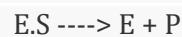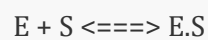# Homework update

dynafit

前面的作业已用 mcr_als matlab 工具包将动力学实验数据分解成了光谱矩阵和浓度矩阵。这里使用得到的各浓度矩阵进行动力学建模。各模型基于米氏方程，使用软件为 dynafit。

- **漆酶+底物体系（LAC_SUB）**

两组分体系，酶和底物，机理为：

```
E + S <===> E.S
E.S ----> E + P
```

运行 dynafit 脚本如下：

```
[task]
   task = fit
   data = progress discontinuous
[mechanism]
   E + S <===> E.S   :   k1+.S   k1-.S
   E.S ----> E + P    :   k2+.P
[constants]
   k1+.S = 1 ?
   k1-.S = 0.01 ?
   k2+.P = 1 ?
[concentrations]
   S = 47
   E = 0.5
[responses]
   P = 10 ?
[data]
   directory D:/Appsetup/DynaFit4/examples/HW1
   sheet LAC_SUB_1.csv
   column 2
   offset auto ?
[output]
   XAxisLabel = time, sec
   YAxiaLabel = product, %
[end]
```

结果

三个平行实验组模型回归评估 summary 依次如下

Regression Summary
Trust-Region Algorithm

unweighted sum of squares	396.188
weighted sum of squares	396.188
mean square	0.662521
r.m.s. deviation	0.813954
relative r.m.s. (%)	5.73591
R^2 ... [a]	0.960442
R^2_{adj} ... [a]	0.960175
log(determinant)	0
data points	598
optimized parameters	5
iterations	46
elapsed time (sec)	0.224

组 1

Regression Summary
Trust-Region Algorithm

unweighted sum of squares	486.783
weighted sum of squares	486.783
mean square	0.814018
r.m.s. deviation	0.902229
relative r.m.s. (%)	6.95249
R^2 ... [a]	0.949609
R^2_{adj} ... [a]	0.949269
log(determinant)	0
data points	598
optimized parameters	5
iterations	39
elapsed time (sec)	0.135

组 2

Regression Summary
Trust-Region Algorithm

unweighted sum of squares	439.018
weighted sum of squares	439.018
mean square	0.734144
r.m.s. deviation	0.856822
relative r.m.s. (%)	7.24605
R^2 ... [a]	0.950657
R^2_{adj} ... [a]	0.950325
log(determinant)	0
data points	598
optimized parameters	5
iterations	281
elapsed time (sec)	0.842

组 3

三个平行实验组数据和模型可视化依次如下

组 1

组 2

组 3
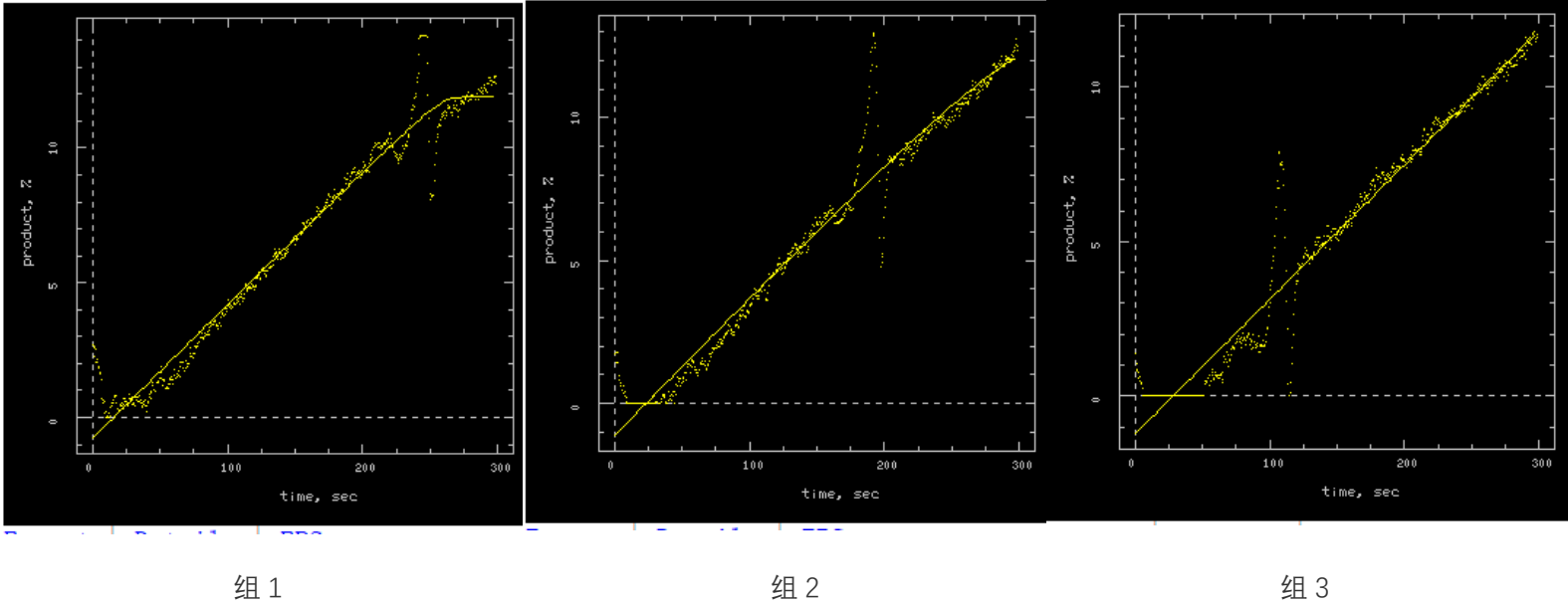
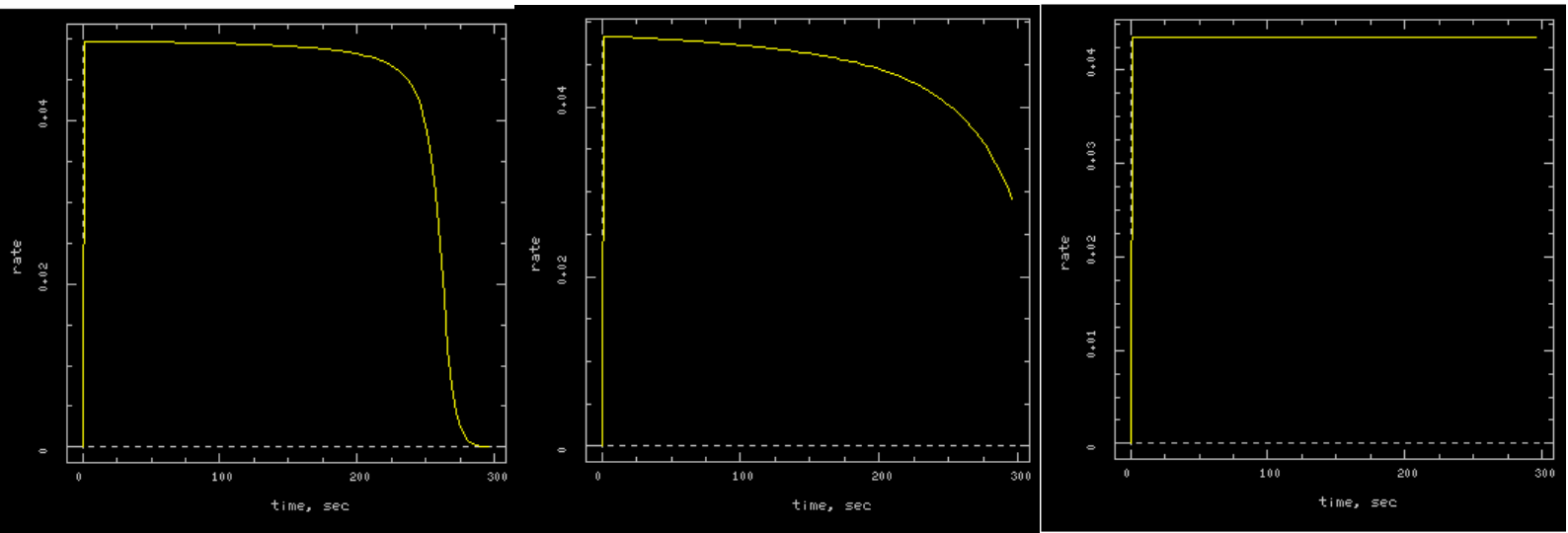反应速率图

组 1   组 2   组 3

初始反应速率:

组 1: 0.0497098

组 2: 0.048394

组 3: 0.0435876

模型各参数:

Parameters

Trust Region Algorithm

Optimized Parameters

No.	Par#Set	Initial	Final	Std. Error	CV (%)	Note
#1	k1+.S	1	240	670000	278877.6	
#2	k1-.S	0.01	97	270000	282183.8	
#3	k2+.P	1	0.372	0.0071	1.9	
#4	r(P)	10	0.2696	0.0035	1.3	
#5	offset#1	2.69613	-0.776	0.086	11.0	

组 1

Parameters

Trust Region Algorithm

Optimized Parameters

No.	Par#Set	Initial	Final	Std. Error	CV (%)	Note
#1	k1+.S	1	4.7	6800	144209.6	
#2	k1-.S	0.01	9.5	14000	148840.6	
#3	k2+.P	1	0.336	0.031	9.3	
#4	r(P)	10	0.301	0.054	18.1	
#5	offset#1	1.72302	-1.13	0.37	32.5	

组 2

Parameters

Trust Region Algorithm

Optimized Parameters

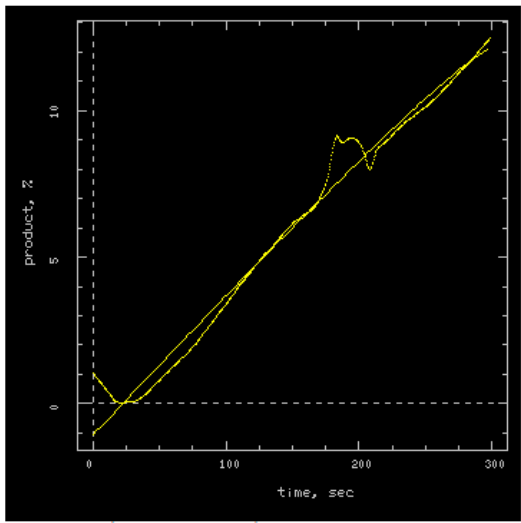| No.	Par#Set	Initial	Final	Std. Error	CV (%)	Note
#1	k1+.S	1	8	81000	1008811.4	
#2	k1-.S	0.01	7.6	27000	355758.8	
#3	k2+.P	1	0.011	120	1109002.4	
#4	r(P)	10	8.1	92000	1130001.9	
#5	offset#1	1.39777	-1.2	1.1	91.7	

组 3

残差分布图:
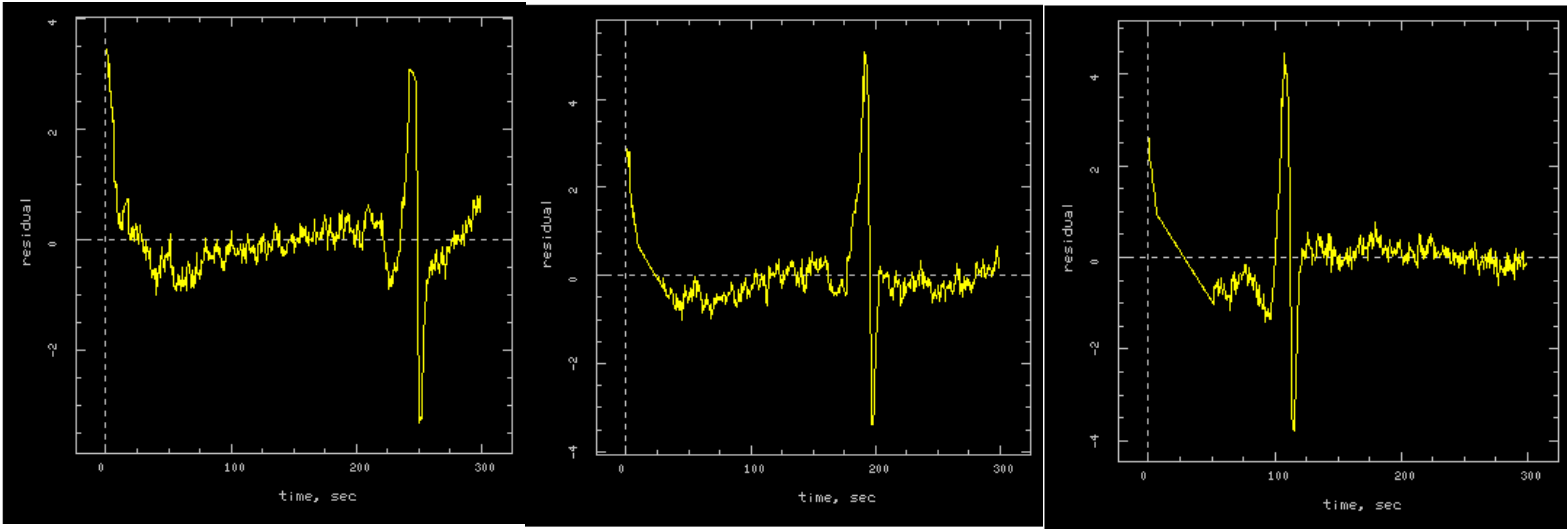
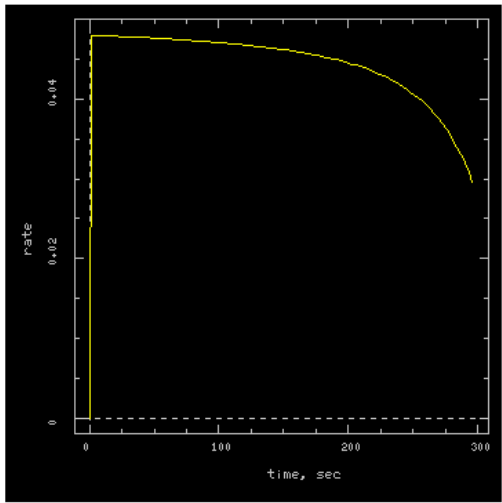组 1   组 2   组 3

为了减小数据误差，使用 origin 将曲线进行光滑，使用光滑后的数据再次进行建模。
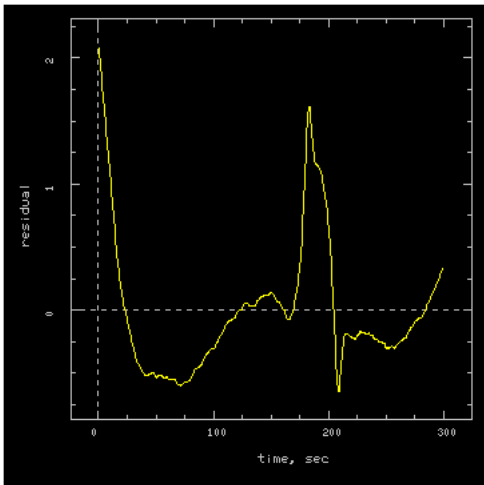此处由于篇幅问题，只展示组 2 光滑后的数据
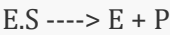

Data&Model

Reaction Rate

Parameters

Residual

可见光滑处理后误差有所减小，拟合更优。

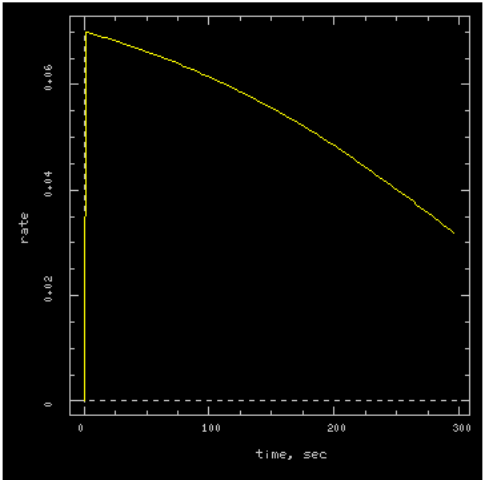- 漆酶+介体 TEMPO+底物体系（LAC_TEMPO_SUB）

  鉴于篇幅，只选取第三组进行展示
  1. 若为两组分体系，模型依然为：

```
E + S <===> E.S
E.S ----> E + P
```
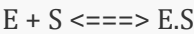
运行脚本与之前相同，只需更改输入文件。
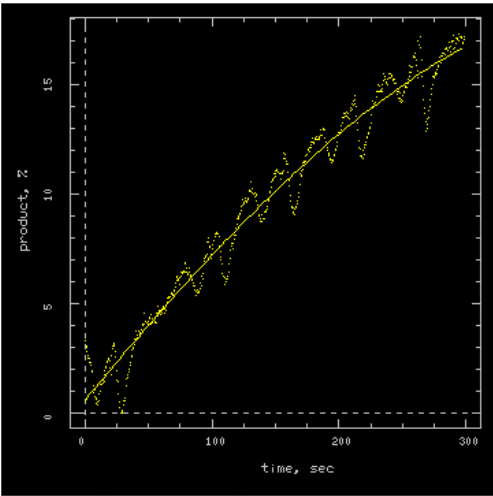
浓度-时间模型图

反应速率图

Parameters

Trust Region Algorithm

Optimized Parameters

No.	Par#Set	Initial	Final	Std. Error	CV (%)
#1	k1+.S	1	0.61	93	15268.5
#2	k1-.S	0.01	11	1700	15076.1
#3	k2+.P	1	0.461	0.06	12.9
#4	r(P)	10	0.421	0.095	22.6
#5	offset#1	3.30555	0.6	0.3	49.9

模型参数
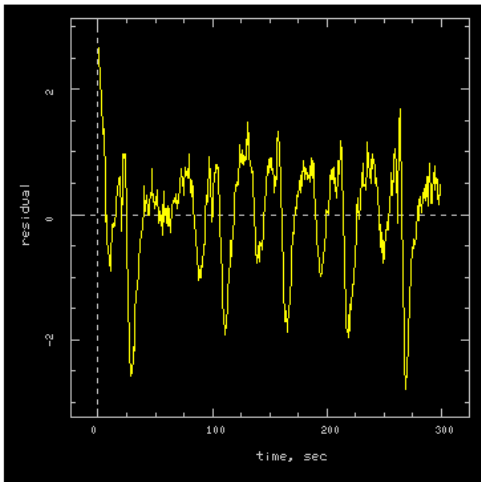
残差图

Initial reaction rates

No. Dataset	Time Rate
1 ./examples/HW1/LAC_SUB_TEMPO2_1.csv:col(2) 1	0.0700487

初始反应速率

2. 若为三组分体系，模型 1：

```
E + S <===> ES
ES ----> E + P
E + M <===> EM
EM ----> E + M*
M* + S ----> M + P
```

Dynafit 运行脚本：

```
[task]
   task = fit
   data = progress discontinuous
[mechanism]
   E + S <===> E.S   :   k1+.S   k1-.S
   E.S ----> E + P   :   k2+.P
[constants]
   k1+.S = 1 ?
   k1-.S = 0.01 ?
   k2+.P = 1 ?
[concentrations]
   S = 47
   E = 0.5
[responses]
   P = 10 ?
[data]
   directory D:/Appsetup/DynaFit4/examples/HW1
   sheet LAC_SUB_1.csv
   column 2
   offset auto ?
[output]
   XAxisLabel = time, sec
   YAxiaLabel = product, %
[end]
```

运行结果:

Initial reaction rates

```
No. Dataset                                          Time Rate
1   ./examples/HW1/LAC_SUB_TEMPO_3.csv:col(3) 1      0.00224822
```
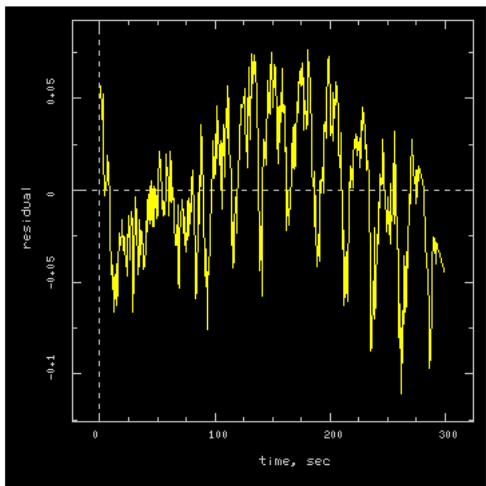

Regression Summary

Trust-Region Algorithm

unweighted sum of squares	0.782961
weighted sum of squares	0.782961
mean square	0.0013093
r.m.s. deviation	0.0361842
relative r.m.s. (%)	4.00497
R^2 ... (a)	0.973415
R^2_{adj} ... (a)	0.973054
log(determinant)	0
data points	598
optimized parameters	9
iterations	947
elapsed time (sec)	5.149

Parameters

Trust Region Algorithm

Optimized Parameters

No.	Par#Set	Initial	Final	Std. Error	CV (%)	Note
#1	k1+.S	1	0.00077	720	93477810.7	
#2	k1-.S	0.01	2.1	11000	544959.5	
#3	k2+.P	1	0.05	46000	91042589.9	
#4	k3+.M	1	1e-006	0.94	93632070.7	MIN
#5	k3-.M	0.01	2.3	9e+007	3907456322.1	
#6	k4+.M*	1	0.94	7.4e+007	7837796796.4	
#7	k5+.P	1	1e-006	52	5241033491.3	MIN
#8	r(P)	15	6.2	260000	4199516.0	
#9	offset#1	0.245479	0.188	0.045	24.1	

3. 三组分模型 2:

```
E + M <===> EM
EM ----> E + M*
M* + S ----> M + P
```
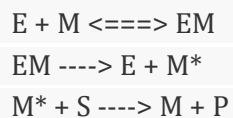
Dynafit 运行脚本：

```
[task]
   task = fit
   data = progress discontinuous
[mechanism]
   E + M <===> EM    :    k1+.M k1-.M
   EM ----> E + M*    :    k2.M*
   M* + S ----> M + P    :    k3.P

[constants]
   k1+.M = 1 ?
   k1-.M = 0.01 ?
   k2.M* = 1 ?
   k3.P = 1 ?
[concentrations] ; nM
   S = 47
   E = 0.5
   M = 0.5
[responses]
   P = 15 ?
[data]
   directory ./examples/HW1
   sheet LAC_SUB_TEMPO_3.csv
   column 3
   offset auto ?
[settings]
{Output}
   XAxisLabel = time, sec
   YAxisLabel = product, %
[end]
```

由建模结果比较可知，在漆酶+介体 TEMPO+底物体系中，应选二组份模型（只有酶和底物参与了反应过程）

建模结果:
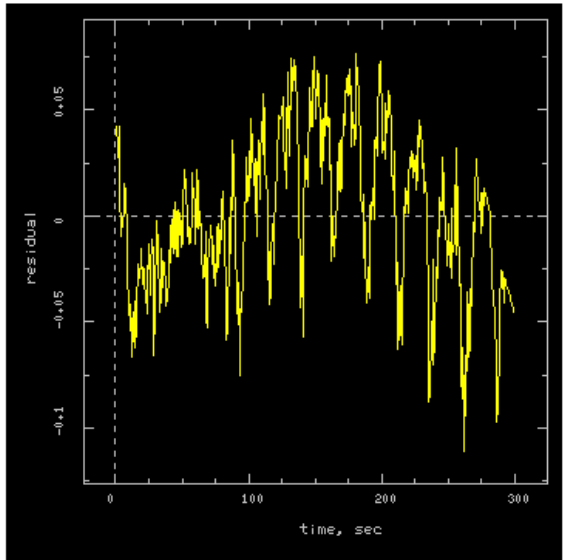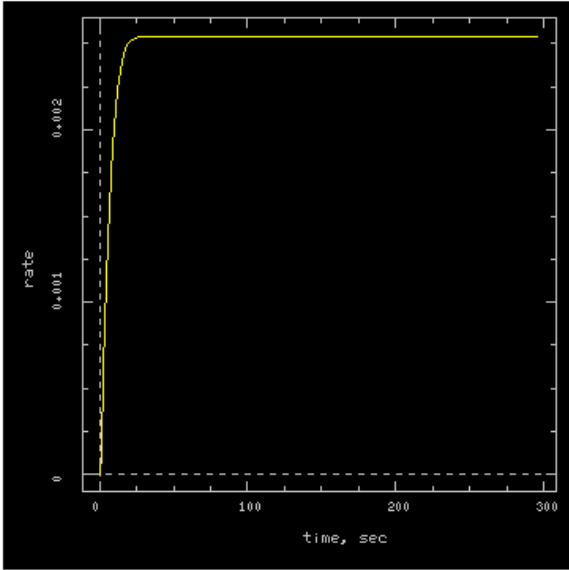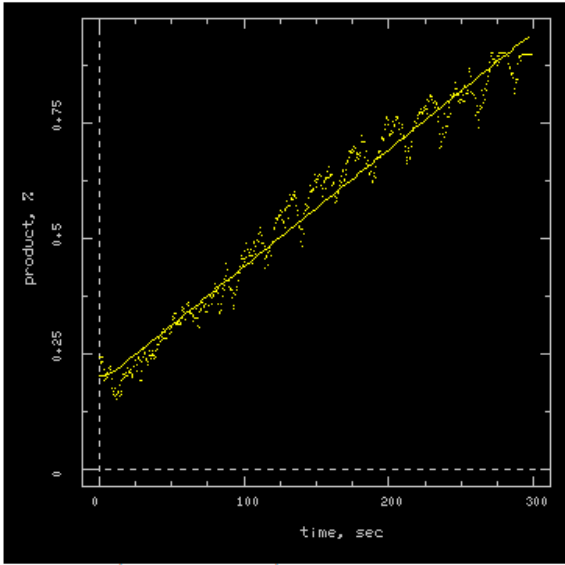
Initial reaction rates

No.	Dataset	Time	Rate
1	./examples/HW1/LAC_SUB_TEMPO_3.csv:col(3)	1	0.000113121

Regression Summary

Trust-Region Algorithm

unweighted sum of squares	0.778727
weighted sum of squares	0.778727
mean square	0.00130222
r.m.s. deviation	0.0360863
relative r.m.s. (%)	3.99412
R^2 ... (a)	0.973559
R^2_{adj} ... (a)	0.973336
log(determinant)	0
data points	598
optimized parameters	6
iterations	117
elapsed time (sec)	0.382

Parameters

Trust Region Algorithm

Optimized Parameters

No.	Par#Set	Initial	Final	Std. Error	CV (%)	Note
#1	k1+.M	1	0.75	260	34993.0	
#2	k1-.M	0.01	1e-008	2.3	23076441404.1	
#3	k2.M*	1	0.33	94	28523.5	
#4	k3.P	1	8.6e-006	0.00058	6726.5	
#5	r(P)	15	13	840	6438.0	
#6	offset#1	0.245479	0.203	0.012	6.0	