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EXPERIENCES WITH THE KINETICAL EVALUATION OF CALORIMETRIC DIFFERENTIAL THERMAL ANALYSIS TRACES

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ABSTRACT

Due to automatic computation the determination of kinetical data of chemical reactions is a routine today. Based on several years of experience in this field this paper shows — after a short introduction into the measuring principle — how to get reliable results and how to control arising difficulties.

BASIC PRINCIPLE

In calorimetric differential thermal analysis (DTA) the heat flow to or from a sample is transduced to a proportional electrical signal which is normally recorded

Fig. 1. Mettler TA2000, calorimetric DTA equipment with data transfer system and Hewlett–Packard desk top calculator for automatic evaluation.

versus time. Figure 1 shows the calorimetric DTA instrument, the Mettler TA2000, with a temperature range from ambient to +500°C, with which experiments were performed.

As sample container hermetically sealed gold or aluminium crucibles as well as Nimonic 80A high pressure crucibles (up to 100 bars) were used (Fig. 2). Figure 3 shows a DTA-diagram with the two ordinate scales of interest: heat flow to sample dH/dt in mW and the reaction rate dn/dt in μmol sec^{-1}. The DTA curve on the left-hand side is typical for an exothermal reaction with a linear temperature increase of 5°C min^{-1}. The equation describing this curve is a combination of the basic

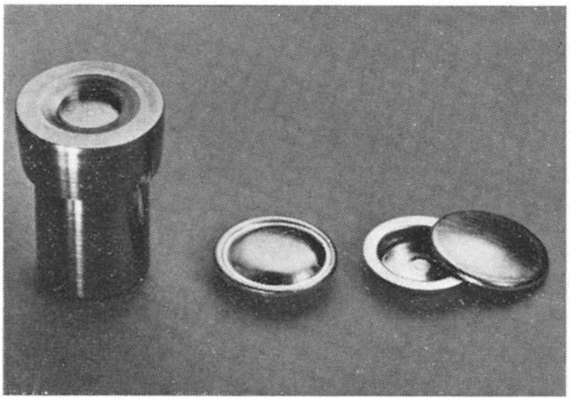

Fig. 2. High pressure crucible (Nimonic 80 A, 500 μl) and standard crucibles (Al, 40 μl).

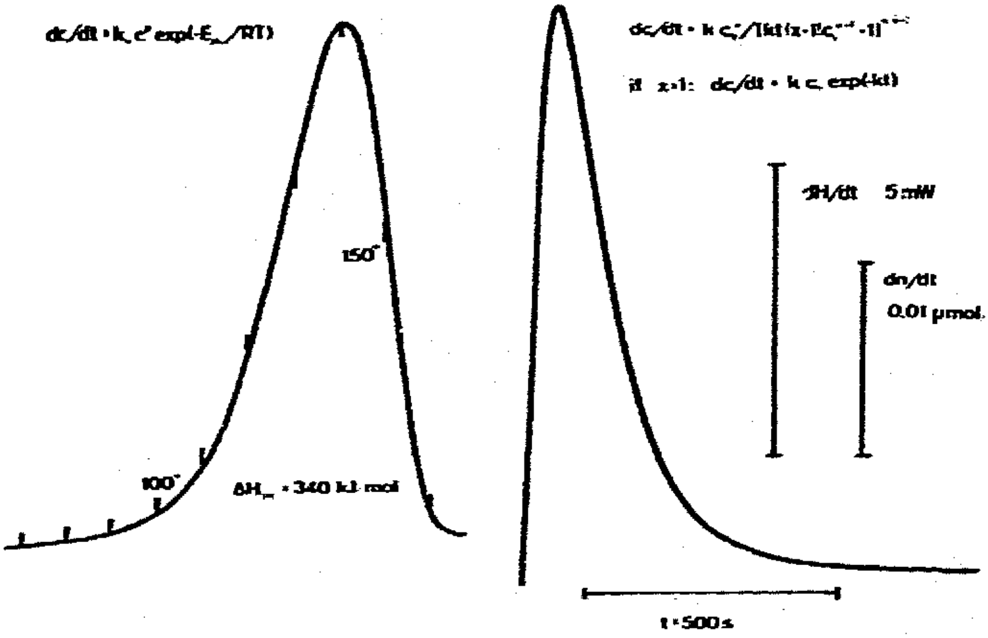

Fig. 3. Scan of an exothermic reaction (left) and isothermic reaction (right) with the respective equations.

equation of kinetics ($dc/dt = k \cdot c^x$) and the Arrhenius equation ($\ln k = \ln k_0 - E_A/RT$).

The curve on the right-hand side represents the same chemical reaction this time under isothermal conditions. The reaction rate reaches its maximum immediately after placing the sample container into the measuring cell preheated to reaction temperature. According to reaction rate constant, temperature and reaction order, the zero level is approached more or less rapidly. Generally, the dynamic experiment ("scanning mode") is preferred because all kinetical data are available in one single experiment.

EXPERIMENTAL REQUIREMENTS

(1) The basic equation of kinetics

$$dc/dt = k \cdot c^x$$

and the Arrhenius equation

$$\ln k = \ln k_0 - E_A/RT$$

must be valid for the investigated temperature range.
These requirements can be checked very simply by running experiments at different scan speeds: Thus, different degrees of conversion are produced at the same temperature, whereas kinetical data like reaction order, frequency factor and activation energy should be invariant ("scan speed check").

(2) The experiment should be started at least 20°C below the onset of the reaction which is generally performed by sufficient cooling of the reaction mixture.

(3) No interference by components, reaction products or solvents with high vapour pressure. Evaporation is suppressed using hermetically sealed — if necessary high pressure type — crucibles.

(4) No overlapping of competitive or consecutive reactions. Should it not be possible to avoid consecutive reactions with experimental measures, evaluation can still be possible, since kinetical information is contained in the first part of the DTA curve. The specific reaction enthalpy must then be known from the literature, calculation or an isothermal DTA experiment.

EVALUATION METHOD FOR DYNAMIC EXPERIMENTS

Essentially, the well-known Freeman–Carroll[1] evaluation method is applied, where at least 3, normally 5 to 10 data points of the DTA curve are used for calculation. Our modification consists in only using data points before the peak maximum thus avoiding errors which might be caused by consecutive reactions. Figure 1 shows a system for on-line evaluation: Mettler TA2000, Mettler data transfer system, Hewlett–Packard desk top calculator HP9810A. Whereas for manual evaluation more than an hour is needed, our evaluation program (Mettler software) displays not only

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METTLER  TA 2000
KINETICS      OF                                                  120.000
CHEM.  REACTIONS                                                   -6.595
****************       REACTION ORDER                              36.956
DBP                              1.200                           1023.000
****************
RANGE         MYV       ACTIVATION                                130.000
        100.000         ENERGY  CAL/MOL                            -5.613
SCAN SPEED K/MIN             30820.000                             98.676
          2.000                                                   383.000
CAL.SENSITIVITY         EXOTHERMIC
E(IN) MYV/MCAL/S                REACTION                          140.000
         34.200         DELTA H  CAL PER                           -4.679
REACTANT OR                QUANTITY UNIT                          251.242
SAMPLE QUANTITY                 323.209                           150.000
          5.423
VOLUME        MYL                                                 150.000
        135.570                                                    -3.788
START TEMP. DEGC                                                  612.054
         75.000          LN K (0)                                  62.000
                                 32.998
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Fig. 4. Calculator printout of the kinetic evaluation of the decomposition of dibenzoylperoxide solution in dibutylphthalate. The figures on the right-hand side are: temperature (°C), natural logarithm of the reaction rate constant, initial heat flow produced by 1 liter of the reaction mixture (kcal sec^{-1}), reaction time for 90% conversion (sec).

kinetical data after a few seconds, but also a table with the following data on a /10°C basis (Fig. 4):

temperature (°C);
natural logarithm of reaction rate constant at indicated temperature;
initial heat power of reaction mixture (kcal l^{-1} sec^{-1});
reaction time for a 90% conversion (sec).

RESULTS

Figure 5 shows DTA curves of the polyaddition reaction of a liquid epoxy resin with anhydride-type hardener with different scan speeds.

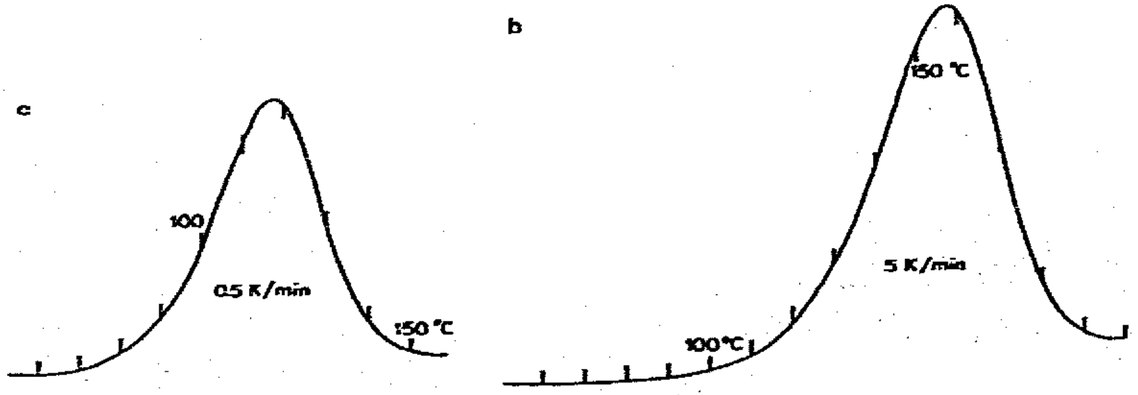

Fig. 5. Scans of the polyaddition reaction of an epoxy resin with anhydride curing agent with different scan speeds.

The kinetical evaluation of these curves is used for the scan speed check (Table 1). Data are independent of applied scan speed and hence reliable.

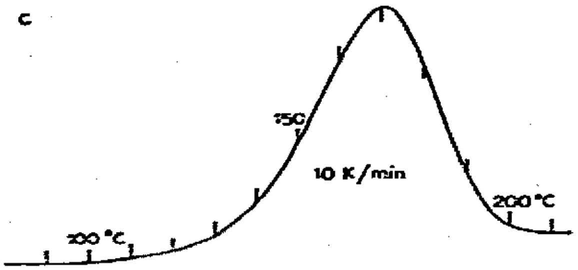

Fig. 5c.

TABLE 1

"SCAN SPEED CHECK" FOR THE EPOXY CURING

Scan speed (K min^{-1})	*Reaction order x*	*E_A (kcal mol^{-1})*	*ln k_0*
0.5	1.35	27.2	25.6
1	1.42	27.8	25.5
2.5	1.32	27.6	25.5
5	1.27	26.9	24.8
10	1.25	28.2	26.3
Mean values	1.32	27.5	25.5

The decomposition reaction of dibenzoylperoxide in dibutylphthalate as a solvent is an example for the evaluation of an incomplete DTA curve (Fig. 6). Sample quantity was 1.426 mg. The hermetically sealed crucible blew up at about 150°C.

From an isothermal experiment at 120°C (Fig. 7) the specific reaction enthalpy

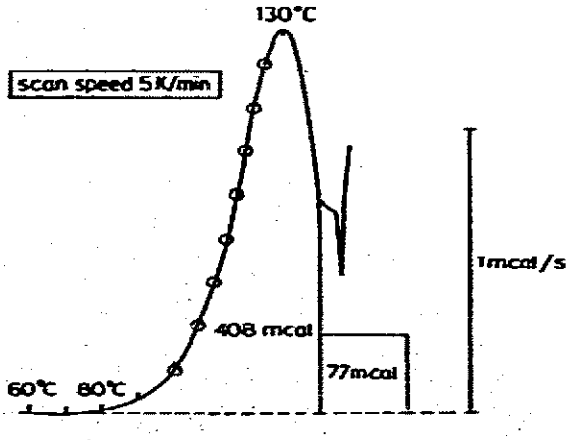

Fig. 6. Dynamic decomposition of peroxide solution in standard crucible. Incomplete curve due to blow up of crucible at 160°C.

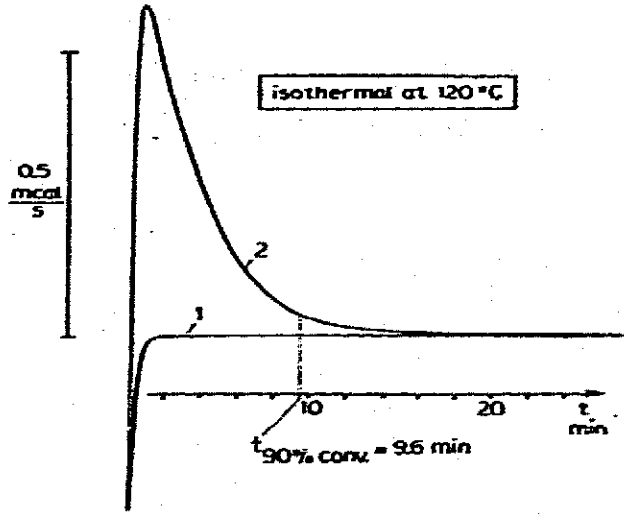

Fig. 7. Isothermal[2] decomposition of peroxide solution in standard crucible.

TABLE 2

COMPARISON OF DATA EVALUATED FROM AN INCOMPLETE AND A COMPLETE CURVE

	Incomplete trace, Fig. 6	*Complete trace, Fig. 8*	
crucible	Al	Nimonic 80 A	
max. pressure	2	100	bar
mass of dibenzoyl-peroxide	1.426	5.423	mg
ΔH_{spec}	340	323	cal g^{-1}
reaction order	1.10	1.20	
activation energy	28.5	30.8	kcal mol^{-1}
ln k_0	30.5	33.0	

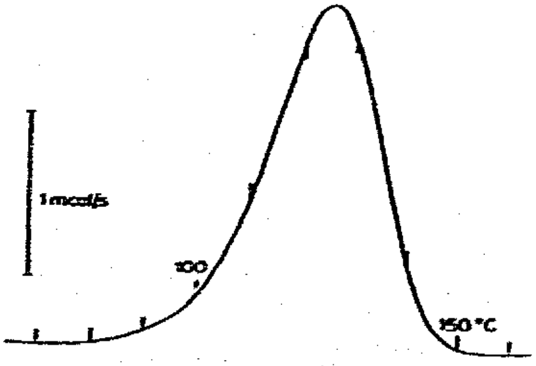

Fig. 8. Dynamic decomposition of 5.42 mg dibenzoyl peroxide dissolved in dibutylphthalate in the high pressure crucible. Scan speed 2 °C min^{-1}. Automatic evaluated results in Fig. 4.

was determined to be 340 cal g^{-1} which allowed to calculate the missing 77 mcal of the incomplete dynamic run.

Kinetical data of this experiment are now compared (Table 2) with a complete high pressure crucible experiment (Fig. 8). Since only minor differences occur, our considerations concerning the evaluation of incomplete DTA curves are obviously correct.

APPLIED SYMBOLS

c	actual concentration	dn/dt	rate of reaction
c_0	initial conc.	R	gas constant
dc/dt	rate of reaction	t	time
E_A	activation energy	V	volume
k	reaction rate const.	x	order of reaction
k_0	frequency factor	ΔH	enthalpy change
n	actual amount of unreacted material	ΔH_{spec}	specific enthalpy change
		dH/dt	heat flow to sample

REFERENCES

1 E. S. Freeman and B. Carroll, *J. Phys. Chem.*, 62 (1958) 394.
2 G. Widmann, *Thermochim. Acta*, 11 (1975) 331.