Model discrimination through ICAS-MoT (related to lecture 6)

By

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Model discrimination through ICAS-MoT

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PROBLEM STATEMENT

The following case study shows the model discrimination through ICAS-MoT.

A hypothetical reaction

$$A + B \longrightarrow C + D$$

takes place in a differential reactor.

A feed stream $v_o = 100.0\ cm^3/\min$ is fed to a reactor, which contains $W = 0.0001\, kg$ of catalyst. The reactor is operated in differential mode and the outlet concentrations P_A, P_B and P_C in [atm.] are measured, the conversion χ of the reaction is calculated and used to determine the rate of reaction from the design equation:

$$r = \chi v_o C_{Ao} / W = \chi v_0 Pa_0 / RTW \quad [gmol / kgCat / \min]$$

Carry out a nonlinear least-square analysis on the data given in Table 1, to determine which of the following rate laws best describes the data:

Model 1 $$r = \frac{k_4 K_1 K_2 P_A P_B}{(1 + K_1 P_A + K_2 P_B + K_3 P_C)^2}$$

Model 2 $$r = \frac{k_4 K_1 P_A P_B}{1 + K_1 P_A + K_3 P_C}$$

Model 3 $$r = \frac{k_4 K_2 P_A P_B}{1 + K_2 P_B + K_3 P_C}$$

Model 4 $$r = k_4 P_A^{\alpha} P_B^{\beta} P_c^{\gamma}$$

Where

$$k_4 = k_{40} \exp(-E_4 / RT)$$
$$K_1 = K_{10} \exp(-\Delta H_1 / RT)$$
$$K_2 = K_{20} \exp(-\Delta H_2 / RT)$$
$$K_3 = K_{30} \exp(-\Delta H_3 / RT)$$

For models 1, 2 and 3 (Langmuir-Hinshelwood kinetics) the model parameters are: $\{k_{40}, E_4, K_{10}, \Delta H_1, K_{20}, \Delta H_2, K_{30}, \Delta H_3\}$; while for model 4 (power law kinetics) estimate the model parameters are: $\{k_{40}, E_4, \alpha, \beta, \gamma\}$.

From the four above models, select the most appropriate one(s).

Table 1. Differential reactor data

Run *no.*	*Temp* *[K]*	P_{Ao} *[atm]*	P_{Bo} *[atm]*	P_{Co} *[atm]*	*Rate, r* *[gmol/Kg cat/min]*	*Conv,* χ	P_A *[atm]*	P_B *[atm]*	P_C *[atm]*
1	650	1.05	1.05	0.10	0.7947824	0.01081	1.03865	1.0387	0.111346
2	600	0.10	0.10	0.00	0.0395129	0.00854	0.09915	0.0991	0.000854
3	600	2.00	0.10	0.00	0.0741632	0.00011	1.99978	0.0998	0.000222
4	600	0.10	2.00	0.00	0.3449568	0.03959	0.09604	1.996	0.003959
5	600	2.00	2.00	0.00	1.197896	0.00221	1.99558	1.9956	0.004422
6	600	0.10	0.10	0.20	0.0012132	0.00049	0.09995	0.1	0.200049
7	600	2.00	0.10	0.20	0.0098456	9.5E-05	1.99981	0.0998	0.200189
8	600	0.10	2.00	0.20	0.0178852	0.00977	0.09902	1.999	0.200977
9	600	2.00	2.00	0.20	0.3425765	0.00189	1.99622	1.9962	0.203777
10	650	1.05	1.05	0.10	0.8671039	0.01081	1.03865	1.0387	0.111346
11	650	0.10	0.10	0.00	0.0014893	0.00729	0.09927	0.0993	0.000729
12	650	2.00	0.10	0.00	0.1356959	0.00065	1.99869	0.0987	0.001305
13	650	0.10	2.00	0.00	0.326404	0.12557	0.08744	1.9874	0.012557
14	650	2.00	2.00	0.00	3.3834579	0.01284	1.97432	1.9743	0.025685
15	650	0.10	0.10	0.20	0.0058049	0.00258	0.09974	0.0997	0.200258
16	650	2.00	0.10	0.20	0.0906307	0.00056	1.99888	0.0989	0.201122
17	650	0.10	2.00	0.20	0.1200444	0.04913	0.09509	1.9951	0.204913
18	650	2.00	2.00	0.20	1.4929583	0.01107	1.97786	1.9779	0.222144
19	650	1.05	1.05	0.10	0.7068661	0.01081	1.03865	1.0387	0.111346
20	700	0.10	0.10	0.00	0.018718	0.00737	0.09926	0.0993	0.000737
21	700	2.00	0.10	0.00	0.1853618	0.00232	1.99535	0.0954	0.004649
22	700	0.10	2.00	0.00	0.1910585	0.1288	0.08712	1.9871	0.01288
23	700	2.00	2.00	0.00	3.6766623	0.04408	1.91183	1.9118	0.088167
34	700	0.10	0.10	0.20	0.0107313	0.00533	0.09947	0.0995	0.200533
25	700	2.00	0.10	0.20	0.1492342	0.00207	1.99585	0.0959	0.204147
26	700	0.10	2.00	0.20	0.1948485	0.09651	0.09035	1.9903	0.209651
27	700	2.00	2.00	0.20	3.0341589	0.03958	1.92084	1.9208	0.279156
28	650	1.05	1.05	0.10	0.7988874	0.01081	1.03865	1.0387	0.111346
29	600	0.10	0.10	0.00	0.0640631	0.00208	0.09979	0.0998	0.000208
30	700	2.00	2.00	0.20	2.9393335	0.03958	1.92084	1.9208	0.279156
31	600	2.00	2.00	0.20	0.4496993	0.00189	1.99622	1.9962	0.203777
32	700	0.10	0.10	0.00	0.006409	0.00737	0.09926	0.0993	0.000737

PART I. LEAST SQUARES MINIMIZATION

1. Data Analysis

From the original data points we can see that the following data points (1, 10, 19, 28), (27, 30) and (20, 32) cannot be fitted simultaneously. Taking an average value for each of the data sets for the repeated points we generate a new data points as: point a = (9, 31), point b = (1, 10, 19, 28), point c = (20, 32) and point d = (27, 30).

Table 1b. Differential reactor data

Run no.	*Temp [K]*	P_{Ao} [atm]	P_{Bo} [atm]	P_{Co} [atm]	*Rate, r [gmol/Kg cat/min]*	*Conv,* χ	P_A [atm]	P_B [atm]	P_C [atm]
2	600	0.10	0.10	0.00	0.0395129	0.00854	0.09915	0.0991	0.000854
3	600	2.00	0.10	0.00	0.0741632	0.00011	1.99978	0.0998	0.000222
4	600	0.10	2.00	0.00	0.3449568	0.03959	0.09604	1.996	0.003959
5	600	2.00	2.00	0.00	1.197896	0.00221	1.99558	1.9956	0.004422
6	600	0.10	0.10	0.20	0.0012132	0.00049	0.09995	0.1	0.200049
7	600	2.00	0.10	0.20	0.0098456	9.5E-05	1.99981	0.0998	0.200189
8	600	0.10	2.00	0.20	0.0178852	0.00977	0.09902	1.999	0.200977
11	650	0.10	0.10	0.00	0.0014893	0.00729	0.09927	0.0993	0.000729
12	650	2.00	0.10	0.00	0.1356959	0.00065	1.99869	0.0987	0.001305
13	650	0.10	2.00	0.00	0.326404	0.12557	0.08744	1.9874	0.012557
14	650	2.00	2.00	0.00	3.3834579	0.01284	1.97432	1.9743	0.025685
15	650	0.10	0.10	0.20	0.0058049	0.00258	0.09974	0.0997	0.200258
16	650	2.00	0.10	0.20	0.0906307	0.00056	1.99888	0.0989	0.201122
17	650	0.10	2.00	0.20	0.1200444	0.04913	0.09509	1.9951	0.204913
18	650	2.00	2.00	0.20	1.4929583	0.01107	1.97786	1.9779	0.222144
21	700	2.00	0.10	0.00	0.1853618	0.00232	1.99535	0.0954	0.004649
22	700	0.10	2.00	0.00	0.1910585	0.1288	0.08712	1.9871	0.01288
23	700	2.00	2.00	0.00	3.6766623	0.04408	1.91183	1.9118	0.088167
34	700	0.10	0.10	0.20	0.0107313	0.00533	0.09947	0.0995	0.200533
25	700	2.00	0.10	0.20	0.1492342	0.00207	1.99585	0.0959	0.204147
26	700	0.10	2.00	0.20	0.1948485	0.09651	0.09035	1.9903	0.209651
29	600	0.10	0.10	0.00	0.0640631	0.00208	0.09979	0.0998	0.000208
a	600	2	2	0.2	0.39614	0.00189	1.99622	1.99622	0.20378
b	650	1.05	1.05	0.1	0.79191	0.01081	1.03865	1.03865	0.11135
c	700	0.1	0.1	0	0.01256	0.00737	0.09926	0.09926	0.00074
d	700	2	2	0.2	2.98675	0.03958	1.92084	1.92084	0.27916

2. Power Law Kinetics (Model 4)

First we will consider the following pseudo kinetic model given by a power-law kinetics:

$$r = k_4 P_A^{\alpha} P_B^{\beta} P_c^{\gamma} \tag{1}$$

For this model the orders of the reactions α, β and γ as well as pre-exponential factor k_{4o} and activation energy E_4 for the Arrhenius relationship will be estimate

$$k_4 = k_{4o} \exp(-E_4 / RT) \tag{2}$$

This is, the estimation of the following model parameters:

$$P = \{ \alpha, \beta, \gamma, k_{40}, E_4 \} \tag{3}$$

This pseudo kinetic model is useful to compare the optimization methods and to get starting guesses or *insights* into the three Langmuir-Hinshelwood (L-H) models. For that purpose first the model parameters will be estimated using a linear approach (through a minimization by least squares), which does not require an initial condition. Then based on this solution, the initial condition and bound values are stated for the nonlinear problem.

2.1 Linear solution

Taking the logarithm of both sides of Eq. (1)

$$\ln(r) = \ln(k_4) + \alpha \ln(P_A) + \beta \ln(P_B) + \gamma \ln(P_C) \tag{4}$$

Substituting Eq. (2) in Eq. (4)

$$\ln(r) = \ln(k_{40}) + \left(\frac{-E_4}{R}\right)\left(\frac{1}{T}\right) + \alpha \ln(P_A) + \beta \ln(P_B) + \gamma \ln(P_C) \tag{5}$$

Let

$$Y = \ln(r),\ X_1 = \frac{1}{T},\ X_2 = \ln(P_A),\ X_3 = \ln(P_B),\ X_4 = \ln(P_C) \tag{6}$$

$$a_0 = \ln(k_{40}),\ a_1 = \frac{-E_4}{R},\ a_2 = \alpha,\ a_3 = \beta,\ a_4 = \gamma \tag{7}$$

Then

$$Y = a_0 + a_1 X_1 + a_2 X_2 + a_3 X_3 + a_4 X_4 \tag{8}$$

If we now carry out N experimental runs, for the jth run, Eq. (8) takes the form:

$$Y_j = a_0 + a_1 X_{1j} + a_2 X_{2j} + a_3 X_{3j} + a_4 X_{4j} \tag{9}$$

where $X_{1j} = 1/T_j$, $X_{2j} = \ln\left(P_{A0j}\right)$, $X_{3j} = \ln\left(P_{B0j}\right)$ and $X_{4j} = \ln\left(P_{C0j}\right)$, with ($T_j$, P_{A0}, P_{B0}, P_{C0}) being the measurements for the jth run.

The approach used in linear regression is to minimize the sum of the squares of the differences between the data and a line; that is, finding the values of a_0, a_1, a_2, a_3, and a_4 that minimize the sum

$$f = \sum_{j}^{N} \left(Y_j - Y_{j,\exp}\right)^2 \tag{10}$$

Substituting Eq. (9) into (10)

$$f = \sum_{j=1}^{N} \left(a_0 + a_1 X_{1j} + a_2 X_{2j} + a_3 X_{3j} + a_4 X_{4j} - Y_j\right)^2 \tag{11}$$

Minimizing this sum is called least squares minimization. The minimum of the sum above will occur at a critical point. By the first derivative test from calculus, we can find critical points by solving the system

$$\frac{\partial f}{\partial a_k} = 0, \qquad k = 0, \ldots, 4 \tag{12}$$

Specifically, finding the partial derivatives and rewriting them, the following five linear equations are obtained:

$$N a_0 + a_1 \sum_{j=1}^{N} X_{1j} + a_2 \sum_{j=1}^{N} X_{2j} + a_3 \sum_{j=1}^{N} X_{3j} + a_4 \sum_{j=1}^{N} X_{4j} - \sum_{j=1}^{N} Y_j = 0 \tag{13}$$

$$a_0 \sum_{j=1}^{N} X_{1j} + a_1 \sum_{j=1}^{N} \left(X_{1j}\right)^2 + a_2 \sum_{j=1}^{N} \left(X_{1j} X_{2j}\right) + a_3 \sum_{j=1}^{N} \left(X_{1j} X_{3j}\right) + a_4 \sum_{j=1}^{N} \left(X_{1j} X_{4j}\right) - \sum_{j=1}^{N} \left(Y_j X_{1j}\right) = 0 \tag{14}$$

$$a_0 \sum_{j=1}^{N} X_{2j} + a_1 \sum_{j=1}^{N} \left(X_{1j} X_{2j}\right) + a_2 \sum_{j=1}^{N} \left(X_{2j}\right)^2 + a_3 \sum_{j=1}^{N} \left(X_{2j} X_{3j}\right) + a_4 \sum_{j=1}^{N} \left(X_{2j} X_{4j}\right) - \sum_{j=1}^{N} \left(Y_j X_{2j}\right) = 0 \tag{15}$$

$$a_0 \sum_{j=1}^{N} X_{3j} + a_1 \sum_{j=1}^{N} \left(X_{1j} X_{3j}\right) + a_2 \sum_{j=1}^{N} \left(X_{3j} X_{2j}\right) + a_3 \sum_{j=1}^{N} \left(X_{3j}\right)^2 + a_4 \sum_{j=1}^{N} \left(X_{3j} X_{4j}\right) - \sum_{j=1}^{N} \left(Y_j X_{3j}\right) = 0 \tag{16}$$

$$a_0 \sum_{j=1}^{N} X_{4j} + a_1 \sum_{j=1}^{N} \left(X_{1j} X_{4j}\right) + a_2 \sum_{j=1}^{N} \left(X_{4j} X_{2j}\right) + a_3 \sum_{j=1}^{N} \left(X_{4j} X_{3j}\right) + a_4 \sum_{j=1}^{N} \left(X_{4j}\right)^2 - \sum_{j=1}^{N} \left(Y_j X_{4j}\right) = 0 \tag{17}$$

This system [Eqs. (13)-(17)] can be solved for the five unknown variables a_0, a_1, a_2, a_3, and a_4. The system was solved using ICAS-MoT (see the corresponding code in Appendix) obtaining the following solution:

$$a_0 = 6.77080$$
$$a_1 = -5315.23$$
$$a_2 = 0.82535$$
$$a_3 = 1.12517$$
$$a_4 = -0.24615$$

Afterwards the values of k_4, E_4, α, β and γ can be obtained from Eq. (7):

$$k_{40} = \exp(a_0) = 872.00522$$
$$E_4 = -a_1 R = 436115.98$$
$$\alpha = a_2 = 0.825347$$
$$\beta = a_3 = 1.125166$$
$$\gamma = a_4 = -0.246146$$

The corresponding calculated rate values in comparison with the experimental ones are given in Table 2, some regression plots are shown in Figures 1, and the statistics report for this linear regression is given in Table 3.

Table 2. Experimental and calculated rate values for Model 4 (linear fit)

No. Point	r_{exp}	r_{calc}
2	0.039513	0.007776
3	0.074163	0.130267
4	0.344957	0.152223
5	1.197896	1.811431
6	0.001213	0.002062
7	0.009846	0.024406
8	0.017885	0.059478
11	0.001489	0.016018
12	0.135696	0.164341
13	0.326404	0.208598
14	3.383458	2.274230
15	0.005805	0.004059
16	0.090631	0.047664

No. Point	r_{exp}	r_{calc}
17	0.120044	0.112909
18	1.492958	1.341914
21	0.185362	0.207109
22	0.191058	0.370561
23	3.676662	2.827598
24	0.010731	0.007237
25	0.149234	0.082138
26	0.194848	0.192517
29	0.064063	0.011145
a	0.396138	0.706048
b	0.791910	0.452849
c	0.012564	0.028645
d	2.986746	2.148796

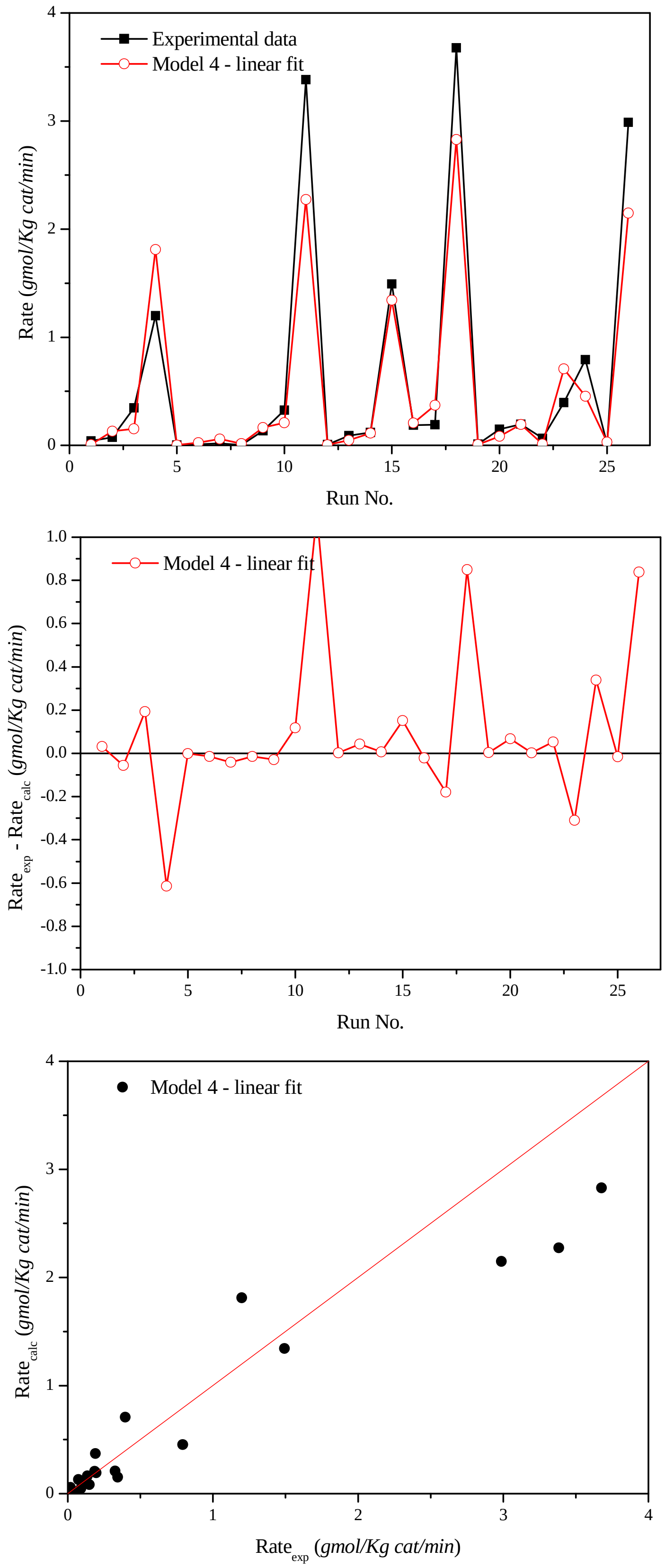

Figure 1. Regression plots for Model 4 – linear case

Table 3. Statistics report for Model 4 (linear fit)

Statistics	
Correlation	0.965515
R^2	0.884074
Adjusted R^2	0.879244
Standard Error	0.374390
$\Sigma(Y_{j,exp} - Y_j)^2$	3.3641

ANOVA

	DOF	*SS*	*MS*	*F*	*Significance F*
Regression	1	25.65473	25.65473	183.02857	1.00E-12
Residual	24	3.36403	0.14017		
Total	25	29.01875			

Where:

Source	***DOF* (degrees of freedom)**	***SS* (Sum of Squares)**	***MS* (Mean Square)**	***F***	***SigF***
Regression (or model)	$DOFN = K$	$SSR = \sum(\hat{y}_i - \bar{y})^2$	$MSR = \frac{SSR}{K}$	$F = \frac{MSR}{MSE}$	*
Residual (or error)	$DOFD = N - K - 1$	$SSE = \sum(y_i - \hat{y}_i)^2$	$MSE = \frac{SSE}{N-K-1}$		
Total	$DOFT = N - 1$	$SST = \sum(y_i - \bar{y})^2$			

Where:

N = number of points

K = number of independent variables

$$\bar{y} = \frac{\sum_i y_i}{N} \text{ and } \bar{\hat{y}} = \frac{\sum_i \hat{y}_i}{N}$$

$$R^2 = 1 - \frac{SSE}{SST}$$

$$R^2_{Adjusted} = 1 - \frac{(N-1)(1-R^2)}{N-K-1}$$

2.2 Nonlinear solution

The best values of the parameters $\{\alpha, \beta, \gamma, k_{40}, E_4\}$ are found by solving the minimization problem

$$\min_{\alpha,\beta,\gamma,k_{40},E_4} f = \sum_j^N \left(r_j - r_{j,\exp}\right)^2 \tag{18}$$

subject to

$$k_{4j} = k_{4o}\exp(-E_4 / RT_j) \tag{19}$$

$$r_j = k_{4j} P_{Aj}{}^{\alpha} P_{Bj}^{\beta} P_{cj}^{\gamma} \tag{20}$$

with initial condition and bounds given in the Table 4.

Table 4. Bounds and initial values for Model 4 (nonlinear fit)

Parameter	*Lower bound*	*Upper bound*	*Initial value*	*Optimal value*
k_{40}	0	$1x10^6$	872.0052	13468.37
E_4	0	$1x10^6$	436115	579587.2
α	-1	2	0.825347	0.921559
β	-1	2	1.125166	1.159066
γ	-1	2	-0.24615	-0.24907

The optimal values found using ICAS-MoT (see the corresponding code in Appendix) are reported also in Table 4, the corresponding calculated rate values in comparison with the experimental ones are given in Table 5, some regression plots are shown in Figures 2, and the statistics report is given in Table 6.

Table 5. Experimental and calculated rate values for Model 4 (nonlinear fit)

No. Point	r_{exp}	r_{calc}	***No. Point***	r_{exp}	r_{calc}
2	0.039513	0.004923	17	0.120044	0.097067
3	0.074163	0.110573	18	1.492958	1.544013
4	0.344957	0.105898	21	0.185362	0.263757
5	1.197896	1.686778	22	0.191058	0.385874
6	0.001213	0.001286	23	3.676662	3.935937
7	0.009846	0.020309	24	0.010731	0.006841
8	0.017885	0.041028	25	0.149234	0.103476
11	0.001489	0.012698	26	0.194848	0.199555
12	0.135696	0.173575	29	0.064063	0.007091
13	0.326404	0.179323	a	0.396138	0.650178
14	3.383458	2.632659	b	0.791910	0.480131
15	0.005805	0.003167	c	0.012564	0.027517
16	0.090631	0.049611	d	2.986746	2.982841

Table 6. Statistics report for Model 4 (nonlinear fit)

Statistics	
Correlation	0.979672
R^2	0.959691
Adjusted R^2	0.958011
Standard Error	0.220767
$\Sigma(Y_{j,exp} - Y_j)^2$	1.1687

ANOVA					
	DOF	*SS*	*MS*	*F*	*Significance F*
Regression	1	27.84904	27.84904	571.39963	3.02E-18
Residual	24	1.16972	0.04874		
Total	25	29.01875			

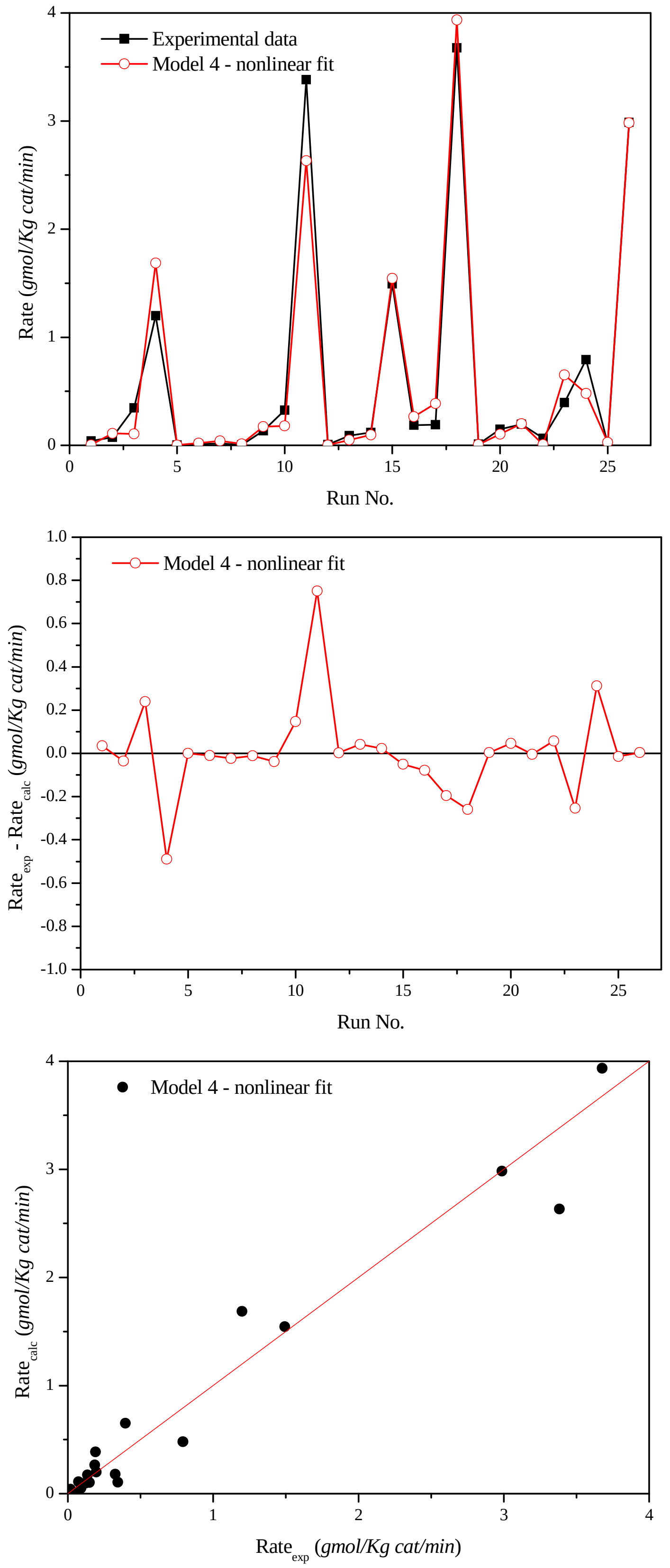

Figure 2. Regression plots for Model 4 – nonlinear case

3. Langmuir-Hinshelwood Kinetics (Models 1, 2 and 3)

Consider the three LH kinetic models described in section 1, which for the *j*th run can be written as follows:

Model 1 $$r_j = \frac{k_{4j}K_{1j}K_{2j}P_{Aj}P_{Bj}}{\left(1+K_{1j}P_{Aj}+K_{2j}P_{Bj}+K_{3j}P_{Cj}\right)^2} \qquad (21)$$

Model 2 $$r_j = \frac{k_{4j}K_{1j}P_{Aj}P_{Bj}}{1+K_{1j}P_{Aj}+K_{3j}P_{Cj}} \qquad (22)$$

Model 3 $$r_j = \frac{k_{4j}K_{2j}P_{Aj}P_{Bj}}{1+K_{2j}P_{Bj}+K_{3j}P_{Cj}} \qquad (23)$$

Where the kinetic rate constants follows the Arrenhius-type:

$$k_{4j} = k_{4o}\exp(-E_4/RT_j) \qquad (24)$$

$$K_{1j} = K_{10}\exp(-\Delta H_1/RT_j) \qquad (25)$$

$$K_{2j} = K_{20}\exp(-\Delta H_2/RT_j) \qquad (26)$$

$$K_{3j} = K_{30}\exp(-\Delta H_3/RT_j) \qquad (27)$$

For these models, the kinetic parameters to be estimated are:

Model 1 $$P_1 = \{k_{40}, E_4, K_{10}, \Delta H_1, K_{20}, \Delta H_2, K_{30}, \Delta H_3\} \qquad (28)$$

Model 2 $$P_2 = \{k_{40}, E_4, K_{10}, \Delta H_1, K_{30}, \Delta H_3\} \qquad (29)$$

Model 3 $$P_3 = \{k_{40}, E_4, K_{20}, \Delta H_2, K_{30}, \Delta H_3\} \qquad (30)$$

Then, the optimal values of the parameters for each model are found by solving the following minimization problem:

$$\min_{P_k} f = \sum_j^N \left(r_j - r_{j,\exp}\right)^2 \qquad k = Model \quad No. \qquad (31)$$

with initial condition and bounds given in the Table 7.

Table 7. Bounds and initial values for Models 1, 2 and 3.

Parameter	***Lower bound***	***Upper bound***	***Initial value Model 1***	***Initial value Model 2***	***Initial value Model 3***
k_{40}	0	$1x10^8$	1	1	1
E_4	0	$1x10^8$	$1x10^4$	$1x10^4$	$1x10^4$
K_{10}	0	$1x10^8$	1	1	-
ΔH_1	$-1x10^8$	$1x10^8$	$-1x10^4$	$1x10^4$	-
K_{20}	0	$1x10^8$	1	-	1
ΔH_2	0	$1x10^8$	$-1x10^4$	-	$1x10^4$
K_{30}	0	$1x10^8$	1	1	1
ΔH_3	$-1x10^8$	$1x10^8$	$-1x10^4$	$1x10^4$	$1x10^4$

The optimal values found using ICAS-MoT (see the corresponding codes in Appendix) are reported also in Table 8; the corresponding calculated rate values in comparison with the experimental ones are given in Table 9; some regression plots are shown in Figures 3, 4 and 5; and the statistics reports are given in Table 10.

Table 8. Optimal parameter values for Models 1, 2 and 3.

Parameter	***Model 1***	***Model 2***	***Model 3***
k_{40}	196.1408	202.8362	71.3988
E_4	36626.1839	218319.7693	43709.5858
K_{10}	25.9840	297.2284	-
ΔH_1	263454.9708	347710.2856	-
K_{20}	14.2753	-	56.1734
ΔH_2	261885.0297	-	407674.7719
K_{30}	0.0015	0.0329	0.7508
ΔH_3	-406345.7434	-299822.8755	-92610.8372

Table 9. Experimental and calculated rate values for Models 1, 2 and 3.

		Model 1	***Model 2***	***Model 3***
No. Point	r_{exp}	r_{calc}	r_{calc}	r_{calc}
2	0.039513	0.007522	0.005799	0.004086
3	0.074163	0.101710	0.080776	0.081021
4	0.344957	0.111659	0.108456	0.078502
5	1.197896	1.606558	1.550592	1.585252
6	0.001213	0.001737	0.001554	0.002102
7	0.009846	0.028198	0.027642	0.041420
8	0.017885	0.030388	0.030692	0.041554
11	0.001489	0.017895	0.013911	0.008292
12	0.135696	0.198270	0.154914	0.157594
13	0.326404	0.210364	0.223512	0.139296
14	3.383458	2.758698	2.753032	2.837511
15	0.005805	0.007246	0.005144	0.004536
16	0.090631	0.096975	0.079042	0.087528
17	0.120044	0.108125	0.096737	0.085584
18	1.492958	1.504825	1.491171	1.655304
21	0.185362	0.324396	0.248612	0.265482
22	0.191058	0.393744	0.480743	0.254792
23	3.676662	3.961218	4.026789	3.985320
24	0.010731	0.021007	0.013661	0.008710
25	0.149234	0.217907	0.166415	0.159218
26	0.194848	0.259501	0.243085	0.155317
29	0.064063	0.007673	0.005928	0.004153
a	0.396138	0.497341	0.545519	0.819737
b	0.791910	0.778701	0.647789	0.607642
c	0.012564	0.037160	0.029031	0.015152
d	2.986746	2.909168	2.888178	2.670529

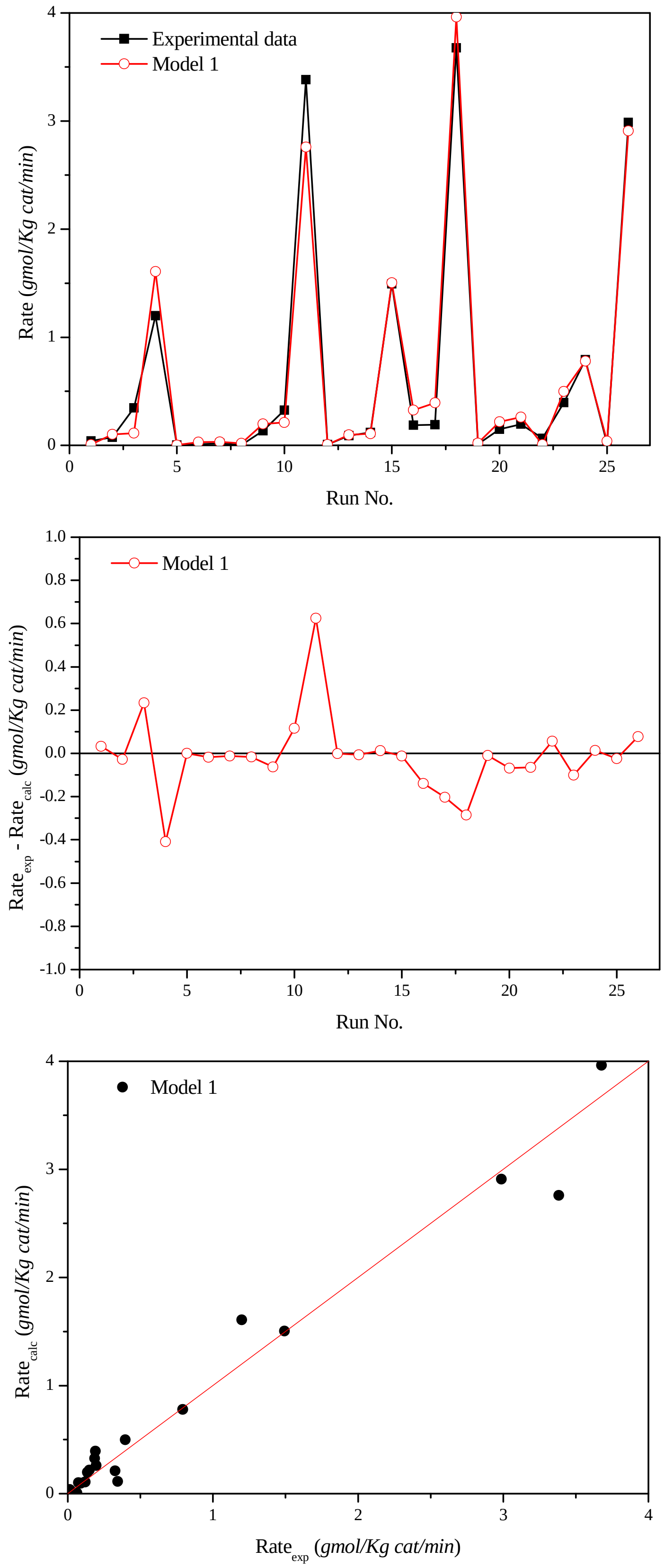

Figure 3. Regression plots for Model 1.

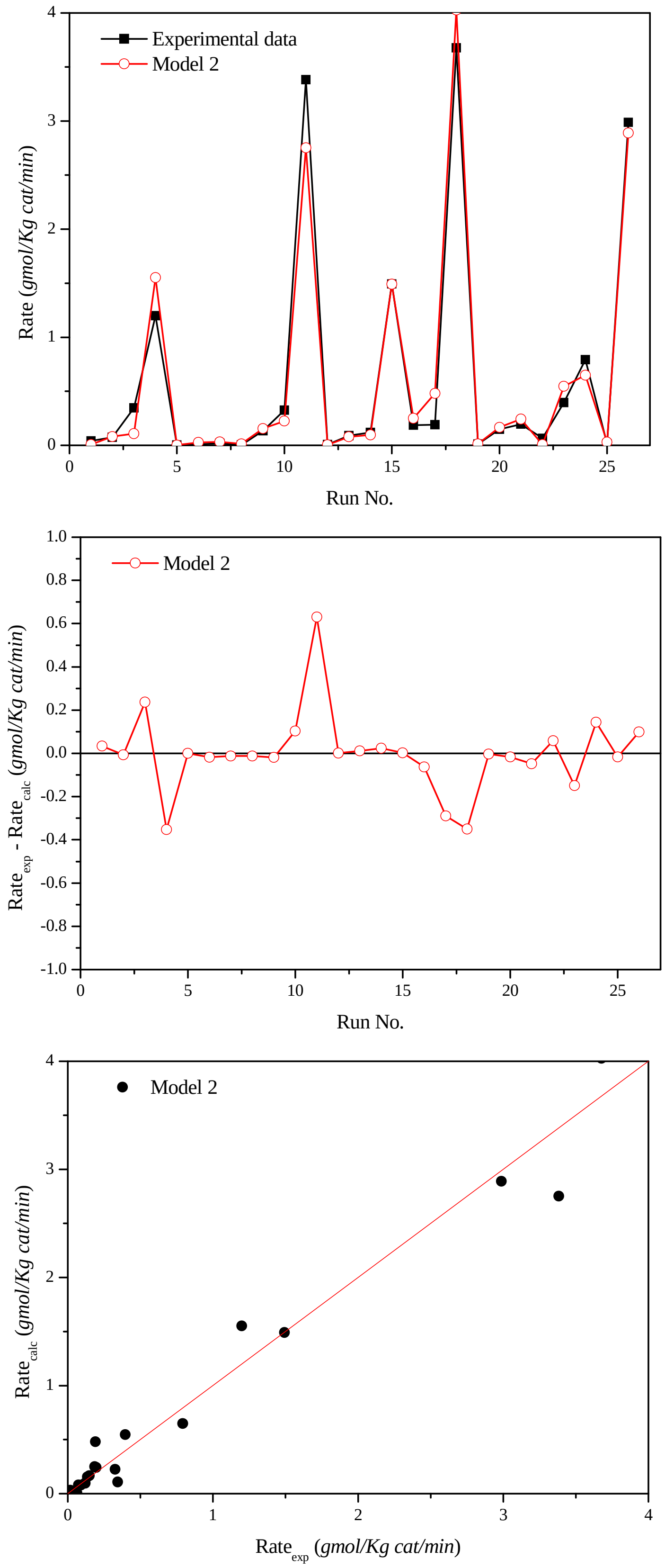

Figure 4. Regression plots for Model 2.

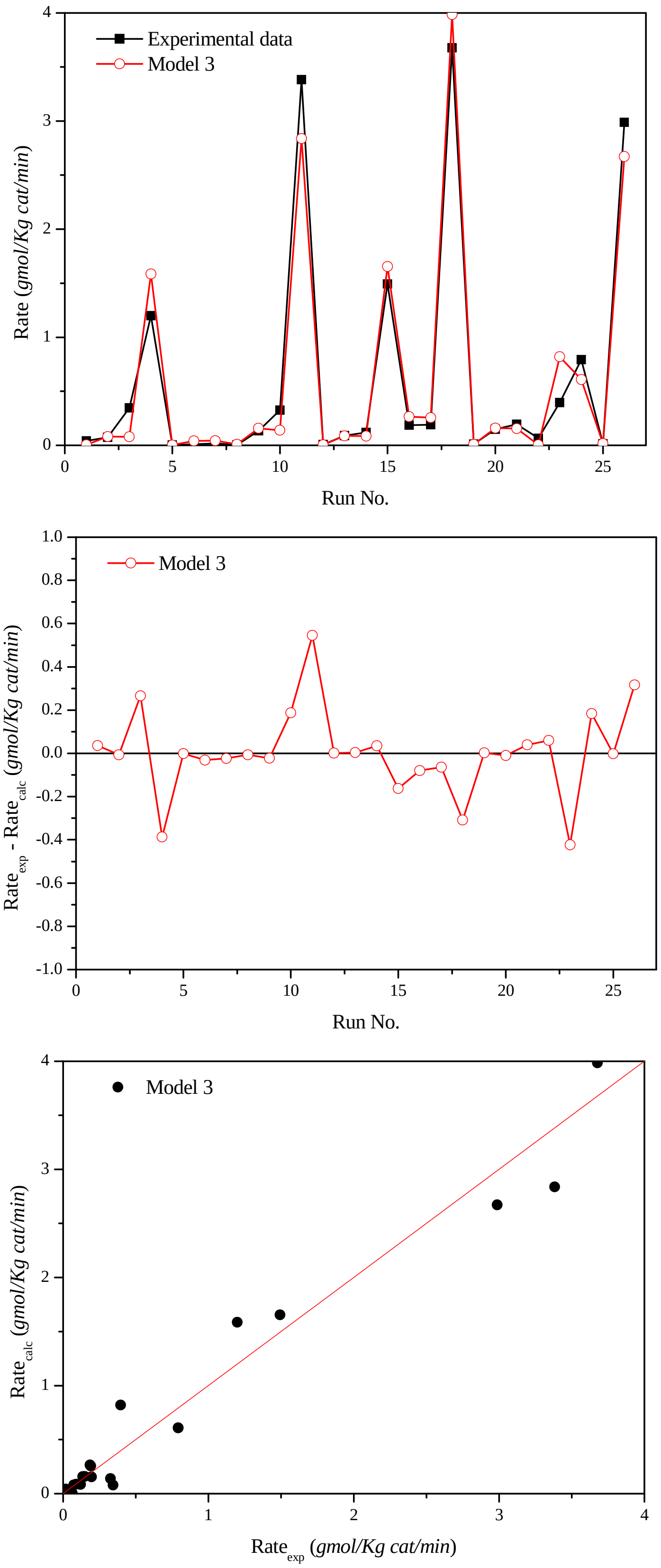

Figure 5. Regression plots for Model 3.

Table 10. Statistics reports for Model 1, 2 and 3

Statistics	*Model 1*	*Model 2*	*Model 3*
Correlation	0.986151	0.985057	0.982468
R^2	0.972342	0.970336	0.965214
Adjusted R^2	0.971189	0.969100	0.963765
Standard Error	0.182872	0.189386	0.205086
$\Sigma(Y_{j,exp} - Y_j)^2$	0.8026	0.8608	1.0165

ANOVA: Model 1

	DOF	*SS*	*MS*	*F*	*Significance F*
Regression	1	28.21614	28.21614	843.72775	3.27E-20
Residual	24	0.80261	0.03344		
Total	25	29.01875			

ANOVA: Model 2

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	28.15795	28.15795	785.06798	7.59E-20
Residual	24	0.86081	0.03587		
Total	25	29.01875			

ANOVA: Model 3

	DOF	*SS*	*MS*	*F*	*Significance F*
Regression	1	28.00931	28.00931	665.93188	5.14E-19
Residual	24	1.00945	0.04206		
Total	25	29.01875			

Parameter	*Model 1*	$\pm CI_{95\%}$	*Model 2*	$\pm CI_{95\%}$	*Model 3*	$\pm CI_{95\%}$
k_{40}	196.1408	78.07151552	202.8362	81.23557314	71.3988	28.51805
E_4	36626.184	14578.61743	218319.7693	87436.71784	43709.586	17458.447
K_{10}	25.984	10.34262254	297.2284	119.039498	-	-
ΔH_1	263454.97	104865.1216	347710.2856	139257.4123	-	-
K_{20}	14.2753	5.682113592	-	-	56.1734	22.436734
ΔH_2	261885.03	104240.2252	-	-	407674.77	162833.12
K_{30}	0.0015	0.000597057	0.0329	0.013176397	0.7508	0.2998839
ΔH_3	-406345.74	-161741.0963	-299822.8755	-120078.5813	-92610.837	-36990.545

The width of the confidence interval gives us some idea about how uncertain we are about the unknown parameter. A very wide interval may indicate that more data should be collected before anything very definite can be said about the parameter.

4. Model Discrimination

For the model discrimination, a statistic summarize is done in the following table:

Table 11. Statistic summarize

Statistics	***Model 1***	***Model 2***	***Model 3***	***Model 4 (Linear)***	***Model 4 (Nonlinear)***
Correlation	0.986151	0.985057	0.982468	0.965515	0.979672
R^2	0.972342	0.970336	0.965214	0.884074	0.959691
Adjusted R^2	0.971189	0.969100	0.963765	0.879244	0.958011
Standard Error	0.182872	0.189386	0.205086	0.374390	0.220767
$\Sigma(Y_{j,exp} - Y_j)^2$	0.8026	0.8608	1.0165	3.3641	1.1687
F-significance	3.27E-20	7.59E-20	5.14E-19	1.00E-12	3.02E-18

According to these results, Model 1 has the best correlation values for all the statistical parameters. And as expected, Model 4 gives the worst correlation (since this is a pseudo model not proper for describing the kinetics).

PART II. MAXIMUM LIKELIHOOD APPROACH

1. Principle of Maximum Likelihood

The maximum likelihood estimates are derived from the probability density function of the measurement errors. Under certain assumptions these estimates coincide with the OLS or WLS estimates. The idea behind maximum likelihood parameter estimation is to determine the parameters that maximize the probability (likelihood) of the sample data.

Mathematically, the likelihood is defined as the probability of making the set of measurements. If we have *N* observations of different quantities x_j, for instance, then the likelihood is defined as:

$$L = p\left(x_1, x_2, x_3, \ldots, x_N\right) \tag{32}$$

Notice (as indicated by the commas) that this is a joint probability distribution of all the measurements. Often the measurements will be independent of one another, in which case the joint probability is simply the product of all the individual probabilities:

$$L = \prod_{j=1}^{N} p\left(x_j\right) \tag{33}$$

The assumption of independent probabilities certainly makes life simpler, because joint distributions can be extremely difficult to work with! But we may lose something if the errors are correlated, so it is important to be careful.

Sums are easier to deal with than products (and the product of a lot of small numbers may be too small to represent on a computer), so we generally work with the log of the likelihood. The log varies monotonically with its argument (i.e. $ln(x)$ increases when x does and decreases when it does), so the log of a function will have its maximum at the same position. Usually what one is interested in is finding the position of the maximum of the likelihood function.

$$LL = \ln\left(L\right) = \sum_{j=1}^{N} \ln\left[p\left(x_j\right)\right] \tag{34}$$

In fact, to make the analogy with least-squares more obvious, it is often minimised minus log likelihood.

One way to think about likelihood is that we imagine we have not measured the data yet. We have a model, with various parameters to adjust, and some idea of sources of error and how they would propagate. This allows calculating the probability of any possible set of measurements. Finally, we bring in the actual measurements and see how well they agree with the model.

Let us apply maximum likelihood to the problem where the errors in predicting the observations follow a Gaussian distribution. With a few simple manipulations, maximum likelihood is equivalent to least squares in this case.

First, remember the equation for a Gaussian probability distribution.

$$p(x_j) = \frac{1}{\sqrt{2\pi\sigma_j^2}} \exp\left[-\frac{1}{2\sigma_j^2} \left(x_j - \hat{x}_j \right)^2 \right] \tag{35}$$

where $\hat{x}_j$ is the predicted value of x_j.

In log likelihood, we will need the log of this probability distribution

$$\ln\left[p(x_j) \right] = -\frac{1}{2}\ln(2\pi) - \ln(\sigma_j) - \frac{1}{2\sigma_j^2}\left(x_j - \hat{x}_j \right)^2 \tag{36}$$

Now, the likelihood is the probability of making the entire set of observations. As before, we are assuming that the observations are independent, so that the likelihood is the product of all the individual probabilities and the log likelihood is the sum of the logs. To make the comparison with least-squares minimisation clearer, let us stick a minus sign in front and show the equation for minus log likelihood.

$$-LL = \sum_{j=1}^{N} \left[\frac{1}{2}\ln(2\pi) + \ln(\sigma_j) + \frac{1}{2\sigma_j^2}\left(x_j - \hat{x}_j \right)^2 \right] \tag{37}$$

1.1 Parameter estimation problem for Models 1, 2, 3 and 4

To estimate the parameters using likelihood estimation, we have to consider that the data were generated using the following probability distribution:

$$y_i = r_i (1 + r_i^{\gamma^* - 1} \varepsilon) \tag{38}$$

where

$$\varepsilon \approx NID(0, \omega r_{\max}) \tag{39}$$

The parameters γ^* and ω of the error distribution will be estimated as well the parameters for each model.

2. Power Law Kinetics (Model 4: Nonlinear solution)

Consider the power-law kinetics model given by Eq. (1). Then applying the maximum likelihood approach afore described, the best values of the parameters $\{\alpha, \beta, \gamma, k_{40}, E_4, \omega, \gamma^*\}$ using ICAS-MoT (see the corresponding code in Appendix B) are shown in the following table:

Table 12. Bounds and initial values for Model 4 (nonlinear fit)

Parameter	***Lower bound***	***Upper bound***	***Initial value***	***Optimal value***
k_{40}	0	$1x10^6$	872.0052	13043.1192
E_4	0	$1x10^6$	436115	569231.7415
α	-1	2	0.825347	0.8457
β	-1	2	1.125166	1.0367
γ	-1	2	-0.24615	-0.2398
ω	0	$1x10^8$	0.1	0.1151
γ^*	0	$1x10^8$	0.1	0.0989

The corresponding calculated rate values in comparison with the experimental ones are given in Table 13, some regression plots are shown in Figures 6, and the statistics report is given in Table 14

Table 13. Experimental and calculated rate values for Model 4 (Maximum Likelihood)

No. Point	r_{exp}	r_{calc}	No. Point	r_{exp}	r_{calc}
1	0.794782	0.548594	17	0.120044	0.123085
2	0.039513	0.008352	18	1.492958	1.563611
3	0.074163	0.153299	19	0.706866	0.548594
4	0.344957	0.131515	20	0.018718	0.046773
5	1.197896	1.671512	21	0.185362	0.367785
6	0.001213	0.002071	22	0.191058	0.475035
7	0.009846	0.029673	23	3.676662	3.924778
8	0.017885	0.052458	24	0.010731	0.011975
9	0.342577	0.667116	25	0.149234	0.149049
10	0.867104	0.548594	26	0.194848	0.251111
11	0.001489	0.021685	27	3.034159	3.003266
12	0.135696	0.241364	28	0.798887	0.548594
13	0.326404	0.223474	29	0.064063	0.012003
14	3.383458	2.614794	30	2.939333	3.003266
15	0.005805	0.005445	31	0.449699	0.667116
16	0.090631	0.071951	32	0.006409	0.046773

Table 14. Statistics report for Model 4 (Maximum Likelihood)

Statistics	
Correlation	0.978541
R^2	0.957538
Adjusted R^2	0.956122
Standard Error	0.222727
$\Sigma(Y_{j,exp} - Y_j)^2$	1.488222

ANOVA

	DOF	*SS*	*MS*	*F*	*Significance F*
Regression	1	33.559931	33.559931	676.510396	3.87814E-22
Residual	30	1.488222	0.049607		
Total	31	35.048153			

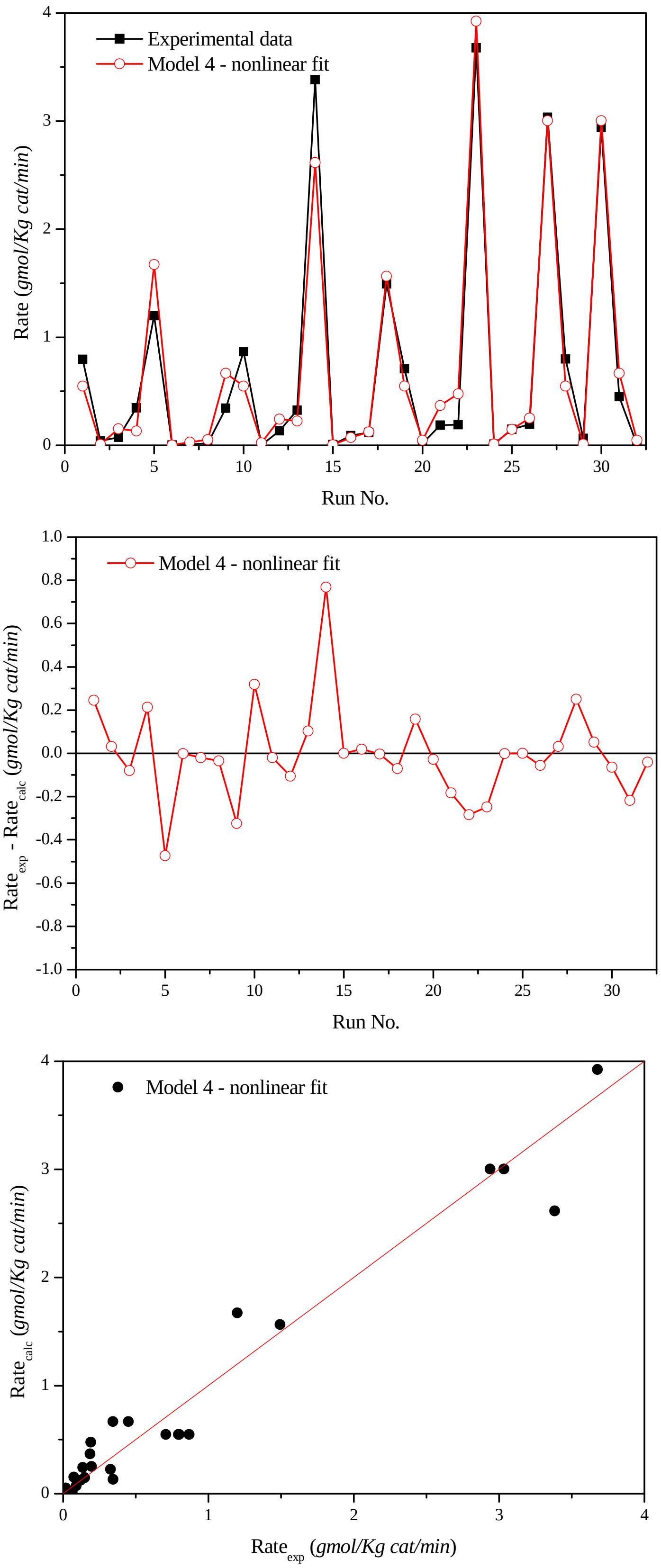

Figure 6. Regression plots for Model 4 (Maximum Likelihood)

3. Langmuir-Hinshelwood Kinetics (Models 1, 2 and 3)

Consider the three LH kinetic models described by Eqs.

Then the maximum likelihood approach is applied and the models are solved using ICAS-MoT (see the corresponding codes in Appendix B). the bounds and initial values for each model are shown in Table 15. The optimal values are reported also in Table 16; the corresponding calculated rate values in comparison with the experimental ones are given in Table 17; and some regression plots are shown in Figures 7, 8 and 9; and the statistics reports are given in Table 18.

Table 15. Bounds and initial values for Models 1, 2 and 3 (Maximum Likelihood).

Parameter	***Lower bound***	***Upper bound***	***Initial value Model 1***	***Initial value Model 2***	***Initial value Model 3***
k_{40}	0	$1x10^8$	1	1	1
E_4	0	$1x10^8$	$1x10^4$	$-1x10^4$	$1x10^4$
K_{10}	0	$1x10^8$	1	1	-
ΔH_1	$-1x10^8$	$1x10^8$	$-1x10^4$	$-1x10^4$	-
K_{20}	0	$1x10^8$	1	-	1
ΔH_2	$-1x10^8$	$1x10^8$	$-1x10^4$	-	$1x10^4$
K_{30}	0	$1x10^8$	1	1	1
ΔH_3	$-1x10^8$	$1x10^8$	$-1x10^4$	$1x10^4$	$1x10^4$
ω	0	$1x10^8$	0.1	0.1	0.1
γ^*	0	$1x10^8$	0.1	0.1	0.1

Table 16. Optimal parameter values for Models 1, 2 and 3 (Maximum Likelihood).

Parameter	***Model 1***	***Model 2***	***Model 3***
k_{40}	682.9912	486.9774	136.8862
E_4	101301.4651	272397.6240	166177.5668
K_{10}	24.2761	122.3300	-
ΔH_1	265139.6407	286917.8500	-
K_{20}	52.0747	-	31.9079
ΔH_2	332626.3729	-	276654.5649
K_{30}	9.6917	0.0355	0.0019
ΔH_3	78781.8933	-299901.9718	-430713.9655
ω	0.0333	0.1220	0.0352
γ^*	0.0855	0.0976	0.1307

Table 17. Experimental and calculated rate values for Models 1, 2 and 3 (Maximum Likelihood).

		Model 1	***Model 2***	***Model 3***
No. Point	r_{exp}	r_{calc}	r_{calc}	r_{calc}
1	0.794782	0.810609	0.668596	0.624787
2	0.039513	0.005460	0.006119	0.005122
3	0.074163	0.077528	0.079776	0.106428
4	0.344957	0.086670	0.120686	0.081086
5	1.197896	1.281408	1.543512	1.679673
6	0.001213	0.002858	0.001330	0.001508
7	0.009846	0.044573	0.028045	0.031528
8	0.017885	0.049885	0.032337	0.029294
9	0.342577	0.772102	0.561634	0.586445
10	0.867104	0.810609	0.668596	0.624787
11	0.001489	0.016209	0.014990	0.010333
12	0.135696	0.189704	0.152649	0.207958
13	0.326404	0.196341	0.245699	0.131239
14	3.383458	2.700834	2.737282	2.793893
15	0.005805	0.007956	0.005100	0.004706
16	0.090631	0.107775	0.079593	0.094891
17	0.120044	0.118689	0.102353	0.078462
18	1.492958	1.670124	1.512501	1.559162
19	0.706866	0.810609	0.668596	0.624787
20	0.018718	0.040474	0.031410	0.018657
21	0.185362	0.374946	0.248676	0.357805
22	0.191058	0.412912	0.525314	0.217483
23	3.676662	4.167522	4.061234	3.981653
24	0.010731	0.018702	0.014082	0.011189
25	0.149234	0.214394	0.167829	0.216662
26	0.194848	0.233744	0.257205	0.157337
27	3.034159	2.740376	2.930159	2.939801
28	0.798887	0.810609	0.668596	0.624787
29	0.064063	0.005545	0.006266	0.005230
30	2.939333	2.740376	2.930159	2.939801
31	0.449699	0.772102	0.561634	0.586445
32	0.006409	0.040474	0.031410	0.018657

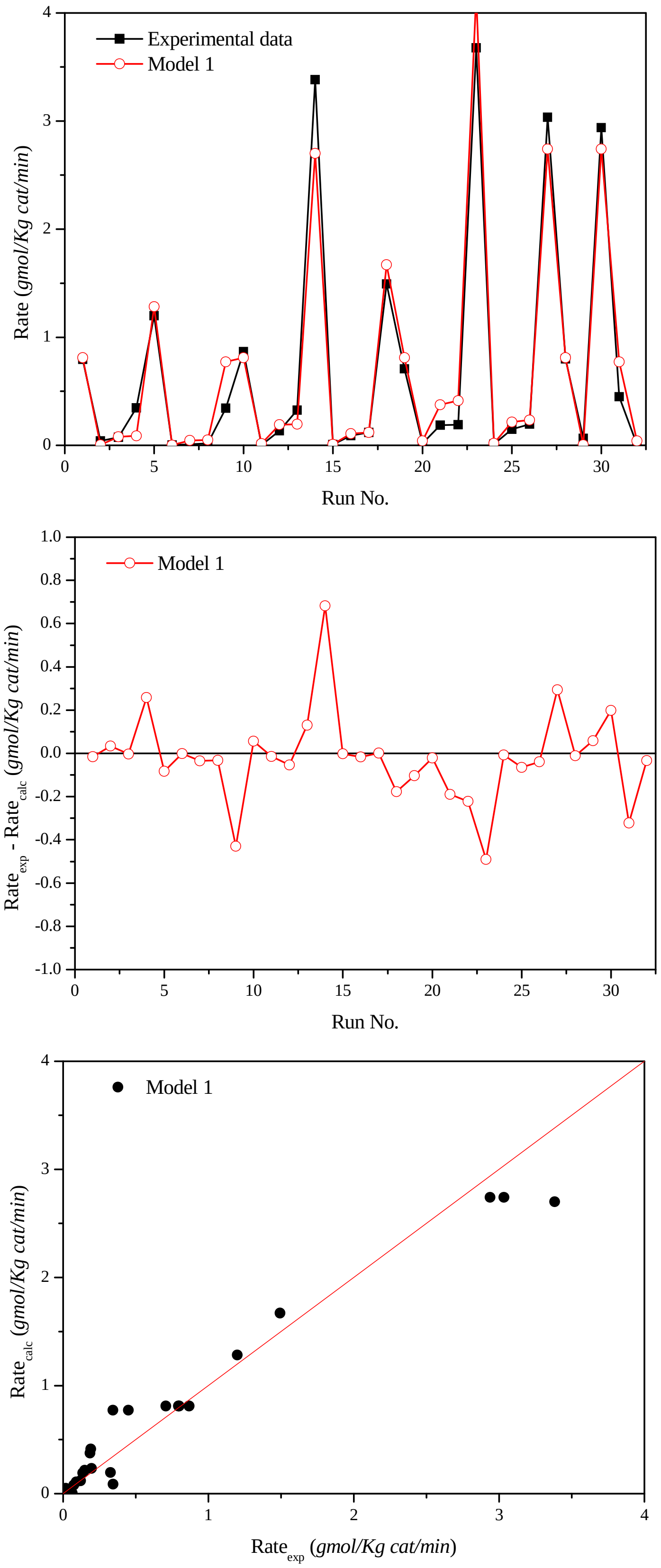

Figure 7. Regression plots for Model 1 (Maximum Likelihood).

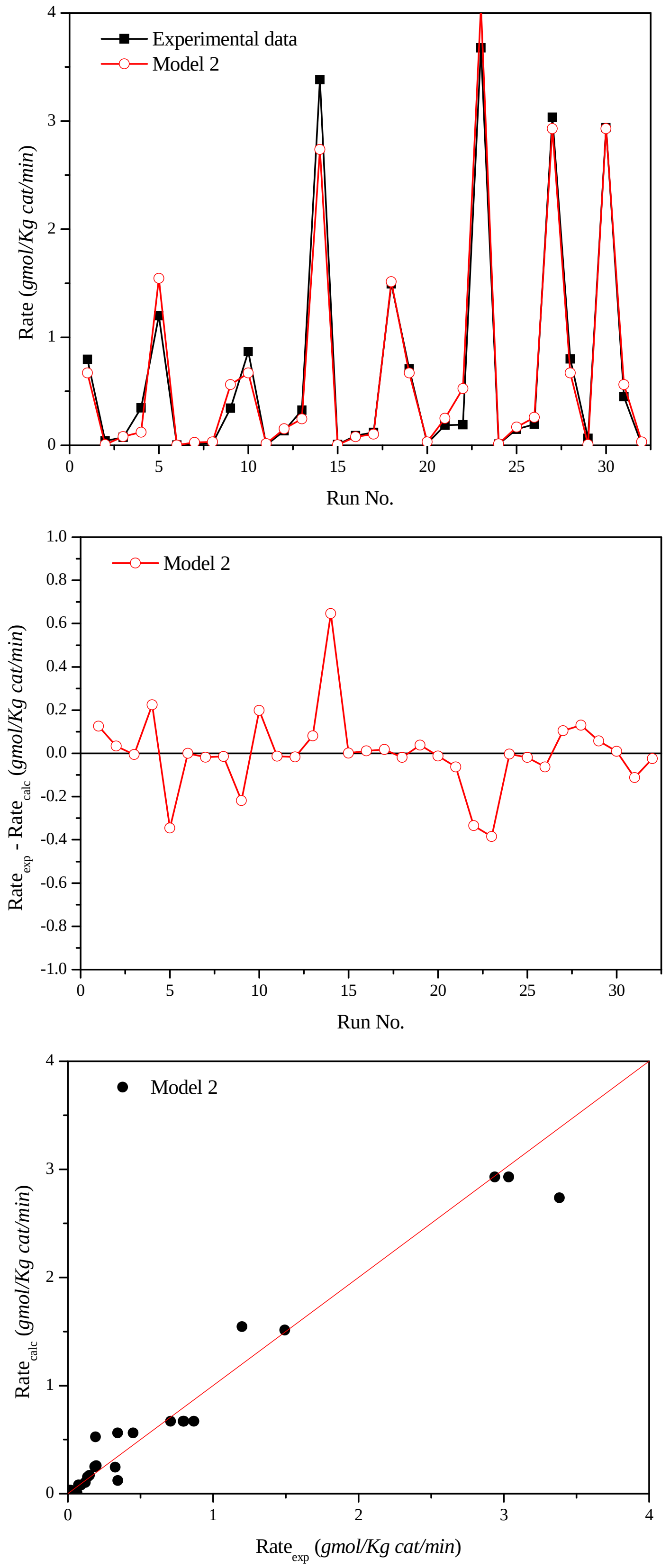

Figure 8. Regression plots for Model 2 (Maximum Likelihood).

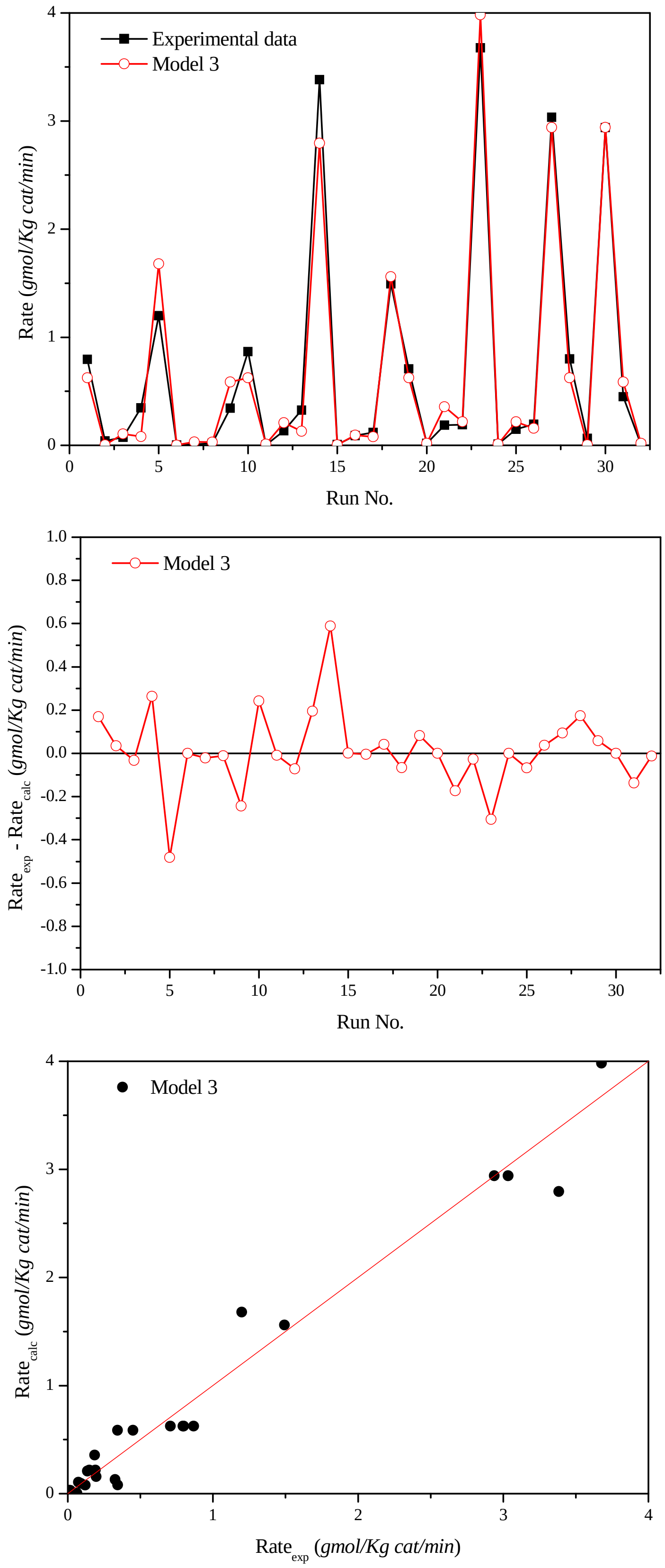

Figure 9. Regression plots for Model 3 (Maximum Likelihood).

Table 18. Statistics reports for Model 1, 2 and 3 (Maximum Likelihood).

Statistics	***Model 1***	***Model 2***	***Model 3***
Correlation	0.980671	0.985430	0.985035
R^2	0.961183	0.971069	0.970143
Adjusted R^2	0.959889	0.970105	0.969148
Standard Error	0.212952	0.183845	0.186764
$\Sigma(Y_{j,exp} - Y_j)^2$	1.360460	1.013964	1.046428

ANOVA: Model 1					
	DOF	*SS*	*MS*	*F*	*Significance F*
Regression	1	33.687694	33.687694	742.859769	1.00721E-22
Residual	30	1.360460	0.045349		
Total	31	35.048153			

ANOVA: Model 2					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	34.034189	34.034189	1006.964025	1.21926E-24
Residual	30	1.013964	0.033799		
Total	31	35.048153			

ANOVA: Model 3					
	DOF	*SS*	*MS*	*F*	*Significance F*
Regression	1	34.001726	34.001726	974.794495	1.95698E-24
Residual	30	1.046428	0.034881		
Total	31	35.048153			

Parameter	***Model 1***	$\pm CI_{95\%}$	***Model 2***	$\pm CI_{95\%}$	***Model 3***	$\pm CI_{95\%}$
k_{40}	682.9912	239.8865515	486.9774	174.2776525	136.8862	54.66783477
E_4	101301.47	35580.04719	272397.624	97484.64398	166177.57	66365.84086
K_{10}	24.2761	8.526478693	122.33	43.77900337	-	-
ΔH_1	265139.64	93124.82223	286917.85	102681.0882	-	-
K_{20}	52.0747	18.29016275	-	-	31.9079	12.74296317
ΔH_2	332626.37	116828.143	-	-	276654.56	110486.7112
K_{30}	9.6917	3.404009439	0.0355	0.012704607	0.0019	0.000758797
ΔH_3	78781.893	27670.51275	-299901.9718	-107327.7972	-430713.97	-172012.956

4. Model Discrimination

For the model discrimination, a statistic summarize is done in the following table:

Table 19. Statistic summarize (Maximum Likelihood)

Statistics	*Model 1*	*Model 2*	*Model 3*	*Model 4 (Nonlinear)*
Correlation	0.980671	0.985430	0.985035	0.978541
R^2	0.961183	0.971069	0.970143	0.957538
Adjusted R^2	0.959889	0.970105	0.969148	0.956122
Standard Error	0.212952	0.183845	0.186764	0.222727
$\Sigma(Y_{j,exp} - Y_j)^2$	1.360460	1.013964	1.046428	1.488222
F-significance	1.00721E-22	1.21926E-24	1.95698E-24	3.87814E-22

According to these results, <u>Model 2 has the best correlation values</u> for all the statistical parameters.

Remarks

There are two generally accepted methods of parameter estimation. They are least-squares estimation (LSE) or weighted least-squares(WLS) and maximum likelihood estimation (MLE). MLE is not widely recognized among modellers. LSE might be useful for obtaining a descriptive measure for the purpose of summarizing observed data, but MLE is more suitable for statistical inference such as model comparison (i.e., which model should we choose). LSE has no basis for constructing confidence intervals or testing hypotheses whereas both are naturally built into MLE. For example, MLE is a prerequisite for the chi-square test, the G-square test, Bayesian modelling, and many model selection criteria such as the Akaike Information Criterion and the Bayesian Information Criteria. In a sense, LSE can be thought of as a special application of MLE.

Both the linear and nonlinear least-squares analyses presented assume that the variance is constant throughout the range of the measured variables. This is not the case for the discrimination problem presented, then a weighted least-squares or Maximum likelihood analysis must be used to obtain better estimates of the rate law parameters.

From a statistical point of view, the method of maximum likelihood (MLE) is considered to be more robust (with some exceptions) and yields estimators with good statistical properties. In other words, MLE methods are versatile and apply to most models and to different types of data. In addition, they provide efficient methods for quantifying uncertainty through confidence bounds.

In the present analysis we have implemented both methods and the results are shown in the previous sections.

Appendix A. MoT Codes: Least Square Minimization

MODEL 1

```
R = 82.05

K1[j]  = K10*exp(-H1/R/T[j])
K2[j]  = K20*exp(-H2/R/T[j])
K3[j]  = K30*exp(-H3/R/T[j])
k4[j]  = k40*exp(-E4/R/T[j])

f_a[j] = K1[j]*Pa[j]
f_b[j] = K2[j]*Pb[j]
f_c[j] = K3[j]*Pc[j]

r_calc[j] = k4[j]*K1[j]*K2[j]*Pa[j]*Pb[j] / (1 + f_a[j] + f_b[j] + f_c[j])^2

error[j] = (r_exp[j] - r_calc[j])^2
OBJ      = sum_j( w[j]*error[j] )
```

MODEL 2

```
R = 82.05

K1[j]  = K10*exp(-H1/R/T[j])
K3[j]  = K30*exp(-H3/R/T[j])
k4[j]  = k40*exp(-E4/R/T[j])

f_a[j] = K1[j]*Pa[j]
f_c[j] = K3[j]*Pc[j]

r_calc[j] = k4[j]*K1[j]*Pa[j]*Pb[j] / (1 + f_a[j] + f_c[j])

error[j] = (r_exp[j] - r_calc[j])^2
OBJ      = sum_j( w[j]*error[j] )
```

MODEL 3

```
R = 82.05

K2[j]  = K20*exp(-H2/R/T[j])
K3[j]  = K30*exp(-H3/R/T[j])
k4[j]  = k40*exp(-E4/R/T[j])

f_b[j] = K2[j]*Pb[j]
f_c[j] = K3[j]*Pc[j]

r_calc[j] = k4[j]*K2[j]*Pa[j]*Pb[j] / (1 + f_b[j] + f_c[j])

error[j] = (r_exp[j] - r_calc[j])^2
OBJ      = sum_j( w[j]*error[j] )
```

MODEL 4: NONLINEAR

```
R = 82.05

k4[j]  = k40*exp(-E4/R/T[j])
f_a[j] = Pa[j]^alpha
f_b[j] = Pb[j]^beta
f_c[j] = Pc[j]^gama

r_calc[j] = k4[j]*f_a[j]*f_b[j]*f_c[j]

error[j] = (r_exp[j] - r_calc[j])^2
OBJ      = sum_j( w[j]*error[j] )
```

MODEL 4: LINEAR

```
 y[j] = ln(r_exp[j])
x1[j] = 1/T[j]
x2[j] = ln(Pa[j])
x3[j] = ln(Pb[j])
x4[j] = ln(Pc[j])

SUMY    = sum_j(y[j])
SUMX1   = sum_j(x1[j])
SUMX2   = sum_j(x2[j])
SUMX3   = sum_j(x3[j])
SUMX4   = sum_j(x4[j])

SUMYX1  = sum_j(y[j]*x1[j])
SUMYX2  = sum_j(y[j]*x2[j])
SUMYX3  = sum_j(y[j]*x3[j])
SUMYX4  = sum_j(y[j]*x4[j])

SUMX1X1 = sum_j(x1[j]*x1[j])
SUMX2X1 = sum_j(x2[j]*x1[j])
SUMX3X1 = sum_j(x3[j]*x1[j])
SUMX4X1 = sum_j(x4[j]*x1[j])

SUMX1X2 = sum_j(x1[j]*x2[j])
SUMX2X2 = sum_j(x2[j]*x2[j])
SUMX3X2 = sum_j(x3[j]*x2[j])
SUMX4X2 = sum_j(x4[j]*x2[j])

SUMX1X3 = sum_j(x1[j]*x3[j])
SUMX2X3 = sum_j(x2[j]*x3[j])
SUMX3X3 = sum_j(x3[j]*x3[j])
SUMX4X3 = sum_j(x4[j]*x3[j])

SUMX1X4 = sum_j(x1[j]*x4[j])
SUMX2X4 = sum_j(x2[j]*x4[j])
SUMX3X4 = sum_j(x3[j]*x4[j])
SUMX4X4 = sum_j(x4[j]*x4[j])

0 = a0*N      + a1*SUMX1   + a2*SUMX2   + a3*SUMX3   + a4*SUMX4   - SUMY
0 = a0*SUMX1  + a1*SUMX1X1 + a2*SUMX1X2 + a3*SUMX1X3 + a4*SUMX1X4 - SUMYX1
0 = a0*SUMX2  + a1*SUMX2X1 + a2*SUMX2X2 + a3*SUMX2X3 + a4*SUMX2X4 - SUMYX2
0 = a0*SUMX3  + a1*SUMX3X1 + a2*SUMX3X2 + a3*SUMX3X3 + a4*SUMX3X4 - SUMYX3
0 = a0*SUMX4  + a1*SUMX4X1 + a2*SUMX4X2 + a3*SUMX4X3 + a4*SUMX4X4 - SUMYX4

R = 82.05

k40   = exp(a0)
E4    = - a1*R
alpha = a2
beta  = a3
gama  = a4

k4[j]  = k40*exp(-E4/R/T[j])

r_calc[j] = k4[j]*(Pa[j]^alpha)*(Pb[j]^beta)*Pc[j]^gama

error[j] = (r_exp[j] - r_calc[j])^2
SUMerror  = sum_j( w[j]*error[j] )
```

Appendix B. MoT Codes: Maximum Likelihood Approach

MODEL 1

```
#Constant variables
PI   = acos(-1)
N    = 32
SEED = 2
R    = 82.05
rmax = 3.676662

#Reaction rate mode1 1
;kinetic parameter - Arrhenius dependence
K1[j]  = K10*exp(-H1/R/T[j])
K2[j]  = K20*exp(-H2/R/T[j])
K3[j]  = K30*exp(-H3/R/T[j])
k4[j]  = k40*exp(-E4/R/T[j])

;Auxiliary functions
f_a[j] = K1[j]*Pa[j]
f_b[j] = K2[j]*Pb[j]
f_c[j] = K3[j]*Pc[j]

r_model[j] = k4[j]*K1[j]*K2[j]*Pa[j]*Pb[j] / (1 + f_a[j] + f_b[j] + f_c[j])^2

#Probability Distribution Function
EPSILON = (random(SEED)-0.5)*OMMEGA*rmax

y_model[j] = r_model[j]*(1 - r_model[j]^(GAMMA-1)*EPSILON)

#Maximum likelihood funtion for a normal distribution
  error[j] = (y_exp[j] - y_model[j])^2
  SSUM      = sum_j(error[j])

 Obj_lnf  = -(-0.5*N*ln(2*PI) - N*ln(SIGMA) - SSUM/(2*SIGMA^2) )
```

MODEL 2

```
#Constant variables
PI   = acos(-1)
N    = 32
SEED = 2
R    = 82.05
rmax = 3.676662

#Reaction rate mode1 1
;kinetic parameter - Arrhenius dependence

K1[j]  = K10*exp(-H1/R/T[j])
K3[j]  = K30*exp(-H3/R/T[j])
k4[j]  = k40*exp(-E4/R/T[j])

f_a[j] = K1[j]*Pa[j]
f_c[j] = K3[j]*Pc[j]

r_model[j] = k4[j]*K1[j]*Pa[j]*Pb[j] / (1 + f_a[j] + f_c[j])


#Probability Distribution Function
EPSILON = (random(SEED)-0.5)*OMMEGA*rmax

y_model[j] = r_model[j]*(1 - r_model[j]^(GAMMA-1)*EPSILON)

#Maximum likelihood funtion for a normal distribution
  error[j] = (y_exp[j] - y_model[j])^2
```

```
  SSUM      = sum_j(error[j])

 Obj_lnf  = -(-0.5*N*ln(2*PI) - N*ln(SIGMA) - SSUM/(2*SIGMA^2) )
```

MODEL 3

```
#Constant variables
PI   = acos(-1)
N    = 32
SEED = 2
R    = 82.05
rmax = 3.676662

#Reaction rate mode1 1
;kinetic parameter - Arrhenius dependence

K2[j]  = K20*exp(-H2/R/T[j])
K3[j]  = K30*exp(-H3/R/T[j])
k4[j]  = k40*exp(-E4/R/T[j])

f_b[j] = K2[j]*Pb[j]
f_c[j] = K3[j]*Pc[j]

r_model[j] = k4[j]*K2[j]*Pa[j]*Pb[j] / (1 + f_b[j] + f_c[j])


#Probability Distribution Function
EPSILON = (random(SEED)-0.5)*OMMEGA*rmax

y_model[j] = r_model[j]*(1 - r_model[j]^(GAMMA-1)*EPSILON)

#Maximum likelihood funtion for a normal distribution
  error[j] = (y_exp[j] - y_model[j])^2
  SSUM      = sum_j(error[j])

 Obj_lnf  = -(-0.5*N*ln(2*PI) - N*ln(SIGMA) - SSUM/(2*SIGMA^2) )
```

MODEL 4: NONLINEAR

```
#Constant variables
PI   = acos(-1)
N    = 32
SEED = 2
R    = 82.05
rmax = 3.676662

#Reaction rate mode1 1
;kinetic parameter - Arrhenius dependence

  k4[j]  = k40*exp(-E4/R/T[j])
  f_a[j] = Pa[j]^alpha
  f_b[j] = Pb[j]^beta
  f_c[j] = Pc[j]^gama

r_model[j] = k4[j]*f_a[j]*f_b[j]*f_c[j]


#Probability Distribution Function
EPSILON = (random(SEED)-0.5)*OMMEGA*rmax

y_model[j] = r_model[j]*(1 - r_model[j]^(GAMMA-1)*EPSILON)

#Maximum likelihood funtion for a normal distribution
  error[j] = (y_exp[j] - y_model[j])^2
  SSUM      = sum_j(error[j])

 Obj_lnf  = -(-0.5*N*ln(2*PI) - N*ln(SIGMA) - SSUM/(2*SIGMA^2) )
```