

THE SOLUBILITY OF ZINCITE IN BASIC HYDROTHERMAL SOLVENTS

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ABSTRACT

The solubility of ZnO was determined under hydrothermal conditions between 270 and 1380 bars between 200 and 500° C. in NaOH and KOH solutions between about 0.6 and 9.0 m. The solubility was found to be independent of pressure and almost linearly dependent upon base concentration. The dependence on temperature was found to approximately obey Van't Hoff's Equation with ΔH of solution ranging from 0.4-1.1 kcal/mol.

The solubility data suggest that in $(OH)^-$ solutions the predominant species are a variety of zincates and that the reaction with $(OH)^-$ does not go to completion. Comparisons with the solubilities of SiO_2 and Al_2O_3 are presented and deductions relative to ZnO growth are made.

INTRODUCTION

Zinc oxide single crystals have been grown hydrothermally from basic solutions by Walker (1953) and Laudise and Ballman (1960), and it was of interest to determine solubilities at the conditions used for growth. Flawing, spontaneous nucleation and slow rates have long been problems in growing ZnO hydrothermally, and it was hoped that solubility studies could aid in the choice of solvent and conditions most advantageous for growth. These studies have resulted in new conditions for ZnO growth and have been useful in kinetic studies of ZnO crystallization which are reported elsewhere (Laudise, *et al.* to be publ.).

Hydrothermal solubility studies of quartz (Laudise and Ballman, 1961) and α -corundum (Barns, *et al.*, in press) in several mineralizers have recently been carried out in these laboratories, and it would be useful to extend these results to new hydrothermal systems.

EXPERIMENTAL

The equipment and procedure were essentially the same as those employed in the corundum studies (Barns, *et al.*, in press) so that only a brief description, together with significant variations, will be given here. Solubility was determined by means of weight loss determinations carried out on crystalline ZnO contained in welded platinum capsules. The capsules were filled with the desired basic solvent whose concentration had been adjusted after determination by titration against potassium acid phthalate. The crystalline ZnO had been obtained by selection from spontaneously nucleated crystals formed in hydrothermal growth runs. The nutrient ZnO in these runs was reagent purity as were all materials used in this work. The capsules were heated in Tuttle test tube type autoclaves (Laudise and Nielsen, 1961) and the pressure was established by pumping water into these vessels. Furnace control was accurate $\pm 3^\circ$ C.

and the pressure measuring Bourdon gauges had been calibrated to ± 10 bars with a dead weight gauge. Pressure was controlled to no better than ± 30 bars.

Care was exercised during the warm-up so as not to overshoot the temperature and all experiments were run at least in duplicate for two different lengths of time. Results are reported only where the weight loss was independent of further increases in the time of the experiment. Occasionally abnormally high solubilities were observed, presumably due to the loss of a crystal during transfer before weighing at the conclusion of the run. When such results occurred, further replication of runs was made. At the end of each run, the autoclaves were quenched with cold water. Phase equilibria studies were conducted by equilibrating finely powdered ZnO or Zn(OH)₂ under conditions identical with those used for solubilities. Phases were identified by *x*-ray powder diffraction.

Using six replicate determinations of solubility in 6.47 m KOH at 360° C. and 550 bars the standard deviation of the mean, σ , was $\pm 0.09\%$ and the mean of the solubility was 4.62%. This was the highest reproducibility obtained. A more representative standard deviation was that obtained at 200° C. and 550 bars in 6.47 m KOH. Here the result of three replicate determinations was a solubility of $3.57 \pm 0.16\%$, that is, σ was 0.16%. The bar heights on the curves in 6.47 m KOH in Figs. 1 and 3 represent the approximate $\pm 3\sigma$ limits for those points. In sodium hydroxide,

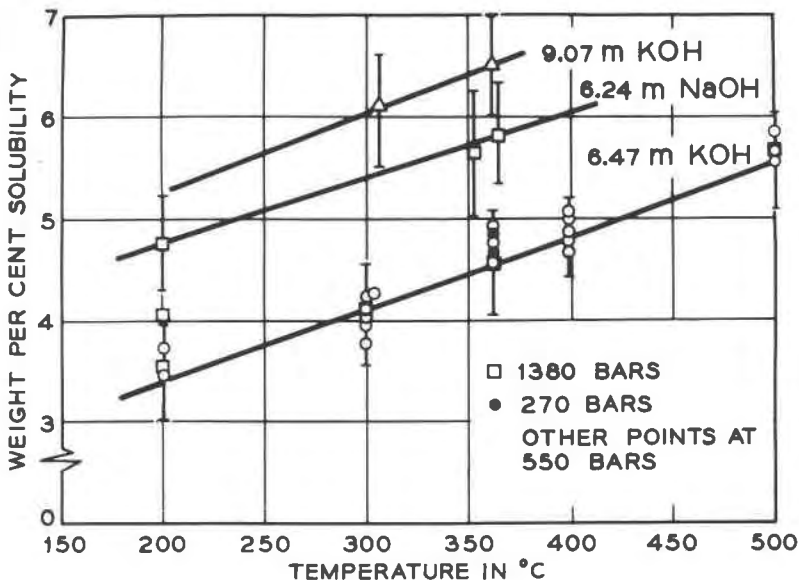


FIG. 1. Wgt. per cent solubility of ZnO vs. temperature in 6.47 m KOH at 1380, 550, and 270 bars and in 9.07 m KOH and 6.24 m NaOH at 550 bars.

in KOH at concentrations other than 6.47 m and in 6.47 m KOH at pressures other than 550 bars, insufficient replication was made to make error estimates meaningful, but it may be assumed that the errors are of the same magnitude as in 6.47 m KOH at 550 bars and similar bar heights are shown on the curves.

RESULTS

The apparent solubility of zincite at all conditions was found to be the same at 4, 7, and 14 days. All runs were for at least seven days. Sapphire solubility studies (Barns *et al.*, in press) indicate that the equilibrium time is probably much shorter, but for experimental convenience, shorter times were not investigated. Solubilities are reported only for those conditions where the solid phase is ZnO. Per cent solubility was calculated as wt. of ZnO lost $\times 100$ /wgt. of water + wgt. of mineralizer. Mineralizer concentrations are expressed in terms of molality, m, calculated from the normality at 25° C. by the use of the measured densities.¹ In general, solubility measurements were confined to two mineralizers, NaOH and KOH. KOH determinations were more extensive because this mineralizer appears more promising in crystal growth.

Solubility dependence on temperature and pressure. Figure 1 shows the solubility dependence on pressure and temperature in 6.47 m KOH, 9.07 m KOH and 6.24 m NaOH. As can be seen, the solubility is a nearly linear function of temperature between 200° and 500° C. and is independent of pressure. Within experimental error the slopes are the same for all the mineralizers, and the solubility is pressure independent between 270 and 1380 bars in KOH.

Solubility dependence on base concentration. Figure 2 shows the solubility dependence on base concentration in NaOH and KOH at 360°. As can be seen, the solubility is a nearly linear function of base concentration of both mineralizers.

¹ It is of interest to report the room temperature normalities, (N), of the solution used in this work.

KOH N(25° C.)	m	NaOH N(25° C.)	m
0.604	0.618	0.60	0.608
2.03	2.08	2.00	2.02
4.06	4.31	3.95	3.98
6.04	6.47	6.04	6.24
7.94	9.07		

The measured 25° densities were used to convert normality (equivalents (OH)⁻/liter) to molality (moles(OH)⁻/1000 gm H₂O). The solubilities are reported with respect to molality which will not be a function of density. The density of the solutions at the p-t conditions where solubilities were measured was, of course, not known.

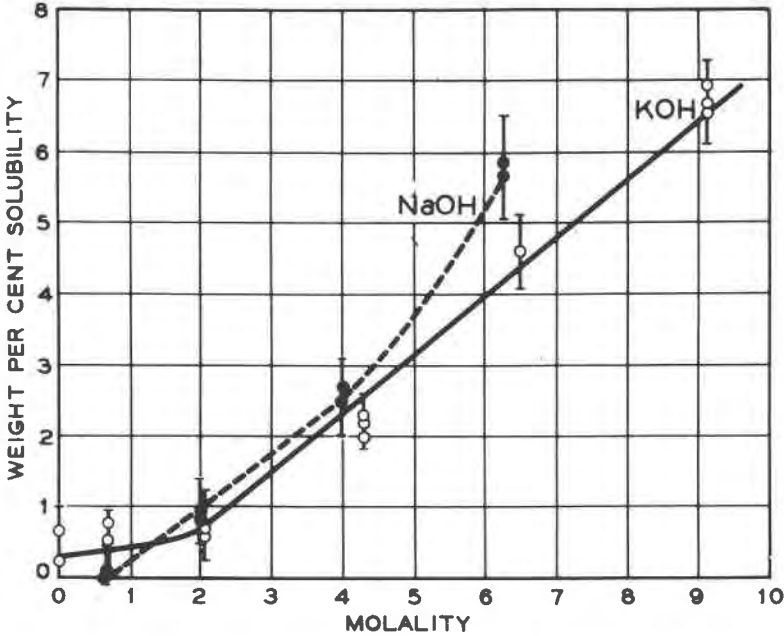
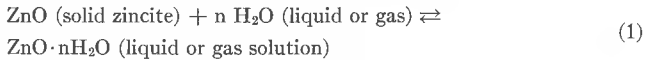


FIG. 2. Wgt. per cent solubility of ZnO vs. molal concentration of NaOH and KOH at 360°C and 550 bars.

DISCUSSION

Solubility in bases. By analogy with previous work on quartz (Laudise and Ballman, 1961) and sapphire (Barns *et al.* to be publ.) in pure water the dissolving reaction for ZnO can be expressed as:



Equation (1) assumes no ionization of the zinc hydroxide formed.

The value of n cannot be determined without accurate solubility data as a function of solution density in pure water and the present method lacked sufficient precision to determine such data. A qualitative determination at 550 bars indicated, however, that the solubility was about 0.25%.

Again by analogy with past work (Laudise and Ballman, 1961; Barns *et al.*, to be publ.) we would expect that the solubility in basic media could be described by



Equation (2) assumes complete ionization of the zincates formed.

Since the solubility is independent of pressure, we must assume that the Δv of Eq. (2) is negligible. The ratio $\text{ZnO}/(\text{OH})^-$ may be calculated from the data of Figure 2. In KOH it varies from about 0.048 at 2 m to about 0.14 at 9 m, while in NaOH it varies from about 0.05 at 2 m to about 0.15 at 6 m. In both solvents the ratio is strongly dependent upon base concentration which suggests a variety of zincates in equilibrium with one another. The small values of the ratio in both solvents is at first sight surprising, especially in view of the larger values obtained for the analogous ratios for SiO_2 (Laudise and Ballman, 1961) and Al_2O_3 (Barns *et al.* to be publ.). It is improbable that as the ratios suggest 6–15 $(\text{OH})^-$'s react with every ZnO. Apparently, Eq. (2) does not proceed anywhere near to completion. It is perhaps to be expected that Eq. (2) would not proceed as far to completion in the case of ZnO as for SiO_2 and Al_2O_3 , since the order for expected acidic character of these oxides based on size

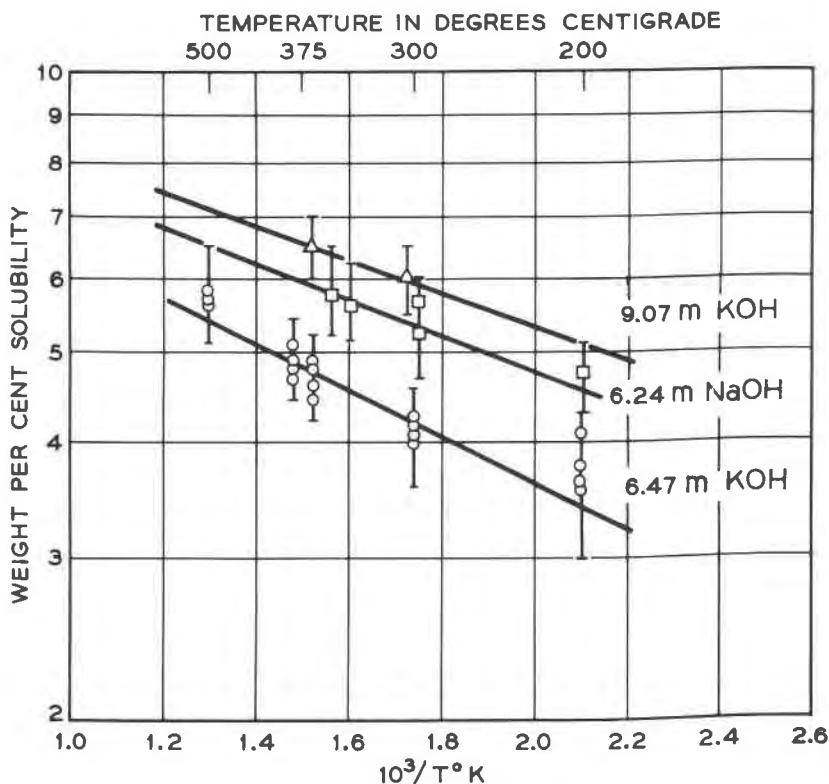


FIG. 3. Wgt. per cent solubility of ZnO vs. the reciprocal of the absolute temperature in 6.47 and 9.07 m KOH and in 6.24 m NaOH at 550 bars.

and electronegativity considerations of the respective cations would be $\text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{ZnO}$. The slightly higher solubility in NaOH cannot be readily explained. However, even though Eq. (2) does not go to completion for ZnO in view of the marked increase in solubility in $(\text{OH})^-$ compared to pure water it is justified to assume that zincates are the principal species in $(\text{OH})^-$ solutions.

Dependence on temperature. Figure 3 shows that within experimental error the Van't Hoff equation is approximately obeyed for the solubility of ZnO in 6.47 m KOH and 6.24 m NaOH while in 9.07 m KOH we have assumed a similar relationship. Thus, as might be expected, the assumptions of approach to ideality are not extremely valid. The respective heats of solution are

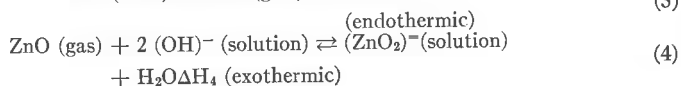
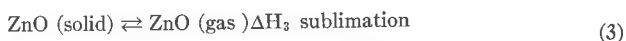
$$\Delta H_{6.47 \text{ m KOH}} \cong 1.1 \pm 0.5 \text{ k cal/mole}$$

$$\Delta H_{9.07 \text{ m KOH}} \cong 0.8 \pm 0.5 \text{ k cal/mole}$$

$$\Delta H_{6.24 \text{ m KOH NaOH}} \cong 0.4 \pm 0.5 \text{ k cal/mole}$$

The error estimates were made from an estimate in slope error in Fig. 3.

Comparisons of ΔH values can perhaps best be made if we consider the dissolving of ZnO in basic media to be principally described by Eq. (2) and examine this reaction in several steps. For simplicity we shall write the zincate species as $(\text{ZnO}_2)^=$



Since

$$\Delta H_2 = \Delta H_3 + \Delta H_4$$

where ΔH_2 is the heat of solution for Eq. (2), then

$$\Delta H_4(6.47 \text{ m KOH}) > \Delta H_4(9.07 \text{ m KOH}) > \Delta H_4(6.24 \text{ m NaOH}).$$

The values of ΔH_2 obtained for ZnO are similar to those obtained for SiO_2 in $(\text{OH})^-$, but higher than those obtained for Al_2O_3 . This is probably due to the fact that while ΔH_3 in all three cases is about the same ΔH_4 for Al_2O_3 is markedly smaller than for SiO_2 and ZnO.

Implications for growth. It is interesting to point out that while solubilities are generally similar in all the solvents studied, growth rates, nucleation tendency and perfection were quite different (Laudise, *et al.*, to be publ.). All of the mineralizers are suitable with respect to solubility and temperature coefficient. All are attractive in that fairly high solubilities are obtained at lower pressures well within the range of noble

metal lined Morey bombs (Laudise and Nielsen, 1961). It should be pointed out that since higher $(\text{OH})^-$ concentrations are required to effect appreciable solubility for ZnO in comparison to Al_2O_3 and SiO_2 it may be expected that diffusion problems in ZnO growth will be appreciable. Experimental results indicated this to be the case (Laudise, *et al.*, to be publ.). However, the high mineralizer concentrations required do serve to lower the water pressures at the temperature range useful for crystal growth to a point where low pressure lined autoclaves are useable.

ACKNOWLEDGEMENTS

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