

Before concluding, the authors wish to thank the Standard Oil Development Company for the samples of *n*-amyl alcohol, *tert*-amyl alcohol and isopropyl ether used in this investigation.

### Summary

1. The specific heats of ten organic compounds containing oxygen or nitrogen have been measured over a wide range of temperatures. Heats of fusion and of transition have also been determined in five cases.

2. The entropies of the ten compounds have been calculated from these heat capacity data. In general, the results are in good agreement with the corresponding values predicted by the use of some empirical entropy regularities.

3. The corresponding free energies for nine of these compounds have also been calculated. The result in the case of urea provides an excellent check upon the third law of thermodynamics.

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RECEIVED FEBRUARY 27, 1933

PUBLISHED JULY 6, 1933

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY,  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 30]

## Indium Sulfate

BY RALPH P. SEWARD

The only sulfates of indium, with the exception of the alums and other double salts, discussed by Mellor<sup>1</sup> are the acid salt  $\text{In}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$  attributed to R. E. Meyer<sup>2</sup> and  $\text{In}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  prepared by C. Winkler<sup>3</sup> by evaporation of indium sulfate solution to dryness at 100°. The observations reported here are in substantial agreement with those of R. E. Meyer but not with those of C. Winkler. Some additional data on the properties of indium sulfate have been secured.

The source of indium for the work was "99.99" pure metallic indium obtained from the Grasselli Company. A sulfate solution was first prepared by the addition of sulfuric acid in slight excess to a suspension of indium hydroxide. On concentration a thick sirup formed from which crystals were secured with some difficulty. Analysis of the product showed the presence of 1.8 moles of sulfate per atom of indium. Since it appeared that the material might be a mixture, the effect of changing the amount of free sulfuric acid was investigated.

**Indium Acid Sulfate.**—When indium sulfate solution containing a large excess of sulfuric acid was concentrated at about 50°, crystallization occurred readily. After washing with acetic acid and drying, the product was analyzed for indium by precipita-

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(1) J. W. Mellor, "Comprehensive Treatise," Vol. V, p. 404.

(2) R. E. Meyer, "Das Indium," Leipzig, 1868.

(3) C. Winkler, *J. prakt. Chem.*, [1] **102**, 373 (1867).

tion of the hydroxide with ammonia, ignition and weighing as the oxide. The sulfate content was determined in the usual way as barium sulfate. Since Thiel and Koelsch<sup>4</sup> have shown that some decomposition of indium oxide occurs at temperatures above 850°, weighed samples of the metal were dissolved in acid, the hydroxide precipitated and ignited in a small porcelain crucible with the full flame of a "Meker" burner. No appreciable decomposition was found. Samples of the crystals had the following composition: In, 30.90, 30.86; SO<sub>4</sub>, 51.83, 52.15. Calcd. for In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>SO<sub>4</sub>·7H<sub>2</sub>O: In, 31.00; SO<sub>4</sub>, 51.75. These values are in reasonable agreement with the formula In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>SO<sub>4</sub>·7H<sub>2</sub>O. It is probable that this is the compound prepared by R. E. Meyer.

The crystals are shining diamond-shaped plates belonging to the orthorhombic system. This salt is not deliquescent and is stable under ordinary atmospheric conditions. On heating to about 250°, fumes of sulfuric acid appear and a residue of the anhydrous normal sulfate is left.

**Normal Indium Sulfate.**—If the acid salt is heated until no more fuming occurs the residue is completely soluble in water. By slow evaporation of the solution at room temperature, small well-defined, prismatic crystals belonging to the monoclinic system are formed. The crystallized product is not deliquescent under ordinary atmospheric conditions. Analysis of this product after drying on filter paper indicated that it is a hydrate of the normal salt In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>: Subs., 0.2520, 0.2675 g.; In<sub>2</sub>O<sub>3</sub>, 0.1015, 0.1058 g.; BaSO<sub>4</sub>, 0.2558, 0.2677 g.; moles SO<sub>3</sub> per mole In<sub>2</sub>O<sub>3</sub>, 3.00, 3.01.

A sample of clear solution which had been in contact with the crystals for two days at room temperature, 25 ± 2° was found to have a specific gravity of 1.83 and contained 0.621 g. of anhydrous sulfate per gram of solution. The solid phase was indicated by the following investigation to be In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O.

**Hydrates of Normal Indium Sulfate.**—The high solubility of indium sulfate makes it difficult to secure complete removal of the solution from the crystals without danger of dehydrating them. For this reason a study of the decomposition pressures at 25° of hydrated indium sulfate was made to establish the composition of the crystals prepared above. This study was made by progressively pumping off water from a solution of the sulfate, measuring the pressure of water vapor in equilibrium with the solution and, when this had disappeared, with the solid hydrates. The pressures were measured with a mercury manometer. The indium sulfate was contained in a glass tube, immersed in a thermostat at 25°, which was connected through a ground-glass joint with the vacuum pump and manometer. This tube could be detached and weighed after every pressure measurement and the composition of the material in the tube calculated from this weight and the known weight of anhydrous indium sulfate. The equilibrium pressures for a series of compositions are given in Table I and the accompanying figure.

TABLE I

Moles H <sub>2</sub> O per mole In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	P, mm.	Moles H <sub>2</sub> O per mole In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	P, mm.	Moles H <sub>2</sub> O per mole In <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	P, mm.
18.00	17.6	12.09	15.2	6.34	12.8
15.53	17.0	9.21	15.0	6.14	10.0
14.00	15.6	9.03	12.0	5.92	1.5
13.20	15.2	7.17	12.5	5.26	1.5

Inspection of Fig. 1 shows a pressure of about 15 mm. for the saturated solution in equilibrium with the hydrate In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O. The constant value of the pressure between 9 moles and 6 indicates the appearance in this region of In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O. The existence of lower hydrates is indicated by the following experiment. The hydrate heated to constant weight at 100° retained an amount of water equivalent to three moles.

(4) Thiel and Koelsch, *Z. anorg. Chem.*, **66**, 288 (1910).

This result is not in agreement with that of C. Winkler, whose weights indicate 9 moles of water of hydration at this temperature.

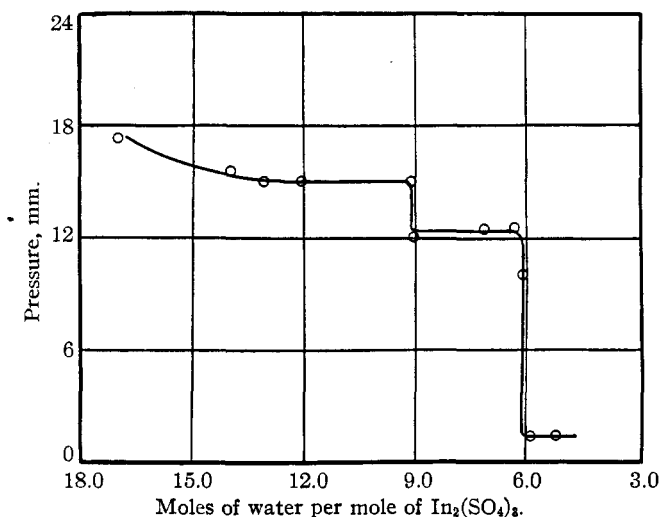


Fig. 1.—Decomposition pressures of hydrates of indium sulfate at 25°.

**Basic Indium Sulfate.**—No systematic study of the formation of basic sulfates was made. Since the solid precipitated by the addition of alcohol to indium sulfate solution was found to be a basic salt, it is described here. Microscopic examination showed this material to consist of small bi-axial positive crystals, probably monoclinic. It was found to be very slightly soluble in water. The analysis follows: In, 42.40, 42.58;  $\text{SO}_4$ , 35.08, 35.10; calcd. for  $\text{In}_2\text{O}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ ; In, 42.10;  $\text{SO}_4$ , 35.19.

**Decomposition Pressures of Anhydrous Indium Sulfate.**—The decomposition of anhydrous indium sulfate was studied by measuring the pressure of the gaseous products of decomposition in equilibrium with the solids at several temperatures. The sulfate, previously dried at 500°, was placed in a silica tube in an electric furnace and the pressure developed at different temperatures was measured with a mercury manometer. To protect the mercury from attack it was separated from the sulfate by a stopcock and a pressure of air admitted on the manometer side. After several trials a pressure of air was arrived at so that no change in the mercury level took place on opening the stopcock. At each temperature this process was repeated two or more times, pumping out the system after each measurement. Since successive pressure readings at a given temperature were in good agreement, it is considered that they represent true equilibrium values within the limits of temperature control,  $\pm 5^\circ$ . The pressures for a series of temperatures are recorded in Table II and shown graphically in Fig. 2, and for comparison those of the more familiar sulfates of aluminum and zinc as given by Willard and Fowler.<sup>5</sup>

TABLE II  
DECOMPOSITION PRESSURES OF ANHYDROUS INDIUM SULFATE

<i>T</i> , °C.....	645	682	705	771	780	803	815	820
<i>P</i> , mm.....	10	40	67	250	315	600	790	900

(5) Willard and Fowler, *THIS JOURNAL*, **54**, 496 (1932).

Pumping off the gaseous decomposition products at 800° brought about complete removal of the sulfate without any falling off in the pressure, indicating that the sulfate decomposes directly to the oxide and not to a basic sulfate.

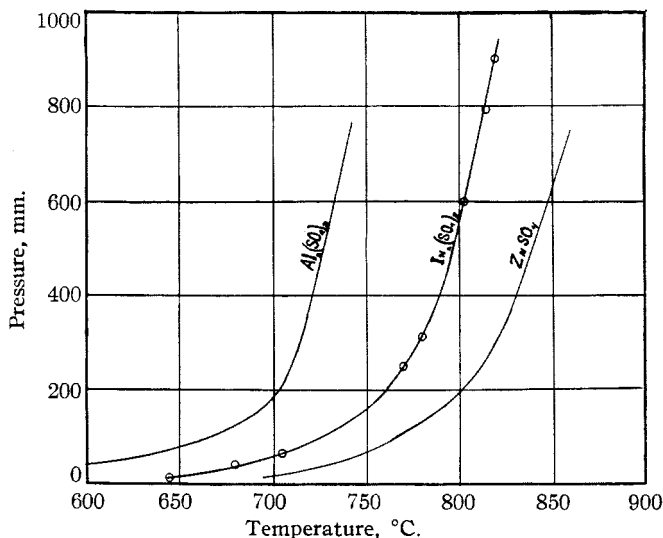


Fig. 2.—Decomposition pressures of aluminum, indium and zinc sulfate.

**Hydrolysis of Indium Sulfate.**—*P<sub>H</sub>* measurements on indium sulfate solutions by means of the quinhydrone electrode indicate a considerable degree of hydrolysis at room temperature. Solutions were prepared in two ways to ensure freedom from free sulfuric acid. One sample of sulfate was heated to 550° in a current of air for several hours and then dissolved in water. The second was a solution of indium sulfate which had stood in contact with a suspension of indium hydroxide for several days. The more dilute solutions were made by adding water to the original solutions. Solutions prepared by the second method gave the following values:

Concn. in moles per liter.....	0.140	0.042	0.0136
<i>P<sub>H</sub></i> .....	1.85	2.25	2.74

Solutions prepared by the first method gave *P<sub>H</sub>* values about 0.2 of a unit lower. These solutions show considerably greater acidity than solutions of aluminum sulfate of the same concentration. The measurements of Davis and Farnham<sup>6</sup> indicate a *P<sub>H</sub>* of about 2.85 for 0.14 molar aluminum sulfate. Since calculation of the per cent. hydrolysis requires an assumption as to the mechanism of the reaction, this has not been done.

### Summary

1. Indium sulfate was crystallized at room temperature, from solutions free from excess acid, as  $In_2(SO_4)_3 \cdot 9H_2O$ . The acid salt  $In_2(SO_4)_3 \cdot H_2SO_4 \cdot 7H_2O$  was formed in the presence of excess sulfuric acid and a basic salt  $In_2O(SO_4)_2 \cdot 6H_2O$  was precipitated by the addition of alcohol.

(6) Davis and Farnham, *J. Phys. Chem.*, **36**, 1057 (1932).

2. The decomposition pressure of the anhydrous normal sulfate reaches one atmosphere at about  $810^{\circ}$ .

3. *PH* measurements of indium sulfate solutions show that a considerable degree of hydrolysis occurs.

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RECEIVED FEBRUARY 28, 1933

PUBLISHED JULY 6, 1933

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

## Heat Capacity Curves of the Simpler Gases. III. Heat Capacity, Entropy and Free Energy of Neutral OH from Near Zero Absolute to $5000^{\circ}\text{K}$ .

BY HERRICK L. JOHNSTON AND DAVID H. DAWSON<sup>1</sup>

One of the interesting developments in chemistry during the past decade has been the discovery of hitherto unsuspected, and even unorthodox, molecules which often play important roles during the intermediate stages of chemical reactions. Among the more important of these is the neutral OH molecule, present in flames and often formed in gaseous reactions in which hydrogen and oxygen are present in either the free or combined forms. The importance of this molecule, particularly in connection with reactions at high temperatures, warrants the computation of tables of its thermodynamic properties, for use in equilibrium calculations. Its spectrum, although complicated, has been satisfactorily worked out and so permits application of the accurate methods employed in earlier papers<sup>2</sup> of this series. Added interest is attached to the heat capacity curve at low temperatures due to the influence of an unusually large  $\Lambda$  type doubling. While no immediate practical importance attaches to this in connection with OH itself it typifies an effect sometimes present to a lesser degree in the heat capacity curves of other, more stable molecules.

In the following pages we make tabulations of heat capacity, entropy, "free energy" and "total" energy to a maximum temperature of  $5000^{\circ}\text{K}$ . For a description of the details of the methods which we have employed in our calculations and for the meanings of symbols which are employed in the following pages without redefinition the reader is referred to the paper by Johnston and Chapman.<sup>2a</sup>

**Spectroscopic Interpretation of Neutral OH.**—The ultraviolet "water vapor" bands were among the earliest molecular spectra to undergo examination,<sup>3</sup> and have been the subject of numerous subsequent investiga-

(1) Du Pont Fellow in Chemistry, Academic Year 1932-1933.

(2) (a) Johnston and Chapman, *THIS JOURNAL*, **55**, 153 (1933); (b) Johnston and Walker, *ibid.*, **55**, 172, 187 (1933).

(3) Liveing and Dewar, *Proc. Roy. Soc. (London)*, **30**, 498, 580 (1880); *ibid.*, **33**, 274 (1882); *Phil. Trans.*, **129**, 271 (1880); cf. also Deslandres, *Ann. chim. phys.*, **14**, 257 (1888); *Compt. rend.*, **100**, 854 (1888).