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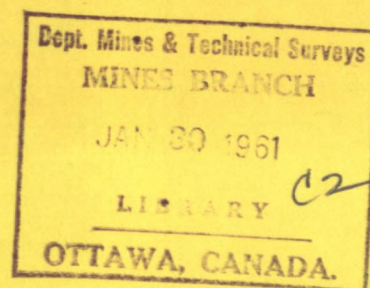
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DECOMPOSITION PRESSURES OF FERRIC SULPHATE AND ALUMINUM SULPHATE



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DECOMPOSITION PRESSURES OF FERRIC SULPHATE AND ALUMINUM SULPHATE¹

N. A. WARNER² AND T. R. INGRAHAM³

ABSTRACT

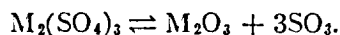
The gas pressures over samples of anhydrous ferric sulphate and anhydrous aluminum sulphate have been measured in a static system, using a mercury manometer in which the exposed surface was covered with a flexible Pyrex bellows. The calculated ΔH for the decomposition of $\text{Fe}_2(\text{SO}_4)_3$ was +135.4 kcal/mole. It was not possible to calculate the ΔH for the $\text{Al}_2(\text{SO}_4)_3$ decomposition, because a discrete aluminum oxide with singular thermodynamic properties was not obtained.

In the $\text{Fe}_2(\text{SO}_4)_3$ system, the fraction of SO_3 in the gas phase was found to be almost constant over the range of temperature and pressure changes used in the study.

At any given temperature, the decomposition pressure over a ferric sulphate sample is greater than that over an aluminum sulphate sample, thus indicating that preferential decomposition of ferric sulphate should be thermodynamically feasible in mixtures of ferric sulphate and aluminum sulphate.

INTRODUCTION

When metallic sulphates are heated *in vacuo* or in a neutral atmosphere, they can be decomposed to oxides, e.g.,



The ease with which this decomposition can be brought about varies widely with the different metallic sulphates. This variation has been utilized commercially in the separation of some sulphates. For example, copper sulphate is more stable than ferric sulphate. Hence, when some ores which contain copper and iron compounds are roasted in controlled sulphating atmospheres, it is possible to prepare copper sulphate almost selectively, while the iron is retained as oxide. Simple leaching techniques effectively separate the soluble copper sulphate from the insoluble iron oxide. The same basic principle of selective sulphate formation or decomposition has been applied industrially for the separation of cadmium and zinc compounds when they occur together in smelting dusts (1).

One of the recently patented methods for separating the constituents of clays and shales (2) would seem to depend on the fact that aluminum sulphate is more stable than ferric sulphate. Since the problem of utilizing the constituents of shale is an important one, the literature was searched to determine whether this assumption were true. Very little information is available on the stability of either compound, and the published data (3) fail to satisfy the critical tests of Kelley (4). Hence, it seemed worth while to measure the decomposition pressures of both of these compounds to determine whether the separation would be thermodynamically possible.

APPARATUS AND PROCEDURE

Because of its simplicity, a static method was chosen for measuring the equilibrium dissociation pressures of the sulphates. The apparatus assembled for the measurements

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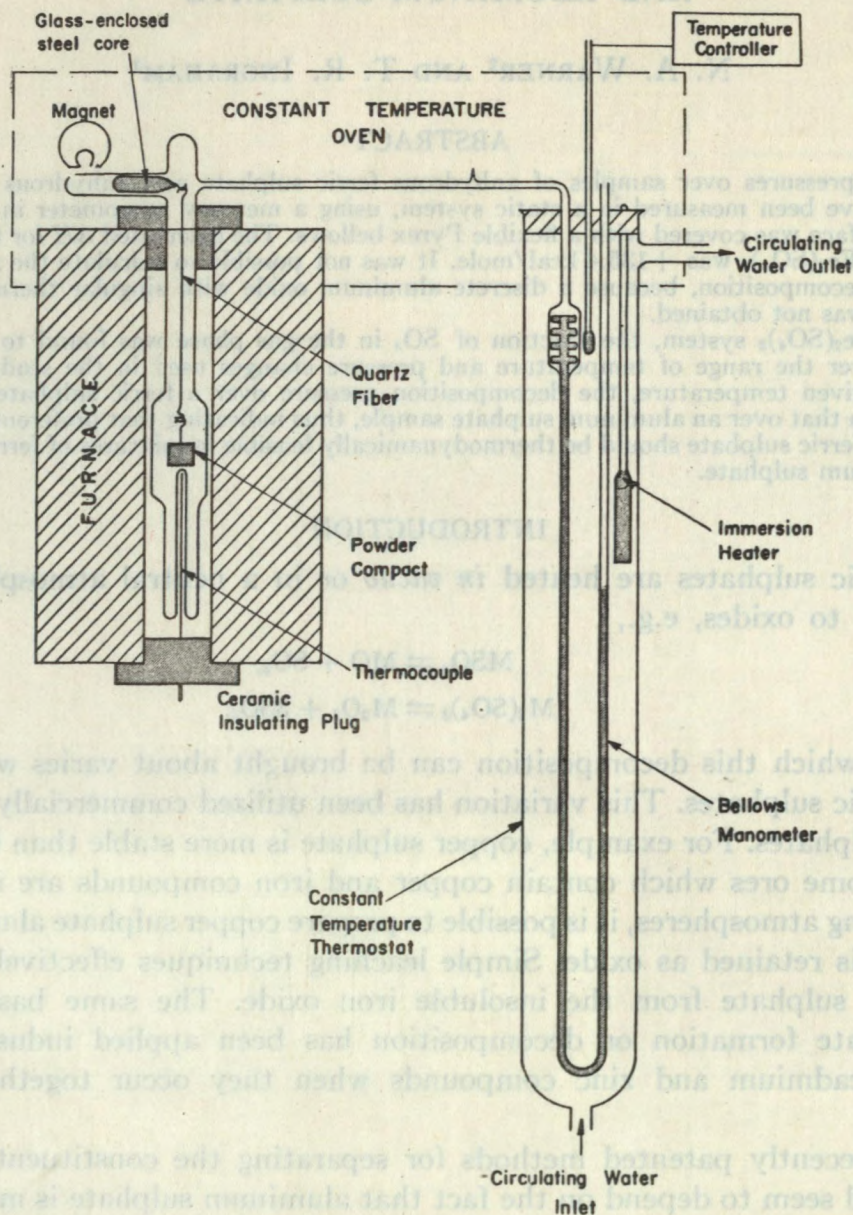


FIG. 1. Apparatus for measuring decomposition pressures of anhydrous sulphates.

is shown diagrammatically in Fig. 1. The most important feature of the apparatus is the glass-bellows mercury manometer. The design of the manometer is based on one originated by Spence (5). However, in the present version the mercury displacement has been modified from horizontal to vertical, and an appreciable increase in sensitivity has resulted (6).

The apparatus was constructed entirely from Pyrex and Vycor glass. The Vycor section extended out to the cool zone of the furnace, where it was joined through graded seals to the Pyrex part of the apparatus.

To avoid complications that might be introduced by the condensation of sulphur trioxide, the bellows manometer and the connecting tubing were thermostatically controlled at a temperature of 60° C.

For convenience in handling, powder compacts of anhydrous ferric sulphate and aluminum sulphate were pressed with a small platinum wire anchored in the pellet. The pellets were suspended by this platinum wire and a small quartz fiber which was attached

to a magnetically moveable hook. The hook was made moveable to permit free access for installing and removing the pellet through the top of the furnace tube.

After installation of each pellet, the reaction tube was sealed and the apparatus was evacuated. During the period of evacuation the pellet was heated to a temperature of about 650° C to remove the last traces of moisture. After several hours at this temperature, the vacuum line was sealed and the temperature raised to the point at which displacement of the mercury column indicated that decomposition of the sulphate had begun. Readings of the pressure were made at 24-hour intervals in the study of the ferric sulphate system, and at 48-hour intervals in the study of the aluminum sulphate system. The experiment was continued until a steady state had been reached.

Displacement of the mercury column in the manometer was observed with a cathetometer, and was corrected for changes in barometric pressure. With small changes in pressure, some sticking of the mercury in the column was noted. Sticking was relieved by rapping the manometer sharply just before readings were made.

RESULTS AND DISCUSSION

The results obtained in experiments with ferric sulphate, with aluminum sulphate, and with 1:1 mole mixtures of aluminum sulphate with iron oxide are shown in Table I.

TABLE I
Decomposition pressures over ferric sulphate, aluminum sulphate, and an aluminum sulphate - iron oxide mixture

Ferric sulphate		Aluminum sulphate		Aluminum sulphate - ferric oxide (mole ratio 1:1)	
Temp. (°C)	Pressure (cm of Hg)	Temp. (°C)	Pressure (cm of Hg)	Temp. (°C)	Pressure (cm of Hg)
				627	1.0
630*	7.3				
638	8.4	652*	1.4		
658	14.7				
660*	16.8	673*	2.4	679	3.2
680*	27.1	680	2.4		
685	28.6	694	3.6		
700	41.9				
705*	48.1	708	4.5		
715	61.1				
724	72.0	730	7.8	724	14.1
				736	49.6
				742	54.3
		743	13.5		
		753	19.4	752	71.7
		762	28.2		
		769	40.0		
		777	72.0		

*Measurements made with temperature decreasing. All other measurements made with temperature increasing.

Ferric Sulphate

When the results shown in Table I were plotted on a $\log p$ versus reciprocal of absolute temperature graph, Fig. 2 was obtained. It will be noted from Fig. 2 that the linearity

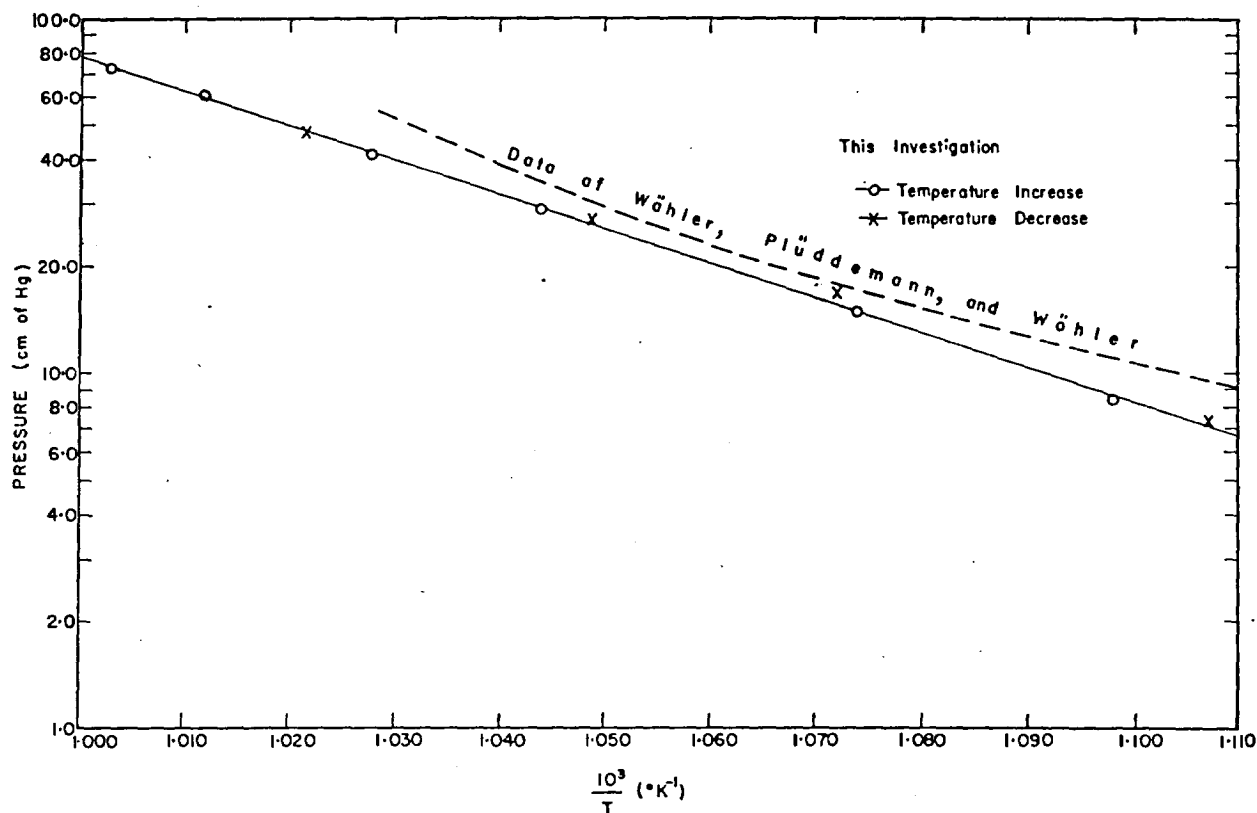


FIG. 2. Pressure vs. reciprocal temperature relationship for anhydrous ferric sulphate.

of the results is good, thus indicating that over the temperature range of the experiments there is not an appreciable change in the heat of the decomposition reaction. The linearity of the results and the demonstrated reversibility of the system indicate that true equilibrium had been reached in the experiments and that the gas phase probably contained only SO_2 , SO_3 , and O_2 . It seems unlikely that polymers of SO_3 were present. The iron oxide product was identified as hematite.

When the static method of measuring the decomposition pressures was selected, the selection was made with some misgiving. From preliminary experiments it had been established that the dynamic method might be subject to substantial errors, because the rate of attainment of equilibrium decreases as equilibrium is approached, and it would be easy to assume that equilibrium had been reached, when in fact the reaction was still proceeding slowly.

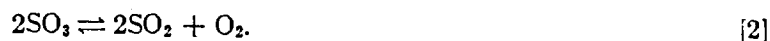
Alternatively, the measurement of pressures in a static system containing a substantial temperature gradient and gases of different molecular weights is also subject to error. In this instance, due to thermal diffusion, the lighter molecules tend to congregate in the hotter zone. This means that the 2:1 molar ratio of SO_2 : O_2 , produced by the decomposition of SO_3 , is reduced to somewhat less than 2:1 in the hot zone, and increased to somewhat more than 2:1 in the cold zone. This departure from exact stoichiometry can lead to errors in any quantities, e.g. degree of dissociation, etc., calculated on the basis of the 2:1 stoichiometry.

The magnitude of the error caused by thermal diffusion is difficult to assess on a purely theoretical basis (7), but the linearity of the results shown in Fig. 2 would favor the conclusion that the error is small or at least comparable with the other errors of measurement. Recently a novel method of studying sulphate equilibria, through the measurement of only one gas pressure, was developed by Kellogg (8). It is expected that when similar systems have been examined by both methods, it may be possible to assess the magnitude of the thermal diffusion error.

Having measured the decomposition pressure exerted by the mixed gases SO_3 , SO_2 , and O_2 , over a ferric sulphate sample, it was of interest to calculate the heat of the decomposition reaction



from the variation of the equilibrium constant of the reaction with temperature. For this calculation it was necessary to know p_{SO_3} , since $K'_p = p^3_{\text{SO}_3}$ for reaction 1. The magnitude of p_{SO_3} was calculated on the assumption that p_{SO_3} satisfied both equation 1 and the equation for the decomposition of SO_3 ,



The calculation was made by obtaining the equilibrium constant K_p , for reaction 2, from the data of Evans and Wagman (9) and converting this K_p to K_x (the equilibrium constant in terms of mole fractions) by dividing by the total pressure at each of a series of temperatures. For convenience and to minimize errors, interpolated temperatures from Fig. 2 were used.

When K_x had been calculated, it was equated to the equilibrium constant which was set up in mole fraction form on the basis that α is the fraction of 1 mole of SO_3 dissociated at a given temperature. Thus, $\{2(1-\alpha)\}/\{(2+\alpha)\}$ represents the mole fractions of SO_3 , and $K_x = 4\alpha^3/(4\alpha^3 - 12\alpha + 8)$. It should be noted that in this calculation an exact $\text{SO}_2:\text{O}_2$ ratio of 2:1 is implicitly assumed.

When K_x was calculated, it was found to be almost constant, with an average deviation of 1% over the temperature range 920 to 1000° K. The average K_x was used in calculations, and $\alpha = 0.538$ and a mole fraction of $\text{SO}_3 = 0.364$ were obtained.

The implications of the constancy of the mole fraction of SO_3 are of interest. Once the value 0.364 is known, the pressure of SO_3 in a system can be set very conveniently by including an excess of ferric sulphate in the system and then heating the system until the total pressure, reduced by the factor 0.364, produces the required partial pressure of SO_3 .

When $\log K'_p = p^3_{\text{SO}_3}$ was plotted against reciprocal absolute temperature, a linear relationship was obtained. The relationship can be described by the equation:

$$\log K'_p = 28.34 - (29,600/T).$$

When this equation was used to calculate the heat of reaction for the dissociation of ferric sulphate, a ΔH of +135.4 kcal was obtained.

Aluminum Sulphate

The results obtained from a study of the decomposition of aluminum sulphate and 1:1 mole mixtures of aluminum sulphate with ferric oxide are shown in Table I and as a log P versus reciprocal temperature relationship in Fig. 3. The curvature of the relationship indicates that the type of treatment accorded the ferric sulphate results to obtain a heat of decomposition would not be valid for the aluminum sulphate systems. It would

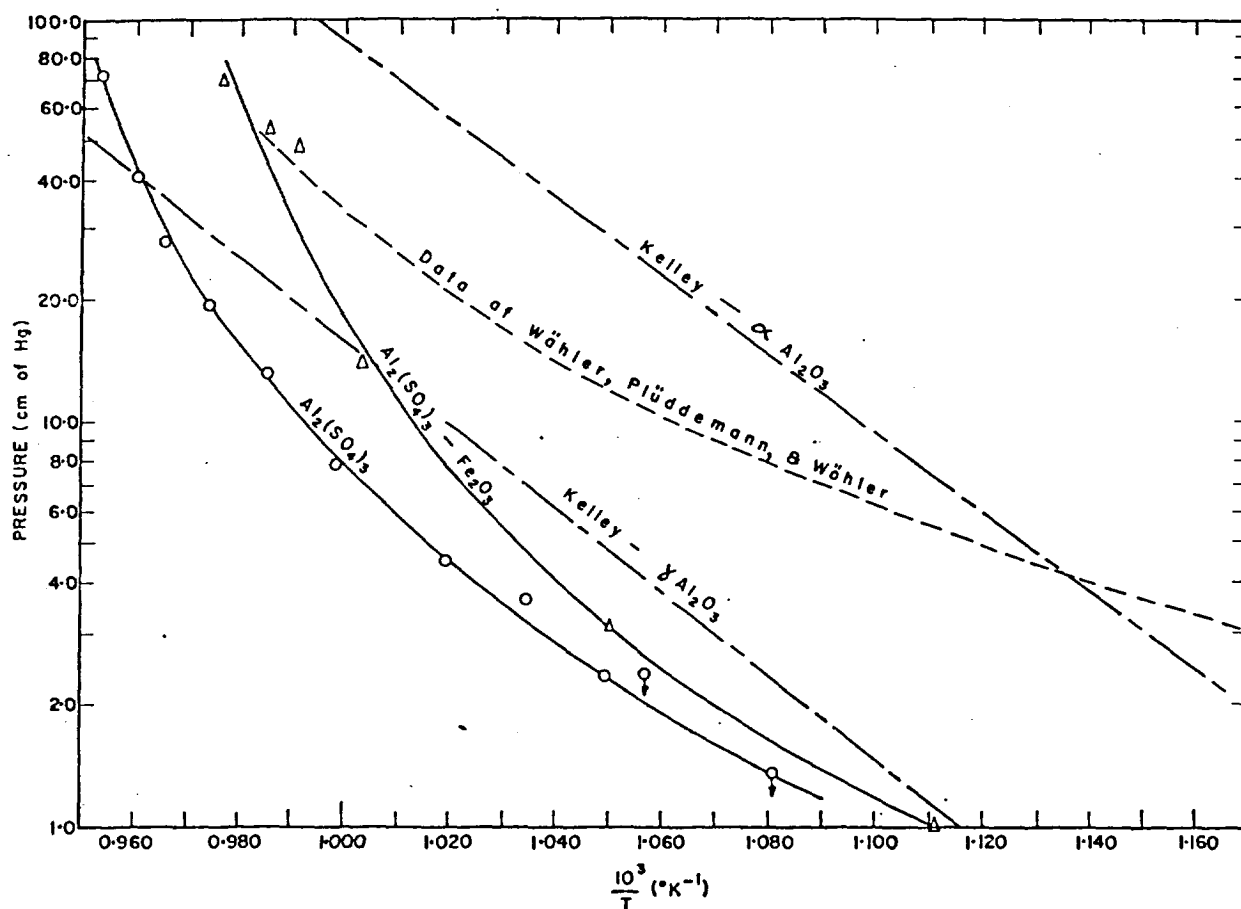


FIG. 3. Pressure vs. reciprocal temperature relationship for anhydrous aluminum sulphate and aluminum sulphate - iron oxide mixtures.

therefore seem sufficient to seek an explanation for the lack of linearity of the results, and to compare the pressures with the corresponding pressures for ferric sulphate, under similar conditions of temperature.

When the partly decomposed and completely decomposed pellets of aluminum sulphate were examined by X-ray diffraction, it was observed that gamma alumina was present. In one pellet which had been heated for a long time at a high temperature, alpha alumina was found. This is in general agreement with the observations of Kelley (10): "In actual decomposition of $\text{Al}_2(\text{SO}_4)_3$, there is not obtained Al_2O_3 (alpha) but a less stable variety usually designated Al_2O_3 (gamma). Unfortunately the latter appears not to have unique thermodynamic properties; available information indicates that there may be two varieties of Al_2O_3 (gamma) or at any rate that its properties depend upon the temperature to which it is heated and the time of heating." From the foregoing, it would seem possible that the results shown in Fig. 3 represent steady-state pressures over a metastable system of aluminum sulphate and some modification of gamma alumina. The curvature of the line in Fig. 3 could be interpreted as representing the presence of an increasingly stable modification of alumina, as the temperature of the experiments was increased. From a few experiments, there was an indication that the pressure measurements, although steady, were not readily reversible if the temperature of the specimen had previously been raised to appreciably above the temperature of the measurement. This would tend to confirm the presence of the more stable form of alumina at higher temperatures. Time did not permit a more extensive investigation of this point.

It is of interest to note, in Fig. 3, that the stable pressures over the aluminum sulphate -

ferric oxide system are, at all temperatures, greater than those over pure aluminum sulphate. This has been resolved by considering that ferric oxide acts as a catalyst in promoting the formation of the more stable forms of alumina. Higher equilibrium pressures are to be expected over the more stable forms of alumina.

Finally, it is of interest to compare, in Table I, the steady-state pressures over the ferric sulphate and aluminum sulphate systems at various temperatures. The comparison shows clearly that at all temperatures the pressure at any given temperature is always greater over the ferric sulphate system than over an aluminum sulphate system.

TABLE II
Calculations made to determine ΔH for the reaction $\text{Fe}_2(\text{SO}_4)_3 \rightleftharpoons \text{Fe}_2\text{O}_3 + 3\text{SO}_2$

T (°K)	K_p	P (atm)	K_x	α	N_{SO_2}	K'_p
920	0.0415	0.1466	0.283	0.538	0.364	1.519×10^{-4}
940	0.0706	0.2480	0.284			7.356×10^{-4}
960	0.1172	0.4046	0.290			3.194×10^{-3}
980	0.1914	0.6650	0.288			1.418×10^{-2}
1000	0.3050	1.047	0.291			5.535×10^{-2}
			Average 0.287 ± 0.003			

CONCLUSIONS

From an examination of the steady-state gas pressures over ferric sulphate and aluminum sulphate samples heated in a closed system, it has been concluded that the pressure at any given temperature is always substantially greater over a ferric sulphate sample. Hence, it would seem thermodynamically feasible to separate aluminum sulphate from ferric sulphate by roasting the compounds under conditions selected to decompose the ferric sulphate only, and then leaching the water-soluble aluminum sulphate from the roasted mixture. The practical limitations affecting the application of this approach will be discussed in a later communication.

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