

Isoconversional Analysis

Vyazovkin (e.g., Vyazovkin, 1997; Vyazovkin and Wight, 1998; Vyazovkin and Wight, 1999; Vyazovkin, 2001) has sparked renewed interest within the thermal analysis community in isoconversional kinetic analysis. He coined the term “model free” to distinguish it from the common poor practice in the thermal analysis community of fitting a variety of models to a single heating-rate experiment, often accompanied with the assertion that the best fitting model gives mechanistic insight. The deficiencies of single heating rate model fitting demonstrated by Vyazovkin are reminiscent of our own work along those lines (Braun and Burnham, 1987), which was directed primarily towards systems with distributed reactivity, while Vyazovkin addressed primarily acceleratory reactions.

Two unfortunate side effects of the term “model free” are that (1) it implies that no assumptions about mechanism are made, which is not true, and (2) it might be unfairly inferred from the criticism of model fitting that multiple heating rate model fitting methods are not good, which is also not true. Despite the controversy surrounding this method, our experience is that it works well, so we have enhanced its implementation in **Kinetics2015**. However, we do avoid the term “model free” because of its possible misinterpretation.

Isoconversional kinetic analysis has a long history dating to the 1960s (Friedman, 1965; Flynn and Wall, 1966; Ozawa, 1965; Ozawa, 1970; Flynn, 1983; Flynn, 1991). Friedman’s method uses reaction rates, and the Ozawa-Flynn-Wall method uses cumulative reacted data along various methods of integrating the rate law. Isoconversional analysis in earlier versions of KINETICS reported kinetic parameters at 10% conversion intervals by Friedman’s method and a modified (i.e., multiple heating rate) Coats-Redfern method (Coats and Redfern, 1964, as enhanced by Burnham and Braun, 1999). The Friedman analysis works with any thermal history, but the modified Coats-Redfern method two required a constant heating rate. These analyses are still done as a preliminary kinetic analysis prior to all nonlinear methods to assist in choosing initial guesses for refinement—see the tutorial on Approximate Analysis. For both methods, the 10% and 90% values are usually unreliable because they are highly sensitive to uncertainties in the data.

The basic Friedman equation solves the simple nth-order reaction rate equation for k:

$$dx/dt = -kx^n \tag{1}$$

For any set of experiments with different, arbitrary thermal histories, a plot of $\ln(-dx/dt)$ versus $1/T$ has a slope of $-E/R$ and an intercept $\ln[Ax^n]$. If one truly has an nth-order reaction with n not equal to one, it is theoretically possible to obtain a constant activation energy and extract a reaction order, but this rarely happens in practice. Instead, the conventional approach currently is to absorb any model dependence (i.e., changing reaction interface area) into the frequency factor, which is a good approximation for any reaction that follows the same trajectory independent of temperature, as long as the A and E are determined at closely spaced conversion intervals. It is not obviously a good approximation when competing reactions occur, but in practice, it still seems to work pretty well.

The enhanced isoconversional analysis in **Kinetics2015** uses Friedman’s rate method combined with cubic-spline smoothing to derive first-order A and E values at one percent intervals up to the lowest final conversion level in any of the data input files. The A and E values are reported for the center of the

interval—e.g., at 0.5% for the interval from 0 to 1% conversion. The cubic-spline method uses the generalized cross-validation and mean-squared prediction-error criteria method of Craven and Wahba (1979). It assumes uncorrelated additive noise and the points can be unevenly spaced. The smoothing is done over a 5% moving interval and is necessary to reduce noise in the Arrhenius parameters to an acceptable level. Even with spline smoothing, however, the parameters near 0 and 100% are sensitive the way the baseline is chosen so should be interpreted with due caution. The isoconversional parameters are linked to the apply mode using an explicit integration step of 10^{-6} fractional conversion.

Even though extensive smoothing is done automatically, the user has a higher level of responsibility for this method to achieve satisfactory results. First, the user must provide the data either as fractions reacted or absolute reaction rates. The program does not renormalize the data, which would introduce an error for when the data really does not go to completion. If the data are relative reaction rates, the user can convert them absolute reaction rates by setting the baseline and temperature interval, integrating the data, making any additional minor baseline adjustment needed, normalizing the data, and then differentiating it to recover absolute reaction rates. Alternatively, the user can leave the data as fractions reacted. Even so, the isoconversional method is temperamental, and the user must be careful to set the baseline and fraction reacted well, or the method will be unreliable or fail. For example, if a slight endotherm precedes an exotherm in DSC data, it should be eliminated, and the user's best judgment applied to set the starting temperature and baseline so that the initial reaction rate is zero and that the cumulative reacted does not become significantly zero. This can be accomplished using the zoom, baseline, and integrate/differentiate features of the data preprocessing window.

REFERENCES

- Burnham A. K. and Braun R. L. (1999) Global kinetic analysis of complex reactions, *Energy & Fuels* **13**, 1-2.
- Braun R. L. and Burnham A. K. (1987) Analysis of chemical reaction kinetics using a distribution of activation energies and simpler models, *Energy & Fuels* **1**, 153-161.
- Coats A. W. and Redfern J. P (1964) Kinetic parameters from thermogravimetric data. *Nature* **201**, 68-69.
- Craven P. and Wahba G. (1979) *Numerische Mathematik* **31**, 377-403.
- Flynn J. H. and Wall L. A. (1966) General treatment of thermogravimetry of polymers. *J. Res Nat. Bur. Stand.* **70A**, 487-523.
- Flynn J. H. (1983) The isoconversional method for determination of energy of activation at constant heating rates. *J. Therm. Anal.* **27**, 95-102.
- Flynn J. H. (1991) A general differential technique for the determination of parameters for $d\alpha/dt = f(\alpha)A\exp(-E/RT)$. *J. Therm. Anal.* **37**, 293-305.
- Friedman H. L. (1963) *J. Polym. Sci., Part C*, **6**, 183-195.

- Ozawa T. (1965) A new method of analyzing thermogravimetric data. *Bull. Chem. Soc. Jap.* **38**, 1881-1886.
- Ozawa T. (1970) Kinetic analysis of derivative curves in thermal analysis. *J. Therm. Anal.* **2**, 301-324.
- Vyazovkin S. (1997) Advanced isoconversional method. *J. Therm. Anal.* **49**, 1493-1499.
- Vyazovkin S. and Wight C. A. (1998) Isothermal and nonisothermal kinetics of thermally stimulated reactions of solids. *Int. Rev. in Phys. Chem.* **17**, 407-433.
- Vyazovkin S. and Wight C. A. (1999) Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data. *Thermochim. Acta* **340-341**, 53-68.
- Vyazovkin S. (2001) Modification of the integral isoconversional method to account for variation in the activation energy. *J. Computational Chem.* **22**, 178-183.