Journal of Thermal Analysis, Vol. 37 (1991) 1785-1792

TG AND DSC KINETICS OF THERMAL DECOMPOSITION AND CRYSTALLIZATION PROCESSES

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The simple n^{th} order model equation combined with the Arrhenius approach of the temperature dependency of the reaction rate constant is widely used in thermal analysis.

The new Mettler software package for thermal analysis, GraphWare TA72 allows to access a full model comprising the power law and the crystallization kinetics (Avrami-Erofe'ev).

The kinetics of the following reactions are studied to illustrate some applications:

- thermal decomposition of dissolved dibenzoylperoxide, (dynamic and isothermal DSC measurement)
- crystallization of polyethylene terephthalate (PET) (isothermal DSC measurements).

The kinetic model applied and the accuracy of the kinetic data obtained are discussed by means of a comparison of a predicted behaviour with the kinetic data measured isothermally.

Introduction

Thermoanalytical measurements mainly comprise physical phenomena such as glass transition, melting and crystallization, as well as chemical reactions e.g. polymerization (including polyaddition, polycondensation, vulcanization) and thermal decomposition in an inert or oxidative atmosphere. Contrary to physical transitions, chemical reactions are not characterized by simple temperatures such as onset or peak temperature, but by their kinetic data. These data allow the computation of the rate of reaction at any given condition.

The simple n^{th} order model equation combined with the Arrhenius approach of the temperature function of the reaction rate constant is:

$d\alpha/dt = k_0 \exp\left(-E_a/RT\right) \cdot (1-\alpha)^n$, $d\alpha/dt$ = Rate of reaction in s^{-1}, k_0 = Preexponential factor, E_a = Activation energy in $J \cdot mol^{-1}$, R = Gas constant = $8.31\ J \cdot mol^{-1} \cdot K^{-1}$, T = Sample temperature in K, α = Degree of conversion, n = Order of reaction

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The properties $d\alpha/dt$ and α in the range of investigation are obtained from DSC or TG curves as follows:

DSC: $d\alpha/dt$ = DSC signal deviation from baseline [mW] divided by total peak area [mJ]. α = partial area [mJ] up to the corresponding temperature divided by total peak area [mJ].

TG: $d\alpha/dt$ = DTG signal [$\mathrm{mg \cdot s^{-1}}$] divided by total weight step [mg] α = partial weight step [mg] divided by total weight step [mg].

The full model [1] comprises the power law and the nucleation term (Avrami):

$$\frac{d\alpha}{dt} = k_o \exp\left(-E_a/RT\right) \cdot (1-\alpha)^n \cdot \alpha^m \cdot \left(-\ln(1-\alpha)\right)^p$$

m = Exponent of the power law, p = Avrami exponent

The kinetic evaluation for reactions measured with TG or DSC is based on a multi dimensional least square method [2] using a number of curve points in a selectable range of conversion. This allows the simultaneous determination of the unknowns.

With the new software an individual model can be selected by any combination of n, m and p. Instead of calculating a respective parameter it also can be fixed to a certain value.

Table of some model types [3, 4]

Name	Function of α	n	m	p
Wilhelmy, n^{th} order	$(1-\alpha)^n$	calculated	–	–
First order	$(1-\alpha)$	1	–	–
Second order	$(1-\alpha)^2$	2	–	–
Interfacial	$(1-\alpha)^{1/2}$	0.5	–	–
Reactions	$(1-\alpha)^{1/3}$	0.333	–	–
Power law	α^m	–	calculated	–
One dimens. diffusion	α^{-1}	–	–1	–
Two dimens. diffusion	$(-\ln(1-\alpha))^{-1}$	–	–	–1
Avrami	$(1-\alpha)\cdot(-\ln(1-\alpha))^p$	1	–	calculated

Experimental

The experiments are performed on a Mettler TA4000 system with a measuring cell DSC25. The system is connected to a personal computer IBM PS/2-60 where the data is stored and evaluated by means of the GraphWare

TA72.5 software package. The curves are drawn by the x-y plotter Fujitsu ImageGraph.

Dynamical decomposition of dibenzoylperoxide

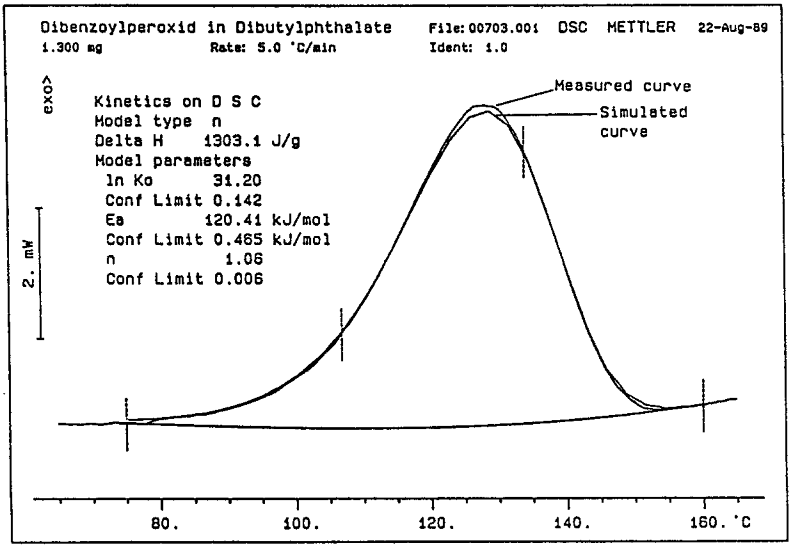


Fig. 1 Dynamical DSC curve of the decomposition of 1.3 mg dibenzoylperoxide dissolved in dibutylphthalate. Heating rate 5 deg/min, pierced aluminum crucible. The chosen baseline type "spline" corresponds to a third order polynomial defined by the baseline start point and end point and their respective slopes. The model type n indicates that the n-th order model is applied. The enthalpy change of the reaction corresponds to the area between baseline and DSC curve.
The natural logarithm of the preexponential factor ($\ln k_0$) the energy of activation (E_a) and the order of the reaction (n) are computed with the corresponding 95% confidence limits. The investigated range of the reaction normally is 10% to 80% conversion. For the n-th order model a computer simulated curve based on the obtained kinetic data allows a visual comparison with the actual measured curve

The reliability of the computed degree of conversion, α, depends on the validity of the applied theories and can be checked by isothermal measurements.

Isothermal decomposition of dibenzoylperoxide

Samples of the same peroxide solution (Fig. 1) are measured in the DSC cell at 3 isothermal temperatures using pierced aluminium crucibles.

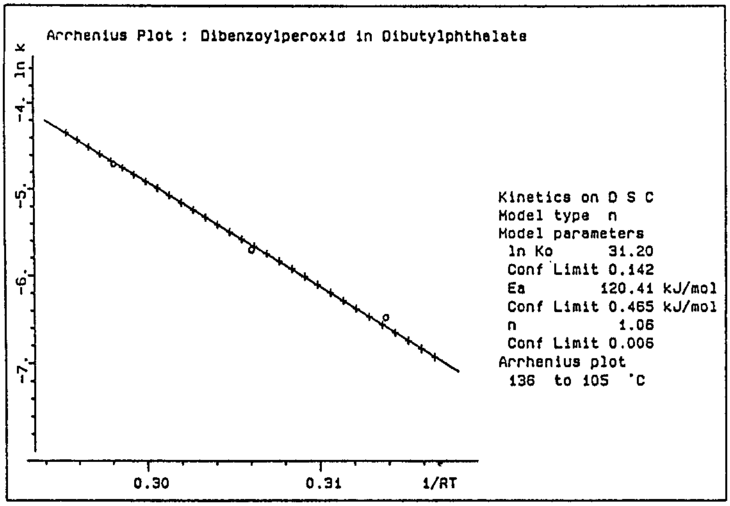


Fig. 2 The Arrhenius plot illustrates the temperature function of the rate constant k, according to the Arrhenius equation: $k = k_0 \exp(-E_a/RT)$. The marks (+) represent the experimental points and allow, together with the confident intervals for 95% probability to qualify the fit. The 3 marks (o) show the values obtained from isothermal measurements (see Fig. 4)

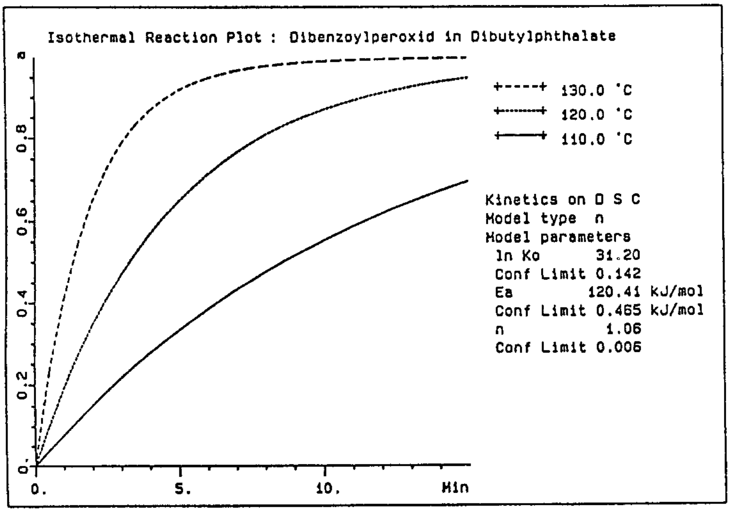


Fig. 3 The kinetic data are used to predict the behaviour of the reaction under isothermal conditions: The computed degree of conversion α, as a function of reaction time is represented for three isothermal temperatures 110 °C, 120 °C and 130 °C

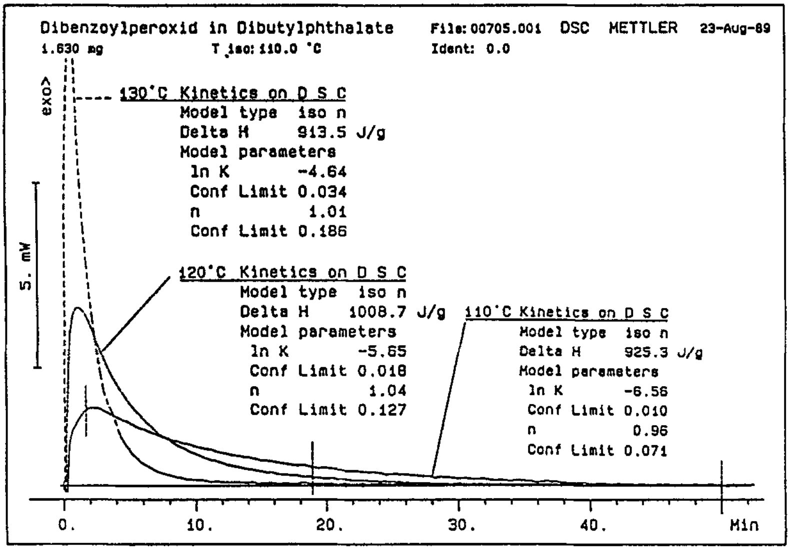


Fig. 4 Isothermal DSC curves of the decomposition of ≈1.6 mg dibenzoylperoxide at 110°C, 120°C and 130°C. The model type *n* indicates that the *n*-th order model is activated. The enthalpy change of the reaction corresponds to the area between the horizontal baseline and the DSC curve. The natural logarithm of the rate constant, ln *k*, and the reaction order, *n*, are computed with the corresponding 95% confidence limits. The investigated range of the reaction is 10% to 80% conversion. For comparison purpose the ln *k* values are manually drawn into the Arrhenius plot (Fig. 2)

As in the case of the dynamic measurement (Fig. 3) the kinetic data based on isothermal curves are used to calculate and plot the degree of conversion, α, as a function of the reaction time.

Furthermore – in addition to the graph (Fig. 5) – a reaction table gives the heat production at the start of the reaction and the reaction time to reach 3 selected degrees of conversion, α.

Finally reaction times up to a certain degree of conversion can directly be obtained by integrating the isothermal DSC curve:

$$\alpha = 20\% : 1.36 \text{ min}, \quad \alpha = 50\% : 3.55 \text{ min}, \quad \alpha = 90\% : 11.7 \text{ min}$$

As the reaction times are close to the ones of Fig. 6 they prove the validity of the model chosen which is also indicated by the good correlation of the rate constants based on a dynamic measurement with the ones based on 3 isothermal experiments in the Arrhenius plot (Fig. 2).

Sometimes the shape of a dynamic DSC curve is similar to the one of the n^{th} order model but an isothermal curve shows an induction period at the beginning thus indicating an other model (e.g. crystallization of PET). In such a case, the kinetic parameters are better defined by isothermal measurements.

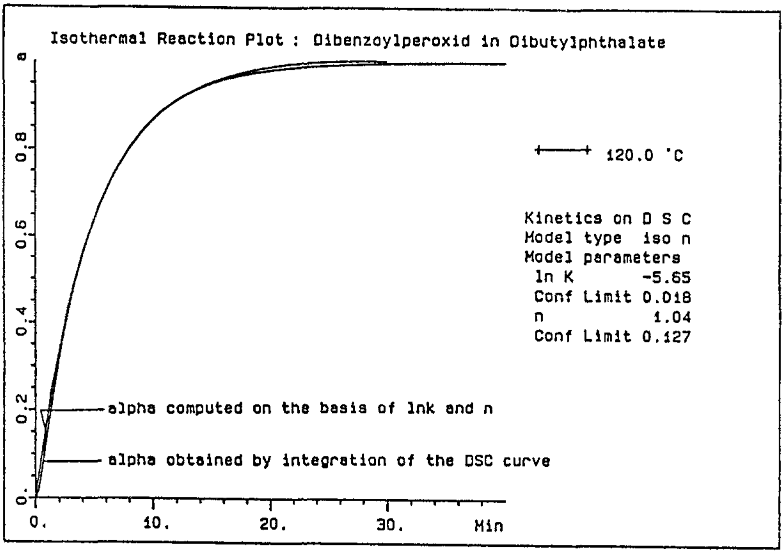
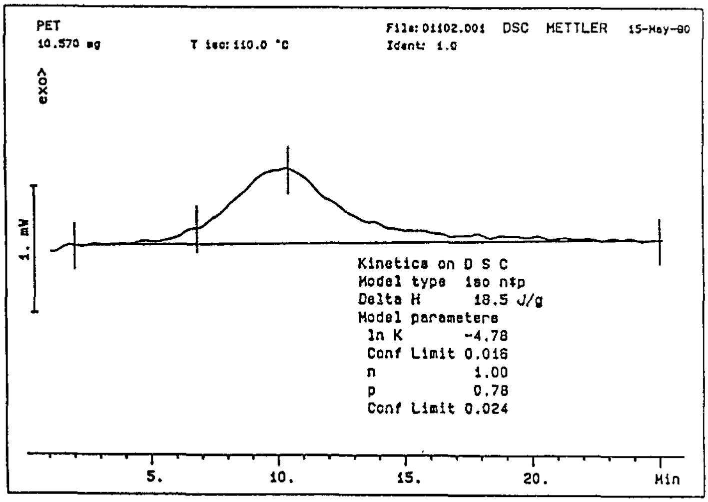


Fig. 5 The degree of conversion α, at 120°C as a function of the reaction time computed on the basis of the kinetic parameters of the isothermal measurement at 120°C (Fig. 4). This computed curve is copied together with a curve obtained by direct partial area integration of the DSC curve of Fig. 4. The good agreement of the 2 curves proves the validity of the chosen model

	Reaction–Table on DSC		Reaction–Table on DSC
Temp.	120.0°C	Temp.	120.0°C
ln K	–5.65	ln K	–5.63
P start	3533 W / kg	P start	4663 W / kg
	Reaction times		Reaction times
α., %	time	α., %	time
20	64.0 s	20	62.7 s
50	3.3 min	50	3.3 min
90	11.5 min	90	11.4 min

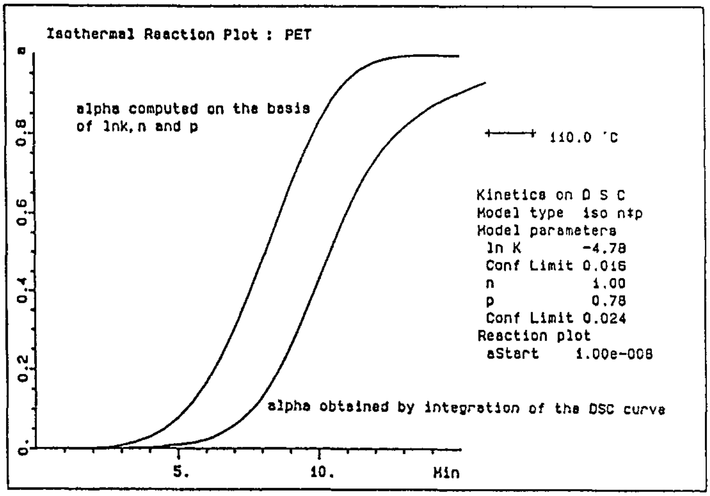
Fig. 6 Left: Reaction table obtained by the kinetic data of the isothermal DSC curve. Right: the same but based on a dynamical measurement for comparison. "P start" is the initial heat production rate and therefore is given for $\alpha = 0$. The calculated reaction times correspond to a conversion of 20, 50 and 90% respectively

Isothermal crystallization of amorphous PET



Kinetics on D S C
Model type iso n*p
Delta H 18.5 J/g
Model parameters
ln K -4.78
Conf Limit 0.016
n 1.00
p 0.78
Conf Limit 0.024

Fig. 7 Isothermal DSC curve of 10.57 mg polyethylene terephthalate at 110°C. With an induction period of approx 6 min it is obvious that the *n*-th order model does not fit. The model type *n** *p* indicates that the Avrami Erofe'ev model is applied. *n** means that *n* is fixed to 1. The evaluation range of the reaction is 5% to 50% conversion i.e. concentrating on the portion of the curve of increasing rate of crystallization



Kinetics on D S C
Model type iso n*p
Model parameters
ln K -4.78
Conf Limit 0.016
n 1.00
p 0.78
Conf Limit 0.024
Reaction plot
aStart 1.00e-008

Fig. 8 Isothermal reaction plot computed on the basis of the kinetic data of Fig. 7 copied together with the alpha curve determined by integration of the DSC curve of Fig. 7. The sigmoidal shape of the two curves is the same, but there is a time shift of 2 min.
Due to mathematical reasons (numerical integration) a certain value of α start >0 is necessary

Conclusions

The Mettler software package for thermal analysis GraphWare TA72 (Version 72.5) allows an easy determination of the kinetic parameters for different kinetic models. Dynamic and isothermal measurements can be evaluated. Often the results from dynamic and isothermal experiments are in good agreement proving the proper choice of the kinetic model. Isothermal experiments are superior to define the kinetic model. The kinetic data are the basis of calculating a reaction at any isothermal temperature.

References

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3 J. Šesták, Thermophysical Properties of Solids, Academia Prague 1984; in Wilson and Wilson's, Comprehensive Analytical Chemistry, Vol. 12, part D, Elsevier, Amsterdam.
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Zusammenfassung — Das einfache kinetische Modell n-ter Ordnung, kombiniert mit der Temperaturabhängigkeit der Reaktionsgeschwindigkeitskonstanten nach der Gleichung von Arrhenius, wird oft angewendet bei der thermischen Analyse von chemischen Reaktionen.

Das neue Mettler Computerprogramm für thermische Analyse, GraphWare TA72, verfügt neben dem einfachen Modell über das Potenzgesetz und die Keimbildungs/Keimwachstumskinetik (Avrami-Erofe'ev).

Die Kinetik der folgenden Reaktionen wird untersucht um einige Anwendungen zu demonstrieren:

- thermische Zersetzung von gelöstem Dibenzoylperoxid (dynamische und isotherme DDK Messungen).
- Kristallisation von Polyethylenterephthalat (PET) (isotherme DDK Messungen).

Durch den Vergleich des aus dynamischen Messungen berechneten isothermen Verhaltens mit demjenigen isothermer Messungen kann die Genauigkeit der kinetischen Daten und die Anwendbarkeit eines kinetischen Modells beurteilt werden.