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EQUILIBRIUM PARAMETERS OF NICKEL SULPHATE DECOMPOSITION AND ITS RATE

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ABSTRACT

This paper presents the results of the nickel sulphate decomposition by a static and a kinetic method.

The first allows to define the equilibrium pressures of gases as a result of this decomposition.

Hence, the free energy and the inversion temperature has been obtained. By the other method, based on thermogravimetric analysis the values of the stable rate and of the activation energy, can be found for this process.

The authors also pay attention to the excess oxygen appearing in the nickel oxide phase.

The amount of this excess speaking about nonstoichiometry proves that this compound depends clearly on the decomposition parameters.

1. INTRODUCTION

Nickel sulphate won from waste electrolyte after copper electrorefining may be used, after prior treatment, as parent substance for oxide production.

The oxygen concentration in nickel oxide—a typical stoichiometric compound—exceeds the stoichiometric value. This is proved by the amount of so-called excess oxygen which ought to be accompanied by an adequate number of Ni^{3+} ions if the electric inertness of the NiO crystalline lattice should be preserved.

The results obtained by the authors during their research[1-3] prove that the larger part of excess oxygen is chemically adsorbed at the NiO surface. On the other hand, Charman et al.[4] state the presence of some quantities of crystalline oxygen. Excess oxygen concentration in NiO depends on the time and the temperature of the decomposition process as well as of the parent substance nature[1, 5, 6]. No information is found in the literature about the effect of nickel sulphate decomposition conditions on the characteristics of the oxide won in the process.

Literature on the decomposition of anhydrous nickel sulphate is very discordant.

According to Hoffman and Wanjukow[7], the process starts at 702°C and its development becomes quite intensive at 764°C. The authors of refs. 8–11 state, on the basis of TG and DTA curve analysis, that decomposition temperatures remain within the range between 675 and 855°C. The alluded discrepancies are quite comprehensible when taking into consideration the fact that, in the adopted investigation, the most important parameters are heating rate, gaseous phase flow-rate as well as the mass of the preparation subjected to the analysis.

No data are available in the literature about the decomposition rate of nickel sulphate under isothermic conditions, and the only information found is the value of activation energy 27.6 kcal mol^{-1} cited in ref. 12.

Some minor discrepancies appear in data on the inversion temperature of NiSO$_4$. They remain within the temperature range between 840 and 890°C.

The discrepancies mentioned above induced the authors of the present paper to investigate nickel sulphate decomposition under static and kinetic conditions. The results of the research will be discussed below.

2. EQUILIBRIUM PRESSURES OF GASES GENERATED IN THE NICKEL SULPHATE DECOMPOSITION PROCESS

When developing the procedure of NiO obtained by thermal nickel salt de-

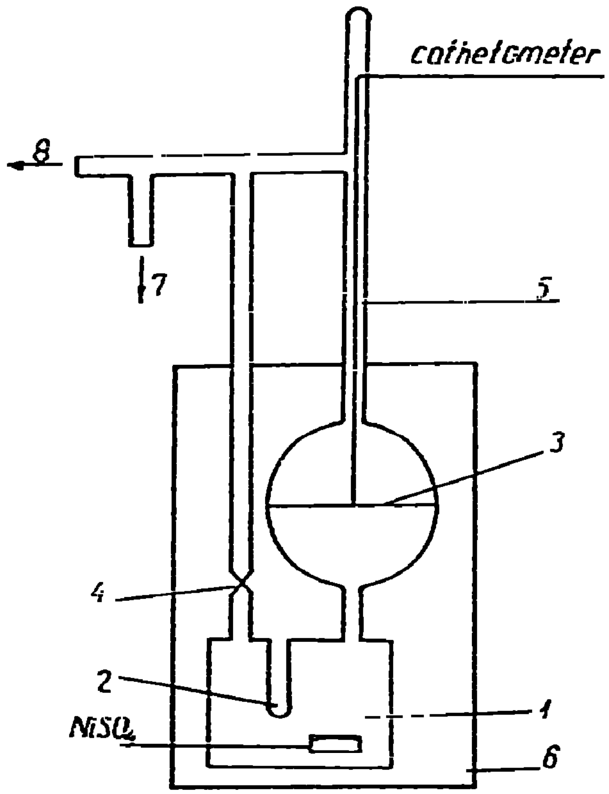

Fig. 1. Schematic drawing of the measurement apparatus: 1 – closed thermodynamic space; 2 – thermocouple seat; 3 – quartz membrane; 4 – point where space 1 was closed by melting the end of the quartz tube; 5 = quartz rod; the displacement of its upper end was followed-up by a cathetometer; 6 = furnace; 7 = needle valve for pressure variation compensation within space 1.

composition, it is very important to know not only the data related to the kinetics but also those on the equilibrium. The latter allow, as we know, to determine the dependence of pressure and composition of the appearing gas phase on temperature. Hitherto, this type of test was performed only by Marchal[7] within the temperature range 700 to 950°C.

In order to determine the relationships mentioned above, the authors of the present paper had adopted a manometric method for the measurement of pressure variation within a closed system. The schematic drawing of the measurement apparatus is shown in Fig. 1.

The tests were carried out on specpure nickel sulphate ($NiSO_4 \cdot 7H_2O$) subjected previously to dehydration at 600°C under 10^{-2} Tr pressure. The principle on which the measurements were based is described below.

At a given temperature "*T*" the gases generated at the equilibrium state have a pressure value "*P*" originating a deflection of the quartz membrane[1]. Under the effect of these alterations, the end of a quartz bar changes its position, this displacement being followed up by a cathetometer. The pressure above the membrane is controlled by means of a needle valve[7] down to the neutral position of the membrane.

TABLE 1

VALUES OF EQUILIBRIUM PRESSURES DEPENDING ON TEMPERATURE IN NICKEL SULPHATE DECOMPOSITION (MEASUREMENTS RESULTS)

T (K)	*P (mm Hg)*
1064	68
1074	96
1080	117
1091	151
1095	166
1102	192
1104	206
1105	211
1107	238
1109	247
1114	257
1117	272
1120	286
1125	312
1130	343
1135	376
1140	423
1141	431
1144	470
1146	498
1150	524
1154	555
1156	575
1158	591

The pressure value read on the manometer[8] is assumed to be equal to the pressure in the system. It should also be pointed out that, at the neutral position of the membrane, the pressure value in the system was equal to the ambient pressure.

Since this position was a temperature function, each measurement was followed by adequate calibration. After preliminary operations, the preparation was inserted in the space of system[1] and the system closed subsequently at point[4]. Variations of the equilibrium values with temperature were then recorded.

The accuracy of the method adopted is of the order of 1 Torr. It is due to the fact that pressure variations of 1 mm Hg in the system originate from a membrane deflection of 0.03 mm and the accuracy of the cathetometer reading is 0.01 mm. The measurement results are recapitulated in Table 1.

The following scheme of process development was adopted for partial equilibrium pressures according to the information found in the literature:

$$\begin{aligned} &(1)\ NiSO_4 \rightarrow NiO + SO_3 \\ &(2)\ SO_3 \rightarrow SO_2 + 1/2\, O_2 \end{aligned} \qquad (2.1)$$

At the equilibrium state, each of the reactions cited above is thus in equilibrium. Consequently, the tested system may be described by the equations below:

$$\begin{aligned} &(1)\ K_1 = \frac{P_{SO_3}}{760} \\ &(2)\ K_2 = \frac{P_{SO_2} \cdot P_{O_2}^{1/2}}{760^{1/2} \cdot P_{SO_3}} \\ &(3)\ P = P_{SO_3} + P_{SO_2} + P_{O_2} \\ &(4)\ P_{SO_2} = 2\, P_{O_2} \end{aligned} \qquad (2.2)$$

where: K_1, K_2 are constant equilibrium values for the first and second reaction, (2.1) respectively; and P_i is partial pressure of gaseous phase components.

When applying Kubaschewski's relationship

$$\Delta G_2 = 22\,600 - 21.36\, T$$

which interprets free enthalpy variations with temperature in the second reaction of (2.1), one may calculate K_2 and, consequently, P_{O_2}, P_{SO_2}, P_{SO_3} from eqns 2, 3, 4 of (2.2).

With known P_{SO_3} and on the basis of eqn 1 of (2.2), we calculate K_1 and subsequently the variation of free enthalpy:

$$\Delta G_1 = -RT \ln K_1$$

The variability of this function with temperature is illustrated by the linear relationship

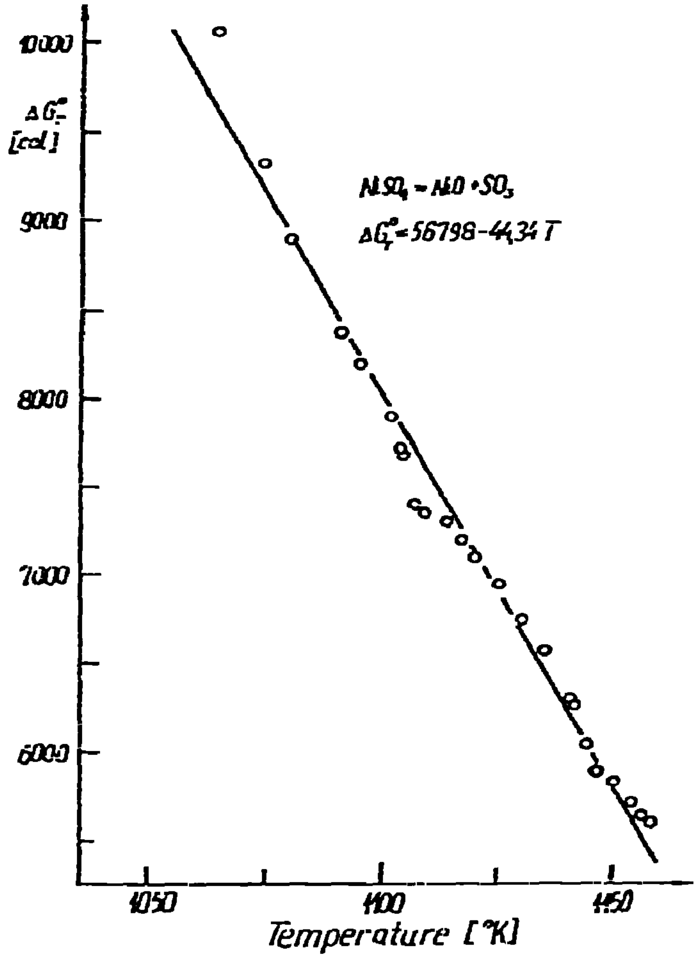

Fig. 2. Variation of free enthalpy with temperature for $NiSO_4 \rightarrow NiO + SO_3$ reaction (tested by the authors).

$$\Delta G_1 = 56\,798 - 44.34\,T$$

represented in Fig. 2.

In Fig. 3, the obtained results are compared with Marchal's data[7] as well as with the ones cited by Barin[13].

The value of partial equilibrium pressure, of stable equilibrium and free enthalpy variations are specified in Table 2.

The obtained relationship for free enthalpy variations with temperature is similar to the Marchal's function[7] (Fig. 3). Both lines, however, deviate considerably in values from Barin's data[13].

Presumably, the temperature of 600 °C was too low to achieve an entire elimination of water. With the measurement techniques adopted, even insignificant quantities of water may originate a shift of the $P = f(T)$ curve, i.e., even such concentration of H_2O which cannot be detected on the TG curve in thermogravimetric tests. The conditions of preparation dehydration were determined on the basis of thermogravimetric test results.

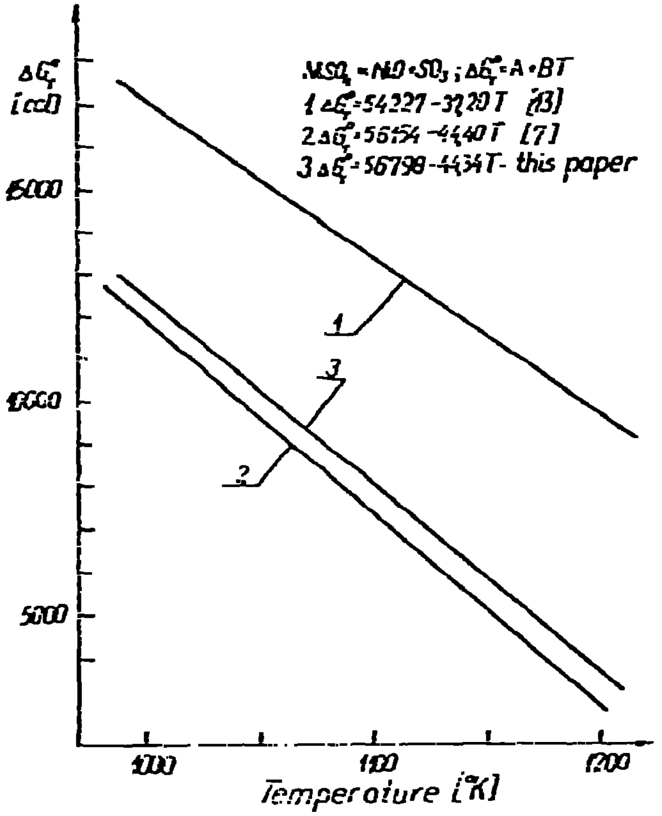

Fig. 3. Variation of free enthalpy with temperature for $NiSO_4 = NiO + SO_3$.

On the basis of the information specified above, the temperature of nickel sulphate inversion may be determined. For the condition $P_{SO_3} = 1$ atm, it is of 1008°C, whereas with the assumption $P = P_{SO_3} + P_{SO_2} + P_{O_2} = 1$ atm it is 900°C.

3. INVESTIGATION OF $NiSO_4$ DECOMPOSITION KINETICS

The tests were carried out with the purpose to find the relationship between the speed of the $NiSO_4$ decomposition reaction and the temperature and duration of the process. The first stage of testing consisted of the determination of the temperature range in the dehydration of hydrous nickel sulphate and its decomposition into NiO and SO_3. The second stage concerned the examination of the reaction of anhydrous nickel sulphate decomposition under isothermic conditions.

The process of dehydration and decomposition of pure nickel sulphate $NiSO_4 \cdot 7H_2O$ was carried out after the thermogravimetric method on a Mettler TA-1 thermoanalyzer. The obtained thermogram is shown in Fig. 4. The development of the recorded mass variations TG and DTG as well as of the heat of reaction DTA as a temperature function shows that the dehydration of hydrous nickel sulphate develops in three subsequent stages, this being proved by the peaks on DTG and DTA. Thus, the process is developing itself at the following temperatures determined from DTG and DTA peaks: $T_1 = 125°C$, $T_2 = 155°C$.

TABLE 2

EQUILIBRIUM VALUES OF PARTIAL PRESSURES, STABLE EQUILIBRIUM AND FREE ENTHALPY IN $NiSO_4 = NiO + SO_3$ REACTION

T (K)	P_{SO_3} *(mm Hg)*	SO_3 *(%)*	P_{SO_2} *(mm Hg)*	P_{O_2} *(mm Hg)*	$NiSO_4 = NiO + SO_3$ K_1	G_1 *(cal)*
1064	6.5	9.55	41	20.5	0.008553	10066
1074	9.6	10	57.6	28.8	0.01263	9329
1080	12	10.26	70	35	0.01579	8902
1091	16	10.6	90	45	0.02105	8369
1095	17.5	10.54	99	49.5	0.02303	8204
1102	20.6	10.46	117.6	58.8	0.02711	7899
1104	22.4	10.87	122.4	61.2	0.02947	7731
1105	22.9	10.85	125.4	62.7	0.03013	7689
1107	26.5	11.13	141	70.5	0.03487	7382
1109	27.1	10.97	146.6	73.3	0.03566	7346
1114	28.1	10.93	152.6	76.3	0.03697	7299
1117	29.6	10.88	161.6	80.8	0.03895	7203
1120	31.3	10.94	169.8	84.9	0.04118	7099
1125	34.2	10.96	185.2	92.6	0.045	6932
1130	37.6	10.96	203.6	101.8	0.04947	6750
1135	41.2	10.96	223.2	111.6	0.05421	6573
1140	46.8	11.06	250.8	125.4	0.06158	6313
1141	47.6	11.04	255.6	127.8	0.06263	6281
1144	53	11.28	278	139	0.06974	6053
1146	57	11.45	294	147	0.075	5898
1150	59	11.26	310	155	0.07763	5839
1154	62.4	11.24	328.4	164.2	0.08211	5731
1156	65	11.30	340	170	0.08553	5648
1158	66.3	11.22	349.8	174.9	0.08724	5612

The first and the second dehydration stages develop within a narrow temperature range, which does not allow to determine each stage separately. The residual water is lost at 385°C.

Within the temperature range between 450 and 700°C, the preparation does not alter its mass which proves that a complete sulphate dehydration took place. Above 700°C, a minor deviation from the line may be noticed on TG, DTG and DTA, which indicates the beginning of the nickel sulphate decomposition reaction which reaches its maximum speed at 845°C.

In the investigations of the kinetics of the nickel sulphate decomposition reaction, we used an anhydrous preparation obtained by keeping hydrous salts at a temperature of 600°C till a solid mass was obtained. This temperature ensured a complete dehydration without originate decomposition. The sample was put into a furnace, heated to the required temperature at a rate of 25 and 100°C min^{-1}. The decomposition was carried out under air atmosphere flowing through the furnace at a rate of 5 l h^{-1}. The calculation of mass decrement started at the moment when the temperature in the furnace reached the set values. The decrements were recorded with

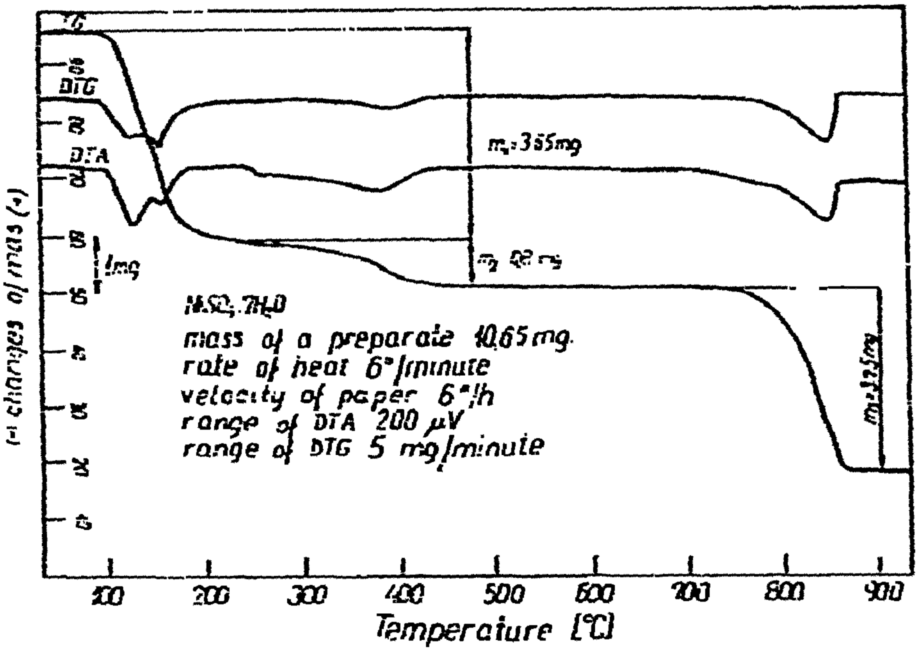

Fig. 4. Thermogram of $NiSO_4 \cdot 7H_2O$ decomposition under air atmosphere.

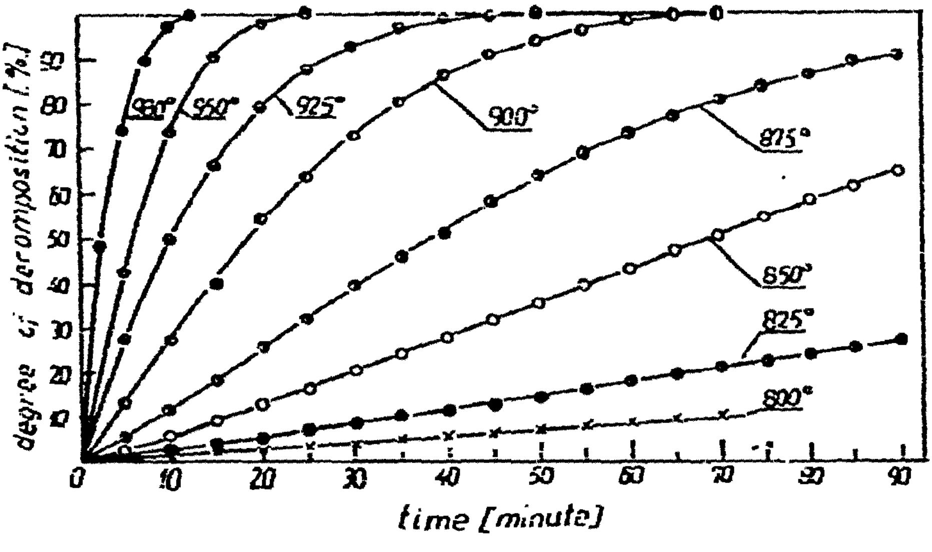

Fig. 5. Degree of $NiSO_4$ decomposition depending on time and temperature.

an accuracy of up to 1 mg. With the known SO_3 concentration in the parent substance the degrees of the decomposition could be easily calculated.

The obtained results are illustrated by the graph in Fig. 5. As can be seen from this graph, process temperature has an essential effect on the degree of decomposition. Within the temperature range between 800 and 900°C, each temperature increment by 25°C originates a nearly double increment of the reaction rate.

In order to obtain a more clear picture of this regularity, the obtained degrees of decomposition depending on time and temperature are compared in Table 3.

The obtained results related to nickel sulphate decomposition degree at various

TABLE 3

INFLUENCE OF TIME AND TEMPERATURE ON THE DEGREE OF NICKEL SULPHATE DECOMPOSITION

Temperature (°C)	*Process duration time (min)*	*Decomposition degree (%)*
800	70	11
825	90	28
850	90	65
875	90	91
900	70	100
925	50	100
950	25	100
980	15	100

TABLE 4

CALCULATION RESULTS OF KINETIC EQUATIONS, THE CALCULATIONS BEING CARRIED AFTER THE METHOD OF LINEAR CORRELATION ANALYSIS

Decomposition temp. (°C)	*Standard deviation*		*Correlation coefficient, R*	*Value of initial ordinate for $t \to 0$*	*Regression coefficient, K'*	*Confidence interval of K'*
	S_x	S_y				
800	22.36068	0.01184125	0.998987	1.0007398	− 0.00052902	− 0.00051475 − 0.00054329
825	28.13657	0.0322963	0.998597	1.0032368	− 0.00114623	− 0.00111513 − 0.00117333
850	28.13657	0.0936248	0.995195	1.018567	− 0.00331153	− 0.0031448 − 0.0034782
875	28.13657	0.1796491	0.998484	1.0257706	− 0.00637522	− 0.0061954 − 0.0065550
900	18.027756	0.2804758	0.9891756	1.0555212	− 0.0153896	− 0.0137811 − 0.0169980
925	15.1382518	0.2941635	0.999519	0.99185886	− 0.0194224	− 0.0189313 − 0.0199136
950	7.905694	0.3119020	0.996550	1.0193614	− 0.0393167	− 0.03330152 − 0.04533195
980	3.952847	0.2765746	0.9996413	0.9896413	− 0.0699257	− 0.0654344 − 0.0744170

temperatures were taken as a basis for kinetic equations. It was assumed at their derivation that the characteristics within the entire $NiSO_4$–NiO interface are identical and that the rate of reaction depends merely on the processes of interface displacement. For each case, the reaction rate expressed by the reactant volume transformed within a time unit may be described by the equation

$$-\frac{dm}{dt} = k \cdot S_i \qquad (3.1)$$

where: dm/dt is the reaction rate; k is the constant reaction rate; S_i is interphase.

The analysis of reaction kinetics after the formula (3.1) consists merely in the calculation of the interface S_i at each moment based on a geometrical model which takes into account the shape and the original position of the interface as well as its displacement speed during the decomposition process. After performing a series of mathematical operations required for the calculation of interface area S_i on the basis of mass decrement a reasonable relationship is obtained:

$$\sqrt[3]{\frac{m_{SO_3} - \Delta m_{SO_3}}{m_{SO_3}}} = 1 - K' t \qquad (3.2)$$

where: m_{SO_3} = original SO_3 concentration in the sample (mg); m_{SO_3} = mass decrement of the sample (mg); K' - constant proportional to reaction rate; t = time period of the process.

After the measurement points had been plotted on the graph according to relationship (3.2), it appeared that they take a linear course. This is also another evidence of the regularity of the equation adopted for the calculations. By taking this into consideration, the results obtained at various temperatures had been analyzed according to the linear correlation method which allowed to calculate kinetic equations for the process. The results of calculations carried out on the significance level 0.05 are specified in Table 4 and plotted on the graphs in Fig. 6.

The calculated regression lines display a quite good compatibility with the test results. This is proved also by the very high coefficients of linear correlation ($R > 0.99$) cited in Table 4.

In the calculated kinetic equations of the $NiSO_4$ decomposition reaction, the attention should be drawn to the initial ordinate for $t = 0$. As it results from equation

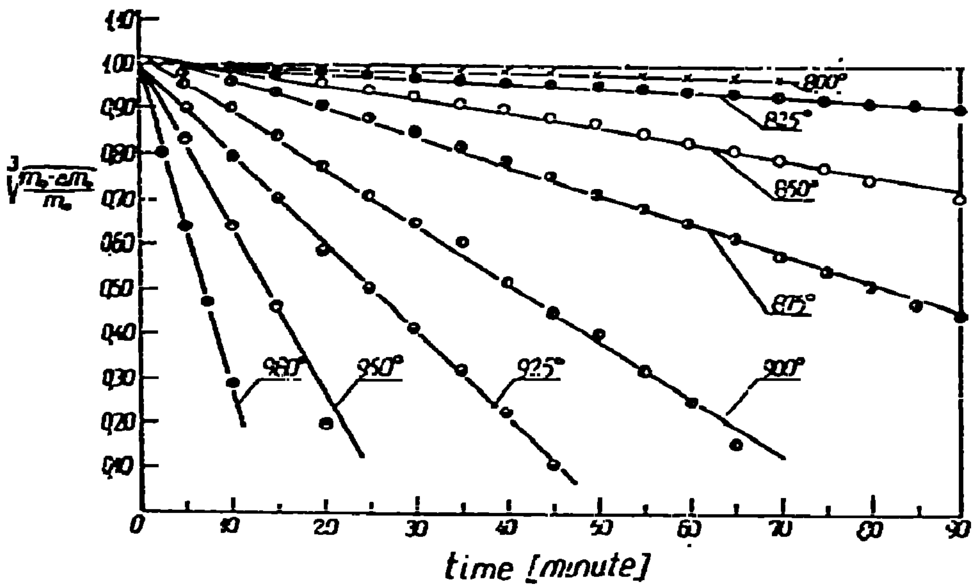

Fig. 6. Development of kinetic equations for the process of $NiSO_4$ decomposition depending on time and temperature.

(3.2) adopted in the calculations, this constant for $t = 0$ should take the value of 1. The calculation results show, however, that this constant differs from the theoretic value of the initial ordinate, the deviations being both positive and negative.

It should be pointed out, however, that the discrepancies between the calculated initial ordinate and the one derived from eqn (3.2) are not essential. This is proved by the very good compatibility between the test results and the equations.

The calculated kinetic equations allowed to find the relationship between the reaction rate and the temperature according to Arrhenius equation: $\log K' = A - B$ as well as to determine the energy of the process of nickel sulphate decomposition. The regression coefficients of the calculated equations (Table 4) correspond to constant K' in eqn (3.2). These constants plotted in the system $\log K' = f(1/T)$ had taken a linear pattern, this allowing to calculate the relationship. The calculation was carried out on the significance level 0.05 and the obtained results are:

standard deviation	$S_x =$	0.04634593
standard deviation	$S_y =$	0.7414884
correlation coefficient	$R =$	0.994532
constant *A*	$A =$	11.615833
constant *B*	$B =$	−0.15911515

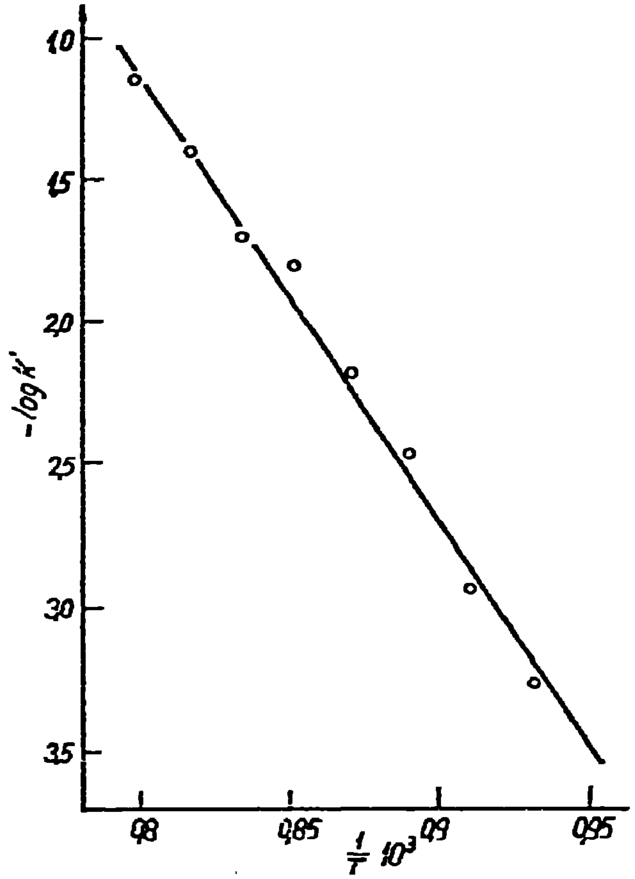

Fig. 7. Dependence of constant reaction rate on temperature.

confidence interval B from $= -0.142424126$
through $= -0.175806182$

The calculation results have been plotted on the graph in Fig. 7.

Activation energy determined on the basis of the calculated value B is of 72795 ± 7636 cal mol^{-1}.

The linear relationship $\log K' = f(1/T)$ within the entire temperature range as well as the high activation energy value are a proof that $NiSO_4$ decomposition reaction takes place within the kinetic area.

4. INFLUENCE OF $NiSO_4$ DECOMPOSITION CONDITIONS ON THE CONCENTRATION OF EXCESS IN NICKEL OXIDE

A subsequent stage of our investigation was the determination of the relationship between decomposition temperature and excess oxygen concentration in nickel oxide.

With this purpose, nickel oxide obtained by nickel sulphate decomposition at 900°C was subjected to X-ray analysis in a "TUR-M62" diffractometer. X-ray analysis carried out within the entire range of the angle θ allowed to state that the single phase appearing is nickel oxide NiO. This fact indicates that the presence of Ni_2O_3 is below the determination limit.

With the purpose to find the relationship between decomposition temperature and excess oxygen concentration in NiO, nickel sulphate was roasted at 900, 950 and 1000°C under air atmosphere and at 900°C under $2 \cdot 10^{-2}$ Tr vacuum. Each time the process lasted 120 min.

Excess oxygen concentration in NiO was determined after the modified Bunsen's and Rupp's method[14, 15]. The obtained results are recapitulated in Table 5 and indicate that nickel oxide won at 900°C through the decomposition of nickel sulphate contains 0.33% of excess oxygen.

This concentration diminishes proportionally to the rise of decomposition

TABLE 5

EXCESS OXYGEN CONCENTRATION IN NiO WON FROM $NiSO_4$ DECOMPOSITION

Atmosphere	*Decomposition temp. (°C)*	*Concentration (%)*				*% at. of excess oxygen*
		Ni^{2+}	*NiO*	*Ni^{3+}*	*Excess oxygen*	
air	900	76.8	97.73	0.17	0.0695	0.33
	950	77.0	97.98	0.15	0.0613	0.29
	1000	77.1	98.11	0.13	0.0531	0.25
vacuum	900	77.5	98.62	none	none	none

$2 \cdot 10^{-2}$ Tr

temperature. Far better effects are achieved when carrying out the decomposition process under vacuum conditions, where nickel oxide of stoichiometric composition may be obtained already at a temperature of 900°C.

In the decomposition process carried out under air atmosphere, excess oxygen cannot be removed completely even at a temperature of 1000°C order and, on the other hand, such conditions may originate sintering and growth of nickel oxide crystalline grains. Therefore, it seems more advisable to carry out the decomposition process under vacuum conditions.

5. CONCLUSIONS

The test results allowed to state that:

(1) Inversion temperature determined on the basis of equilibrium system examination, calculated for $P_{SO_3} = 1$ atm is of 1008°C, whereas its value for $P_{SO_3} + P_{SO_2} + P_{O_2} = 1$ atm is of 900°C.

(2) Decomposition rate under isothermic conditions, measured after the thermogravimetric method may be described by the equation:

$$-\frac{dm}{dt} = k\,S_i$$

According to the analysis result for the constant k in this equation, within the temperature range of 800–980°C: a temperature increase by 25°C is followed by a double increase of decomposition rate; the value of decomposition activation energy is 72795 ± 7636 cal mol^{-1}.

(3) Physical and chemical properties of nickel oxide depend on conditions of sulphate decomposition. This compound contains a certain quantity of excess oxygen, this being a proof that it is a non-stoichiometric compound. Nickel sulphate subjected to decomposition under air atmosphere within the temperature range between 900 and 1000°C gives a product which contains respectively 0.33 to 0.25 at.-% of excess oxygen, whereas, under vacuum conditions of 10^{-2} Tr at 900°C, it gives a product that has a stoichiometric composition.

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