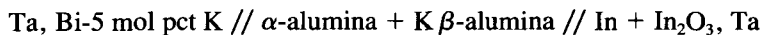


Thermodynamic Stability of K β -Alumina

G.M. KALE and K.T. JACOB

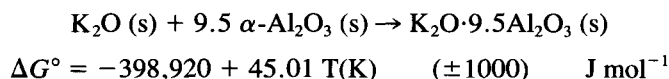
The activity of K₂O in a mixture of α -alumina and K β -alumina has been determined using the solid state galvanic cell:



in the temperature range 600 to 1000 K. The cell is written such that the right hand electrode is positive. The solid electrolyte consisted of a dispersion of α -alumina (~15 vol pct) in a matrix of K β -alumina. The emf of the cell was found to be reversible and to vary linearly with temperature. From the emf and auxiliary data on In₂O₃ and K₂O from the literature, the activity of K₂O in the two-phase mixture is obtained as

$$\log a_{\text{K}_2\text{O}} = 2.368 - \frac{20,850}{T(\text{K})} \quad (\pm 0.015)$$

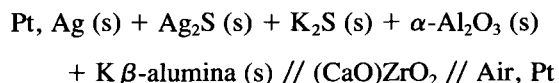
The standard free energy of formation of K β -alumina from component oxides is given by



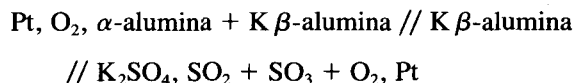
I. INTRODUCTION

THE sodium β -^[1,2] and β'' -alumina^[3] are well-known superionic conductors of Na⁺ ions. The Na⁺ ions in β - and β'' -alumina can be easily exchanged with other cations in molten salts.^[4] Many investigators have synthesized the β - and β'' -alumina of monovalent (Ag⁺, K⁺, Li⁺, Cu⁺, Rb⁺, Tl⁺, In⁺, Ga⁺),^[4-6] divalent (Ca⁺², Ba⁺², Sr⁺²)^[7,8,9] and trivalent (La⁺³)^[10] metal ions. These β - and β'' -alumina analogues show high ionic mobility and, hence, are potential materials for solid-state sensors and batteries. Recently, substituted β - and β'' -alumina have been used in thermodynamic measurements as the solid electrolytes.^[9,11]

The activity of K₂O in the two-phase region between α -alumina and K β -alumina in K₂O-Al₂O₃ system has been determined by Kumar and Kay^[10] using an oxygen concentration cell:

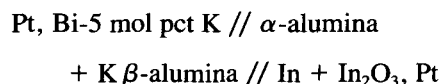


in the temperature range 970 to 1080 K. In order to establish the oxygen potential over the left hand electrode, five condensed phases have to be in equilibrium. Itoh and Kozuka^[12] determined the activity of K₂O in K β -alumina employing the solid-state galvanic cell:



in the temperature range 961 to 1274 K. The standard free energy of formation of K β -alumina from component oxides obtained in these studies differ by ~92 kJ mol⁻¹ at 1000 K and ~99 kJ mol⁻¹ at 1100 K. The re-

sults of Kumar and Kay^[10] are more positive compared to those of Itoh and Kozuka.^[12] In order to resolve the discrepancy, new measurements have been undertaken using the solid-state galvanic cell:



in the temperature range 600 to 1000 K.

II. EXPERIMENTAL

A. Materials

Puratronic grade bismuth, potassium, indium, and indium (III) oxide were obtained from Johnson and Matthey Chemicals, Ltd., London. The Bi-5 mol pct K alloy was prepared by melting the appropriate amount of Bi and K *in situ* in a solid electrolyte tube under an argon atmosphere, free from traces of oxygen. The alloy composition was determined by chemical analysis at the end of the experiment. The K β -alumina powder was prepared by dissolving Al₂(NO₃)₃·9H₂O and K₂CO₃·1.5H₂O in warm water and evaporating to dryness with constant agitation. The dry powder thus obtained was calcined at 1073 K for 360 ks, pressed into pellets, and fired at 1873 K for 8 ks. The material had excess K₂O to partially compensate the loss of K₂O during firing. The product was identified as K β -alumina by X-ray diffraction analysis. This was mixed with 10 vol pct α -alumina and the mixture was ground to a very fine powder having an average particle size of 2 μ . The powder was dried at 473 K for 18 ks. The dried powder was mixed with dry methanol to form a suspension and was slip cast into a tube following the procedure by Rivier and Pelton.^[13] The solid electrolyte tube was enclosed in an alumina container, packed with loose K β -alumina powder, and sintered at 1873 K for 7.5 ks. The density of the resulting alumina

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tube was found to be ~96 pct of the theoretical value. This compares favorably with a value of ~98 pct obtained by Rivier and Pelton^[13] for Na β -alumina. The tube contained almost 15 vol pct α -alumina in a matrix of K β -alumina. The composition of K β -alumina in contact with α -alumina was determined by EDAX as $K_2O \cdot 9.5Al_2O_3$. Yao and Kummer^[4] and Beevers and Brohult^[5] report synthesis of $K_2O \cdot 11Al_2O_3$ having β -alumina structure. This suggests that K β -alumina has a significant homogeneity range.

B. Apparatus and Procedure

A schematic diagram of the cell arrangement using the biphasic electrolyte tube is shown in Figure 1. The Bi-5 mol pct K alloy was taken inside the electrolyte tube. It established the activity of K at the left hand electrode. The tube was packed with dehydrated powder mixture of α -alumina and K β -alumina to minimize the loss of K by vaporization at high temperature. The electrolyte tube was covered at the top with an alumina lid.

The two-phase electrode consisting of 3:1 molar ratio of In and In_2O_3 was taken inside an alumina crucible. The closed end of the biphasic solid electrolyte tube was dipped into liquid indium saturated with In_2O_3 . The electrical contact to both electrodes was made by Ta wires,

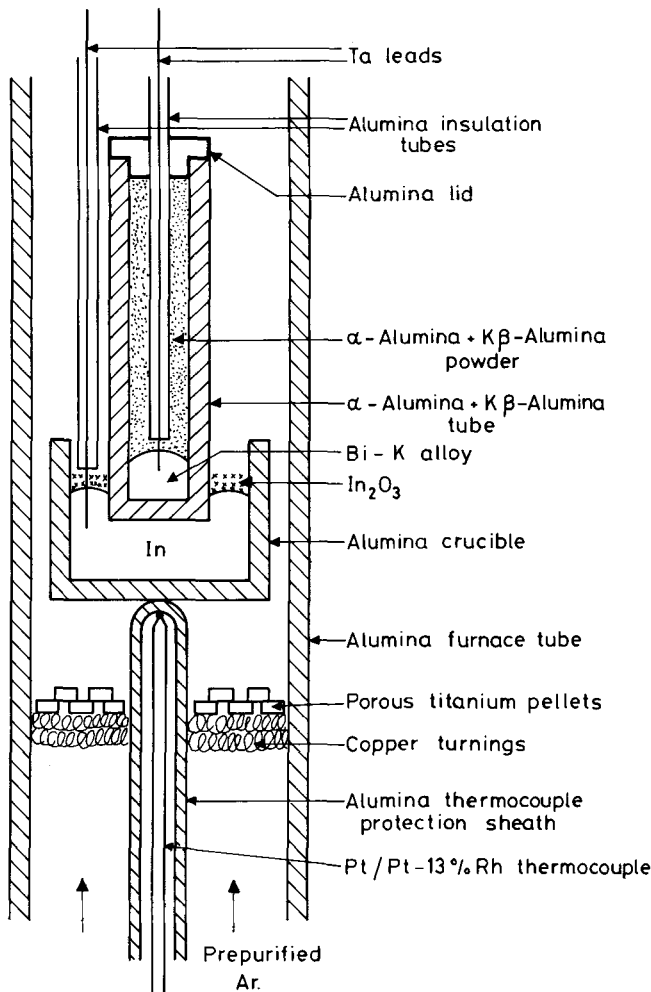


Fig. 1—A schematic diagram of the cell.

which were protected by alumina insulation tubes. The alumina crucible containing liquid In was supported on an alumina thermocouple protection sheath inside a high density alumina tube housing the cell assembly. Below the level of the crucible, the alumina tube was packed with copper turnings on which were placed porous titanium pellets. These were used as an internal getters for oxygen. Deoxidized argon gas was admitted into the outer alumina tube from the bottom.

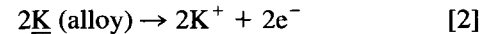
The emf of the cell was measured with a high impedance ($>10^{12}\Omega$) digital voltmeter. The reversibility of the cell was checked by passing a small current ($\sim 50\mu A$) through the cell in either direction for 100 seconds. In each case the emf was found to return to the original value before the titration. The emf was found to be independent of the flow rate of argon in the range of 2 to 4 ml s^{-1} . The emf was reproducible during the heating and cooling cycles. The temperature of the cell was measured by a Pt/Pt-13 pct Rh thermocouple. The steady state emf was obtained in 0.5 to 1.0 ks, depending on the temperature of measurement. The emf was not completely reversible below 600 K. The loss of potassium from the alloy by vaporization sets the upper limit for the operation of the cell at 1000 K.

III. RESULTS

The reversible emf of the cell can be represented as a function of temperature as

$$E = 1397 - 0.418 T(K) \quad (\pm 1.5) \quad \text{mV} \quad [1]$$

The temperature dependence of emf is shown in Figure 2. The numbers on the plot indicate the sequence of measurement. The cathodic reaction of the cell can be represented as



and the anodic reaction as

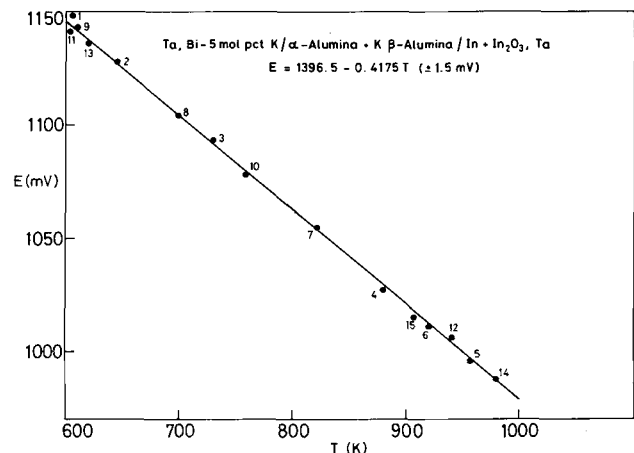
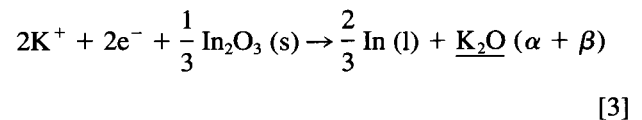
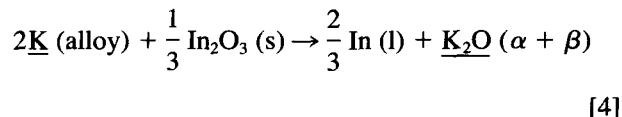


Fig. 2—Temperature dependence of the cell emf.

where \underline{K}_2O ($\alpha + \beta$) denotes K_2O in $K\beta$ -alumina saturated with α -alumina.

The net cell reaction can be represented as



The emf of the cell is related to the Gibbs energy change for reaction [4] by the Nernst equation:

$$-nFE = \Delta G_4 = \Delta G_4^\circ + RT \ln \frac{a_{K_2O(\alpha+\beta)}}{a_{K(\text{alloy})}^2} \quad [5]$$

where n is the number of electrons involved in the electrode reaction, F is the Faraday's constant, and E is the cell voltage. Therefore, the relative chemical potential of K_2O in the phase mixture α -alumina and β -alumina is given by

$$\Delta\mu_{K_2O(\alpha+\beta)} = -nFE - \Delta G_4^\circ + 2RT \ln a_{K(\text{alloy})} \quad [6]$$

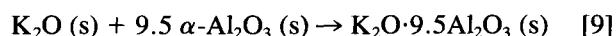
The standard Gibbs energy change for reaction [4] is obtained from the thermodynamic data for In_2O_3 from Jacob^[14] and K_2O from Janaf.^[15] The activity of K in Bi-5 mol pct K alloy is taken from a recent measurement of Petric *et al.*^[16] as

$$\ln a_{K(\text{alloy})} = 19.27 - \frac{12,965}{T(\text{K})} - 2.559 \ln T(\text{K}) \quad [7]$$

This gives the log a_{K_2O} in the α -alumina + $K\beta$ -alumina mixture as

$$\log a_{K_2O} = 2.368 - \frac{20,850}{T(\text{K})} \quad (\pm 0.015) \quad [8]$$

The formation of $K\beta$ -alumina can be represented by the equation



for which the standard free energy change can be calculated from activity data for K_2O in equilibrium with α -alumina and $K\beta$ -alumina at unit activity as

$$\Delta G_9^\circ = -398,920 + 45.01 T(\text{K}) \quad (\pm 1000) \quad \text{J mol}^{-1} \quad [10]$$

The uncertainty limit corresponds to twice the standard deviation in emf measurement. It does not include uncertainties in auxiliary thermodynamic data on In_2O_3 , K_2O , and activity of potassium in the alloy.

IV. DISCUSSION

The standard Gibbs energy of formation of $K\beta$ -alumina from component oxides obtained in this study is plotted in Figure 3 in comparison with the values suggested by Kumar and Kay^[10] and Itoh and Kozuka.^[12] It is clear that the present measurements are in better agreement with Itoh and Kozuka.^[12] In the cell used by Kumar and Kay,^[10] five condensed phases, Ag , Ag_2S , K_2S , $\alpha\text{-Al}_2\text{O}_3$, and $K\beta$ -alumina, must come into equilibrium to estab-

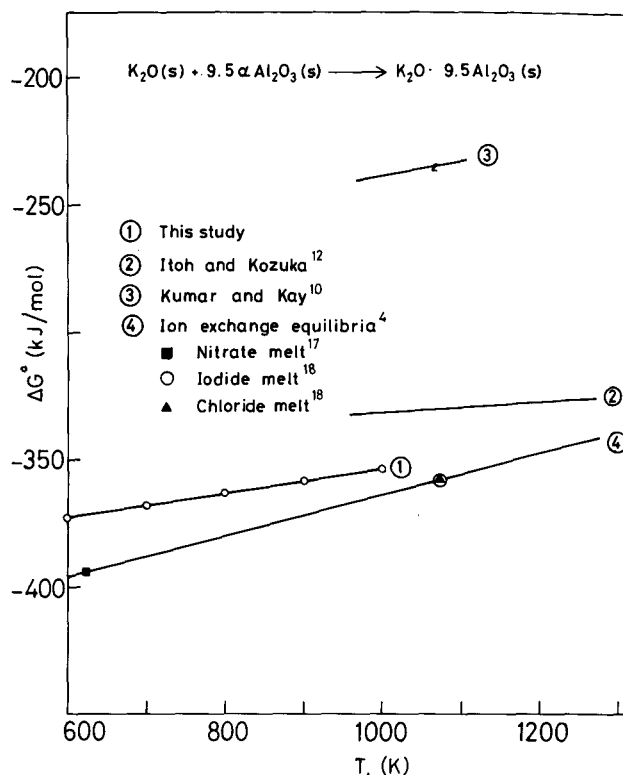


Fig. 3—Comparison of the standard free energy of formation of $K\beta$ -alumina from component oxides as a function of temperature.

lish oxygen potential at the measuring electrode. Kumar and Kay^[10] did not test for the reversibility of the cell by microcoulometric titration in both directions. Also, they did not check for the dependence of emf on the flow rate of gases. The large difference in oxygen potential between the two electrodes of their cell could have resulted in a significant semipermeability flux of oxygen through their calciastabilized zirconia solid electrolyte and consequent polarization of electrodes. Although $(\text{CaO})\text{ZrO}_2$ is a predominantly oxygen ion conductor, there is a finite concentration of electrons in this material which is dependent on temperature and oxygen partial pressure. Coupled transport of oxygen ions and electrons gives rise to oxygen semipermeability of the solid electrolyte. The results obtained in this study are approximately 22 kJ mol^{-1} more negative than the values reported by Itoh and Kozuka^[12] at 1000 K.

An independent assessment of the stability of $K\beta$ -alumina relative to $\text{Na}\beta$ -alumina can be obtained from the ionic distribution measurements between $(\text{Na}, \text{K})\beta$ -alumina and (Na, K) nitrate melt at 623 K and (Na, K) chloride melt and (Na, K) iodide melt at 1073 K. Yao and Kummer^[4] measured the distribution of K^+ ions between the melt and solid β -alumina as a function of composition. From the distribution measurements and data on activity coefficients of nitrate,^[17] chloride,^[18] and iodide^[18] melts, activity coefficients in the $(\text{Na}, \text{K})\beta$ -alumina solid solution can be derived:^[19]

$$\log \gamma_{K_{O_{0.5} \cdot 9.5Al_{0.5}}} = - \int_0^{X_{Na(\beta)}} X_{Na(\beta)} d \log Z \quad [11]$$

where $X_{\text{Na}(\beta)}$ equals the molar ratio, $n_{\text{Na}}/(n_{\text{Na}} + n_{\text{K}})$, in β -alumina and Z is defined as

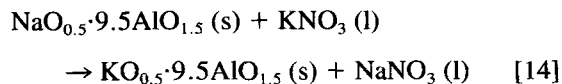
$$Z = \frac{X_{\text{NaNO}_3}(\text{l}) \cdot \gamma_{\text{NaNO}_3}(\text{l}) \cdot X_{\text{K}(\beta)}}{X_{\text{KNO}_3}(\text{l}) \cdot \gamma_{\text{KNO}_3}(\text{l}) \cdot X_{\text{Na}(\beta)}} \quad [12]$$

Components of β -alumina solid solution are chosen as $\text{KO}_{0.5} \cdot 9.5\text{AlO}_{1.5}$ and $\text{NaO}_{0.5} \cdot 9.5\text{AlO}_{1.5}$ so that activity coefficients do not tend to zero at low concentrations. The activity coefficient of $\text{NaO}_{0.5} \cdot 9.5\text{AlO}_{1.5}$ is given by

$$\log \gamma_{\text{NaO}_{0.5} \cdot 9.5\text{AlO}_{1.5}} = \int_0^{X_{\text{K}(\beta)}} X_{\text{K}(\beta)} d \log Z \quad [13]$$

The Gibbs-Duhem integration plot is shown in Figure 4. The derivation of activity coefficients of β -alumina solid solution does not assume any specific value for the equilibrium constant for the exchange reaction.^[19] The activity-composition relationship in the (Na, K) β -alumina solid solution derived from the distribution studies of Yao and Kummer^[4] is shown in Figure 5. The activities in the (Na, K) β -alumina solid solution obtained from the distribution studies with the nitrate and iodide melts indicate mild negative deviation from ideality, whereas the data from distribution equilibria with the chloride melt show approximately ideal behavior.

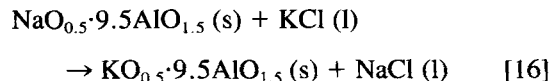
From the distribution equilibria, activities in the fused salt and the derived activity coefficients in (Na, K) β -alumina solid solution, equilibrium constant for the reaction



is obtained as 7.32 at 623 K. The standard free energy change for reaction [14] at 623 K is

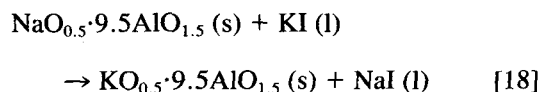
$$\Delta G_{14}^\circ = -RT \ln K_{14} = -10,310 \quad \text{J mol}^{-1} \quad [15]$$

where K_{14} is the equilibrium constant for the reaction [14]. The standard free energy change for similar ion exchange reactions using chloride and iodide melts can be obtained at 1073 K. For the reaction



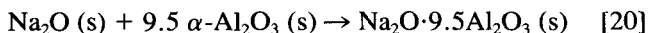
$$\Delta G_{16}^\circ = -RT \ln K_{16} = -5450 \quad \text{J mol}^{-1} \quad [17]$$

and for the reaction



$$\Delta G_{18}^\circ = -RT \ln K_{18} = -5140 \quad \text{J mol}^{-1} \quad [19]$$

Combining the standard free energy of formation of KNO_3 and NaNO_3 from Robie *et al.*,^[20] K_2O and Na_2O from Janaf,^[15] and the standard free energy of formation of $\text{NaO}_{0.5} \cdot 9.5\text{AlO}_{1.5}$ from Jacob *et al.*^[21] given by



$$\Delta G_{20}^\circ = -272,250 + 25.5 T(\text{K}) \quad (\pm 1500) \quad \text{J mol}^{-1} \quad [21]$$

the standard free energy of formation of $\text{KO}_{0.5} \cdot 9.5\text{AlO}_{1.5}$ from component oxides was computed at 623 K. Similar

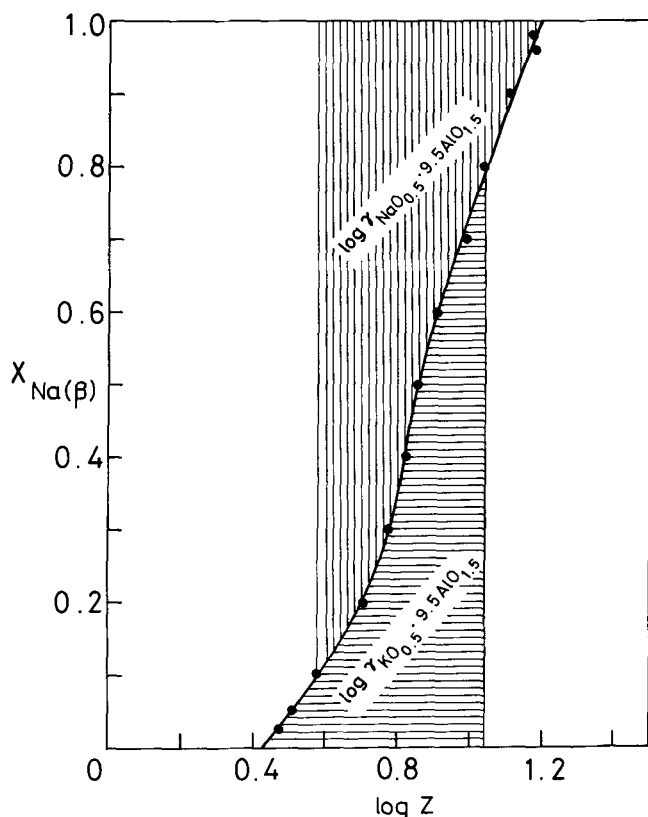


Fig. 4—Gibbs-Duhem integration plot for deriving the activity coefficients of $\text{NaO}_{0.5} \cdot 9.5\text{AlO}_{1.5}$ and $\text{KO}_{0.5} \cdot 9.5\text{AlO}_{1.5}$ from distribution equilibria between (Na, K) nitrate melt and (Na, K) β -alumina equilibrium at 623 K.

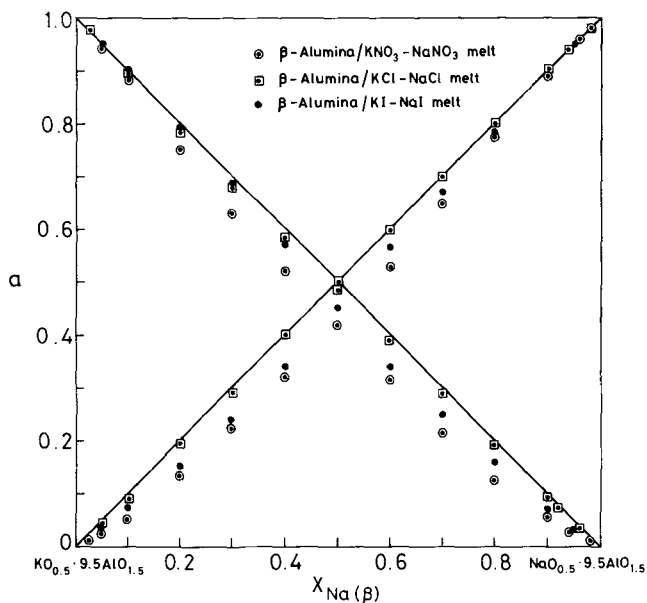


Fig. 5—Activity-composition relationship in (Na, K) β -alumina from distribution studies using nitrate (623 K), chloride (1073 K), and iodide (1073 K) melts.

computations were carried out to obtain the standard free energy of formation of $\text{K}_2\text{O}\cdot 9.5\text{Al}_2\text{O}_3$ from component oxides at 1073 K using chloride and iodide melt for exchange equilibria. The standard free energy of formation of KCl, NaCl, KI, and NaI was taken from Janaf.^[15] The derived standard free energy of formation of K β -alumina from component oxides using ion exchange equilibria are compared in Figure 3 with the present results. Distribution studies yield Gibbs energies which are more negative by 10 to 22 kJ mol⁻¹ depending on temperature. This difference may be caused by combined errors in auxiliary thermodynamic data used in the evaluation. The Gibbs energy of formation of Na β -alumina has been measured by several investigators.^[21-29] Although the data used in this calculation^[21] are in good agreement with those reported by Elrefaie and Smeltzer,^[22] Dewing,^[23] Fray,^[24] and Rog *et al.*,^[25] they differ significantly from the data suggested by Choudhury^[26] and Dubreuil *et al.*^[27] The measurements of Itoh *et al.*^[28] and Brisley and Fray^[29] agree with the Gibbs energy for Na β -alumina used in this study at 1200 K, but their temperature coefficients differ considerably. Considering all the studies, the error limit on the Gibbs energy of formation of Na β -alumina from component oxides is ± 8 kJ mol⁻¹. The Gibbs energy of formation of K_2O is also associated with a large uncertainty, ± 15 kJ mol⁻¹.

The direct experimental data for Gibbs energy of formation of K β -alumina from the component oxides obtained in this study is in better agreement with the data derived from distribution measurements than the values suggested by Kumar and Kay^[10] and Itoh and Kozuka.^[12] It would be interesting to obtain calorimetric information on the enthalpy of formation and heat capacity of $\text{K}_2\text{O}\cdot 9.5\text{Al}_2\text{O}_3$ so that a more complete assessment of thermodynamic data for this compound can be given.

V. SUMMARY

The present study resolves the discrepancy in the reported thermodynamic stability of K β -alumina. The Gibbs energy of formation of K β -alumina from component oxides is

$$\Delta G^\circ = -398,920 + 45.01 T(\text{K}) \quad (\pm 1000) \quad \text{J mol}^{-1}$$

in reasonable accord with the data of Itoh and Kozuka^[12] and distribution measurements.^[4] The results of Kumar and Kay^[10] appear to be less reliable.

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