	0.0
10	1.36324	0.00262812
20	1.25882	0.0700394
30	1.17918	0.184363
40	0.972102	0.354008
50	0.825203	0.469777
60	0.697109	0.607359
80	0.421451	0.852431
100	0.232296	1.03535
120	0.128095	1.16413
140	0.0289817	1.30053
160	0.00962368	1.31971

Table 6.4Data for the Catalytic Hydrogenation of 3-Hydroxypropanal (HPA) to 1,3-Propanediol (PD) at 5.15 Mpa and 80℃

t (*min*)	C_{HPA} (*mol/L*)	C_{PD} (*mol/L*)
0.0	1.34953	0.0
5	0.873513	0.388568
10	0.44727	0.816032
15	0.140925	0.967017
20	0.0350076	1.05125
25	0.0130859	1.08239
30	0.00581597	1.12024

In order to use our standard notation we introduce the following vectors:

$$\mathbf{x} = [x_1, x_2, x_3]^T = [C_{HPA}, C_{PD}, C_{Ac}]^T$$

$$\mathbf{k} = [k_1, k_2, k_3, k_4, k_5, k_6, k_7]^T = [k_1, k_2, k_3, k_{-3}, k_4, K_1, K_2]^T$$

$$\mathbf{y} = [y_1, y_2]^T = [C_{HPA}, C_{PD}]^T$$

Hence, the differential equation model takes the form,

$$\frac{dx_1}{dt} = f_1(x_1, x_2, x_3; k_1, k_2, \ldots, k_7; u_1, u_2) \qquad (6.61a)$$

$$\frac{dx_2}{dt} = f_2(x_1, x_2, x_3; k_1, k_2, ..., k_7; u_1, u_2) \qquad (6.61b)$$

$$\frac{dx_3}{dt} = f_3(x_1, x_2, x_3; k_1, k_2, ..., k_7; u_1, u_2) \qquad (6.61c)$$

and the *observation matrix* is

$$\mathbf{C} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \qquad (6.62)$$

In Eqns 6.61

u_1 is the concentration of catalyst present in the reactor (C_k)

u_2 the hydrogen pressure (P).

Equations 6.61 are rewritten as following

$$\frac{dx_1}{dt} = -u_1(r_1+r_2)-(k_3x_1+k_5x_3x_1-k_4x_3) \qquad (6.63a)$$

$$\frac{dx_2}{dt} = u_1(r_1-r_2) \qquad (6.63b)$$

$$\frac{dx_3}{dt} = (k_3x_1-k_5x_3x_1-k_4x_3) \qquad (6.63c)$$

where

$$r_1 = \frac{k_1 u_2 x_1}{H\left[1+\left(\frac{k_6 u_2}{H}\right)^{0.5} + k_7 x_1\right]^3} \qquad (6.64a)$$

$$r_2 = \frac{k_2 x_2 x_1}{1+\left(\frac{k_6 u_2}{H}\right)^{0.5} + k_7 x_1} \qquad (6.64b)$$

$$r_3 = k_3 x_1 \qquad (6.64c)$$

$$r_{-3} = k_4 x_3 \qquad (6.64d)$$

$$r_4 = k_5 x_3 x_1 \qquad (6.64e)$$

The sensitivity matrix, $\mathbf{G}(t)$, is a (3×7)*-dimensional* matrix with elements:

$$\mathbf{G}(t) = [\mathbf{g}_1(t), \mathbf{g}_2(t), ..., \mathbf{g}_7(t)] = \left[\left(\frac{\partial \mathbf{x}}{\partial k_1}\right), \left(\frac{\partial \mathbf{x}}{\partial k_2}\right), ..., \left(\frac{\partial \mathbf{x}}{\partial k_7}\right)\right] \qquad (6.65a)$$

$$\mathbf{G}(t) = \begin{bmatrix} G_{11}(t) & . & . & . & G_{17}(t) \\ G_{21}(t) & . & . & . & G_{27}(t) \\ G_{31}(t) & . & . & . & G_{37}(t) \end{bmatrix} = \begin{bmatrix} \left(\frac{\partial x_1}{\partial k_1}\right) & . & . & . & \left(\frac{\partial x_1}{\partial k_7}\right) \\ \left(\frac{\partial x_2}{\partial k_1}\right) & . & . & . & \left(\frac{\partial x_2}{\partial k_7}\right) \\ \left(\frac{\partial x_3}{\partial k_1}\right) & . & . & . & \left(\frac{\partial x_3}{\partial k_7}\right) \end{bmatrix} \tag{6.65b}$$

Eqns 6.16 then become,

$$\frac{d\mathbf{g}_1(t)}{dt} = \left(\frac{\partial \mathbf{f}^T}{\partial \mathbf{x}}\right)^T \mathbf{g}_1(t) + \left(\frac{\partial \mathbf{f}}{\partial k_1}\right) \quad ; \mathbf{g}_1(t_0)=\mathbf{0} \tag{6.66a}$$

$$\frac{d\mathbf{g}_2(t)}{dt} = \left(\frac{\partial \mathbf{f}^T}{\partial \mathbf{x}}\right)^T \mathbf{g}_2(t) + \left(\frac{\partial \mathbf{f}}{\partial k_2}\right); \ \mathbf{g}_2(t_0)=\mathbf{0} \tag{6.66b}$$

$$\vdots$$

$$\frac{d\mathbf{g}_7(t)}{dt} = \left(\frac{\partial \mathbf{f}^T}{\partial \mathbf{x}}\right)^T \mathbf{g}_7(t) + \left(\frac{\partial \mathbf{f}}{\partial k_7}\right); \ \mathbf{g}_7(t_0)=\mathbf{0} \tag{6.66c}$$

where

$$\left(\frac{\partial \mathbf{f}^T}{\partial \mathbf{x}}\right)^T = \begin{bmatrix} \left(\frac{\partial f_1}{\partial x_1}\right) & \left(\frac{\partial f_1}{\partial x_2}\right) & \left(\frac{\partial f_1}{\partial x_3}\right) \\ \left(\frac{\partial f_2}{\partial x_1}\right) & \left(\frac{\partial f_2}{\partial x_2}\right) & \left(\frac{\partial f_2}{\partial x_3}\right) \\ \left(\frac{\partial f_3}{\partial x_1}\right) & \left(\frac{\partial f_3}{\partial x_2}\right) & \left(\frac{\partial f_3}{\partial x_3}\right) \end{bmatrix} \tag{6.67a}$$

and

$$\left(\frac{\partial \mathbf{f}}{\partial k_j}\right) = \begin{bmatrix} \left(\frac{\partial f_1}{\partial k_j}\right) \\ \left(\frac{\partial f_2}{\partial k_j}\right) \\ \left(\frac{\partial f_3}{\partial k_j}\right) \end{bmatrix} \quad ; \quad j=1,2,\ldots,7 \tag{6.67b}$$

Taking into account the above equations we obtain

$$
\left.\begin{aligned}
\frac{dG_{11}}{dt} &= \left(\frac{\partial f_1}{\partial x_1}\right)G_{11} + \left(\frac{\partial f_1}{\partial x_2}\right)G_{21} + \left(\frac{\partial f_1}{\partial x_3}\right)G_{31} + \frac{\partial f_1}{\partial k_1} \;;\quad G_{11}(0) = 0 \\
\frac{dG_{21}}{dt} &= \left(\frac{\partial f_2}{\partial x_1}\right)G_{11} + \left(\frac{\partial f_2}{\partial x_2}\right)G_{21} + \left(\frac{\partial f_2}{\partial x_3}\right)G_{31} + \frac{\partial f_2}{\partial k_1} \;;\quad G_{21}(0) = 0 \\
&\vdots \\
\frac{dG_{17}}{dt} &= \left(\frac{\partial f_1}{\partial x_1}\right)G_{17} + \left(\frac{\partial f_1}{\partial x_2}\right)G_{27} + \left(\frac{\partial f_1}{\partial x_3}\right)G_{37} + \frac{\partial f_1}{\partial k_7} \;;\quad G_{17}(0) = 0 \\
\frac{dG_{27}}{dt} &= \left(\frac{\partial f_2}{\partial x_1}\right)G_{17} + \left(\frac{\partial f_2}{\partial x_2}\right)G_{27} + \left(\frac{\partial f_2}{\partial x_3}\right)G_{37} + \frac{\partial f_2}{\partial k_7} \;;\quad G_{27}(0) = 0
\end{aligned}\right\} \quad (6.68)
$$

$$\vdots$$

$$\frac{dG_{37}}{dt} = \left(\frac{\partial f_3}{\partial x_1}\right)G_{17} + \left(\frac{\partial f_3}{\partial x_2}\right)G_{27} + \left(\frac{\partial f_3}{\partial x_3}\right)G_{37} + \frac{\partial f_3}{\partial k_7} \;;\quad G_{37}(0) = 0$$

The partial derivatives in Eqn 6.67a are given next

$$\left(\frac{\partial f_1}{\partial x_1}\right) = -u_1\left(\frac{\partial r_1}{\partial x_1} + \frac{\partial r_2}{\partial x_1}\right) - k_3 - k_5 x_3 \tag{6.69a}$$

$$\left(\frac{\partial f_1}{\partial x_2}\right) = -u_1\left(\frac{\partial r_2}{\partial x_2}\right) = -u_1 \frac{r_2}{x_2} \tag{6.69b}$$

$$\left(\frac{\partial f_1}{\partial x_3}\right) = k_4 - k_5 x_1 \tag{6.69c}$$

$$\left(\frac{\partial f_2}{\partial x_1}\right) = u_1\left(\frac{\partial r_1}{\partial x_1} - \frac{\partial r_2}{\partial x_1}\right) \tag{6.69d}$$

$$\left(\frac{\partial f_2}{\partial x_2}\right) = -u_1\left(\frac{\partial r_2}{\partial x_2}\right) = -u_1 \frac{r_2}{x_2} \tag{6.69e}$$

$$\left(\frac{\partial f_2}{\partial x_3}\right) = 0 \tag{6.69f}$$

$$\left(\frac{\partial f_3}{\partial x_1}\right) = k_3 - k_5 x_3 \tag{6.69g}$$

$$\left(\frac{\partial f_3}{\partial x_2}\right) = 0 \tag{6.69h}$$

$$\left(\frac{\partial f_3}{\partial x_3}\right) = -k_5 x_1 - k_4 \tag{6.69i}$$

The partial derivatives w.r.t. the parameters are given next

$$\left(\frac{\partial \mathbf{f}}{\partial k_1}\right) = \begin{bmatrix} \left(\frac{\partial f_1}{\partial k_1}\right) \\ \left(\frac{\partial f_2}{\partial k_1}\right) \\ \left(\frac{\partial f_3}{\partial k_1}\right) \end{bmatrix} = \begin{bmatrix} -u_1\left(\frac{\partial r_1}{\partial k_1}\right) \\ u_1\left(\frac{\partial r_1}{\partial k_1}\right) \\ 0 \end{bmatrix} \tag{6.70a}$$

$$\left(\frac{\partial \mathbf{f}}{\partial k_2}\right) = \begin{bmatrix} \left(\frac{\partial f_1}{\partial k_2}\right) \\ \left(\frac{\partial f_2}{\partial k_2}\right) \\ \left(\frac{\partial f_3}{\partial k_2}\right) \end{bmatrix} = \begin{bmatrix} -u_1\left(\frac{\partial r_2}{\partial k_2}\right) \\ -u_1\left(\frac{\partial r_2}{\partial k_2}\right) \\ 0 \end{bmatrix} \tag{6.70b}$$

$$\left(\frac{\partial \mathbf{f}}{\partial k_3}\right) = \begin{bmatrix} \left(\frac{\partial f_1}{\partial k_3}\right) \\ \left(\frac{\partial f_2}{\partial k_3}\right) \\ \left(\frac{\partial f_3}{\partial k_3}\right) \end{bmatrix} = \begin{bmatrix} -x_1 \\ 0 \\ x_1 \end{bmatrix} \tag{6.70c}$$

$$\left(\frac{\partial \mathbf{f}}{\partial k_4}\right) = \begin{bmatrix} \left(\frac{\partial f_1}{\partial k_4}\right) \\ \left(\frac{\partial f_2}{\partial k_4}\right) \\ \left(\frac{\partial f_3}{\partial k_4}\right) \end{bmatrix} = \begin{bmatrix} x_3 \\ 0 \\ -x_3 \end{bmatrix} \qquad (6.70d)$$

$$\left(\frac{\partial \mathbf{f}}{\partial k_5}\right) = \begin{bmatrix} \left(\frac{\partial f_1}{\partial k_5}\right) \\ \left(\frac{\partial f_2}{\partial k_5}\right) \\ \left(\frac{\partial f_3}{\partial k_5}\right) \end{bmatrix} = \begin{bmatrix} -x_3 x_1 \\ 0 \\ -x_3 x_1 \end{bmatrix} \qquad (6.70e)$$

$$\left(\frac{\partial \mathbf{f}}{\partial k_6}\right) = \begin{bmatrix} \left(\frac{\partial f_1}{\partial k_6}\right) \\ \left(\frac{\partial f_2}{\partial k_6}\right) \\ \left(\frac{\partial f_3}{\partial k_6}\right) \end{bmatrix} = \begin{bmatrix} -u_1\left(\frac{\partial r_1}{\partial k_6} + \frac{\partial r_2}{\partial k_6}\right) \\ u_1\left(\frac{\partial r_1}{\partial k_6} - \frac{\partial r_2}{\partial k_6}\right) \\ 0 \end{bmatrix} \qquad (6.70f)$$

$$\left(\frac{\partial \mathbf{f}}{\partial k_7}\right) = \begin{bmatrix} \left(\frac{\partial f_1}{\partial k_7}\right) \\ \left(\frac{\partial f_2}{\partial k_7}\right) \\ \left(\frac{\partial f_3}{\partial k_7}\right) \end{bmatrix} = \begin{bmatrix} -u_1\left(\frac{\partial r_1}{\partial k_7} + \frac{\partial r_2}{\partial k_7}\right) \\ u_1\left(\frac{\partial r_1}{\partial k_7} - \frac{\partial r_2}{\partial k_7}\right) \\ 0 \end{bmatrix} \qquad (6.70g)$$

The 21 *sensitivity equations* (Eqn 6.68) should be solved simultaneously with the three *state equations* (Eqn 6.64) to yield **x**(t) and **G**(t) which are used in setting up matrix **A** and vector **b** at each iteration of the Gauss-Newton method.