

DTA STUDY OF THE KINETICS  
OF SODIUM HYDRIDE DECOMPOSITION

J. ŠUBRT and K. TOBOLA

*Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Řeč u Prahy, CSSR*

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A trial was performed to study the thermal decomposition of sodium hydride with DTA within the temperature range of 500 to 800 K. The best description of this process is provided by the Avrami equation  $\alpha = 1 - e^{-kt^3}$ . The activation energy of this process  $E_a = 115$  kJ/mole and the frequency factor  $Z = 2 \cdot 10^7$  sec<sup>-1</sup> were determined.

The method derived by Borchard and Daniels [1] was employed for the calculation of the degree of conversion from DTA curves. These authors defined the experimental conditions under which Eq. 1 can be used for the description of the reaction rate:

$$-\frac{dn}{dt} = \frac{n_0}{\Delta H} \left( C \frac{d\Delta T}{dt} + k\Delta T \right) \quad (1)$$

Its use for heterogeneous reactions is described, for instance, by Škvára and Šatava [2]. Given that at the beginning of the DTA peak (at time  $t_0$ ) the reaction rate is equal to zero, the total area under the DTA peak ( $A_t$ ) is proportional to the reaction heat:

$$A_t = \frac{\Delta H}{K}$$

The degree of conversion ( $\alpha$ ) at time  $t$  can be calculated via Eq. 3 where  $a$  is the part of the area under the DTA peak within the  $t_0 - t$  range [2].

$$\alpha = \frac{n_0 - n}{n_0} = \frac{1}{A_t} \left( \frac{C}{K} \Delta T + a \right) \quad (3)$$

The  $A_t$  and  $a$  values can be determined from the DTA recording through integration of the peak, and the  $C/K$  value can be determined from the cooling curve [3].

Provided that the reaction is studied in a region far enough from equilibrium, the course of the reaction rate ( $d\alpha/dt$ ) can be described by Eq. 4:

$$\frac{d\alpha}{dt} = Z \cdot e^{-\frac{E_a}{RT}} \cdot f(\alpha) \quad (4)$$

At a constant heating rate  $\left(v = \frac{dT}{dt}\right)$ , Eq. 4 can be converted to the following form:

$$\frac{d\alpha}{f(\alpha)} = \frac{Z}{v} \cdot e^{-\frac{E_a}{RT}} \cdot dT \quad (5)$$

integration of which to temperature  $T_\alpha$ , at which the degree of conversion  $\alpha$  is reached, gives the following relation:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{Z \cdot E_a}{R \cdot v} \cdot p(x) \quad (6)$$

where the quantities  $x$  and  $p(x)$  are defined by Eqs 7 and 8:

$$x = \frac{E_a}{R \cdot T} \quad (7)$$

$$p(x) = \frac{e^{-x}}{x} - \int_{-x}^{\infty} \frac{e^{-u}}{u} \cdot du \quad (8)$$

The quantity  $u$  is defined by relation 9:

$$u = \frac{E_a}{R \cdot T} \quad (9)$$

The logarithmic calculation of Eq. 6 gives the following relation:

$$\log g(\alpha) - \log p(x) = \log \frac{Z \cdot E_a}{R \cdot v} \quad (10)$$

Due to the fact that the right side of Eq. 10 contains only constants, and the dependence of  $\log p(x)$  on  $1/T$  is linear for higher  $x$  values, the dependence of  $\log g(\alpha)$  on  $1/T$  must also be linear if the function  $f(\alpha)$  expresses the actual mechanism of the process [2, 4]. These facts can be used to see whether or not the proposed function  $f(\alpha)$  expresses the course of the process under study and to calculate the activation energy  $E_a$  and the frequency factor  $Z$  of the reaction studied.

### Experimental

The decomposition of sodium hydride is an endothermic reaction ( $\Delta H_r = 56.898$  kJ/mole (13.6 kcal/mole) [5]) involving a very small weight change (4%) in the course of decomposition. Hence, DTA is a method suitable for its study. The apparatus used was developed and made in the Institute of Inorganic Chemistry, its detailed description having already been published [9].