

# Chemiluminescence Data Analysis

## Differential Isoconversional Kinetic Analysis

Differential isoconversional analysis of oxidation reaction activation parameters and prediction of the life time.

### Introduction

The noticeable weakness of the 'single curve' methods (determination of the kinetic parameters from single run recorded with one heating rate or isothermal condition only) has led to the introduction of 'multi curve' methods over the past few years, as discussed in the International ICTAC kinetics project.

Degradation reactions are often too complex to be described in terms of a single pair of Arrhenius parameters and the commonly applied set of reaction models. As a general rule, these reactions demonstrate profoundly multi-step characteristics. They can involve several processes with different activation energies and mechanisms. In such situations, the reaction rate can be described only by complex equations, where the activation energy term is no longer constant but dependent on the reaction progress  $\alpha$  ( $E \neq \text{const}$  but  $E = E(\alpha)$ ).

The isoconversional methods were introduced by Friedman and Ozawa-Flynn-Wall. A detailed analysis of the various isoconversional methods (i.e. the isoconversional differential and integral methods) for the determination of the activation energy was presented by Budrugeac. The convergence of the activation energy values obtained by means of a differential method (Friedman) with those resulting from using integral methods (Ozawa-Flynn-Wall) comes from the fundamentals of the differential and integral calculus:

The differential isoconversional method of Friedman is based on the Arrhenius equation

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT(t)}\right) f(\alpha)$$

with

$f(\alpha)$ : the model function

$A$ : the pre-exponential factor

$E$ : the activation energy

$R$ : the universal gas constant

$T$ : the temperature

$t$ : the time

Friedman has applied the logarithm of the conversion rate  $d\alpha/dt$  as a function of the reciprocal temperature at any conversion  $\alpha$ :

As  $f(\alpha)$  is a constant in the last term at any fixed  $\alpha$ , the logarithm of the conversion rate  $d\alpha/dt$  over  $1/T$  shows a straight-line dependence with the curve of  $m = -E/R$ .

$$\frac{d\alpha}{dt} = A(\alpha) \exp\left(-\frac{E(\alpha)}{RT(t)}\right) f(\alpha)$$

By the extension of the expression

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(A(\alpha)) - \frac{E(\alpha)}{RT(t)} + \ln(f(\alpha))$$

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(A'(\alpha)) - \frac{E(\alpha)}{RT(t)}$$

with

$$A'(\alpha) = A(\alpha) f(\alpha)$$

one can predict the reaction rate or reaction progress having determined and using the following expression:

$$\frac{d\alpha}{dt} = A'(\alpha) \exp\left(-\frac{E(\alpha)}{RT(t)}\right)$$

### Chemiluminescence Data

The data from at least 3 experiments is required for the analysis of the oxidation kinetics. The more experiments carried out, the more accurate the analysis of the kinetic parameters (as a result of the linear regression for  $\alpha_i$ ). Isotherms ( $T = \text{static}$ ) as well as non-isotherms ( $T = \text{dynamic}$ ) can be analyzed. However, moderate static measurement conditions (e.g. 90, 100, 110, 120°C) are recommended in principle for oxidation reactions. This enables the targeted prevention during the experiments of temperature-related changes in the reaction kinetics caused by secondary phase transitions (e.g. melting, softening etc.).

## Example

The procedure concerning differential isoconversional analysis is explained and illustrated below in the example of unstabilized natural rubber (isoprene polymer, mainly *cis*-1,4-polyisoprene):

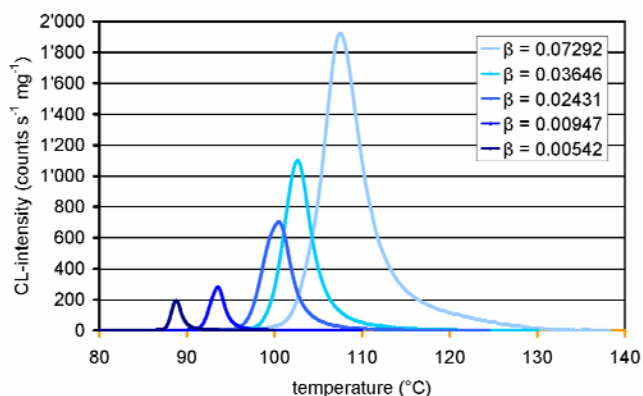


Fig. 1: Oxidation behavior of unstabilized natural rubber at different non-isothermal temperature profiles (heating rate  $\beta = 0.073..0.005\text{Kmin}^{-1}$ ) in synthetic air measured with the chemiluminescence method (basic configuration 1<sup>10</sup> of ACL Instruments).

The time/temperature-dependent reaction progress  $\alpha$  of the measurement data is now evaluated.

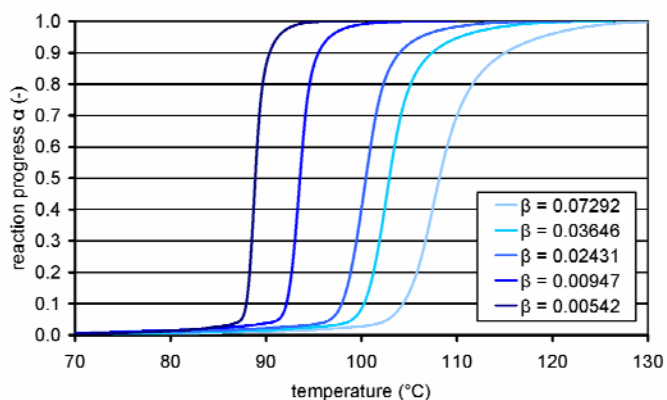


Fig. 2: reaction progress  $\alpha$  of the relevant CL experiments depending on experimental temperature profiles.

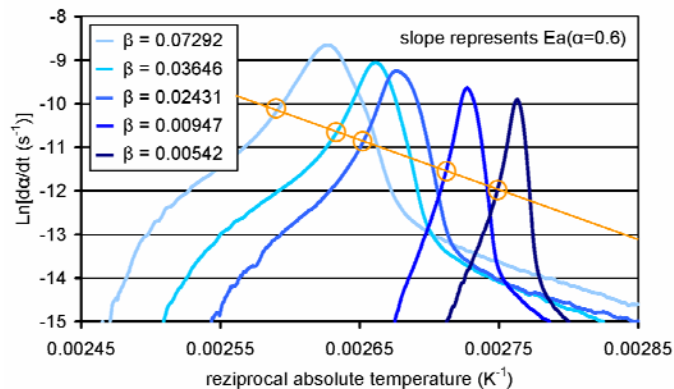


Fig. 3: Presentation of measurement data in the Arrhenius diagram with regression analysis for  $\alpha_i$  (e.g.  $\alpha = 60\%$ ).

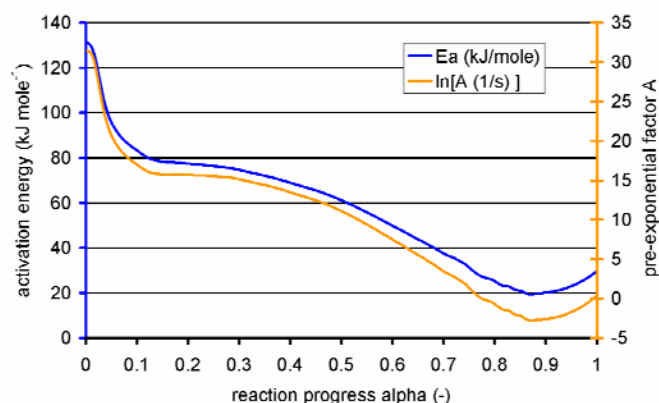


Fig 4: Activation parameters (activation energy  $E_A$  and pre-exponential factor  $A$ ) of the oxidation of unstabilized natural rubber as a function of reaction progress  $\alpha$ .

## Benefit

ACL Instruments' chemiluminescence method enables the characterization of organic solids and liquids at moderate temperature conditions. Measurement data obtained in this way is particularly suitable for the analysis of activation parameters and the prognosis of products and formulations under individual application conditions.

ACL Instruments recommends the use of AKTS Thermokinetics ([www.akts.com](http://www.akts.com)) software for the analysis of activation parameters of chemical reactions.

