

Model Discrimination in Chemical Kinetics

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Abstract: In studies on chemical kinetics, generally after the rate data have been taken, a mechanism and an associated rate law model are proposed based on the data taken. Frequently, more than one mechanism and rate law may be consistent with data. In order to find the correct rate law, regression techniques (model discrimination) are applied to identify which model equation best fits the data by choosing the one with the smaller sum of squares. With this non-linear regression technique, rate parameters with 95% confidence limits are calculated along with residues. Of course, model parameters must be realistic. For example, reaction rate constants, activation energies or adsorption equilibrium constants must be positive by comparing the calculated value of parameters with 95% confidence limits, one can judge about the validity of the model.

In this paper, model discrimination will be applied to certain data from the literature along with the suggested heterogeneous catalytic models such as Langmuir-Hinshelwood Kinetic Model or Rideal-Eley Model.

A reaction of $A + B \rightarrow C + D$ type have been selected (like methanation) with the rate laws given below:

$$-r_A = kP_A P_B / (1 + K_A P_A + K_B P_B + K_C P_C + K_D P_D)^2 \quad \text{dual-site Langmuir-Hinshelwood Model}$$

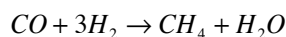
$$-r_A = kP_A P_B / (1 + K_A P_A + K_B P_B + K_C P_C + K_D P_D) \quad \text{single-site Langmuir-Hinshelwood Model}$$

$$-r_A = kP_A P_B / (1 + K_A P_A + K_B P_B)^2 \quad \text{only reactants are adsorbed}$$

$$-r_A = kP_A P_B / (1 + K_A P_A)^2 \quad \text{dual-site Rideal-Eley Model}$$

$$-r_A = kP_A^a \cdot P_B^b \quad \text{power-law}$$

In this study,



reaction rate data were tested for five different models to find the most suitable rate expression by model discrimination method taking the advantage of powerful POLYMATH package program.

INTRODUCTION

Regression Techniques

In empirical studies, in order to determine the parameters for the postulated model, very powerful regression techniques (methods) are used.

Regression methods basically are as follows [1]

- Linear regression* (like $y = ax + b$), where a and b are to be determined.
- Multiple regression* (like $y = a_1 x_1 + a_2 x_2 + \dots + a_n x_n$), where a_i 's are parameters to be determined.
- Polynomial regression* (like $y = a_n x^n + a_{n-1} x^{n-1} + \dots + a_1 x + a_0$), a_i 's are parameter to be determined from regression.

- Non-linear regression* [2].

This is very common and can be used almost under any condition. General form is $y = f(x_1, x_2, \dots, x_n, a_1, a_2, \dots, a_n)$, where $n = \#$ of experiments, $m = \#$ of parameters to be determined providing $n > m+1$.

The common features of the above regression techniques are that it is to make the variance minimum, and to make the correction factor as close to unity as possible. After determination of parameters, the next step is to check to see whether they are physically meaningful or not. For example, if adsorption equilibrium constant is one of the parameters, then it must decrease with increasing temperature as adsorption is an exothermic process (Le Chatelier Principle)

In kinetic studies, generally one faces very complicated rate expressions on heterogeneous catalysts. Those rate expressions may obey Langmuir-Hinshelwood or Rideal-Eley model [3, 4].

In general, if we have a reaction of $A + B \rightarrow C$ we may have possible rate expressions as

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$$-r_A = \frac{kP_A P_B}{(1 + K_A P_A + K_B P_B + K_C P_C)^2} \quad (\text{Dual-site model})$$

$$-r_A = \frac{kP_A P_B}{(1 + K_A P_A + K_B P_B + K_C P_C)} \quad (\text{Single-site model})$$

$$-r_A = \frac{kP_A P_B}{(1 + K_A P_A)^2} \quad (\text{Dual-site, Rideal-Eley})$$

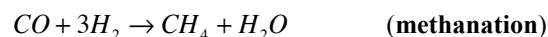
$$-r_A = kP_A^a P_B^b \quad (\text{Apparent power-law expression})$$

In kinetic studies, for example, one may have three different mechanisms and three different rate-determining steps. Therefore, one will have nine different rate expressions. In order to determine the correct rate expression, **model discrimination method** is being used. The essence of this method is not only to minimize the variance, but also to keep the correction factor as close to one (unity) as possible. In addition to the above two criteria, one also has to check the physical validity of the determined parameters.

RESULTS

Now we will chose the reaction of methanation [4] on Ni catalyst where initial rates are taken at constant temperature at variety partial pressures of reactants and products.

Consider the reaction



Assuming the following runs were carried out under the given conditions (see Table 1).

Table 1. Initial Rates Obtained at Various Partial Pressures

Run #	r_A^*	P_{CO}^{**}	$P_{H_2}^{**}$	$P_{H_2O}^{**}$	$P_{CH_4}^{**}$
1	0.1219	1	1	0	0
2	0.0944	1	1	1	1
3	0.0943	1	1	1	2
4	0.0753	1	1	2	1
5	0.0753	1	1	2	2
6	0.0512	1	1	4	1
7	0.0280	1	1	8	1
8	0.1274	1	2	1	1
9	0.1056	1	2	2	2
10	0.1203	1	4	2	2
11	0.1189	1	8	1	1
12	0.0782	2	1	1	1
13	0.1204	2	2	1	1
14	0.1057	2	2	2	0
15	0.1056	2	2	2	1
16	0.1056	2	2	2	2
17	0.1552	2	4	1	1
18	0.0533	4	1	1	1
19	0.0911	4	2	1	1
20	0.0317	8	1	1	1
21	0.1476	8	8	1	1

* r_A [mole/kg.cat.s], ** P_i [atm].

We will consider the following plausible rate expressions and by **model discrimination** we will reach hopefully to the true rate expression.

- a) All reactants and products are adsorbed with dual-site mechanism:

$$-r_A = \frac{kP_{CO} \cdot P_{H_2}}{(1 + K_{CO} \cdot P_{CO} + K_{H_2} \cdot P_{H_2} + K_{H_2O} \cdot P_{H_2O} + K_{CH_4} \cdot P_{CH_4})^2} \quad (\text{Dual-site})$$

- b) All reactants and products are adsorbed with single-site mechanism:

$$-r_A = \frac{kP_{CO} \cdot P_{H_2}}{(1 + K_{CO} \cdot P_{CO} + K_{H_2} \cdot P_{H_2} + K_{H_2O} \cdot P_{H_2O} + K_{CH_4} \cdot P_{CH_4})} \quad (\text{Single-site})$$

- c) Only reactants are adsorbed with dual-site mechanism:

$$-r_A = \frac{kP_{CO} \cdot P_{H_2}}{(1 + K_{CO} \cdot P_{CO} + K_{H_2} \cdot P_{H_2})^2} \quad (\text{Only reactants are adsorbed, dual-site})$$

- d) Only CO is adsorbed; H₂ comes directly from gas phase and reacts with adsorbed CO (Rideal-Eley Mechanism)

$$-r_A = \frac{kP_{CO} \cdot P_{H_2}}{(1 + K_{CO} \cdot P_{CO})^2} \quad (\text{Rideal-Eley, dual-site})$$

- e) A power-law expression:

$$-r_A = k \cdot P_{CO}^a \cdot P_{H_2}^b \quad (\text{Power-Law})$$

In the following pages, these five different models were tried on Polymath[®] program. The results are self explanatory, and are given in Figs. (1-5).

Model a:

$$-r_A = \frac{kP_{CO} \cdot P_{H_2}}{(1 + K_{CO} \cdot P_{CO} + K_{H_2} \cdot P_{H_2} + K_{H_2O} \cdot P_{H_2O} + K_{CH_4} \cdot P_{CH_4})^2}$$

Output of Model a:

$$r_A = kP_{CO} P_{H_2} / (1 + K_{CO} P_{CO} + K_H P_H + K_{H_2O} P_{H_2O} + K_{CH_4} P_{CH_4})^2$$

POLYMATH Results

Nonlinear Regression (L-M)

Variable	Ini. Guess	Value	95% Confidence
k	4	7.9628870	0.0367133
KCO	2	5.0877643	0.0124837
KH	4	1.9950241	0.0047754
KH ₂ O	5	1.0969188	0.0030085
KCH ₄	1	0.0046140	0.0015179

Nonlinear regression settings.

Max # iterations = 64

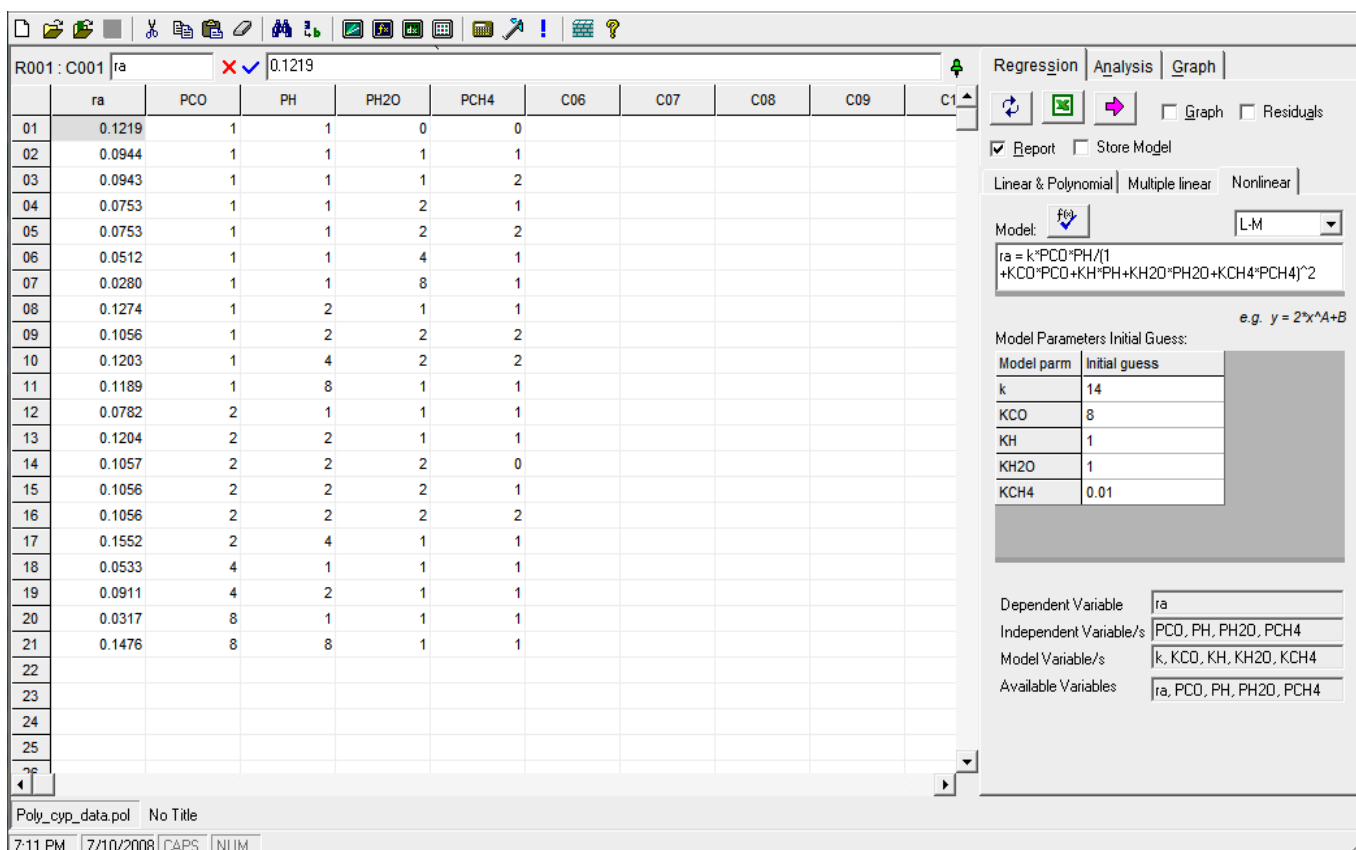


Fig. (1). Input of the data in POLYMATH Screen for Model a.

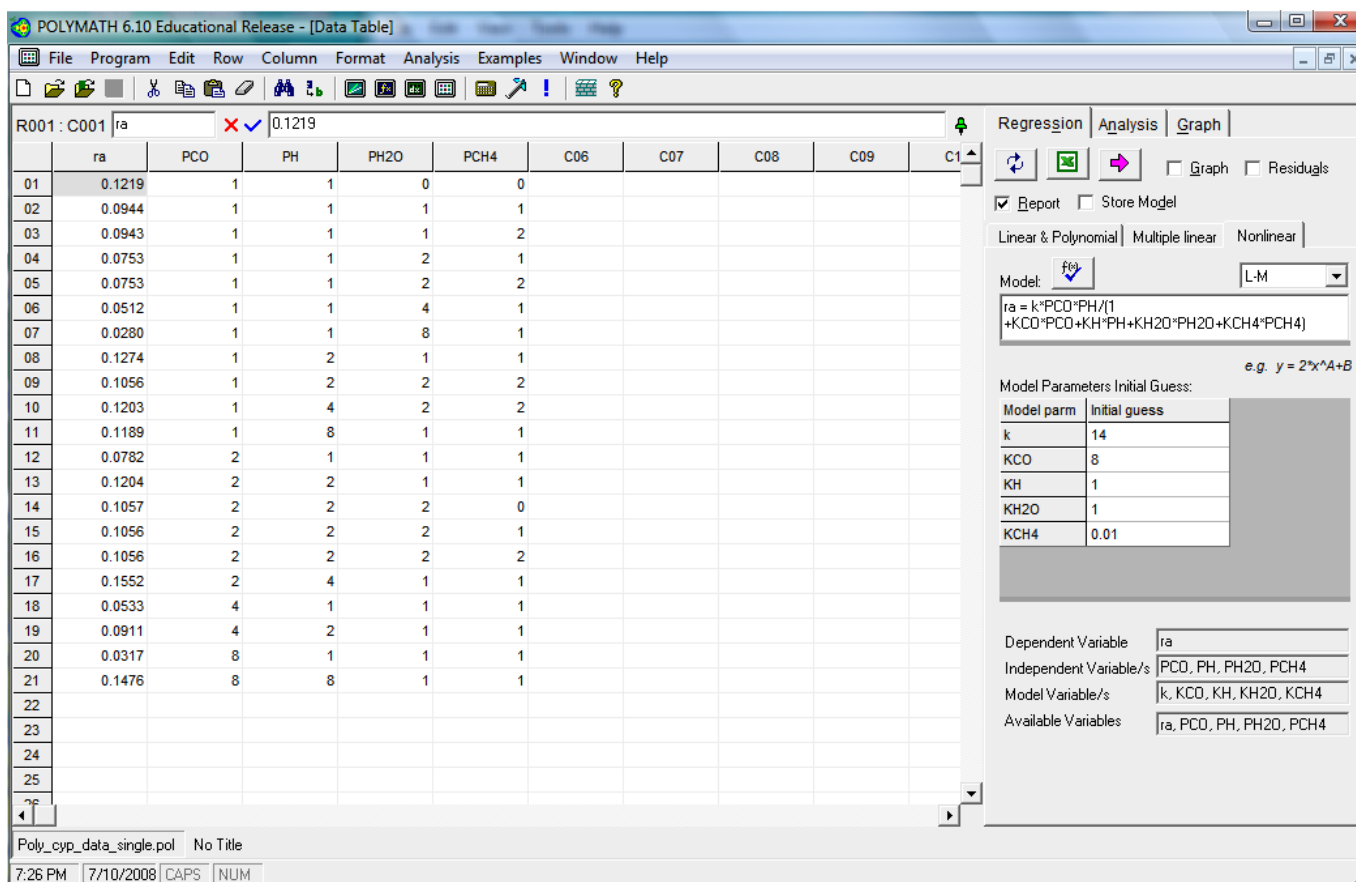


Fig. (2). Input of the data in POLYMATH Screen for Model b.

Precision

$R^2 = 0.9999995$
 $R^2_{adj} = 0.9999993$
 Rmsd = 5.321E-06
 Variance = 7.804E-10

Model b:

$$-r_A = \frac{kP_{CO} \cdot P_{H_2}}{(1 + K_{CO} \cdot P_{CO} + K_{H_2} \cdot P_{H_2} + K_{H_2O} \cdot P_{H_2O} + K_{CH_4} \cdot P_{CH_4})}$$

Output of Model b:

$$r_A = kP_{CO} P_H / (1 + K_{CO} P_{CO} + K_H P_H + K_{H_2O} P_{H_2O} + K_{CH_4} P_{CH_4})^2$$

Variable	Ini guess	Value	95% Confidence
k	14.0	2.747922	0.0023620
KCO	8.0	51.41168	0.0593556
KH	1.0	12.89503	0.0368865
KH ₂ O	1.0	2.123223	0.0692380
KCH ₄	0.01	-1.989895	0.0982922

Nonlinear regression settings

Max # iterations = 64

Precision

$R^2 = -1.586834$
 $R^2_{adj} = -2.233542$
 Rmsd = 0.011789
 Variance = 0.0038306

Model c: $-r_A = \frac{kP_{CO} \cdot P_{H_2}}{(1 + K_{CO} \cdot P_{CO} + K_{H_2} \cdot P_{H_2})^2}$

Output of Model c: $r_A = kP_{CO} P_H / (1 + K_{CO} P_{CO} + K_H P_H)^2$

Variable	Ini guess	Value	95% Confidence
k	14.0	0.7700806	0.6088063
KCO	8.0	1.540737	0.7859312
KH	1.0	0.5896616	0.3142481

Precision

$R^2 = 0.7311287$
 $R^2_{adj} = 0.7012541$
 Rmsd = 0.0038007
 Variance = 0.0003539

Model d: $-r_A = \frac{kP_{CO} \cdot P_{H_2}}{(1 + K_{CO} \cdot P_{CO})^2}$

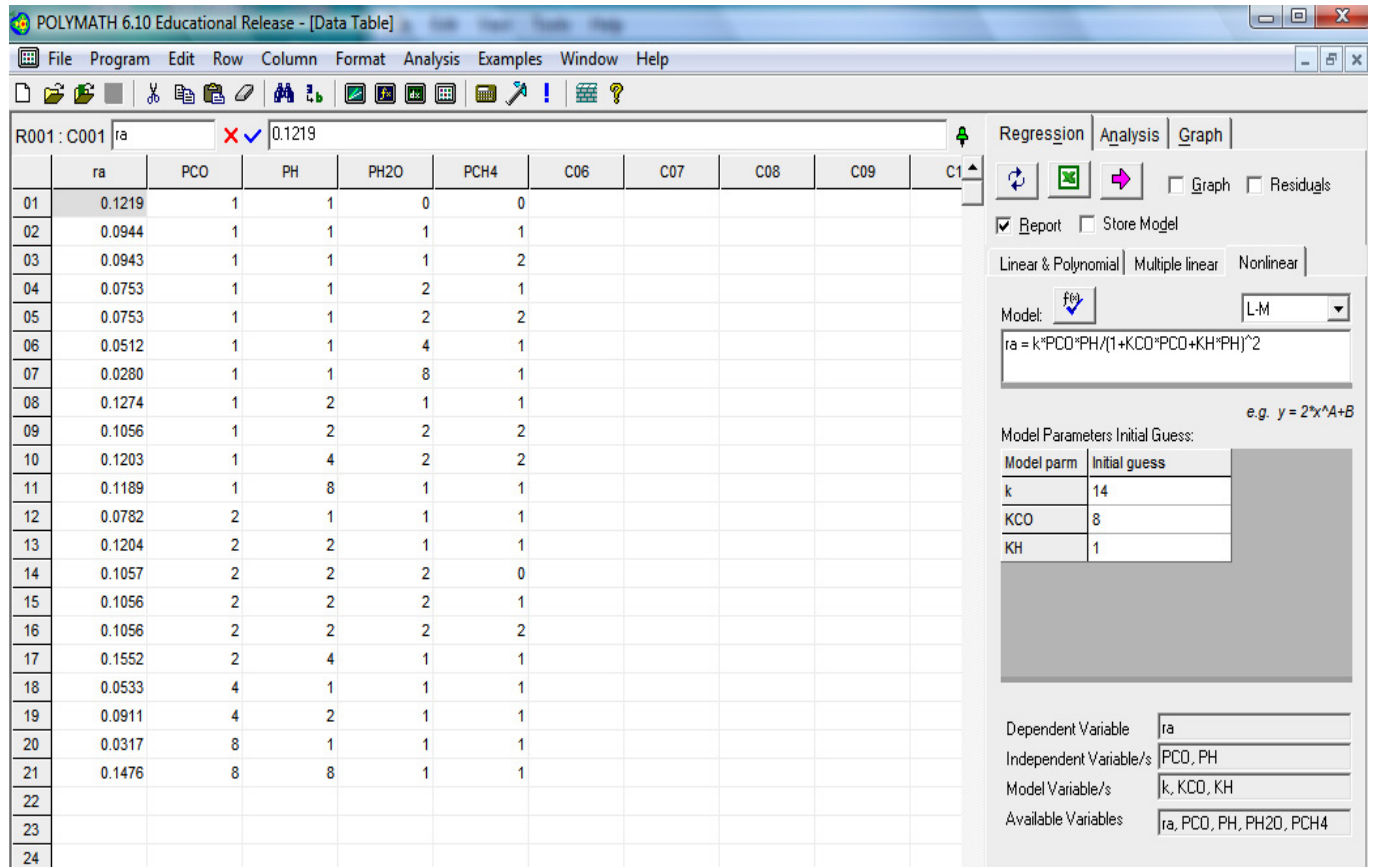


Fig. (3). Input of the data in POLYMATH Screen for Model c.

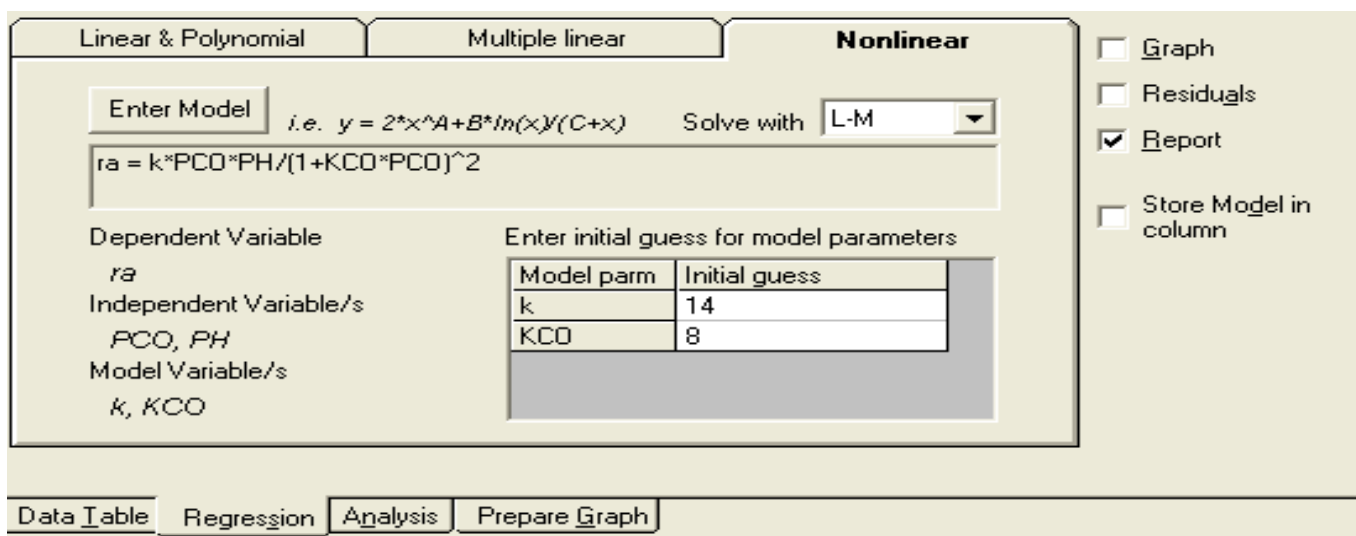


Fig. (4). Input of the data in POLYMATH Screen for Model d.

Output of Model d: $r_A = kP_{CO}P_H / (1 + K_{CO}P_{CO})^2$

Variable	Ini Guess	Value	95% Confidence
k	14.0	0.062234	5.47E-06
KCO	8.0	0.453103	3.977E-05

Precision

R² = -1.282797
 R²adj = -1.402944
 Rmsd = 0.0110745
 Variance = 0.0028467

Nonlinear regression settings.

Max # iterations = 64

Model e: $-r_A = k.P_{CO}^a.P_{H_2}^b$

Output of Model e: $ra = k*PCO^a*PH^b$

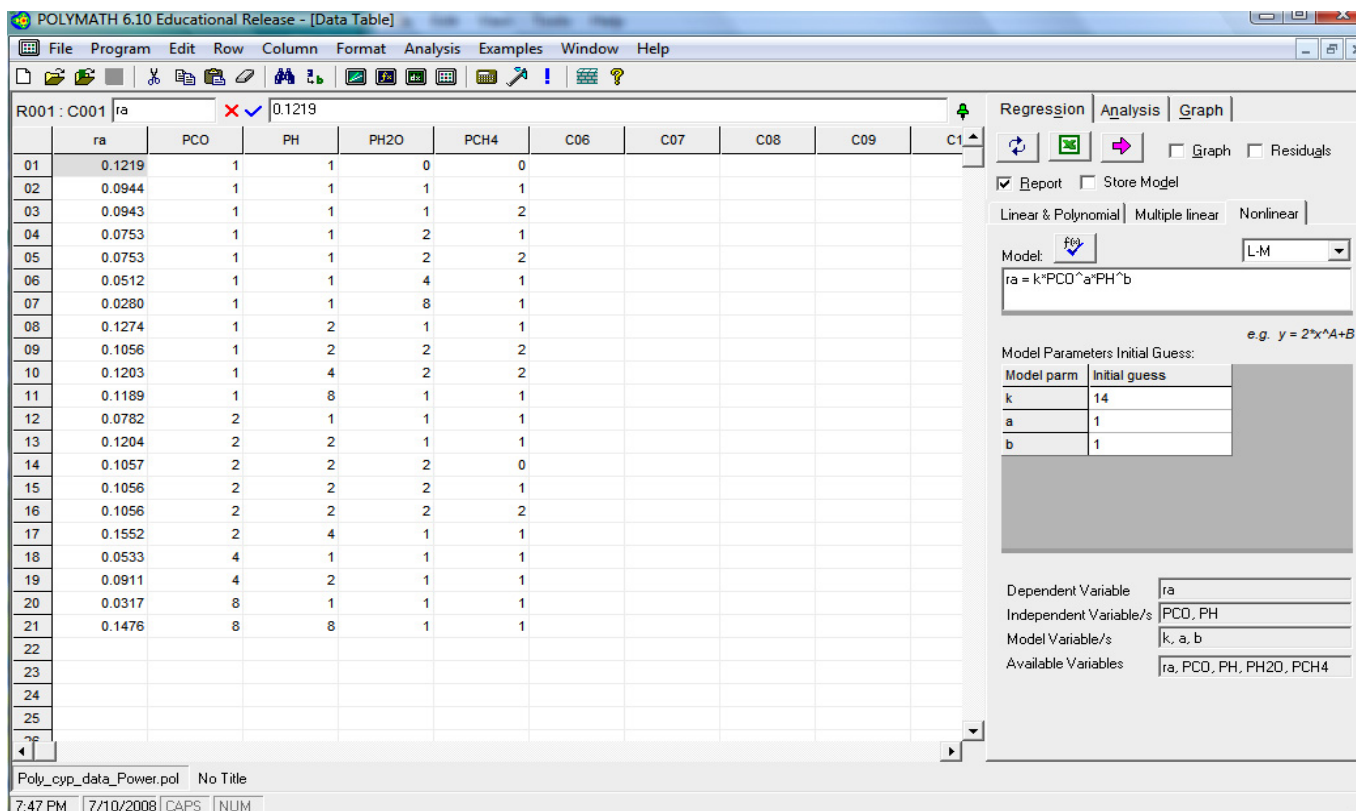


Fig. (5). Input of the data in POLYMATH Screen for Model e.

Variable	Ini Guess	Value	95% Confidence
k	14.0	0.0806184	3.076E-06
a	1.0	-0.0554411	4.271E-05
b	1.0	0.3205555	3.242E-05

Nonlinear regression settings.

Max # iterations = 64

Precision

R² = 0.4902824

R²adj = 0.4336471

Rmsd = 0.0052331

Variance = 6.709E-04

When variance, correction factor (coefficient) and the physical meaningfulness of the parameters are considered, one can clearly see that the **model a** fits the data in a perfect manner. In the remaining other models (i.e. **b**, **c**, **d** and **e**) either because of variance or correction factor or 95% confidence interval or combination thereof, the models seem to be inadequate and as a result they are eliminated.

CONCLUSIONS

No matter how the chemical kinetic expressions are complicated, either linear, multiple linear, non-linear or polynomial, one can find a satisfactory rate expression by means of model discrimination method. This discrimination processes are eased especially after the advent of powerful ready package programs such as POLYMATH, MATLAB, MATHCAD [5], and others. One, still, has to be very cautious in that finding the satisfactory rate expression does not mean the true (absolute) rate expression and mechanism are found [6].

ACKNOWLEDGEMENTS

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