ELECTROMOTIVE FORCE MEASUREMENTS ON CELLS INVOLVING \( \beta \)-ALUMINA SOLID ELECTROLYTE

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Open-circuit emf measurements have been made to demonstrate that a two-phase, polycrystalline mixture of β-alumina and α-alumina could be used as a solid electrolyte in galvanic cells with reversible electrodes fixing oxygen or aluminum chemical potentials. These measurements indicate that such a two-phase solid electrolyte can be used to monitor oxygen chemical potentials as low as that corresponding to Al, Al₂O₃ coexistence (10⁻⁴² N/m² ≈ 10⁻⁴⁷ atm at 1000 K). The activity of Na₂O in β-alumina in coexistence with α-alumina was also determined by emf measurements.
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\( \beta \)-ALUMINA SOLID ELECTROLYTE

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SUMMARY

Open-circuit electromotive force (emf) measurements have been made to demonstrate that a two-phase, polycrystalline mixture of \( \beta \)-alumina and \( \alpha \)-alumina could be used as a solid electrolyte in galvanic cells with reversible electrodes fixing oxygen or aluminum chemical potentials. These measurements indicate that such a two-phase solid electrolyte may be used to monitor oxygen chemical potentials as low as that corresponding to Al, \( \text{Al}_2\text{O}_3 \) coexistence (\( 10^{-42} \text{ N/m}^2 \approx 10^{-47} \) atm at 1000 K). The activity of \( \text{Na}_2\text{O} \) in \( \beta \)-alumina in coexistence with \( \alpha \)-alumina was also determined by emf measurements.

INTRODUCTION

Normally available polycrystalline \( \beta \)-alumina (nominal composition \( \text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3 \)) has been shown (refs. 1 to 4) to be really a two-phase mixture of \( \beta \)-alumina (approximate composition \( \text{Na}_2\text{O} \cdot 9\text{Al}_2\text{O}_3 \)) and \( \alpha \)-alumina (\( \text{Al}_2\text{O}_3 \) with negligible or no doped sodium oxide). The three-component, two-phase system has three degrees of freedom (\( F = C - P + 2 \)); and at a particular temperature and pressure (which is nominally fixed at 1 atm), this is reduced to only one. Thus the thermodynamic state of the system at a particular temperature and pressure is completely defined if the chemical potential of any one of the components, namely \( \text{Na}, \text{O}, \) or \( \text{Al} \), is fixed.

These considerations do not include electronic defects. However, if electronic defects are also considered, the local electroneutrality condition (together with the various chemical equilibria between electrons, ions, and neutral species) must also be taken into account, in effect providing an additional constraint. Moreover, \( \beta \)-alumina is known to be a good \( \text{Na}^+ \) ion conductor with negligible or no electronic conduction.

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(refs. 5 and 6), and α-alumina is an excellent insulator. Therefore, the measured open-circuit electromotive forces (emf's), in an electrochemical cell with β-alumina solid electrolyte, do not depart significantly from the thermodynamic emf's (ref. 6). These results were also confirmed by recent experiments conducted by W. L. Fielder of Lewis.

In all previous investigations (refs. 6, 7) involving open-circuit emf measurements with β-alumina solid electrolyte, the Na chemical potential has been controlled at both electrodes. The purpose of the present investigation is to determine if meaningful open-circuit emf's can be measured with electrodes when O or Al is the fixed chemical potential. (Illustrative electrode reactions are given in the appendix.) If the phase rule applies as just described, fixing the O or Al chemical potential is equivalent to fixing the Na chemical potential.

EXPERIMENTAL TECHNIQUE

The β-alumina solid electrolyte disks were prepared in this laboratory from β-alumina powder (<325 mesh) supplied by Aluminum Corporation of America. The powder was pressed into 19.05×10^{-3}-meter (3/4-in.) diameter, 3.175×10^{-3}-meter (1/8-in.) thick disks at 379.225×10^6
dN/m^2 (55 000 psi) and sintered with β-alumina powder in dry air at 1690°C for 1 hour. The resulting material had 60 to 65 percent theoretical density and was supplied by W. L. Fielder of the Lewis Research Center.

The cell for measuring emf consisted of solid reversible electrodes and a β-alumina solid electrolyte disk. The electrodes were held in contact with the β-alumina disk by spring pressure applied through α-alumina tubes, which constituted the cell assembly. The design was similar to that described by Skelton and Patterson (ref. 8). Platinum lead wires connected to the electrodes and a platinum/platinum - 13-percent rhodium thermocouple were insulated from each other by α-alumina insulating tubes. The tip of the thermocouple was positioned close to the cell. The cell assembly, enclosed in a closed-end α-alumina furnace tube, formed a gas-tight system. Insulated feed-throughs were used to provide electrical connections external to the system. The heating system consisted of a wire-wound (Kanthal) tube furnace with a controller to maintain the cell temperature to within ±1 K. The α-alumina furnace tube was shielded by a grounded stainless-steel tube to minimize electrical noise. All electrical connections external to the furnace were made with shielded cables, with the shields appropriately grounded.

The cell emf's were monitored with an electrometer (input impedance, 10^{14} ohms) or a digital voltmeter (input impedance, 10^9 ohms). The temperature was monitored with a potentiometer in conjunction with a null detector. An electronic cold junction compensator was used to provide compensation for the cold junction temperature of the thermocouple.
At the beginning of each run, the system was evacuated to 1.33 N/m$^2$ (10^{-2} \text{ torr}), flushed with helium, and evacuated again. This procedure was repeated several times. The helium was purified by passing it through copper turnings held at 673 K (400° C) and a liquid nitrogen cold trap before it entered the system. Subsequent to the flushing and evacuation procedure the system was filled with helium, and a slow and steady flow of helium was maintained through the system. The furnace was then brought to the measuring temperatures. The emf's were recorded after a wait of at least 1/2 hour at each temperature. The attainment of equilibration was indicated by reproducibility of the recorded emf's on cycling the cell temperature within the range of measurements.

RESULTS AND DISCUSSION

Electrodes Fixing Oxygen Chemical Potential

Stable and reproducible open-circuit emf's were obtained from the following cells with electrodes fixing oxygen partial pressures:

- $\text{Fe, FeO/\beta\text{-alumina/Ni, NiO}}$ \hspace{1cm} I
- $\text{Ni, NiO/\beta\text{-alumina/Cu, Cu}_2\text{O}}$ \hspace{1cm} II

Figure 1 illustrates the data obtained from 962 to 1263 K (689° to 990° C) for cell I. Kiukkola and Wagner's (ref. 9) data for the cell Fe, FeO/CaO, ZrO$_2$/Ni, NiO are indicated in figure 1 as the solid line. The data for cell II are shown in figure 2 along with Lasker and Rapp's (ref. 10) estimated thermodynamic emf for the cell. It is apparent that the open-circuit emf's observed with \beta-alumina are in good agreement with the previously measured (with oxygen-ion-conducting solid electrolyte) and calculated thermodynamic emf's. It should be noted that the rate of equilibration at lower temperatures was progressively sluggish. For example, at 923 K (650° C) cell II attained equilibrium only after 12 hours. In a few of the runs with Cu, Cu$_2$O electrodes, a considerable amount of Cu penetration was visually observed in the \beta-alumina disks.

Another cell - Ti, TiO/\beta-alumina/Nb, NbO - was also investigated. The starting electrode mixtures were Ti, TiO$_2$ and Nb, Nb$_2$O$_5$ with excess metals, so that at high temperatures the electrodes were expected to equilibrate to the desired Ti, TiO and Nb, NbO coexistence. However, the observed emf's were much lower than the thermodynamic emf's and were not reproducible. The reason may be the failure of the elec-
trodes to equilibrate even at 1273 K (1000° C) - the highest temperature achievable with the furnace system.

Determination of Na₂O Activity in β-Alumina

Consider the reaction

Na₂O + 9Al₂O₃ = Na₂O·9Al₂O₃

Because both β-alumina and α-alumina coexist in the standard state in the solid electrolyte, the standard free-energy change for this reaction is given by RT ln aNa₂O, where aNa₂O is the activity of Na₂O in β-alumina in coexistence with α-alumina. This may be determined with a cell of the type M, MX₂, NaX/β-alumina/M', M'O provided M, MX₂, and NaX coexist in the standard state. The open-circuit emf for this cell is given by

\[ E = \frac{RT}{F} \ln \frac{a_{Na}^{(R)}}{a_{Na}^{(L)}} \]  

(1)

The Na activities in the left and right sides of the cell are given by

\[ RT \ln a_{Na}^{(L)} = \Delta G_{NaX}^{0} - \frac{1}{2} \Delta G_{MX_{2}}^{0} \]  

(2)

\[ RT \ln a_{Na}^{(R)} = \frac{1}{2} RT \ln a_{Na_{2}O} + \frac{1}{2} \Delta G_{Na_{2}O}^{0} - \frac{1}{2} \Delta G_{M'O}^{0} \]  

(3)

Combining equations (1) to (3) yields

\[ RT \ln a_{Na_{2}O} = -2EF + 2 \Delta G_{NaX}^{0} - \Delta G_{MX_{2}}^{0} + \Delta G_{M'O}^{0} - \Delta G_{Na_{2}O}^{0} \]  

(4)

\[ \text{Ni, NiF}_2, \text{NaF}/\beta-\text{alumina/Cu, Cu}_2\text{O} \]

was the one investigated in the present study. That Ni, NiF₂, and NaF coexist in the standard state at least to 1033 K (760° C) was confirmed by measuring the open-circuit emf of the cell

\[ \text{Co, CoF}_2, \text{NaF}/\beta-\text{alumina/Ni, NiF}_2, \text{NaF} \]
The observed emf's of cell IV between 763 and 1037 K (490° and 764° C) were in good agreement (fig. 3) with those measured by Skelton and Patterson (ref. 8) with the cell Co, CoF$_2$/CaF$_2$/Ni, NiF$_2$. The solid line in figure 3 represents the least-square best fit of Skelton and Patterson's (ref. 8) data. It should be noted that NaF and NiF$_2$ form an eutectic at around 1063 K (790° C) (ref. 11) and this limits the use of the Ni, NiF$_2$, NaF electrode to below this temperature.

Reproducible emf's were obtained for the cell Ni, NiF$_2$, NaF/β-alumina/Cu, Cu$_2$O between 849 and 998 K (576° and 725° C). The emf data for cell III are given in table I and also illustrated in figure 4.

The least-square best fit of the data between 850 and 1000 K is given by

\[
E(\text{III}) \text{mV} = (646.5 - 0.190 T) + 1
\]

where \( T \) is in K.

Above 998 K (725° C) the emf's were low and irreproducible, presumably because of excessive evaporation of NaF affecting the Cu, Cu$_2$O electrode.

The standard free energies of formation of NiF$_2$ and NaF can be obtained from publications of Skelton and Patterson (ref. 8) and Steinmetz and Roth (ref. 12). The \( \Delta G^0_{\text{Na}_2\text{O}} \) and \( \Delta G^0_{\text{Cu}_2\text{O}} \) values can be obtained from JANAF tables (ref. 13). Using these values, we can calculate the activity of Na$_2$O in β-alumina from equations (4) and (5). For example, at 1000 K, \( RT \ln a_{\text{Na}_2\text{O}} = -322.17 \times 10^3 \text{ J/mole} \) (-77.0 kcal/mole); at 900 K, \( RT \ln a_{\text{Na}_2\text{O}} = -325.51 \times 10^3 \text{ J/mole} \) (-77.8 kcal/mole); at 800 K, \( RT \ln a_{\text{Na}_2\text{O}} = -329.28 \times 10^3 \text{ J/mole} \) (-78.7 kcal/mole). The corresponding \( a_{\text{Na}_2\text{O}} \) values at 1000, 900, and 800 K are $10^{-16.83}$, $10^{-18.89}$, and $10^{-21.50}$, respectively.

Electrodes Fixing Aluminum Chemical Potential

Metallic aluminum was used as the anode fixing the aluminum chemical potential in the following cells

\[
\text{Al/β-alumina/AlF}_3, \text{NiF}_2, \text{Ni} \quad \text{V}
\]

and

\[
\text{Al/β-alumina/NaF, NiF}_2, \text{Ni} \quad \text{VI}
\]

Emf measurements with compacted aluminum powder electrodes were not successful.
However, reasonably stable emf's were obtained with Al electrodes in the form of a foil (1.6×10⁻³ m (1/16 in.) thick). These cells had relatively short lives. It was further observed that the cell life could be prolonged by operating it under vacuum instead of in flowing helium. It is believed that rapid oxidation of aluminum at elevated temperatures is the cause of poor cell lives. However, under vacuum the cells lasted for 8 to 12 hours, during which the open-circuit emf data could be recorded.

The open-circuit emf of cell V is given by \( E_V = -\frac{1}{3F}RT \ln a_{\text{Al}} \), where \( a_{\text{Al}} \) is the activity of aluminum at the cathode. Therefore, the emf \( E_V \) is also given by

\[
E_V = -\frac{1}{3F} \left( \Delta G_{\text{AlF}_3}^0 - \frac{3}{2} \Delta G_{\text{NiF}_2}^0 \right)
\]

(Skelton and Patterson (ref. 8) have measured the open-circuit emf of the cell \( \text{Al, AlF}_3/\text{CaF}_2/\text{Ni, NiF}_2 \), which is also given by equation (6). The data for cell V are plotted in figure 5, which also shows the least-square best fit line of Skelton and Patterson's (ref. 8) data. The agreement seems to be satisfactory at temperatures above 817 K (540° C). At temperatures below 817 K (540° C) the observed open-circuit emf's of cell V fall significantly below those observed by Skelton and Patterson (ref. 8). The reason for this may be sluggish electrode equilibration and/or departure from the proposed equilibrium of \( \alpha \)-alumina and \( \beta \)-alumina in the electrolyte.

Open-circuit emf data for cell VI are given in table II and plotted in figure 6. The least-square best fit of the data from 836 to 929 K (563° to 656° C) is given by

\[
E(\text{VI})_{\text{mV}} = (1414 - 0.023 T) + 3
\]

The departure of the observed emf at 817 K (540° C) from the linear relation is similar to that observed with cell V and can be accounted for in the same way.

Equations (5) and (7) can be combined to obtain the open-circuit emf between \( \text{Al, Al}_2\text{O}_3 \), and \( \text{Cu, Cu}_2\text{O} \) electrodes. Attempts to directly measure the open-circuit emf of such a cell below the melting point of aluminum (933 K (660° C)) were not successful. The reason for this is presumably the inability of the \( \text{Cu, Cu}_2\text{O} \) electrode to achieve equilibration in a relatively short time (8 to 12 hr) at these temperatures. Though not pursued in the present investigation, such measurements may be feasible at higher temperatures with different cell geometries. For example, the \( \beta \)-alumina solid electrolyte may be in the form of a flat-bottomed cup with molten aluminum inside and the \( \text{Cu, Cu}_2\text{O} \) electrode contacting the outer flat surface of the electrolyte.

The free energy of formation of \( \text{Al}_2\text{O}_3 \) was calculated from equations (5) and (7) and the \( \Delta G_{\text{Cu}_2\text{O}}^0 \) (ref. 13) values. This is given by equation (8) for the limited temperature range of 833 to 933 K (560° to 660° C).
\[
\Delta G_{Al_2O_3}^0 = -(1693.7 \pm 2.5) \times 10^3 + 339 \text{ T joules/mole}
\]

\[
= -(404.8 \pm 0.6) + 0.081 \text{ T kcal/mole}
\]

Figure 7 compares the \( \Delta G_{Al_2O_3}^0 \) values, according to equation (8) with those given in JANAF tables (ref. 13). The agreement seems to be quite satisfactory in view of the scatter in the data of cell VI and the different methods of estimation.

Reaction Between Sodium and Alumina

Consider the reaction

\[6Na + Al_2O_3 = 3Na_2O + 2Al\]  \hspace{1cm} (9)

The standard free-energy change for this reaction is given by

\[
\left( 3 \Delta G_{Na_2O}^0 - \Delta G_{Al_2O_3}^0 \right)
\]

It has been discussed in the section Determination of Na\(_2\)O Activity in \( \beta \)-Alumina that the standard free-energy change of the reaction

\[Na_2O + 9Al_2O_3 = Na_2O \cdot 9Al_2O_3\]  \hspace{1cm} (10)

is given by \( RT \ln a_{Na_2O} \) where \( a_{Na_2O} \) is the activity of Na\(_2\)O in \( \beta \)-alumina in coexistence with \( \alpha \)-alumina.

When equations (9) and (10) are combined, the free-energy change for the reaction

\[6Na + 28Al_2O_3 = 3(Na_2O \cdot 9Al_2O_3) + 2Al\]  \hspace{1cm} (11)

is given by

\[
\Delta G^0 = 3 \Delta G_{Na_2O}^0 - \Delta G_{Al_2O_3}^0 + 3RT \ln a_{Na_2O}
\]

When we use the data from JANAF tables (ref. 13) for \( \Delta G_{Na_2O}^0 \) and \( \Delta G_{Al_2O_3}^0 \) and
the RT in a \( \text{Na}_2\text{O} \) value of \(-322.17 \times 10^3 \) J/mole (-77.0 kcal/mole) (see p. 5), the estimated \( \Delta G^0 \) for reaction (11) at 1000 K is \(-446.85 \times 10^3 \) J (-106.8 kcal). The value of \( \Delta G^0 \) at 573 K is \(-540.99 \times 10^3 \) J (-129.3 kcal). The negative value of the \( \Delta G^0 \) indicates that polycrystalline two-phase \( \beta \)-alumina (i.e., mixture of \( \alpha \)-alumina and \( \beta \)-alumina) in equilibrium with Na is able to liberate free aluminum at the interface. Miles and Wynn Jones (ref. 14) observed that \( \beta \)-alumina in contact with Na at 573 K did not initially show any electronic conductivity. However, after some time there was significant electronic conduction. This electronic conduction was metallic in nature. They concluded that this was the result of Na metal penetration in the \( \beta \)-alumina. In view of the negative \( \Delta G^0 \) value of reaction (eq. 11), it may be possible that there was formation of metallic aluminum in the \( \beta \)-alumina membrane (instead of Na penetration), giving rise to the electronic conduction.

Possible Use of Two-Phase Polycrystalline \( \beta \)-Alumina in Solid Electrolyte Oxygen Pressure Gages

The fact that \( \beta \)-alumina behaves as a solid electrolyte at the extremely low oxygen partial pressure of Al, \( \text{Al}_2\text{O}_3 \) coexistence (\( P_{\text{O}_2} \approx 10^{-42} \text{ N/m}^2 \approx 10^{-47} \text{ atm at 1000 K} \)) suggests that it may be used to monitor very low oxygen chemical potentials. The commonly known oxygen-ion-conducting solid electrolyte \( P_{\text{O}_2} \) gages are limited by the onset of electronic conduction to oxygen partial pressures of around \( 10^{-32} \text{ N/m}^2 \) (10^{-37} \text{ atm}) at 1000 K (ref. 15). Although the upper \( P_{\text{O}_2} \) limit in this investigation corresponded to \( \text{Cu, Cu}_2\text{O} \) equilibrium, it is probable that \( \beta \)-alumina may be used as a solid electrolyte at higher oxygen partial pressures without significant hole conduction. The low-temperature limit for sufficiently fast equilibration in \( \beta \)-alumina for use as an oxygen monitor seems to be around 823 K (550° C). This temperature is lower than the operating temperatures of known oxygen-ion-conducting solid electrolytes, in which the limiting factor is poor ionic conductivity. Beta-alumina being a much better conductor, by some three orders of magnitude, suggests the possibility of reducing the operating temperature below 823 K (550° C) with better material and cell design. Thus \( P_{\text{O}_2} \) gages constructed with \( \beta \)-alumina solid electrolyte may offer the advantages of lower operating
temperature and wider response (especially at extremely low $P_{O_2}$) and may find applications in semiconductor and metallurgical industries.

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503-25.
APPENDIX - ILLUSTRATIVE ELECTRODE REACTORS

In order to derive the thermodynamic relations for the various couples studied in this work, we combined appropriate anodes and cathodes and following the relevant equations:

(1) M, MO coexistence electrode as anode

\[ \text{Na}_2\text{O} \cdot 9\text{Al}_2\text{O}_3 = \text{Na}_2\text{O} + 9\text{Al}_2\text{O}_3 \]

\[ \text{Na}_2\text{O} = 2\text{Na} + \frac{1}{2} \text{O}_2 \]

\[ \text{M} + \frac{1}{2} \text{O}_2 = \text{MO} \]

\[ \text{Na} = \text{Na}^+ + e \]

(2) M', M'O coexistence electrode as cathode

\[ \text{Na}^+ + e = \text{Na} \]

\[ \text{M}'\text{O} = \text{M}' + \frac{1}{2} \text{O}_2 \]

\[ 2\text{Na} + \frac{1}{2} \text{O}_2 = \text{Na}_2\text{O} \]

\[ \text{Na}_2\text{O} + 9\text{Al}_2\text{O}_3 = \text{Na}_2\text{O} \cdot 9\text{Al}_2\text{O}_3 \]

(3) Al electrode as anode

\[ \text{Na}_2\text{O} \cdot 9\text{Al}_2\text{O}_3 = \text{Na}_2\text{O} + 9\text{Al}_2\text{O}_3 \]

\[ \text{Na}_2\text{O} = 2\text{Na} + \frac{1}{2} \text{O}_2 \]

\[ 2\text{Al} + \frac{3}{2} \text{O}_2 = \text{Al}_2\text{O}_3 \]

\[ \text{Na} = \text{Na}^+ + e \]
(4) $\text{AlF}_3, \text{NiF}_2, \text{Ni}$ coexistence electrode as cathode

\[
\text{NiF}_2 = \text{Ni} + \text{F}_2
\]

\[
2\text{Al} + \frac{3}{2} \text{F}_2 = \text{AlF}_3
\]

\[
\text{Al}_2\text{O}_3 = 2\text{Al} + \frac{3}{2} \text{O}_2
\]

\[
\text{Na}^+ + e = \text{Na}
\]

\[
2\text{Na} + \frac{1}{2} \text{O}_2 = \text{Na}_2\text{O}
\]

\[
\text{Na}_2\text{O} + 9\text{Al}_2\text{O}_3 = \text{Na}_2\text{O} \cdot 9\text{Al}_2\text{O}_3
\]

(5) $\text{NaF}, \text{MF}_2, M$ as cathode

\[
\text{Na}^+ + e = \text{Na}
\]

\[
\text{MF}_2 = \text{M} + \text{F}_2
\]

\[
\text{Na} + \frac{1}{2} \text{F}_2 = \text{NaF}
\]

(6) $\text{NaF}, \text{M'}\text{F}_2, \text{M'}$ as anode

\[
\text{NaF} = \text{Na} + \frac{1}{2} \text{F}_2
\]

\[
\text{M'} + \text{F}_2 = \text{M'}\text{F}_2
\]

\[
\text{Na} = \text{Na}^+ + e
\]
REFERENCES


TABLE I. - ELECTROMOTIVE FORCE OF CELL III
[Ni, NiF₂, NaF/β-alumina/Cu, Cu₂O₃]

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TABLE II. - ELECTROMOTIVE FORCE OF CELL VI
[Al/β-alumina/NaF, NiF₂, Ni]

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Figure 1. - Open-circuit electromotive force against temperature for cell I: Fe, FeO/β-alumina/Ni, NiO.

Figure 2. - Open-circuit electromotive force against temperature for cell II: Ni, NiO/β-alumina/Cu, CuO₂.
Figure 3 - Open-circuit electromotive force against temperature for cell IV: Co, CoF₂, NaF/β-alumina/NaF, NiF₂, Ni.

Figure 4 - Open-circuit electromotive force against temperature for cell III: Ni, NiF₂, NaF/β-alumina/Cu, CuO.

Figure 5 - Open-circuit electromotive force against temperature for cell V: Al/β-alumina/AlF₃, NiF₂, Ni.

Figure 6 - Open-circuit electromotive force against temperature for cell VI: Al/β-alumina/NaF, NiF₂, Ni.
Figure 7. - Free energy of formation of Al$_2$O$_3$ against temperature, comparing values estimated in present investigation with those tabulated in JANAF tables (ref. 13).
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—National Aeronautics and Space Act of 1958

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