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Thermochimica Acta 397 (2003) 1–3

thermochimica acta

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Comment

Some comments to the paper of J.D. Sewry and M.E. Brown: "Model-free" kinetic analysis?

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We have two main objections concerning Section 2 in the paper by Sewry and Brown.

1. Model-free methods

Sewry and Brown [1] emphasize correctly in their abstract: "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. A major reason for doing this is that misidentification of the kinetic model has a marked effect on the values obtained for the Arrhenius parameters in both isothermal and non-isothermal kinetic analyses". But the following formulation in their conclusions is then at least not clear: "Vyazovkin has shown, by numerous examples, the advantages of isoconversional methods and the necessity of testing Arrhenius parameters for dependence upon extent of reaction. Such a dependence usually indicates some inadequacy in the kinetic model that is assumed to apply". To our opinion, this is a contradiction in terms: the activation energy, estimated by model-free algorithms, is by definition not dependent upon a kinetic model. Assuming high quality, reliable experimental data sets, an observed dependence of $E_A = f(\alpha)$ is always a clear indication that the reaction under investigation doesn't proceed as a single-step reaction. The possibly dramatic influence of erroneous measurements is a different problem.

Vice versa: If no dependence of $E_A = f(\alpha)$ is observed, then there exists a high probability for the presence of a single-step reaction. Now additionally to the estimation of the activation energy, we have also the possibility to estimate the most probable kinetic model.

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha=\alpha_j} = \ln\ f(\alpha)|_{\alpha=\alpha_j} + \ln A - \frac{E}{RT_{j,m}} \qquad (1)$$

whereby j is the index of the α-value and m the index of the heating rate and/or the temperature.

Eq. (1) shows that the sum of the two terms $\ln f(\alpha)$ and $\ln A$ should be (approximately) constant for the true kinetic model. Testing the whole set of standard conversion functions $f(\alpha)$ [2], that conversion function is the most probable one for which the dependence of the sum $[\ln f(\alpha) + \ln A - \ln f_{\text{test}}(\alpha)]$ achieves a minimum. As shown in Fig. 1, this produces a horizontal line in a plot $\ln A = f(\alpha)$. A dependence of $\ln A$ on α can be an indication that no function from the standard set is able to describe the course of reaction or a hidden multiple-step reaction taking place.

Figs. 2–5 of the paper by Sewry and Brown present the dependence of activation energies on α for non-appropriately selected conversion functions $g^*(\alpha)$ in the case of isothermal measurements. These examples are not relevant concerning the model-free

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PII: S0040-6031(02)00224-1

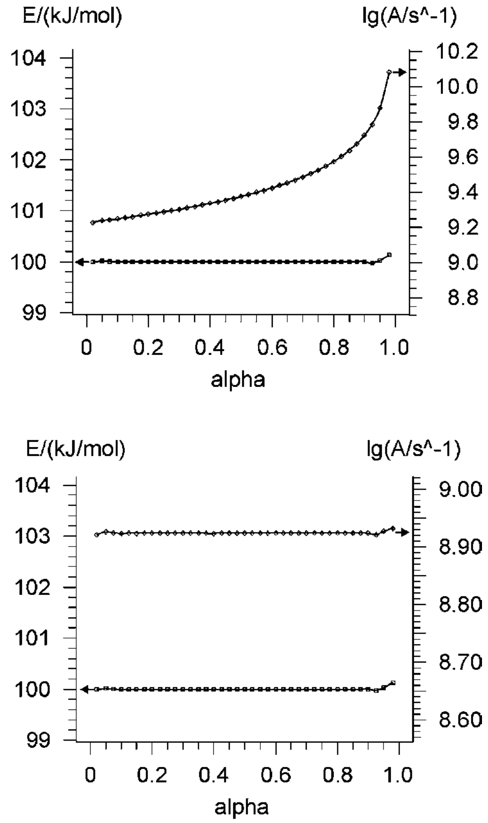

Fig. 1. Model-free analysis of a data set, simulated using $f(\alpha) = 2(1-\alpha)^{0.5}$ (R2) and heating rates of 0.25, 1, 5, and 20 K/min; $\ln A = 8.924\,\mathrm{s}^{-1}$; $E_A = 100\,\mathrm{kJ/mol}$; (a) test function F1; (b) test function R2.

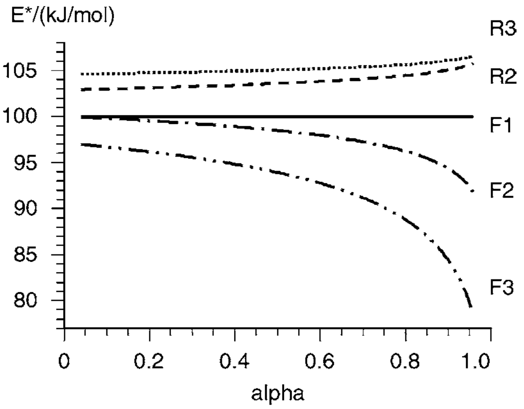

Fig. 2. E^* vs. α, based on Eq. (2b), $g(\alpha) = -\ln(1-\alpha)$; (F1) with $E_A = 100\,\mathrm{kJ\,mol^{-1}}$ and $T = 500\,\mathrm{K}$.

estimation of activation energies: there is no selection of the conversion function as per definition.

2. Determination of the two parameters of the Arrhenius equation, A and E_A, after selection of a conversion function using isothermal measurements

In the model-based determination of kinetic parameters, there is no possibility to estimate one parameter of the kinetic triplet separately. Consequently, it is not allowed to handle separately one of the three elements of the kinetic triplet $f(\alpha)$, A and E_A. On the contrary, in the paper by Sewry and Brown, it is assumed that one of the two Arrhenius parameters, A is correctly estimated and then it is investigated how a wrongly chosen conversion function influences the other parameter, E_A.

The basis of their investigation is Eq. (2):

$$E^* = -RT\ln\left(\frac{g^*(\alpha)}{At}\right) \tag{2}$$

whereby E^* is the incorrect activation energy, $g^*(\alpha)$ the incorrect conversion function, α the conversion at time t, and A the pre-exponential, estimated with the correct conversion function.

Adequately, Eq. (2a) is valid for the correct conversion function $g(\alpha)$:

$$E = -RT\ln\left(\frac{g(\alpha)}{At}\right) \tag{2a}$$

Subtracting Eq. (2a) from Eq. (2), we obtain Eq. (2b):

$$E^* = E - RT\ln\left(\frac{g^*(\alpha)}{g(\alpha)}\right) \tag{2b}$$

Fig. 2 corresponds to the similar Figs. 2–5 in [1]. The deviations from the reference value 100 have opposite algebraic sign compared to values in [1]; maybe there is an error in the algebraic sign. But we neither see the reason nor the message of Figs. 2–5. If, for instance, calculated isothermal runs for a certain type of single-step reactions, F1, A3 and R3 are evaluated (at constant pre-exponential factor A) by some other model functions, then it is clear that the parameter E^* must be dependent on α. But E^* for only one temperature and one α is some calculating parameter

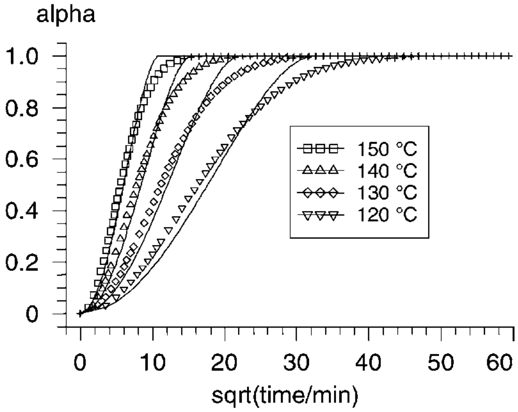

Fig. 3. Isothermal data set (symbols), simulated with F1 as conversion function and fitted by R2 as conversion function (solid lines). The data points indicated by '+' symbol, are outside the analysis range and therefore not taken into account.

but by no means the activation energy E_A. In order to study the effect of misidentified kinetic models, it is necessary that several data sets at different temperatures are simultaneously evaluated. If the reaction under investigation is actually a single-step reaction (as assumed in [1]) and the experimental data set is of excellent quality (comparable to calculated ones), the correct model including its kinetic parameters can be obtained definitely by non-linear regression and use of statistical tests. This is valid for both, isothermal and non-isothermal experiments. In any case, this should be much better than using the so-called reduced-time plots for isothermal runs.

A wrongly chosen conversion function always results in error in both parameters, $\ln A$ and E_A. But despite of a poor fit quality (Fig. 3), it is remarkable that applying simultaneous analysis by non-linear regression, the differences between the true activation energy and the estimated values are always much smaller as the values given in Fig. 2! This is shown in Table 1 for some misidentified conversion functions.

Table 1
Kinetic parameters, determined using misidentified conversion functions (R2, R3, F2 and F3 instead of F1)

Conversion function	E_A (kJ mol^{-1})	$\ln A$ (s^{-1})	Correlation coefficient
F1	100.00	8.924	1.0000
R3	100.08	8.357	0.9918
R2	100.05	8.486	0.9830
F2	100.02	9.265	0.9469
F3	99.88	9.613	0.8510

Analysis range: $0.01 < \alpha < 0.99$ (see Fig. 3).

3. Conclusion

If model-free evaluation methods are applied on single-step reactions, the activation energy does not depend on the conversion degree and by definition not from a misidentified kinetic model. Otherwise, assuming high quality measurements, a dependence $E_A = f(\alpha)$ can be an indication for a multiple-step reaction. Additionally, using the power of modern evaluation techniques, it is no longer difficult to obtain the so-called kinetic triplet for single-step reactions. The true difficulties result from imperfect measurements and in the case of activation energies dependent upon alpha degree from identifying the correct model with the smallest number of reaction steps which describe the overall reaction.

References

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[2] A.K. Galwey, M.E. Brown (Authors), Kinetic background to thermal analysis and calorimetry, in: M.E. Brown (Eds.), Handbook of Thermal Analysis and Calorimetry: Principles and Practice, Vol. 1, Elsevier, Amsterdam, 1998, Chapter 3, pp. 169–171.