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EXTRACTION METALLURGY DIVISION

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SUMMARY

Comparative differential thermal analysis was used to estimate that 124 kcal/mole were required to dehydrate $MgSO_4 \cdot 7H_2O$. Fifty percent of the water was expelled rapidly in a stream of nitrogen at temperatures near 100° C. The remaining water was removed very slowly and dehydration was completed only at temperatures of about 300° C. When the dehydration was done under reduced pressure, an amorphous to crystalline transition followed the removal of the last traces of water. It released 6.58 kcal/mole of $MgSO_4$ at 285° C.

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INTRODUCTION

During a visit by one of the writers (TRI) to the Gordon Research Laboratories of The International Nickel Co. of Canada Ltd. at Sheraton Park on May 27, 1971, the subject of sulphur dioxide recovery and sulphate stability was discussed with Dr. S. Warner, Director of the laboratories, and Prof. H.H. Kellogg of Columbia University, a consultant. Dr. Warner was particularly interested in the amount of energy required to a) recover anhydrous $MgSO_4$ from the various hydrates and to b) decompose the sulphate for the recovery of MgO and SO_2. He pointed out that he would welcome any assistance we could provide on the heat requirements for either or both processes. Published values are in substantial disagreement. The problem was discussed with Dr. K.W. Downes and it was felt that, because of prior experience with these materials, we might be able to assist INCO at this time.

EXPERIMENTAL RESULTS AND DISCUSSION

Over a period of years, we have developed in these laboratories a reliable technique of semi-quantitative differential thermal analysis. By conducting DTA experiments under carefully controlled and reproduceable conditions, it is possible to estimate heats of reaction or of transition[1] within ± 4% or better.

In the first experiment, a known weight of reagent-grade stoichiometric $MgSO_4 \cdot 7H_2O$ was dehydrated in a stream of nigrogen in the DTA cell. The cell was heated at a rate of 1° C/min. The DTA curve consisted of two peaks. About half of the water was removed during the endotherm represented by the peak near 100° C. The remainder was removed slowly as the temperature was raised to 300° C. The area beneath the base line and the curve, per mole of $MgSO_4$, is proportional to the heat required for the dehydration. By dehydrating a known weight of $BaCl_2 \cdot 2H_2O$ under identical circumstances, it was possible to estimate the heat of dehydration of $MgSO_4 \cdot 7H_2O$ from the known heat of dehydration of $BaCl_2 \cdot 2H_2O$[(2)].

When $MgSO_4 \cdot 7H_2O$ was dehydrated under reduced pressure (10 Torr and 2° C/min.), the fine structure of the dehydration process became evident. Under these circumstances, it was possible to see two endotherms and the exotherm for the re-crystallization of the dehydrated material to the stable form of the anhydrous $MgSO_4$ crystal. The curve is shown in Figure 1. The heat of this transition was estimated by the comparative DTA technique using silver sulphate[(3)] as the standard material. It is important to note that the dehydration process is endothermic and the recrystallization exothermic. When dehydration was done in a stream of nitrogen, only the net effect was

shown. When the experiment was done under reduced pressure, both stages were evident. The actual dehydration enthalpy is greater than the net dehydration enthalpy by the heat of recrystallization.

The results of the experiments are shown in Table 1.

TABLE 1

COMPARISON OF DEHYDRATION AND RECRYSTALLIZATION ENTHALPIES

Compound	Enthalpy (kcal/mole)	Net Change (kcal/mole)
$BaCl_2 \cdot 2H_2O$	35.50	
Ag_2SO_4	4.460	
$MgSO_4 \cdot 7H_2O$ to $MgSO_4$ (amorphous)	132.9	
$MgSO_4$ (amorphous to crystal)	-6.58	126.3
$MgSO_4 \cdot 7H_2O$ crystal to $MgSO_4$ crystal	121.6 121.9	121.7
Average		124.0±5
Average estimate based on entropy and Nernst calculation[3]		135.1±10

Within experimental error, our results are in good agreement with the average of estimates by Berg and Pribylov[3], but the results are somewhat higher than those shown in the National Bureau of Standards Circular 500[5].

ACKNOWLEDGEMENTS

Mr. P. Belanger made the X-ray diffraction analyses to identify the compounds and Mr. Y. Lavoie did some of the experimental work.

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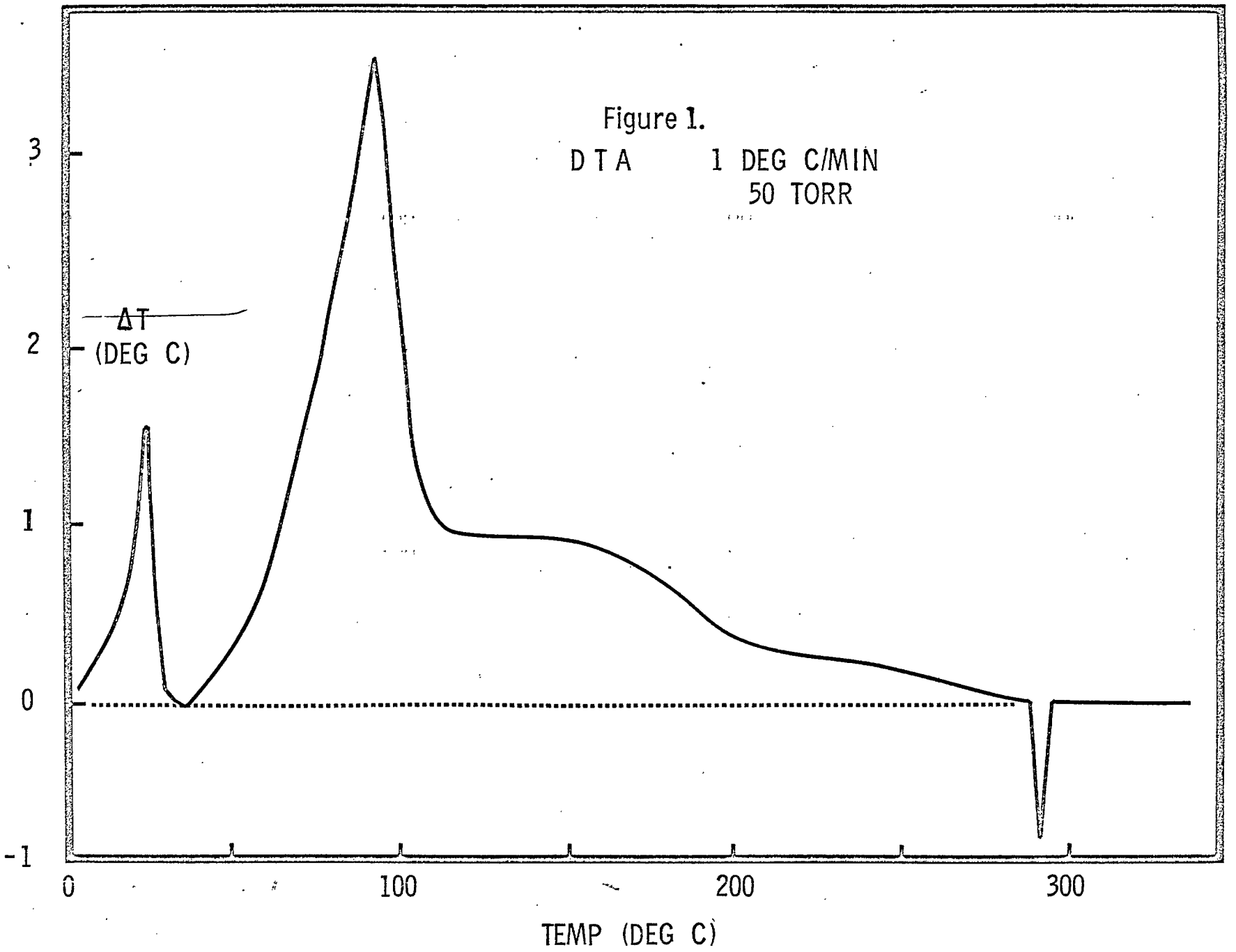
Figure 1.
D T A 1 DEG C/MIN
50 TORR
ΔT
(DEG C)
3
2
1
0
-1
0
100
200
300
TEMP (DEG C)