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Critical review of the thermodynamics of the Na–Al–O system

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The free energies of formation of various phases in the Na–Al–O systems are critically reviewed for the composition range between pure alumina and sodium-aluminate. The results clearly indicate that in the temperature range between 600 and 1100 K neither β-alumina nor β''-alumina ($Na_2O.5Al_2O_3$) are stable with respect to sodium; the most stable phase in that range being sodium aluminate. Least square fitting and statistical analysis of all the available data on the free energy of formation of β-alumina deemed accurate yields

$$\Delta G^\circ_{\mathrm{form}}\ (\text{from oxides}) = -8772 + 1.53T\ (\text{J/mole of O}) \quad (600 \leqslant T \leqslant 1200\,\mathrm{K})$$

If the composition of β-alumina is assumed to be $Na_2O.11Al_2O_3$ then

$$\Delta G^\circ_{\mathrm{form}}\ (Na_{1/17}Al_{11/17}O,\ \text{from elements}) = -565\,100 + 109.6T$$
$$(\text{J mole of O}) \quad (600 \leqslant T \leqslant 1200\,\mathrm{K})$$

If the composition is assumed to be 1 : 9 then:

$$\Delta G^\circ_{\mathrm{form}}\ (Na_{1/14}Al_{9/14}O,\ \text{from elements}) = -564\,000 + 109.6\ T$$
$$(\text{J/mole of O}) \quad (600 \leqslant T \leqslant 1200\,\mathrm{K})$$

Based on the only study to date, the best estimate for the free energy of formation of β''-alumina is

$$\Delta G^\circ_{\mathrm{form}}\ (Na_{1/8}Al_{5/8}O,\ \text{from the elements}) = -567\,860 + 114\ T$$
$$(\text{J/mole of O}) \quad (600 \leqslant T \leqslant 1200\,\mathrm{K})$$

The uncertainty (95% confidence band) is estimated to be about ±200 J/mole of O. Based on these results β''-alumina should be thermodynamically stable at lower temperatures, but become unstable at temperatures > 900 K and should, kinetics permitting, dissociate into β-alumina and sodium aluminate. Experimental evidence, however exists that conclusively shows that β''-alumina is thermodynamically stable at much higher temperatures than 900 K which leads to the conclusion that $\Delta G^\circ_{\mathrm{form}}$ for β''-alumina reported to date is too high and should be more negative.

1. Introduction

Despite the technological importance of β- and β''-alumina in such devices as Na–S high energy batteries and the use of α-alumina as envelopes for high pressure sodium lamps, the question of the chemical stability of these phases with respect to each other and with respect to sodium has to date not been conclusively resolved. Part of the reason for this state of affairs has been that, until quite recently, the free energy of formation of β''-alumina had not been measured. Recently, however, Choudhury [1, 2] reported data for the free energy of formation of β'', allowing for the first time, for a complete analysis of the thermodynamics of the Na–Al–O system.

The thermodynamic data are presented in both tabular and graphical form. In graphical form, the compositional dependences of the free energies of formation of the various compounds, *normalized to a per mole of oxygen basis*, are plotted in graphs similar to the one shown in Fig. 1. The free energies of formation of the binary oxides, M_xO and N_yO, from their elements, are plotted on either side of the graph with the normalized free energy of formation data for the ternaries in between. The composition is expressed as a mole fraction of N_yO. For example, in the Al_2O_3–Na_2O system the x-axis would represent the mole fraction of $Al_{2/3}O$. The advantages of presenting the data in the format shown in Fig. 1 are several and include the following.

(1) The most stable compound in a given system at a given temperature is the one with the lowest free energy of formation (e.g. compound II in Fig. 1).

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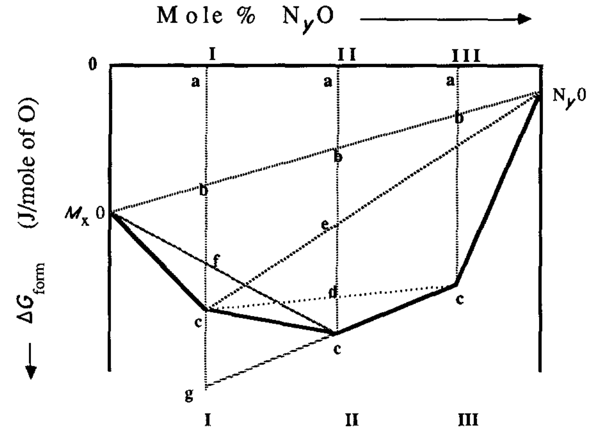

Figure 1 Geometrical construction of compositional dependence of Gibbs free energy of formation per mole oxygen plotted against composition. The most stable compound in this system is II.

This in turn implies that the compound is thermodynamically stable with respect to the pure alkali metal (sodium in this case).

(2) The free energy of formation (per mole of oxygen) of any compound *from its elements* is given by the distance ac, whereas the free energy of formation from the *parent oxides* is given by the distance bc.

(3) The line joining any two compounds represents the free energy of formation of non-interacting mixtures of the phases in question. Consequently, the free energy of formation of any ternary compound from any two adjacent phases is given by the vertical distance between the line joining these phases and the free energy of formation of the ternary compound in question. For example, the free energy of formation of compound II starting with compounds I and II is given by the distance dc. Similarly, the free energy formation of the same compound from N_yO and I is represented by the distance ce, etc.

(4) The thermodynamic data have to be self consistent in that the free energy of formation of each ternary compound must lie within a range of values determined by the free energy of formation of the phases adjacent to it. For example, if the free energy of formation of M_xO and compound II are known then the free energy data for compound I can only take the values between points f and g. For more details on the various methods by which thermodynamic data can be graphically depicted and the advantages of each, the reader is referred to several papers that have addressed these issues [3, 4].

2. Review of pertinent thermodynamic data

β-alumina is a general term that refers to a family of non-stoichiometric compounds of soda and alumina [5]. The structure is known to be layered consisting of blocks of spinel separated by loosely packed layers forming the ion conduction planes. Large variations in the sodium content is possible whilst retaining the alumina structure [5]. Given the uncertainty in the composition of β-alumina the analysis in this paper was carried out assuming the composition to be either $Na_20.11Al_2O_3$ or $Na_20.9Al_2O_3$.

It should be pointed out that despite the fact that β-alumina may exhibit a wide range of stoichiometry the composition in equilibrium with α or β'' alumina will, once a third variable is fixed, such as the oxygen partial pressure or sodium activity for example, have a unique fixed composition according to the Gibbs phase rule.

Similarly it is assumed that the composition of β''-alumina, in equilibrium with β-alumina is Na_2 $0.5Al_2O_3$ [5, 23]. As discussed in more detail below, the composition of these phases would have to be

TABLE I Summary of thermodynamic data

Compound	Free energy of formation (kJ/mole of O)				Reference
	600 K	800 K	1000 K	1200 K	
α-Alumina*(α-$Al_{2/3}O$)	**−495.77 ± 0.5**	**−474.98 ± 0.5**	**−453.81 ± 0.5**	**−431.74 ± 0.5**	[6]
$Na_{1/17}Al_{11/17}O$ (β-alumina)					
From oxides ⇒	−8.0 ± 1.3*	−7.6 ± 1.3*	−7.2 ± 1.3	−6.8 ± 1.3	[7]
[7] corrected (see text)	−7.36	−7.1*	−6.83	−6.66	
	−7.85*	−7.5 ± 0.5*	−7.1 ± 0.5	−6.8 ± 0.5	[8]
	−6.47 ± 0.2*	−6.48 ± 0.2	−6.48 ± 0.2	−6.49 ± 0.2	[9]
[9] corrected (see text)	−5.0 ± 0.2	−5.2 ± 0.2	−5.3	−5.5	
			−7.27		[10]
				−6.65 @ 1273 K	[11]
				−6.58	[13]
	−8.32 ±	−8.0	−7.76	−7.5	[14]
Best fit (Equation 9)	−7.85	−7.55	−7.24	−6.9	
From elements					
$Na_{1/17}Al_{11/17}O$ ⇒	**−499.0 ± 0.5**	**−477.7 ± 0.5**	**−456 ± 0.5**	**−433.2 ± 0.5**	
$Na_{1/14}Al_{9/14}O$ ⇒	**−498.0**	**−476.5**	**−455**	**−432**	
$Na_{1/8}Al_{5/8}O$ (β''-alumina)					
From oxides ⇒	−14.5 ± 0.2*	−13.5 ± 0.2	−12.3 ± 0.2	−11.4 ± 0.2	[1]
[1] corrected (see text)	−13.09	−12.54	−11.47	−10.11	
From elements ⇒	**−499 ± 0.2***	**−477.0***	**−454.5**	**−430.5**	
$Na_{1/2}Al_{1/2}O$ (sodium-aluminate)					
From elements ⇒	**−501.2 ± 0.5**	**−479.0 ± 0.5**	**−456.7 ± 0.5**	**−432.6 ± 0.5**	[6]
Na_2O	**−336.41**	**−308.07**	**−280.54**	**−249.215**	[6]

*extrapolated

Bold faced numbers refer to the free energy of formation from the elements based on the free energy data listed in this table for the binary oxides and are not necessarily the ones reported in the original references.

dramatically different from the ones assumed here to alter the general conclusions.

Based on these compositions for β and β'' alumina, the free energies of formation, $\Delta G^\circ_{\mathrm{form}}$, of the following phases, in order of increasing soda content are of importance and are reviewed: α-alumina (α-Al_2O_3), β-alumina ($Na_20.11Al_2O_3$ or $Na_20.9Al_2O_3$), β''-alumina ($Na_20.5Al_2O_3$), sodium aluminate ($Na_2O.Al_2O_3$) and Na_2O. The occurrence of other soda-rich phases e.g. Na_5AlO_4, $Na_7Al_3O_4$ are not germane to this paper and are not considered.

The free energy data, on a per mole of oxygen basis, for the various compounds are summarized in Table I and are discussed below.

2.1. Alumina

$\Delta G^\circ_{\mathrm{form}}$ for alumina is fairly well established and the values used in this paper are the ones listed in the latest JANAF tables [6]. Least square regression analysis of the data yields

$$\Delta G^\circ_f(Al_{2/3}O) = -560041.3 + 106.0\,T$$
$$(\text{J/mole of O}) \quad 600 < T < 1200 \qquad (1)$$

The uncertainty is estimated to be ± 500 J/mole of O.

2.2. β-alumina ($Na_20.11Al_2O_3$)

$\Delta G^\circ_{\mathrm{form}}$ of β-alumina was measured by a number of investigators [7–14] and, with two exceptions, namely Dubreuil *et al.* [9] and Choudhury [12], the results agree within experimental error.

Elrefaie and Smeltzer [7] measured the EMF (900 to 1200 K) generated across the cell

$$\mathrm{Pt}\,|\,\mathrm{W},\ WS_2 \text{ and } Na_2S\,|\,\alpha \text{ and } \beta\text{-}Al_2O_3\,|\,\mathrm{M}',\ \mathrm{M}'_nO\,|\,\mathrm{Pt} \qquad (\mathrm{I})$$

On the left-hand side, the sodium activity was fixed by the three phase mixture, W, WS_2 and Na_2S*. On the right hand side, the sodium activity was set by fixing the oxygen partial pressure P_{O_2}, using various M′, M'_nO mixtures, and the two phase mixture of α and β-Al_2O_3 (in the electrolyte). Three different electrodes were used namely: Ni–NiO, Fe–FeO, Cu–Cu_2O. A fourth cell where the metal–metal oxide was replaced by a NaF, NiF_2 and nickel mixture was also used†. The e.m.f.s were measured for both increasing and decreasing temperatures. All the cells gave consistent results and ΔG°_f (normalized to a per mole of oxygen basis) for β-alumina was calculated from the e.m.f. results and found to be

$$\Delta G^\circ_f(\text{from oxides}) = -9235 + 2.0\,T\,(\text{J/mole of O}) \qquad (2)$$

with an uncertainty of ± 1200 J/mole of O. Equation 2 is listed in Table I and plotted in Fig. 2.

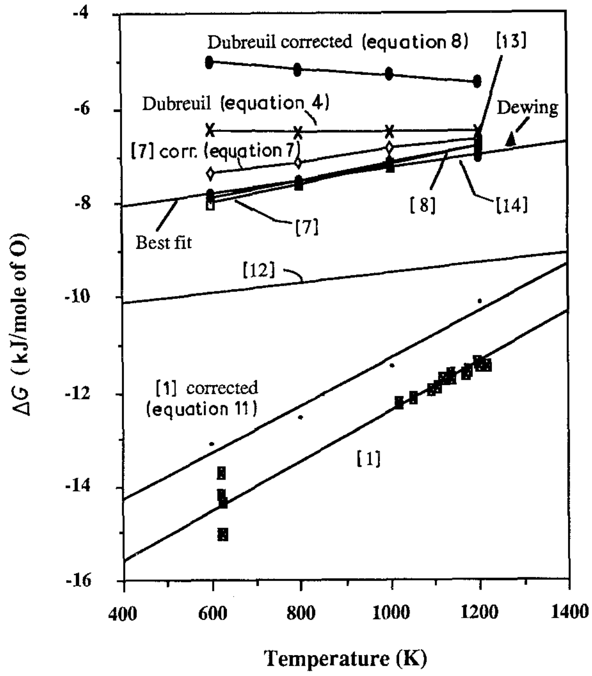

Figure 2 Summary of the free energies of formation from oxides per mole of oxygen for β-alumina and β''-alumina (lower two lines).

Rog *et al.* [8] measured ΔG°_f of β-alumina (970 to 1220 K) using the galvanic cell

$$\mathrm{Pt}\,|\,Na_2O\ (\mathrm{NASICON})\,||\,\mathrm{NASICON}\,|$$
$$|\,\alpha \text{ and } \beta\text{-}Al_2O_3\,|\ \mathrm{Pt}. \qquad (\mathrm{II})$$

The sodium activity on the right-hand side was fixed by the three phases: α and β-Al_2O_3 (present in the electrolyte) and ambient oxygen. On the left half-cell, the Na_2O activity was unity. ΔG°_f for β-alumina was calculated from the e.m.f.s measured to be

$$\Delta G^\circ_f(\text{from oxides}) = -8910 + 1.76\,T\,(\text{J/mole of O}) \qquad (3)$$

The results are listed in Table I and plotted in Fig. 2. The uncertainty in this case is ± 500 kJ mol^{-1}.

Dubreuil *et al.* [9] used two types of cells to measure the free energy of formation of β-Al_2O_3 namely

$$\text{Chromel (W) } Na_{\mathrm{liq}}\,|\,Na_20.11Al_2O_3,\,|\,(NaNO_3$$
$$+\ NaNO_2)_{\mathrm{liq}}\,|\,\alpha + \beta\text{-}Al_2O_3\,|\,O_2\ (\mathrm{Pt}) \qquad (\mathrm{III})$$

in the range 573 to 773 K, and

$$(\mathrm{Pt})\,|\,\mathrm{W},\ WS_2,\ Na_2S\,|\,\alpha\text{-}Al_2O_3$$
$$+\ \beta\text{-}Al_2O_3\,|\,ZrO_2\text{-}Y_2O_3\,|\,O_2\ (0.21\ \mathrm{atm})\ (\mathrm{Pt}) \qquad (\mathrm{IV})$$

in the range 873 to 1073 K. The two sets of data were plotted and joined together with chronopotentiometric experiments performed over the range 85 to 140° C to determine the activity of Na that corresponds to equilibrium between α- and β-alumina. The three

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*The free energy data in Table III in [7] are incorrectly labelled as being in cal/mol when in fact they are in J/mol^{-1}.

†The cell

$$\mathrm{Pt}\,|\,\mathrm{W}\ WS_2 \text{ and } Na_2S\,|\,\alpha \text{ and } \beta\text{-}Al_2O_3\,|\,NiF_2,\ \mathrm{Ni}, \text{ and NaF}\,|\,\mathrm{Pt}$$

used by Elrefaie and Smeltzer does not yield any information about the free energy of formation of the electrolyte since at each electrode the sodium activity is fixed by the three-phase mixture; the electrolyte simply acts as a sodium activity sensor.

sets of data were in agreement with each other and resulted in

$$\Delta G_f^\circ(\text{from oxides}) = -6470 - 0.017\,T\,(\text{J/mole of O}) \quad (4)$$

Equation 4 is plotted in Fig. 2 and the results listed in Table I. It is to be noted that contrary to other investigations, the slope of the free energy versus temperature data is negative. For this reason, as well as the fact that when the data are corrected (see below) the results of Dubreuil *et al.* are even further removed from the rest of the data, they were not included in the final analysis.

The value of -7.27 kJ/mole of O determined by Fray [10] at 1000 K is in general agreement with the rest of the data. It should be pointed out, however, that Fray's determination was based on a single data point for a run that lasted only a few minutes. Also, in accordance with the rest of the data is the value of -6.65 kJ/mole of O (from oxides) at 1273 K, determined by Dewing [11].

Weber [13] measured the free energy change for the reaction

$$2\,\text{NaAlO}_2 + 10\,\text{Al}_2\text{O}_3 \Leftrightarrow \text{Na}_2\text{0.11Al}_2\text{O}_3 \quad (5)$$

Using his e.m.f. data and the free energies of formation for $Na_2O.Al_2O_3$ and Al_2O_3 listed in Table I, ΔG_f° of β-alumina (from oxides) at 1200 K is calculated to be -6.33 kJ/mole of O. Weber's results extrapolate to 0 at 140° C, which is incompatible with the rest of the data that indicates that the free energy changes for reaction 5 become more, rather than less, negative with increasing temperature. For this reason this data was not included in the final analysis. Also plotted in Fig. 2 are the results of Choudhury [12] for the free energy of formation of β-alumina, which clearly are anomalously negative. Using Chauvenet's criteria [26] it can be shown that Choudhury's data should be rejected or at best suspect. These results were thus not used in the final analysis.

Brisley and Fray [14] measured the free energy of formation of β-alumina using the cell

$$\text{Fe}\,|\,\text{Na(l)}\,|\,\alpha \text{ and } \beta\text{-Al}_2\text{O}_3\,|\,\text{Cu, Cu}_2\text{O}\,|\,\text{Pt} \quad (\text{I})$$

as a function of temperature from 673 to 873 K. Their results, which are listed in Table I and plotted in Fig. 2, are given by

$$\Delta G_f^\circ(\text{from oxides}) = -9098.5 + 1.3\,T\,(\text{J/mole of O}) \quad (6)$$

It is interesting to note that Brisley and Fray also concluded that the results of Choudhury [12] and Dubreuil *et al.* [9] were too low and too high, respectively.

To calculate the equilibrium sodium activity of their reference electrodes Elrefaie and Smeltzer [7] and Dubreuil *et al.* [9] used the values listed in Table II (columns 3 and 4). The latest available free energy data [6] for the same compounds also listed in Table II, (columns 6 to 8), some of which are clearly different from the original set. $\Delta G_f^\circ$of β-alumina determined by Elrefaie and Smeltzer [7] and Dubreuil *et al.* [9] were thus recalculated using the latest free energy data listed in Table II. The correction is non-trivial and Equation 2 becomes:

$$\Delta G_f^\circ(\text{from oxides}) = -8091 + 1.224\,T\,(\text{J/mole of O}) \quad (7)$$

while Equation 4 changes to

$$\Delta G_f^\circ(\text{from oxides}) = -4530 - 0.8\,T\,(\text{J/mole O}) \quad (8)$$

The corrected values, i.e. Equations 7 and 8, are plotted in Fig. 2 and listed in Table I. The correction moves both sets of results farther away than the rest of the data. Rog *et al.* [8] did not use a reference electrode and hence their results remain unchanged. Brisley and Fray [14] used the JANAF tables and hence their results remain unchanged as well.

The good agreement between the results of Rog *et al.* and Elrefaie and Smeltzer, and Brisely and Fray is notable given that very different cell arrangements were used in each case and lends validity to all the results. The results of Choudhury, Weber and Dubreuil *et al.* were not used in the final analysis.

Statistical analysis of the β-alumina data using Equations 3, 6, 7 and the results of [10] and [11] yields

$$\Delta G_f^\circ(\text{from oxides}) = -8772 + 1.53\,T\,(\text{J/mole O}) \quad (9)$$

Equation 9, labelled best fit, is plotted in Fig. 2. It is

TABLE II Summary of thermochemical data (J/mole) used in original references (columns 3 and 4) and the ones adopted in this paper, all from [6] (columns 6 to 8)

1 Compound	2 Temperature range (K)	3 $\Delta G^\circ = A + BT$	4	5 Reference	6 $\Delta G^\circ = C + DT + ET^2$	7	8
		A	B		C	D	E
Al_2O_3	600–1200	−1 680 126	319.9	[7, 9]	same		
NiO	900–1400	−234 158	84.893	[7]	same		
Cu_2O	900–1300	−167 046	71.463	[7]	same		
FeO	873–1600	−264 575	65.4	[7]	same		
Na_2O	400–1100	−420 015	146.02	[7]	−422 220	142.5	
	400–1100	−405 600	128.9	[9]	−422 220	142.5	
Na_2S*	500–1100	−440 232	131.38	[7, 9]	−348 550	−29.17	0.073
WS_2	1370–1565	−336 394	156.48	[7, 9]	same		

*A lamba transition at 1276 K in Na_2S causes a marked curvature in the temperature dependence of the free energy. Hence the need for a second-order polynomial.

important to note that Equation 9 is independent of composition. With reference to Fig. 1, Equation 9 represents the vertical distance bc.

2.3. β''-alumina ($Na_2O.5Al_2O_3$)

To date, the only data for the free energy of formation of β'' were reported by Choudhury [1] who measured the e.m.f., between 1020 and 1220 K, generated by cells of the type

$$\mathrm{Pt}\,|\,\mathrm{W,\ WS_2,\ Na_2S}\,|\,\beta \text{ and } \beta''\text{-}\mathrm{Al_2O_3}\,|\,\mathrm{O_2}\,|\,\mathrm{Pt} \quad (\mathrm{V})$$

where the sodium activity, on the right-hand side, was fixed by the equilibrium between pure oxygen and β and β'' (in the electrolyte). In some runs the oxygen was replaced by oxygen–argon mixtures. At lower temperatures (≈ 623 K) the e.m.f. between sodium and a test electrode (mercury or indium) in a molten $NaNO_3$ bath was used to calculate the Na_2O activity in the two phase (β and β'' electrolyte). The calculations were based on the following reaction

$$[\mathrm{Na_2O}] + n\mathrm{M} \Leftrightarrow \mathrm{M}_n\mathrm{O} + 2\mathrm{Na}^+ + 2\mathrm{e}$$

where M was either indium or mercury. The scatter in the low temperature results was fairly large (see Fig. 2) and fluctuations of 50 MV in the e.m.f.s were observed which renders the low temperature data less reliable than the high temperature data. Nevertheless, a least square fit of the data gives

$$\Delta G^{\circ}_{\mathrm{form}}\ (\text{from oxides})$$
$$= -17666 + 5.23\ T\ (\text{J/mole O}) \quad (10)$$

The uncertainty (95% confidence band) 600 K is ± 200 J/mole of O. As before, Table II was used to correct the data, resulting in

$$\Delta G^{\circ}_{\mathrm{form}}\ (\beta'',\ \text{from oxides})$$
$$= -16307 + 5\ T\ (\text{J/mole of O}) \quad (11)$$

The corrected values are listed in Table I and Equation 11 is plotted in Fig. 2. However, as discussed in more detail in the discussion section there is strong evidence in the literature that suggests that the values given by Equation 11 are too high and should be more negative.

2.4. Sodium aluminate ($Na_2O.Al_2O_3$)

The free energy data for sodium aluminate reported in JANAF are based on [15–17]. A least square fit (600 to 1200 K) results in

$$\Delta G^{\circ}_{\mathrm{form}}\ (\mathrm{Na_{1/2}Al_{1/2}O},\ \text{from elements})$$
$$= -569\,458 + 113.5\ T\ (\text{J/mole of O}) \quad (12)$$

Based on the original papers the uncertainty was conservatively estimated to be about ± 500 J/mole of O. More recently the enthalpy of formation at 298 K for $NaAlO_2$ was remeasured [18] and found to be 2795 J/mol^{-1} more negative than originally reported. This correction would make the free energy results (i.e. Equation 12) even more negative (by about 1.4 kJ/mole of O) than those listed in Table I and therefore further strengthens the arguments made in the next section concerning the most stable phase in the system at lower temperatures.

2.5. Sodium oxide, Na_2O

ΔG°_{f} for Na_2O according to the JANAF (Listing: June 1968) are shown in Table I. More recently Sreedharan *et al.* [19] reviewed ΔG°_{f} for Na_2O and their values are almost identical to the JANAF results. The values adopted for the free energy of formation of Na_2O are thus those listed in JANAF (see Table II) namely

$$\Delta G^{\circ}_{\mathrm{form}}\ (\mathrm{Na_2O}) = -422\,220 + 142.5\ T$$
$$(\text{J/mole of O}) \quad (600 \text{ to } 1200\ \mathrm{K}) \quad (13)$$

2.6. Free energy of formation from the elements

To calculate the free energies of formation of β and β'' alumina from the elements the value of the free energy data of the parent oxides have to be known as well as their exact compositions. Elrefaie and Smeltzer used Elliot and Gleiser's [20] results while Dubreuil *et al.* used a third source [21] (both listed in Table II) for the free energy of Na_2O. The obvious variability of these values is in turn reflected in the final free energy of formation (from elements) values reported in each case. To eliminate this variable the free energies of β and β'' were recalculated based on the free energies of formation of Al_2O_3 and Na_2O listed in Table II. (namely Equations 1 and 13). In other words, referring to Fig. 1, the M_2O–N_2O line (corresponding to the $Al_{2/3}O$–Na_2O line in this paper) is constructed and all the free energy data, whenever possible, are referred to that line. Using these values the free energy of formation of β-alumina from the elements, assuming the 1 : 11 composition is

$$\Delta G^{\circ}_{\mathrm{form}}\ (\mathrm{Na_{1/17}Al_{11/17}O},\ \text{from elements})$$
$$= -565\,100 + 109.6\ T\ (\text{J/mole of O}) \quad (14)$$

If the composition is assumed to be 1 : 9 then

$$\Delta G^{\circ}_{\mathrm{form}}\ (\mathrm{Na_{1/14}Al_{9/14}O},\ \text{from elements})$$
$$= -564\,000 + 109.6\ T\ (\text{J/mole of O}) \quad (15)$$

Similarly for β''-alumina:

$$\Delta G^{\circ}_{\mathrm{form}}\ (\mathrm{Na_{1/8}Al_{5/8}O},\ \text{from elements})$$
$$= -567\,860 + 114\ T\ (\text{J/mole of O}) \quad (16)$$

Equations 14 to 16 are the ones plotted in Fig. 3.

3. Discussion

The normalized free energy results (corrected values, from elements) listed in Table I are plotted as a function of temperature and composition in Fig. 3 from which the following conclusions can be drawn. (i) β''-alumina is a stable phase at lower temperatures but becomes unstable as the temperature increases. (ii) At lower temperatures neither β nor β''-alumina are thermodynamically stable with respect to sodium; the stable phase being sodium-aluminate. (iii) At higher temperatures β-alumina appears to become stable with respect to Na.

3.1. Stability of β''-alumina

There are several phase equilibria studies that have shown β''-alumina to be unstable *vis-a-vis* β-alumina at higher temperatures. At temperatures greater than

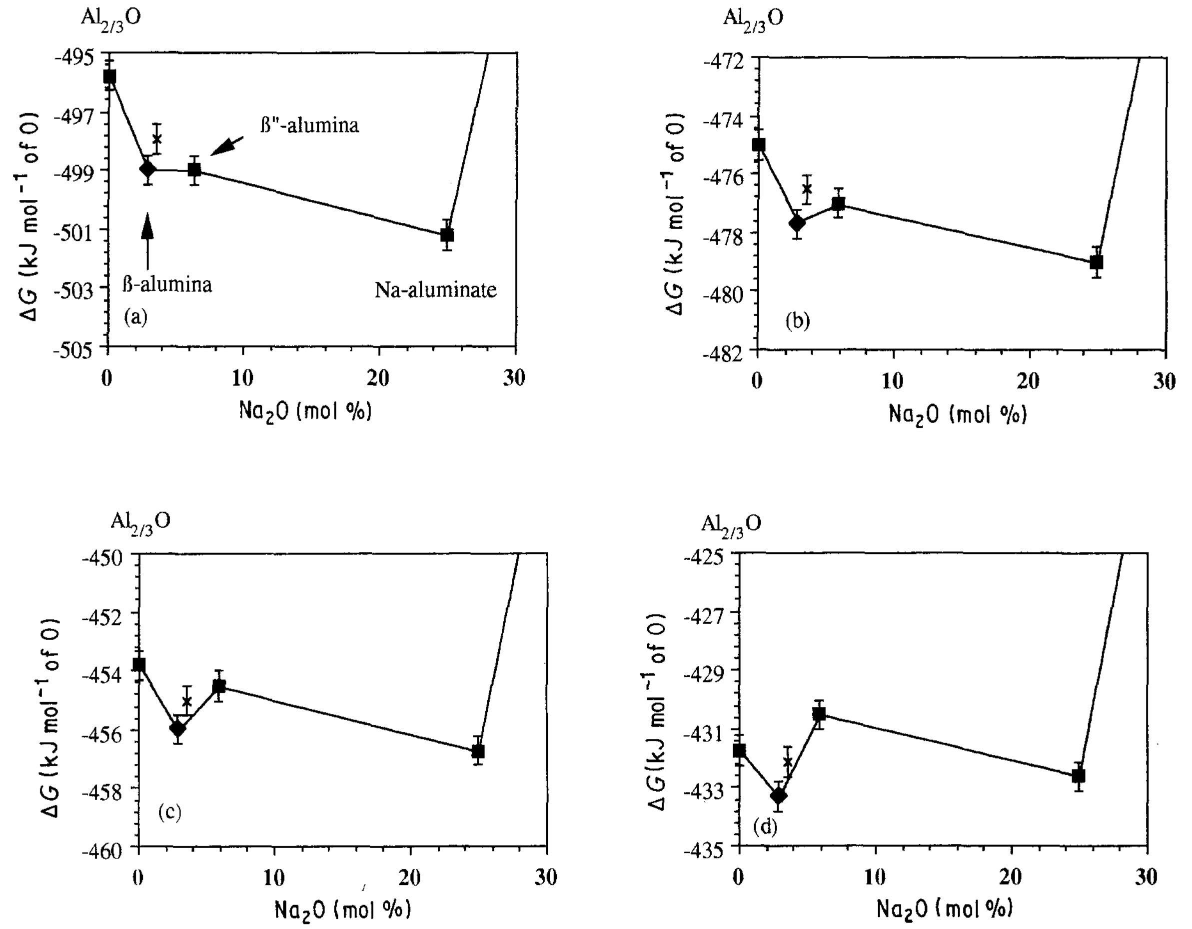

Figure 3 Compositional dependence of the free energy of formation from elements per mole of oxygen at four different temperatures. (a) 600 K, (b) 800 K, (c) 1000 K, (d) 1200 K. (Diamonds assume β-alumina composition to be 1 : 11, crosses the 1 : 9 composition.)

1500° C, β''-alumina will convert to β-alumina and sodium aluminate [5]. Hodge [22] has shown that annealing samples containing β- and β''-alumina, in the temperature range 1400 to 1530° C, resulted in the growth of β at the expense of β'' providing convincing evidence that β''-alumina is thermodynamically unstable at those temperatures. LeCars *et al.* [23] reported the complete disappearance of the β''-phase from β- and β''-alumina mixtures when the latter were heated to temperatures greater than 1550° C. The results shown in Fig. 3 are in complete agreement with the phase equilibria studies since they unequivocally show that the trend is for β''-alumina to become unstable at higher temperatures. According to Fig. 3 at temperatures greater than 1000 K, β'' should, kinetics permitting, dissociate into β-alumina and sodium-aluminate.

The question of whether β''-alumina is a thermodynamically stable phase at lower temperatures, however, has to date remained unanswered, partially because phase equilibria reaction kinetics at temperatures lower than 1400° C are too sluggish to follow [22, 23].

Before addressing the question of the thermodynamic stability of β''-alumina it is important to note that conclusive experimental evidence exists indicating that the free energy values for β''-alumina reported in [1] and plotted in Fig. 3 are too high. For instance, LeCars *et al.* [23] reported that mixtures of sodium-aluminate and α-alumina (in sealed platinum envelopes to prevent Na_2O evaporation) reacted in the temperature range 1200 to 1500° C to form mixtures of β- and β''-alumina. The same authors also reported that prolonged heating of sodium-aluminate powders in air resulted in the formation of β''-alumina as a result of Na_2O evaporation at 1223 and 1323 K. According to Fig. 3 these reactions would be impossible at temperatures higher than 1000 K since that would result in an *increase* in the free energy of the system. For these reactions to be feasible the free energy of β''-alumina would have to be lower than the tie-line joining alumina to sodium-aluminate. It is thus concluded that the free energy of formation of β''-alumina has to be more negative than reported in [1].

This conclusion has important implications. Firstly, lowering the free energy of formation of β''-alumina would most probably render it thermodynamically stable at lower temperatures. This is especially true if the β-alumina composition is assumed to be 1 : 9 (see Fig. 3a). It is interesting to note that if the composition of β-alumina is assumed to be 1 : 9 the lowest possible value for the free energy of formation of β''-alumina at 600 K would be 501 kJ/mole of O. (The free energy of formation of β''-alumina has to be more positive than the extension of the line joining α and β alumina.) Similarly the results of LeCars *et al.* [23] also have implications for the maximum Na_2O content of β-alumina. In Fig. 3d the tie-line joining α-alumina with sodium-aluminate is slightly above the point for β-alumina assuming the 1 : 9 composition. Higher soda contents would shift that point further to the right hand corner and across the line, which would be incompatible with the results of LeCars *et al.*

3.2. Stability in molten sodium

The stability of β- and β''-alumina in contact with molten sodium is a vital importance because of their use as solid electrolytes in sodium–sulphur batteries, where the electrolyte is exposed to molten sodium at temperatures between 300 to 350° C. The results shown in Fig. 3 clearly indicate that in the temperature range 600 to 1000 K, neither β- nor β''-alumina are stable in contact with molten sodium; the stable phase being sodium-aluminate. This conclusion is bolstered by the fact that the more recent data regarding the free energy of formation of sodium-aluminate would render it even more negative than shown in Fig. 3. Interestingly enough, the trend is for β-alumina to become the more stable phase at higher temperatures. This is especially true at temperatures greater than 1400 K (not shown).

Hence, the apparent stability of β-alumina in molten sodium environments has to be attributed to the sluggishness of the reaction kinetics at lower temperatures. Furthermore, doping with more stable oxides such as CaO, Y_2O_3 etc. to form solid solutions with β-alumina would further lower its free energy and further diminish the driving force for reaction with liquid sodium.

A manifestation of the chemical instabilities of β and β''-aluminas when in contact with molten sodium is their propensity for blackening [24, 25]. The blackening has been attributed to a reduction process in which oxygen diffuses from the electrolyte into the sodium electrode [24]. Such a mechanism is a thermodynamic impossibility for the following reasons.

Assuming that sodium would react with β-alumina to form β''alumina and aluminium according to

$$0.0662\ \mathrm{Na} + \mathrm{Na}_{1/17}\mathrm{Al}_{11/17}\mathrm{O} \Leftrightarrow \mathrm{Na}_{1/8}\mathrm{Al}_{5/8}\mathrm{O} + 0.022\ \mathrm{Al(s)} \qquad (17)$$

further assuming, for the sake of illustration, that ΔG° of β''-alumina is 1 kJ/mole of O more negative than β-alumina, (1 : 11 composition) then at 600 K, the equilibrium sodium activity is calculated to be $\ln a_{\mathrm{Na}} = -3 \pm 1.2$ ($a_{\mathrm{Na}} = 0.05$). (In all subsequent calculations the temperature is taken to be 600 K.) A similar reaction to the one shown above has been shown to occur when alumina is exposed to lithium of varying activities; the products in that case were found to be lithium–aluminate and aluminium [3].

Implicit in writing reaction 17 is that the compatibility triangles in the Na–Al–O system are the ones shown in Fig. 4. Also implicit in writing reaction 17 is that the oxygen partial pressure is determined by the Al–$\mathrm{Al_2O_3}$ equilibrium or

$$0.022\ \mathrm{Al} + 0.0165\ \mathrm{O}_2 \Leftrightarrow 0.033\ \mathrm{Al}_{2/3}\mathrm{O} \qquad (18)$$

which at 600 K is calculated to be $P_{\mathrm{O}_2} = 4.7 \times 10^{-87}$.

The Na_2O activity at the interface between β- and β''-alumina can be calculated from the equilibrium reaction

$$2\ \mathrm{Na} + \tfrac{1}{2}\ \mathrm{O}_2 \Leftrightarrow \mathrm{Na_2O} \qquad (19)$$

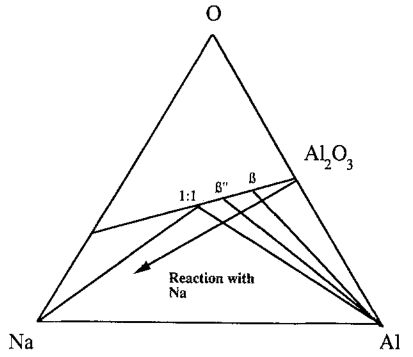

Figure 4 Ternary stability diagram and compatibility triangles in the Al–O–Na system at 600 K.

for which the corresponding mass action expression is

$$\frac{a_{\mathrm{Na_2O}}}{a_{\mathrm{Na}}^2 P_{\mathrm{O}_2}^{1/2}} = K \qquad (20)$$

since both P_{O2} and a_{Na} are known. At 600 K that activity is 4.3×10^{-17}. The same activity can be determined from the following equilibrium reaction

$$0.0331\ \mathrm{Na_2O} + \mathrm{Na}_{1/17}\mathrm{Al}_{11/17}\mathrm{O} \Leftrightarrow \mathrm{Na}_{1/8}\mathrm{Al}_{5/8}\mathrm{O} + 0.033\ \mathrm{Al}_{2/3}\mathrm{O}$$

The oxygen partial pressure in an oxygen saturated sodium electrode, (where both a_{Na} and $a_{\mathrm{Na_2O}} = 1$) can also be calculated from Equation 20 as well and yields 2.65×10^{-59}. (Unless extreme care is taken in protecting the sodium electrode from oxygen, the formation of Na_2O is unavoidable given the extremely low P_{O_2} for reaction 19.)

A summary of the interfacial conditions, assuming equilibrium at 600 K are shown in Fig. 5. If β-alumina is exposed to an oxygen-saturated Na electrode, reaction 17 would proceed to the right, i.e. the first layer to form would be β''-alumina, followed by sodium-aluminate. The sodium activity at the β–β'' interface would be fixed at 0.05 and that of oxygen at 4.7×10^{-87}. Meanwhile the oxygen activity in the oxygen saturated sodium electrode is 2.65×10^{-59}. Clearly under those circumstances diffusion of oxygen out of the electrolyte is impossible and hence cannot be responsible for the colouration.

An alternate mechanism for the colouration which is thermodynamically possible, has been proposed elsewhere [3]. The blackening is probably due to Na

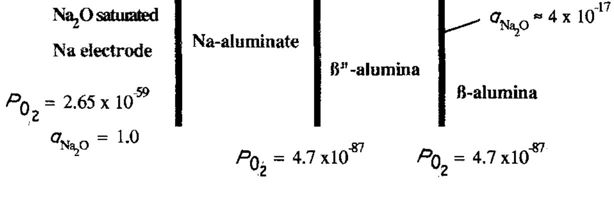

Figure 5 Summary of equilibrium conditions at interfaces when an oxygen saturated sodium electrode reacts with β-alumina to form higher soda containing phases at 600 K. Composition of β-alumina is assumed to be 1 : 11 and ΔG of formation of β''-alumina is assumed to be 1 kJ/mole of O more negative than β-alumina.

atoms diffusing interstitially into the electrolyte according to the defect reaction

$$2\ \mathrm{Na}\ (\text{electrode}) \Rightarrow 2\ \mathrm{Na}_i' + 2e^{-1} \qquad (24)$$

followed by the trapping of the electrons by oxygen vacancies to form the colour centres

$$V_O'' + 2e^{-1} \Rightarrow V_O^x$$

This scheme is thermodynamically possible, and the results are consistent with data presented by Staikov *et al.* [25] that indicates that the colouration is enhanced in the presence of an electric field in such a way that the charge on the rate limiting step has to be negative [3].

4. Conclusions

The thermodynamic data available for the Na–Al–O system were critically reviewed and the following conclusions were reached.

(1) In the temperature range 600 to 1200 K, the free energy of formation of β-alumina (from oxides) is given by

$$\Delta G^\circ_{\text{form}} = -8772 + 1.53\,T$$
$$(\text{J/mole of O}) \quad (600 < T < 1200\,\text{k})$$

(2) In the temperature range 600 to 1000 K, sodium-aluminate is the most stable phase while β and β″ are thermodynamically unstable with respect to sodium.

(3) β″-alumina is a stable phase at lower temperatures but becomes thermodynamically unstable and should, kinetics permitting dissociate into β-alumina and sodium-aluminate at higher temperatures.

(4) Convincing experimental evidence exists that suggests that the only data available for the free energy of formation of β″-alumina are too high and should be more negative.

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