Polymath Examples:

Nonlinear Algebraic Equation

and Regression Problems

Problem

Flash evaporation of an ideal multicomponent mixture

Concept

Calculation of bubble point and dew point temperatures and associated vapor and liquid compositions for flash evaporation of an ideal multicomponent mixture.

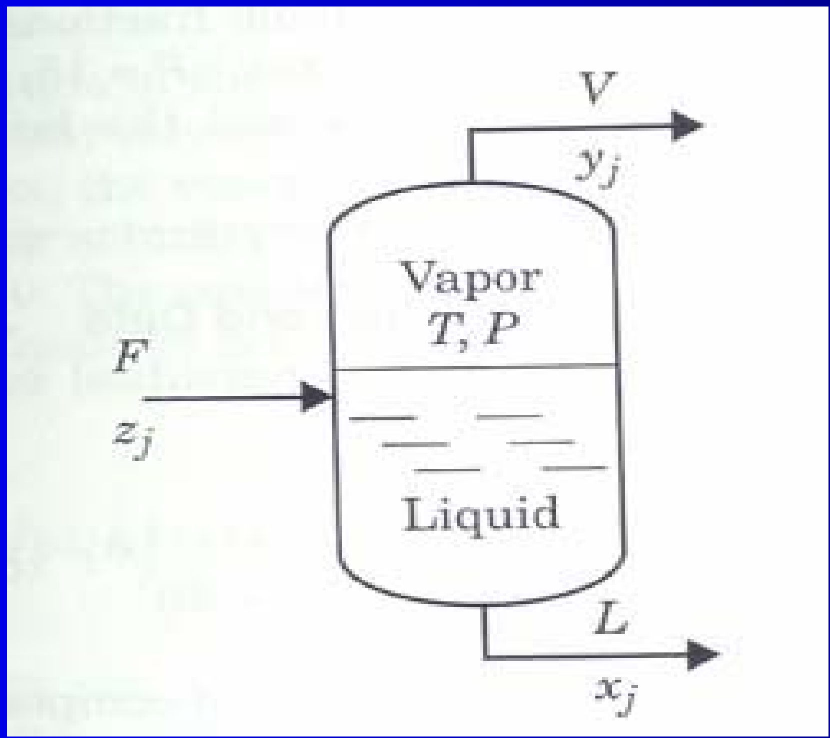
Numerical methods utilized

Solution of a single nonlinear algebraic equation.

Problem statement

A flash evaporator must separate ethylene and ethane from a feed stream which contains propane and n-butane.

Flash Evaporator



The evaporator will operate under high pressure ,between 15 and 25 atm with a feed stream at 50 ℃

Table. Liquid composition and Antoine equation constant

component	mole fraction	A	B	C
Ethylene	0.1	6.64380	395.74	266.681
Ethane	0.25	6.82915	663.72	256.681
Propane	0.5	6.80338	804.00	247.04
n-Butane	0.15	6.80776	935.77	238.789

problem

- Calculate the percent of the total feed at 50℃ that is evaporated and the corresponding mole fractions in the liquid and vapor streams for the following pressures: P=15,17,19,21,23,and 25atm.

Solution

This problem is calculated by a single nonlinear algebraic equation, from this equation, we can calculate the vapor to feed ratio and mole fractions.

$$f(a) = \sum_{j=1}^{n_c} (x_j - y_j) = \sum_{j=1}^{n_c} \frac{z_j (1 - k_j)}{1 + a(k_j - 1)} = 0$$

and

$$x_j = \frac{z_j}{1 + a(k_j - 1)}$$

$$y_j = k_j x_j$$

$$P_j = 10^{[A_j - (\frac{B_j}{C_j + T})]}$$

$$k_j = \frac{P_j}{P}$$

then

$$f(a) = \sum_{j=1}^{n_c} x_j (1 - k_j)$$

Solution

The equations are entered into POLYMATH *Simultaneous Algebraic Equation Solver* for the case of P=20 atm and T=50℃ are given as follows:

equations:

```
f(alpha)=x1*(1-k1)+x2*(1-k2)+x3*(1-k3)+x4*(1-k4)
q=20*760
TC=50
k1=10^(6.6438-395.74/(266.681+TC))/P
k2=10^(6.82915-663.72/(256.681+TC))/P
k3=10^(6.80338-804/(247.04+TC))/P
k4=10^(6.80776-935.77/(238.789+TC))/P
x1=0.1/(1+alpha*(k1-1))
x2=0.25/(1+alpha*(k2-2))
x3=0.5/(1+alpha*(k3-3))
x4=0.15/(1+alpha*(k4-4))
y1=k1*x1
y2=k2*x2
y3=k3*x3
y4=k4*x4
alpha(min)=0,alpha(max)=1
```

Result

NLE Solution

Variable	Value	f(x)	Ini Guess
alpha	0.6967064	2.121E-14	0.5
P	1.52E+04		
TC	50		
k1	16.304509		
k2	3.0416078		
k3	0.8219213		
k4	0.2429921		
x1	0.0085743		
x2	0.1032034		
x3	0.5708209		
x4	0.3174014		
y1	0.1397999		
y2	0.3139042		
y3	0.4691699		
y4	0.077126		

NLE Report (safenewt)

Nonlinear equations

[1] f(alpha) = x1*(1-k1)+x2*(1-k2)+x3*(1-k3)+x4*(1-k4) = 0

Explicit equations

[1] P = 20*760

[2] TC = 50

[3] k1 = 10^(6.6438-395.74/(266.681+TC))/P

[4] k2 = 10^(6.82915-663.72/(256.681+TC))/P

[5] k3 = 10^(6.80338-804/(247.04+TC))/P

[6] k4 = 10^(6.80776-935.77/(238.789+TC))/P

[7] x1 = 0.1/(1+alpha*(k1-1))

[8] x2 = 0.25/(1+alpha*(k2-1))

[9] x3 = 0.5/(1+alpha*(k3-1))

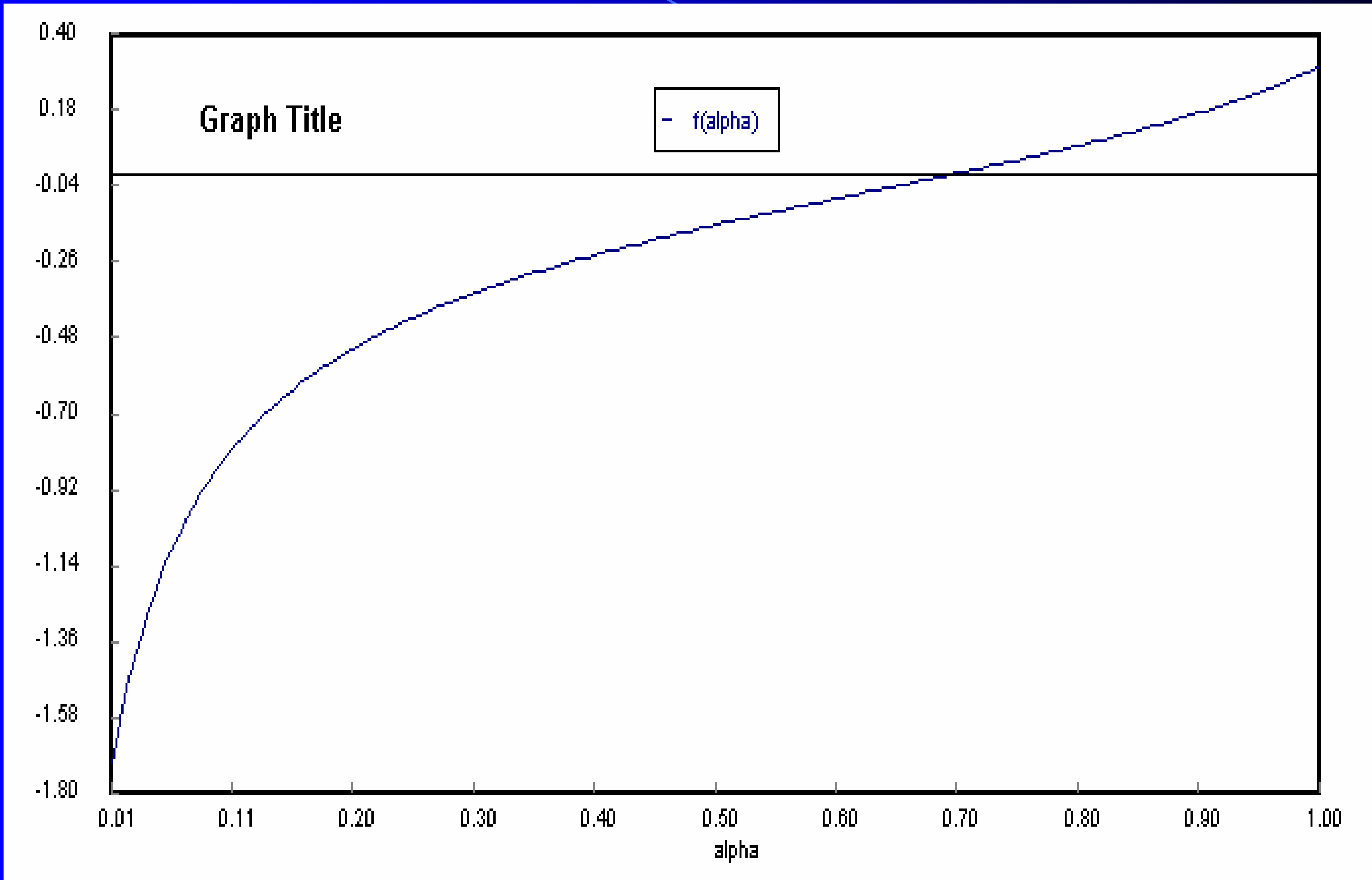
[10] x4 = 0.15/(1+alpha*(k4-1))

[11] y1 = k1*x1

[12] y2 = k2*x2

[13] y3 = k3*x3

[14] y4 = k4*x4



Graph Title
f(alpha)
0.40
0.18
-0.04
-0.26
-0.48
-0.70
-0.92
-1.14
-1.36
-1.58
-1.80
0.01
0.11
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
alpha

Result

NLE Solution

Variable	Value	f(x)	Ini Guess
alpha	1.0159791	5.901E-09	0.5
P	1.14E+04		
TC	50		
k1	21.739345		
k2	4.0554771		
k3	1.0958951		
k4	0.3239895		
x1	0.0045309		
x2	0.0609117		
x3	0.455611		
x4	0.4789464		
y1	0.0984985		
y2	0.2470261		
y3	0.4993019		
y4	0.1551736		

NLE Report (safenewt)

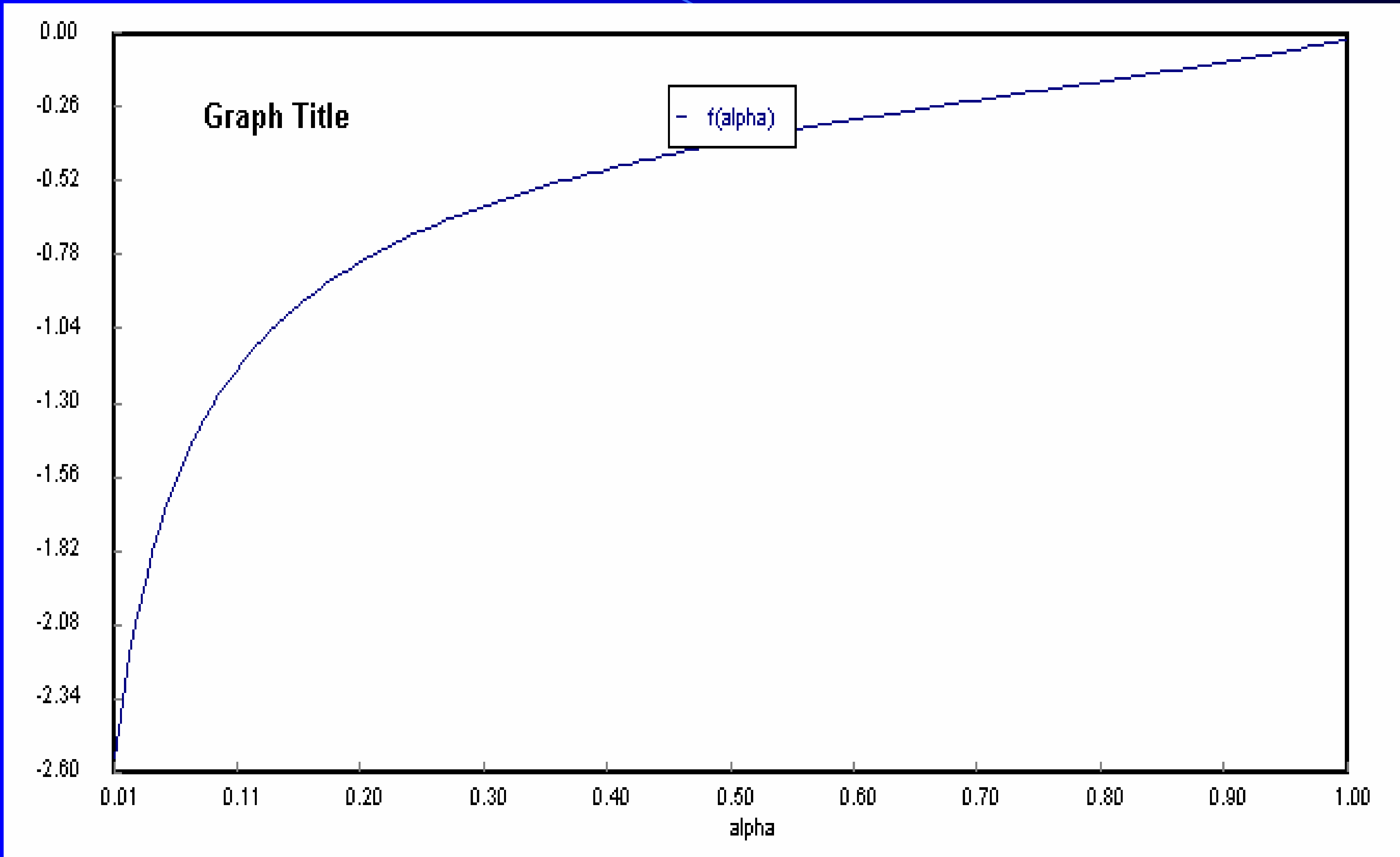
Nonlinear equations

[1] f(alpha) = x1*(1-k1)+x2*(1-k2)+x3*(1-k3)+x4*(1-k4) = 0

Explicit equations

[1] P = 15*760
[2] TC = 50
[3] k1 = 10^(6.6438-395.74/(266.681+TC))/P
[4] k2 = 10^(6.82915-663.72/(256.681+TC))/P
[5] k3 = 10^(6.80338-804/(247.04+TC))/P
[6] k4 = 10^(6.80776-935.77/(238.789+TC))/P
[7] x1 = 0.1/(1+alpha*(k1-1))
[8] x2 = 0.25/(1+alpha*(k2-1))
[9] x3 = 0.5/(1+alpha*(k3-1))
[10] x4 = 0.15/(1+alpha*(k4-1))
[11] y1 = k1*x1
[12] y2 = k2*x2
[13] y3 = k3*x3
[14] y4 = k4*x4

Result



Graph Title
f(alpha)
0.00
-0.26
-0.52
-0.78
-1.04
-1.30
-1.56
-1.82
-2.08
-2.34
-2.60
0.01
0.11
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
alpha

Result

NLE Solution

Variable	Value	f(x)	Ini Guess
alpha	0.8785873	2.652E-12	0.5
P	1.292E+04		
TC	50		
k1	19.181775		
k2	3.5783622		
k3	0.9669663		
k4	0.2858731		
x1	0.0058913		
x2	0.0765623		
x3	0.5149453		
x4	0.4026012		
y1	0.113005		
y2	0.2739675		
y3	0.4979347		
y4	0.1150928		

NLE Report (safenewt)

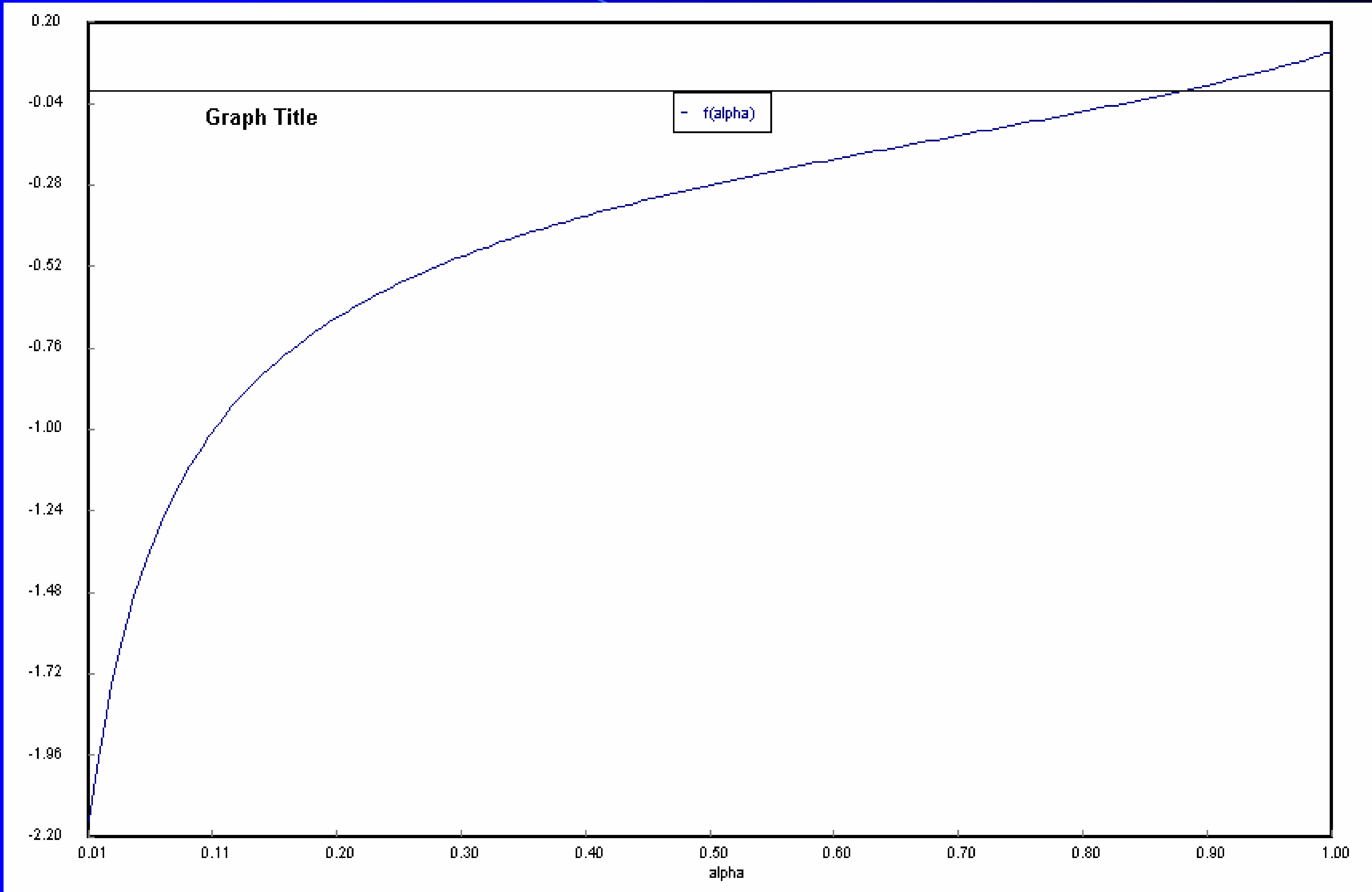
Nonlinear equations

[1] f(alpha) = x1*(1-k1)+x2*(1-k2)+x3*(1-k3)+x4*(1-k4) = 0

Explicit equations

[1] P = 17*760
[2] TC = 50
[3] k1 = 10^(6.6438-395.74/(266.681+TC))/P
[4] k2 = 10^(6.82915-663.72/(256.681+TC))/P
[5] k3 = 10^(6.80338-804/(247.04+TC))/P
[6] k4 = 10^(6.80776-935.77/(238.789+TC))/P
[7] x1 = 0.1/(1+alpha*(k1-1))
[8] x2 = 0.25/(1+alpha*(k2-1))
[9] x3 = 0.5/(1+alpha*(k3-1))
[10] x4 = 0.15/(1+alpha*(k4-1))
[11] y1 = k1*x1
[12] y2 = k2*x2
[13] y3 = k3*x3
[14] y4 = k4*x4

Result



Graph Title
f(alpha)
0.20
-0.04
-0.28
-0.52
-0.76
-1.00
-1.24
-1.48
-1.72
-1.96
-2.20
0.01
0.11
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
alpha

Result

NLE Solution

Variable	Value	f(x)	Ini Guess
alpha	0.7541049	5.294E-12	0.5
P	1.444E+04		
TC	50		
k1	17.162641		
k2	3.2016925		
k3	0.8651803		
k4	0.2557812		
x1	0.0075825		
x2	0.0939741		
x3	0.5565872		
x4	0.3418562		
y1	0.1301351		
y2	0.3008762		
y3	0.4815483		
y4	0.0874404		

NLE Report (safenewt)

Nonlinear equations

[1] f(alpha) = x1*(1-k1)+x2*(1-k2)+x3*(1-k3)+x4*(1-k4) = 0

Explicit equations

[1] P = 19*760

[2] TC = 50

[3] k1 = 10^(6.6438-395.74/(266.681+TC))/P

[4] k2 = 10^(6.82915-663.72/(256.681+TC))/P

[5] k3 = 10^(6.80338-804/(247.04+TC))/P

[6] k4 = 10^(6.80776-935.77/(238.789+TC))/P

[7] x1 = 0.1/(1+alpha*(k1-1))

[8] x2 = 0.25/(1+alpha*(k2-1))

[9] x3 = 0.5/(1+alpha*(k3-1))

[10] x4 = 0.15/(1+alpha*(k4-1))

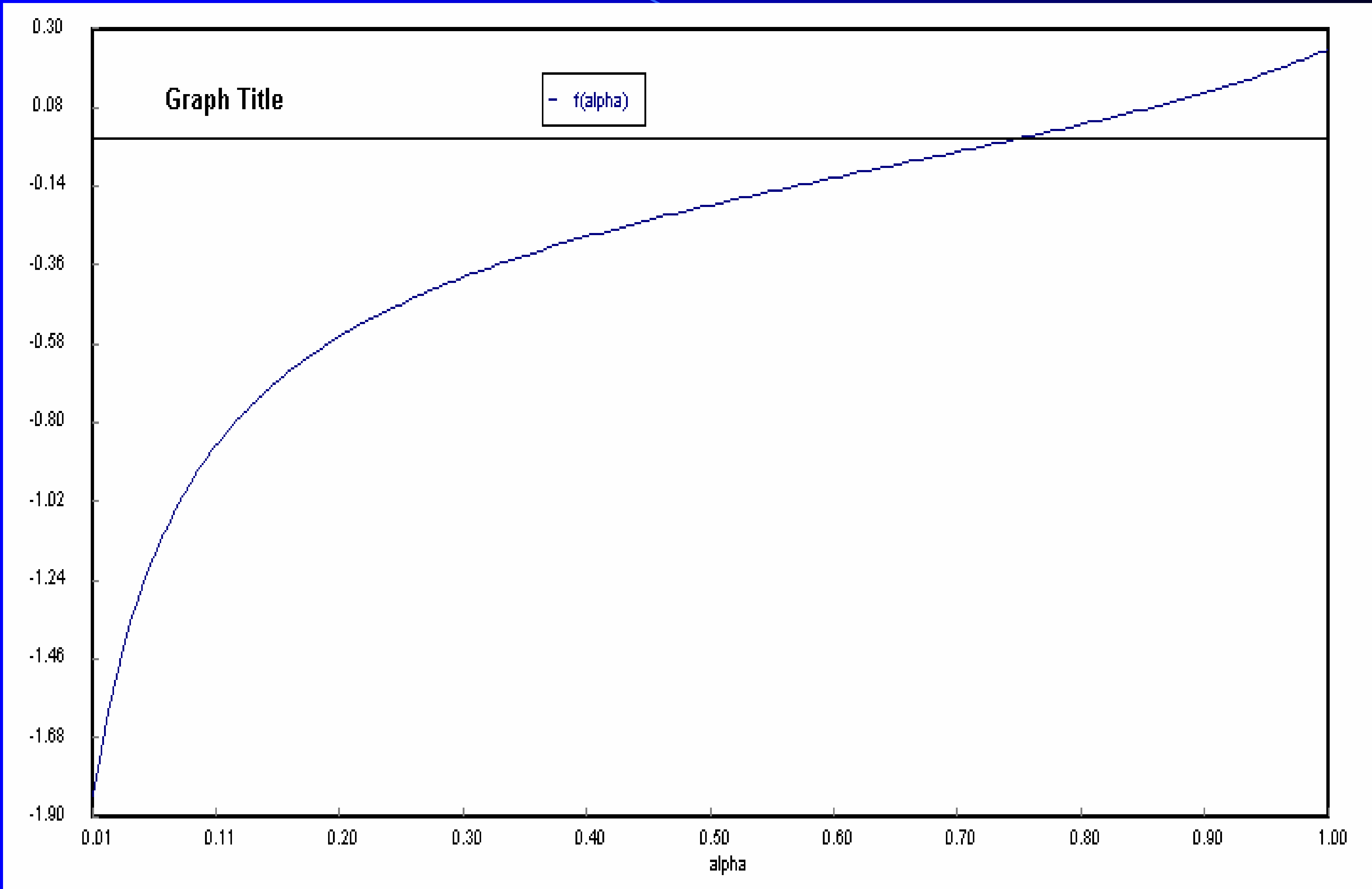
[11] y1 = k1*x1

[12] y2 = k2*x2

[13] y3 = k3*x3

[14] y4 = k4*x4

Result



Graph Title
f(alpha)
0.30
0.08
-0.14
-0.36
-0.58
-0.80
-1.02
-1.24
-1.46
-1.68
-1.90
0.01
0.11
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
alpha

Result

NLE Solution

Variable	Value	f(x)	Ini Guess
alpha	0.642934	6.236E-08	0.5
P	1.596E+04		
TC	50		
k1	15.528103		
k2	2.8967694		
k3	0.7827822		
k4	0.2314211		
x1	0.0096706		
x2	0.1126381		
x3	0.5811634		
x4	0.296528		
y1	0.1501662		
y2	0.3262866		
y3	0.4549243		
y4	0.0686228		

NLE Report (safenewt)

Nonlinear equations

[1] f(alpha) = x1*(1-k1)+x2*(1-k2)+x3*(1-k3)+x4*(1-k4) = 0

Explicit equations

[1] P = 21*760

[2] TC = 50

[3] k1 = 10^(6.6438-395.74/(266.681+TC))/P

[4] k2 = 10^(6.82915-663.72/(256.681+TC))/P

[5] k3 = 10^(6.80338-804/(247.04+TC))/P

[6] k4 = 10^(6.80776-935.77/(238.789+TC))/P

[7] x1 = 0.1/(1+alpha*(k1-1))

[8] x2 = 0.25/(1+alpha*(k2-1))

[9] x3 = 0.5/(1+alpha*(k3-1))

[10] x4 = 0.15/(1+alpha*(k4-1))

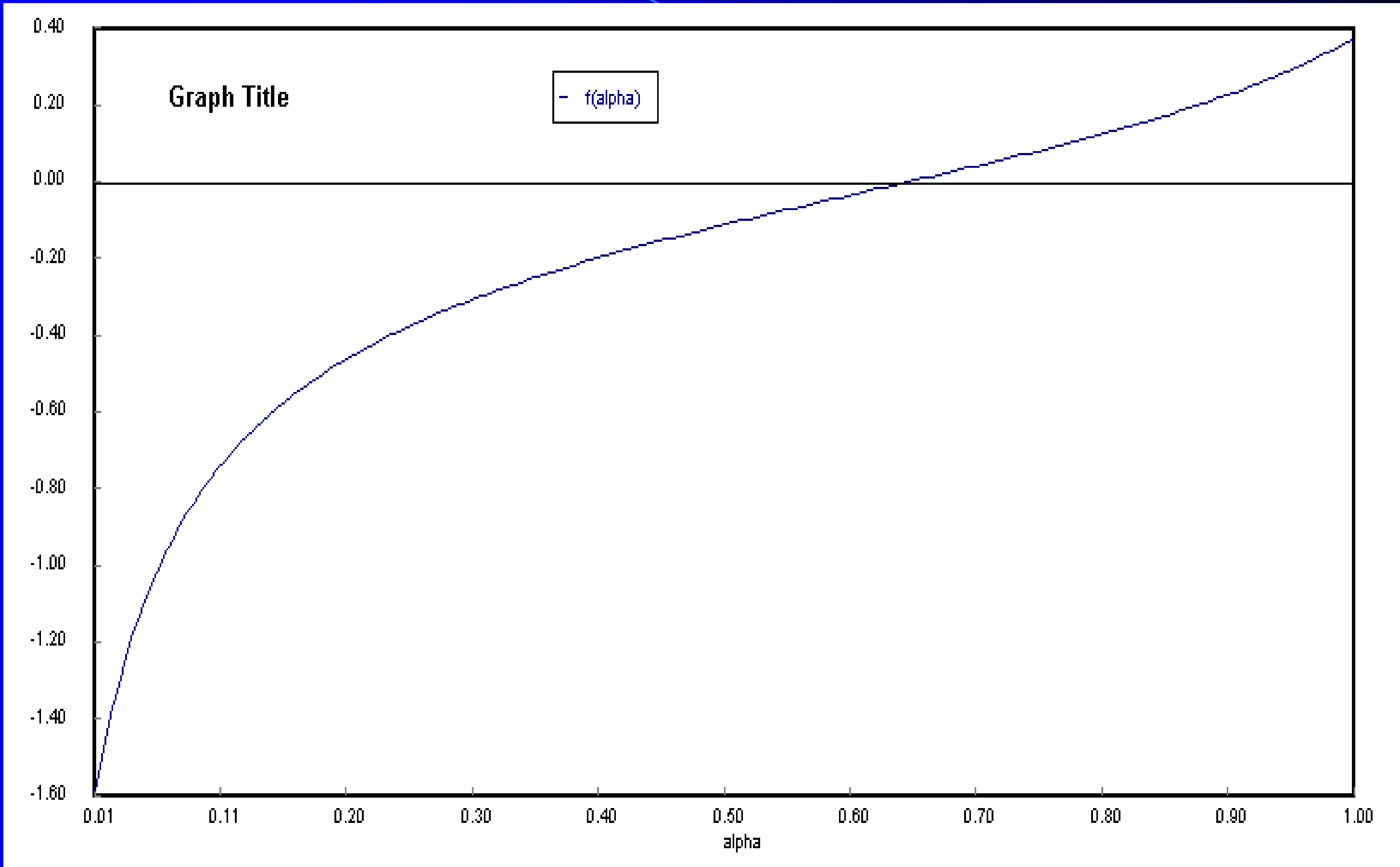
[11] y1 = k1*x1

[12] y2 = k2*x2

[13] y3 = k3*x3

[14] y4 = k4*x4

Result


Graph Title
f(alpha)
0.40
0.20
0.00
-0.20
-0.40
-0.60
-0.80
-1.00
-1.20
-1.40
-1.60
0.01
0.11
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
alpha

Result

NLE Solution

Variable	Value	f(x)	Ini Guess
alpha	0.4657069	-6.665E-13	0.5
P	1.9E+04		
TC	50		
k1	13.043607		
k2	2.4332863		
k3	0.6575371		
k4	0.1943937		
x1	0.0151314		
x2	0.1499258		
x3	0.5948751		
x4	0.2400678		
y1	0.1973675		
y2	0.3648124		
y3	0.3911524		
y4	0.0466677		

NLE Report (safenewt)

Nonlinear equations

[1] f(alpha) = x1*(1-k1)+x2*(1-k2)+x3*(1-k3)+x4*(1-k4) = 0

Explicit equations

[1] P = 25*760

[2] TC = 50

[3] k1 = 10^(6.6438-395.74/(266.681+TC))/P

[4] k2 = 10^(6.82915-663.72/(256.681+TC))/P

[5] k3 = 10^(6.80338-804/(247.04+TC))/P

[6] k4 = 10^(6.80776-935.77/(238.789+TC))/P

[7] x1 = 0.1/(1+alpha*(k1-1))

[8] x2 = 0.25/(1+alpha*(k2-1))

[9] x3 = 0.5/(1+alpha*(k3-1))

[10] x4 = 0.15/(1+alpha*(k4-1))

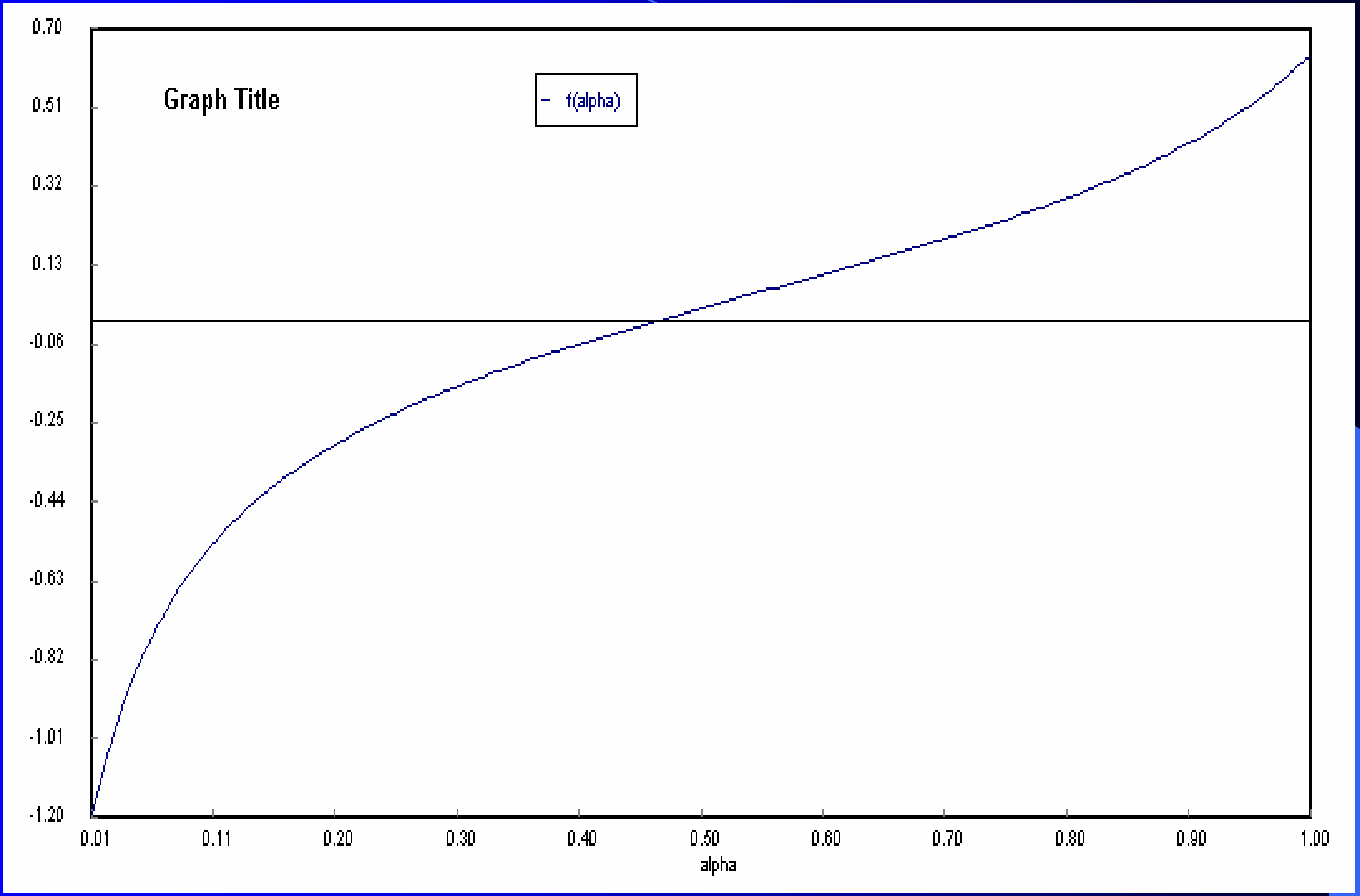
[11] y1 = k1*x1

[12] y2 = k2*x2

[13] y3 = k3*x3

[14] y4 = k4*x4

Result



alpha

Result

component mole fractions		Ethylene	Ethane	Propane	n-Butane
feed		0.1	0.25	0.5	0.15
P=20	vapor (y_j)	0.1398	0.313904	0.46917	0.077126
	liquid (x_j)	0.008574	0.103203	0.570821	0.317401
P=15	vapor (y_j)	0. 098499	0. 247026	0. 499302	0. 1551736
	liquid (x_j)	0. 004531	0. 060912	0. 455611	0. 4789464
P=17	vapor (y_j)	0. 113005	0. 273968	0. 497935	0. 1150928
	liquid (x_j)	0. 005891	0. 076562	0. 514945	0. 4026012
P=19	vapor (y_j)	0. 130135	0. 300876	0. 481548	0. 0874404
	liquid (x_j)	0. 007583	0. 093974	0. 556587	0. 3418562
P=21	vapor (y_j)	0. 150166	0. 326287	0. 454924	0. 0686228
	liquid (x_j)	0. 009671	0. 112638	0. 581163	0. 296528
P=23	vapor (y_j)	0. 172757	0. 34809	0. 423419	0. 055735
	liquid (x_j)	0. 012185	0. 131609	0. 592431	0. 263775
P=25	vapor (y_j)	0. 197368	0. 364812	0. 391152	0. 0466677
	liquid (x_j)	0. 015131	0. 149926	0. 594875	0. 2400678

Problem

Correlation of activity coefficients with the Van Laar equations

Concept

Estimation of parameters in the Van Laar equations for the correlation of binary activity coefficients.

Numerical methods utilized

Linear and nonlinear regression, transformation of data for regression, calculation and comparisons of confidence intervals, residual plots, and sum of squares.

Problem statement

(a) Use linear regression on equation (3) with the data of TABLE to determine A and B in the Van Laar equations for the benzene and n-heptane binary system.

(b) Estimate A and B by employing nonlinear regression on Equation (3) and a single equation that is the sum of Equations(1) and (2) .

(c) Compare the results of the regressions in (a) and (b) using parameter confidence intervals, residual plots, and sums of squares of errors (least-squares summations calculated with both activity coefficients).

Solution

TABLE . The activity coefficients for the system Benzene (1) and n-Heptane(2)

No.	x_1	γ_1	γ_2
1	0.0464	1.2968	0.9985
2	0.0861	1.2798	0.9998
3	0.2004	1.2358	1.0068
4	0.2792	1.1988	1.0159
5	0.3842	1.1598	1.0359
6	0.4857	1.1196	1.0676
7	0.5824	1.0838	1.1096
8	0.6904	1.0538	1.1664

Solution

(a) Linear regression of excess Gibbs energy equation

$$g = G_E / RT = x_1 \ln\gamma_1 + x_2 \ln\gamma_2 = ABx_1x_2/(Ax_1 + Bx_2) \quad (3)$$

The upper equation can be rewritten in a linearized form for the determination of A and B using linear regression as

$$\frac{x_1}{x_1 \ln\gamma_1 + x_2 \ln\gamma_2} = \frac{1}{A} + \frac{1}{B}\frac{x_1}{x_2} = a_0 + a_1 X_1$$

$a_0 = 1/A \quad a_1 = 1/B$

Thus the final one transformation column needed for linear regression can be defined as $X_1 = x_1/x_2$ and $G = x_1/(x_1 \ln\gamma_1 + x_2 \ln\gamma_2)$

Result

Linear Regression Report

Model: G = a0 + a1*X1

Variable	Value	95% confidence
a0	3.7787592	0.1894029
a1	2.0173762	0.0605644

General
Regression including free parameter
Number of observations = 10

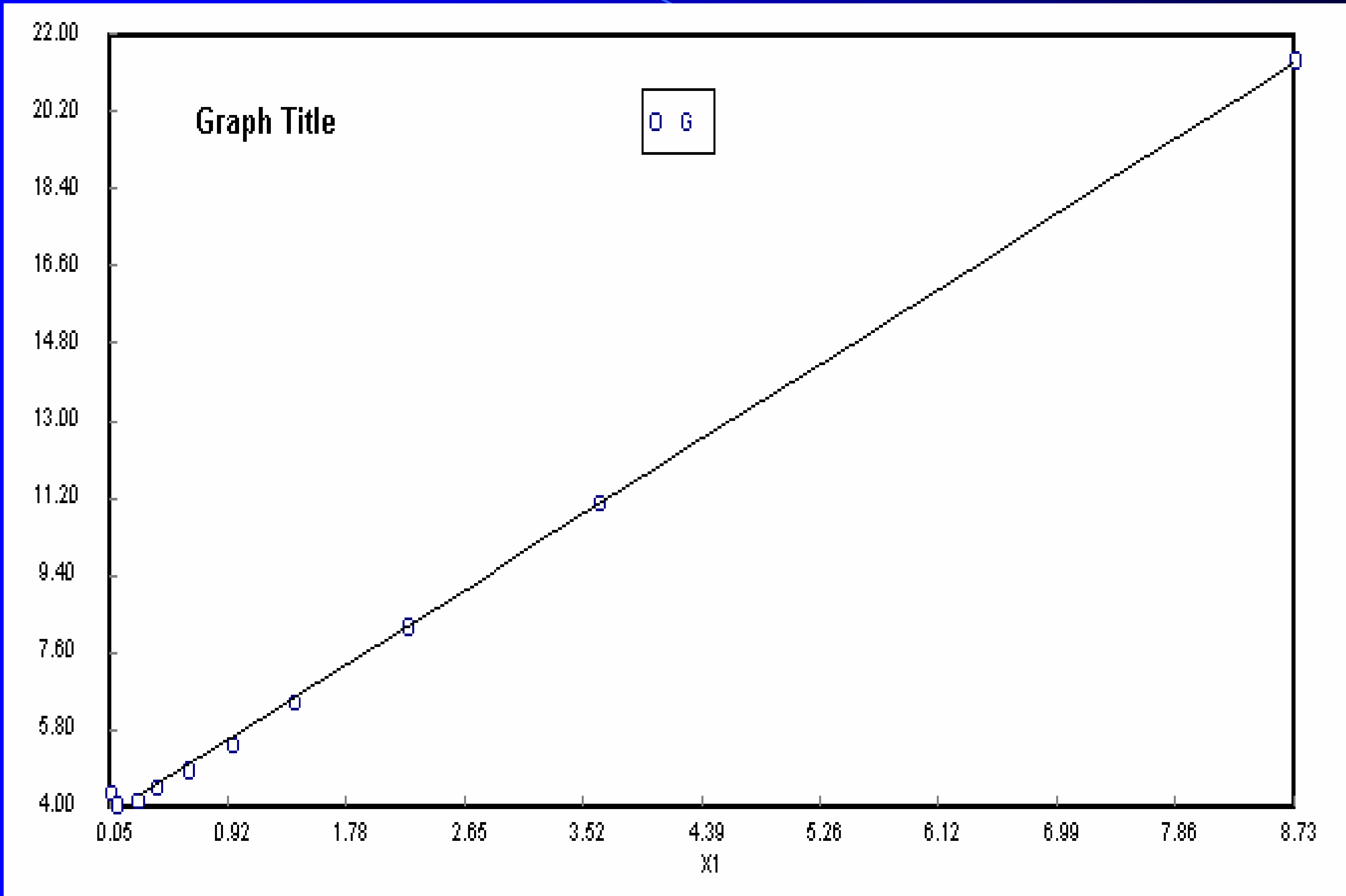
Statistics
R^2 = 0.9986459
R^2adj = 0.9984767
Rmsd = 0.0595125
Variance = 0.0442718

Through calculation, we can get the value of A and B

$A=1/a_0=1/3.7787592=0.2646$

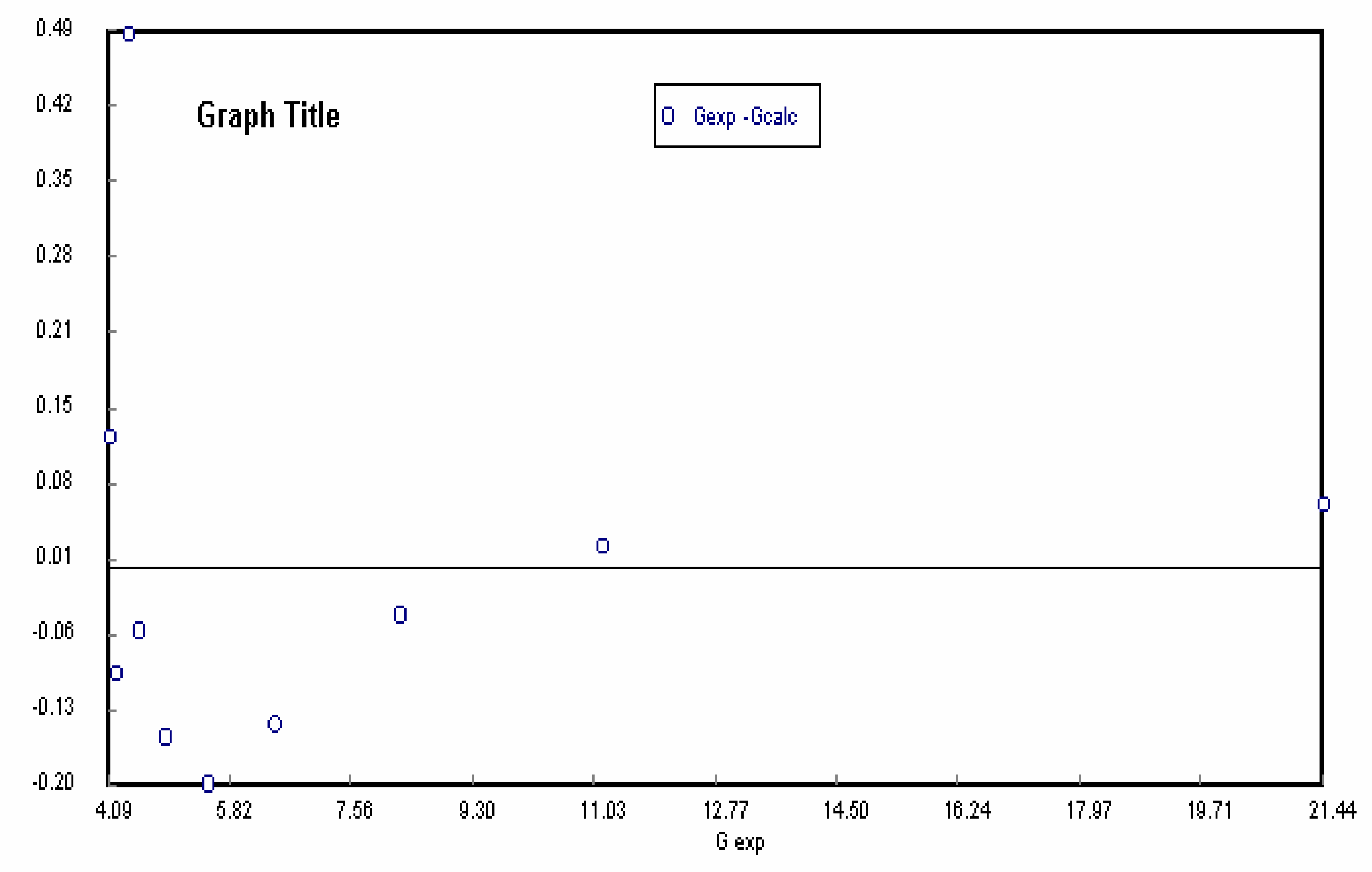
$B=1/a_1=1/2.0173762=0.4957$

Result



Graph Title
O G
22.00
20.20
18.40
16.60
14.80
13.00
11.20
9.40
7.60
5.80
4.00
0.05
0.92
1.78
2.65
3.52
4.39
5.26
6.12
6.99
7.86
8.73
X1

Result



Graph Title
Gexp -Gcalc
0.49
0.42
0.35
0.28
0.21
0.15
0.08
0.01
-0.06
-0.13
-0.20
4.09
5.82
7.56
9.30
11.03
12.77
14.50
16.24
17.97
19.71
21.44
G exp

(b) Nonlinear regression for sum of γ 1 and γ 2

$$\gamma_1 = \exp\left\{A/\left[1+(x_1/x_2)(A/B)\right]^2\right\} \quad (1)$$

$$\gamma_2 = \exp\left\{B/\left[1+(x_2/x_1)(B/A)\right]^2\right\} \quad (2)$$

$$gsum = \exp\left\{A/\left[1+(x_1/x_2)(A/B)\right]^2\right\} + \exp\left\{B/\left[1+(x_2/x_1)(B/A)\right]^2\right\}$$

Introduce gsum equation into the nonlinear regression program in the polymath. We can get the value of A and B.

Result

Nonlinear regression (L-M)

Model: gsum = exp(A/(1+(x1/x2)*(A/B))^2)+exp(B/(1+(x2/x1)*(B/A))^2)

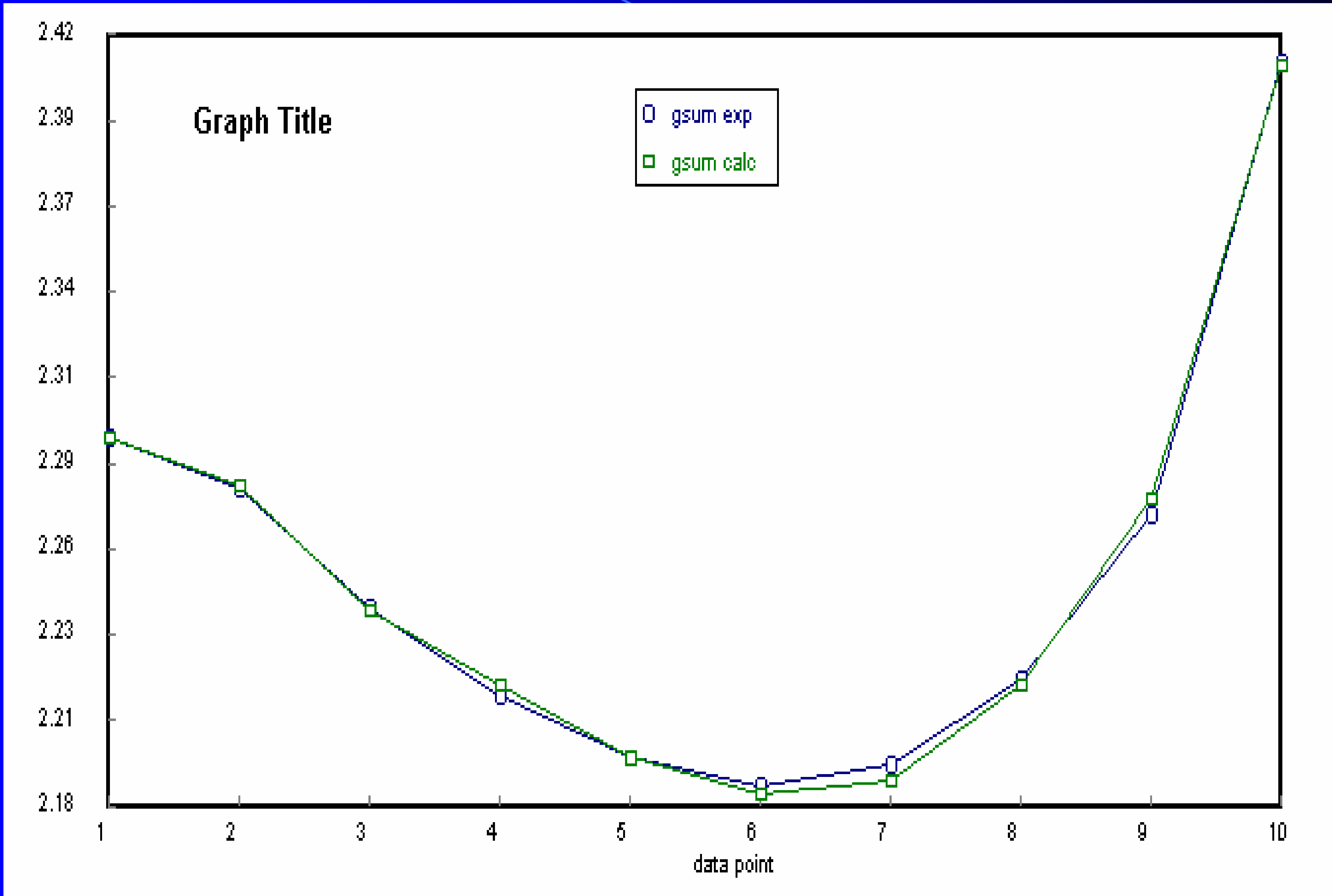
Variable	Ini guess	Value	95% confidence
A	0.25	0.2722954	0.0040212
B	0.46	0.493803	0.0114727

Nonlinear regression settings
Max # iterations = 64

Precision
R^2 = 0.9981693
R^2adj = 0.9979404
Rmsd = 8.744E-04
Variance = 9.557E-06

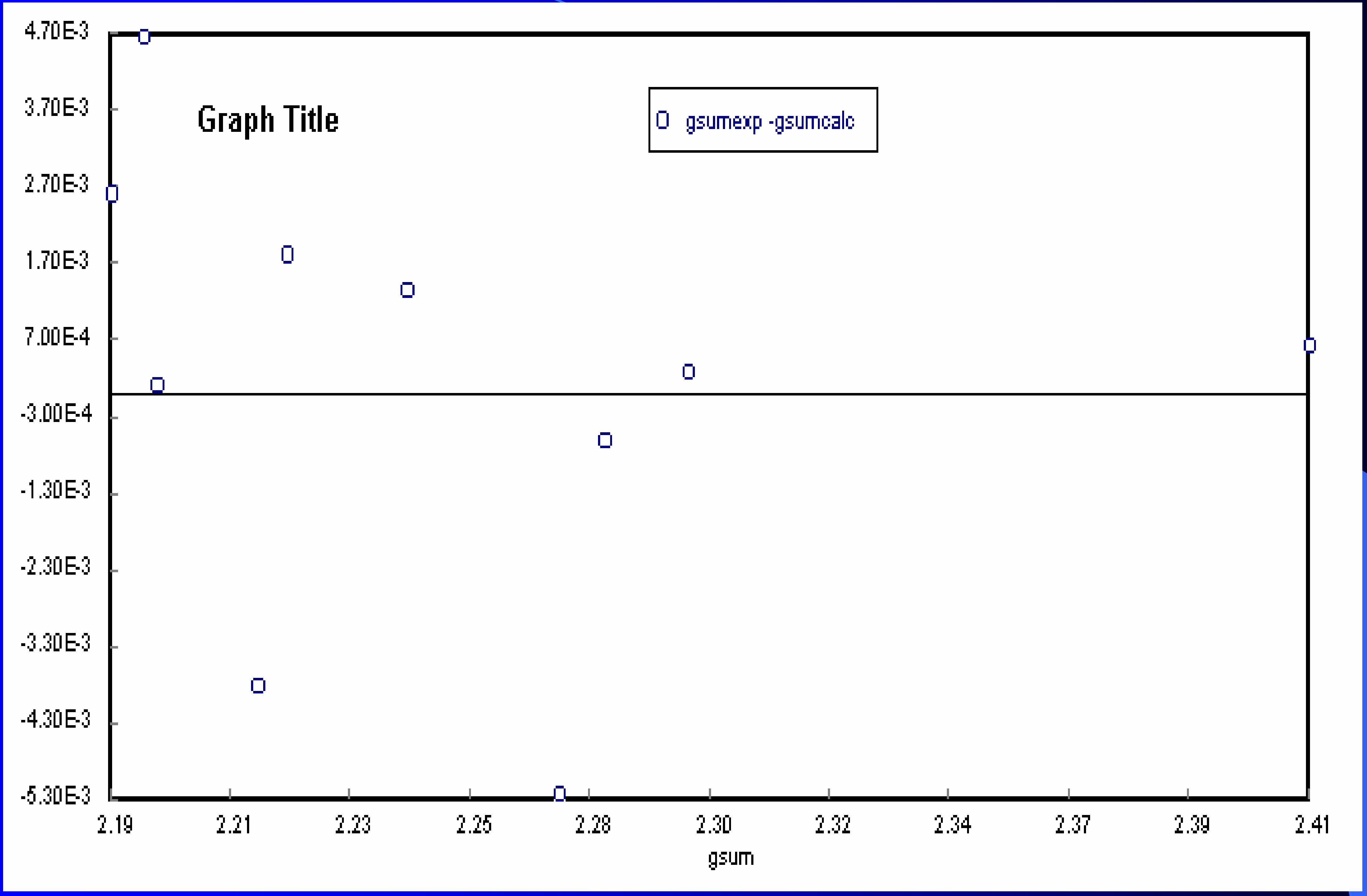
General
Sample size = 10
Model vars = 2
Indep vars = 2
Iterations = 3

Result



Graph Title
gsum exp
gsum calc
2.42
2.39
2.37
2.34
2.31
2.29
2.26
2.23
2.21
2.18
1
2
3
4
5
6
7
8
9
10
data point

Result



Graph Title
gsumexp -gsumcalc
4.70E-3
3.70E-3
2.70E-3
1.70E-3
7.00E-4
-3.00E-4
-1.30E-3
-2.30E-3
-3.30E-3
-4.30E-3
-5.30E-3
2.19
2.21
2.23
2.25
2.28
2.30
2.32
2.34
2.37
2.39
2.41
gsum

(c) Compare the results of the regressions in (a) and (b)

A and B of the linear regression calculated and the nonlinear regression calculated is entered into the equation of γ_1 and γ_2. The resulting values from γ_1 and γ_2 are defined as γ_{1calc} and γ_{2calc}, and then introduced the γ_1, γ_2, γ_{1calc} and γ_{2calc} into the SS equation to calculate the SS in the POLYMATH.

$$SS = \sum_{i=1}^{N} [(\gamma_{1i} - \gamma_{1i(calc)})^2 + (\gamma_{2i} - \gamma_{2i(calc)})^2]$$

We can get SS of the linear regression and the nonlinear regression through sum of each data.

$$SS = 0.788 \times 10^{-3}$$ (for linear regression)

$$SS = 3.91 \times 10^{-4}$$ (for nonlinear regression)