



Figure 2. Deviation plots of the density data from the equation of state proposed by Kagawa et al. along the 340 K isotherm.

results agree well with the data by Michels (9) and those by Zander (10) within  $\pm 0.2\%$  in pressure deviation.

We calculated the derivatives of density with respect to temperature at constant pressure and those of density with respect to pressure at constant temperature from the data given in Table I by approximation as differences of these

quantities. The values of the volume expansion coefficient and the isothermal compressibility thus obtained are given in Tables II and III, respectively.

#### Acknowledgment

M. Yamamoto, Y. Takiguchi, and K. Nakagima have provided valuable assistance in the present work. The National Research Laboratory of Metrology, Tsukuba, Japan, kindly calibrated the platinum resistance thermometer. We are greatly indebted to Professor K. Watanabe, Keio University, for his kind support to use the research-grade pure sample.

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Received for review May 2, 1990. Accepted July 26, 1990.

## Solubility Products of the Trivalent Rare-Earth Phosphates

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The solubility and solubility products of 14 rare-earth phosphates in aqueous solution have been determined at  $25 \pm 1$  °C. The most soluble compound is yttrium phosphate ( $pK = 24.76$ ). The least soluble ones are lanthanum phosphate ( $pK = 26.15$ ) and ytterbium phosphate ( $pK = 26.17$ ). The rare-earth phosphates were prepared by precipitation from homogeneous solution. Saturated solutions were analyzed for pH, the concentrations of some rare-earth cations, and the total concentration of phosphate. Activity products were calculated from the experimental data. The solubilities of the rare-earth phosphates are so low that the solubility products and the activity products are essentially the same value. The rare-earth phosphates are more insoluble at higher temperatures. Lanthanum phosphate has a  $pK$  of 26.49 at 70 °C. Twelve values for the activity product of rare-earth phosphates at elevated temperatures were determined.

#### Introduction

Previous work by Jonasson, Bancroft, and Nesbitt (1) reported on the solubilities of only the lanthanum, praseodymium, neodymium, and erbium phosphates. Limited experimental in-

formation was presented. The study reported here involved the entire trivalent rare-earth series, excluding scandium and cerium. Solubilities at 25 °C and at higher temperatures are reported.

#### Experimental Section

Commercial rare-earth phosphates were unsatisfactory for use in this study. Colloidal suspensions formed that did not settle out of solution even after months of standing.

Satisfactory crystals of rare-earth phosphates were prepared by precipitation from homogeneous solution using the hydrolysis of urea.

Equimolar amounts (0.005 mol) of rare-earth cation and phosphoric acid were added to a 1-L beaker with 5 mL of 70% HClO<sub>4</sub> to prevent the rare-earth phosphate from precipitating. Deionized water was added to bring the volume to about 900 mL. A 3–5-g amount of urea was slowly added with constant stirring. The solution was heated to hydrolyze the urea, increase the pH, and bring about the precipitation of the rare-earth phosphate. The solution was heated for an additional hour after precipitation began. The resulting crystals were washed 10–15 times with deionized water. The last two washings were made with a 0.10 M perchloric acid solution to eliminate the possibility of rare-earth carbonate being present. No fizzing