

Kinetics and Mechanism of Solid-State Reaction between Cyclooctasulfur and Nickel Oxide

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The mechanism of reaction between sulfur and nickel oxide in the solid state was studied by chemical analysis, TGA, and capillary diffusion methods. Nickel oxide and sulfur react in the molar ratio 3 : 1 to give $\text{Ni}_3\text{S}_5 \cdot 3\text{H}_2\text{O}$. The data for lateral diffusion fit best in the equation $g = kt$. It has been also suggested by thermal analysis that S^{-2} ions are formed which are exchanged by O^{-2} ions.

Introduction

The solid-state reaction between powder sulfur and nickel oxide becomes interesting from the point of view of the S_8 ring. The formation of the final compound, hydrated trinickelpentasulfide ($\text{Ni}_3\text{S}_5 \cdot 3\text{H}_2\text{O}$), leads to a conclusion that molecular sulfur (I) becomes ionic sulfur by breaking of the S_8 ring during the course of solid-state reactions between sulfur and nickel oxide, $\text{NiO}_{1+x} \cdot \frac{1}{3}\text{H}_2\text{O}$, where $x \approx 1$, surplus oxygen. The breaking of the S_8 ring tempted us to investigate this reaction. The present paper describes the kinetics and mechanism of solid-state reaction between sulfur powder (S_8) and nickel oxide ($\text{NiO}_{1+x} \cdot \frac{1}{3}\text{H}_2\text{O}$), where $\text{Ni}_3\text{S}_5 \cdot 3\text{H}_2\text{O}$ is the final product.

Experimental

Materials

Nickel oxide ($\text{NiO}_{1+x} \cdot \frac{1}{3}\text{H}_2\text{O}$, $x \approx 1$, surplus oxygen). The basic nickel carbonate used was of 99.98% purity (Sarabhai Chem-

icals). Its decomposition temperature is reported to be 230°C (2). Nickel oxide ($\text{NiO}_{1+x} \cdot \frac{1}{3}\text{H}_2\text{O}$), where $x \approx 1$, surplus oxygen (2-4), was prepared by heating basic nickel carbonate $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ at 240°C for 6 hr. The presence of H_2O molecule in $\text{NiO}_{1+x} \cdot \frac{1}{3}\text{H}_2\text{O}$ has been confirmed by TG analysis.

The dynamic TGA of nickel oxide, carried out with the help of a thermogravimetric analyser (Fertilizer Corporation of India Ltd., Sindri) in a platinum crucible, given in Fig. 1, shows that dehydration occurs from $80-240^\circ\text{C}$. The calculated amount of $\frac{1}{3}$ water molecule comes out to be 6.2% against an observed value of 6.6%. M. Prasad, M. G. Tendulkar, M. Le Blanc, and H. Sachse (2) have reported that black-color nickel oxide contains one atom of surplus oxygen interstitially associated with the lattice. On heating to 800°C the green-color compound of NiO has also been confirmed by them. They have also reported that black nickel oxide containing surplus oxygen becomes reactive in the presence of other reactants (2). D. K. Goralevitsch (2)

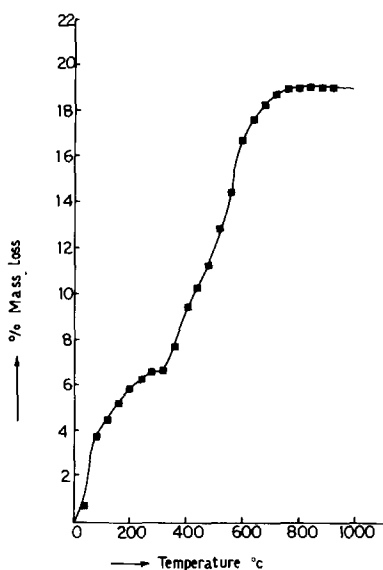


FIG. 1. Dynamic TG analysis of nickel oxide.

has reported that hydrated nickelous oxide containing surplus oxygen liberates its surplus (active) oxygen by the action of $\text{con} \cdot \text{H}_2\text{SO}_4 \cdot (\text{AR})$. As soon as nickel oxide was reacted with sulfuric acid, the residue turned green (NiO) from black, and finally dissolved on stirring with a glass rod. This shows that surplus oxygen was liberated by the action of sulfuric acid. The TGA also indicates a steep loss from 360–800°C. The observed value (12.4%) for the loss of one atom of oxygen from nickel oxide agrees within experimental error with respect to the calculated value (16.5%).

Cyclooctasulfur. Cyclooctasulfur (BDH) was used at 99.9% purity. The molecular weight determination (Rast's method using naphthalene as solvent) showed that the observed value (255) corresponds to the theoretical value (256) for the S_8 molecule.

Preparation of Compound

Fresh nickel oxide ($\text{NiO}_{1+x} \cdot \frac{1}{3}\text{H}_2\text{O}$, 100 mesh) and cyclooctasulfur (S_8 , 100 mesh) were mixed in a 3:1 molar ratio and crushed in an agate mortar. The mixture was heated in an air oven at $105 \pm 1^\circ\text{C}$ for

17 hr. The process of heating and crushing was repeated several times in order to get a homogeneous compound. Chemical analysis of Ni and S (5) as given in Table IV showed that the compound is $\text{Ni}_3\text{S}_5 \cdot 3\text{H}_2\text{O}$.

Rate measurement. The kinetics of reaction in solid state were studied by pressing $\text{NiO}_{1+x} \cdot \frac{1}{3}\text{H}_2\text{O}$ over powder sulfur S_8 (each 100 mesh) in a Pyrex capillary of internal diameter 0.25 cm (6). One end of the capillary was sealed with asbestos powder. The capillary was then held vertical and the sulfur powder was gently pressed by placing a thinner glass rod into the reaction capillary. $\text{NiO}_{1+x} \cdot \frac{1}{3}\text{H}_2\text{O}$ was placed over the sulfur layer in the capillary with the help of a glass rod. The capillary was tapered vertically in order to get nice packing and a sharp distinguished line of demarcation between the black and yellow colors, as shown in Fig. 2. The progress of the reaction was followed by measuring with a traveling microscope (least count 0.001 cm) the total thickness of the product layer $(l_2 - l_1) = \xi$, given in Table I, formed at the interface.

Each experiment was run in triplicate and the average values of the different sets reported are quite satisfactory. After the placement of the capillary in the oven at $100 \pm 1^\circ\text{C}$, an ash color first appeared and was then converted to black. The kinetics were studied at different temperatures. The data are given in Table II.

TGA (isothermal.) The fresh $\text{NiO}_{1+x} \cdot \frac{1}{3}\text{H}_2\text{O}$ was prepared by heating basic nickel carbonate ($\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) in an oven at $240 \pm 1^\circ\text{C}$ for 6 hr. The experimental value of $\text{NiO}_{1+x} \cdot \frac{1}{3}\text{H}_2\text{O}$ obtained by isothermal TGA agrees well with the theoretical value given in Table III. A mixture of freshly prepared

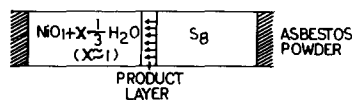


FIG. 2. Direction of diffusion of sulfur.

TABLE I
DIFFUSION STUDY OF S_8 AND $NiO_{1+x} \cdot \frac{3}{2}H_2O$ AT DIFFERENT TEMPERATURES (ξ = BAND WIDTH IN cm)

95°C		100°C		105°C		110°C		115°C	
Time (hr)	$\xi \times 10^{-3}$ (cm)	Time (hr)	$\xi \times 10^{-3}$ (cm)	Time (hr)	$\xi \times 10^{-3}$ (cm)	Time (hr)	$\xi \times 10^{-3}$ (cm)	Time (hr)	$\xi \times 10^{-3}$ (cm)
4	44.6	4	52.6	4	87.5	4	76.0	4	93.3
10	70.3	10	75.6	6	100.0	10	138.3	8	131.3
14	75.6	14	80.6	10	113.5	15	153.3	12	162.6
22	111.0	20	114.3	18	135.5	28	241.6	16	184.0
33	120.0	25	131.6	25	178.5	34	261.6	20	210.0
37	125.6	38	163.3	34	242.5	46	300.0	24	231.3
44	136.3	44	181.6	38	249.0	52	316.6	28	255.3
52	147.0	48	198.3	44	255.0	60	336.6	32	268.6
		55	206.6	50	263.5			36	288.6
				58	268.5			40	305.6
								44	311.6
								48	331.3
								52	348.0
								58	366.6

$NiO_{1+x} \cdot \frac{3}{2}H_2O$ and S_8 in a 3:1 molar ratio was heated at $105 \pm 1^\circ C$ for 17 hr in order to get the final product. The isothermal TGA data indicated that a favorable experimental quantity remained at the end with respect to the theoretically calculated value for $Ni_3S_5 \cdot 3H_2O$ given in Table III. During the course of reaction SO_2 gas evolved in two steps, shown in Fig. 3, and gave a weight loss in isothermal TG analysis which corresponded to the theoretical value given in Table III.

Comparison of X-ray powder diffraction patterns of the reactants and product. The powder X-ray diffraction patterns of the reactants and product were taken with an X-ray diffractometer at Bhabha Atomic Re-

search Centre, Bombay, using $CuK\alpha$ radiation.

In order to establish the identity of $Ni_3S_5 \cdot 3H_2O$ with respect to other phases participating in the reaction, a comparative

TABLE II

Temp. (°C)	K cm ² /hr	n error in n	Activation energy
95	2.761×10^{-4}	2.17 + 0.17	25.5 kcal/mole
100	6.918×10^{-4}	2.00 - 0.00	
105	13.62×10^{-4}	1.99 - 0.01	
110	22.28×10^{-4}	1.95 - 0.05	
115	28.44×10^{-4}	1.92 - 0.08	

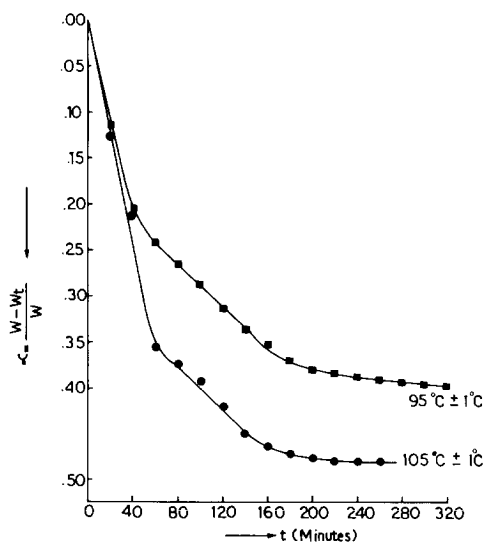


FIG. 3. Isothermal TG analysis of a mixture (3:1) of nickel oxide and cyclooctasulfur; Plot of α (fractional mass loss) vs time at different temperatures.

TABLE III
TGA OF BASIC NICKEL CARBONATE, NICKEL OXIDE, AND HYDRATED TRINICKEL
PENTASULFIDE

	Calculated value (g)	Observed value (g)	Error (%)
Amount of basic nickel carbonate taken = 0.4220 g			
H ₂ O (in NiCO ₃ · 2Ni(OH) ₂ · 4H ₂ O)	0.0806	0.0759	1.1
NiO _{1+x} (x ≈ 1, surplus oxygen)	0.2700	0.2650	1.8
NiO _{1+x} · ½H ₂ O (x ≈ 1)	0.2870	0.2860	1.5
H ₂ O in NiO _{1+x} · ½H ₂ O	0.0261	0.0278	0.4
Amount of mixture taken = 0.5560 g			
Ni ₃ S ₅	0.3427	0.3376	1.7
Ni ₃ S ₅ · 3H ₂ O	0.3900	0.3810	2.5
SO ₂ + H ₂ O	0.2142	0.2190	2.2
H ₂ O in Ni ₃ S ₅ · 3H ₂ O	14%	13%	1

study of X-ray powder patterns has been given in Table V. The *d* values of the final product do not tally with the reported *d* values for NiS, NiS₂, Ni₃S₂, Ni₃S₄, and Ni₆S₅ (7). This also indicates that a new compound has been obtained.

Discussion

For a comprehensive understanding of the solid-state reaction between sulfur and nickel oxide, the following aspects are considered to be important.

1. Diffusion tendency of sulfur in nickel oxide.
2. Mechanism of chemical interaction between cyclooctasulfur and nickel oxide.

1. Diffusion Tendency of Sulfur in Nickel Oxide

It has been observed that sulfur diffuses in black nickel oxide when both are packed in a capillary and produces an ash-color band which gradually increases and becomes black with time. A sharp boundary was found at the interface and the thickness of the sulfur band was not changed with time, while the thickness of the nickel oxide band was decreased gradually. This shows that only sulfur diffuses (3) toward nickel oxide. Chang *et al.* (8) have also reported the diffusion of sulfur in nickel oxide. The thickness of the product band increases with time and the reaction continues. The

TABLE IV
CHEMICAL ANALYSIS FOR Ni AND S IN BASIC NICKEL CARBONATE, NICKEL OXIDE, AND
HYDRATED TRINICKEL PENTASULFIDE

	Calculated value (%)	Observed value (%)	Error (%)
Ni (in NiCO ₃ · 2Ni(OH) ₂ · 4H ₂ O)	46.8	45.1	1.7
Ni (in NiO _{1+x} · ½H ₂ O)	64.7	66.6	1.9
Ni (in Ni ₃ S ₅ · 3H ₂ O)	45.1	47	1.9
S (in Ni ₃ S ₅ · 3H ₂ O)	41	39	2

TABLE V
COMPARISON OF X-RAY POWDER DIFFRACTION PATTERNS OF THE REACTANTS AND PRODUCT

Reactant $\text{NiO}_{1+x} \cdot \frac{1}{3}\text{H}_2\text{O}$			Reactant (S_8)			Intermediate compound $3\text{NiO} \cdot 6.5\text{S}^{2-}$ First stage			Compound ($\text{Ni}_3\text{S}_5 \cdot 3\text{H}_2\text{O}$)		
$2\theta^\circ$	d values (\AA)	I/I_0	$2\theta^\circ$	d values (\AA)	I/I_0	$2\theta^\circ$	d values (\AA)	I/I_0	$2\theta^\circ$	d values (\AA)	I/I_0
20.0	4.4394	20.9	11.6	7.6283	7.17	15.4	5.7536	18	19.5	4.5521	37.5
37.2	2.4169	70	15.5	5.7166	13.45	21.9	4.0583	21	20.9	4.2502	100
43.2	2.0941	100	22.0	4.0401	15.69	22.7	3.9171	16	26.3	3.3885	13.1
62.9	1.4776	58.9	22.8	3.9001	14.34	23.0	3.8667	100	30.1	2.9688	22.4
75.1	1.2649	23.9	23.1	3.8502	100.00	25.9	3.4399	30	31.5	2.8400	29.2
78.5	1.2184	24.0	26.0	3.4269	37.66	26.7	3.3386	40	32.9	2.7223	15.4
			26.8	3.3264	18.83	27.7	3.2203	51	34.9	2.5707	17.07
			27.8	3.2090	48.43	28.6	3.1210	28	35.3	2.5425	17.07
			28.8	3.0998	21.07	28.9	3.0893	26	38.5	2.3382	22.40
			29.0	3.0789	14.79	31.4	2.8488	23	42.5	2.1270	9.20
			31.4	2.8488	15.11	34.1	2.6292	15	45.3	2.0018	8.90
			34.2	2.6217	11.21	35.8	2.5081	18	53.2	1.7217	16.50
			35.9	2.5014	10.31	37.0	2.4295	26	53.6	1.7098	19.0
			37.0	2.4295	14.34	42.6	2.1222	25			
			42.9	2.1080	12.55	43.2	2.0941	23			
			47.9	1.8990	13.0	47.8	1.9028	13			
			51.3	1.7609	14.79	51.2	1.7841	14			
			53.1	1.7247	10.76	53.1	1.7247	14			
			55.8	1.6474	8.96	53.9	1.7009	16			
						62.3	1.4903	13			

capillary experiment confirms the diffusion tendency of sulfur toward nickel oxide. The energy needed to break the S_8 ring is reported (1) to be 14.5 kcal/mole. In the capillary diffusion method, the overall energy of activation is found to be 25.5 kcal/mole. Thus this amount of energy will be sufficient to break the S_8 ring into ionic sulfur, which reacts with nickel ions present in nickel oxide (9).

The TGA data fit best in Jander's equation $[1 - (1 - \alpha)^{1/3}]^2 = kt$. A plot given in Fig. 4 indicates that the overall energy of activation of the reaction is 20.6 kcal/mole. This further explains that energy greater than 14.5 kcal/mole will be sufficient to break the S_8 ring. Consequently ionic sulfur reacts with nickel ions.

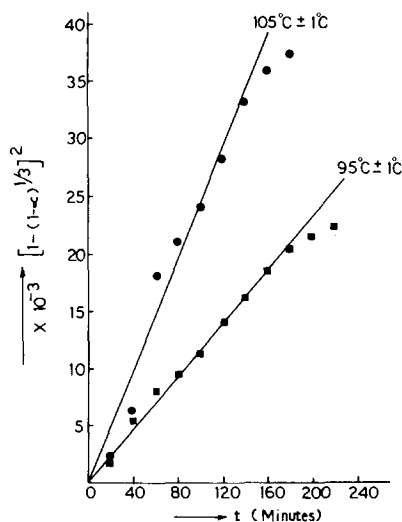


FIG. 4. Test of Jander's equation. Plot of $[1 - (1 - \alpha)^{1/3}]^2$ vs t .

TABLE VI
ISOTHERMAL TG ANALYSIS OF
MIXTURE OF SULFUR AND NICKEL
OXIDE AT DIFFERENT TEMPERATURES,
(α = FRACTIONAL WEIGHT LOSS)

Time (min)	Temperature	
	95°C $\alpha \times 10^{-3}$	105°C $\alpha \times 10^{-3}$
0.0	0.0	0.0
20	116.5	128
40	207	214
60	244	356
80	266	374
100	289	394
120	314	420
140	337	451
160	354	463
180	370	473
200	376	479
220	383.5	482
240	388.5	482
260	392	—
280	393.5	—
300	395	—
320	395.5	—
340	395.5	—

In order to study the kinetics of the reaction, the kinetic data fit best in the equation $\xi^n = kt$, where ξ is the thickness of the product band ($l_2 - l_1$) at time t , n is a constant, and k is the rate of diffusion. The plot of ξ vs t is given in Fig. 5. The slope of the test equation $n \log \xi = \log k + \log t$ gives the values of n and k , which are given in Table

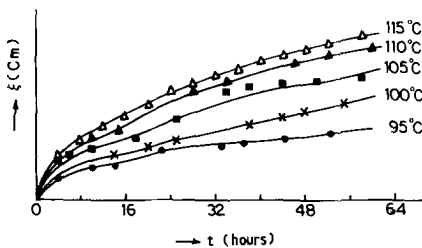


FIG. 5. Capillary diffusion of nickel oxide and cyclooctasulfur at different temperatures. Plot of band width (ξ) vs time.

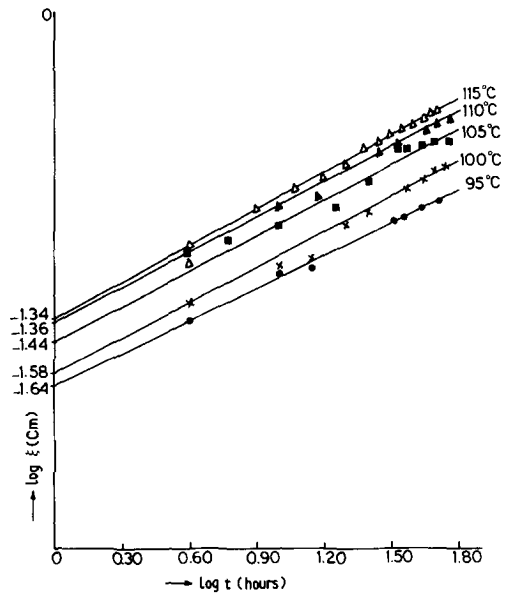


FIG. 6. Plot of $\log \xi$ vs $\log t$ (by the equation $\xi^n = kt$).

II, and the plot of $\log \xi$ vs $\log t$ is given in Fig. 6. The plot of the Arrhenius equation,

$$\log \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right),$$

shown in Fig. 7, gives the energy of activation.

It has been concluded from the kinetic data of the capillary method that the value of n is found to be $2 \pm 1^\circ\text{C}$.

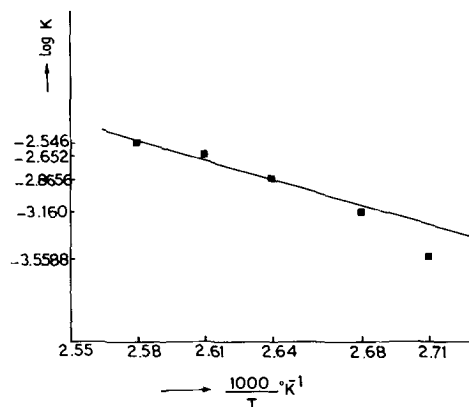


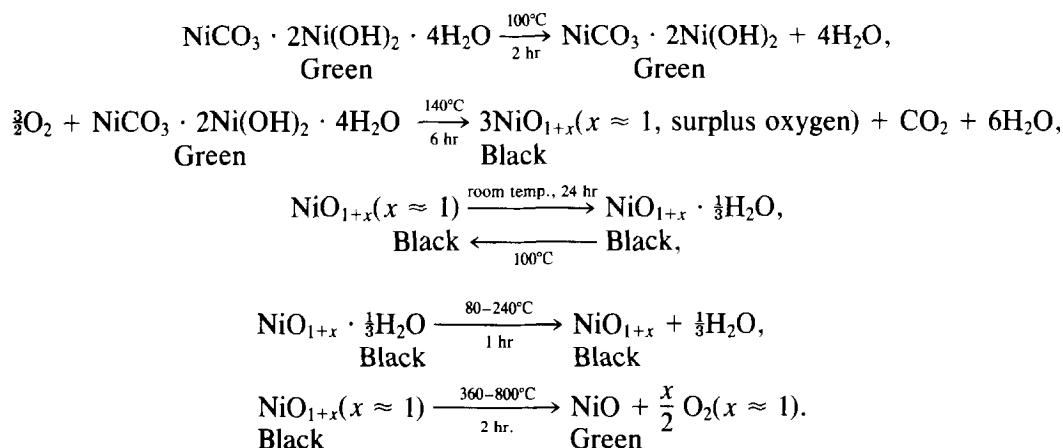
FIG. 7. Arrhenius plot of $\log K$ vs $1/T$ for activation energy.

2. Mechanism of Chemical Interaction between Nickel Oxide and Sulfur

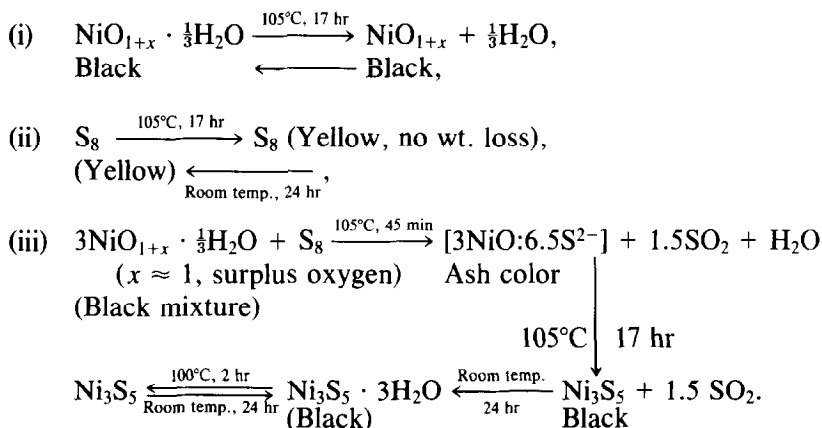
Isothermal gravimetric analysis showed

that $\text{NiO}_{1+x} \cdot \frac{1}{3}\text{H}_2\text{O}$ and S_8 react in a 3 : 1 molar ratio. The whole reaction has been explained with the help of TG analysis given below:

1. TG analysis for nickel oxide from basic nickel carbonate.



2. TG analysis for nickel sulfide.



The mechanism of the reaction probably proceeds via a dehydration process of nickel oxide at 100°C . The dehydration process will produce cracks in the lattice of $\text{NiO}_{1+x} \cdot \frac{1}{3}\text{H}_2\text{O}$. In these cracks sulfur diffuses into the dehydrated lattice of NiO_{1+x} . The diffusion tendency of sulfur has been confirmed by the capillary experiment and, as a consequence, the diffusing S_8 ring,

having a bigger size, creates disturbances in the lattice of NiO_{1+x} , reacts with adsorbed active oxygen, and itself gets broken into ionic sulfur. At this stage, evolution of SO_2 gas takes place and the color of the mixture changes from black to ash. The change in color suggests that probably, at such a low temperature, the green color NiO lattice, which has lost adsorbed oxygen with the

evolution of SO_2 gas, is present (2). This whole process occurs within 45 min. The X-ray analysis of the ash color compound shows the presence of d values of sulfur and NiO. Finally, a black color compound is obtained with the further evolution of SO_2 gas which involves breaking of the Ni-O bond by interaction with ionic sulfur. By virtue of this, the final product, hydrated trinickel pentasulfide, $\text{Ni}_3\text{S}_5 \cdot 3\text{H}_2\text{O}$, is obtained, as given in Tables III and VI. This compound absorbs three molecules of water from the atmosphere. It loses the water molecule on heating at 100°C within an hour and regains the water molecule from the atmosphere. Each and every step has been confirmed by TGA experiment and chemical analysis of nickel and sulfur. The evolution of SO_2 gas has further been confirmed by passing the gas into $\text{K}_2\text{Cr}_2\text{O}_7$ solution, giving rise to a green color due to $\text{Cr}_2(\text{SO}_4)_3$.

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