Chapter 06.04
Nonlinear Models for Regression-More Examples
Chemical Engineering

Example 1

Below is given the FT-IR (Fourier Transform Infra Red) data of a 1:1 (by weight) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Absorbance P is given as a function of wavenumber, m.

Table 1 Absorbance as a function of wavenumber.

Wavenumber, m (cm^{-1})	Absorbance, P (arbitrary unit)
804.184	0.1591
827.326	0.0439
846.611	0.0050
869.753	0.0073
889.038	0.0448
892.895	0.0649
900.609	0.1204

Regress the above data to a second order polynomial

$$P = a_0 + a_1 m + a_2 m^2$$

Find the absorbance at $m = 1000\ \text{cm}^{-1}$

Solution

Table 2 shows the summations needed for the calculations of the constants of the regression model.

Table 2 Summations for calculating constants of model.

i	Wavenumber, m (cm^{-1})	Absorbance, P (arbitrary unit)	m^2	m^3	m^4	$m \times P$	$m^2 \times P$
1	804.18	0.1591	6.4671×10^5	5.2008×10^8	4.1824×10^{11}	127.95	1.0289×10^5
2	827.33	0.0439	6.8447×10^5	5.6628×10^8	4.6849×10^{11}	36.319	3.0048×10^4
3	846.61	0.0050	7.1675×10^5	6.0681×10^8	5.1373×10^{11}	4.233	3.583×10^3
4	869.75	0.0073	7.5647×10^5	6.5794×10^8	5.7225×10^{11}	6.349	5.522×10^3
5	889.04	0.0448	7.9039×10^5	7.0269×10^8	6.2471×10^{11}	39.828	3.5409×10^4
6	892.90	0.0649	7.9726×10^5	7.1187×10^8	6.3563×10^{11}	57.948	5.1742×10^4
7	900.61	0.1204	8.1110×10^5	7.3048×10^8	6.5787×10^{11}	108.43	9.7655×10^4
$\sum_{i=1}^{7}$	6030.4	0.4454	5.2031×10^6	4.4961×10^9	3.8909×10^{12}	381.06	3.2685×10^5

$P = a_0 + a_1 m + a_2 m^2$ is the quadratic relationship between the absorbance and the wavenumber where the coefficients a_0, a_1, a_2 are found as follows

$$\begin{bmatrix} n & \left(\sum_{i=1}^{n} m_i\right) & \left(\sum_{i=1}^{n} m_i^2\right) \\ \left(\sum_{i=1}^{n} m_i\right) & \left(\sum_{i=1}^{n} m_i^2\right) & \left(\sum_{i=1}^{n} m_i^3\right) \\ \left(\sum_{i=1}^{n} m_i^2\right) & \left(\sum_{i=1}^{n} m_i^3\right) & \left(\sum_{i=1}^{n} m_i^4\right) \end{bmatrix} \begin{bmatrix} a_0 \\ a_1 \\ a_2 \end{bmatrix} = \begin{bmatrix} \sum_{i=1}^{n} P_i \\ \sum_{i=1}^{n} m_i \ P_i \\ \sum_{i=1}^{n} m_i^2 P_i \end{bmatrix}$$

$n = 7$

$\sum_{i=1}^{7} m_i = 6.0304 \times 10^3$

$\sum_{i=1}^{7} m_i^2 = 5.2031 \times 10^6$

$\sum_{i=1}^{7} m_i^3 = 4.4961 \times 10^9$

$\sum_{i=1}^{7} m_i^4 = 3.8909 \times 10^{12}$

$\sum_{i=1}^{7} P_i = 0.4454$

$\sum_{i=1}^{7} m_i P_i = 381.06$

$\sum_{i=1}^{7} m_i^2 P_i = 3.2685 \times 10^5$

We have

$$\begin{bmatrix} 7.0000 & 6.0304 \times 10^3 & 5.2031 \times 10^6 \\ 6.0304 \times 10^3 & 5.2031 \times 10^6 & 4.4961 \times 10^9 \\ 5.2031 \times 10^6 & 4.4961 \times 10^9 & 3.8909 \times 10^{12} \end{bmatrix} \begin{bmatrix} a_0 \\ a_1 \\ a_2 \end{bmatrix} = \begin{bmatrix} 0.4454 \\ 381.06 \\ 3.2685 \times 10^5 \end{bmatrix}$$

Solve the above system of simultaneous linear equations, we get

$$\begin{bmatrix} a_0 \\ a_1 \\ a_2 \end{bmatrix} = \begin{bmatrix} 43.985 \\ -0.10268 \\ -5.9922 \times 10^{-5} \end{bmatrix}$$

The polynomial regression model is

$$P = a_0 + a_1 m + a_2 m^2$$
$$= 43.985 - 0.10268m - 5.9922 \times 10^{-5} m^2$$

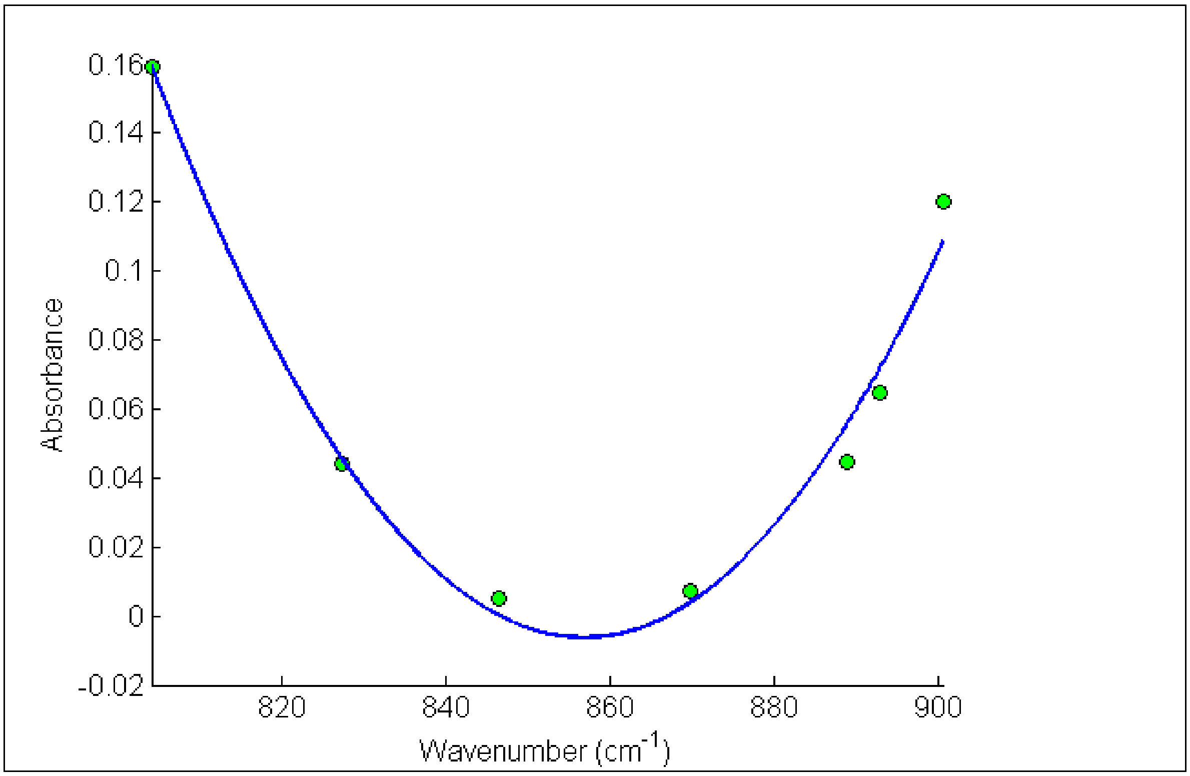

Figure 1 Second order polynomial regression model for absorbance as a function of wavenumber.

To find P where $m = 1000\ \text{cm}^{-1}$:

$$P = a_0 + a_1 m + a_2 m^2$$
$$= 43.985 - 0.10268m - 5.9922 \times 10^{-5} m^2$$
$$= 43.9855 - 0.10268 \times (1000) - 5.9922 \times 10^{-5} \times (1000)^2$$
$$= 1.2221$$

Example 2

The mechanism of polymer degradation reaction kinetics is suspected to follow Avrami or random nucleation reaction,

$$f(\alpha) = A\frac{(T - T_0)}{b} e^{-\frac{E}{RT}}$$

where $f(\alpha) = -\ln(1-\alpha)$, T is the absolute temperature (K), b is the heating rate in K/min, A is the frequency factor with units of rate constant, R is the gas constant (8.314 kJ/kmol-K) and T_0 is the activation temperature. Given that $T_0 = 338.75$ K, $b = 10$ K/min and conversion, α, at different temperatures are as given in table 3. Use the method of least squares to determine the values of $A$and$E$.

Table 3 Conversion at given different temperatures

Temp (K)	360	370	380	390	400	410	420	430	440
Conversion, α	0.1055	0.2010	0.3425	0.5146	0.6757	0.8026	0.8924	0.9544	1.00

Solution

To set-up the table, we must re-write equation

$$-\ln(1-\alpha) = A\frac{(T-T_0)}{b}e^{-\frac{E}{RT}}$$

as

$$-\frac{b\ln(1-\alpha)}{(T-T_0)} = Ae^{-\frac{E}{RT}}$$

Taking natural log of both sides of the above equation, we obtain

$$\ln\left[-\frac{b\ln(1-\alpha)}{(T-T_0)}\right] = \ln(A) - \frac{E}{RT}$$

so that the equation is in the form $y = \beta_0 + \beta_1 x$ where

$$y = \ln\left[-\frac{b\ln(1-\alpha)}{(T-T_0)}\right]$$

$$\beta_0 = \ln(A)$$

$$\beta_1 = -\frac{E}{R}$$

$$x = \frac{1}{T}$$

$$\beta_1 = \frac{n\sum_{i=1}^{n} x_i y_i - \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i}{n\sum_{i=1}^{n} x_1^2 - \left(\sum_{i=1}^{n} x_i\right)^2}$$

$$\beta_0 = \left(\frac{\sum_{i=1}^{n} y_i}{n}\right) - \beta_1\left(\frac{\sum_{i=1}^{n} x_i}{n}\right)$$

Table 4 Example on nonlinear exponential problem.

i	T	α	x	y	x^2	$x \times y$
1	360	0.1055	2.7778×10^{-3}	-2.9476	7.7160×10^{-6}	-8.1877×10^{-3}
2	370	0.2010	2.7027×10^{-3}	-2.6338	7.3046×10^{-6}	-7.1183×10^{-3}
3	380	0.3425	2.6316×10^{-3}	-2.2862	6.9252×10^{-6}	-6.0163×10^{-3}
4	390	0.5146	2.5641×10^{-3}	-1.9588	6.5746×10^{-6}	-5.0225×10^{-3}
5	400	0.6757	2.5000×10^{-3}	-1.6936	6.2500×10^{-6}	-4.2341×10^{-3}
6	410	0.8026	2.4390×10^{-3}	-1.4796	5.9488×10^{-6}	-3.6088×10^{-3}
7	420	0.8924	2.3810×10^{-3}	-1.2932	5.6689×10^{-6}	-3.0791×10^{-3}
8	430	0.9544	2.3256×10^{-3}	-1.0835	5.4083×10^{-6}	-2.5199×10^{-3}
$\sum$			2.0322×10^{-2}	-1.5376×10^{1}	5.1797×10^{-5}	-3.9787×10^{-2}

$n = 8$

$$\sum_{i=1}^{8} x_i = 2.0322 \times 10^{-2}$$

$\sum_{i=1}^{8} y_i = -1.5376 \times 10^{1}$

$\sum_{i=1}^{8} x_i y_i = -3.9787 \times 10^{-2}$

$\sum_{i=1}^{8} x_i^2 = 5.1797.10^{-5}$

$$\beta_1 = \frac{8(-3.9787\times10^{-2})-(2.0322\times10^{-2})(-1.5376\times10^{-1})}{8(5.1797\times10^{-5})-(2.0322\times10^{-2})^2}$$

$$= -4.1561 \times 10^{3}$$

$$\beta_0 = \frac{-1.5376 \times 10^{1}}{8} - (-4.1561 \times 10^{3})\frac{2.0322 \times 10^{-2}}{8}$$

$$= 8.6352$$

$$A = e^{\beta_0}$$

$$= e^{8.6352}$$

$$= 5.6264 \times 10^{3}$$

$$E = -\beta_1 R$$

$$= -(-4.1561.10^{3}) \times 8.3140$$

$$= 3.4553 \times 10^{4}$$

This gives the model as

$$-\ln(1-\alpha) = 5.6264 \times 10^{3}\,\frac{(T-338.75)}{10} \times e^{-\frac{4.1561\times 10^{3}}{T}}$$

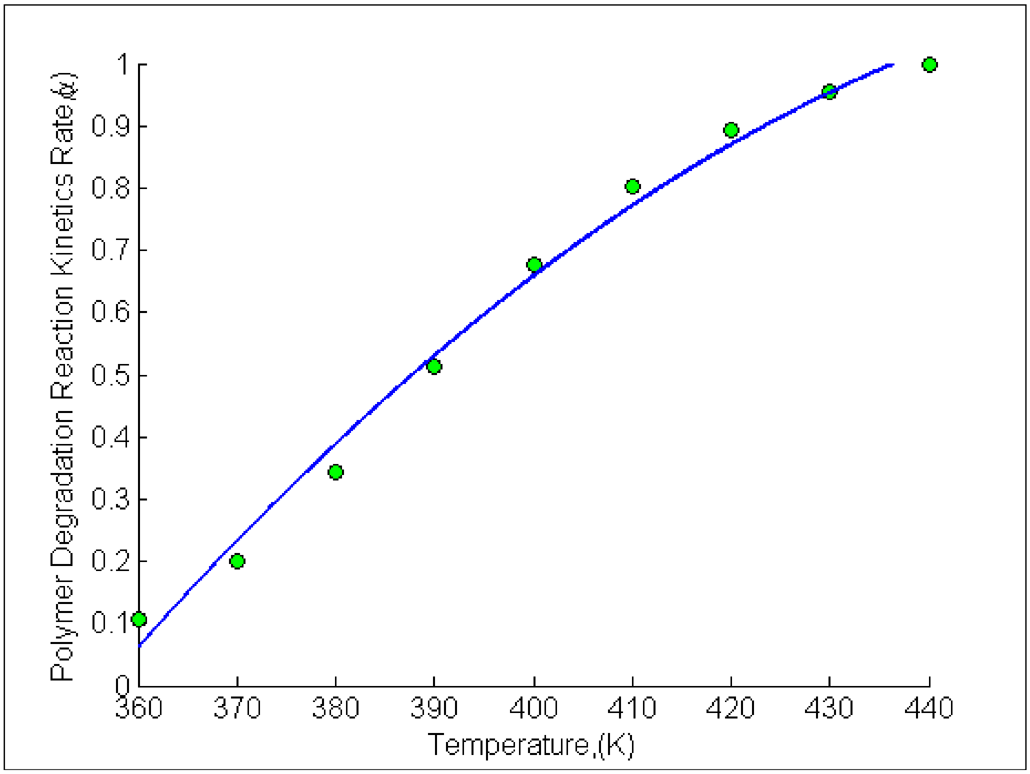

Figure 2 Polymer degradation reaction kinetics rate as a function of temperature.

Example 3

The progress of a homogeneous chemical reaction is followed and it is desired to evaluate the rate constant and the order of the reaction. The rate law expression for the reaction is known to follow the power function form

$$-r \quad = kC^n. \tag{1}$$

Use the data provided in the table to obtain n and$k$.

Table 11 Chemical kinetics

C_A(gmol/l)	4	2.25	1.45	1.0	0.65	0.25	0.06
$-r_A$ gmol/ls	0.398	0.298	0.238	0.198	0.158	0.098	0.048

Solution

Taking natural log of both sides of Equation (1), we obtain

$$\ln(-r \quad) = \ln(k) + n\ln(C \quad)$$

Let

$$\ln(-r \quad) = z$$

$$\ln(C \quad) = w$$

$$\ln(k) = a_0 \text{ from which } k = e^{a_0} \tag{2}$$

$$n = a_1 \tag{3}$$

We get

$$z = a_0 + a_1 w$$

This is a linear relation between z and w, where

$$a_1 = \frac{\sum_{i=1}^{m} w_i z_i - \sum_{i=1}^{m} w_i \sum_{i=1}^{m} z_i}{m\sum_{i=1}^{m} w_i^2 - \left(\sum_{i=1}^{m} w_i\right)^2}$$

$$a_0 = \frac{\sum_{i=1}^{m} z_i}{m} - a_1 \frac{\sum_{i=1}^{m} w_i}{m} \tag{4a,b}$$

Table 6 Kinetics rate law using power function.

i	C	$-r$	w	z	$w \times z$	w^2
1	4	0.398	1.3863	−0.92130	−1.2772	1.9218
2	2.25	0.298	0.8109	−1.2107	−0.9818	0.65761
3	1.45	0.238	0.3716	−1.4355	−0.5334	0.13806
4	1	0.198	0.0000	−1.6195	0.0000	0.00000
5	0.65	0.158	−0.4308	−1.8452	0.7949	0.18557
6	0.25	0.098	−1.3863	−2.3228	3.2201	1.9218
7	0.06	0.048	−2.8134	−3.0366	8.5431	7.9153
$\sum_{i=1}^{7}$			−2.0617	−12.391	9.7657	12.7401

$m = 7$
$\sum_{i=1}^{7} w_i = -2.0617$
$\sum_{i=1}^{7} z_i = -12.391$
$\sum_{i=1}^{7} w_i z_i = 9.7657$
$\sum_{i=1}^{7} w_i^2 = 12.7401$

From Equation (4a, b)

$$a_1 = \frac{7\times(9.7657)-(-2.0617)\times(-12.391)}{7\times12.7401-(-2.0617)^2}$$
$$= 0.50408$$

$$a_0 = \frac{-12.391}{7} - (-0.50408)\frac{-2.0617}{7}$$
$$= -1.6217$$

From Equations (2) and (3), we obtain

$$k = e^{-1.6217}$$
$$= 0.19755$$

$$n = a_1$$
$$= 0.50408$$

Finally, the model of progress of that chemical reaction is

$$-r = 0.19755 \times C^{0.50408}$$

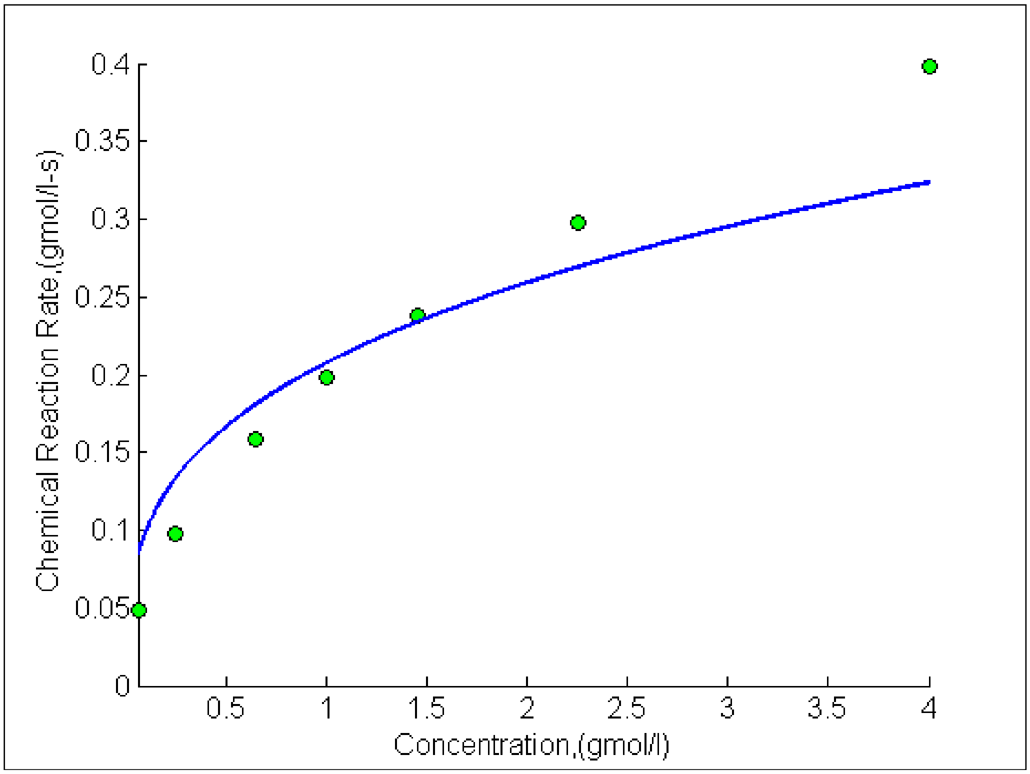

Figure 3 Kinetic chemical reaction rate as a function of concentration.