

Computational aspects of kinetic analysis. Part D: The ICTAC kinetics project — multi-thermal–history model-fitting methods and their relation to isoconversional methods

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Abstract

This paper is Part D of a discussion of the computational stage of solid-state reactions as applied to the data sets of the ICTAC Kinetic Analysis Project. This Part critically evaluates the results from the various participants and finds that kinetic analysis programs used by Burnham, Roduit, and Opfermann give very similar results. Isoconversional methods give kinetic parameters that agree qualitatively with those from subsequent nonlinear regression to appropriate models. Single-heating-rate methods work poorly and should not be used or published. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The results of kinetic analysis of numerical data supplied to participants in the ICTAC Kinetics Project have been presented in Part A [1]. In this Part, the methods and results are compared and discussed. To avoid confusion, please note that all but one references to tables are to those of Part A, while the references to figures are all in this part.

2. Discussion

The clearest test of a kinetic analysis program is its ability to recover the correct parameters from a synthetic data set in a blind test for which the constructing

parameters are known exactly. Burnham, Opfermann, Roduit, and to a lesser extent, Nomen and Sempere, give nearly identical results in Tables 7 and 8 of Part A for fits of a concurrent reaction model to the ICTAC simulated data, yielding two equally weighted first-order reactions having activation energies of about 80 and 120 kJ mol⁻¹ [1]. Essentially identical parameters are obtained from fitting isothermal data (see Table 8 of Part A), constant heating rate data (see Table 7 of Part A), or both (see Table 7 of Part A). The non-linear regression parameters are similar to those estimated from the initial, and final, stages of the reaction by the Friedman, modified Coats–Redfern, and Flynn–Wall–Ozawa isoconversional methods. The residual sum of squares of the nonlinear regression analysis of Burnham is several orders of magnitude lower than ordinarily observed for real data, giving confidence that the concurrent first-order model is correctly identified. The quality of the fit is shown in Fig. 1. Similarly, the

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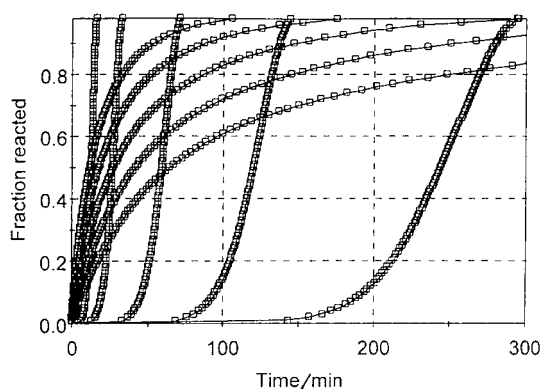


Fig. 1. Comparison of observed and calculated fractions reacted for a simultaneous fit to both, the isothermal and constant heating rate synthetic data by the LLNL program Kinetics98.

standard errors for kinetic parameters from the Opfermann fits are lowest for the concurrent first-order reaction model. The actual values used to create the synthetic data set, subsequently revealed and confirmed that the correct parameters had been recovered.

In an attempt to distinguish among the minor variations for the concurrent reaction models, the residual sum of squares were calculated for several sets of kinetic parameters. The results are compared in Table 1 of this part. The differences in residuals among Burnham, Opfermann, and Roduit are close to differences due to the round-off errors for the number of significant figures reported. These three programs appear to be on solid numerical ground. Although their method seems sound in principle, the parameters from Nomen and Sempere seem to be significantly less precise, and this difference is outside any potential effect of round-off errors. Also, the n th-order reaction model parameters of Anderson lead to substantially

higher residuals of 0.26, which is not surprising since it is not the correct model.

Returning to real experimental data, the activation energies and frequency factors of the various methods give very disparate results for calcium carbonate in Table 1 of Part A, with the activation energy varying by more than a factor of four. The single heating rate results of Desseyn are the most diverse, which is not surprising when one considers the well-known unreliability of single heating rate. The isoconversional methods give a narrower set of results and uniformly agree that the activation energy decreases during conversion. Agreement is particularly good for the Friedman method at high conversion, giving about 90 kJ mol^{-1} from the analysis of Burnham, Desseyn, Opfermann, and Roduit. Just viewing the parameters, however, does not give a good view of how accurately they describe the data. The LLNL fit to a Sestak–Berggren model is shown in Fig. 2; it is good but not outstanding. Addition of a nonunity reaction order reduces the residual sum of squares from 0.15 to 0.12 without affecting the values of A and E_a . The mean activation energy of $115.7 \text{ kJ mol}^{-1}$ agrees well with the mid-range of the isoconversional methods and the $109.6 \text{ kJ mol}^{-1}$ value from single n -dimensional Avrami fit of Opfermann. The values of m and n from Burnham are similar to those derived by Nomen and Sempere, but the activation energies and frequency factors are significantly different. A change in q from 0.99 to 0.99999 in Kinetics98 reduced the residuals from 0.119 to 0.110 and caused m and n (0.411 and 0.761, respectively) to approach the values of Nomen and Sempere, but the activation energy and frequency factor did not change significantly ($115.6 \text{ kJ mol}^{-1}$ and $\ln(A \text{ s}^{-1})=10.08$), thereby leaving the 10 kJ mol^{-1} discrepancy. Opfermann and Roduit presumably

Table 1

Comparison of residual sum of squares (RSS) for kinetic parameters from different fits to a concurrent reaction model^a

Analyst	RSS from hr data	RSS from iso data	Comment
Burnham	2.1E-06	5.2E-06	from nonlinear regression analysis
Burnham	3.8E-04	2.9E-04	from Tables 7 and 8 of Part A
Burnham	9.6E-05	2.2E-04	From Tables 8 and 7 (switched)
Opfermann	5.7E-04	3.2E-05	From Tables 7 and 8
Roduit	7.9E-04	2.2E-04	From Tables 7 and 8
Nomen and Sempere	0.85	n.a.	From Tables 7 and 8

^a Switched means using the isothermal (iso) parameters with the heating rate (hr) data and vice versa.

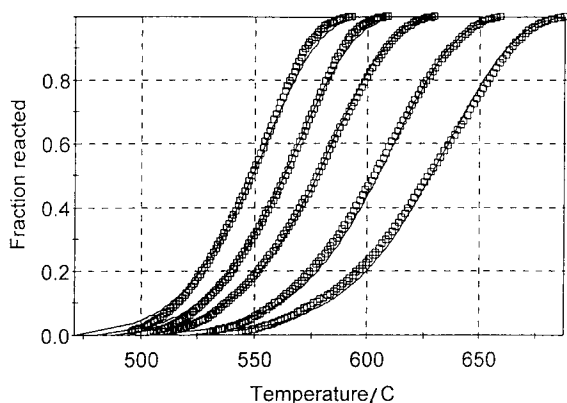


Fig. 2. Comparison of measured and calculated data for a fit of the n th-order nucleation model (Sestak–Berggren) by Kinetics98 to decomposition of calcium carbonate in a vacuum at various heating rates. The agreement is very good but not perfect.

obtained a better fit by using two reactions, but I did not pursue that option.

The agreement among the various methods is better for the isothermal decomposition of calcium carbonate in a vacuum (see Table 3 of Part A). The Friedman analysis of Burnham suggests a slight increase in activation energy with conversion, unlike for a constant heating rate. Single-reaction fits of Anderson, Burnham, Opfermann, and Roduit all give similar activation energies of about 222 kJ mol^{-1} . Anderson uses an n th-order reaction, while Burnham, Opfermann, and Roduit use nucleation reactions. The latter can be seen to be more appropriate when examining the differentiated isothermal data, as shown in Fig. 3. Here, the reaction rates show a clear acceleratory phase. One can also see oscillations, which may be due either to temperature instability or, less likely, to an intrinsic chemical effect. (The actual temperatures were not supplied with the data, so it is not possible to determine which is the case.) The Avrami parameters of Opfermann and Roduit agree very well with each other and qualitatively with the nucleation order (m) of 0.495 derived by Burnham. Burnham et al. [2] showed that $n=1.6$ in the Avrami equation gives a result very close to $m=0.45$ in the Sestak–Berggren equation.

The case for temperature oscillation becomes stronger when looking at the isothermal data for calcium carbonate decomposition in nitrogen, as shown in Fig. 4. If the actual temperatures were supplied, Kinetics98 would match the oscillations, because

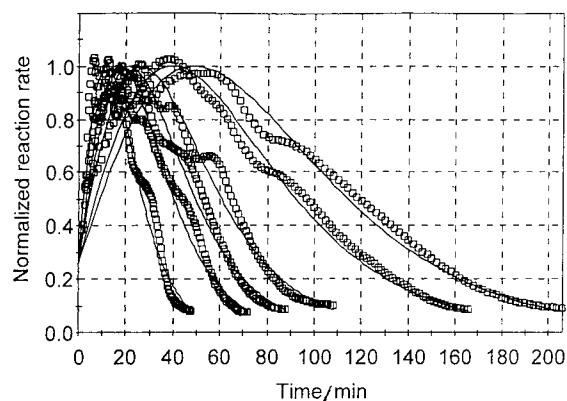


Fig. 3. Comparison of measured and calculated reaction rates for the isothermal decomposition of calcium carbonate in a vacuum. The calculations are for a fit of a first-order nucleation model by Burnham.

the rate equation is integrated numerically over the exact thermal history. Even so, one can easily see that the decomposition in nitrogen is qualitatively different to that in vacuum. The acceleratory characteristic is much weaker (better heat transfer?), and the reaction rate rapidly heads to zero at high conversion, which is characteristic of a receding interface reaction. As a result, the nucleation order (m) is only 0.087 and the reaction order is very low (0.155) from Burnham's fit. Similarly, Anderson used a zero reaction order, Opfermann obtained a reaction order of 0.067, and Roduit

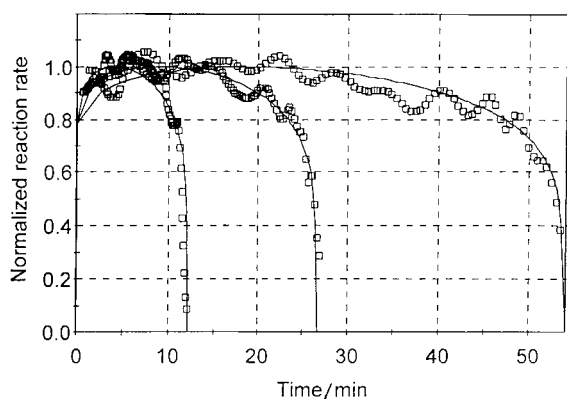


Fig. 4. Comparison of measured and calculated data for isothermal decomposition of calcium carbonate in flowing N_2 . The fit is an n th-order nucleation model (Sestak–Berggren) derived by Burnham.

derived a reaction order of 0.09. Again, the activation energies by the four workers agree well, ranging from only 175 to 181 kJ mol⁻¹ (see Table 4 of Part A).

Similarly, Anderson, Burnham, Opfermann, and Roduit all obtained about 193 kJ mol⁻¹, using an *n*th-order model for calcium carbonate decomposition under nitrogen at constant heating rates (see Table 2 of Part A). Anderson again used a zero-order reaction. Burnham obtained *n*=0.176 and *m*=0.011 (or *n*=0.160 when *m* is constrained to zero), while Opfermann obtained *n*=0.146 and Roduit obtained *n*=0.177. Opfermann also reports *n*=0.164 for second and largest of two consecutive reactions, but the activation energy increased to 198 kJ mol⁻¹. Nomen and Sempere obtained a similar reaction order (*n*=0.126), but their activation energy is significantly lower (181 kJ mol⁻¹). In contrast, the various results of Desseyn et al. vary all over the map, with the Freeman–Carroll method seemingly the worst. The isoconversional methods agree much better than the single heating rate methods with the nonlinear regression results, with Friedman's method yielding 180–200 kJ mol⁻¹ from Burnham, Desseyn, Opfermann, Roduit, and Li and Tang.

The isothermal and dynamic heating experiments for calcium carbonate in nitrogen were fitted simultaneously by Anderson, Burnham, Opfermann, and Malek and Mitsuhashi. The first three workers obtained activation energies ranging from 184 to 191 kJ mol⁻¹. The activation energy of 103 kJ mol⁻¹ from Malek and Mitsuhashi seems to be seriously in error. Opfermann obtained a reaction order of 0.060. Burnham used an *n*th-order nucleation model, and the reaction order of 0.222 was the parameter dominating the deviation from first-order behavior. Reaction order was not specified for Anderson, and his activation energy is significantly lower than those of Burnham and Opfermann. While the simultaneous fit works fairly well, there is a noticeable discrepancy between isothermal and constant heating rate data, as shown in Fig. 5. The fitted kinetic parameters underestimate the reaction rate for the lowest isothermal experiment and overestimate the reaction rate for the slowest heating rate. This could be due to either a mechanistic effect or a slight error in temperature calibration.

The ammonium perchlorate data provides a more interesting challenge for kinetic modeling. For the constant heating rate data (see Table 5 of Part A),

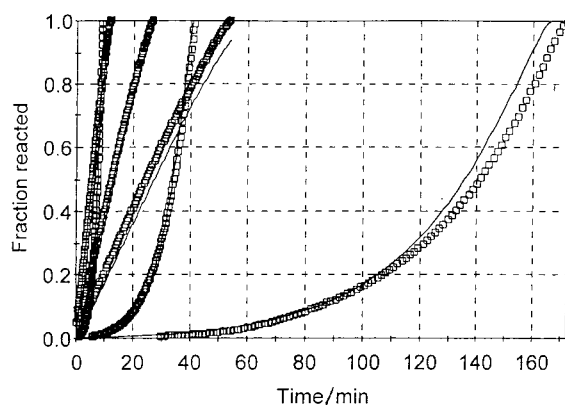


Fig. 5. Comparison of observed and calculated rates for calcium carbonate decomposition in N₂ for both isothermal and dynamic heating conditions. The line is a model fit to an *n*th-order nucleation model (Sestak and Berggren).

Burnham, Opfermann, and Roduit all found that the activation energy increased during the course of the reaction by isoconversional methods. According to Friedman's approach, *E_a* increased from 80 to 83 kJ/mol in the early stages to about 115 kJ/mol in the later stages. The various integral isoconversional methods had *E_a* increase during the reaction from about 94 to 102 kJ/mol for Burnham and Opfermann and from about 104 to about 116 kJ/mol for Roduit. Burnham, Nomen and Sempere, Opfermann, and Roduit all used two-component models for more advanced modeling of the data, with the faster reaction being sigmoidal and the second being a receding interface. In all cases, these four sets of workers found the faster reaction to have an activation energy similar to the lowest value from the isoconversional analysis and the slower reaction to have an activation energy similar to the highest value from the isoconversional analysis. The agreement between Burnham and Opfermann is especially good, with roughly a 25%/75% split between the two components and a second activation energy of 113 kJ/mol. Burnham obtained a slightly higher activation energy for first reaction responsible for the acceleratory phase. Comparison of data and fitted curves are shown in Fig. 5. The agreement with the fractions reacted is excellent. The correspondence of the measured and calculated reaction rates is not quite as good, but this could be improved by nonlinear regression to the rates, if desired.

For the constant-temperature data for ammonium perchlorate decomposition (see Table 6 of Part A), the Friedman isoconversional analysis of Burnham found a similar increase in activation energy from the earlier to latter stages of the reaction. Again, two-component models fitted the data well, with Burnham, Opfermann, and Roduit all using a sigmoidal fast reaction and a slower receding interface reaction. Burnham constrained the nucleation order (m) to one and zero, respectively, for these two reactions. Opfermann used similar models, with the sigmoidal reaction being either an n -dimensional Avrami model or an autocatalytic reaction. Again, the fractional distribution between the two components is similar for the two workers, and the activation energies for the receding

interface portion of the reaction are virtually identical. The fits are visually very good for both, the isothermal and constant heating rate experiments, as shown in Figs. 6 and 7.

While the kinetic parameters from the isothermal experiments agree qualitatively with those from the constant heating rate experiments, they differ in detail. Attempts to fit both, the isothermal and constant heating-rate data were marginally successful. As found for the calcium carbonate data in Fig. 5, there appears to be a shift in reactivity between the isothermal and constant heating rate data; in this case, the constant heating rate data seems to be slightly faster. Shifting the temperatures of the constant heating-rate data upwards by 5°C eliminates the discrepancy, but it is not certain whether a small temperature error or a limitation of the kinetic model is responsible for the discrepancy.

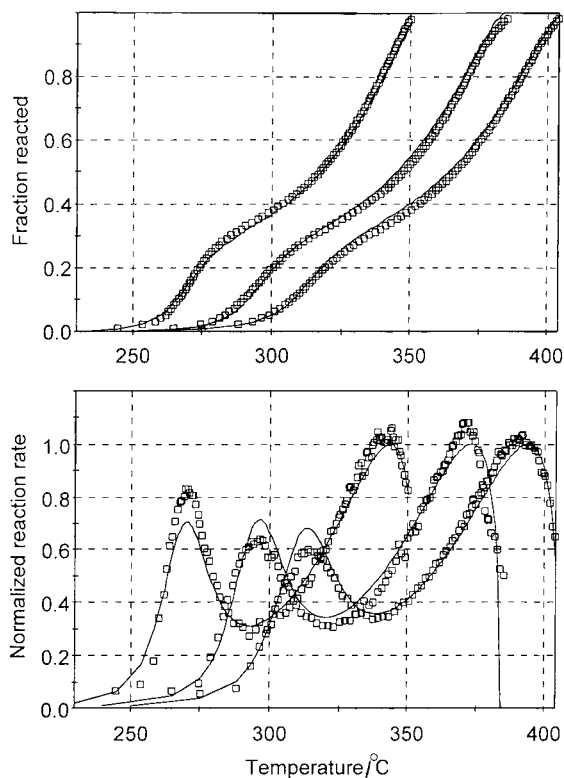


Fig. 6. Comparison of measured and calculated data for decomposition of ammonium perchlorate at three constant heating rates. The line is a fit of the fractions reacted to two concurrent reactions, the faster of which is an n th-order nucleation reaction and the second of which is a receding interface. The lower figure shows the reaction rates derived from differentiation of both, the measured and calculated data.

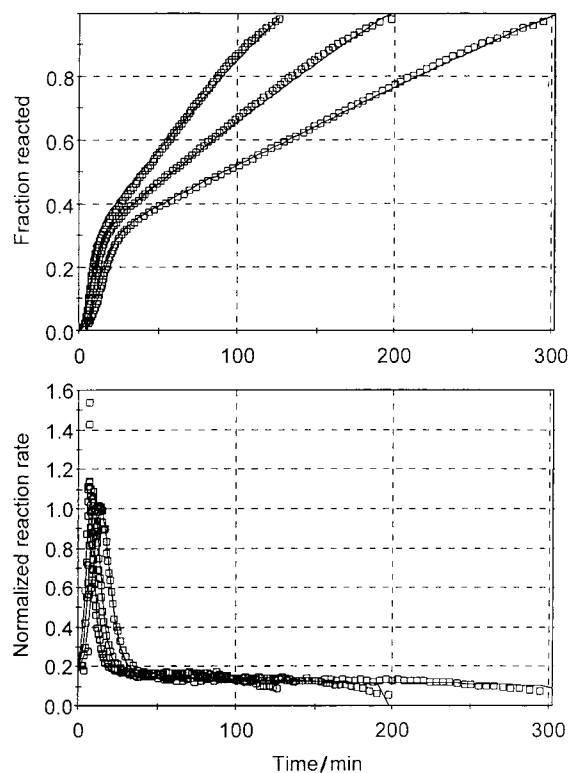


Fig. 7. Comparison of measured and calculated fractions reacted and reaction rates for isothermal decomposition of ammonium perchlorate. The solid line is a fit of the fraction-reacted data to a two-component model by Burnham.

3. Conclusions

In summary, the isoconversional analyses of various workers tend to agree fairly well and give qualitatively good predictions of the activation energies ultimately obtained from non-linear regression to appropriate models. The nonlinear regression results from Burnham, Opfermann, and Roduit (plus Anderson and Nomen and Sempere to a lesser extent) are always similar, and sometimes very close. With the ready availability of these and potentially other good analysis programs, kinetic analysis using single heating-rate methods should no longer be considered acceptable in the thermal analysis community.

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