Nonlinear Regression

Major: Chemical Engineering

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Nonlinear Regression

Given *n* data points $(x_1, y_1), (x_2, y_2), \ldots, (x_n, y_n)$ best fit $y = f(x)$ to the data, where $f(x)$ is a nonlinear function of x .

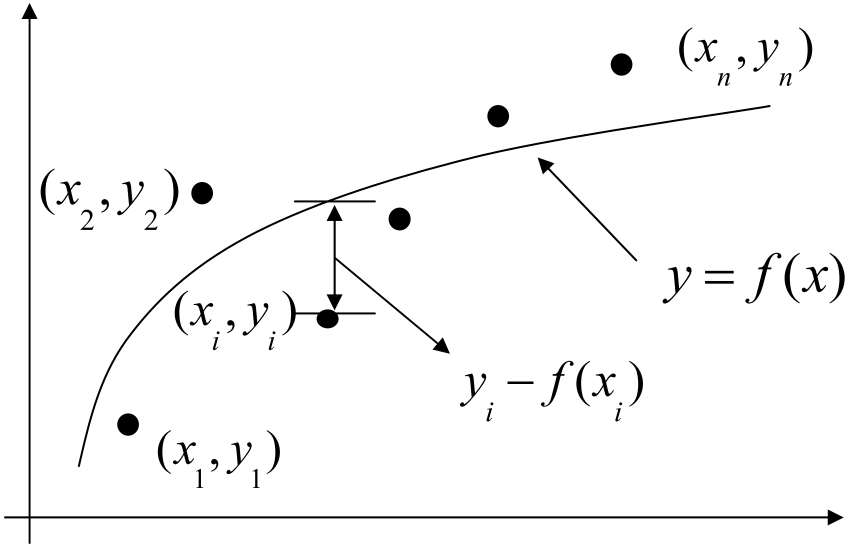

Figure. Nonlinear regression model for discrete y vs. x data

Nonlinear Regression

Some popular nonlinear regression models:

1. Exponential model: $(y = ae^{bx})$
2. Power model: $(y = ax^{b})$
3. Saturation growth model: $\left(y = \frac{ax}{b+x}\right)$
4. Polynomial model: $(y = a_0 + a_1 x + \ldots + a_m x^m)$

Exponential Model

Given $(x_1, y_1), (x_2, y_2), \ldots, (x_n, y_n)$ best fit $y = ae^{bx}$ to the data.

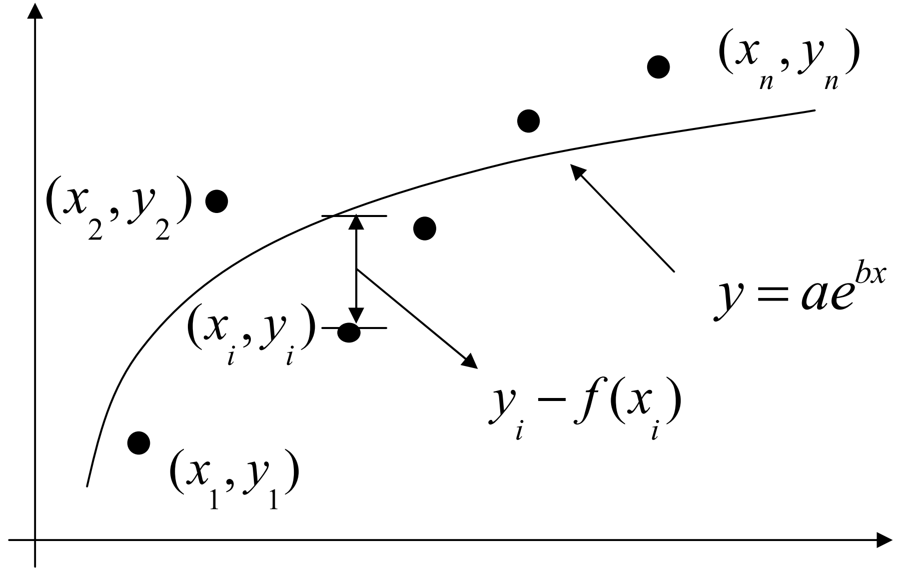

Figure. Exponential model of nonlinear regression for y vs. x data

Finding constants of Exponential Model

The sum of the square of the residuals is defined as

$$S_r = \sum_{i=1}^{n} \left(y_i - a e^{b x_i} \right)^2$$

Differentiate with respect to a and b

$$\frac{\partial S_r}{\partial a} = \sum_{i=1}^{n} 2\left(y_i - a e^{b x_i} \right)\left(-e^{b x_i} \right) = 0$$

$$\frac{\partial S_r}{\partial b} = \sum_{i=1}^{n} 2\left(y_i - a e^{b x_i} \right)\left(-a x_i e^{b x_i} \right) = 0$$

Finding constants of Exponential Model

Rewriting the equations, we obtain

$$-\sum_{i=1}^{n} y_i e^{bx_i} + a\sum_{i=1}^{n} e^{2bx_i} = 0$$

$$\sum_{i=1}^{n} y_i x_i e^{bx_i} - a\sum_{i=1}^{n} x_i e^{2bx_i} = 0$$

Finding constants of Exponential Model

Solving the first equation for a yields

$$a = \frac{\sum_{i=1}^{n} y_i e^{bx_i}}{\sum_{i=1}^{n} e^{2bx_i}}$$

Substituting a back into the previous equation

$$\sum_{i=1}^{n} y_i x_i e^{bx_i} - \frac{\sum_{i=1}^{n} y_i e^{bx_i}}{\sum_{i=1}^{n} e^{2bx_i}} \sum_{i=1}^{n} x_i e^{2bx_i} = 0$$

Nonlinear equation in terms of b

The constant b can be found through numerical methods such as the bisection method or secant method.

Example 1-Exponential Model

Many patients get concerned when a test involves injection of a radioactive material. For example for scanning a gallbladder, a few drops of Technetium-99m isotope is used. Half of the techritium-99m would be gone in about *6* hours. It, however, takes about *24* hours for the radiation levels to reach what we are exposed to in day-to-day activities. Below is given the relative intensity of radiation as a function of time.

Table. Relative intensity of radiation as a function of time

t(hrs)	0	1	3	5	7	9
γ	1.000	0.892	0.708	0.562	0.447	0.355

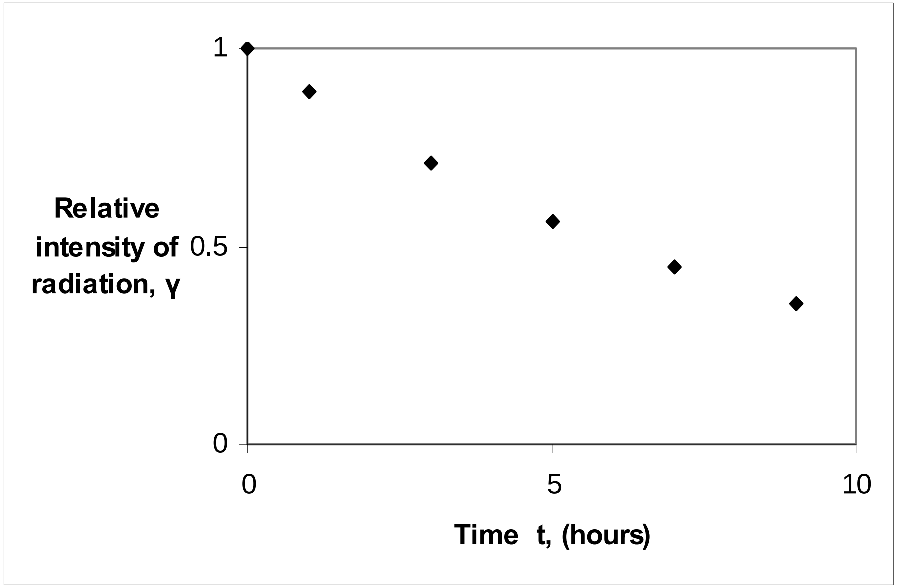

Figure. Data points of relative radiation intensity vs. time

Example 1-Exponential Model cont.

Find:

a) The value of the regression constants A and λ

b) The half-life of Technium-99m

c) Radiation intensity after 24 hours

The relative intensity is related to time by the equation

$$\gamma = Ae^{\lambda t}$$

Example 1-Exponential Model cont.

The value for λ is found by solving the nonlinear equation

$$f(\lambda)=\sum_{i=1}^{n}\gamma_i t_i e^{\lambda t_i}-\frac{\sum_{i=1}^{n}\gamma_i e^{\lambda t_i}}{\sum_{i=1}^{n}e^{2\lambda t_i}}\sum_{i=1}^{n}t_i e^{2\lambda t_i}=0$$

Numerical methods such as bisection method, or secant method are the best method to solve for λ

The value for A is then found by solving

$$A=\frac{\sum_{i=1}^{n}\gamma_i e^{\lambda t_i}}{\sum_{i=1}^{n}e^{2\lambda t_i}}$$

Example 1-Exponential Model cont.

Using bisection method, we may estimate the initial bracket for λ to be $\lambda = [-0.23105, -0.077016]$

The table below shows $f(\lambda)$ evaluated at $f(-0.23105)$.

Table. Summation value for calculation of constants of model

i	t_i	γ_i	$\gamma_i t_i e^{\lambda t_i}$	$\gamma_i e^{\lambda t_i}$	$e^{2\lambda t_i}$	$t_i e^{2\lambda t_i}$
1	0	1	0.00000	1.00000	1.00000	0.00000
2	1	0.891	0.70719	0.70719	0.62996	0.62996
3	3	0.708	1.0620	0.35400	0.25000	0.75000
4	5	0.562	0.88509	0.17702	0.09921	0.49606
5	7	0.447	0.62087	0.08870	0.03937	0.27560
6	9	0.355	0.39937	0.04437	0.01562	0.14062
$\sum_{i=1}^{6}$			3.6745	2.3713	2.0342	2.2922

Example 1-Exponential Model cont.

From Table,

$$\sum_{i=1}^{6} \gamma_i t_i e^{-0.23105 t_i} = 3.6745$$

$$\sum_{i=1}^{6} \gamma_i e^{-0.23105 t_i} = 2.3713$$

$$\sum_{i=1}^{6} e^{2(-0.23105) t_i} = 2.0342$$

$$\sum_{i=1}^{6} t_i e^{2(-0.23105) t_i} = 2.2922$$

$$f(-0.23105) = (3.6745) - \frac{2.3713}{2.0342}(2.2922) = 1.0024$$

Example 1-Exponential Model cont.

Using the same procedure with $\lambda = -0.077016$ we find

$$f(-0.0077016) = -0.39201$$

Since $f(-0.23105) \times f(-0.0077016) < 0$ the value of λ falls in the bracket $[-0.23105, -0.0077016]$

Continuing the bisection method, we eventually find that the root of $f(\lambda) = 0$ is $\lambda = -0.11508$.

This was calculated after twenty iterations with an absolute relative approximate error of 0.0002%.

Example 1-Exponential Model cont.

The value A can now be calculated

$$A = \frac{\sum_{i=1}^{6} \gamma_i e^{\lambda t_i}}{\sum_{i=1}^{6} e^{2\lambda t_i}}$$

$$= \frac{\begin{array}{c} 1 \times e^{-0.11508(0)} + 0.891 \times e^{-0.11508(1)} + 0.708 \times e^{-0.11508(3)} + \\ 0.562 \times e^{-0.11508(5)} + 0.447 \times e^{-0.11508(7)} + 0.355 \times e^{-0.11508(9)} \end{array}}{\begin{array}{c} e^{2(-0.11508)(0)} + e^{2(-0.11508)(1)} + e^{2(-0.11508)(3)} + \\ e^{2(-0.11508)(5)} + e^{2(-0.11508)(7)} + e^{2(-0.11508)(9)} \end{array}} = 0.99983$$

The exponential regression model then is $\gamma = 0.99983\, e^{-0.11508t}$

Example 1-Exponential Model cont.

Resulting model $\gamma = 0.99983\, e^{-0.11508t}$

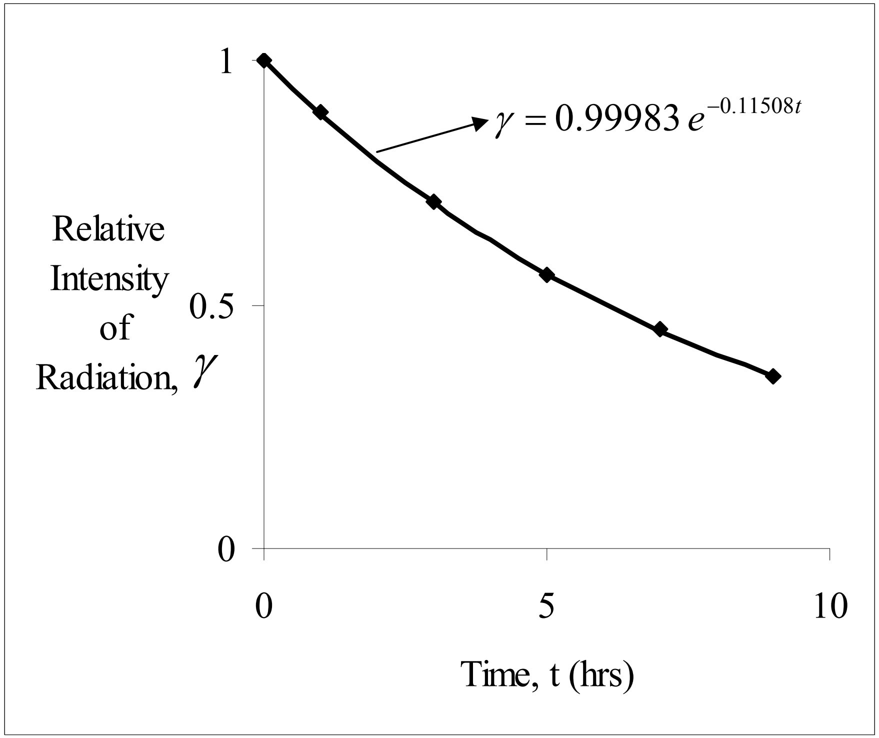

Figure. Relative intensity of radiation as a function of time using an exponential regression model.

Example 1-Exponential Model cont.

b) Half life of Technetium 99-m is when $\gamma = \frac{1}{2}\gamma\Big|_{t=0}$

$$0.99983 \times e^{-0.11508t} = \frac{1}{2}(0.99983)e^{-0.11508(0)}$$

$$e^{-0.11508t} = 0.5$$

$$-0.11508t = \ln(0.5)$$

$$t = 6.0232\,hours$$

c) The relative intensity of radiation after 24 hours

$$\gamma = 0.99983 \times e^{-0.11508(24)}$$

$$= 6.3160 \times 10^{-2}$$

This result implies that only $\frac{6.3160 \times 10^{-2}}{0.99983} \times 100 = 6.3171\%$ of the initial radioactive intensity is left after 24 hours.

Polynomial Model

Given $(x_1, y_1), (x_2, y_2), \ldots, (x_n, y_n)$ best fit $y = a_0 + a_1 x + \ldots + a_m x^m$ $(m \le n-2)$ to a given data set.

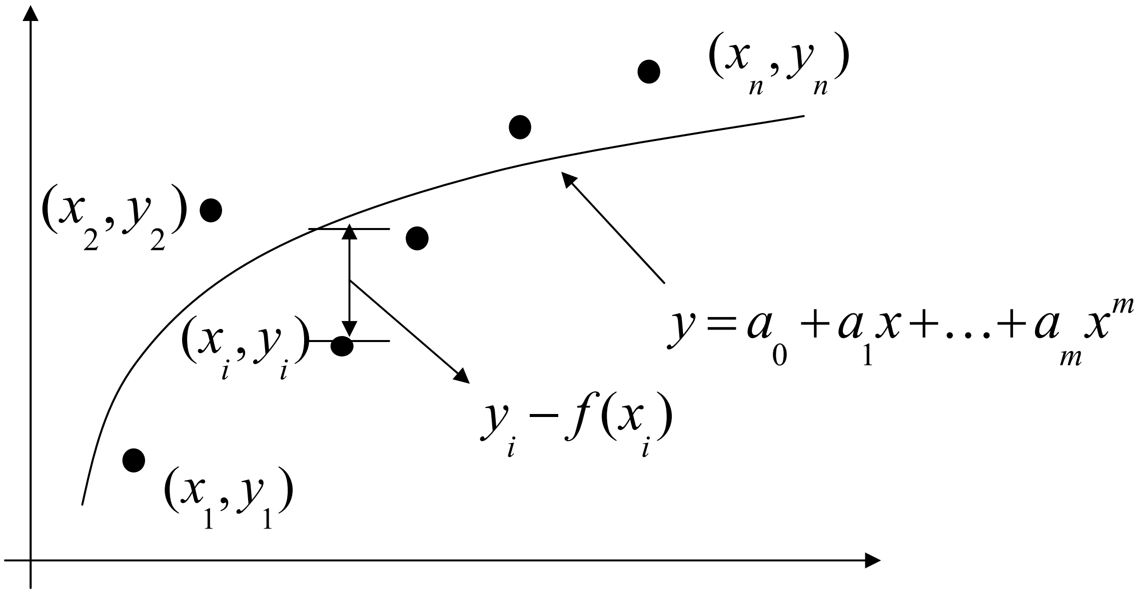

Figure. Polynomial model for nonlinear regression of y vs. x data

Polynomial Model cont.

The residual at each data point is given by

$$E_i = y_i - a_0 - a_1 x_i - . \; . \; . - a_m x_i^m$$

The sum of the square of the residuals then is

$$S_r = \sum_{i=1}^{n} E_i^2$$

$$= \sum_{i=1}^{n} \left(y_i - a_0 - a_1 x_i - . \; . \; . - a_m x_i^m \right)^2$$

Polynomial Model cont.

To find the constants of the polynomial model, we set the derivatives with respect to a_i where $i = 1, \ldots m,$ equal to zero.

$$\frac{\partial S_r}{\partial a_0} = \sum_{i=1}^{n} 2.\left(y_i - a_0 - a_1 x_i - .\ .\ . - a_m x_i^m\right)(-1) = 0$$

$$\frac{\partial S_r}{\partial a_1} = \sum_{i=1}^{n} 2.\left(y_i - a_0 - a_1 x_i - .\ .\ . - a_m x_i^m\right)(-x_i) = 0$$

$$\vdots \qquad \vdots \qquad\qquad \vdots \qquad\qquad\qquad \vdots$$

$$\frac{\partial S_r}{\partial a_m} = \sum_{i=1}^{n} 2.\left(y_i - a_0 - a_1 x_i - .\ .\ . - a_m x_i^m\right)(-x_i^m) = 0$$

Polynomial Model cont.

These equations in matrix form are given by

$$\begin{bmatrix} n & \left(\sum_{i=1}^{n} x_i\right) & . \; . \; . & \left(\sum_{i=1}^{n} x_i^m\right) \\ \left(\sum_{i=1}^{n} x_i\right) & \left(\sum_{i=1}^{n} x_i^2\right) & . \; . \; . & \left(\sum_{i=1}^{n} x_i^{m+1}\right) \\ . \; . \; . & . \; . \; . & . \; . \; . & . \; . \; . \\ \left(\sum_{i=1}^{n} x_i^m\right) & \left(\sum_{i=1}^{n} x_i^{m+1}\right) & . \; . \; . & \left(\sum_{i=1}^{n} x_i^{2m}\right) \end{bmatrix} \begin{bmatrix} a_0 \\ a_1 \\ . \; . \; . \\ a_m \end{bmatrix} = \begin{bmatrix} \sum_{i=1}^{n} y_i \\ \sum_{i=1}^{n} x_i y_i \\ . \; . \; . \\ \sum_{i=1}^{n} x_i^m y_i \end{bmatrix}$$

The above equations are then solved for $a_0, a_1, \ldots, a_m$

Example 2-Polynomial Model

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. Absorbance vs Wavenumber data

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

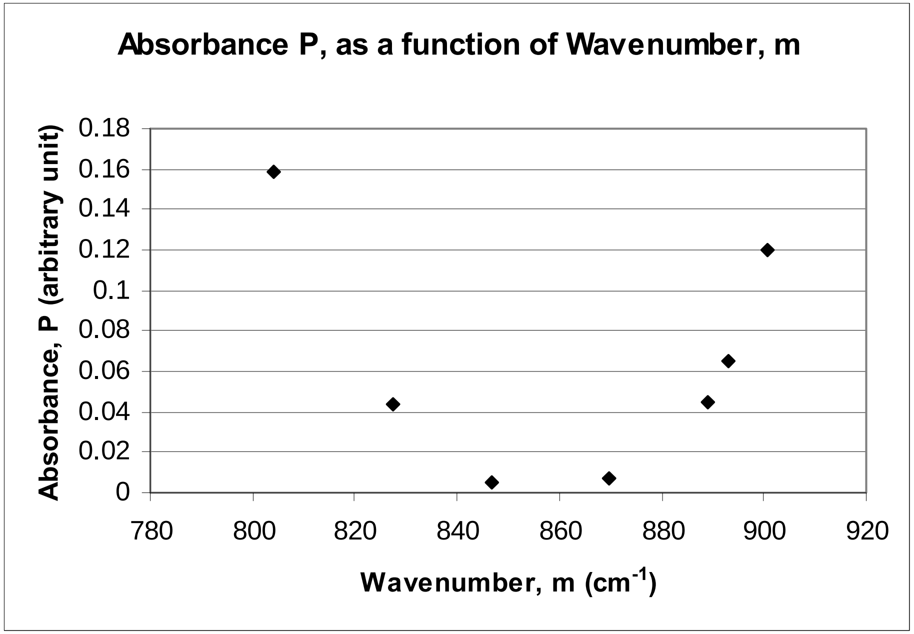

Figure. Absorbance vs. Wavenumber data

Example 2-Polynomial Model cont.

Regress the data to a second order polynomial where

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

and find the absorbance at $\mathrm{m} = 1000\mathrm{cm}^{-1}$

The coefficients a_0, a_1, a_2 are found as follows

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

Example 2-Polynomial Model cont.

The necessary summations are as follows

Table. Necessary summations for calculation of polynomial model constants

i	**Wavenumber, m (cm^{-1})**	**Absorbance, P (arbitrary unit)**	**m^2**	**m^3**
1	804.184	0.1591	$6.46711\text{x}10^5$	$5.20075\text{x}10^8$
2	827.326	0.0439	$6.84468\text{x}10^5$	$5.66278\text{x}10^8$
3	846.611	0.0050	$7.1675\text{x}10^5$	$6.06808\text{x}10^8$
4	869.753	0.0073	$7.5647\text{x}10^5$	$6.57942\text{x}10^8$
5	889.038	0.0448	$7.90388\text{x}10^5$	$7.02685\text{x}10^8$
6	892.895	0.0649	$7.97261\text{x}10^5$	$7.11870\text{x}10^8$
7	900.609	0.1204	$8.11096\text{x}10^5$	$7.30480\text{x}10^8$
$\sum_{i=1}^{7}$	6030.416	0.4454	$5.203144\text{x}10^6$	$4.496138\text{x}10^9$

Example 2-Polynomial Model cont.

Necessary summations continued:

Table. Necessary summations for calculation of polynomial model constants.

i	**m^4**	**m x P**	**m^2x P**
1	$4.1824\text{x}10^{11}$	127.946	$1.0289\text{x}10^5$
2	$4.6849\text{x}10^{11}$	36.319	$3.0048\text{x}10^4$
3	$5.1373\text{x}10^{11}$	4.233	$3.583\text{x}10^3$
4	$5.7225\text{x}10^{11}$	6.349	$5.522\text{x}10^3$
5	$6.2471\text{x}10^{11}$	39.828	$3.5409\text{x}10^4$
6	$6.3563\text{x}10^{11}$	57.948	$5.1742\text{x}10^4$
7	$6.5787\text{x}10^{11}$	108.433	$9.7655\text{x}10^4$
$\sum_{i=1}^{7}$	$3.8909\text{x}10^{12}$	381.056	$3.2685\text{x}10^5$

Example 2-Polynomial Model cont.

Using these summations we have

$$\begin{bmatrix} 7.0000 & 6.0304\times10^{3} & 5.2031\times10^{6} \\ 6.0304\times10^{3} & 5.2031\times10^{6} & 4.4961\times10^{9} \\ 5.2031\times10^{6} & 4.4961\times10^{9} & 3.8909\times10^{12} \end{bmatrix}\begin{bmatrix} a_0 \\ a_1 \\ a_2 \end{bmatrix}=\begin{bmatrix} 0.4454 \\ 381.056 \\ 3.2685\times10^{5} \end{bmatrix}$$

Solving this system of equations we find

$$\begin{bmatrix} a_0 \\ a_1 \\ a_2 \end{bmatrix}=\begin{bmatrix} -4.59194 \\ 0.011219 \\ -0.674058 \end{bmatrix}$$

The regression model is then

$$\mathrm{P}=a_0+a_1m+a_2m^2$$

$$=\text{-}4.59194+0.011219m-0.674058m^2$$

Example 2-Polynomial Model cont.

With $P = -4.59194 + 0.011219\,m - 0.674058\,m^2$ the model is given by

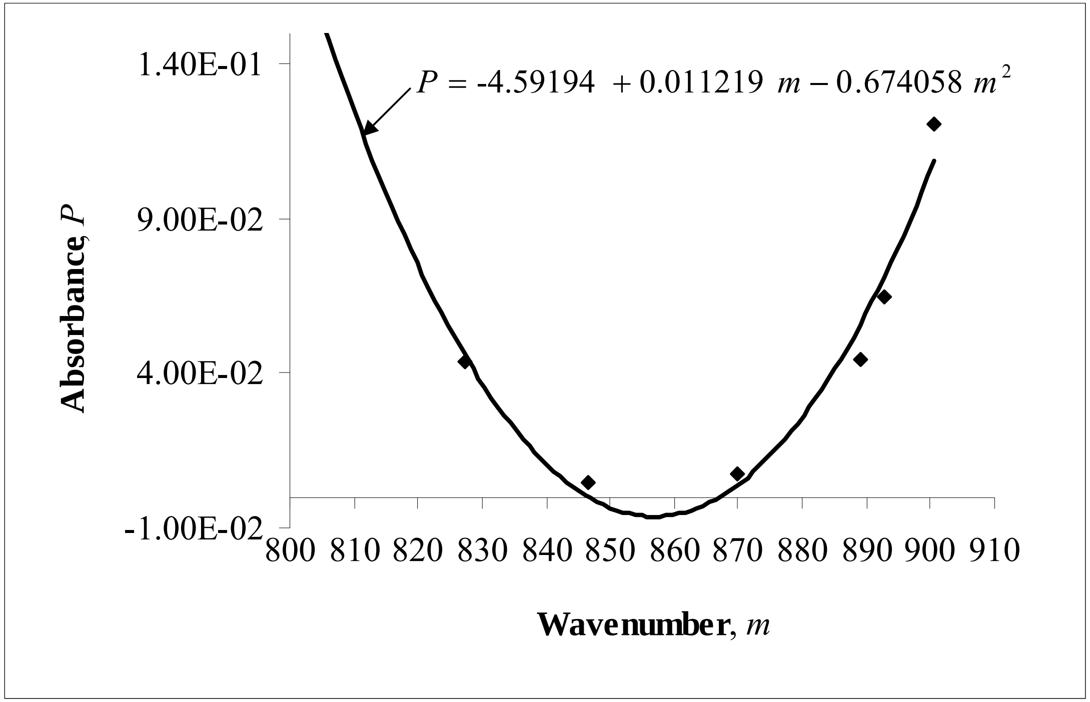

Figure. Polynomial model of Absorbance vs. Wavenumber.

Example 2-Polynomial Model cont.

To find P where $\mathrm{m} = 1000\mathrm{cm}^{-1}$ we have

$$\begin{aligned}
\mathrm{P} &= a_0 + a_1 m + a_2 m^2 \\
&= -4.59194 + 0.011219m - 0.674058m^2 \\
&= -4.59194 + 0.011219 \times (1000) - 0.674058 \times (1000)^2 \\
&= 0.1512
\end{aligned}$$

Linearization of Data

To find the constants of many nonlinear models, it results in solving simultaneous nonlinear equations. For mathematical convenience, some of the data for such models can be linearized. For example, the data for an exponential model can be linearized.

As shown in the previous example, many chemical and physical processes are governed by the equation,

$$y = ae^{bx}$$

Taking the natural log of both sides yields,

$$\ln y = \ln a + bx$$

Let $z = \ln y$ and $a_0 = \ln a$

We now have a linear regression model where $z = a_0 + a_1 x$

(implying) $a = e^{a_o}$ with $a_1 = b$

Linearization of data cont.

Using linear model regression methods,

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

$$a_0 = \bar{z} - a_1 \bar{x}$$

Once a_o, a_1 are found, the original constants of the model are found as

$$b = a_1$$

$$a = e^{a_0}$$

Example 3-Linearization of data

Many patients get concerned when a test involves injection of a radioactive material. For example for scanning a gallbladder, a few drops of Technetium-99m isotope is used. Half of the techritium-99m would be gone in about *6* hours. It, however, takes about *24* hours for the radiation levels to reach what we are exposed to in day-to-day activities. Below is given the relative intensity of radiation as a function of time.

Table. Relative intensity of radiation as a function of time

t(hrs)	0	1	3	5	7	9
γ	1.000	0.892	0.708	0.562	0.447	0.355

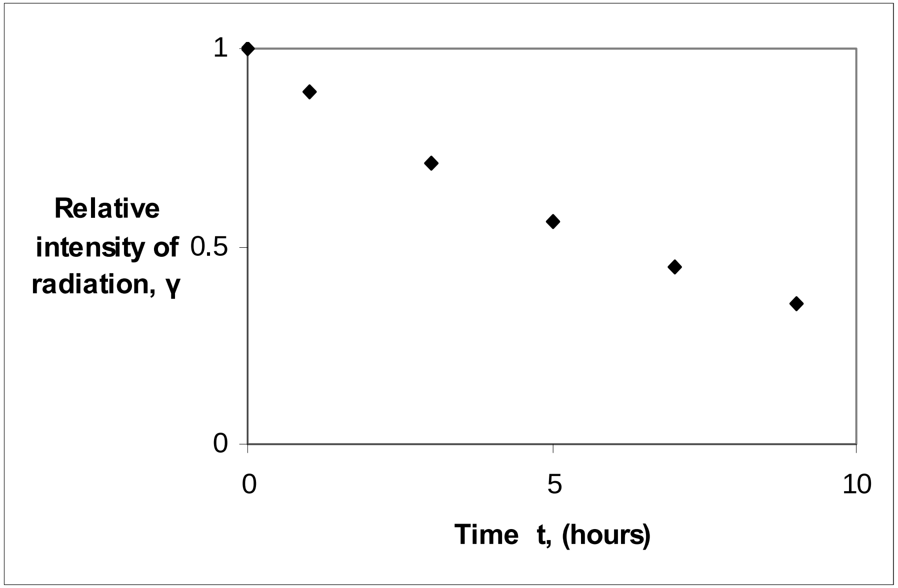

Figure. Data points of relative radiation intensity vs. time

Example 3-Linearization of data cont.

Find:

a) The value of the regression constants A and λ

b) The half-life of Technium-99m

c) Radiation intensity after 24 hours

The relative intensity is related to time by the equation

$$\gamma = Ae^{\lambda t}$$

Example 3-Linearization of data cont.

Exponential model given as,

$$\gamma = Ae^{\lambda t}$$

$$\ln(\gamma) = \ln(A) + \lambda t$$

Assuming $z = \ln \gamma$, $a_o = \ln(A)$ and $a_1 = \lambda$ we obtain

$$z = a_0 + a_1 t$$

This is a linear relationship between z and t

Example 3-Linearization of data cont.

Using this linear relationship, we can calculate a_0, a_1 where

$$a_1 = \frac{n\sum_{i=1}^{n} t_i z_i - \sum_{i=1}^{n} t_i \sum_{i=1}^{n} z_i}{n\sum_{i=1}^{n} t_1^2 - \left(\sum_{i=1}^{n} t_i\right)^2}$$

and

$$a_0 = \bar{z} - a_1 \bar{t}$$

$$\lambda = a_1$$

$$A = e^{a_0}$$

Example 3-Linearization of Data cont.

Summations for data linearization are as follows

Table. Summation data for linearization of data model

i	t_i	γ_i	$z_i = \ln \gamma_i$	$t_i z_i$	t_i^2
1	0	1	0.00000	0.0000	0.0000
2	1	0.891	-0.11541	-0.11541	1.0000
3	3	0.708	-0.34531	-1.0359	9.0000
4	5	0.562	-0.57625	-2.8813	25.000
5	7	0.447	-0.80520	-5.6364	49.000
6	9	0.355	-1.0356	-9.3207	81.000
$\sum$	25.000		-2.8778	-18.990	165.00

With $n = 6$

$$\sum_{i=1}^{6} t_i = 25.000$$

$$\sum_{i=1}^{6} z_i = -2.8778$$

$$\sum_{i=1}^{6} t_i z_i = -18.990$$

$$\sum_{i=1}^{6} t_i^2 = 165.00$$

Example 3-Linearization of Data cont.

Calculating a_0, a_1

$$a_1 = \frac{6(-18.990) - (25)(-2.8778)}{6(165.00) - (25)^2} \qquad = -0.11505$$

$$a_0 = \frac{-2.8778}{6} - (-0.11505)\frac{25}{6} \qquad = -2.6150 \times 10^{-4}$$

Since

$$a_0 = \ln(A)$$

$$A = e^{a_0}$$

$$= e^{-2.6150 \times 10^{-4}} \quad = 0.99974$$

also

$$\lambda = a_1 = -0.11505$$

Example 3-Linearization of Data cont.

Resulting model is $\gamma = 0.99974 \times e^{-0.11505t}$

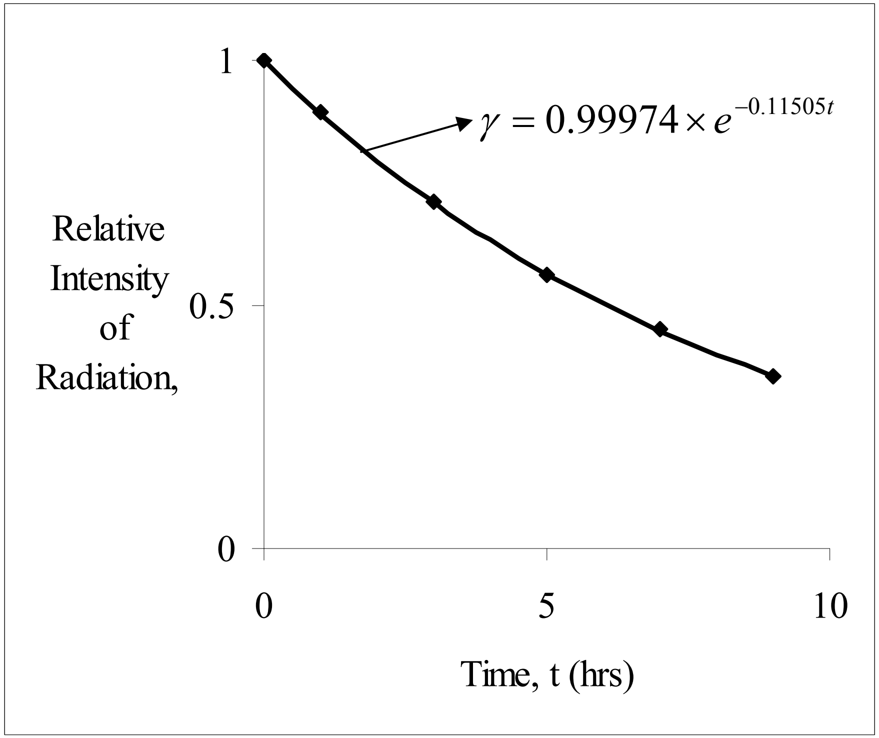

Figure. Relative intensity of radiation as a function of temperature using linearization of data model.

Example 3-Linearization of Data cont.

The regression formula is then

$$\gamma = 0.99974 \times e^{-0.11505t}$$

b) Half life of Technetium 99 is when $\gamma = \frac{1}{2}\gamma\Big|_{t=0}$

$$0.99974 \times e^{-0.11505t} = \frac{1}{2}\left(0.99974\right)e^{-0.11505(0)}$$

$$e^{-0.11508t} = 0.5$$

$$-0.11505t = \ln(0.5)$$

$$t = 6.0247 \ hours$$

Example 3-Linearization of Data cont.

c) The relative intensity of radiation after 24 hours is then

$$\begin{aligned}\gamma &= 0.99974e^{-0.11505(24)} \\ &= 0.063200\end{aligned}$$

This implies that only $\frac{6.3200\times 10^{-2}}{0.99983}\times 100 = 6.3211\%$ of the radioactive material is left after 24 hours.

Comparison

Comparison of exponential model with and without data linearization:

Table. Comparison for exponential model with and without data linearization.

	With data linearization (Example 3)	Without data linearization (Example 1)
A	0.99974	0.99983
λ	-0.11505	-0.11508
Half-Life (hrs)	6.0247	6.0232
Relative intensity after 2 hrs.	6.3160×10^{-2}	6.3200×10^{-2}

The values are very similar so data linearization was suitable to find the constants of the nonlinear exponential model in his case.