

---

**Comparison of several computational procedures for evaluating the kinetics of thermally stimulated condensed phase reactions**

*Nicolas Sbirrazzuoli, Luc Vincent, Sergey Vyazovkin*

Published in *Chemometrics and Intelligent Laboratory Systems 54 2000 53–60*

---

**or some comments on how to implement comparative analysis**

*A. Kossoy, CISP Ltd*

**Abstract**

About 13 years ago the article “Comparison of several computational procedures for evaluating the kinetics of thermally stimulated condensed phase reactions” published in Chemometrics and Intelligent Laboratory Systems compared model-free method and model-based method presented by ForK - one of the CISP- developed programs for kinetics evaluation – which resulted in unfavorable conclusions with regard to ForK capabilities. We found it important to analyze the origins of such an unfavorable opinion of the authors, to show that the comparison had been implemented without due attention to all the details, and to give the results of more objective and accurate comparison. We believe that this paper may be of general interest.

**Introduction**

No doubt comparative analysis of different methods used for solving certain problem is very useful. It allows revealing merits and limitations of every method thus providing a researcher with the guidance on when and why one or another method can be more informative and efficient – as a matter of fact there is no one universal method equally applicable to all the cases.

As it follows from the article title its aim was to compare several computational procedures of kinetics evaluation or, to be more precise, to compare two approaches to kinetics evaluation – model-free and model based ones. The ForK program developed by CISP [1] was used as an example of software designed for practical application of the model-based approach.

The real value and usefulness of such an analysis depends on its objectivity. In the case of the above-mentioned article we have found that some results and conclusions presented there suffer from the lack of this very objectivity and our program has come in for undeserved criticism. This is the reason why we decided to write these comments. Unfortunately the journal where the article was published is unfamiliar to us therefore we happened to read the article after more than 10 years since it has been published. Then these notes waited for their time for additional 3 years. Nevertheless they say “the written word remains” and “better late than never” therefore we decided to make this material available for visitors of our site in believe that it may be of general interest.

**Some general observations**

1. In section 1 (Introduction) we find the statement

*“The first class of methods enables Arrhenius parameters to be estimated by fitting kinetic data to assumed reaction models. When applied to data obtained at a single heating rate, these methods produce highly uncertain values of the activation energy and of the pre-exponential factor, which are strongly correlated with each other.” (p. 54 of the article)*

It is hard to argue with this statement as it is the axiom in thermal analysis and, more generally, in chemical kinetics theory. It equally concerns any method of kinetic analysis which means in particular that if a method doesn't allow simultaneous processing of several data sets that correspond to different thermal modes then this method shouldn't be taken seriously at all. Let us remember this.

Then it is stated:

**“As an alternative.... This class involves so-called isoconversional methods, which yield the activation energy as a function of the extent of conversion. Because *estimating this sole dependence is sufficient for both making kinetic predictions and drawing mechanistic conclusions*, the use of the isoconversional methods give rise to completely model-free kinetic analysis” (p. 54 of the article)**

This is definitely an overstatement of the method's capabilities. The sole dependence E(conversion) cannot answer all the questions with regard to kinetics.

**As an alternative...** This is the first point of our principal disagreement with the authors – by no means should isoconversional and model-based methods be considered as the antagonistic alternatives. Contrary to this in many cases they turn out to be mutually complementary.

There were several papers published in Thermochemica Acta that gave well- weighed evaluation of the role and limitations of the isoconversional method, for instance [2-4]

In [4] we can find precise conclusion which conveys the very idea about complementarity of these approaches:

**“”Model-free” methods of kinetic analysis postpone the problem of identifying a suitable kinetic model until an estimate of the activation energy has been made”**

**Making kinetic predictions** is impossible without knowledge of pre-exponent – kinetic prediction means first of all the possibility to predict the reaction rate.

**... drawing mechanistic conclusions** is also problematic if to deal only with the dependence E(conversion). For example one cannot distinguish between autocatalytic and non self-accelerating reactions: autocatalytic reactions are often described by the single value of E as well as simple reactions of N-order type therefore for single-stage reaction E will always be constant irrespective of specific reaction mechanism.

Let us note that simple enhancement of the isoconversional method allows simultaneous estimate of both functions E(conversion) and Ko(conversion) which really gives the possibility not only to recognize overall features of a reaction but also to predict reaction course under conditions of interest - though with due precautions.

2. Section 3.4 begins with the statement that really surprised us:

**“The commercial software package ForK Version 1.5 allows one to estimate kinetic parameters from several isothermal, or a single nonisothermal experiment...” (p. 58).**

We cannot agree with this statement. From the very beginning ForK (and its DOS-predecessor MK for that matter) has been purposefully designed to process simultaneously several data sets that correspond to different thermal modes (isothermal and non-isothermal data, data at different heating rates, non-adiabatic and adiabatic data, data with responses of different physical quantity, etc). Moreover, there are several examples in the Tutorial demonstrating that only the simultaneous analysis of different data can give reliable results (see [1] for more information). The same recommendations can be found in our presentations and articles, e.g. [5-7].

As you can see this is the unfounded statement. Perhaps the authors took no notice of the main principle ForK is based, though it would be only natural to expect that to provide objective comparative analysis of certain methods one had to make detailed acquaintance with these methods.

### **Analysis of dynamic data treatment presented in the article.**

7 data sets at different heating rates where used. They were simulated and then distorted by adding the Gaussian noises. It is the good basis for further analysis. Very provocative complex two-stage reaction A->B, C->D was created so that the curves don't reveal its complexity. It makes the test even more rigorous.

Then the whole bunch of data was used for creation of model-free kinetics. The advanced isoconversional method proposed by S. Vyazovkin has been applied for this purpose.

**“The extreme values of the E variation 80 and 130 kJ/mol” (p.58)** were obtained which give more or less acceptable estimates of real values (74 and 143 kJ/mol respectively).

Then, to verify the ability of ForK to create correct kinetics, only one curve for 1 K/min has been chosen in apparent violation of the main principle of kinetic analysis. Why had it been done?

Is it because ForK doesn't allow simultaneous treatment of several data sets?

No, as we have emphasized already, it is not.

Is it because the analysts just didn't know what ForK is capable of?

Believing in good faith of the authors we have to assume that this is the reason.

Was it to prove once more the axiom?

It seems there is no need in further evidences, but if it was the purpose then ForK specifically has nothing to do with it. In such the cases it is more pertinent and correct to take and use some anonymous method.

Nevertheless let us see what was obtained with ForK when it has been put in such an unfavorable conditions

From non-disturbed single curve (heating rate 1 K/min) ForK was able to evaluate practically exact values of all the 8 parameters (Tab. 4, p.58 of the article)! It is fantastic result taking into account that the approach was wrong. The estimates of activation energies obtained from disturbed data were about 103 and 130 kJ/mol - not bad provided that, again, the main principle has been violated. Let me remind that isoconversional method being applied to the whole bunch of data wasn't able to reconstruct exact values either.

### **Analysis of isothermal data treatment presented in the article.**

The set of isothermal data for temperatures within the range 100-220 °C had been simulated and distorted in the same way as DSC data.

Isoconversional method gave the following results:

*"For this narrower temperature region (i.e. 170-220 °C) one obtains the extreme values of E 115 and 135 kJ/mol. Although the extreme values of the E variation do not give the exact values of the activation energies of the individual reactions, **they appear to be quite reasonable approximations.**" (p. 58)*

Note that the errors of the estimates are 55% for the first stage and 6% for the second one.

What was obtained with ForK? For the same temperature region the worst estimates are 96 and 160 kJ/mol, which gives the following errors: 30% for the first stage and 12% for the second one. If to compare the results without any prejudice we should conclude that ForK-generated estimates are at least not worse than that obtained by isoconversional method. But what is the conclusion presented in the article?

**"ForK failed to produce the correct values"**. (p.59) ??

**Such principal difference in conclusions seems to be very strange if not unfair.**

Another example of very specific estimate of ForK capabilities can be found on the same page:

*The correct values can, however, be estimated from the data over the wider temperature region 373-494 K, which does not seem realistic from the experiment standpoint.*

To tell the truth we do not comprehend in full measure how this result based on simulated data may relate to experiment. Is it because isoconversional method being applied to data from the same wider temperature region failed to estimate correct parameters? As a matter of fact the estimates of activation energy were ~100 and 140 kJ/mol (p.58).

### **Demonstration of real capabilities of ForK.**

This part represents more correct comparison of isoconversional and model-based methods. The same sample data as described in the article have been simulated and the noises were added.

The original isoconversional method developed by CISP and introduced by the IsoKin program has been applied. It allows simultaneous estimation of dependences  $K_0(\text{conversion})$  and  $E(\text{conversion})$  but only the last function is presented in comparison with the original results from

the article.

### Processing of dynamic data.

Results of the isoconversional analysis are shown in Fig.1 (curve 2) along with the results from the article (curve 1). It is evident that they are very similar and that isoconversional method gives only approximate values of the activation energies (about 76 and 128 kJ/mol instead of 74 and 143 kJ/mol respectively).

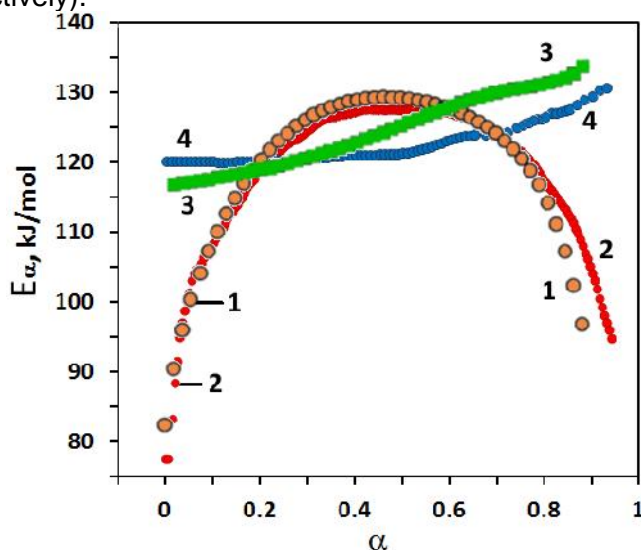


Fig. 1. Results of applying the isoconversional method  
linear heating mode: 1 – results from the article, 2 – IsoKin results;  
isothermal mode: 3 – results from the article, 4 – IsoKin results

Then ForK was used for evaluation of the kinetic model. Two variants have been examined:

- by using only one disturbed data set for 1 K/min (as in the article);
- by using 3 disturbed data sets for 1, 2 and 5 K/min.

When it comes to applying non-linear optimization for parameters estimation the important point is the initial guess on parameters that has been accepted. In both the cases the following set was used (Tab. 1).

**Table 1**

Parameter	Units	Value	
		1-st stage	2-nd stage
ln(k0)	ln(1/s)	26.8 (11.7)	33 (29.4)
E	kJ/mol	130 (74)	160 (143)
n	-	1.00 (1.0)	1.00 (1.2)
c	-	0.45 (0.3)	0.55 (0.7)

One can see that the parameters are quite far from the exact values (here and hereafter these figures are given in parentheses) though they provide reasonable initial fit of “experimental” data.

The resultant parameters evaluated from the single data set are presented in Tab.2.

**Table 2**

Parameter	Units	Value	
		1-st stage	2-nd stage
ln(k0)	ln(1/s)	12.89 (11.7)	30.84 (29.4)
E	kJ/mol	78.02 (74)	148.79 (143)
n	-	0.91 (1.0)	1.29 (1.2)
c	-	0.31 (0.3)	0.69 (0.7)

These results are very good taking into account that only one data set was used for estimation. We can only guess why they are better than that mentioned in the article. Most likely it is because the authors used the default parameters for numerical methods (for instance default values of the absolute and relative errors of numerical integration are  $10^{-4}$ ) whereas we used higher precision  $10^{-6}$ . It is no wonder that due attention should be paid to these matters, specifically, higher precision is required for processing data with noises.

3 disturbed data sets allowed obtaining almost exact values of the parameters (Tab.3).

**Table 3**

Parameter	Units	Value	
		1-st stage	2-nd stage
$\ln(k_0)$	$\ln(1/s)$	11.75 (11.7)	29.5 (29.5)
E	kJ/mol	74.15 (74)	143.41 (143)
n	-	1.00 (1.0)	1.202 (1.2)
c	-	0.31 (0.3)	0.69 (0.7)

Fig.2 demonstrates very good correspondence between “experimental” (asterisks) and simulated (solid lines) data.

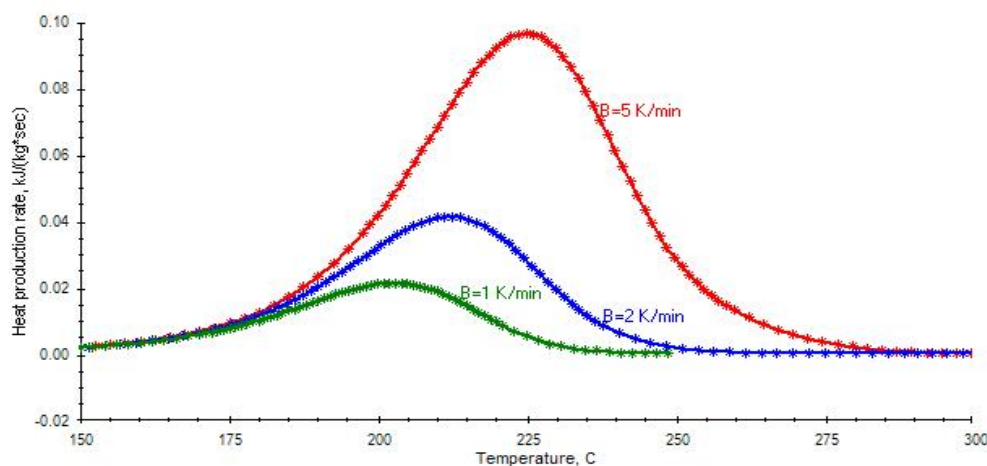


Fig. 2 Results of applying model-based method (ForK) for analysis of dynamic data

### Processing of isothermal data.

The narrow temperature range 170 – 220 °C has been chosen deliberately because, as it was shown in the article, expanded range simplifies obtaining better results.

As in previous case both variants of the isoconversional method give similar results (Fig. 1 curves 3 and 4) and the estimates of activation energies are quite rough - about 120 and 132 kJ/mol.

3 disturbed data sets at 180, 200 and 220 °C were used for kinetics evaluation by using ForK. Optimization started from the same initial parameters vector as in Tab.1. Fig.3 shows that ‘experimental’ data (asterisks) are perfectly fitted by the simulated ones (solid lines). The estimates of the model parameters are much closer to the exact values than the estimates generated by the isoconversional method (Tab. 4).

**Table 4**

Parameter	Units	Value	
		1-st stage	2-nd stage
$\ln(k_0)$	$\ln(1/s)$	10.99 (11.7)	29.16 (29.4)
E	kJ/mol	71.23 (74)	142.1 (143)
n	-	0.97 (1.0)	1.20 (1.2)
c	-	0.28 (0.3)	0.72 (0.7)

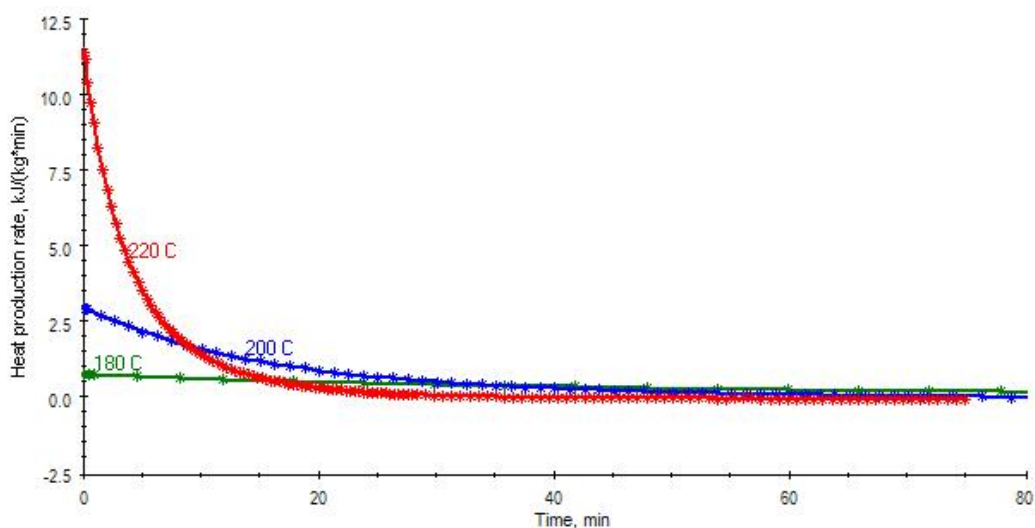


Fig. 3 Results of applying model-based method (Fork) for analysis of isothermal data

## Conclusion

1. The analysis presented here demonstrates once again the usefulness of isoconversional method in revealing complexity of a reaction and in getting preliminary estimates of the range of apparent activation energies.
2. It can be concluded from the data presented here (and the results from the article show the same) that isoconversional method is less efficient for processing of isothermal data.
3. The model-based method allows getting the final kinetics suitable for further practical use provided that it complies with the main principles of kinetics evaluation.
4. Fork as a software that implements the model-based approach is really capable of generating detailed and reliable kinetic information provided that a researcher mastered its main features and due attention is paid to the adjustment of math methods used.

## References

1. TSS software <http://www.cisp.spb.ru/fork>
2. Ammar Khawam and Douglas R. Flanagan, Role of isoconversional methods in varying activation energies of solid-state kinetics. I. isothermal kinetic studies, *Thermochimica Acta*, 429 (2005) 93–102
3. Ammar Khawam and Douglas R. Flanagan, Role of isoconversional methods in varying activation energies of solid-state kinetics II. Nonisothermal kinetic studies, *Thermochimica Acta*, 436, (2005) 101-112
4. Joyce D. Sewry and Michael E. Brown, "Model-free" kinetic analysis?, *Thermochimica acta*, 390; (2002), 217-225
5. Kossoy A.A., Benin A.I., Smikalov P.Yu., Kasakov A.N. A computerized system for research into thermal safety of chemical processes. *Thermoch. Acta*, 203 (1992), 77-92.
6. Kossoy A., Akhmetshin Yu., Specific features of kinetics evaluation in reaction hazard assessment Proceedings of the 3rd Int. Symposium on Runaway Reactions and Pressure Relief Design, Cincinnati, USA, 30 October – 4 November, 2005
7. Kossoy A., Akhmetshin Yu., Identification of kinetic models for the assessment of reaction hazards, *Process Safety Progress*, 26, N3 (2007), 209-220