

# A METHOD FOR EVALUATING AND CORRELATING THERMODYNAMIC DATA

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A useful thermodynamic function has been developed which permits (1) fitting of high-temperature heat content data with algebraic equations by a fast and accurate method; (2) accurate smoothing of high-temperature heat content data; (3) correlation of low-temperature heat capacity data with high-temperature heat content data; (4) accurate evaluation of heats of transition and fusion at high temperatures; (5) accurate calculation of heat capacities at high temperatures from heat content data.

Many laboratories are engaged in measurements of low temperature heat capacities, in which a measured amount of heat is added to a sample to raise its temperature by a relatively small amount. The heat capacity at the mean temperature is calculated from the energy supplied, divided by the temperature rise, the assumption being made that the heat capacity varies linearly with temperature over this small temperature interval. Precisions in the heat capacities measured by this method usually do not exceed a few tenths of one per cent.

Most attempts to use this method at moderately high temperatures have failed, however, so far as accuracy is concerned, because it was impossible to evaluate satisfactorily the corrections for heat interchange with the surroundings. In fact, the experimental plots of most low-temperature heat capacity data will have more scatter of the experimental points in the neighborhood of room temperature than at lower temperatures. Consequently, the experimental method most widely employed for extending thermodynamic data above room temperature has been the method of mixtures, or so-called "drop" method, in which a sample is heated in a furnace to a temperature  $T$ , allowed to drop into a calorimeter maintained at some convenient temperature near room temperature (e.g., 298.16°K.), and the amount of heat delivered to the calorimeter,  $H_T - H_{298.16}$ , measured.

The curves obtained by the usual plot of experimental  $H_T - H_{298.16}$  values vs.  $T$ , barring anomalies such as transitions and fusions, can be roughly approximated as straight lines, with  $H_T - H_{298.16} = 0$ , when  $T = 298.16^\circ\text{K}$ . Such a plot is not satisfactory for obtaining smoothed values of  $H_T - H_{298.16}$ , especially at the lower temperatures, where a certain vertical displacement becomes percentage-wise a much greater error. Some investigators plot the function  $(H_T - H_{298.16})/(T - 298.16)$  vs.  $T$ , which permits some magnification of the vertical scale, since the function is not equal to zero at 298.16°K., but becomes  $C_{p298.16}$  at this temperature.

High-temperature heat content data should not be considered entirely divorced from low-temperature heat capacity data for the same substance, and yet it is difficult to correlate the two sets of data. A few investigators attempt to differentiate graphically their high-temperature heat content curves<sup>1</sup> in order to evaluate the heat capacity at

high temperatures, but such a procedure is difficult and laborious, and its success depends a great deal on how well the heat content curves have been smoothed. There is no assurance that the heat capacities thus obtained will correlate smoothly with low-temperature heat capacities in the neighborhood of room temperature. Most low-temperature investigators graphically integrate their heat capacity curves to obtain low-temperature heat content values. This procedure is not too difficult, but, as mentioned above, the heat content plot is rather insensitive, and is a poor method for trying to correlate the two sets of data.

A few years ago the author<sup>2</sup> presented a graphical method for obtaining the best heat content equation of the form

$$H_T - H_{298.16} = aT + bT^2 + cT^{-1} + d \quad (1)$$

to fit a set of experimental high-temperature heat content data. In its differentiated form the equation becomes

$$C_p = a + 2bT - cT^{-2} \quad (2)$$

If the value of  $C_{p298.16}$  is known from heat capacity measurements at room temperature, one boundary condition is satisfied by setting  $C_p = C_{p298.16}$  in equation 2 when  $T = 298.16^\circ$ . The other boundary condition to be satisfied is that  $H_T - H_{298.16} = 0$  when  $T = 298.16^\circ$  in equation 1. This reduces the number of constants to be evaluated to two, and the following relationship can be derived

$$\frac{T[(H_T - H_{298.16}) - C_{p298.16}(T - 298.16)]}{(T - 298.16)^2} = bT + \frac{c}{(298.16)^2} \quad (3)$$

If the function on the left side of equation 3 is evaluated for each measured high-temperature heat content value, and the results are plotted against  $T$ , the resulting plot will be a straight line if the measured data are fitted exactly by equation 1, the slope of the line being  $b$ , and the "y"-intercept  $c/(298.16)^2$ . The constants  $a$  and  $d$  are evaluated from the boundary conditions at 298.16°K. The high-temperature heat content of most substances can be fitted over a wide temperature range by an equation of the form of equation 1 with a maximum error of only a few tenths of a per cent. For example, a straight line drawn in the high-temperature region of the function plot for aluminum oxide (Fig. 1) with a slope of 0.0117 and a "y"-intercept (value of the function at  $T = 0$ ) of 33.75 yields the following

(1) (a) D. C. Ginnings and R. J. Corruccini, *J. Research Natl. Bur. Standards*, **38**, 593 (1947); (b) G. Rutledge, *Phys. Rev.*, **40**, 262 (1932).

(2) C. H. Shomate, *J. Am. Chem. Soc.*, **66**, 928 (1944).

heat content equation, which fits the smoothed data within 0.5% in the range 298–1200°K.

$$H_T - H_{298.16}(\text{abs. j./mole}) = 105.78T + 0.0117T^2 + 3,000,000T^{-1} - 42,641$$

In addition to the utility of the function for fitting high-temperature heat content data with algebraic equations, it has several other practical applications, which will be described.

**Smoothing of High-Temperature Heat Content Data, and Correlating with Low-Temperature Heat Capacity Data.**—In order to apply the function to low temperature heat capacity data, the latter must first be graphically integrated to give heat contents below 298.16°K. In a paper on "Heat Capacity Standards" Ginnings and Furukawa<sup>3</sup> have presented a table of smoothed values of the heat capacity and heat content of aluminum oxide (synthetic sapphire) from 0 to 1200°K. The function curve for these heat content data is shown in Fig. 1. The curve bears a resemblance to the heat capacity curve of aluminum oxide, except that it does not have the pronounced S-shape in the neighborhood of 50–100°K. It should be noted that there is no discontinuity in the curve at 298.16°K.

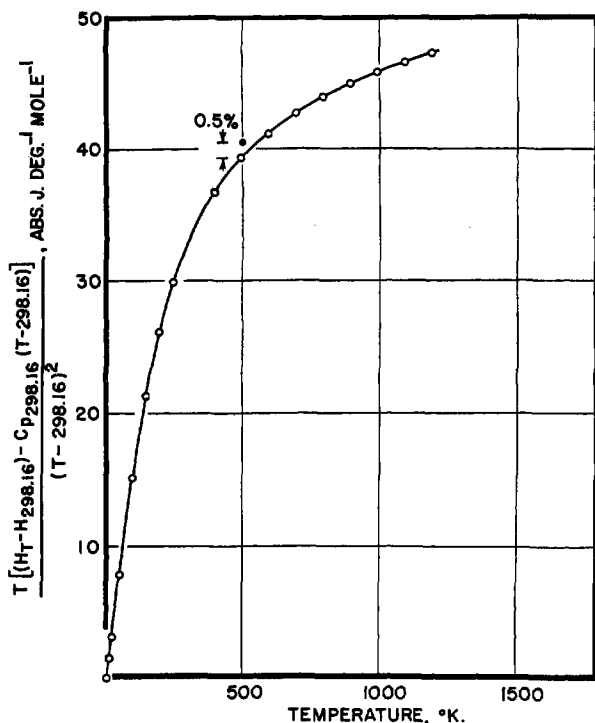


Fig. 1.—Thermodynamic data for  $\text{Al}_2\text{O}_3$  ( $C_{p298.16} = 79.01$  abs. j. deg.<sup>-1</sup> mole<sup>-1</sup>).

The extreme sensitivity of the function curve is indicated by a point above the curve at 500°K., in which the true  $H_{500} - H_{298.16}$  value has been increased by 0.5%. Errors of 0.1% in the heat content are easily detectable in this method of plotting, and since this is approximately the precision being achieved with some high-temperature heat content apparatuses, it is important not to

(3) D. C. Ginnings and G. T. Furukawa, *J. Am. Chem. Soc.*, **75**, 522 (1953).

sacrifice this precision in smoothing the data. Other graphical methods currently used do not have this sensitivity.

The question arises as to what effect an erroneous value of  $C_{p298.16}$  has on the application of the method. As far as smoothing the high-temperature heat content data is concerned, the value adopted for  $C_{p298.16}$  is immaterial, since in recalculating smoothed values of  $H_T - H_{298.16}$  from the function curve the erroneous value is eliminated. However, if a value close to the true value of  $C_{p298.16}$  is adopted, the function curve will have only slight curvature in the high-temperature region.

In applying the function to both high and low temperature data for the same compound, an erroneous value of  $C_{p298.16}$  is easily demonstrated by the function curve. Figure 2 shows a plot of the function for aluminum oxide, in which a value of  $C_{p298.16} = 79.17$  abs. j./deg./mole is used. This is only 0.2% higher than the true value of 79.01 abs. j./deg./mole used in Fig. 1, but the discontinuity at 298.16°K. is quite marked.

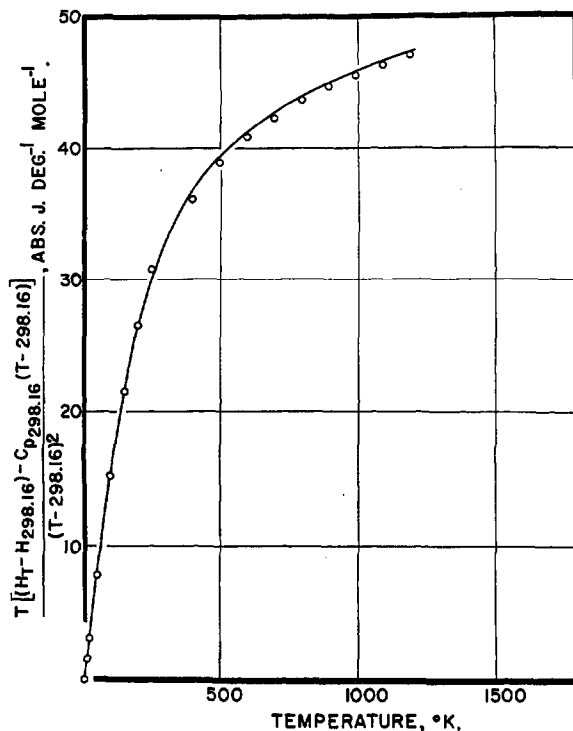


Fig. 2.—Thermodynamic data for  $\text{Al}_2\text{O}_3$  ( $C_{p298.16} = 79.17$  abs. j. deg.<sup>-1</sup> mole<sup>-1</sup>).

A more vivid example is shown in Fig. 3, in which the function is applied to the data for titanium metal taken from a Bureau of Standards compilation.<sup>4</sup> On a heat content plot the discontinuity is undiscernible. Most probably the error here is principally in the high-temperature heat content data, rather than in the value of  $C_{p298.16} = 6.01$  cal./deg./mole used to calculate the function curve.

Even in the absence of high-temperature data, the function is useful in determining how to draw

(4) National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties, Series III" (June 30, 1949).

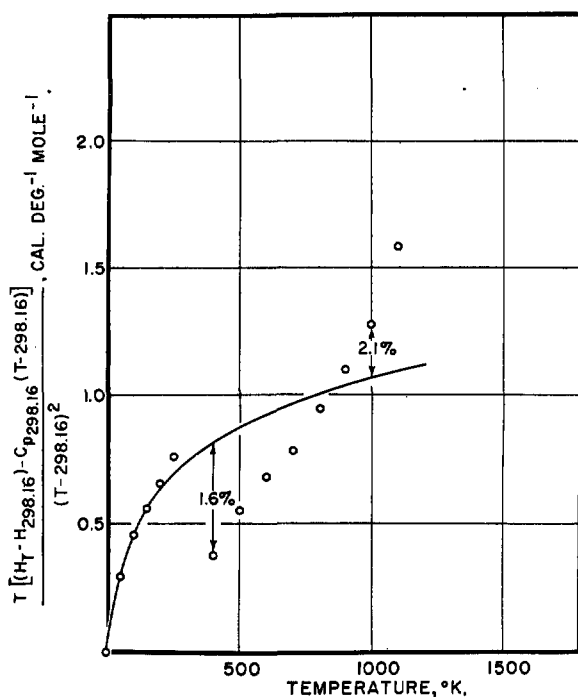


Fig. 3.—Thermodynamic data for Ti ( $C_{p,298.16} = 6.01$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>).

low-temperature heat capacity curves in the neighborhood of room temperature, where the data are least accurate. If the heat capacity curve, as drawn, yields a maximum in the function curve below 298.16°K., then the heat capacity curve should be raised slightly. On the other hand, if the function curve has an inflection point upward below 298.16°K., the heat capacity curve should be lowered slightly in the neighborhood of room temperature. These shifts in the heat capacity curve normally will not exceed a few tenths of a per cent., which is approximately the precision of the experimental data near room temperature.

**Evaluation of Heats of Fusion and Transition at High Temperatures.**—One of the disadvantages attributed to the high-temperature drop method is that it is not always adequate for obtaining heat effects at transition points, especially if the heat of transition is small. For example, Coughlin and Orr<sup>5</sup> reported measurements of the high-temperature heat content of barium metatitanate, and were unable to calculate the heat associated with a Curie-type transition occurring at 393°K. Figure 4 shows a heat content *vs.* temperature plot of their data, in which the transition is almost undiscernible.

Todd and Lorenson<sup>6</sup> made low-temperature heat capacity measurements on barium metatitanate which disclosed the existence of anomalies at 201.6 and 284.9°K., with heats of transition of 12 and 26 cal./mole, respectively. A recomputation of their data showed a heat of 33 cal./mole for the 284.9° transition, the difference being in the judgment on how to draw the "normal" heat capacity curve in that region. Todd and Lorenson also made low-temperature heat ca-

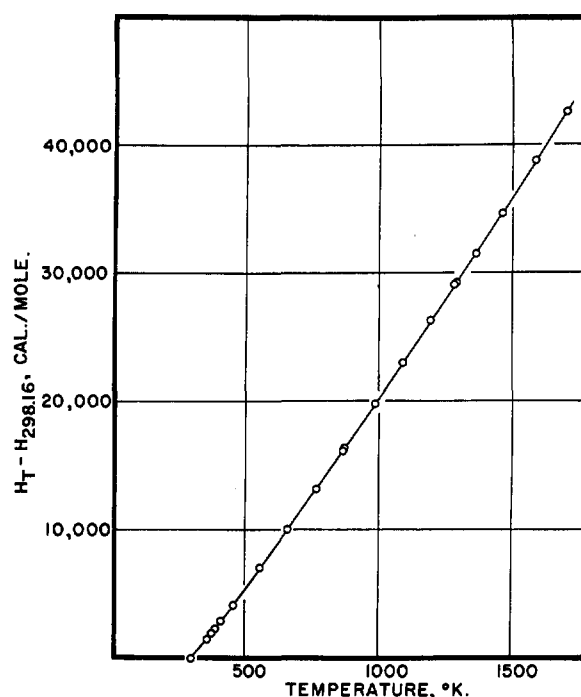


Fig. 4.—High-temperature heat content of BaTiO<sub>3</sub>.

capacity measurements on a crystalline solution of barium and strontium metatitanates (0.543 BaTiO<sub>3</sub>·0.457 SrTiO<sub>3</sub>) in the hope of lowering the 393° Curie point to a temperature within the range of their measurements (below 298°K.). The result, however, was the elimination of all transitions in the range 50–298°K.

The evaluation of the heat of the 393°K. transition is easily accomplished by the application of the function to Todd and Lorenson's "normal" curve for barium metatitanate, and to Coughlin and Orr's experimental data. The results are shown in Fig. 5. If 75, 85 and 95 cal./mole are successively subtracted from Coughlin and Orr's data above 393°K. before applying the function, the three upper curves in Fig. 5 are obtained. It should be noted that Coughlin and Orr rounded their heat content results to the nearest 10 cal./mole, allowing possible rounding errors of 5 cal./mole, which is about the precision to be attached to the heat of the 393°-transition of 85 cal./mole. This uncertainty compares favorably with the uncertainty of the heat of the transition at 284.9°K.

If the heat capacity curves below and above an anomaly (transition or fusion) are markedly different, so that it is difficult to draw a smooth "normal" heat capacity curve through the region of the anomaly, a similar difficulty will be encountered in drawing a continuous function curve in this region after the heat associated with the anomaly is subtracted. However, in the latter case, if the two function curves intersect at the temperature of the anomaly, then the correct heat has been subtracted to obtain the high-temperature curve.

Oftentimes it is difficult to ascertain on a heat content *vs.* temperature plot whether a particular point contains a small amount of premelting or

(5) J. P. Coughlin and R. L. Orr, *J. Am. Chem. Soc.*, **75**, 530 (1953).

(6) S. S. Todd and R. E. Lorenson, *ibid.*, **74**, 2043 (1952).

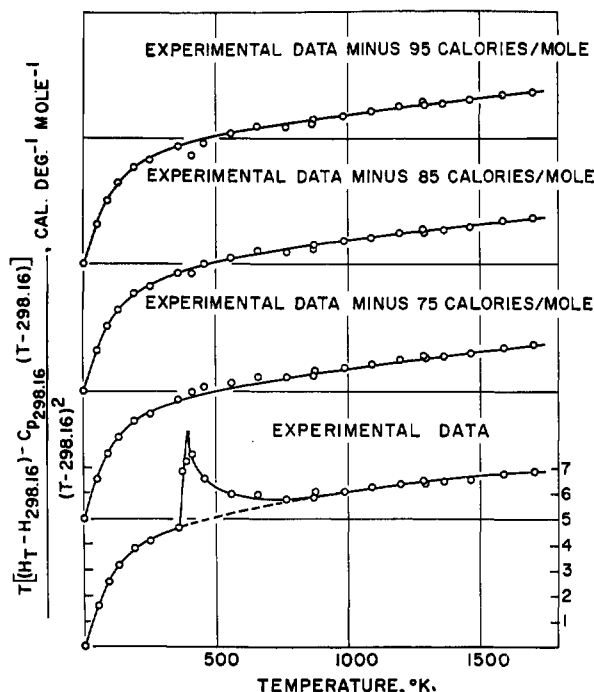


Fig. 5.—Thermodynamic data for  $\text{BaTiO}_3$  ( $C_{p298.16} = 24.49$  cal. deg. $^{-1}$  mole $^{-1}$ ).

pretransition effect, but when the function is applied to the results, these effects are more easily identified. This observation is illustrated with data for potassium sulfate in Figs. 6 and 7. Both the low-temperature heat capacity data<sup>7</sup> and the high-temperature heat content data<sup>8</sup> for potassium sulfate are included in Fig. 7, in which the isothermal transition at 856°K. and the fusion at 1342°K. are greatly magnified.

**Calculation of High-Temperature Heat Capacities.**—Since the function plot is an effective method for smoothing high-temperature heat content data, it also permits accurate calculation of high-temperature heat capacities. For example, in the function plot for aluminum oxide (Fig. 1), the values of 39.09 and 39.51 are read from the curve at 490° and 510°K., respectively, from which are calculated  $H_{490} - H_{298.16} = 18,093$ , and  $H_{510} - H_{298.16} = 20,214$  abs. j./mole.  $C_{p500}$  is then calculated to be  $(20,214 - 18,093)/20$ , or 106.05 abs. j./deg./mole, the value reported by Ginnings and Furukawa.<sup>3</sup>

Since the value for  $H_{500} - H_{298.16}$  usually has been tabulated already, an easier method for calculating  $C_{p500}$  employs the following relationship derived by differentiating the function with respect to  $T$ :  $C_{pT} = (H_T - H_{298.16})(T + 298.16)/(T - 298.16)T - (298.16)(C_{p298.16})/T + (b)(T - 298.16)^2/T$ , where  $b$  is the slope of the function curve at temperature  $T$ . The value of  $C_{pT}$  calculated from this expression is entirely independent of the value adopted for  $C_{p298.16}$ ; any change in  $C_{p298.16}$  is compensated by a corresponding change in  $b$ . At 500°K.  $b$  is calculated to be  $(39.51 - 39.09)/20$ , or 0.0210, and  $C_{p500} = 151.45 - 47.11 + 1.71$ , or 106.05 abs. j./deg./mole. An error

(7) G. E. Moore and K. K. Kelley, *J. Am. Chem. Soc.*, **64**, 2949 (1942).

(8) C. H. Shomate and B. F. Naylor, *ibid.*, **67**, 72 (1945).

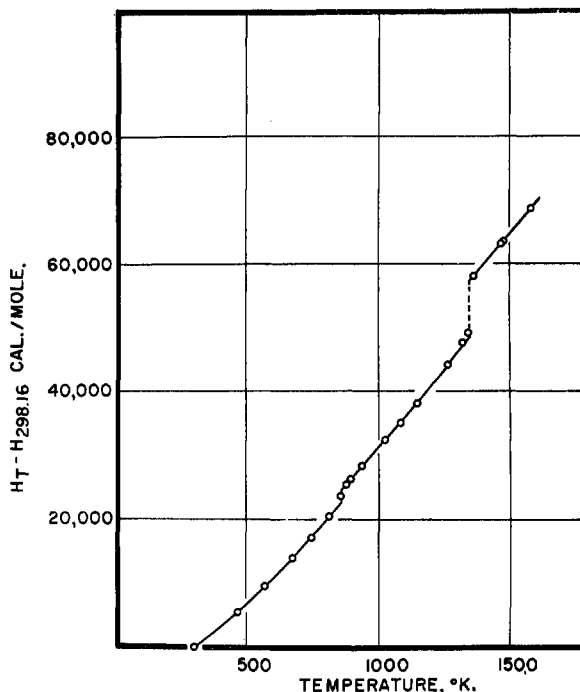


Fig. 6.—High-temperature heat content of  $\text{K}_2\text{SO}_4$ .

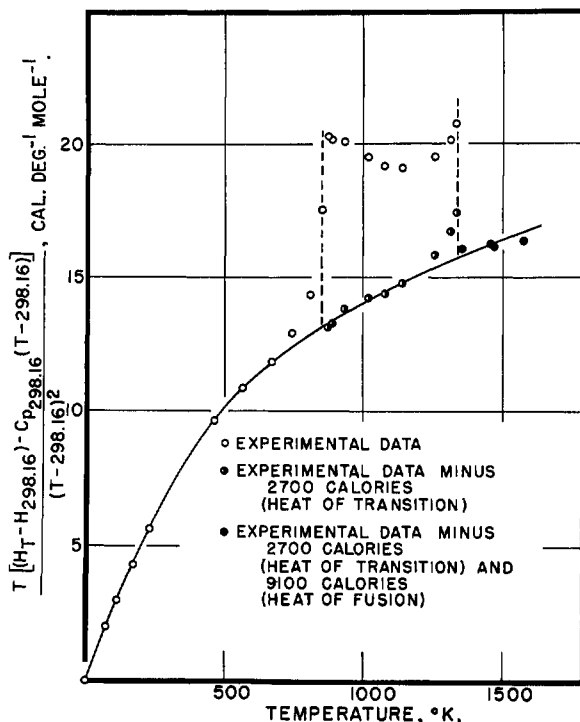


Fig. 7.—Thermodynamic data for  $\text{K}_2\text{SO}_4$  ( $C_{p298.16} = 31.27$  cal. deg. $^{-1}$  mole $^{-1}$ ).

of 10% in the determination of the slope,  $b$ , of the function curve affects this heat capacity result by only 0.17 abs. j./deg./mole, or less than 0.2%, whereas an error of 10% in the slope of the heat content curve directly affects the value of  $C_p$  by 10%.

**Miscellaneous Applications.**—Johnston and Bauer<sup>9</sup> have used the function to derive general

(9) H. L. Johnston and T. W. Bauer, *ibid.*, **73**, 1119 (1951).

expressions for  $\Delta H$ ,  $\Delta S$  and  $\Delta F$  as functions of temperature for a dissociation reaction from heat capacity and thermochemical data at 298.16°K. and dissociation pressure data at higher temperatures.

In some instances base temperatures other than 298.16°K. may be more convenient. For example, 273.16°K. may be a more convenient base for those employing an ice calorimeter in measuring high-temperature heat contents, where values of

$H_T - H_{273.16}$  are recorded. With lower base temperatures the sensitivity of the function plot is decreased. If a base of 0°K. is used, the function simplifies to  $(H_T - H_0)/T$ .

It is suggested that if the thermodynamic data for a substance have been determined with great accuracy up to a temperature  $T_1$ , the data can be extrapolated a few hundred degrees higher with greater certainty by using the function plot than by another graphical method.

## PHASES PRESENT AND PHASE EQUILIBRIUM IN THE SYSTEM $\text{In}_2\text{O}_3\text{-H}_2\text{O}$

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Phase equilibrium relations in the system  $\text{In}_2\text{O}_3\text{-H}_2\text{O}$  have been determined by a static hydrothermal method in the temperature range 25–300° at 500–20,000 p.s.i. A new phase  $\text{InOOH}$ , not isomorphous with any other trivalent oxyhydroxide, has been found and its properties described.

**Introduction.**—As part of a research program investigating equilibrium in systems involving metal oxides and water, our attention has been drawn to the  $\text{In}_2\text{O}_3\text{-H}_2\text{O}$  system. Earlier work in this Laboratory has resulted in new or revised data on compound formation and phase equilibrium in the systems  $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ ,<sup>1</sup>  $\text{Ga}_2\text{O}_3\text{-H}_2\text{O}$ ,<sup>2</sup>  $\text{Al}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-H}_2\text{O}$ ,<sup>3</sup>  $\text{Cr}_2\text{O}_3\text{-H}_2\text{O}$  and  $\text{Sc}_2\text{O}_3\text{-H}_2\text{O}$ ,<sup>4</sup> and the rare earth hydrates.<sup>5</sup> The literature contains less information regarding the hydrates of indium sesquioxide and the rare earth oxides than of any other oxide in this group of the periodic table. In addition since something is known of the structures of the compounds of both the smaller ions (Al–Sc) and the larger ones (Y–La) it was hoped that the indium compounds would fit into the structural picture.

It has been known for a long time (Milligan and Weiser<sup>6</sup>) that the precipitate which forms on the addition of alkali to indium(III) salts, after drying at 100°, has the composition  $\text{In}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . This compound has been shown to be the trihydroxide  $\text{In}(\text{OH})_3$ , and attempts have been made to determine its structure by Milligan and Weiser,<sup>6</sup> Fricke and Seitz,<sup>7</sup> and Palm,<sup>8</sup> and Moeller and Schnizlein.<sup>9</sup> It is cubic, although the above authors report cell-edges of 7.95, 7.90, 7.92 Å., respectively, and the last named a value of 5.40 Å. based on an incorrect unit cell. Carnelley and Walker<sup>10</sup> reported a continuous loss of water from the fresh precipitate and no indication of the existence of a hydrate. Weiser and Milligan on the

other hand reported that the trihydroxide decomposed at 207° to yield directly the sesquioxide. No indication of another hydrate has been reported other than the rather early work of Renz.<sup>11</sup>

Most of the work on the stability of hydrates of the sesquioxides has been done by the dehydration isobar technique. The great disadvantage of such techniques is the fact that at the low partial pressures of water vapor used in most cases, the activation energy necessary for the formation of a new structure from the one that is decomposed on heating is very great. Hence in many cases so-called "amorphous" structures result, and in others metastable phases appear, and incorrect values for equilibrium decomposition temperatures are reached. In the present study, techniques designed for use in studying phase equilibrium in silicate and other systems, where reactions are notoriously sluggish, have been used.

**Experimental.**—The experimental techniques used in these studies have been more fully described in earlier papers<sup>1–5,12</sup> and will only be stated in outline here. The equipment used consists of an assembly of several (30) pressure vessels and furnaces, the former being attachable to a high pressure source of water pressure by a system of valves and fittings. Each vessel can be controlled independently with respect to both temperature and pressure: the temperature of the furnaces is automatically regulated. Two main types of vessels have been used: the vessels designed by Morey and Ingerson<sup>13</sup> and the "test-tube" bomb developed in this Laboratory. Details regarding equipment have been given by Roy and Osborn.<sup>14</sup> For examination of the products the petrographic microscope and X-ray diffraction patterns were used, the former being quite limited in application. The X-ray patterns were obtained on Geiger-counter diffractometers manufactured by G. E. Company (165° unit) or North American Phillips (90° units).  $\text{CuK}$  radiation was used filtered through nickel.

The starting material was prepared from C.P.  $\text{In}_2\text{O}_3$  by dissolving in nitric acid precipitating at room temperature with ammonium hydroxide and washing thoroughly. The  $\text{In}(\text{OH})_3$ ,  $\text{InOOH}$  and  $\text{In}_2\text{O}_3$  prepared from this material were also used as starting materials in various runs. These

- (1) G. Ervin and E. F. Osborn, *J. Geology*, **59**, 4 (1941).
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- (3) V. G. Hill, R. Roy and E. F. Osborn, *J. Am. Cer. Soc.*, **35**, 6 (1952).
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- (5) R. Roy and H. A. McKinstry, *Acta Cryst.*, **6**, Part 4, 365 (1953).
- (6) W. O. Milligan and H. B. Weiser, *J. Am. Chem. Soc.*, **59**, 1670 (1937).
- (7) R. Fricke and A. Seitz, *Z. anorg. Chem.*, **225**, 13 (1947).
- (8) A. Palm, *This Journal*, **52**, 959 (1948).
- (9) T. Moeller and J. Schnizlein, *ibid.*, **51**, 771 (1947).
- (10) T. Carnelley and J. Walker, *J. Chem. Soc.*, **53**, 88 (1888).

- (11) C. Renz, *Ber.*, **36**, 1848, 2754 (1903).
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- (13) G. W. Morey and E. Ingerson, *Am. Mineral.*, **22**, 1121 (1937).
- (14) R. Roy and E. F. Osborn, *Econ. Geol.*, **47**, 717 (1952).