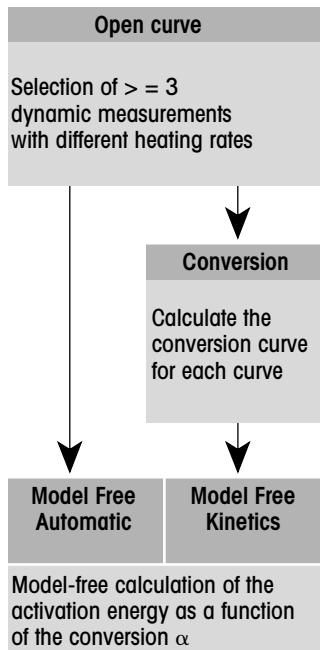
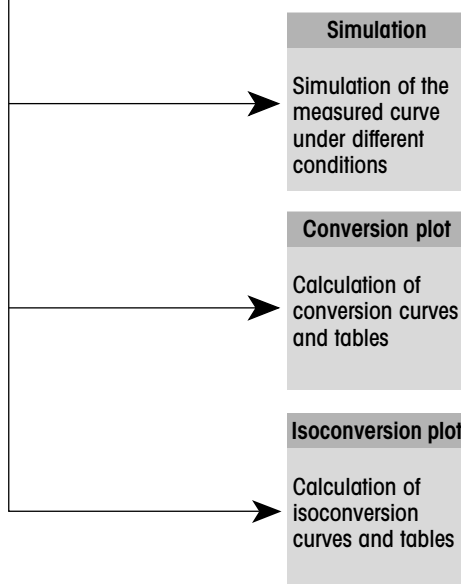


# Model Free Kinetics

This new kinetics software is an extremely powerful tool to help you optimize a process and interpret the reaction sequences. Predictions of the behavior of the sample not only inside and outside the temperature and time range investigated, but also under different isothermal conditions are possible. Without the need for time-consuming lengthy measurements, information on ageing, oxidative stability, product lifetime and process optimization can be gained.



- Usable with simple and complex reactions
- Process optimization
- Safety investigations
- Very simple operation (rapid and dependable, simple check)
- Automation for simple reactions
- Saves experimental time and improves the efficiency
- Applied kinetics (prediction under different conditions)
- Suitable for DSC and TGA measurements
- No physico-chemical model necessary
- Activation energy as a function of the conversion  $\alpha$  provides an insight into the complexity of the reaction.



## Theory

The idea of Vyazovkin is based on the following 2 assumptions:

1. The activation energy is not a constant, but constant only for a particular conversion  $\alpha$ .
2. The Arrhenius expression for the temperature dependence of the rate coefficient retains its validity:

$$\frac{d\alpha}{dt} = k_0 \cdot e^{\frac{-E(\alpha)}{R \cdot T}} \cdot f(\alpha)$$

$$\frac{d\alpha}{dt} = \text{reaction rate}$$

$k_0$ : rate constant at infinite temperature

$f(\alpha)$ : reaction model

$E(\alpha)$ : activation energy as a function of the conversion  $\alpha$

R: universal gas constant

## Flexible result selection

The integrated form of the rate equation has the following appearance:

$$\beta \cdot g(\alpha) = k_0 \int e^{\frac{-E(\alpha)}{R \cdot T}} \cdot dT$$

$$\text{where: } g(\alpha) = \int \frac{1}{f(\alpha)} d\alpha$$

$$\text{with } \frac{2R \cdot T}{E(\alpha)} \ll 1 \text{ we get:}$$

$$\beta \cdot g(\alpha) = k_0 \cdot \frac{RT^2}{E(\alpha)} e^{\frac{-E(\alpha)}{R \cdot T}}$$

The last equation can be used to calculate the associated activation energy  $E_\alpha$  for every conversion if at least 3 dynamic measurements with different heating rates are available.

To use the applied kinetics (simulation, conversion plot, isoconversion plot), this new formulation requires no knowledge of the reaction model ( $f(\alpha)$  or  $g(\alpha)$ ). The information needed for the applied kinetics is implicitly included in the measurements. As there are no formal solutions for the calculations, they must all be solved numerically.

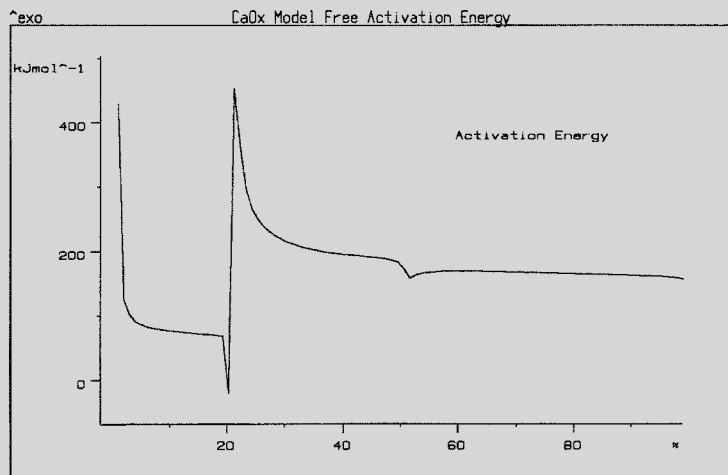
With these new kinetics, selection of the model with all its associated errors is no longer necessary. This leads to improved results as experience has shown that the known models correctly mirror reality only in isolated cases.

## Results

The activation energy curve as a function of the conversion  $\alpha$  is always calculated. This curve is the basis for the further

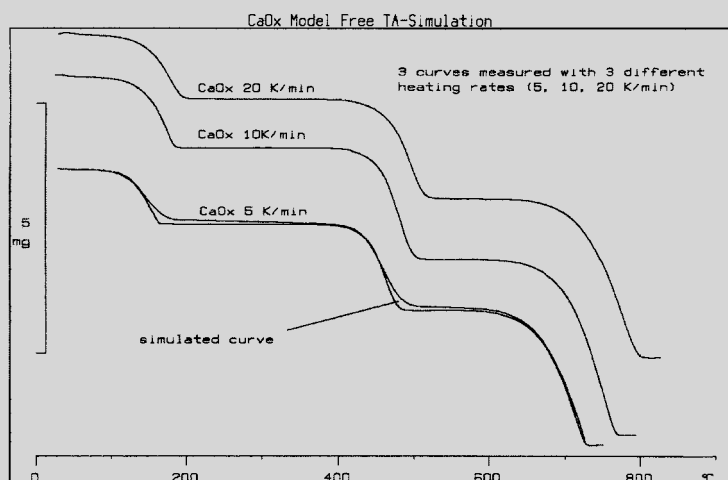
calculations. The number of result curves and tables can be configured very easily.

The representation can be shown in one or several evaluations, depending on requirements.



### Interpretation of the reaction progress

Example of an activation energy curve calculated from three TGA measurements (calcium oxalate monohydrate). The three levels of the activation energy curve with the practically constant activation energies indicate three relatively simple reactions running in succession.



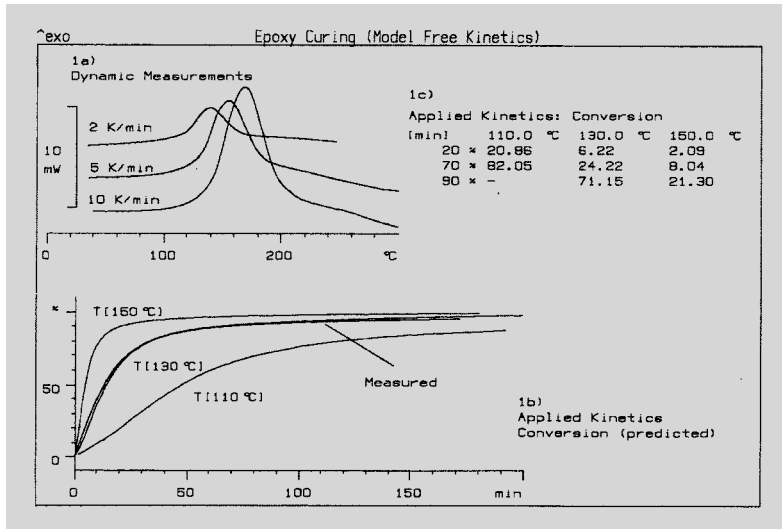
### Simulation of the reaction progress

Example of a simulation over several weight steps in a TGA measurement. The sample comprises approximately 10 mg calcium oxalate monohydrate. The measurements were run at three different heating rates under nitrogen. Anhydrous calcium oxalate, calcium carbonate and finally calcium oxide are formed in steps.

## Application examples

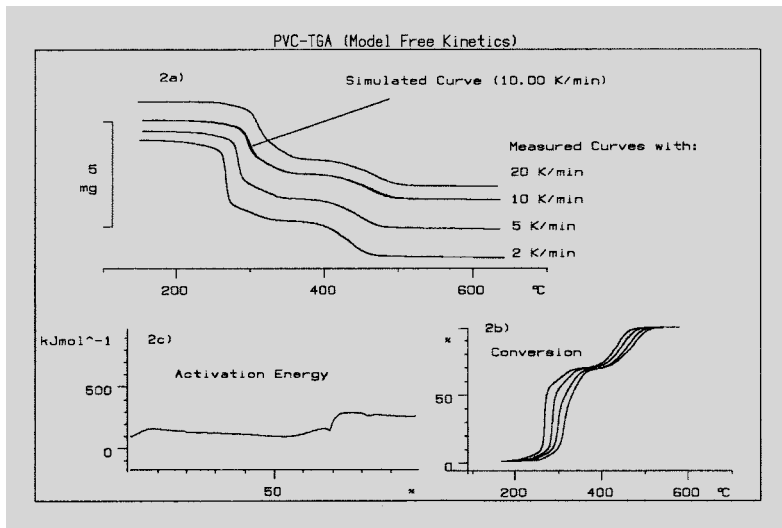
### Curing reaction of an epoxy resin

Epoxy resins are today used in many fields. The chemical reactions which form the basis of the curing behavior are very complex and can thus not be described by simple kinetic models. Reliable prediction of the degree of curing, in other words the conversion of the chemical reaction, which is correlated with the mechanical properties of the product, as a function of temperature without the need to perform numerous time consuming single measurements is thus of great interest. Fig. 1a) shows three dynamic curves of an epoxy resin whose curing reaction was recorded at different heating rates. These curves were automatically analyzed using the model-free kinetics and the activation energy calculated as a function of the conversion.



These curves were automatically analyzed using the model-free kinetics and the activation energy calculated as a function of the conversion.

These data allow prediction of the conversion as a function of the time at different temperatures or heating rates. It is thus possible to use the three dynamic measurements to predict the conversion as a function of time at different temperatures. Fig. 1b) shows the conversion predicted by the model at temperatures between 110 and 150 °C in graphical form, Fig. 1c) the same data in tabular form. To demonstrate how well the model describes reality, a measurement was performed isothermally at 130 °C and its conversion curve compared with the prediction. The good agreement shows that the model-free kinetics allow very accurate prediction of the isothermal behavior.



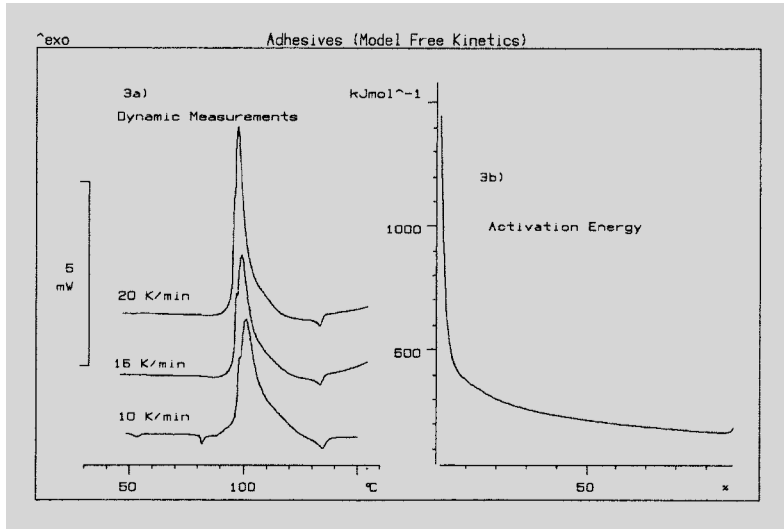
### Decomposition of a polyvinyl chloride sample

Many plastics show signs of decomposition at elevated temperatures which can lead to complete degradation, depending on the experimental conditions used. The illustration opposite shows such decomposition using the example of polyvinyl chloride recorded in the TGA under an N<sub>2</sub> atmosphere up to a temperature of 700 °C.

Fig. 2 a) shows the weight loss detected at four heating rates, which occurs in two clearly separate steps in the case of PVC.

The first is a consequence of the loss of hydrogen chloride. The model-free kinetics can also be used with this reaction investigated by thermogravimetry. Use of the calculated conversions (2b) and the calculated activation energy (2c) allows simulation of this multistage decomposition reaction as Fig. 2 a) shows. The simulation of the weight loss at a heating rate of 10 K/min is identical with the behavior actually measured.

## Application examples



### Curing behavior of an adhesive

Adhesives are expected to exhibit their adhesive properties rapidly and moreover even at low temperatures. This is synonymous with the attainment of a particular chemical conversion „ $\alpha$ “. As this depends on both the temperature and the time, these two influences on the conversion have to be determined before the processing can be optimized. Were this optimization to be under-taken in the normal way, numerous individual measurements under a wide range of conditions would be necessary.

Fig. 3a) shows the required three dynamic DSC measured curves from which the activation energy curve (Fig. 3b) can be calculated automatically. The applied kinetics thus allow prediction of the conversion curve „ $\alpha$ “ as a function of temperature, which is shown both graphically (Fig. 3c) and in tabular form (Fig. 3d). The conditions under which a particular conversion is attained can thus be quickly identified. This information can then be used for simple adjustment of the production conditions to the required degree of cure.

