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DTA STUDY OF THE KINETICS OF SODIUM HYDRIDE DECOMPOSITION

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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^{-1} 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:

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

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 (α) 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].

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

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:

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

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

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

integration of which to temperature T_α, at which the degree of conversion α is reached, gives the following relation:

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

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

$$x = \frac{E_a}{R \cdot T} \tag{7}$$

$$p(x) = \frac{e^{-x}}{x} - \int_{-x}^{\infty} \frac{e^{-u}}{u} \cdot \mathrm{d}u \tag{8}$$

The quantity u is defined by relation 9:

$$u = \frac{E_a}{R \cdot T} \tag{9}$$

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

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

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].

Sodium hydride supplied by the Dynamit Nobel firm was used for the measurement. The material is provided in the form of lentil-shaped monodisperse particles 1 mm in diameter. It is formed of practically pure sodium hydride (purity better than 99%), with only slight surface contamination due to hydrolysis products. Some of the experiments were performed in vacuum (1 mm Hg of H_2 pressure), maintained throughout the measurement, and the others in an O_2-free and H_2O-free hydrogen atmosphere under atmospheric pressure. The measurements were performed at the heating rates of 3.1 and 5.2 K/min. Stainless crucibles 13 mm in height and 10 mm in diameter were used. All operations with sodium hydride (sensitive to moisture) were carried out in an inert nitrogen or argon atmosphere. Annealed Al_2O_3 (analysed reagent grade) was used as reference substance. The amount of NaH used was 0.55 g.

A GIER computer was employed for calculation of the activation energies and frenquency factors, as well as for calculation of the functions $g(\alpha)$ and their dependence on $1/T$. The programme used, in Algol language, is available at the Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences.

Description of the apparatus

A diagram of the measuring equipment is shown in Fig. 1. The measuring part proper (1), enabling work in a closed space up to a temperature of 550° and a pressure of 5 MPa, consisted of a stainless autoclave and holder with crucibles. The whole equipment is electrically heated from outside and is programmable with a linear temperature programmer (2). Temperature and differences of temperature were picked up with chromel-alumel thermocouples, and pressure with tensometric sensors (3). The value of temperature was measured with a digital millivoltmeter (5) and together with the value of pressure was recorded on an XY-recorder (6). The differences of temperature were recorded with a linear compensation recorder (7).

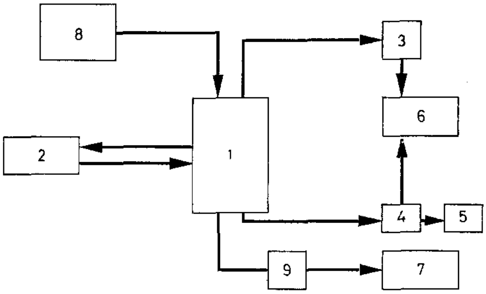

Fig. 1. Block diagram of the DTA equipment. 1 — measuring part proper; 2 — heating with linear temperature programmer; 3 — measurement of pressure in the equipment; 4 — measurement of temperature; 5 — digital millivoltmeter; 6 — XY-plotter; 7 — compensation recorder for the temperature difference measurement; 8 — gas reservoir; 9 — temperature difference measurement

The measuring part is shown in Fig. 2. The stainless autoclave (a) is fitted externally with an electric heating belt (input 2.5 kW) (b) and with thermal insulation (c). The crucible holder (d) also serves for thermocouple leading. The whole equipment has a pressure measurement outlet (i), serving at the same time for filling the apparatus with the required gas. The outlets of the thermocouples (*g*) pass through a pressure bushing.

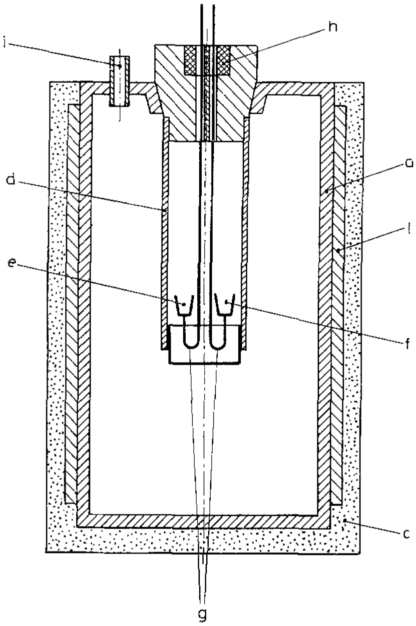

Fig. 2. Diagram of the measuring part proper. *a* — stainless autoclave; *b* — heating; *c* — thermal insulation; *d* — crucible holder; *e* — crucible with the measured substance; *f* — crucible with the reference substance; *g* — thermocouples; *h* — pressure bushing; *i* — pressure measurement spot

Results and discussion

The DTA curve of sodium hydride decomposition at atmospheric pressure and a heating rate of 5.2 K/min is shown in Fig. 3. Table 1 contains equations used in the literature for the description of reactions of solid substances [7] and used in this paper for the calculation of the kinetic parameters from the measured DTA curves. However, it must be noted that the courses of these equations (particularly when derived for the same process controlling the reaction rate) are very similar, and that is often impossible to differentiate between them due to the insufficient accuracy of the experimental data [8].

Table 1

The kinetic equations used

Function	Equation	Reaction rate-controlling process
d 1	$\alpha^2 = kt$	Diffusion
d 2	$(1 - \alpha).\ln(1 - \alpha) + \alpha = kt$	
d 3	$(1 - (1 - \alpha)^{1/3})^2 = kt$	
d 4	$(1 - 2.\alpha/3) - (1 - \alpha)^{2/3} = kt$	
a 1	$\alpha = 1 - \exp(-kt)$	Random nucleation and the growth of nuclei
a 2	$\alpha = 1 - \exp(-kt^2)$	
a 3	$\alpha = 1 - \exp(-kt^3)$	
r 2	$1 - (1 - \alpha)^{1/2} = kt$	Model of the contraction of the unreacted sphere
r 3	$1 - (1 - \alpha)^{1/3} = kt$	

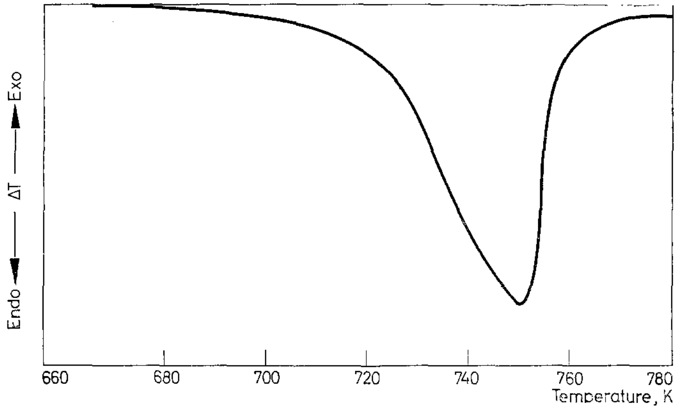

Fig. 3. A recording of the DTA peak for NaH decomposition

Figure 4 shows the dependence of $\log g(\alpha)$ on $1/T$ for the equations presented in Table 1. The smallest deviations from linearity (the standard deviation from linearity calculated from Eq. 11, where p was the gradient of the line with the values of $\log g(\alpha)$ and q was its intercept on the ordinate, was 1 – 3 %) were found via Eq. 3; this is the well-known Avrami equation, where random nucleation and the growth of the nuclei of a newly-arising phase are the processes controlling the reaction. Non-linearity at the very beginning of the process under study (4) is observable only up to $\alpha = 0.3\%$, where the results still bear a considerable experimental error.

$$\sigma = 100 \sqrt{\frac{\sum_{i=1}^{m} (\log g(\alpha)_i - (p/T_i + q))^2}{m - 1}} \tag{11}$$

The calculated value of the activation energy, $E_a = 115$ kJ/mole ± 8 kJ/mole, is in good correspondence with the value obtained from isothermal measurements, 104.1 kJ/mole (24.9 kcal/mole) [6]. Neither a hydrogen pressure change in the apparatus, nor a heating rate change within the limits mentioned above, causes statistically significant deviations of the measured activation energy. The calculated value of the frequency factor Z is 2.10^7 sec^{-1}. If the synthesis and decomposition of sodium hydride take place via the same activated complex, then it must hold true, as indicated in Fig. 5, that

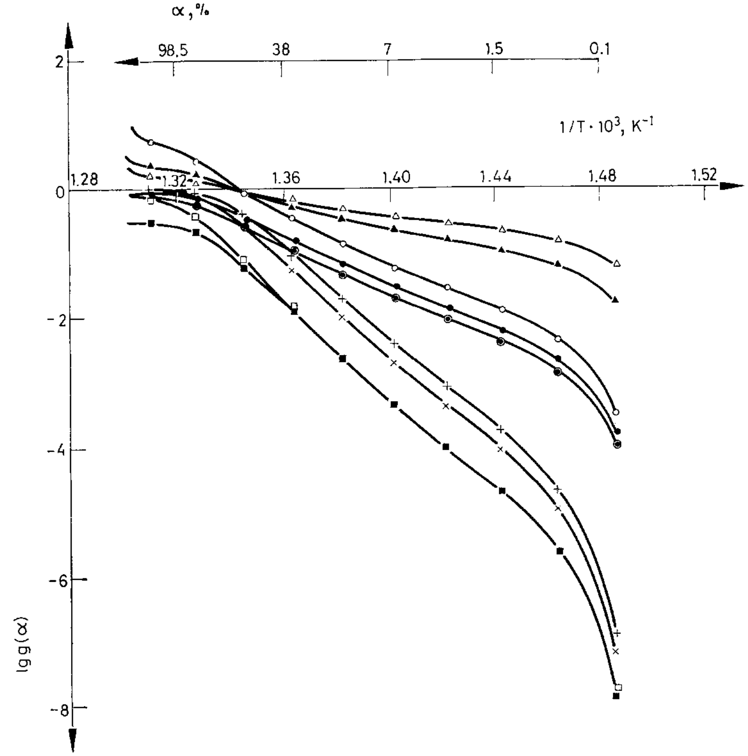

Fig. 4. Dependence of log $g(\alpha)$ on $1/T$. + — d 1; × — d 2; °□ — d 3; ■ — d 4; ○ — a 1; ▲ — a 2; △ — a 3; ● — r 2; ⊙ — r 3

$$E_{a_1} = E_{a_2} + \Delta H_r \tag{12}$$

where E_{a_1} is the activation energy of NaH decomposition, E_{a_2} is the activation energy of its synthesis, and ΔH_r is the reaction enthalpy of NaH production.

We recently studied the kinetics of the synthesis of sodium hydride from melted sodium under an increased hydrogen pressure [8]. The proposed mechanism, in which the reaction rate-controlling process was the passage of sodium hydride through the phase boundary of the liquid phase (sodium saturated with sodium hydride) and the solid phase (non-stoichiometric sodium hydride), provided a very good description of the experimental data of the kinetics of NaH synthesis. The obtained value of the activation energy was 54 kJ/mole. Hence, the value of the activation energy of NaH decomposition calculated from Eq. 12 should be 110.898 kJ/mole, which is in very good correspondence with the value of 115.5 kJ/mole obtained in our study.

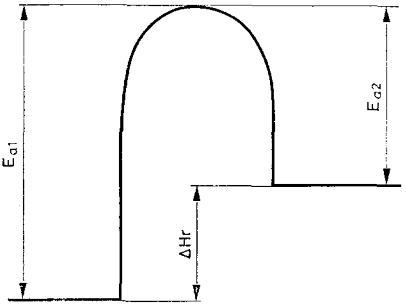

Fig. 5. Relation of the activation energies of the direct and reverse reactions, taking place via the same activated complex

Symbols

t	reaction time (sec)
n	quantity of unreacted NaH at the time of measurement (mole)
n_0	weighed amount of NaH (mole)
K	constant from Eq. 2
C	constant from Eq. 1
ΔT	temperature difference between sample and standard (K)
k	constant from Eq. 1 (K^{-1})
A_t	area of the DTA peak (cm^2)
ΔH	heat released by reaction (J)
α	conversion degree
a	area under the DTA peak from the beginning of the reaction to the moment of measurement (cm^2)
$d\alpha/dt$	reaction rate of NaH decomposition
Z	frequency factor (sec^{-1})
E_a	activation energy (kJ/mole)
$f(\alpha)$	function describing the course of the reaction
v	heating rate (K/min)
R	gas constant (J/mole.K)

T	temperature (K)
T	temperature at which the degree of conversion is obtained
$g(\alpha)$	function defined by Eq. 6
x	quantity defined by Eq. 7
$p(x)$	function defined by Eq. 8
u	quantity defined by Eq. 9
ΔH_r	reaction enthalpy (kJ/mole)
σ	standard deviation
p	gradient of line interlaced with $g(\alpha)$ values as a function of $1/T$
q	intercept of this straight line on the ordinate
m	number of applied values from DTA peak

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Résumé — Etude de la décomposition thermique de l'hydrure de sodium par ATD entre 500 et 800 K. L'équation d'Avrami $\alpha = 1 - c^{-kt^3}$ fournit la meilleure description du processus. Les résultats fournissent les valeurs de $E_a = 115$ kJ mol^{-1} pour l'énergie d'activation et $Z = 2 \cdot 10^7$ sec^{-1} pour le facteur de fréquence.

Zusammenfassung — Es wurde ein Versuch unternommen die thermische Zersetzung von Natriumhydrid im Temperaturbereich von 500 bis 800 K mittels DTA zu untersuchen. Die beste Beschreibung des Vorganges wird durch die Avrami-Gleichung $\alpha = 1 - c^{-kt^3}$ geliefert. Die Aktivierungsenergie $E_a = 115$ kJ/Mol und der Frequenzfaktor $Z = 2 \cdot 10^7$ sec^{-1} wurden bestimmt.

Резюме — Проведено испытание по изучению термического разложения гидрида натрия с помощью DTA в пределах температуры от 500 до 800 К. Процесс разложения наилучшим образом описывается уравнением Аврами $\alpha = 1—e^{-kt^3}$. Определены энергия активации этого процесса и частотный фактор, которые, соответственно, равны 115 кдж/моль и $2 . 10^7$ сек$^{-1}$.