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STEPWISE AND FORCED STEPWISE ISOTHERMAL ANALYSIS

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History

The stepwise isothermal analysis, SIA, was introduced by the author in the late seventies [1]. Together with quasi-isothermal analysis, QIA, introduced by Paulik [3] and the rate controlled thermal analysis, RCTA, introduced by Rouquerol [4], SIA thus is one of the pioneering techniques on which the modern sample controlled thermal analysis (SCTA) is based.

One drawback with SIA is that it is not possible to dertermine the activation energy in kinetic studies as isothermal data is obtained by SIA. In order to overcome this the forced stepwise isothermal analysis (FSIA) was later introduced [5].

Principle

The overall controlling parameter in SIA is the derivative mass (dw/dt) or length (dL/dt) signal, corresponding to the reaction rate, which is calculated in the algorithm after each mass (length) measurement. As long as this signal is smaller than a preselected treshold value, the heating is allowed to proceed at the preset constant heating rate, but the moment this signal becomes larger than the threshold value, then the heating is stopped and the reaction takes place at isothermal conditions. After completion of the reaction the heating is resumed when the derivative signal again becomes smaller than the treshold value and the sample will be heated at constant heating rate until the next reaction temperature is reached. The overall measurement will therefore take place in characteristic isothermal steps depending on the number of reactions for the sample.

A characteristic feature of SIA is also that the treshold value is smaller for the end of the reaction than for the start. In this way it is also possible to measure the tail of the reaction, which for many reactions is very long. This improves the resolution, demostrated in a SIA study of the thermal decomposition of $CuSO_4 \cdot 5H_2O$ [5].

Kinetic studies with SIA and FSIA

Determination of reaction mechanism

The isothermal data obtained with SIA are particularly useful in accurate kinetic studies to establish the reaction mechanism. Some examples from previous studies:

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- Thermal decomposition of Ba-oxalate hemi hydrate ($BaC_2O_4{\cdot}0.5H_2O$); five decomposition steps, for all steps the controlling mechanism was found to be two-dimensional phase-boundary controlled [6].
- Decomposition of Ce-carbonate dihydrate ($Ce_2O(CO_3)_2{\cdot}2H_2O$) in different atmospheres [7]. In air the controlling mechanism was found to be nucleation followed by two-dimensional phase boundary movement; in CO the nucleation was apparently so fast that phase-boundary controlled nuclei growth became the controlling mechanism in this atmosphere.
- Decomposition of rare earth doped cerium carbonates [8] which again showed that the controlling mechanism was nucleation followed by two dimensional growth.

Determination of activation energies

One drawback with this technique is, however, that activation energies cannot be determined from the isothermal data. In order to overcome this problem the forced stepwise isothermal analysis (FSIA) technique was introduced.

As described in [2], FSIA operates in the following way: when the mass changes, which is constantly monitored during the reaction, reaches 10% of the total mass change for a particular reaction, the temperature is forced to increase with 5º. In this way the total reaction is forced to take place in about 10 isothermal steps at increasing temperature. The curves obtained for the thermal decomposition of Ce-carbonates in different atmospheres are shown in Fig. 3 in [2], whereas the corresponding Arrhenius plot obtained from these curves are shown in Fig. 5 still in [2]. For the atmospheres air and CO, the following activation energies and pre-exponential factors were obtained:

	E/kJ mol^{-1}	A/min^{-1}
Air	104.9	$5.91{\cdot}10^9$
CO	297.8	$5.03{\cdot}10^{20}$

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