

LETTER TO THE EDITORS

The "Shape Index" of Temperature-Programmed Desorption Curves

Konvalinka and Scholten have assumed in a very recent and interesting paper (1) that the method formulated by Kissinger (2) for determining the reaction order of thermal decomposition reactions of solids from the "shape index," S , of differential thermal analysis curves (DTA) holds for temperature-programmed desorption (TPD) diagrams as well.

The parameter S has been defined (2) as the ratio of the slopes of the tangents to the DTA curve at the inflection points and it is correlated with the reaction order n through the equation:

$$n = 1.26 \cdot S^{\frac{1}{2}} \quad (1)$$

This expression has been obtained empirically by Kissinger by plotting the S values calculated for different reaction orders against n^2 .

In Ref. (1) there is reported a weakly bound ("type C") hydrogen on the surface of palladium and, bearing in mind previous considerations, a desorption order very close to 1 has been calculated applying Kissinger's criterion to a TPD diagram. Moreover, taking into account these data and comparing the half-value TPD peak broadening with those calculated (3) for first-order desorption, it has been concluded that the desorption of "type C" hydrogen is first order in coverage with freely occurring readsorption.

However, it is necessary to point out that a first-order reaction of thermal decompo-

sition of solids follows the law:

$$\frac{d\alpha}{dt} = A \cdot e^{-E/RT} \cdot (1 - \alpha), \quad (2)$$

where α is the fraction of solid reacted at time t and the other parameters have their usual meaning.

A first-order desorption reaction with freely occurring readsorption follows the kinetic equation:

$$-\frac{d\theta}{dt} = \frac{F}{V_s V_m} \cdot \frac{\theta}{(1 - \theta)} \cdot A^* \cdot e^{-\Delta H/RT} \quad (3)$$

or

$$-\frac{d\theta}{dT} = \frac{F}{V_s \beta V_m} \cdot \frac{\theta}{(1 - \theta)} \cdot A^* \cdot e^{-\Delta H/RT} \quad (3a)$$

where θ is the surface coverage; F is the carrier gas flow rate; V_s is the volume of the solid phase in the catalyst bed; β is the heating rate; A^* stands for $\exp(\Delta S/R)$, ΔS being the adsorption entropy, ΔH the adsorption heat and V_m is the amount of gas adsorbed at full coverage.

Equations (2) and (3) are quite different and, in our opinion, there is no reason for assuming *a priori* that both DTA diagrams of first-order reaction of thermal decomposition of solids and TPD curves of first-order desorption with freely occurring readsorption have the same shape index. In order to check the above assumption we will calculate the parameter of asymmetry S of TPD diagrams described by kinetic Eq. (3).

The shape index can be expressed analytically as

$$S = \left| \frac{\left(\frac{d^2\theta}{dt^2}\right)_1}{\left(\frac{d^2\theta}{dt^2}\right)_2} \right|, \quad (4)$$

where subscripts 1 and 2 refer to the values of this quantity at the inflection points, i.e., where $d^3\theta/dt^3 = 0$.

Differentiating Eq. (3), substituting Eq. (3), and collecting terms one obtains

$$\frac{d^2\theta}{dt^2} = \left[\frac{1}{\theta(1-\theta)} \frac{d\theta}{dt} + \frac{\beta\Delta H}{RT^2} \right] \frac{d\theta}{dt}. \quad (5)$$

Integrating Eq. (3) between an initial coverage θ_0 and θ and taking into account the expression given in Ref. (3) for the integral of the Arrhenius equation, we can write:

$$\begin{aligned} -\ln \theta + \theta - C \\ = \frac{A^*FRT^2}{V_s V_m \beta \Delta H} \cdot g(x) \cdot e^{-\Delta H/RT}, \quad (6) \end{aligned}$$

where $C = (-\ln \theta_0 \div \theta_0)$ and $g(x)$ is a

function given by the following expression:

$$g(x) = 1 - \frac{2!}{x} + \frac{3!}{x^2} - \dots + \frac{(-1)^n \cdot (n+1)!}{x^n}, \quad (7)$$

where $x = \Delta H/RT$.

From Eqs. (3) and (6) we obtain:

$$\frac{d\theta}{dt} = - \frac{\beta\Delta H}{RT^2} \frac{\theta}{1-\theta} (-\ln \theta + \theta - C) \cdot \frac{1}{g(x)}. \quad (8)$$

Setting the first derivative of Eq. (5) equal to zero, taking into account the value of $d\theta/dt$ given by Eq. (8), and rearranging, we obtain the condition that must be fulfilled by θ at the inflection points:

$$\begin{aligned} - \frac{1+2\theta}{(1-\theta)^4} (-\ln \theta + \theta - C)^2 \cdot \frac{1}{g(x)^2} \\ - \frac{3}{g(x)} \frac{1}{(1-\theta)^2} \cdot (-\ln \theta + \theta - C) \\ + \left(1 - \frac{2RT}{\Delta H}\right) = 0. \quad (9) \end{aligned}$$

On the other hand, from Eqs. (4), (5), and (8) there results for the shape index:

$$S = \frac{\left[\frac{1}{g(x)} \frac{-\ln \theta_1 + \theta_1 - C}{(1-\theta_1)^2} + 1 \right] \frac{\theta_1}{(1-\theta_1)} (-\ln \theta_1 + \theta_1 - C)}{\left[\frac{1}{g(x)} \frac{-\ln \theta_2 + \theta_2 - C}{(1-\theta_2)^2} + 1 \right] \frac{\theta_2}{(1-\theta_2)} (-\ln \theta_2 + \theta_2 - C)} \cdot \left(\frac{T_2}{T_1}\right)^4, \quad (10)$$

where θ_1 and θ_2 are the solutions of Eq. (9) at the first and second inflection points, respectively.

We can see from Eqs. (9) and (10) that the shape index depends on the values of both $\Delta H/RT$, T_2/T_1 , and the initial coverage θ_0 . This last parameter has no meaning

in reactions of thermal decomposition of solids, where α_0 is always equal to zero.

If we consider, following Kissinger's paper (2), that $g(x) \cong (1 - 2RT/E) \cong 1$ and that T_2/T_1 varies little from an average value of about 1.08, values of $S = 1.08$ at $\theta_0 = 1$ and $S = 0.77$ at $\theta_0 = 0.25$ are ob-

tained. These data are different from the value calculated from Eq. (1). On the other hand, they show that the shape index strongly depends on the initial coverage.

The previous considerations show rather clearly that the skewness of a DTA curve of a reaction of thermal decomposition of solids is not necessarily the same as that obtained for a TPD curve of a first-order desorption reaction with freely occurring readsorption. Therefore, to determine the order of a desorption reaction from Eq. (1) would be a meaningless exercise.

A study on the shape index of TPD diagrams of first- and second-order desorption reaction without readsorption and with readsorption, respectively, as a function of $\Delta H/RT$, T_2/T_1 ratio, and initial coverage is currently being performed in our laboratory and will be the scope of a further paper.

REFERENCES

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