

## KINETICS OF THE THERMAL DECOMPOSITION OF AMMONIUM THIOCARBAMATE

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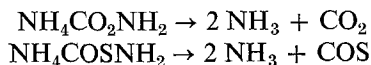
Results of the kinetic study of the thermal decomposition of ammonium thiocarbamate in vacuum (ca.  $10^{-2}$  torr) in the temperature range 303–353 K are presented. Under these conditions ammonium thiocarbamate decomposes into gaseous products ( $\text{NH}_4\text{COSNH}_2 \rightarrow 2\text{NH}_3 + \text{COS}$ ). Fifteen general equations for the kinetics of thermal decomposition of solids were taken into consideration. The following equation describes the experimental results over the whole range of the degree of decomposition:

$$\alpha = \frac{2k_2}{ab} (t - t_0)[a + b - 2k_2(t - t_0)]$$

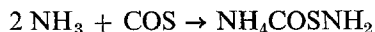
where  $\alpha$  = degree of decomposition,  $t$  = time,  $t_0$  = time required to attain constant growth rate of nuclei, and  $a$  and  $b$  are the dimensions of the crystal.

The temperature-dependence of the rate constant  $k_2$  was determined and the activation energy was found to be 10.7 kcal/mole. An experiment planning scheme was adopted in this study: in a series of experiments, each one was followed by statistical analysis in order to plan successive experiments depending on the results of the previous one.

The aim of this work was to investigate the thermal decomposition of ammonium thiocarbamate in vacuum in the temperature range 303–353 K. Under these conditions ammonium thiocarbamate decomposes into gaseous products. It is generally supposed that the reaction is analogous to the thermal decomposition of ammonium carbamate [1, 2]:



Ammonium thiocarbamate was obtained in the reaction:



carried out in absolute alcohol as solvent. The mechanism of decomposition of ammonium thiocarbamate is incompletely understood. Measurements of the dissociation pressure have been made only in the narrow temperature range 283–293 K [2].

The kinetics of the thermal decompositions of solids are usually expressed by complicated equations [3–7]. Experimental verification of these equations by traditional methods of calculation requires many additional simplifications. A set

Table 1  
Kinetic equations of nucleation according to an exponential law

Degree of freedom ( $\lambda$ ) for growth of nuclei	$\lambda = 1$	$\lambda = 2$	$\lambda = 3$
Nucleation according to the equation			
a) $\frac{dN}{dt} = k_1 N_0 \exp(-k_1 t)$		Rectangular plates, $a \gg c, b \gg c$ $\alpha = \frac{2k_2}{k_1 c} [\exp(-k_1 t) + k_1 t - 1]$ XI  Spherical particles $\alpha = 1 + \exp(-k_1 t) \left[ 3 \frac{k_2}{k_1 a} + 6 \left( \frac{k_2}{k_1 a} \right)^2 + \right.$ $\left. + 6 \left( \frac{k_2}{k_1 a} \right)^3 \right] - \left[ \left( 1 - \frac{k_2 t}{a} \right)^3 + \right.$ $\left. + 3 \left( 1 - \frac{k_2 t}{a} \right) \left( \frac{k_2}{k_1 a} \right) + 6 \left( 1 - \frac{k_2 t}{a} \right) \right]$ XII	$\alpha = C_6 \left( \frac{k_2}{k_1} \right)^3 \left[ \exp(-k_1 t) - 1 + \right.$ $\left. + k_1 t - \frac{(k_1 t)^2}{2} + \frac{(k_1 t)^3}{6} \right]$ XIII  Overlapping of growth nuclei a) $-\ln(1 - \alpha) = C_7 \left( \frac{k_2}{k_1} \right)^3 \left[ \exp \right.$ $\left. (-k_1 t) - 1 + k_1 t - \frac{(k_1 t)^2}{2} + \right.$ $\left. + \frac{(k_1 t)^3}{6} \right]$ XIV  b) $\alpha = 1 - \exp(-C_8 k_2^3 t^3)$ when $t$ is large XV
b) $\frac{dN}{dt} = k_1 N_0$	Branching nuclei, $\frac{dN}{dt} = k_1 N_0 +$ $+ k_3 N$ , no overlap $\alpha = \frac{k_1 k_3 C_2}{k_3^2} [\exp(k_3 t) - k_3 t - 1]$ II		

<p>c) <math>N = N_0</math></p> <p>Branching nuclei, <math>\frac{dN}{dt} = k_3 N</math></p> <p><math>\alpha = \frac{k_3 C_3}{k_3^2} [\exp(k_3 t) - k_3 t - 1]</math> III</p> <p>Branching nuclei, interfering during growth</p> <p>a) <math>k_3</math> independent of <math>t</math></p> <p><math>\ln \frac{\alpha}{1 - \alpha} = k_3 t + C_4</math> IV</p> <p>b) branching coefficient <math>k_3</math> varying with time, <math>k_3 = k_3'/t</math></p> <p><math>\ln \frac{\alpha}{k_3 + 1 - k_3' \alpha} = (k_3' + 1) \ln t + C_5</math> V</p>	<p>Nucleation confined to certain faces only</p>	<p>X</p> <p><math>\alpha = \frac{1}{2} \left[ \frac{k_2}{a} (t - t_0) \right]^3 - \frac{3}{16} \left[ \frac{k_2}{a} (t - t_0) \right]^4</math></p>
<p>Nucleation on all faces</p>	<p>Contracting rectangle, <math>a \gg c</math>, <math>b \gg c</math>. The interface is of constant width equal to the thickness of plates</p> <p><math>\alpha = \frac{2k_2}{ab} (t - t_0)[a + b - 2k_2(t - t_0)]</math> VI</p> <p>Circular plate nucleated at the perimeter, <math>a</math> — initial radius of a plate</p> <p><math>\alpha = \frac{2k_2}{a} (t - t_0) - \left[ \frac{k_2}{a} (t - t_0) \right]^2</math> VII</p> <p>Contracting parallelepipeds, <math>a = b, c</math></p> <p><math>\alpha = 1 - \frac{1}{a^2 b} [a - 2k_2(t - t_0)]^2</math> VIII</p> <p><math>[b - 2k_2(t - t_0)]</math> VIII</p> <p>Spherical particles of initial radius <math>a</math></p> <p><math>\alpha = 1 - \left[ 1 - \frac{k_2}{a} (t - t_0) \right]^3</math> IX</p>	

of kinetic equations is given in the literature [3–7] for different mechanisms of nucleation and growth of the nuclei. Fifteen equations out of those given by Jacobs and Tompkins [4] were considered, in order to find out which of them gives the best description of the investigated reaction. These equations give the relationship between the degree of decomposition ( $\alpha$ ) and time ( $t$ ). The degree of decomposition can be calculated as a ratio of the volume at a given time to the initial volume of a crystal. Equation for nucleation according to the power law is given below; fourteen others are in Table 1.

$$\alpha = C_1(t - t_0)^n \quad (1)$$

In all equations  $k_1$ ,  $k_2$  and  $k_3$  designate the rate constants of nucleation, growth and branching of nuclei respectively,  $t_0$  is the time required for attainment of the constant growth rate of nuclei, or the time required to establish the interface.  $C_1, C_2, \dots$ , are constants.

### Experimental

The kinetics of the thermal decomposition of ammonium thiocarbamate was investigated under isothermal conditions using a McBain balance [8]. The examined compound was synthesized from ammonia and carbon oxysulphide [9–11]. The crystals obtained were sifted and the fraction of sieve mesh 0.75–1.02 mm was stored in a desiccator over  $P_2O_5$  at 277 K. The mean dimensions of this fraction, found via a microscope, were 2.0 and 1.1 mm. The weight of the investigated samples was of the order of 0.10 g.

### Results and discussion

Degree of decomposition ( $\alpha$ ) versus time ( $t/t_{0.9}$ ), where  $t_{0.9}$  is the time needed for 90% decomposition, is plotted in Fig. 1. Graphical analysis showed that the results can be expressed using equation IX (see Fig. 2). Some deviations from this equation were observed at the beginning and at the end of the reaction. Further investigations were aimed at finding an equation describing the experimental results over a wider range of  $\alpha$ .

In order to find which of the fifteen equations gives the best fit to the experimental data, the values of the parameters were calculated by the least-squares method:

$$S_j = \sum_{i=1}^m [\alpha_i - \eta_j(\Theta_j, t_i)]^2 w_i$$

where

- $S_j$  = the weighted sum square for the  $j$ -th equation
- $m$  = number of experimental points
- $\alpha$  = degree of decomposition

$\Theta_j = \|\Theta_{1j}, \Theta_{2j}, \dots, \Theta_{n_jj}\|$  = the vector of parameters of the  $j$ -th equation

$n_j$  = number of parameters in the  $j$ -th equation

$t$  = time counted from the beginning of the reaction

$\eta_j(\Theta_j; t)$  = calculated degree of decomposition from the  $j$ -th equation

$\alpha_i$  = mean value of  $r_i$  experiments

$$\alpha_i = \frac{1}{r_i} \sum_{l=1}^{r_i} \alpha_{il}$$

$\omega_i$  = statistical weight

$$\omega_i = \frac{r_i}{s_i^2}$$

$s_i^2$  = variance [for  $r_i$  experiments]

$$s_i^2 = \frac{1}{r_i - 1} \sum_{l=1}^{r_i} (\alpha_{il} - \alpha_i)^2$$

$r_i - 1 = f_i$  = degrees of freedom for  $s_i^2$ .

The calculations were performed using a "Minuite" programme [12]. The calculated values of the weighted sum squares are given in Table 2. These calculations were performed for the experiments carried out at 339.6 K. One can see from Table 2 that the lowest values of the sum squares are for equations VI, VII and VIII.

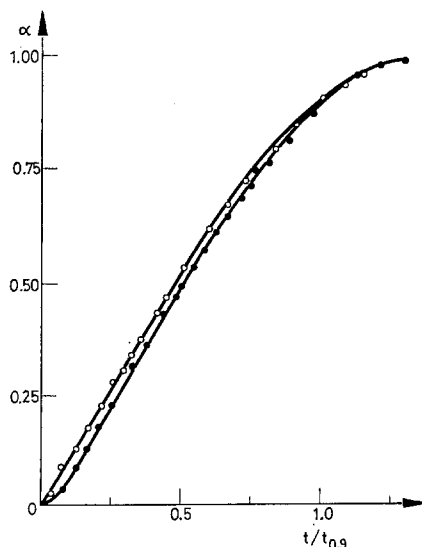


Fig. 1. Dependence of degree of decomposition ( $\alpha$ ) on time ( $t/t_{0.9}$ ). ● 355.2 K,  $t_{0.9} = 24$  min; ○ 313.4 K,  $t_{0.9} = 227$  min

Table 2

Values of weighted sum squares ( $S_j$ ), variances ( $s_{2j}^2$ ) and degrees of freedom ( $f_{2j}$ ), calculated for experiments performed at 339.6 K. Fraction of sieve mesh 0.75–1.02 mm

Model, $j$	$S_j$	$s_{2j}^2$	$f_{2j}$
I	$2.46 \cdot 10^3$		
II	$6.14 \cdot 10^4$		
III	$6.15 \cdot 10^4$		
IV	$1.51 \cdot 10^3$	$1.76 \cdot 10^{-3}$	36
V	$9.54 \cdot 10^3$		
VI	$1.59 \cdot 10^2$	$1.62 \cdot 10^{-4}$	34
VII	$2.50 \cdot 10^2$	$2.19 \cdot 10^{-4}$	36
VIII	$3.88 \cdot 10^2$	$3.62 \cdot 10^{-4}$	34
IX	$1.70 \cdot 10^3$	$1.21 \cdot 10^{-3}$	36
X	$3.72 \cdot 10^3$		
XI	$9.15 \cdot 10^3$		
XII	$8.00 \cdot 10^2$	$7.45 \cdot 10^{-4}$	36
XIII	$1.28 \cdot 10^5$		
XIV	$1.22 \cdot 10^4$		
XV	$1.09 \cdot 10^3$	$1.11 \cdot 10^{-3}$	36

Hence these are the equations of best fit for the obtained experimental data. Equation IX, chosen previously on the basis of graphical analysis, does not fit the experimental results so well as seemed. Variance analysis (test F), applied to compare the variances for equations VI, VII and VIII, showed that these variances are equivalent.

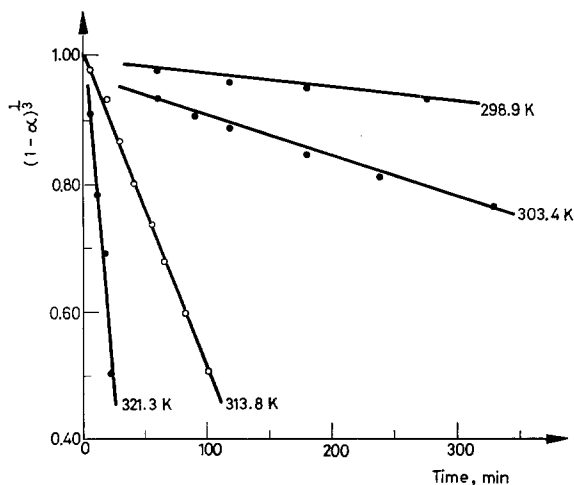


Fig. 2. Dependence of  $(1 - \alpha)^{1/3}$  on time in the temperature range 303–321 K. Fraction of sieve mesh 0.50–0.60 mm

$$S_{2,j}^2 = \frac{S_j^0}{m - n_j}$$

where

- $S_j^0$  = unweighted sum squares
- $f_2$  =  $m - n_j$  = degrees of freedom
- $n_j$  = number of parameters in the  $j$ -th equation.

In the next stage of the attempts to find the best kinetic equation, a series of experiments was carried out. Each one was followed by statistical analysis in order to plan successive experiments depending on the results of the previous one [13–15].

Calculations were carried out with a programme which had the following functions to perform:

1. Calculation and refinement of parameter values for each equation (model). This was done by the least-squares method, minimizing the function  $S_j$  by quasi-linear estimation [15].

$$\Theta_j^{(s+1)} = \Theta_j^{(s)} + M_j^{-1}(\Theta_j^{(s)}) Y_j(\Theta_j^{(s)}), \quad j = 1, 2, \dots, k$$

$$M_j(\Theta_j^{(s)}) = \sum_{i=1}^m \omega_i F_j(\Theta_j^{(s)}, t_i) F_j^T(\Theta_j^{(s)}, t_i)$$

$$Y_j(\Theta_j^{(s)}) = \sum_{i=1}^m \omega_i [\alpha_i - \eta_j(\Theta_j^{(s)}, t_i)] F(\Theta_j^{(s)}, t_i)$$

$$F_j(\Theta, t) = \nabla \eta_j(\Theta, t)$$

$$\nabla^T = \left\| \frac{\partial}{\partial \Theta_1}, \frac{\partial}{\partial \Theta_2}, \dots, \frac{\partial}{\partial \Theta_n} \right\|$$

where

- $M_j(\Theta_j)$  = Fisher's information matrix for the  $j$ -th equation
- $k$  = number of equations.

2. Calculation of the probability function ( $L$ ) and the values of probability ( $q$ ) for each model

$$L_j = (2\pi)^{(n_j-m)/2} \prod_{i=1}^m \omega_i \sqrt{|M_j^{-1}(\Theta_j^{(s+1)})|} \exp [-S_j(\Theta_j^{(s+1)})]$$

$$q_j = p_j L_j / \left( \sum_{i=1}^k p_i L_i \right)$$

where

- $|M_j^{-1}(\Theta_j^{(s+1)})|$  = determinant of the variance matrix calculated for the "best" values of the parameters

$p_j$  = the value of the a priori probability of the  $j$ -th model.

## 3. Planning of the next experiment

- a) in order to obtain more accurate values of the parameters;  
 b) in order to discriminate between the fifteen different hypothetical models.

The solution of this problem was found by a simple method. A table of values of  $\alpha$  functions for equidistance values of time was constructed. For each value of  $t$ , the value of the square root of  $d_j$  and the Kullback measure of divergence [13], [Q], were computed.

$$d_j^{(i)} = F_j^T(\Theta_j^{(s+1)}, t_i) M_j^{-1}(\Theta_j^{(s+1)}) F_j(\Theta_j^{(s+1)}, t_i)$$

$$Q_i = \frac{1}{2} \sum_{l=1}^k \sum_{j=l+1}^k q_l q_j \left\{ \frac{d_l^{(i)} + d_j^{(i)}}{(s_1^2 + d_l^{(i)})(s_1^2 + d_j^{(i)})} + (\eta_l^{(i)} - \eta_j^{(i)})^2 \left( \frac{1}{s_1^2 + d_l^{(i)}} + \frac{1}{s_1^2 + d_j^{(i)}} \right) \right\}$$

where

$s_1^2$  = experimental variance

$$s_1^2 = \frac{\sum_{i=1}^m f_i s_i^2}{f_1}$$

$f_1 = \sum_{i=1}^m f_i$  = degrees of freedom of the variance  $s_1^2$ .

The programme for planning the successive experiments was written on the assumption that the degree of experimental difficulty remains constant throughout the whole reaction range [14, 15]. Following the experiment planning scheme, each

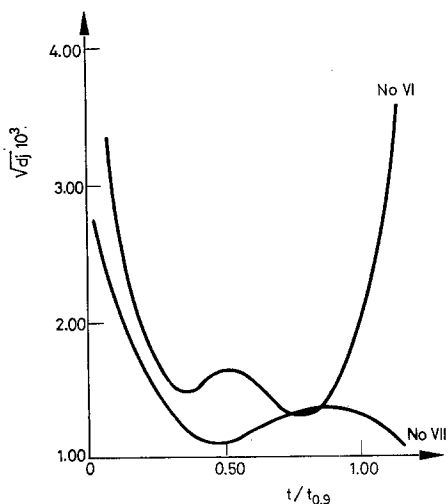


Fig. 3. Dependence of  $d_j$  on time



successive measurement was carried out for those values of time  $[t]$  for which  $d_j$  and  $Q$  had the greatest values. The results are presented in Figs 3–5. Figures 3 and 4 show in turn the dependence of  $d_{VI}$ ,  $d_{VII}$  and  $Q$  on time for experiments performed at 339.6 K. Curve 1 in Fig. 3 corresponds to the initial experiments; curve 2 was obtained after the additional measurements had been made. The changes in the probability values for models VI and VIII are presented in Fig. 5. They were assumed initially equal for both models, and with each successive experiment the value of  $q$  for model VI increased. When  $q$  reached a value of 0.99 for model VI, the experiments were stopped. The values of variances ( $s_2^2$ ), degrees of freedom,  $F$ -test

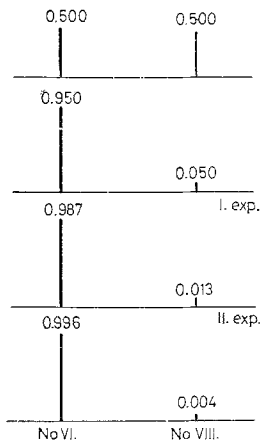


Fig. 4. Dependence of  $Q$  on time. Curve 1. Values of  $Q$  corresponding to the initial data; curve 2. Values of  $Q$  obtained after the additional experiments

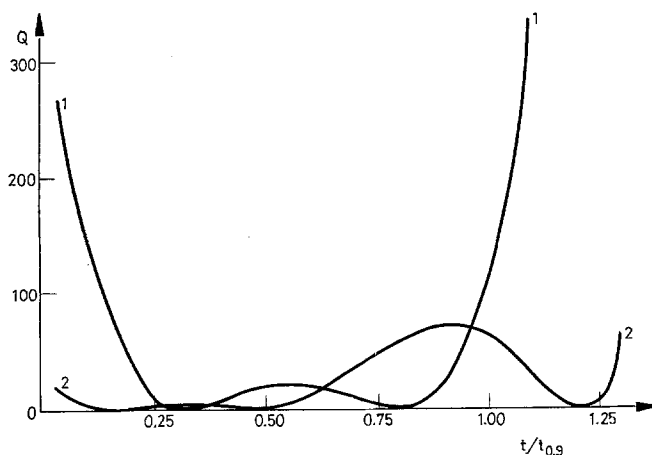


Fig. 5. Changes of probability ( $q$ ) in successive experiments

values and  $F_{0.05}$  values, calculated on the basis of all the experimental data, are given in Table 3. As can be seen from this Table, the  $F$  calculated is smaller than  $F_{0.05}$  only for equation VI, and hence only this equation describes the experimental results in an adequate way.

The values of the degree of decomposition calculated from equation VI and those obtained experimentally are given in Table 4.

Table 3

Values of variances ( $s_{2j}^2$ ), degrees of freedom ( $f_{2j}$ ),  $F$ -test and  $F_{0.05}$  for experiments performed at 339.6 K.  $s_1^2 = 6.83 \cdot 10^{-5}$ ,  $f_1 = 160$

Model, $j$	$s_{2j}^2 \cdot 10^5$	$f_{2j}$	$F$	$F_{0.05}$
IV	85.88	48	12.57	1.43
VI	6.01	46	1.14	1.52
VII	18.88	48	2.76	1.43
VIII	10.58	46	1.55	1.44
IX	85.37	48	12.50	1.43
XII	37.95	48	5.56	1.43
XV	40.79	48	5.97	1.43

Table 4

Experimental values of  $\alpha$  and those calculated from equation VI.  
Temperature 339.6 K

Degree of decomposition $\alpha \cdot 10^3$	
experimental value	value calculated from equation VI
36	25
82	80
111	106
186	184
307	307
398	399
524	525
677	673
838	825
992	992

It was successfully verified for various samples of ammonium thiocarbamate that equation VI adequately describes the kinetics of the studied reaction in the temperature range 303–353 K and over the whole range of  $\alpha$ . Usually two or three equations are needed to describe such a process. In the studied reaction gaseous products were continuously removed during the course of the reaction

and this is the likely explanation of why equation VI fits the experimental results over the whole reaction range.

The calculated values of the parameters for equation VI are presented in Table 5, together with the values of the parameters for equation VIII, for comparison pur-

Table 5

Values of parameters for equations VI and VIII calculated for different temperatures of decomposition of ammonium thiocarbamate

T, K	Values of parameters							
	equation VI				equation VIII			
	$k_2 \cdot 10^3$ mm/min	$t_0$ min	$a$ mm	$b$ mm	$k_2 \cdot 10^3$ mm/min	$t_0$ min	$a$ mm	$b$ mm
313.4	2.847	7.138	1.53	2.81	1.945	7.411	1.03	3.64
323.8	5.675	2.202	1.48	2.77	3.379	5.101	1.35	1.53
339.6	9.810	2.432	1.07	1.98	5.435	2.523	0.59	1.99
343.1	15.066	2.332	1.35	2.44	5.365	2.407	0.54	1.84
352.0	21.003	1.979	1.35	2.46	7.807	1.895	0.49	1.70
355.2	22.653	1.923	1.28	2.35	8.130	1.984	0.45	1.56

poses. The values of  $a$  and  $b$  representing the dimensions of the crystal are, for equation VI, in agreement with the results of the crystal measurements under the microscope. The same does not hold for equation VIII. Both equations were derived with the assumption of the same model for nucleation and growth of the nuclei on the crystal surface, the only difference being that they assumed different crystal shapes.

It was found that the temperature dependences of constants in  $k_2$  and  $t_0$  in equation VI are as follows:

$$k_2 = 8.91 \cdot 10^4 \exp \left( - \frac{10700}{RT} \right)$$

$$t_0 = 5.45 \cdot 10^{-5} \exp \left( \frac{7340}{RT} \right)$$

The calculated value of the activation energy of the thermal decomposition ammonium thiocarbamate is 10.7 kcal/mole.

### Conclusions

1. The process of the thermal decomposition of ammonium thiocarbamate in vacuum is described adequately by equation VI in the temperature range 303–353 K over the entire decomposition range. This was found by the use of statistical analysis.

2. The temperature dependences of  $k_2$  and  $t_0$  for equation VI were found, and an activation energy of 10.7 kcal/mole was calculated.

3. The example of this study illustrates the fact that the successive planning of experiments gives good guidance as to how to carry them out in order to obtain the maximum information in the shortest time.

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RÉSUMÉ — On présente les résultats de l'étude cinétique de la décomposition thermique du thiocarbamate d'ammonium, sous vide (environ  $10^{-2}$  torr), dans l'intervalle de température compris entre 303 et 353 K. Dans ces conditions, le thiocarbamate d'ammonium se décompose en donnant naissance à des produits gazeux ( $\text{NH}_4\text{COSNH}_2 \rightarrow 2\text{NH}_3 + \text{COS}$ ). On a envisagé quinze équations cinétiques générales de décomposition thermique des corps solides. L'équation suivante décrit les résultats expérimentaux dans tout l'intervalle de décomposition:

$$\alpha = \frac{2k_2}{ab}(t - t_0)[a + b - 2k_2(t - t_0)],$$

avec  $\alpha$  = taux de décomposition,  $t$  = le temps,  $t_0$  = le temps nécessaire pour atteindre la vitesse de grossissement constante d'un germe,  $a$  et  $b$  = dimensions du cristal. On a déterminé la relation entre la constante de vitesse  $k_2$  et la température et on a établi la valeur de l'énergie d'activation (10,7 kcal.mol<sup>-2</sup>). Dans cette étude, on a planifié le mode opératoire de la manière suivante: chaque série d'expériences a été suivie d'une étude statistique pour choisir les expériences suivantes dont les résultats dépendent de celles qui ont précédé.

ZUSAMMENFASSUNG — Die Ergebnisse der kinetischen Untersuchungen der thermischen Zersetzung von Ammoniumthiocarbamat im Vakuum (etwa  $10^{-2}$  torr) im Temperaturbereich von 303 bis 353 K werden vorgestellt. Unter diesen Bedingungen wird Ammoniumthiocarbamat in gasförmige Produkte zersetzt ( $\text{NH}_4\text{COSNH}_2 \rightarrow 2\text{NH}_3 + \text{COS}$ ). Fünfzehn allgemeine kinetische Gleichungen der thermischen Zersetzung von Festkörpern wurden in Betracht gezogen. Die folgende Gleichung beschreibt die Versuchsergebnisse im ganzen Bereich der Zersetzungsgrade:

$$\alpha = \frac{2k_2}{ab} (t - t_0)[a + b - 2k_2(t - t_0)],$$

( $\alpha$  = Zersetzungsgrad,  $t$  = Zeit,  $t_0$  = die zur Erreichung der konstanten Wachstumsgeschwindigkeit eines Kerns benötigte Zeit,  $a$  und  $b$  = Abmessungen des Kristalls). Die Temperaturabhängigkeit der Geschwindigkeitskonstante  $k_2$  wurde bestimmt und die Aktivierungsenergie gleich 10,7 Kcal/mol gefunden. Das Schema der Versuchsplanung wurde bei diesen Untersuchungen angenommen. Hierbei wurden in einer Versuchsreihe alle Einzelversuche durch statistische Analyse ausgewertet, um die nachfolgenden Versuche in Abhängigkeit der Ergebnisse der vorhergehenden zu entwerfen.

Резюме — Представлены результаты кинетических исследований термического разложения тиокарбамата аммония в вакууме (около  $10^{-2}$  тор) в области температур 303—353°K. В этих условиях тиокарбамат аммония разлагается на газообразные продукты ( $\text{NH}_4\text{COSNH}_2 \rightarrow 2\text{NH}_3 + \text{COS}$ ). Учитывалось пятнадцать общих уравнений кинетики термического разложения твердых тел. Приведено уравнение, которое описывает экспериментальные результаты степени разложения во всей области температур:

$$\alpha = \frac{2k_2}{ab} (t - t_0)[a + b - 2k_2(t - t_0)],$$

где  $\alpha$ -степень разложения,  $t$ -время,  $t_0$ -время, требуемое для достижения постоянной скорости ядра,  $a$  и  $b$ -параметры кристалла. Была определена температурная зависимость константы скорости  $k_2$  и было найдено, что энергия активации равна 10,7 ккал/моль. В настоящем исследовании был принят эксперимент планирующей схемы: в серии экспериментов за каждым из которых следовал статистический анализ для того, чтобы планировать успешные эксперименты, зависящие от результатов одного из предыдущих.