SULFATION OF CuO, Fe_2O_3, MnO_2 AND NiO WITH $(NH_4)_2SO_4$

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ABSTRACT

An attempt has been made to calculate the free energy values for possible reactions utilising the available thermodynamic data in order to study the sulfation of CuO, Fe_2O_3, MnO_2 and NiO with $(NH_4)_2SO_4$, and further trials have been made to determine the exact reaction through differential thermal analysis. There is no real correlation between the theoretical value of ΔH^0 and that calculated from the DTA peak, which may be due to some uncertainty in the thermodynamic values and the possibility of some side reactions.

INTRODUCTION

Metal oxides, when roasted with $(NH_4)_2SO_4$ at a suitable temperature, may form the respective sulfates. However, to predict the proper reaction it is necessary to make a thorough probe into the equilibrium and kinetic data of sulfation of various simple and complex systems. Though such reviews have been published by Kelley[1] and Kellog[2], sufficient data are not available for the sulfation of metal oxides at temperatures lower than 700 K and data are especially lacking for sulfation with $(NH_4)_2SO_4$. Hence in this paper an attempt has been made to calculate the free energy values for the possible reactions utilizing the available thermodynamic data[3, 4]. Further, the determination of the exact reaction has been attempted through differential thermal analysis.

THERMODYNAMIC CALCULATIONS

The free energy change was calculated from the general equation

$$\Delta G_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ$$

The values of ΔH_{298}°, ΔS_{298}° and C_p for the oxides and sulfates were taken from Kubaschewski et al.[3] and the corresponding values for $(NH_4)_2SO_4$ from Keller[4].

TABLE 1

STANDARD FREE ENERGIES OF THE REACTION[a]

$$\Delta G_T^0 = A + BT\log T + CT^2 + DT$$

Reaction	ΔG^0 (cal)				Temp. range (K)
	A	B	C ($\times 10^{-3}$)	D	
(1) $CuO + (NH_4)_2SO_4 \rightleftharpoons CuSO_4 + H_2O + 2 NH_3$	55548	−14.19	+20.12	−70.26	323–573
(2) $CuO + (NH_4)_2SO_4 + \frac{1}{2} O_2 \rightleftharpoons CuSO_4 + 2H_2O + \frac{4}{3} NH_3 + \frac{1}{3} N_2$	4845	−16.65	+20.92	−68.72	623–823
(3) $MnO_2 + (NH_4)_2SO_4 + O_2 \rightleftharpoons MnSO_4 + 4 H_2O + N_2$	−81418	−36.96	+25.23	−45.90	323–573
(4) $\frac{1}{2} MnO_2 + (NH_4)_2SO_4 + \frac{3}{4} O_2 \rightleftharpoons \frac{1}{2} MnSO_4 + \frac{7}{2} H_2O + \frac{4}{3} NH_3 + \frac{5}{6} N_2 + \frac{1}{2} SO_2$	−26135	−33.09	+25.81	−92.14	623–823
(5) $NiO + (NH_4)_2SO_4 \rightleftharpoons NiSO_4 + H_2O + 2 NH_3$	45275	−31.8	+21.36	−18.73	323–573
(6) $NiO + (NH_4)_2SO_4 + \frac{1}{2} O_2 \rightleftharpoons NiSO_4 + 2 H_2O + \frac{4}{3} NH_3 + \frac{1}{3} N_2$	−5430	−34.3	+22.16	−17.53	623–823

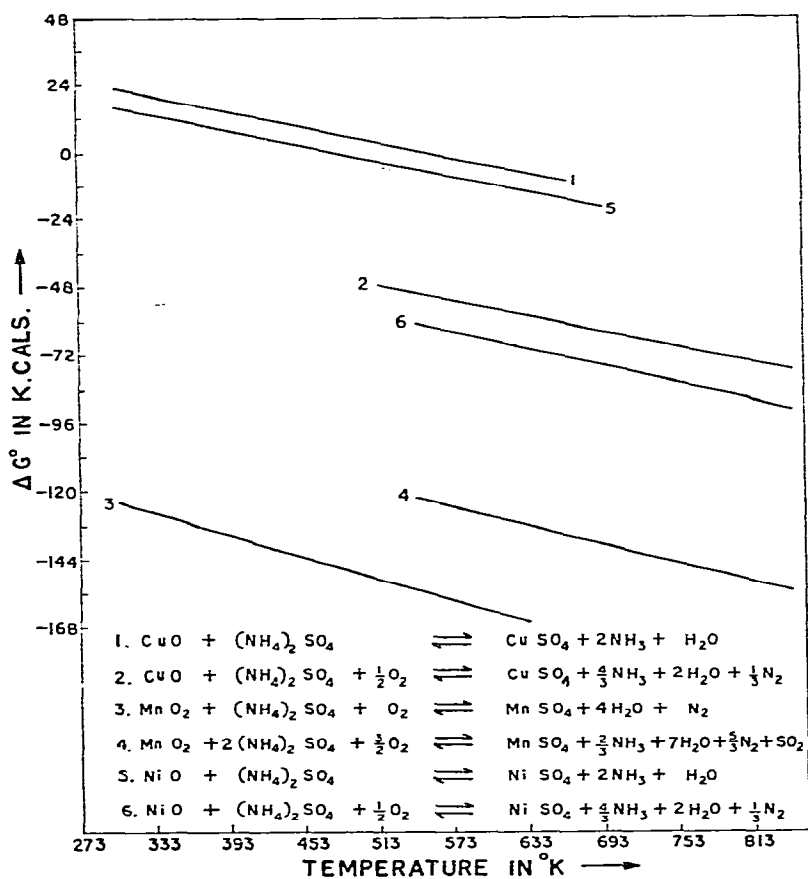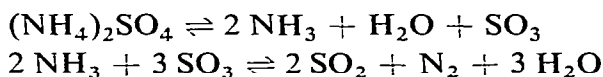[a] Calculations could not be made for Fe_2O_3 as the corresponding thermodynamic data are not available.

Fig. 1. Free-energy vs. temperature for some metal oxide–$(NH_4)_2SO_4$ systems.

As $(NH_4)_2SO_4$ is heated, the following reactions take place[5], the first one at lower temperatures and the latter at higher temperatures.

$$(NH_4)_2SO_4 \rightleftharpoons 2\,NH_3 + H_2O + SO_3$$
$$2\,NH_3 + 3\,SO_3 \rightleftharpoons 2\,SO_2 + N_2 + 3\,H_2O$$

Hence, SO_3 has been assumed to be the reacting gas from 25 to 325 °C and SO_2 from 325 to 550 °C. The calculations have always been made for 1 gmole of $(NH_4)_2SO_4$. For different reactions, the standard free energy change as a function of temperature is given in Table 1 and Fig. 1. The ΔG^0 values reported here have been based on the thermodynamic data taken from different sources, which have been stated to vary within certain error limits. The cumulative errors in this diagram can be of the order of 5–10 kcal.

EXPERIMENTAL

Materials

The metal oxides and ammonium sulfate used were of AnalaR grade.

Apparatus

The thermal analysis experiments were carried out using an equipment supplied by the Hungarian Optical Works, Budapest. The derivatograph (Model No. OD-102) simultaneously records the TG(thermogravimetric), DTG (derivative thermogravimetric) and DTA (differential thermal analysis) curves and the temperature of the sample (in °C) on photographic paper. The thermocouple (Pt/Pt–Rh of 0.35 mm diameter) of the derivatograph measures the temperature of the sample indirectly. It is not directly immersed in the sample, as is the thermocouple of the classic DTA apparatus. Its welded joint is placed across the folded wall of the crucible. The crucible is, of course, in direct contact with the sample.

Procedure for thermal analysis

The oxide and $(NH_4)_2SO_4$ were ground separately and only the −100 B.S.S. fractions were selected for experiments. The samples were dried at 120 °C for 45–60 min and stoichiometric proportions of the reactants mixed thoroughly by means of a vibrator to give a homogeneous mixture. This mixture was placed in a ceramic crucible such that it would not react with the sulfur oxides produced by the decomposition of $(NH_4)_2SO_4$. In all cases the rate of heating was maintained at 10 °C min^{-1} by means of a furnace in the DTA unit. Inert Al_2O_3 powder was used as reference for carrying out DTA. AnalaR grade KNO_3 was considered as the standard and gave a distinct endothermic peak at 370 °C. The heat of fusion of KNO_3 was found[6] to be 28.1 cal g^{-1}.

Procedure for calculating ΔH^0 values from the DTA curve

The endothermic peak was transferred to tracing graph paper and the number

of squares were counted. Similarly, the number of squares were counted for the standard KNO_3 and the ΔH^0 values were calculated. From the TG curves, the amount of the particular sulfate decomposed and hence the amount of $(NH_4)_2SO_4$ utilised to form this sulfate could be determined. The ΔH^0 values were calculated only on the basis of the amount of $(NH_4)_2SO_4$ reacted. This method was followed in the case of CuO, Fe_2O_3 and NiO but in the case of MnO_2 it was not possible from the TG curves to determine the amount of sulfate which decomposed. Hence, for this case, the mixture (in stoichiometric proportions) was roasted under exactly the same conditions of time and temperature as those in the DTA peak, then leached and analysed. From the analysis, it was easy to determine how much sulfate was formed and accordingly, how much of the $(NH_4)_2SO_4$ was used. The remainder of the

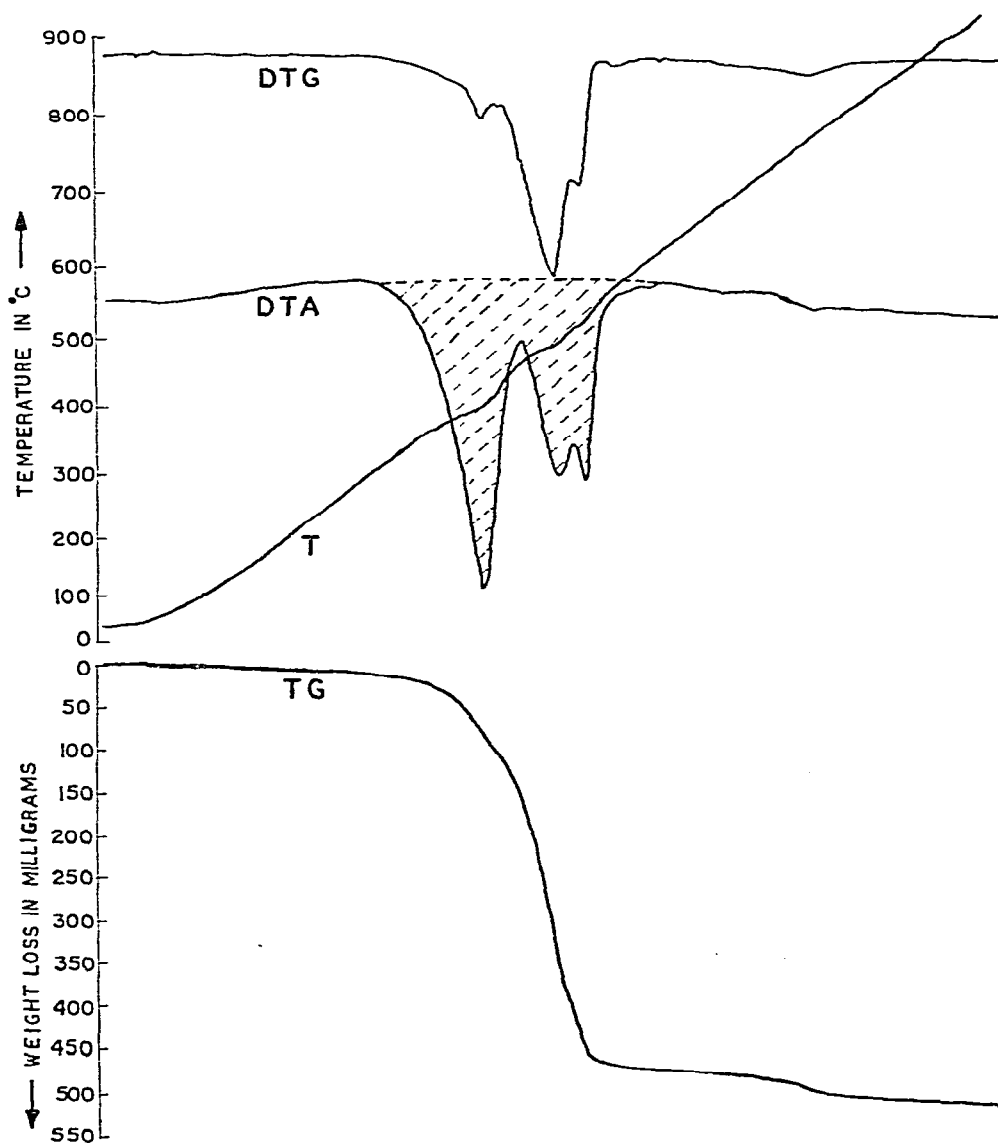

Fig. 2. Sample: ammonium sulfate; amount: 954 mg; TG, 1000 mg; DTA, 1/20; DTG, 1/10.

TABLE 2

POSSIBLE REACTIONS FOR THE DECOMPOSITION OF $(NH_4)_2SO_4$

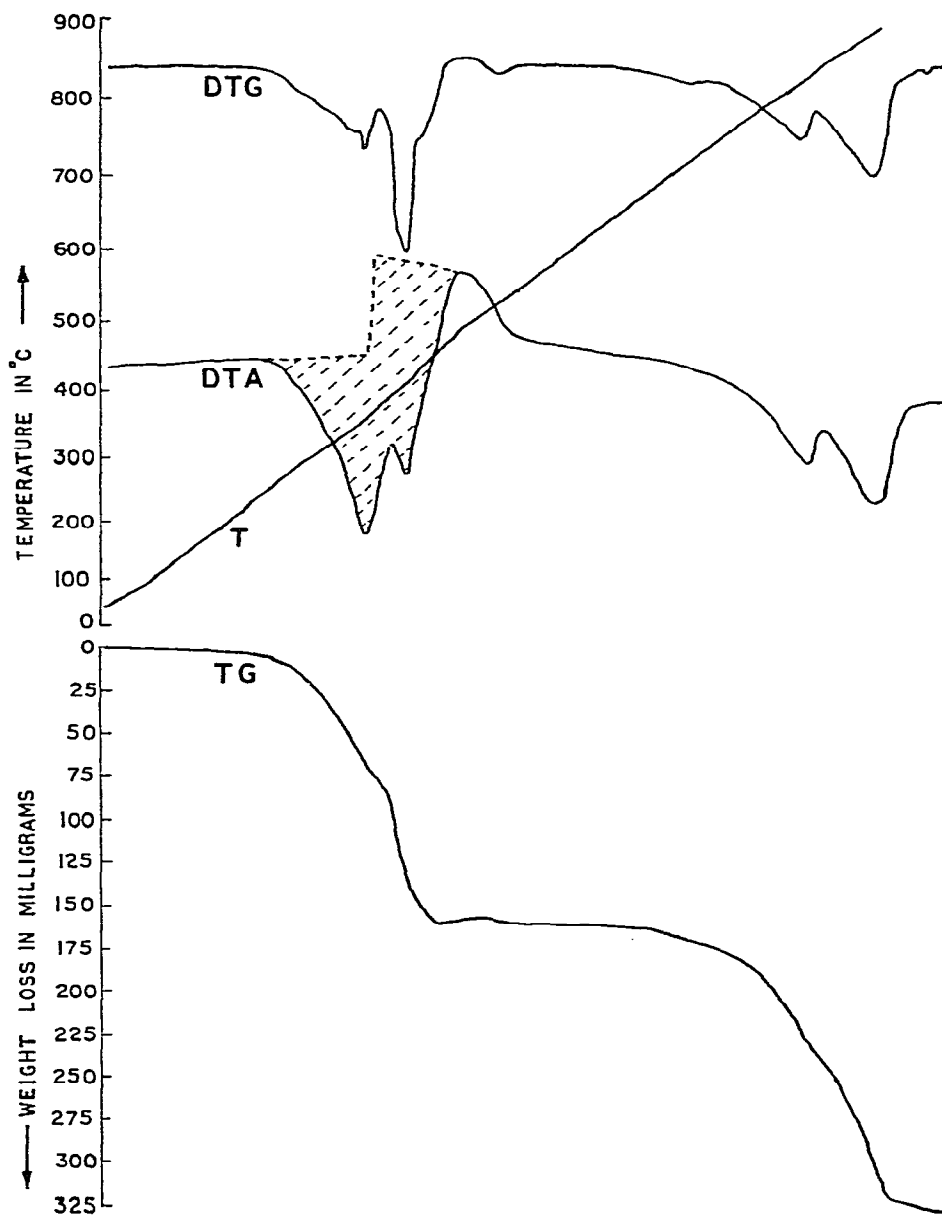| Possible reactions	ΔH_{693}^0 $(kcal\ gmole^{-1})$
(1) $(NH_4)_2SO_4 \rightleftharpoons 2\ NH_3 + H_2O + SO_3$	103.98
(2) $(NH_4)_2SO_4 \rightleftharpoons \frac{4}{3}\ NH_3 + 2\ H_2O + SO_2 + \frac{1}{3}\ N_2$	56.54

Fig. 3. Sample: CuO and ammonium sulfate mixture; amount: 500 mg; TG, 500 mg; DTA, 1/15; DTG, 1/10.

$(NH_4)_2SO_4$ decomposed without taking part in the reaction. From the DTA of the different oxide $-(NH_4)_2SO_4$ systems, the ΔH^0 values at the particular temperature have been calculated and comparison has been made with theoretical calculations. The ΔH^0 values have been calculated with respect to 1 gmole of $(NH_4)_2SO_4$ in each case.

RESULTS AND DISCUSSIONS

Sample: $(NH_4)_2SO_4$

Figure 2 shows DTA and DTG curves for $(NH_4)_2SO_4$. The DTA exhibits an endothermic area at 420°C. It appears that the reaction starts at 300°C and is completed at 600°C. There is another small peak at 520°C but the whole area from 300 to 600°C has been considered for calculation. However, the area under consideration has been indicated by hatching in the case of Figs. 2–6. For the decomposition of $(NH_4)_2SO_4$, the possible reactions and the theoretically calculated ΔH^0 values are shown in Table 2.

The ΔH°_{693} value obtained from the DTA curve is 96.8 kcal gmole^{-1} of $(NH_4)_2SO_4$ and this agrees fairly well with the value in the case of reaction (1) in Table 2. However, in the case of Figs. 3–6, the value obtained from DTA has been used for actual calculations, as roasting was carried out under identical conditions.

Sample: $CuO + (NH_4)_2SO_4$

The different curves for this system are shown in Fig. 3. There is an endothermic area at 350°C and another exothermic area at 480°C. The total area, 260–620°C is taken for calculations. Table 3 shows the possible reactions and the ΔH^0 values calculated from available thermodynamic data.

As the ΔH°_{623} calculated from the DTA curve is only 34 kcal gmole^{-1}, reaction (1) seems to be playing a predominant role. Also, the formation of basic sulfate as reported by Kellog[2] cannot be ruled out. Reaction (1) proceeds via SO_3 and reaction (2) via SO_2. Kinetic studies[7] of CuO in a SO_2–O_2 atmosphere do not show any change in the rate of sulfation due to the presence of V_2O_5. Hence, formation

TABLE 3

POSSIBLE SULFATION REACTIONS FOR THE CuO–(NH₄)₂SO₄ SYSTEM

Possible reactions	ΔH_{623}^0 (kcal gmole^{-1})
(1) $CuO + (NH_4)_2SO_4 \rightleftharpoons CuSO_4 + 2\,NH_3 + H_2O$	50.58
(2) $CuO + (NH_4)_2SO_4 + \frac{1}{2}\,O_2 \rightleftharpoons CuSO_4 + \frac{4}{3}\,NH_3 + 2\,H_2O + \frac{1}{3}\,N_2$	1.23
(3) $CuO + (NH_4)_2SO_4 + \frac{3}{4}\,O_2 \rightleftharpoons CuSO_4 + NH_3 + \frac{5}{2}\,H_2O + \frac{1}{2}\,N_2$	−25.67
(4) $CuO + (NH_4)_2SO_4 + \frac{5}{4}\,O_2 \rightleftharpoons CuSO_4 + \frac{1}{3}\,NH_3 + \frac{7}{2}\,H_2O + \frac{5}{6}\,N_2$	−75.19
(5) $2\,CuO + (NH_4)_2SO_4 \rightleftharpoons CuO \cdot CuSO_4 + 2\,NH_3 + H_2O$	52.93

of either basic sulfate or normal sulfate probably takes place through the reaction of CuO with SO_2. Also, the free energy diagram (Fig. 1) illustrates the reaction of CuO with $(NH_4)_2SO_4$ via SO_2 to be more favourable, depending on the free energy value. In Table 3, reaction (5) proceeds via SO_3 and the ΔH^0 values from eqns. (1) and (5) cannot be differentiated. Finally, it may be that CuO has partly formed basic sulfate with SO_3 and it is difficult to separately identify the different fractions and compare the ΔH^0 value obtained from these reactions with that from the DTA curve.

The superimposition of an exothermic reaction as seen in Fig. 3 may be an explanation for the discrepancy in the values. Reactions (3) and (4) have been pro-
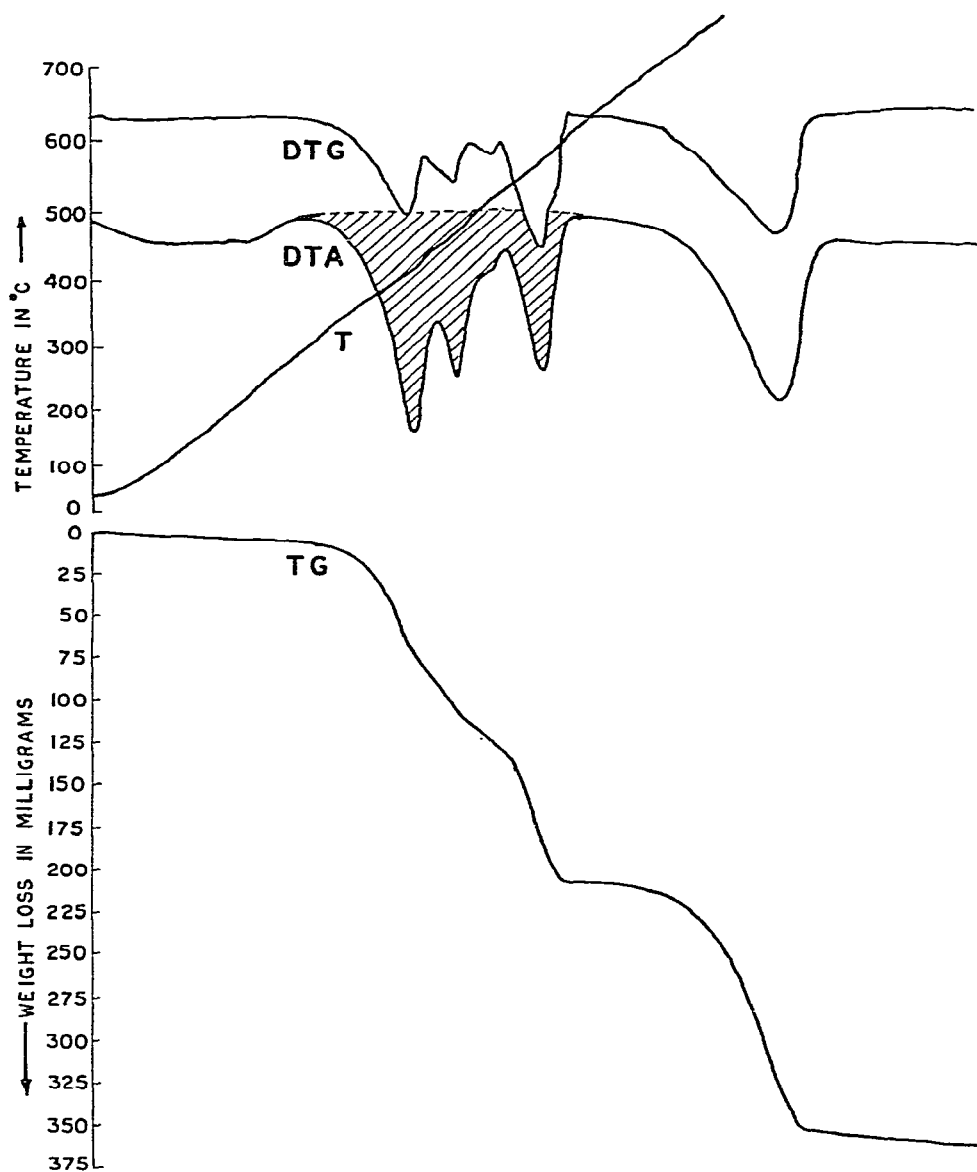

Fig. 4. Sample: Fe_2O_3 and ammonium sulfate mixture; amount: 500 mg; TG, 500 mg; DTA, 1/15; DTG, 1/10.

TABLE 4

POSSIBLE SULFATION REACTIONS FOR THE Fe_2O_3–$(NH_4)_2SO_4$ SYSTEM

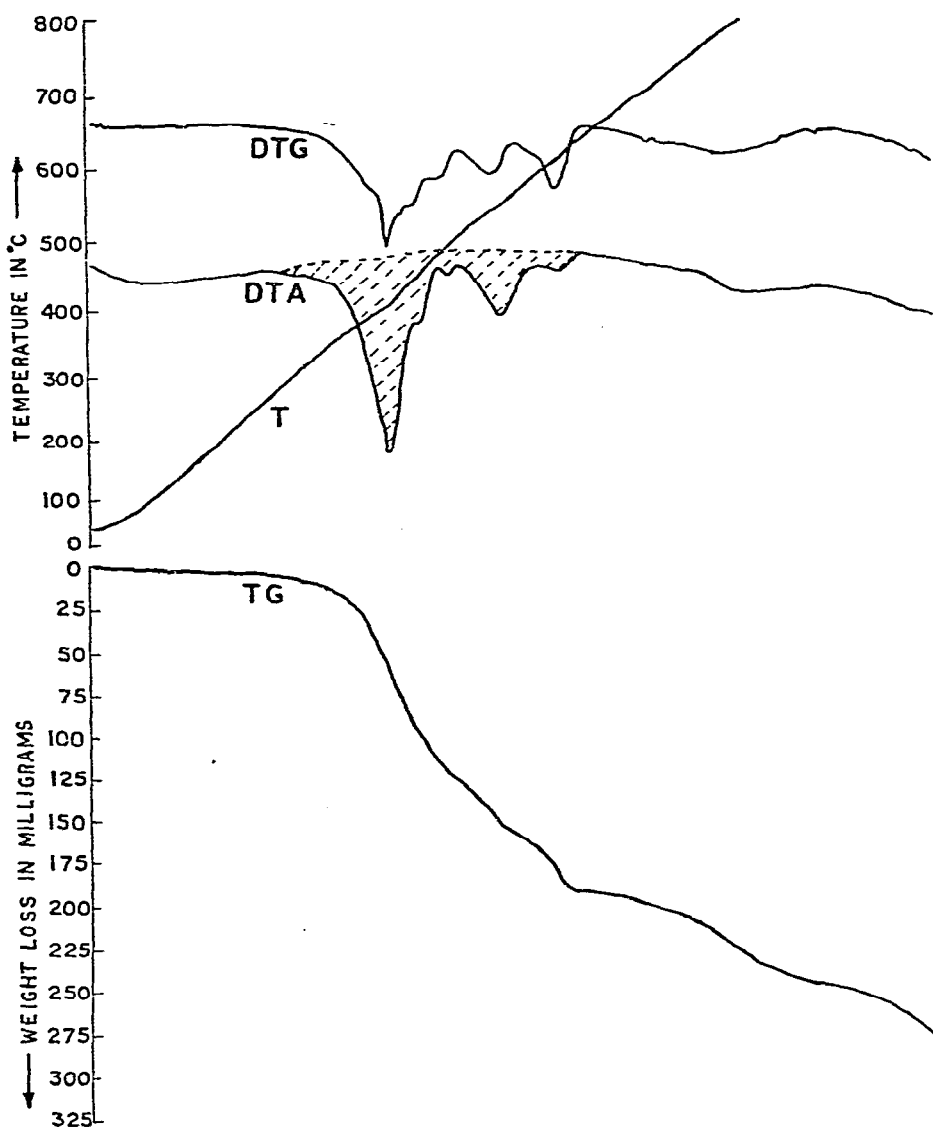| Possible reactions	ΔH^0 values (kcal gmole^{-1})
(1) $\frac{1}{3} Fe_2O_3 + (NH_4)_2SO_4 \rightleftharpoons \frac{1}{3} Fe_2(SO_4)_3 + 2 NH_3 + H_2O$	63.36
(2) $\frac{1}{2} Fe_2O_3 + (NH_4)_2SO_4 + \frac{1}{2} O_2 \rightleftharpoons FeSO_4 + NH_3 + \frac{5}{2} H_2O + \frac{1}{2} N_2$	2.22
(3) $\frac{1}{2} Fe_2O_3 + (NH_4)_2SO_4 + O_2 \rightleftharpoons FeSO_4 + \frac{1}{3} NH_3 + \frac{7}{2} H_2O + \frac{5}{6} N_2$	−21.7
(4) $\frac{1}{2} Fe_2O_3 + (NH_4)_2SO_4 \rightleftharpoons FeSO_4 + \frac{5}{3} NH_3 + \frac{3}{2} H_2O + \frac{1}{6} N_2$	9.1
(5) $\frac{1}{2} Fe_2O_3 + (NH_4)_2SO_4 + \frac{1}{2} O_2 \rightleftharpoons FeSO_4 + NH_3 + \frac{5}{2} H_2O + \frac{1}{2} N_2$	9.6

Fig. 5. Sample: MnO_2 and ammonium sulfate mixture; amount, 500 mg; TG, 500 mg; DTA, 1/15; DTG, 1/10.

posed with CuO being reduced to Cu_2O and then reacting with SO_3 and SO_2. However, the ΔH^0 values from these reactions do not compare with that from the DTA curve.

Sample: Fe_2O_3 + $(NH_4)_2SO_4$

Figure 4 shows the different curves for Fe_2O_3 and $(NH_4)_2SO_4$. There is an endothermic peak at 410 °C and another distinct peak at 570 °C. The reaction starting at 310 °C and finishing at 610 °C has been considered for calculation. Table 4 shows different reactions with corresponding ΔH^0 values.

As sufficient thermodynamic data are not available, ΔH°_{298} was calculated in the case of reactions (2)–(5), whereas in the case of reaction (1), ΔH°_{683} was determined. Reaction (1) proposes the Fe_2O_3–SO_3 system whereas reactions (2)–(5) have been proposed for the FeO–SO_3, FeO–SO_2, Fe_3O_4–SO_3 and Fe_3O_4–SO_2 systems, respectively, i.e. after Fe_2O_3 has been reduced to these lower oxides by NH_3 and O_2; this is feasible from the free energy point of view. Though Alcock et al.[8] reported the formation of basic sulfate ($Fe_2O_3 \cdot SO_3$) below 650 °C, it is not possible to calculate the heat effects for the reactions, as the thermodynamic data at 298 K are not available for basic sulfate.

The value calculated from the DTA curve (ΔH°_{683} = 34.8 kcal gmole^{-1}) does not agree with any of the above observations. However, reaction (1) probably plays a substantial role in the system which means that the sulfation of Fe_2O_3 takes place via the SO_3 route. There may be a superimposition of an extra exothermic component due to the reduction of Fe_2O_3 and hence the difference in the ΔH^0 values. The fluctuations in the DTG may be due to earlier decomposition of basic sulfate and simultaneous sulfation of the decomposed products. This might also serve as an explanation for the difference in the values.

Sample: MnO_2 + $(NH_4)_2SO_4$

Figure 5 shows the different curves for the MnO_2–$(NH_4)_2SO_4$ system. There

TABLE 5

POSSIBLE SULFATION REACTIONS FOR THE MnO_2–$(NH_4)_2SO_4$ SYSTEM

Possible reactions	ΔH_{673}^{0} (kcal gmole^{-1})
(1) $MnO_2 + (NH_4)_2SO_4 \rightleftharpoons MnSO_4 + 2\,H_2O + \frac{4}{3}\,NH_3 + \frac{1}{3}\,N_2$	57.25
(2) $MnO_2 + (NH_4)_2SO_4 \rightleftharpoons MnSO_4 + H_2O + 2\,NH_3 + \frac{1}{2}\,O_2$	69.06
(3) $MnO_2 + (NH_4)_2SO_4 + O_2 \rightleftharpoons MnSO_4 + 4\,H_2O + N_2$	−83.1
(4) $\frac{1}{2}\,MnO_2 + (NH_4)_2SO_4 + \frac{3}{4}\,O_2 \rightleftharpoons \frac{1}{2}\,MnSO_4 + \frac{7}{2}\,H_2O + \frac{1}{3}\,NH_3 + \frac{1}{2}\,N_2$	−14.5
(5) $MnO_2 + (NH_4)_2SO_4 \rightleftharpoons MnSO_4 + 2\,H_2O + \frac{4}{3}\,NH_3 + \frac{1}{3}\,N_2$	17.64
(6) $MnO_2 + (NH_4)_2SO_4 + \frac{1}{2}\,O_2 \rightleftharpoons MnSO_4 + 3\,H_2O + \frac{2}{3}\,NH_3 + \frac{1}{3}\,N_2$	−41.1
(7) $MnO_2 + (NH_4)_2SO_4 + \frac{1}{4}\,O_2 \rightleftharpoons MnSO_4 + \frac{5}{2}\,H_2O + NH_3 + \frac{1}{2}\,N_2$	− 7.86
(8) $MnO_2 + (NH_4)_2SO_4 + \frac{3}{4}\,O_2 \rightleftharpoons MnSO_4 + \frac{7}{2}\,H_2O + \frac{1}{3}\,NH_3 + \frac{5}{6}\,N_2$	−50.62

is an endothermic peak at 400°C and another small endothermic peak at 550°C. However, the curve starting at 300°C and finishing at 640°C has been taken for calculation. Table 5 shows the different possible reactions and the corresponding ΔH^0 values.

Reactions (1) and (2) are for MnO_2–SO_2 and MnO_2–SO_3, respectively, whereas reactions (3)–(8) are for MnO–SO_3, MnO–SO_2–O_2, Mn_3O_4–SO_3, Mn_3O_4–SO_2, Mn_2O_3–SO_3 and Mn_2O_3–SO_2, respectively. The reduction of MnO_2 to its lower oxides by NH_3 is possible from the free energy point of view.
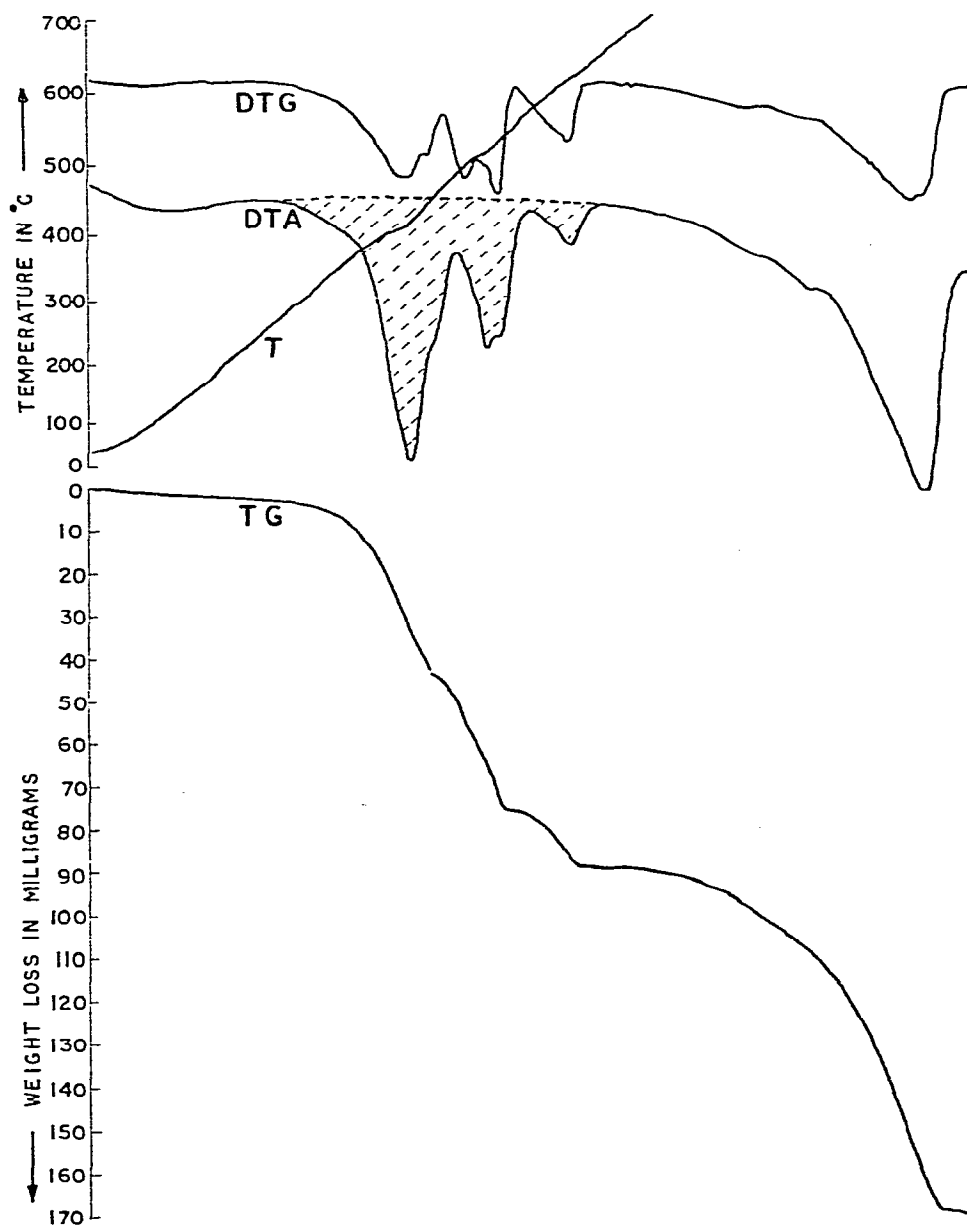

Fig. 6. Sample: NiO and ammonium sulfate mixture; amount: 650 mg, TG, 500 mg; DTA, 1/15; DTG, 1/10.

TABLE 6

POSSIBLE SULFATION REACTIONS FOR THE NiO–(NH$_4$)$_2$SO$_4$ SYSTEM

Possible reactions	ΔH_{693}^0 (kcal gmole^{-1})
(1) NiO + (NH$_4$)$_2$SO$_4$ $\rightleftharpoons$ NiSO$_4$ + 2 NH$_3$ + H$_2$O	44.94
(2) NiO + (NH$_4$)$_2$SO$_4$ + $\frac{1}{2}$ O$_2$ $\rightleftharpoons$ NiSO$_4$ + $\frac{4}{3}$ NH$_3$ + 2 H$_2$O + $\frac{1}{3}$ N$_2$	−5.43

The ΔH^0 values shown in Table 5 do not compare with the ΔH^0 values from the DTA curve $\Delta H_{673}^0 = -143$ kcal gmole^{-1}). However, the ΔH^0 value corresponding to eqn. (3) suggests the possibility of a predominant role of this particular reaction in the system. Between the two DTA peaks (400 and 550 °C), there seems to be a predominant exothermic component. The fluctuations in the DTG curves may be attributed to the simultaneous weight loss due to the reduction of MnO$_2$ to lower oxides and the weight gain due to sulfation of these oxides. From Fig. 1, it is seen that the reaction of MnO$_2$ with both SO$_2$ and SO$_3$ is possible. In kinetic studies[7] this has also been observed, though the rate of sulfation by SO$_3$ is seen to be faster than that by SO$_2$. There is some uncertainty in the thermodynamic data used for the calculations. This may be the explanation for the mismatch obtained here.

Sample: *NiO + (NH$_4$)$_2$SO$_4$*

The system NiO–(NH$_4$)$_2$SO$_4$ is represented in Fig. 6. There is an endothermic peak at 420 °C, but there are another two small peaks at 520 and 620 °C. However, it is assumed to be one peak starting at 300 °C and finishing at 640 °C. The possible reactions and corresponding ΔH^0 values are represented in Table 6.

Reactions (1) and (2) are for the NiO–SO$_3$ and NiO–SO$_2$–O$_2$ systems, respectively. The ΔH^0 value calculated from the DTA curve (-55.2 kcal gmole^{-1}) does not seem to compare well with the predicted value of the reactions. The ΔH^0 value from the DTA curve seems to have an extra exothermic component. NH$_3$ may have been oxidised in the presence of NiO according to the following equation and so contributed this extra value.

$$4\,NH_3 + 3\,O_2 = 6\,H_2O + N_2$$
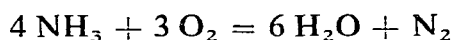
for which $\Delta H_{673}^0 = 303.46$ kcal. It is observed from Fig. 1 that reaction of NiO with SO$_2$ is more favoured than that with SO$_3$. Also, Dhindaw[9] in his sulfation studies on NiO in a SO$_2$–O$_2$ atmosphere found no effect of SO$_3$ over that of SO$_2$. Hence, the SO$_2$ reaction [reaction (2) in Table 6] is assumed to be taking place in the present investigation.

In general, there is no proper agreement between the values calculated from available thermochemical data and from DTA curves. The possibility of some uncertainty in the thermodynamic values and the presence of some side reactions cannot be ruled out. Further work on more oxides is in progress and this may be of considerable help in treating a complex oxide are by a suitable hydrometallurgical method.

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