HYDROTHERMAL SOLUBILITY OF
Al_2O_3 IN $Na_2B_4O_7$ SOLUTION

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Abstract

The solubilities of corundum in aqueous borax solutions were measured by the weight loss method as temperature, pressure, and borax concentrations were varied. Special precautions were taken to ensure accuracy of temperature measurement and uniformity of temperature distribution. The solubility at 417° C. and 28 kpsi varied from 0.54% in 0.1 Molal $Na_2B_4O_7$ to 14.65% in 11.1 Molal solution, and the solubility in 1.5 Molal solution varied from 1.74% at 328° C. to 8.11% at 515° C. Variation of pressure from 5000 psi to 28,000 psi had only a slight effect on solubility.

Introduction

The hydrothermal growth of single crystals requires a system in which:

(a) a sensible solubility difference exists between temperatures imposed on the system to yield the desired gradient,

(b) a fair degree of supersaturation can be supported, and

(c) a sufficient growth rate of the desired phase can be attained to make the process practical.

Solvent systems for corundum employed to date have been NaOH (Laudise and Ballman, 1958; Barns *et al.*, 1963), Na_2CO_3 (Laudise and Ballman, 1958; Ballman *et al.*, 1961; Barns *et al.*, 1963; Kuznestov, 1964), K_2CO_3 (White, 1963; Lambdin *et al.*, 1964) and Rb_2CO_3 (White, 1963).

Corundum was reported to exhibit a pressure independent and very slightly temperature dependent solubility in 2 Molal NaOH, above 430°, (Laudise and Ballman, 1958; Barnes *et al.*, 1963). Growth rates of up to 1 mm per day have been attained in Na_2CO_3 solutions. Lower rates were attained in NaOH solutions, and they required more drastic conditions. The diaspore-corundum phase transitions in these solvents is not accurately known, but is believed to be slightly below 400° C.

The sodium borate-water system as a solvent for corundum was studied in detail because preliminary studies showed a high apparent solubility above 400° C. and a moderate variation of apparent solubility with temperature. This system was also of interest because of the claimed growth of quartz hydrothermally from sodium borate solutions (Frank and de Longchamp, 1949), the crystallization of corundum from borax (Ebelmen, 1851), and the well known use of B_2O_3 as a mineralizer. There is also no previously reported data on hydrothermal solubility in borate solutions.

EXPERIMENTAL

Apparent solubility studies via weight loss measurements were carried out in a modified high-temperature, high-pressure apparatus (TEM-PRES Model HR-1B) in a manner similar to that described by Barnes, Laudise, and Shields (1963). A Linde 0.100″ diameter single crystal α-Al_2O_3 rod, sodium borate pentahydrate (Baker Analyzed) and distilled H_2O, as required, were weighed into annealed platinum capsules which had been cleaned in HCl. The capsules were sealed with a spectrographic graphite tipped D.C. arc welder. Weighings were made with a Mettler M-5 microbalance. Baker and Adamson borax was used to prepare the 5.55 Molal solutions.

The René 41 Tuttle autoclaves had thermocouple wells 1″ apart along their length to determine the temperature gradient over the length of the platinum capsules inside the bomb. The platinum capsules were 2 centimeters long, 0.180″ I.D., and had a 5 mil wall. By suitable space winding of the furnace, the gradient at the capsule location (at the temperature of interest) can be reduced to about 1°/inch as measured at the thermocouple wells closest to the capsule. The furnace was positioned relative to the autoclave with a Lab-Jack. Thermocouple well temperatures were measured with Pt-Pt Rh 10% thermocouples with a reference ice bath, using a potentiometer measuring circuit. The chromel-alumel thermocouple of the furnace controller was compensated by using a constant temperature bath ($\pm 0.05°$ C.) as reference. Variacs were inserted in the furnace heater circuits to prevent temperature overshoot.

In a typical determination the capsule was placed in the autoclave, the latter filled with 500 centipoise Dow-Corning DC 200 silicone oil, and about $\frac{1}{2}$ to $\frac{1}{3}$ the final desired pressure applied by means of a pressure intensifier. The heated furnace was raised into position and the temperature and pressure carefully monitored.

At a few degrees below the final soak temperature, the gradient was reduced to about 1° by adjusting the furnace position, relative to the bomb. Pressure was adjusted continuously by bleeding off fluid from the system. After soaking at the desired temperature and pressure for at least 18 hours the autoclave was quenched. The α-Al_2O_3 seeds, after removal from the capsule were boiled in hot water or dilute HCl and examined microscopically after drying to ascertain that no deposit remained on the crystal before weighing. In all cases the seed was found to be etched. All determinations were carried out in duplicate. The maximum variation was found to be less than 0.2 wt. % from the average. Leaks in the welded capsules were found by weighing.

The use of silicone fluid in the autoclave eliminated pressure variations due to room temperature fluctuations affecting the high pressure tubing

outside the furnace. It is more compressible than water. Pressure could be adjusted to ± 100 psi. In addition, its use allowed a determination of the internal bomb temperature in relation to the thermocouple well reading by a modification of a method suggested by Yoder (1963.) The latter consists of sealing small slivers (a few mgs) of accurately known melting point materials (*e.g.* NBS high purity Pb, 99.999% Zn) into small evacuated borosilicate glass capsules. The capsules were constructed with two chambers that were about 2 cms apart. A capsule was placed in a 2 centimeter platinum tube sealed at one end in order to more closely approximate conditions existing during weight loss measurements. The outside thermocouples were adjusted to within 1° C. of the desired temperature and the autoclave sharply tapped after a few hours soak. (Even on high purity specimens there is usually a thin layer of oxide on the sliver sufficient to hold it in shape even though it is actually melted.) If these measurements were carried out in water the glass was severely attacked and the specimens could not be observed. By bracketing, the internal gradient was found to be within 3° at the Pb and Zn points. Variation in the controller is less than 1° C. Temperatures are reported to $\pm 3°$ C. (including the existing gradient) at the calibration points. Variation in the autoclave pressure from 5 to 30 kpsi did not alter the internal gradient. The calibration was taken as constant over the temperature range. Above 520° C. decomposition of the silicone takes place.

Solubility in Na₂B₄O₇ Solutions

Concentration Dependence. The apparent solubility, S′, in g per 100 g of solvent, of α-Al₂O₃ in Na₂B₄O₇-H₂O solutions as a function of Na₂B₄O₇ concentration at 28.0 kpsi and 417° C. is shown in Fig. 1, Curve 2, from 0.1 to 11.1 Molal. Comparison with weight loss determinations in NaOH (Curve 1) and Na₂CO₃ solutions (Curve 3) (Barns *et al.*, 1963) shows an intermediate apparent solubility at the higher concentrations. At concentrations up to about 3 Molal, S′ in NaOH and Na₂B₄O₇ solutions are comparable.

Temperature and Pressure Dependence. The variation of S′ for corundum in 1.5 Molal Na₂B₄O₇ at 28.0 kpsi as a function of temperature is shown in Fig. 2. The curve changes slope in the vicinity of 400°. In the range 400° to 515° C., S′ is linearly related to the temperature. A plot of log S′ vs 1/T for the same data is shown in Fig. 3. From a least squares determination of the slope in this region $\Delta H_{28.0kpsi}$ was calculated to be 2.62 kcal/mole using the relationship

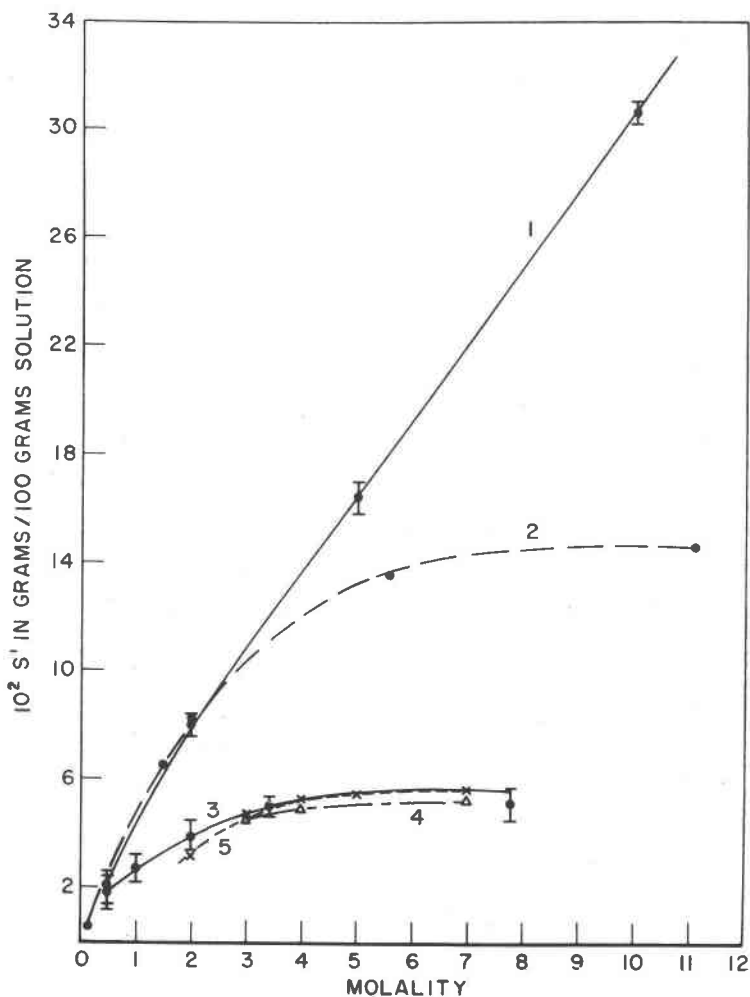$$\ln S_1'/S_2' = \frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

Fig. 1. Apparent solubility of α-Al_2O_3 (single crystal) vs concentration of various alkaline solvents.

Curve 1: NaOH, 430° C., 21 kpsi
Curve 2: $Na_2B_4O_7$, 417° C., 28 kpsi
Curve 3: Na_2CO_3, 430° C., 21 kpsi
Curve 4: K_2CO_3, 430° C., 20 kpsi
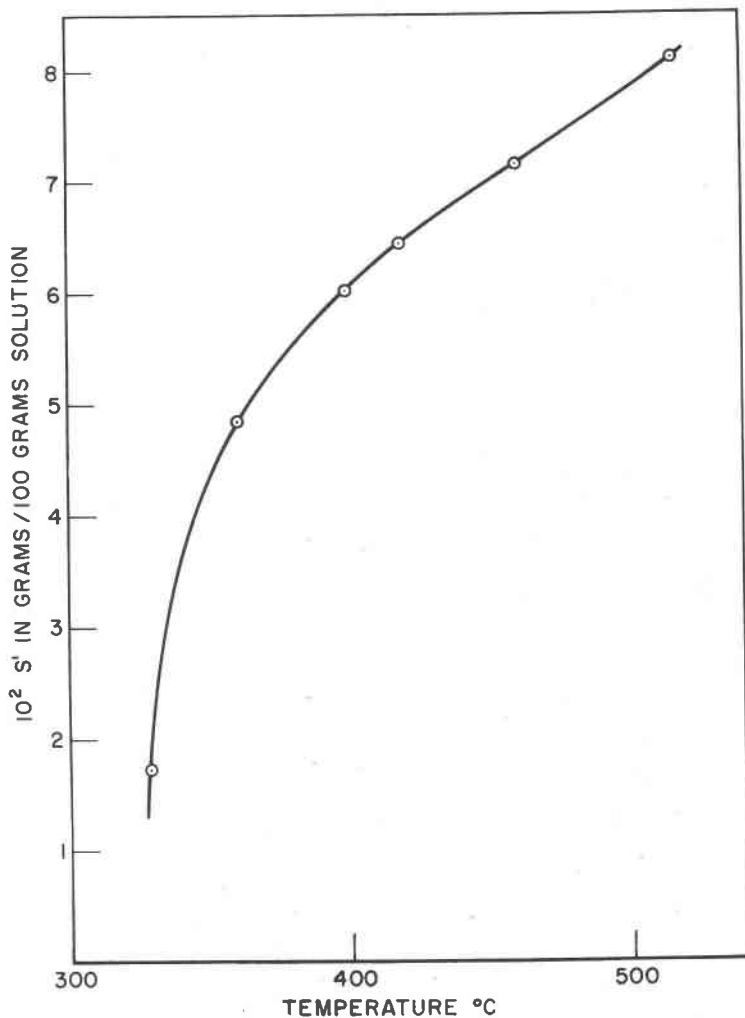Curve 5: K_2CO_3, 430° C., 10 kpsi

Fig. 2. Relationship between apparent solubility and temperature, for α-Al_2O_3 in 1.5 Molal $Na_2B_4O_7$ at 28.0 kpsi.

where

    R = gas constant,
    T = absolute temperature, and
    H = enthalpy.

A small negative pressure dependence for S′ was found in the range of 5.0 to 28.0 kpsi at 417°, in 1.5 Molal $Na_2B_4O_7$ (Fig. 4).

REVERSIBILITY

The $Na_2B_4O_7$-H_2O-Al_2O_3 system was found to be reversible with respect to corundum as the stable phase at 450°. This was demonstrated by crystal growth trials in a temperature gradient in platinum tube 4″
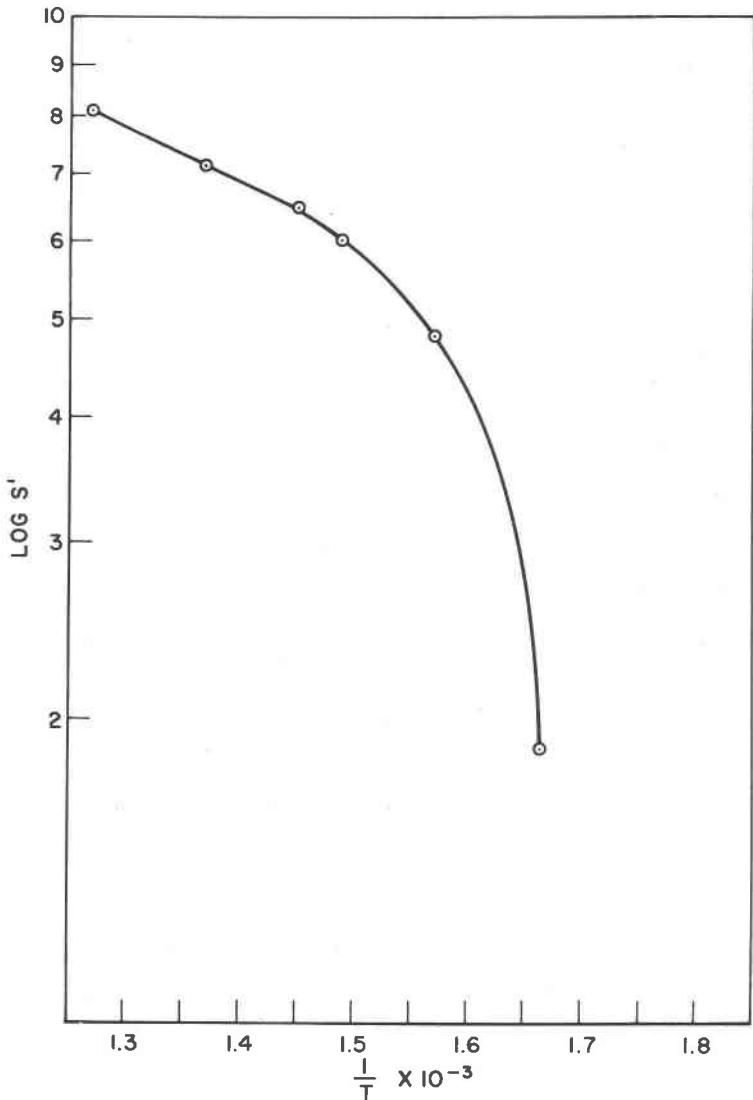

FIG 3. Relationship between logarithm of apparent solubility, and reciprocal of absolute temperature, at 28.0 kpsi in 1.5 Molal $Na_2B_4O_7$.
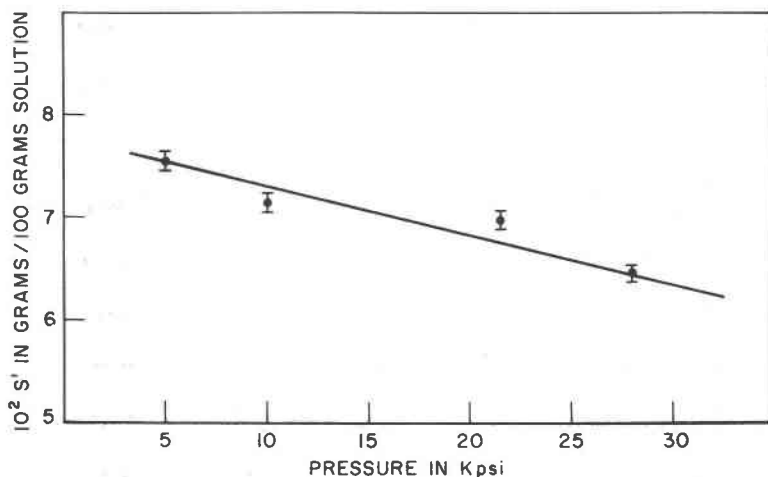
FIG. 4. Pressure dependence of the apparent solubility of α-Al$_2$O$_3$ in 1.5 Molal Na$_2$B$_4$O$_7$ at 417° C.

$\times 0.180''$ I.D. $\times 5$ mil wall, a convenient technique of Laudise *et al.* (1961). Slight growth took place after several days in an 80° gradient at 12 kpsi. In a similar experiment using a solvent 3 Molal in K$_2$CO$_3$ and 1 Molal in K$_2$B$_4$O$_7$, the rate of corundum growth on the seed was greatly reduced (x-ray analysis for α-Al$_2$O$_3$ in the material surrounding the seed is difficult because of the masking effect of Na$_2$B$_4$O$_7 \cdot 10$ H$_2$O).

DISCUSSION

The apparent solubility of corundum in Na$_2$CO$_3$, NaOH, and Na$_2$B$_4$O$_7$ solutions up to about 0.5 Molal and in NaOH and Na$_2$B$_4$O$_7$ solutions up to about 3 Molal are comparable. At higher concentrations, S' appears to be related to the room temperature alkalinity of the various solutions. This is borne out by the fact that in a solubility experiment using 2 Molal K$_2$SO$_4$ as solvent no weight loss could be detected at 420° C. and 28.0 kpsi. The ratio of the number of moles of Al$_2$O$_3$ dissolved per mole of Na$_2$B$_4$O$_7$, r, was found to be constant over the range of concentrations studied ≈ 0.4 at 417° C. This agrees with r $= 0.38$–0.42 found in NaOH solution, by Ballman *et al.* (1961), and indicates that similar ionic species may be involved. For Na$_2$CO$_3$ and K$_2$CO$_3$ solutions r is lower and varies with concentration of carbonate.

However, in view of the absence of any experimental information regarding the nature of the species present, we are reluctant to speculate on the nature and relative concentrations of the various anions which are present. We may also note that a knowledge of the variation of the

critical point with concentration of the various solutes is not known. The number of fluid phases present is still open to determination.

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REFERENCES

BALLMAN, A. A., A. J. CAPORASO AND R. A. LAUDISE (1961) Method of growing corundum crystals. U. S. Patent No. 2,979,413.

BARNS, R. L., R. A. LAUDISE AND R. M. SHIELDS (1963) The solubility of corundum in basic solvents. *Jour. Phys. Chem.* **67**, 835–839.

EBELMEN, J. J. (1851) Sur une nouvelle methode pour obtenir des combinaisons cristalisees par la voie sèche. *Ann. Chim.* **33**, 34–74.

FRANK, I. AND M. H. DE LONGCHAMP (1949) Production de quartz artificel en cristaux de grandes dimensions. *Compt. rend.* **228**, 1136–1137.

KUZNETSOV, V. A. (1964) Growth rates of corundum faces under hydrothermal conditions. *Kristallografia* **9**, 123–124.

LAMBDIN, R. W., J. W. NIELSEN AND R. C. RUTTBACH (1964) Some new hydrothermal investigations on ruby and sapphire. *Ext. Abs. Electronics Divis. Electrochem. Soc.* **13**, (1), 219–221.

LAUDISE, R. A. AND A. A. BALLMAN (1958) Hydrothermal synthesis of sapphire. *Jour. Am. Chem. Soc.* **80**, 2655–2657.

———, J. H. CROCKET AND A. A. BALLMAN (1961) The hydrothermal crystallization of yttrium iron garnet and yttrium gallium garnet and a part of the crystallization diagram $Y_2O_3 - Fe_2O_3 - H_2O - Na_2CO_3$. *Jour. Phys. Chem.* **65**, 359–361.

WHITE, E. A. D. (1963) Private communication.

YODER, H. S. (1963) Private communication.