

INTERPRETATION OF QUASI-ISOTHERMAL THERMOGRAVIMETRIC WEIGHT CURVES

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Abstract

Quasi-isothermal analysis (QIA) is a very useful technique. Compared to conventional non-isothermal thermogravimetry, closely lying reactions can easily be separated by use of this method and kinetic data can be obtained for each intermediate reaction in a single run. This paper discusses the shape of the weight and temperature curves expected in QIA for different controlling mechanisms, and a method is given for calculating the activation energies from these curves. As an example, the QIA curves obtained in thermal decomposition of ammonium-uranyl carbonate (AUC) are analysed and the kinetics of some of the intermediate reactions are determined.

INTRODUCTION

Quasi-isothermal analysis (QIA), which was introduced by Paulik and Paulik (1-2), is a very useful thermogravimetric technique. Compared to conventional non-isothermal thermogravimetry, it has the following advantages: intermediate phases can easily be determined, kinetics (controlling mechanism and activation energy) can be determined for each intermediate reaction step in a single run, and using a crucible arrangement for measurements in self-generated atmospheres, reproducible decomposition temperatures can be determined.

DESCRIPTION OF QIA METHOD

The principle of the QIA method is as follows: when the sample during programmed heating reaches the reaction temperature and a deviation is obtained in the weight curve, a DTG signal proportional to the slope of the weight curve will also be produced in the DTG amplifier. With a regulator, two limits can be preset for the DTG signal: an upper limit where heating is stopped when the DTG signal

becomes larger than this limit, and a lower limit where heating is resumed when the DTG signal becomes smaller than this limit when the reaction is nearly completed.

INTERPRETATION OF QIA CURVES

Shape of weight and temperature curves

Two basic types of behaviour can be expected: A) The DTG signal fluctuates between the two preset limits and a linear weight change will be obtained. The temperature will only increase a few degrees during each step and quasi-isothermal conditions are obtained. B) The DTG signal remains outside the upper preset limit during a large part of the reaction, and a sigmoid weight curve, but strictly isothermal conditions, will be obtained. Considering the $d\alpha/dt$ versus α curves shown in fig. 1 for different controlling mechanisms, one notes that nucleation and three-dimensional growth of nuclei can, depending on the activation energy, give type A behaviour in the first part followed by a type B behaviour, whereas the opposite will be observed for phase-boundary and especially diffusion-controlled reactions. The shape of the weight and temperature curves in a QIA measurement can thus give information on the mechanism controlling the reaction (s).

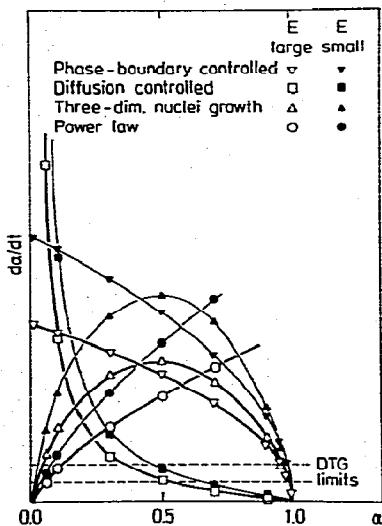


Fig. 1. Reaction rate ($d\alpha/dt$) versus degree of reaction (α) for reactions controlled by different mechanisms according to reference (4)

Calculation of activation energies

For a reaction involving several steps, the reaction rates at the two DTG limits are given by

$$\left(\frac{d\alpha}{dt}\right)_1 = k_\infty \exp(-E/RT_1) \cdot f(\alpha)$$

$$\left(\frac{d\alpha}{dt}\right)_2 = k_\infty \exp(-E/RT_2) \cdot f(\alpha)$$

Thus the ratio between these rates, which is constant (C), becomes

$$C = \exp(-E/RT_1) / \exp(-E/RT_2), \text{ or}$$

$$\log C = \frac{E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = \frac{E}{R} \Delta \left(\frac{1}{T} \right). \quad (1)$$

INTERPRETATION OF QIA CURVES FOR THE THERMAL DECOMPOSITION OF AMMONIUM-URANYL-CARBONATE (AUC)

The weight and temperature curves obtained for thermal decomposition of AUC in hydrogen are shown in fig. 2. An analysis of these curves according to the ideas presented above, shows that the decomposition of AUC takes place in several steps each with a characteristic activation energy in accordance with the results presented in reference 4.

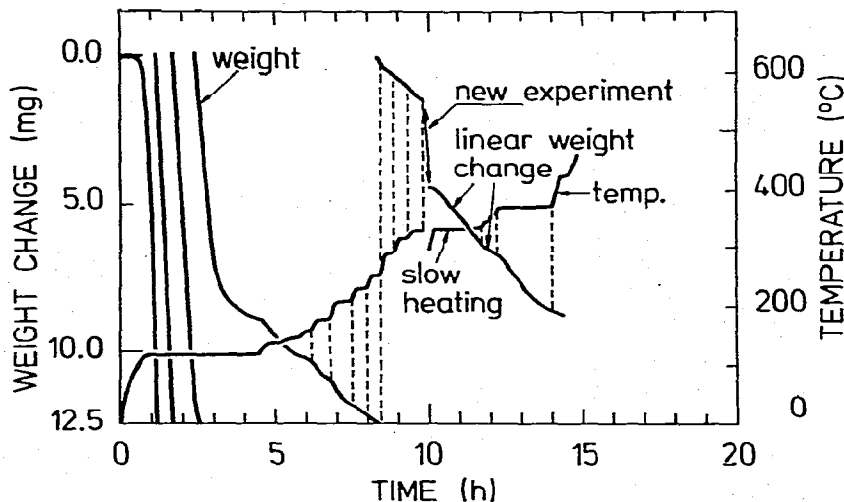


Fig. 2. Weight and temperature curves obtained in a QIA examination of the thermal decomposition of ammonium-uranyl carbonate (AUC) in hydrogen.

Once the extent of the individual intermediate reactions is established, $\alpha (= \Delta W_t / \Delta W_{\max})$ and $d\alpha/dt$ can easily be calculated, and using a $\log f(\alpha) - \log d\alpha/dt$ plot (6) the mechanism controlling the reaction can be determined. Figure 3 shows that a linear relationship is obtained for the $\text{AUC} \rightarrow \text{UO}_3 \cdot \text{H}_2\text{O}_{1.5}$ conversion when

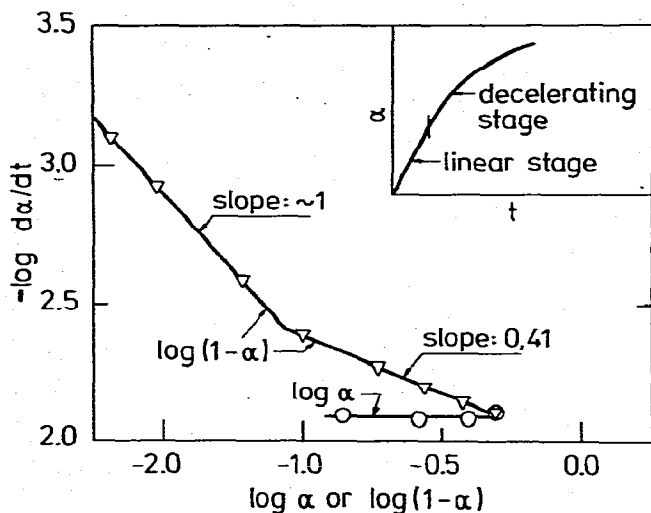


Fig. 3. Log - log plot for the $\text{AUC} \rightarrow \text{UO}_3(\text{H}_2\text{O})_{1.5}$ conversion step.

$\log \alpha$ and $\log(1-\alpha)$ are plotted against $\log d\alpha/dt$, indicating that the first part of this step is phase-boundary controlled (one-dimensional: $f(\alpha) = \alpha^0$, two dimensional $f(\alpha) = (1-\alpha)^{1/2}$) and that nuclei growth is controlling ($f(\alpha) = (1-\alpha)$) in the last part. This does not agree with the results reported for ADU (ammonium diuranate) by Ball et al. (5), who found that this step was controlled by a one-dimensional diffusion mechanism ($f(\alpha) = \alpha^{-1}$). The reason for this discrepancy is not clear, but Ball et al. did use the less precise non-isothermal thermogravimetric technique in their investigation.

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