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SULFATION OF Al_2O_3, CaO, CdO AND ZnO WITH $(NH_4)_2SO_4$

P. K. SAHOO
Regional Research Laboratory, Bhubaneswar-7510 (India)
S. K. BOSE AND S. C. SIRCAR
Department of Metallurgical Engineering, Indian Institute of Technology, Kharagpur-721302 (India)
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ABSTRACT

For studying the sulfation of Al_2O_3, CaO, CdO and ZnO with $(NH_4)_2SO_4$, free energy values have been calculated for possible reactions utilising the available thermodynamic data. Further differential thermal analysis has been carried out to find out the exact reaction. The ΔH^0 values calculated theoretically and that from DTA peak are very close in case of CaO and ZnO, whereas in the other two cases there is no proper match. The mismatch may be due to some uncertainty in the thermodynamic values and the possibility of some side reactions.

INTRODUCTION

In a previous communication[1] results were reported on the sulfation of CuO, Fe_2O_3, MnO_2 and NiO with $(NH_4)_2SO_4$. In this paper results are presented on the sulfation of Al_2O_3, CaO, CdO and ZnO with $(NH_4)_2SO_4$. The thermodynamic calculations, apparatus and the procedure for thermal analysis have been reported earlier[1]. The possible reactions for the sulfation of Al_2O_3, CaO, CdO and ZnO with $(NH_4)_2SO_4$ with the standard free energy change as a function of temperature are shown in Table 1 and Fig. 1.

EXPERIMENTAL

Materials

The metal oxides and ammonium sulfate utilised were all of Analar grade.

PROCEDURE FOR CALCULATING THE ΔH^0 VALUES FROM THE DTA CURVE

The calculations were made for Al_2O_3 as in the case of CuO, Fe_2O_3 and NiO[1] whereas for CaO, CdO and ZnO, a method similar to that of MnO_2[1] was followed.

TABLE 1

STANDARD FREE ENERGIES OF REACTION

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

Reaction	*ΔG⁰ (cals)*				*Temperature range (K)*
	A	*B*	*C*	*D*	
$1/3\ Al_2O_3 + (NH_4)_2SO_4 \rightleftharpoons 1/3\ Al_2(SO_4)_3 + 2\ NH_3 + H_2O$	59370	−38.5	24.34×10^{-3}	−2.26	323–573
$1/3\ Al_2O_3 + (NH_4)_2SO_4 + \frac{1}{2}\ O_2 \rightleftharpoons 1/3\ Al_2(SO_4)_3 + 4/3\ NH_3 + 2\ H_2O + 1/3\ N_2$	8690	−40.9	25.14×10^{-3}	−3.09	623–823
$CaO + (NH_4)_2SO_4 \rightleftharpoons CaSO_4 + 2\ NH_3 + H_2O$	142047	−3.66	15.06×10^{-3}	−98.85	323–573
$CaO + (NH_4)_2SO_4 + \frac{1}{2}\ O_2 \rightleftharpoons CaSO_4 + 4/3\ NH_3 + 2\ H_2O + 1/3\ N_2$	−38243	−6.12	15.86×10^{-3}	−97.31	623–823
$CdO + (NH_4)_2SO_4 \rightleftharpoons CdSO_4 + 2\ NH_3 + H_2O$	43793	−12.7	18.11×10^{-3}	−74.64	323–573
$CdO + (NH_4)_2SO_4 + \frac{1}{2}\ O_2 \rightleftharpoons CdsO_4 + 4/3\ NH_3 + 2\ H_2O + 1/3\ N_2$	−8540	−15.1	18.91×10^{-3}	−73.41	623–823
$ZnO + (NH_4)_2SO_4 \rightleftharpoons ZnSO_4 + 2\ NH_3 + H_2O$	51355	−15.8	17.83×10^{-3}	−69.78	323–573
$ZnO + (NH_4)_2SO_4 + \frac{1}{2}\ O_2 \rightleftharpoons ZnSO_4 + 4/3\ NH_3 + 2\ H_2O + 1/3\ N_2$	+2971	−18.21	18.26×10^{-3}	−69.39	623–823

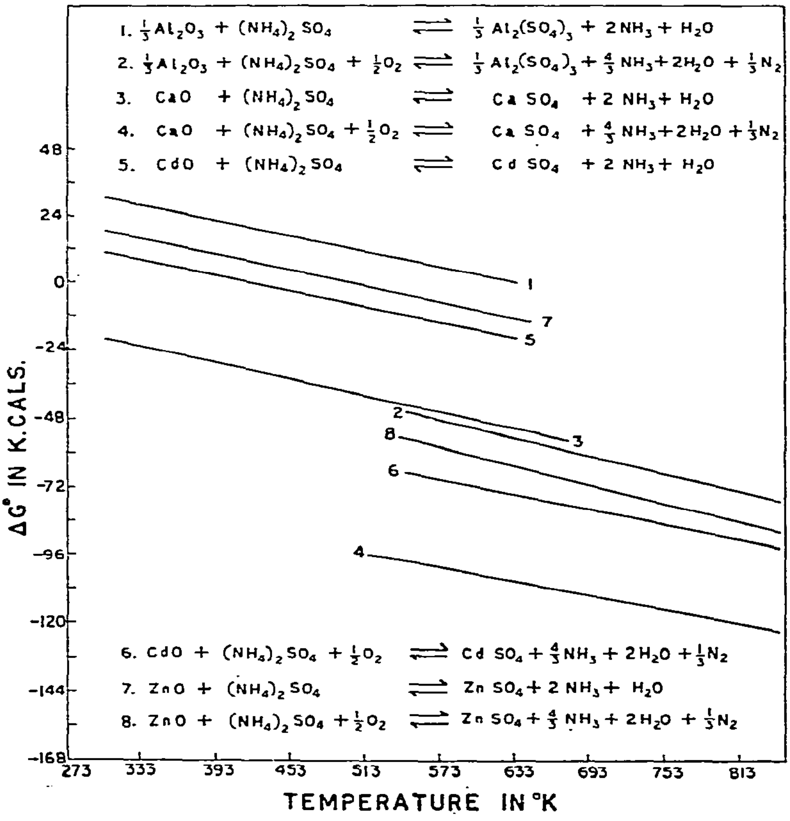

Fig. 1. Free energy against temperature for some metal oxide–$(NH_4)_2SO_4$ systems.

RESULTS AND DISCUSSIONS

$Al_2O_3 + (NH_4)_2SO_4$

In case of $(NH_4)_2SO_4$, the ΔH°_{693K} value from the thermal analysis curves has been utilised as in the previous case[1]. Figure 2 shows an endothermic peak at 420 °C. This peak starts at 320 °C and finishes at 660 °C. However, the area shown by hatching has been considered for calculation in all the cases. There are two more peaks at 530 °C and 640 °C. Table 2 shows the possible reactions and the ΔH^0 values calculated from the available thermodynamic data.

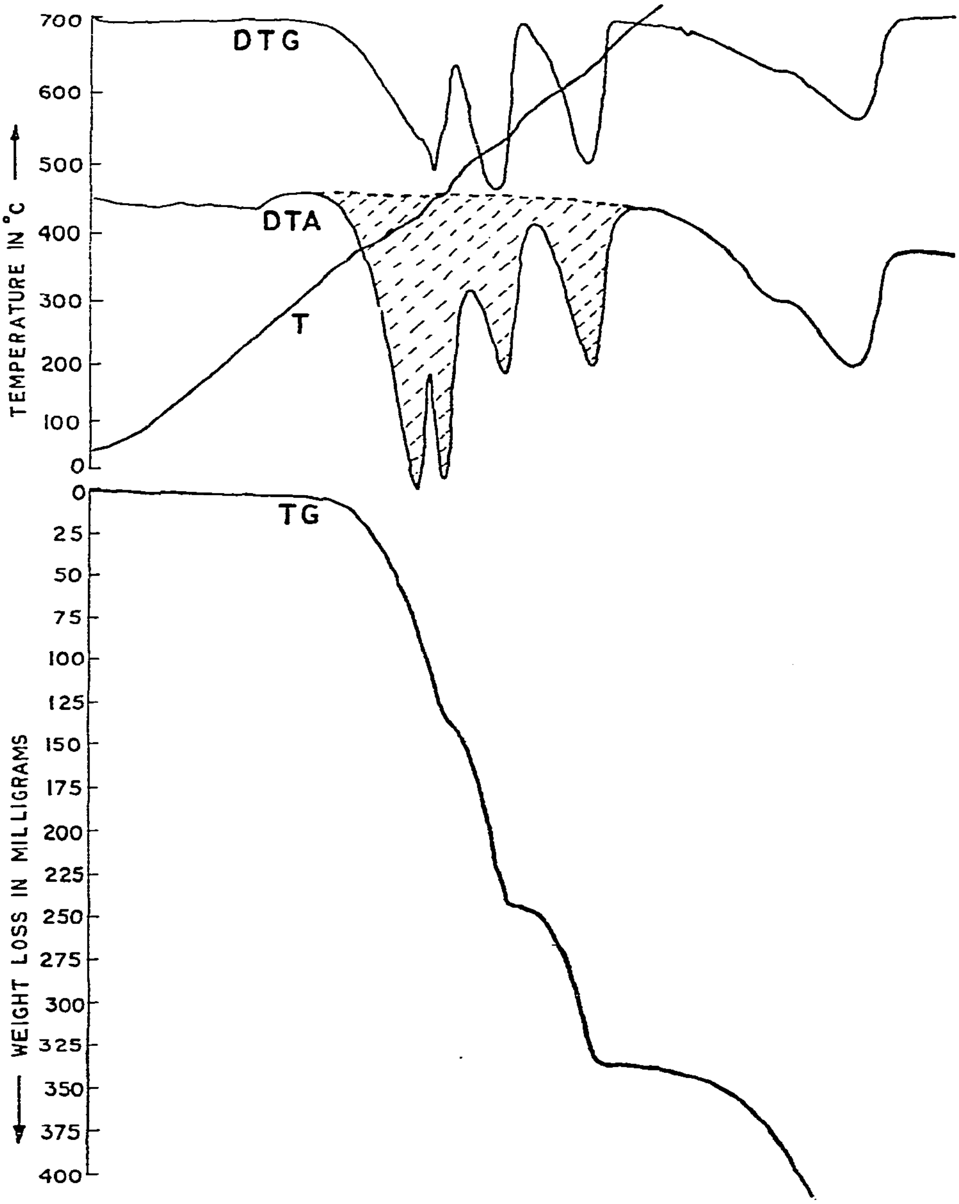

Fig. 2. Sample, Al_2O_3 and ammonium sulfate mixture; amount, 600 mg; TG, 500 mg; DTA, 1/15; DTG, 1/10.

TABLE 2

POSSIBLE SULFATION REACTIONS FOR THE Al_2O_3–$(NH_4)_2SO_4$ SYSTEM

Possible reactions	ΔH^0_{693K} *(kcal g mole^{-1})*
$1/3\ Al_2O_3 + (NH_4)_2SO_4 \rightleftharpoons 1/3\ Al_2(SO_4)_3 + 2\ NH_3 + H_2O$	59.02
$1/3\ Al_2O_3 + (NH_4)_2SO_4 + \frac{1}{2}\ O_2 \rightleftharpoons 1/3\ Al_2(SO_4)_3 + 4/3\ NH_3 + 2\ H_2O + 1/3\ N_2$	9.25

ΔH°_{693K} calculated from the DTA curve is only 35.6 kcals. g mole^{-1}. The extent of mismatch in the ΔH^0 values from the DTA curve and the theoretical calculations can be attributed to the following reasons.

There will be a wide difference in the thermodynamic values for the two grades of Al_2O_3, α and ν variety as printed out by Kellogg[2], who suggested considering the decomposition of $Al_2(SO_4)_3$ to $Al_2O_3(\nu)$ rather than to $Al_2O_3(\alpha)$ under most of the experimental conditions. Thermodynamic properties for $Al_2O_3(\nu)$ are not known definitely because of its high sensitivity to the presence of impurities[2]. It may be that the Al_2O_3 selected in the present investigation was the ν variety and hence the mismatch.

The interesting feature observed here is that there has been appreciable sulfation of the Al_2O_3. Dhindaw[3] could not observe any sulfation of the Al_2O_3 in an SO_2–O_2 atmosphere over a temperature range of 500–800 °C. Probably, the presence of NH_3 along with $SO_2:O_2$ evolved from the decomposition of $(NH_4)_2SO_4$ brings about a favourable situation by maintaining a reducing atmosphere. From the free energy diagram (Fig. 1), it is observed that the reaction of Al_2O_3 via the SO_3 is less favourable than the reaction through the SO_2 route.

$CaO + (NH_4)_2SO_4$

There is an endothermic peak at 400 °C shown in Fig. 3. From the curve it appears that the reaction starts at 300 °C and is complete at 600 °C. The ΔH°_{673K} value calculated from the DTA curve is only 2.2 kcal g mole^{-1}. When compared with the value calculated theoretically, it is seen that the ΔH^0 value calculated from reaction 1 (Table 3) seems to match the ΔH^0 value derived from the DTA curve better. The free energy value calculated on the basis of $\Delta H^0 = 2.2$ kcal lies within an error of $\pm$ 10 kcal, when plotted in Fig. 1.

$CdO + (NH_4)_2SO_4$

Figure 4 shows the DTA, DTG, T and TG curves for this system. In this figure there is an endothermic peak at 400 °C and another small peak at 520 °C. The whole area from 300 to 600 °C is taken for calculation. The ΔH°_{673K} values calculated from the DTA curve is -3.57 kcal g mole^{-1}. The values from theoretical calculations have been reported in Table 4. The ΔH^0 values calculated on the basis of the reactions in this table seem to match comparatively better with the ΔH^0 values obtained from

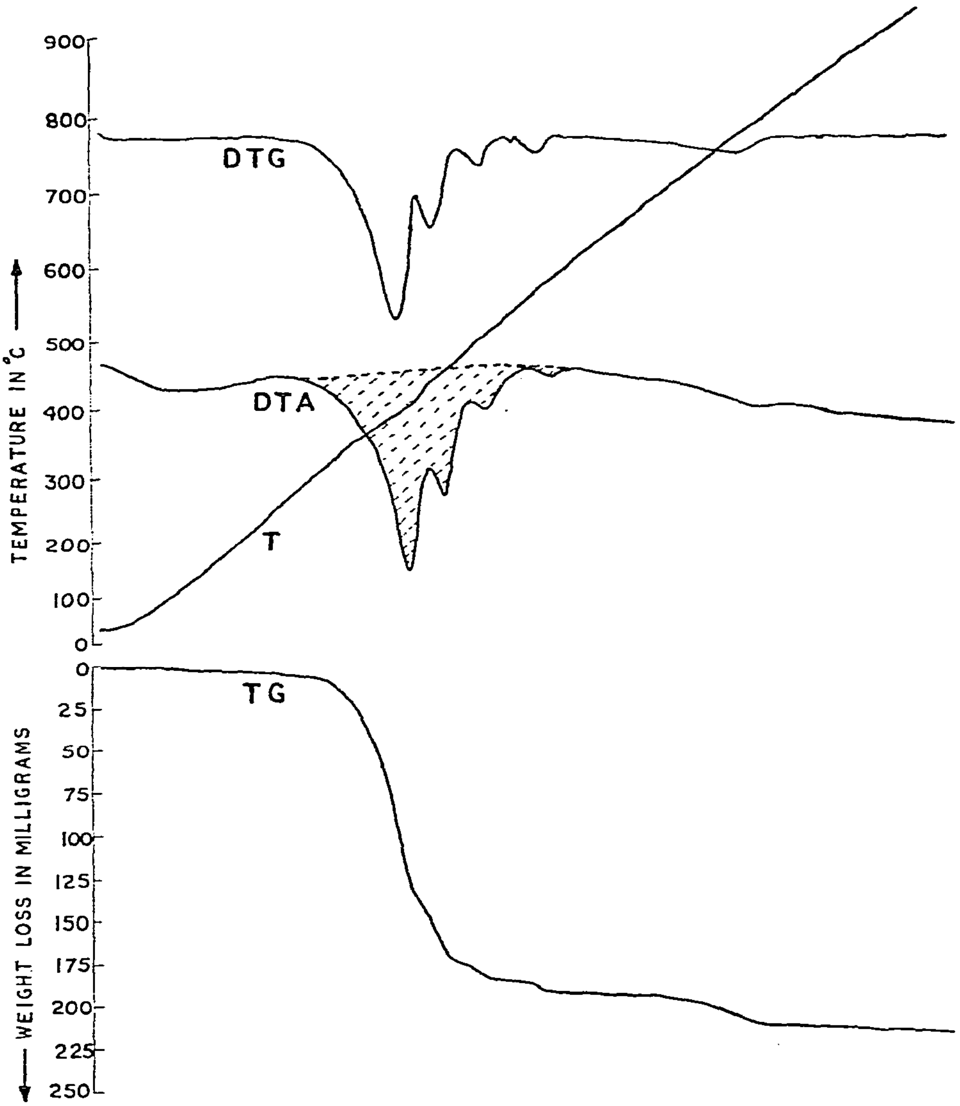

Fig. 3. Sample, CaO and ammonium sulfate mixture; amount, 500 mg; TG, 500 mg; DTA, 1/15; DTG, 1/10.

TABLE 3

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

Possible reactions	ΔH^0_{673K} *(kcal g mole^{-1})*
$CaO + (NH_4)_2SO_4 \rightleftharpoons CaSO_4 + 2\ NH_3 + H_2O$	6.696
$CaO + (NH_4)_2SO_4 + \frac{1}{2}\ O_2 \rightleftharpoons CaSO_4 + 4/3\ NH_3 + 2\ H_2O + 1/3\ N_2$	−43.63

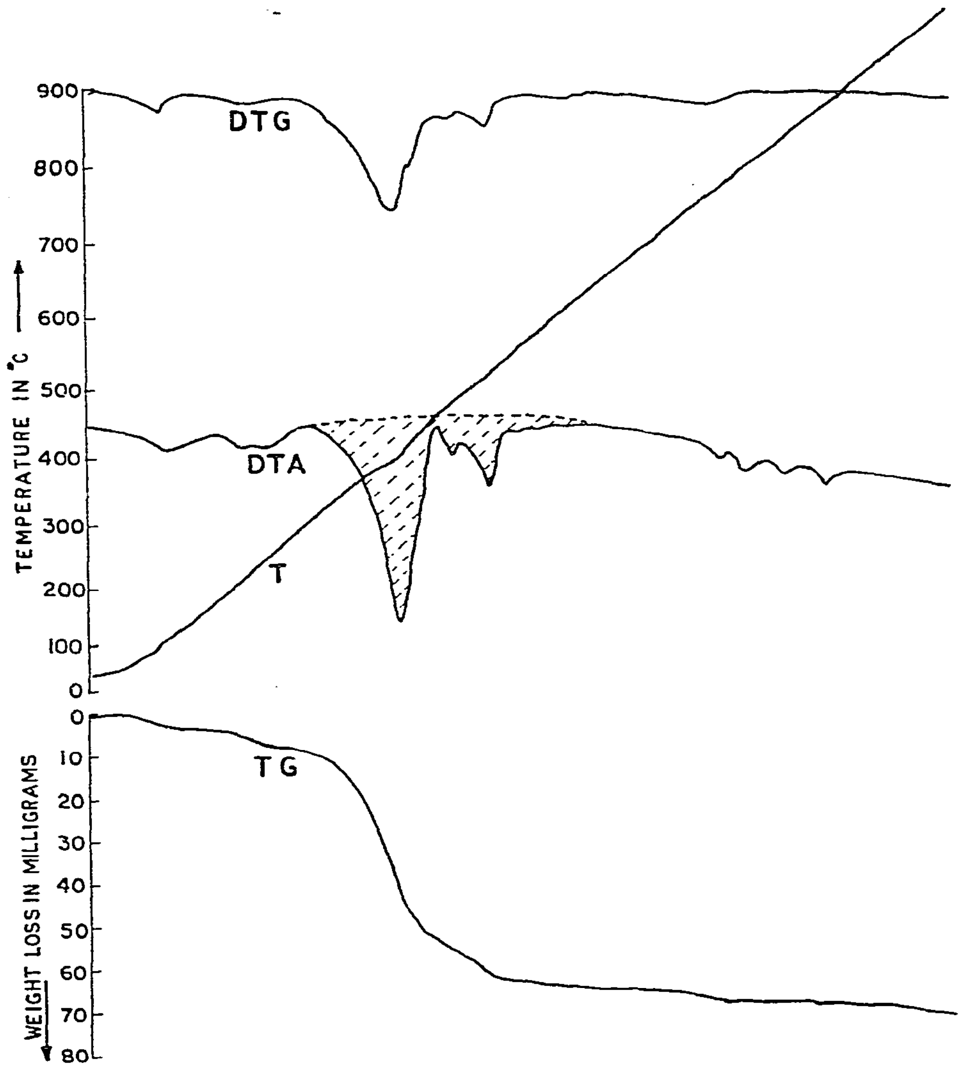

Fig. 4. Sample, CdO and ammonium sulfate mixture; amount, 640 mg; TG, 200 mg; DTA, 1/15; DTG, 1/10.

TABLE 4

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

Possible reactions	ΔH^0_{673K} *(kcal g mole^{-1})*
$CdO + (NH_4)_2SO_4 \rightleftharpoons CdSO_4 + 2\ NH_3 + H_2O$	37.67
$CdO + (NH_4)_2SO_4 + \frac{1}{2}\ O_2 \rightleftharpoons CdSO_4 + 4/3\ NH_3 + 2\ H_2O + 1/3\ N_2$	−12.68

the DTA curve. There is a possibility of basic sulfate ($2\ CdO \cdot CdSO_4$) formation as reported by Margulis et al.[4]. However, as the thermodynamic data at 290 K are not available, it is not possible to calculate the ΔH^0 values in such a case.

ZnO + (NH$_4$)$_2$SO$_4$

As seen from Fig. 5, there is an endothermic peak at 300 °C and another very small peak at 480 °C. However, they are assumed to be one peak starting at 200 °C and finishing at 550 °C. The ΔH°_{573K} value from the DTA curve is only -0.975 kcal g mole^{-1}. This value seems to match perfectly with the calculated value i.e. -0.94 kcal g mole^{-1} (eqn. 2, Table 5). The free energy calculated on the basis of $\Delta H^0 = -0.975$ kcal lies within ± 5 kcal, when plotted in Fig. 1. This suggests a higher feasibility for the sulfation of ZnO via SO$_2$ at 300 °C.

In general, from the sulfation studies of CuO, Fe$_2$O$_3$, MnO$_2$ and NiO[1] and of Al$_2$O$_3$, CaO, CdO and ZnO, the following observations can be made.

(1) The values obtained from the DTA curves clearly indicate a superimposition

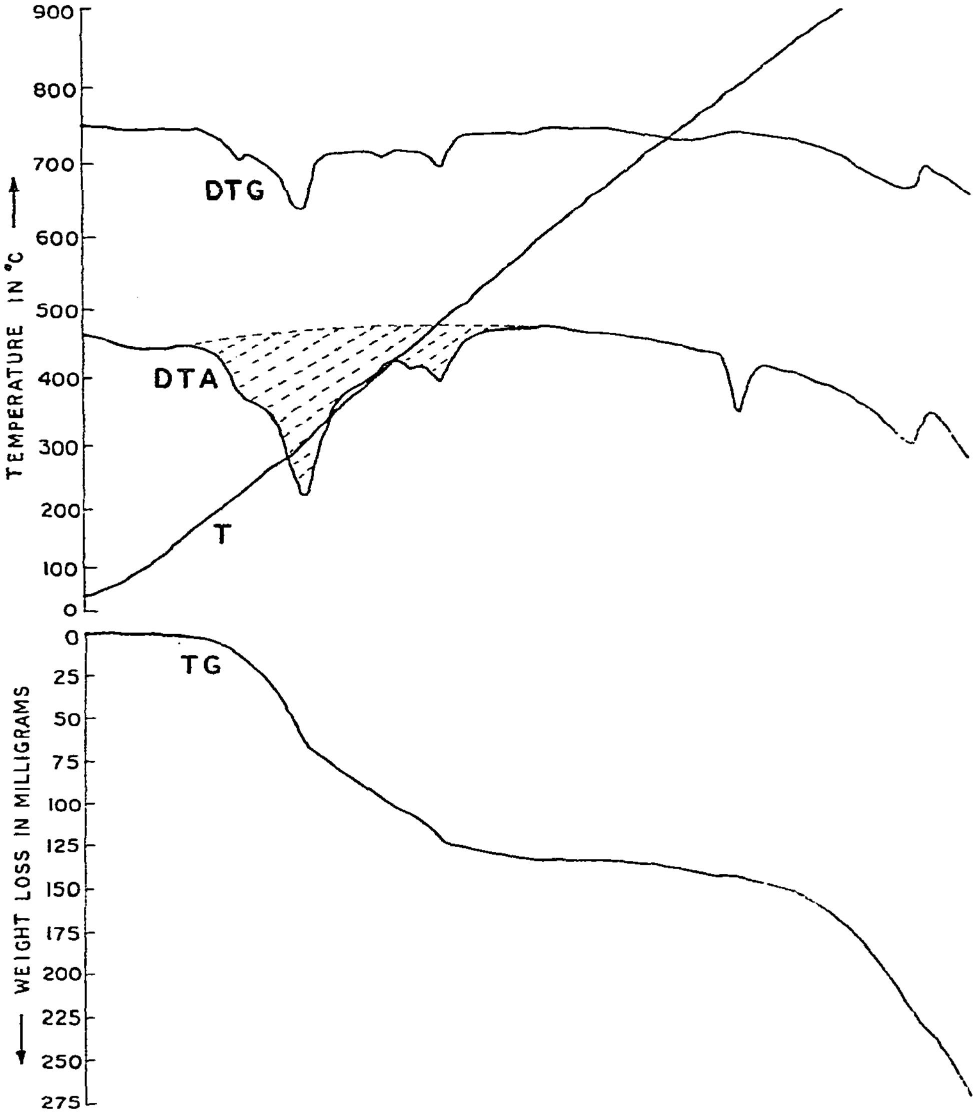

Fig. 5. Sample, ZnO and ammonium sulfate mixture; amount, 500 mg; TG, 500 mg; DTA, 1/15; DTG, 1/10.

TABLE 5

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

Possible reactions	ΔH^0_{573K} *(kcal g mole^{-1})*
$ZnO + (NH_4)_2SO_4 \rightleftharpoons ZnSO_4 + 2\ NH_3 + H_2O$	49.42
$ZnO + (NH_4)_2SO_4 + \frac{1}{2}\ O_2 \rightleftharpoons ZnSO_4 + 4/3\ NH_3 + 2\ H_2O + 1/3\ N_2$	−0.94

of some extra exothermic component. This might be due to either oxidation of SO_2 to SO_3 or that of NH_3 to N_2 and H_2O.

(2) Oxides of multivalent metals show comparatively more deviations than oxides of monovalent metals, which indicates that some complications are arising out of possible reduction reactions taking place simultaneously with sulfation which can not be correctly incorporated in the calculations.

(3) Distinctly basic oxides have shown better matching than less basic ones.

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