THERMODYNAMIC PROPERTIES OF COMPOUNDS OF Na_2O WITH THE
OXIDES OF CHROMIUM, NICKEL AND IRON

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MASTER

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Thermodynamic properties of compounds of Na_2O with the
oxides of chromium, nickel and iron

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I. INTRODUCTION

It has been reported (1,2) that the fast breeder reactor was selected because of its high power density, fuel resources conservation and because it may be effective in solving some of the atmosphere pollution problems. The fast reactor core is typically much smaller than a thermal reactor core with the same heat output because there is no requirement for a moderating material. Designs generally use mixed oxide fuels, such as (Pu,U) oxide, in a pin configuration. The pins will have characteristically about half the diameter of the pins for a thermal reactor. In order to remove the high heat fluxes from the very close lattice that is inherent in the fast reactor, an extremely efficient coolant is required. The choice of the coolant is defined by a number of practical considerations, and to meet these considerations liquid metals are the most suitable primary and secondary working fluids.

Liquid metals generally have excellent heat-transfer characteristics and low moderating capabilities. These are the most important properties for use in fast reactors. In addition, the liquid metals considered have little chemical activity and are particularly resistant to radiation damage. Among about 15 potential liquid-metal coolants, sodium was chosen as the most suitable because of its low pumping-power¹

¹Pumping power is defined by the ratio $\mu^{0.2}/\rho^2 C_p^{2.8}$, where μ is the viscosity in lb/ft-hr, ρ is the density in lb/ft³, and C_p is the specific heat in Btu/lb-°F.

and high temperature-range-ratio.¹ Evaluation based on these parameters results in avoiding an economic penalty in heat transport, high power cycle efficiencies and low pressure in the reactor vessel. This, in turn, makes possible reactor vessels that are low in cost which leads to lower power costs.

A large number of laboratory experiments on the effects of liquid metals on many materials are available in the literature (3-5). Although most materials suffer from attack or corrosion when subjected to liquid sodium, Fe-Cr-Ni alloys show very good behavior and remain the most suitable and satisfactory container material for temperatures up to about 600°C. However, when these alloys are exposed to oxygen contaminated sodium, the formation of various compounds has been observed (6-10). Electron microprobe, X-ray diffraction patterns and metallographic analysis were employed in these works to confirm the formation of NaCrO_2 and depletion of the Cr from stainless steel. This is the most stable compound formed in the presence of oxygen contaminated sodium. In addition, there is experimental evidence for the formation of similar double oxides of Na_2O with iron and nickel oxides. Earlier investigations (6,9,10) indicate that, in the presence of liquid sodium, the compound $(\text{Na}_2\text{O}) \cdot \text{FeO}$ is stable only above 600°C and $(\text{Na}_2\text{O})_2 \cdot \text{FeO}$ only above 800°C. Below these tempera-

¹This quantity is defined by the ratio $(T_b - T_m)/T_w$, where T_b , T_m and T_w are the boiling, melting and outlet absolute temperature of the coolant (°K) respectively.

tures, the compounds are reduced to metallic iron by sodium. Likewise, in the presence of liquid sodium, the compound $(\text{Na}_2\text{O}) \cdot \text{NiO}$ is unstable below 800°C .

The thermodynamic properties of these compounds are of particular importance in explaining the corrosion of Fe-Cr-Ni alloys by oxygen containing sodium. Previous attempts (6,11) to determine the thermodynamic properties of these compounds have led to unrealistic entropy values. The purpose of this investigation is to review this earlier work and to remeasure the emf of cells with solid electrolytes employing a modified procedure. These emf data will permit calculation of the thermodynamic properties of the double oxides and calculation of the critical concentration of oxygen in sodium below which these compounds are unstable.

II. THEORETICAL CONSIDERATIONS AND LITERATURE REVIEW

A. Corrosion of Austenitic Stainless Steel by Liquid Sodium

Austenitic stainless steels are popularly referred to as those steels containing 18 wt % of Cr and 8 wt % or more Ni. None of these elements form intermetallic compounds with pure sodium, however, dissolution of solid metal into liquid sodium may be expected (12-17). With oxygen contaminated sodium, the corrosion rate increases as the oxygen content increases, and consequently the mode of attack becomes both dissolution of solid metal into liquid metal and penetration of sodium into solid metal with the formation of NaCrO_2 . The influence of temperature and oxide content of sodium on the corrosion rates of various stainless steels has been studied by many investigators (18-21). It was found that among the sodium loop conditions, the oxygen content of the liquid sodium appears to be the most important parameter. A roughly linear relationship between metal loss rate and oxygen level has been established by Thorley and Tyzack (17). An expression correlating weight loss with oxygen concentration also has been established by Zebroski et al. (20). They found that reducing the oxygen level from 45-50 ppm to 10-15 ppm reduced the rate by a factor of about 5.

The ability of sodium to dissolve oxygen has been measured and found to follow the relationship

$$\log_{10} C_s = A - BT^{-1} \quad (1)$$

Table 1. Solubility data for oxygen in sodium equilibrated with sodium oxide in
 $\log_{10} C_s (\text{ppm O}) = A - BT^{-1} (^\circ\text{K})$

Workers	Refer- ence	Parameters		Temp. range (°K)	Method
		A	B		
Alcock and Stauroopoulos	(21)	7.076+0.004	2865+180	714-934	galvanic cell
Minushkin and Kissel	(22)	6.46 +0.11	2600	623-823	galvanic cell
Eichelberger	(23)	6.239	2447	623-823	chemical analyses
Isaacs <u>et al.</u>	(24)	6.550	2600	673-973	uranium gettering
Kassner and Smith	(25)	6.940	2801	423-823	Assessment

where C_s is the solubility of oxygen in ppm by weight, A and B are constants and T is the temperature in degrees Kelvin. Some results obtained by various investigators are summarized in Table 1. The agreement between these relationships obtained by different and independent methods is satisfactory. Reviews of data by various authors are given in references (21), (22) and (25). The preferred relation is the one given by Kassner and Smith (25).

The free energy of formation of disodium oxide reported by various workers (21,22,26-30) is summarized in Table 2. The preferred relation is based on the data taken from the JANAF Table (30). This relation reproduces the tabulated data for the temperatures 500 to 1000 K with root mean square deviation of ± 58 cal.

B. Compounds of Na_2O with Cr, Fe and Ni

The formation of $(\text{Na}_2\text{O})_x\text{MO}_y$ and MO_x has been suggested (31) for the reaction of metal M with oxygen-containing sodium. Sven and Edgar (32) and Chiotti et al. (33) have identified the hexagonal sodium chromite, $\text{Na}_2\text{O} \cdot \text{Cr}_2\text{O}_3$, as the main corrosion product of Inconel 600 alloy at temperatures from 650 to 850°C, and concluded that the free energy change for the reaction

must be negative and sufficiently more favorable than the reaction

Table 2. The free energy of formation of disodium oxide, $2\text{Na}(\ell) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{Na}_2\text{O}(\gamma)$
 $\Delta G^\circ = [-A + BT(^{\circ}\text{K})] \pm C$. A in cal/mole, B in cal/mole-K and C in cal/mole

Authors	Parameters		Estimated uncertainty C	Temp. range $^{\circ}\text{K}$	Reference
	A	B			
Alcock and Stauroopoulos	96945	30.83	?	714-934	(21)
Minushkin and Kissel	94900	28.30	?	573-823	(22)
Kelley, K. K.	100460	33.91	3300	500-1000	(26)
Richardson and Jeffes	98500	31.00	10000	500-1000	(27)
Elliot and Gleiser	100500	35.10	?	573-823	(28)
Wick & Block	100471	34.83	100	500-1000	(29)
JANAF ^a	100581	33.60	1500	~500-1000	(30)

^aThis is the preferred data. The uncertainty in $\Delta H_f^\circ(298)$ is given as ± 1.0 kcal and the uncertainty in $\Delta G_f^\circ(\text{Na}_2\text{O})$ is estimated to be within ± 1.5 kcal over the temperature range indicated. The parameters given reproduce the JANAF values with a root mean square error of ± 58 cal.

to exclude the formation of Cr_2O_3 as a reaction product. Barker and Wood (34) also observed that the only corrosion product of chromium in liquid sodium with oxygen contents ranging from 20 ppm to 6200 ppm was sodium chromite, NaCrO_2 . Charles (35) employed thermomagnetic analysis to study the reactions of mixed oxides of iron and chromium with liquid sodium at high temperature (848°K), and suggested the following possible reactions

Clough (36) reported that the standard free energy change for reaction (2) is -11.7 kcal at 298°K . Gross et al. (9) made many different types of experiments at high temperature (773°K) with chromium in contact with sodium containing different initial oxygen concentrations and found that NaCrO_2 is the only double oxide formed. They reported the free energy change for reaction (2) as

$$\Delta G_T^\circ = -8,300 - 19.6T \text{ cal}. \quad (7)$$

They conclude that sodium chromite could form below 850°C even at oxygen contents in sodium as low as 5 ppm. The enthalpy of formation of NaCrO_2 from its constituent oxides was determined from solution calorimetric data to be -24.24 ± 0.24 kcal/mole

at 298°K. This value was combined with literature data to obtain relation 7.

Horsley (37) carried out tests on iron specimens in sodium with oxygen concentrations varying from 0.16 to 10 wt % at 1073°K and identified that the brown scale formed to be the compound $(\text{Na}_2\text{O})_2 \cdot \text{FeO}$. Gross and Wilson (10) studied the reaction of mixtures of iron and Fe_2O_3 with Na_2O at 773-873°K. They reported the formation of $\text{FeO}(\text{Na}_2\text{O})_2$. They determined by solution calorimetry the enthalpy change for the reaction

at 298°K to be -25.07 kcal. The reaction

at 873°K has a free energy change, ΔG° , of -2.2 kcal and they conclude this reaction is not possible at low oxygen concentration and about 1000 ppm oxygen in liquid sodium is needed. It was also suggested (10,38) that other possible double oxides are $(\text{Na}_2\text{O}) \cdot \text{FeO}$ and NaFeO_2 .

Hans and Guenter (18) and Barker and Wood (34) also reported that the free energy change of the reaction of iron with sodium oxide dissolved in sodium according to reaction 9 at 873°K is -2.5 kcal/mole and -2.2 kcal/mole, respectively. The first value is based on work by Issacs et al. (24) and the latter value is from Gross and Wilson (10). Therefore, oxidation of iron should not occur unless the oxygen content

exceeds the value of some hundreds of ppm sodium oxide as Gross and Wilson (10) suggested. However, this content is far higher than that which occurs in practice in commercial liquid sodium circuits.

Based on Horsley's hypothesis (37), the following reaction was proposed by Mottley (39):

Similar reaction was thought to take place with the nickel. The existence of $(\text{Na}_2\text{O}) \cdot \text{NiO}$ has been suggested but is not stable in liquid sodium (10). Wu (6) concluded that the compound $(\text{Na}_2\text{O}) \cdot \text{NiO}$ cannot be stable in liquid sodium below 800°C . He also made the observation that nickel displays the least amount of attack.

C. EMF Measurements with Solid Electrolyte Cell

Electromotive force measurements on galvanic cells involving solid electrolytes have been shown to yield valuable thermodynamic data (40-42).

Consider a cell of the following type:

Wagner (43) postulated that all mass transport in the oxidation process occurred by virtue of ion migration only and predicted the open circuit emf, E , of the cell to be

$$E = \frac{1}{nF} \int_{\mu_{O_2}'}^{\mu_{O_2}''} t_{ion} d\mu_{O_2} \quad (11)$$

where n = the number of equivalents

F = Faraday's constant

μ_{O_2}'' , μ_{O_2}' = the high and low oxygen chemical potentials

which exist at opposite sides of the cell

In the case $t_{ion} = 1$ and is independent of μ_{O_2} , Equation 11 can then be integrated to give

$$E = \frac{1}{nF} (\mu_{O_2}'' - \mu_{O_2}') \quad (12)$$

If all of the active condensed phases of the electrode materials are in their standard states (i.e., unit activity), then the above equation can be rewritten as

$$E_o = -\frac{1}{nF} \Delta G_{Rxn}^{\circ} \quad \text{or} \quad \Delta G_{Rxn}^{\circ} = -nFE_o \quad (13)$$

where ΔG_{Rxn}° is the Gibbs standard free energy change for the cell reaction. It is well known (43-46) that the emf of a cell whose electrolyte has not only ionic, but also electronic conductivity is given by the expression:

$$E = [1 - (\bar{t}_e + \bar{t}_o)] E_o \quad (14)$$

where $\bar{t}_e$ is the charge transport number due to electronic conductivity induced by movement of the electrons present in the conducting zone; $\bar{t}_o$ is the electron transport number due to hole conductivity induced by movement of electrons from the almost filled energy zone; E_o is the thermodynamic value of

the electromotive force of the cell. It is evident that the percentage of the ionic conductivity of the electrolyte, $\bar{t}_{ion}$ is equal to the term $[1-(\bar{t}_e + \bar{t}_o)]$ in Equation 14. Thus, if the $\bar{t}_e + \bar{t}_o$ is sufficiently small, the value t_{ion} will be ≈ 1 and under these conditions, the electromotive force of the cell considered must be close to its thermodynamic value.

The mobility of the ions in solid electrolytes can be greatly enhanced by introducing defects in the lattice. When an oxide such as thoria, ThO_2 , dissolves a lower valent oxide such as Y_2O_3 , oxygen ion, $O^{=}$, vacancies are created in the ThO_2 lattice. Subbarao et al. (46) found that a maximum in the ionic conductivity occurs at 3.75% vacant oxygen sites, which corresponds to a dopant level of 15 mole % $YO_{1.5}$.

Zirconia doped with MgO or CaO also has been successfully employed as a suitable electrolyte for reversible emf cell measurements, but for only a few compositions and a certain range of temperature. Kuikkola and Wagner (40) reported that the solid solutions of ZrO_2 -CaO containing 10-20 mole % calcium oxide are practically purely ionic conductors at high temperature (1000°C). Pal'guev and Neuimin (47) studied the cell $Pt|Fe, FeO|electrolyte|Cu_2O, Cu|Pt$ with electrolytes composed of various oxides and their mixture, and found the solid electrolyte composed of 85 mole % ZrO_2 + 15 mole % CaO is a purely ionic conductor in the temperature range 600°C-1000°C, but the calcia-stabilized thoria (85 mole % ThO_2 +

15 mole % CaO) has a predominantly electrical conductivity.

Calcium fluoride, CaF_2 , is also an ionic solid electrolyte from below room temperature to its melting point at 1418°C . It can similarly be doped with NaF, for example, to create $\bar{\text{F}}$ vacancies. The suitability of solid CaF_2 used as a solid electrolyte at elevated temperature has been established by a number of authors (43,48,49).

Hinze (50) studied the electronic conductivity of CaF_2 and concluded that for the temperature range 823 to 1123°K the $\bar{t}_{\text{ion}}$ is ≥ 0.99 when $\log_{10} P_{\text{F}_2} \geq [10.5 - 6.3 \times 10^4/T]$, where P_{F_2} is fluorine partial pressure in atm, and T is in $^\circ\text{K}$. Schieltz (51) also gave an excellent review of solid electrolyte applications.

High temperature galvanic cells with CaF_2 solid electrolyte have been used in several investigations (42,52-54) for obtaining thermodynamic data. Some equations for the standard free energy of formation of fluorides are listed in Table 3.

D. Thermodynamic Considerations

The employment of the electrochemical method to determine the free energy change of a reaction requires the experimental realization of a cell in which the reaction occurs electrochemically. In general, emf measurements were made on galvanic cells of the type $\text{M}, \text{MO}_x / \text{oxide electrolyte} / \text{M}', \text{M}'\text{O}_y$ or $\text{M}, \text{MF}_x / \text{fluoride electrolyte} / \text{M}', \text{M}'\text{F}_y$ involving oxides MO_x and $\text{M}'\text{O}_y$ or fluorides MF_x and $\text{M}'\text{F}_y$ of metal M and M', respectively.

Table 3. Standard free energy change of formation in literature for some fluoride compounds

Compound MF _x	Temp. Range °K	$\Delta G_f^\circ(T) = (A+BT)$ cal/mole	Reference
CaF ₂	881-1123	-289000+34.04T	(52)
	1128-1193	-304000+47.60T	(52)
	673-1123	-289357+39.98T	(54)
	700-1100	-291180+38.53T	(30)
	700-1100	-288325+38.55T	(29)
NaF	673-1073	-136358+23.67T	(54)
	700-1100	-137390+24.74T	(30)
	700-1300	-135757+23.96T	(29)
NiF ₂	373-1073	-156485+33.02T	(52)
	298	-157200+37.92	(55)
	673-1073	-156531+30.02	(54)

Consider the following cell arrangement:

The reactions at the left and right electrode are respectively

The isothermal, isobaric free energy change per mole of oxygen is given by

$$\Delta G_{\text{Rxn}} = \frac{2}{3}\mu_{M_2O_3} + 2\mu_{M'} - \frac{4}{3}\mu_M - 2\mu_{M'O} \quad (18)$$

where the quantity μ_i , called the chemical potential is de-

defined as $\mu_i = (\partial G / \partial n_i)_{T, P, n_j}$. (19)

For a condensed phase, stoichiometric compound or nominally pure metal, the activity is unity and then

$$\Delta G_{\text{Rxn}} = \Delta G_{\text{Rxn}}^\circ = \frac{2}{3} \mu_{M_2O_3}^\circ + 2\mu_{M'}^\circ - \frac{4}{3} \mu_M^\circ - 2\mu_{M'O}^\circ \quad (20)$$

By adding and subtracting $2\mu_O$, Equation 20 yields the relationship for reaction 17 at any temperature:

$$\Delta G_{\text{Rxn}}^\circ = \frac{2}{3} \Delta G_f^\circ(M_2O_3) - 2\Delta G_f^\circ(M'O) \quad (21)$$

Combining the application 21 with the fact

$$\Delta G_{\text{Rxn}}^\circ = -nFE(\text{Cell})$$

the value of ΔG_f° for any compound can be determined quantitatively from the measured values of $E(\text{cell})$ if the ΔG_f° for the other compounds are known. In fact, extensive tabulations of

ΔG_f° values as functions of temperature are already in existence for many oxide compounds as well as fluorides. Some data for oxides of particular interest to this investigation are listed in Table 4.

The enthalpy change, ΔH_{Rxn}° , and the entropy change, ΔS_{Rxn}° , associated with the displacement reaction can be deduced from the variation of ΔG_{Rxn}° over a temperature range, and consequently also ΔH_f° and ΔS_f° for any compound.

Gibbs-Helmholtz equation gives

$$\Delta G_f^\circ = \Delta H_f^\circ + T \left[\frac{\partial \Delta G_f^\circ}{\partial T} \right]_P = \Delta H_f^\circ - T \Delta S_f^\circ \quad (22)$$

It frequently is convenient to employ the relation

$$\Delta H_f^\circ = \frac{\partial (\Delta G_f^\circ / T)}{\partial (1/T)} \Big|_P \quad (23)$$

Selected literature data for calculations carried out in this thesis are summarized in Table 5.

Table 4. Thermodynamic data for various oxides

Temp. Range (°K)	Compound	Standard free energy of formation (cal/mole = (A+BT(°K)] +C	Reference
700-1100	Cu ₂ O	[-39750+16.00T]	(29)
924-1328	Cu ₂ O	[-39000+17.0T]+50	(56)
1095-1227	Cu ₂ O	[-40040+16.70T]+350	(57)
700-1000	NiO	[-56380+20.70T]+15	(29)
911-1376	NiO	[-55840+20.30T]+50	(56)
1023-1373	NiO	[-56100+20.28T]+185	(57)
298-1725	NiO	[-58450+23.55T]+2000	(58)
903-1540	FeO	[-62950+15.49T]+100	(56)
298-1642	FeO	[-62050+14.95T]+3000	(58)
700-1400	Fe ₂ O ₃	[-193635+59.24T]+45	(30)
298-1460	Fe ₂ O ₃	[-193720+61.04T]+8000	(58)
700-1400	Fe ₃ O ₄	[-261730+72.21T]+60	(30)
298-1642	Fe ₃ O ₄	[-260770+74.75T]+3000	(58)
1300-1600	Cr ₂ O ₃	[-266700+60.0T]+300	(56)
298-2100	Cr ₂ O ₃	[-267750+62.1T]+4000	(58)
700-1100	Cr ₂ O ₃	[-268915+61.00T]+2000	(30)
700-1100	CO ₂ (gas)	[-94260-0.37T]+500	(30)
700-1000	Na ₂ CO ₃	[-268060+64.09T]+1000	(30)

Table 5. Selected literature data for calculations

Standard free energies of formation, $\Delta G_f^\circ = (A+BT) + C$					
Compound	ΔG_f° in cal/mole			Temp. range °K	Ref.
	A	B	C		
Cu ₂ O	-39000	17.0	50 ^a	924-1328	(56)
NiO	-55840	20.30	50 ^a	911-1376	(56)
FeO	-62950	15.49	100 ^a	903-1540	(56)
Fe ₂ O ₃	-193635	59.24	45	700-1400	(30)
Fe ₃ O ₄	-261730	72.21	60	700-1400	(30)
Cr ₂ O ₃	-268915	61.00	~2000	700-1100	(30)
Na ₂ O	-100580	33.60	~1500	500-1000	(30)
CO ₂ (g)	-94260	-0.37	~500	700-1100	(30)
Na ₂ CO ₃	-268060	64.09	~1000	700-1000	(30)
CaF ₂	-291180	38.53	~2000	700-1100	(30)
NaF	-137390	24.74	~1000	700-1100	(30)
NiF ₂	-156530	30.02	~1500	673-1073	(54)

Solubility data for oxygen in sodium; $\log_{10} C_s = A - BT^{-1}$ (°K)

C _s	Parameters		Temp. range= °K	Ref.
	A	B		
(ppm O)	6.940	2801	423-823	(25)
(at.% O)	3.092	2801	423-823	(25)

^aThese are values reported by the authors and presumably are based on the precision of their measurements; all other values are estimated absolute uncertainties.

III. EXPERIMENTAL PROCEDURES

A. Compound Preparation

Reagent grade materials were used to prepare the double oxides of Na_2O with the oxides of chromium, iron and nickel. The procedures employed were similar to those described by Wu (6). Sodium chromite, NaCrO_2 , was synthesized in an open tantalum crucible under vacuum in an induction furnace according to the reaction,

The compound, Na_2NiO_2 was prepared according to the reaction,

Nickel oxide was prepared by roasting the pure nickel powder (99.9%) in a porcelain crucible in air at 800°C for 24 hours. The powder mixture of NiO and Na_2O was placed in a zirconia boat lined with silver foil and heated in a tubular vessel of Inconel. The vessel was kept under a helium atmosphere after evacuation and heated at 600°C for 12 hours. The compound NaFeO_2 was obtained by carrying out reaction 26 in a tantalum crucible under a helium atmosphere for 10 hours,

The compound, Na_2FeO_2 was prepared by the reaction,

FeO was synthesized by reduction of Fe_2O_3 with Fe in the

induction furnace under vacuum at 1000°C. The powder mixture of FeO and Na₂O was put in an iron crucible and heated at 600°C for 24 hours under a helium atmosphere. Other compounds NaNiO₂ and (Na₂O)₂FeO were previously prepared by Wu et al. (59).

X-ray powder diffraction patterns were taken to identify the products obtained from each of the above reactions. Some of the compounds with hygroscopic nature were enclosed in glass capillary tubes for Debye-Scherrer powder patterns. The characterization of all these reaction products has been reported (6). The physical constants and X-ray diffraction data are given in Appendix A.

B. Cell Arrangement and Apparatus

Zirconia or calcium fluoride, all obtained from commercial vendors, were employed as solid electrolyte for the galvanic cells. The ZrO₂·15 mole % CaO electrolyte, obtained from Zirconium Corporation of America, Solon, Ohio, was in the form of discs 1/8 inch thick and 7/8 inch in diameter. The CaF₂ single crystal electrolyte was in the form of discs 1 inch in diameter and 1/8 inch thick as well as in the form of crucibles 1 inch outside diameter, 3/4 inch inside diameter and 3/4 inch high with 1/8 inch wall and bottom. These were purchased from Harshaw Chemical Company, Solon, Ohio. The electrodes were made by mixing the desired phases of components and pressing them in the form of pellets or the powder

mixture was contained in a suitable crucible. The preparation of the electrodes as well as the assemblage of the cells were all done in a controlled atmosphere glove box filled with helium. The helium was purified by circulating it through a molecular sieve to remove moisture and through zirconium chips and titanium sponge at 650°C to remove oxygen, nitrogen or other reactive gases.

A schematic diagram of the apparatus with a cell (K) in place is shown in Figure 1. A spring loaded Al_2O_3 push rod (Q and P) was used so that the contact between electrodes and electrolyte could be maintained. Nickel wires provided the electrical leads between the reversible electrodes and the external circuit. The cell emf was measured with a differential voltmeter, Model 1002 made by Precision Standards Corporation. The temperature of the cell was measured with a chromel-alumel thermocouple with the cold junction in an ice bath in order to negate any ambient temperature changes. The emf was read with a Leeds and Northrup K-3 potentiometer.

The furnace tube containing the cell could be evacuated or filled with purified helium. The cell was heated by an electric furnace which was powered by a Powerstat transformer.

The cell was first heated in a vacuum of 10^{-2} Torr at 500°C for about 12 hours in order to eliminate any moisture or extraneous gases and then refilled with purified helium from the glove box. An atmosphere of helium was maintained in the

Figure 1. Apparatus used for emf measurements

- A. EMF lead wires
- B. Al_2O_3 two hole insulation
- C. "O" ring seal
- D. Vacuum line
- E. Cooling water inlet
- F. Water jacket
- G. Quartz or stainless steel furnace tube
- H. Supporting disc
- I. Supporting rod
- J. Heating furnace
- K. EMF cell
- L. Ceramic disc
- M. Fire brick
- N. T.C. junction
- O. Insulator
- P. Al_2O_3 rod
- Q. Spring
- S. Cooling water outlet
- T. Glove box bottom
- U. Cap of furnace tube
- V. T.C. lead wire

cell while the emf was being measured.

C. EMF Measurements Employed to Check the Apparatus

EMF measurement of the cell $\text{Ni, NiO/ZrO}_2 \cdot 15 \text{ m\% CaO/Cu}_2\text{O, Cu}$ was made to check the experimental apparatus. The emf of this cell is known (29,56,57). Each electrode was in the form of a pressed tablet of a powder mixture of metal and its oxide. The equilibrium reaction at the respective electrode-electrolyte interfaces are

and

The anodic and cathodic reactions for the cell can be written as

Since the activity of the elements or compounds for this cell could be considered to be unity, the free energy change for the overall reaction can be expressed by the relationship:

$$\Delta G_{\text{Rxn}}^{\circ} = \Delta G_{\text{NiO}}^{\circ} - \Delta G_{\text{Cu}_2\text{O}}^{\circ} = -nFE \quad (33)$$

The comparison of the measured emf values with the values calculated from known thermodynamic data is shown in Figure 2 and linear equations for the curves shown are given in Table 6.

Figure 2. Measured and literature emf versus temperature for the cell $\text{Ni, NiO/ZrO}_2 \cdot 15 \text{ mole } \% \text{ CaO/Cu}_2\text{O, Cu}$

Table 6. Measured and calculated emf versus temperature equations for cell of Ni,NiO/ZrO₂·15 mole % CaO/Cu₂O,Cu

Temp. range °K	E(volt)=[A+BT]+C	Reference
760-1060	$E=[0.3647-8.774 \times 10^{-5}T]+1.54 \times 10^{-3}$	This work
660-1040	$E=[0.3389-5.886 \times 10^{-5}T]+6.8 \times 10^{-4}$	This work
911-1376	$E=[0.3651-7.16 \times 10^{-5}T]+2.75 \times 10^{-6}$	(56)
1023-1373	$E=[0.3482-7.76 \times 10^{-5}T]+2.74 \times 10^{-6}$	(57)
700-1400	$E=[0.3578-9.88 \times 10^{-5}T]+2.9 \times 10^{-6}$	(29)

Data taken at elevated temperature by Rapp and Shores (56) and Vasil'eva et al. (57) are extrapolated to lower temperatures in Fig. 2. Rapp and Shores' data lie approximately 10-15 mV higher and Vasil'eva et al.'s. data lie about 5-10 mV below the data obtained in the present investigation. In these experiments high purity helium was circulated past the emf cell by thermal convection, but a vacuum was not applied prior to measurements as was done in subsequent experiments.

D. Measurements for Free Energy of Formation of NaCrO₂

One of the cells used to measure the emf for determining the free energy of formation of NaCrO₂ was

The cell is presented schematically in Figure 3. This modified cell was designed for improving the contact between the

Figure 3. Arrangement for Ca/CaF₂/NaCrO₂,Cr,Cr₂O₃,NaF

electrodes and electrolyte in order to yield consistent and reproducible data from which reliable thermodynamic values may be calculated. For this cell, the anode, cathode and overall cell reactions are

$$\text{and } \Delta G_{\text{Rxn}}^{\circ} = -nFE_{\text{cell}}$$

$$\begin{aligned} &= \Delta G_{\text{f}}^{\circ}[\text{NaCrO}_2] + \frac{1}{2}\Delta G_{\text{f}}^{\circ}[\text{CaF}_2] - \Delta G_{\text{f}}^{\circ}[\text{NaF}] \\ &\quad - \frac{2}{3}\Delta G_{\text{f}}^{\circ}[\text{Cr}_2\text{O}_3] \end{aligned} \quad (37)$$

from which $\Delta G_{\text{f}}^{\circ}[\text{NaCrO}_2]$ can be calculated by the relation,

$$\begin{aligned} \Delta G_{\text{f}}^{\circ}[\text{NaCrO}_2] &= -nFE_{\text{cell}} - \frac{1}{2}\Delta G_{\text{f}}^{\circ}[\text{CaF}_2] + \Delta G_{\text{f}}^{\circ}[\text{NaF}] \\ &\quad + \frac{2}{3}\Delta G_{\text{f}}^{\circ}[\text{Cr}_2\text{O}_3] \end{aligned} \quad (38)$$

According to the overall reaction 36, the number of electrons transferred, n , is 1. Faraday's constant, F , is 23060 cal/volt-equivalent. The standard free energy change for the formation of the compounds CaF_2 , NaF and Cr_2O_3 can be calculated from the relations given previously in Table 5.

Another cell (Figure 4) also with CaF_2 electrolyte used to measure the emf for determining $\Delta G_{\text{f}}^{\circ}[\text{NaCrO}_2]$ was of the type,

Figure 4. Arrangement for $\text{Ni, NiF}_2/\text{CaF}_2/\text{NaF, Cr}_2\text{O}_3, \text{Cr, NaCrO}_2$

Since the standard electromotive force of NaF is greater than that of NiF (53), the anodic and cathodic reactions for this cell can be written as

and hence

$$\Delta G_f^\circ[\text{NaCrO}_2] = \frac{1}{3}\{3FE_{\text{cell}} - \frac{3}{2}\Delta G_f^\circ[\text{NiF}_2] + 3\Delta G_f^\circ[\text{NaF}] + 2\Delta G_f^\circ[\text{Cr}_2\text{O}_3]\} \quad (42)$$

The values of emf were obtained in the temperature range of 500-800°C. Since there is a eutectic reaction between CaF_2 and NaF at 810°C (60), the upper temperature is limited. EMF measurements were recorded every hour and the final valid value was taken when the emf remained constant to within ± 2 mV for 2-3 hours at a given temperature. The time necessary to establish the equilibrium value of the emf was normally 6 to 8 hours after the temperature had been attained.

E. Measurements for Free Energy of Formation of Compounds

The cell with the fluoride electrolyte and with the oxide electrolyte was used to determine the standard free energy of formation of Na_2NiO_2 and that of NaNiO_2 , respectively. The cells may be represented as:

and

The cell arrangements are shown in Figure 5 and Figure 6, respectively. The anode, cathode, and overall cell reactions are:

and hence, the standard free energies of formation of Na_2NiO_2 and NaNiO_2 can be expressed as,

$$\Delta G_f^\circ[\text{Na}_2\text{NiO}_2] = -2FE - \Delta G_f^\circ[\text{CaF}_2] + 2\Delta G_f^\circ[\text{NiO}] + 2\Delta G_f^\circ[\text{NaF}] \quad (49)$$

and

$$\Delta G_f^\circ[\text{NaNiO}_2] = \frac{1}{2}\{-2FE + \Delta G_f^\circ[\text{Na}_2\text{NiO}_2] + \Delta G_f^\circ[\text{NiO}] + \Delta G_f^\circ[\text{Cu}_2\text{O}]\} \quad (50)$$

The values for $\Delta G_f^\circ[\text{NaNiO}_2]$ in Equation 50 can be derived by using the thermodynamic data for the compound Na_2NiO_2 calculated from Equation 49.

Figure 5. Arrangement for Ca/CaF₂/NaF, NiO, Ni, Na₂NiO₂ cell

Figure 6. Arrangement for $\text{NaNiO}_2, \text{Na}_2\text{NiO}_2 / \text{ZrO}_2 \cdot \text{CaO} / \text{Cu}_2\text{O}, \text{Cu}$ cell

F. Measurements for Free Energy of Formation of Compounds

The standard free energy of formation of the compound Na_2FeO_2 was investigated by the cell

with the virtual cell reaction

and hence

$$\Delta G_f^\circ[\text{Na}_2\text{FeO}_2] = -2FE - \Delta G_f^\circ[\text{CaF}_2] + 2\Delta G_f^\circ[\text{NaF}] + 2\Delta G_f^\circ[\text{FeO}] \quad (52)$$

An attempt was also made to study the standard free energy of formation of NaFeO_2 and $(\text{Na}_2\text{O})_2\text{FeO}$ by using the following cells:

and

For these cells, the reactions are

and

The standard free energy of formation can be written as

$$\Delta G_f^\circ[\text{NaFeO}_2] = \frac{1}{2}\{-2FE_{\text{cell}} + \Delta G_f^\circ(\text{Na}_2\text{FeO}_2) + \Delta G_f^\circ[\text{FeO}] + \Delta G_f^\circ[\text{Cu}_2\text{O}]\} \quad (59)$$

$$\Delta G_f^\circ[(\text{Na}_2\text{O})_2\text{FeO}] = 4FE_{\text{cell}} + 4\Delta G_f^\circ[\text{NaFeO}_2] - 3\Delta G_f^\circ[\text{FeO}] - 2\Delta G_f^\circ[\text{Cu}_2\text{O}] \quad (60)$$

The standard derivation for the $\Delta G_f^\circ[(\text{Na}_2\text{O})_2\text{FeO}]$ in Equation 60 depended upon the data of $\Delta G_f^\circ[\text{NaFeO}_2]$ calculated in 59, and the calculation of $\Delta G_f^\circ[\text{NaFeO}_2]$ was derived by using the data of $\Delta G_f^\circ[\text{Na}_2\text{FeO}_2]$ in Equation 52.

IV. RESULTS

A. Thermodynamic Properties of Compounds

Heating and cooling data were obtained with each cell for the open circuit emf versus temperature plots. The data are shown graphically in Figures 7-9 and are tabulated in Appendix A. The least square linear equations for the emfs are summarized in Table 7 and the derived standard free energy of formation relations for the compounds are given in Table 8. The uncertainty indicated for the compounds is based on the experimental inaccuracy in the galvanic cell measurement and estimates of the uncertainty in the free energy of formation of the compounds involved in the cell reactions.

The data for cell VII was very erratic, probably due to interaction between FeO and $(\text{Na}_2\text{O})_2 \cdot \text{FeO}$ to produce $(\text{Na}_2\text{O}) \cdot \text{FeO}$. Consideration of the data obtained with other cells and literature data show that this reaction is favorable and consequently the anticipated cell reactions 56-58 are not valid.

The temperature dependence of the emf of cell V was also found to be erratic for temperatures above 911°K . These data were also discarded and account for the relatively short temperature span for this cell as indicated in Table 7. The reason for this unexpected behavior is not known.

The free energy of formation for the compound Na_4FeO_3 or $(\text{Na}_2\text{O})_2 \cdot \text{FeO}$, is based on the calorimetric data of Gross and Wilson (10). They employed solution calorimetry to obtain the

Figure 7. Measured emf versus temperature values

Figure 8. Measured emf versus temperature values

Figure 9. Measured emf versus temperature values

Table 7. Temperature dependence of cell emfs

Cell no.	Reaction	E(volt) = (A+BT) + C ^a			Temp. range °K
		A	Bx10 ⁵	Cx10 ³	
I.	1/2Ca+NaF+2/3Cr ₂ O ₃ →	1.737	-18.38	4.9	824-1020
	1/2CaF ₂ +NaCrO ₂ +1/3Cr	+0.0198	+2.16		
II.	Cr+3NaCrO ₂ +3/2NiF ₂ →	1.376	-3.622	3.6	797-1041
	3NaF+3/2Ni+2Cr ₂ O ₃	+0.0156	+1.67		
III.	Ca+2NaF+2NiO→	0.9991	22.8	3.2	807-1067
	Na ₂ NiO ₂ +CaF ₂ +Ni	+0.0125	+1.311		
IV.	Na ₂ NiO ₂ +NiO+Cu ₂ O→	-0.2059	27.18	8.4	826-1044
	2NaNiO ₂ +2Cu	+0.0337	+3.787		
V.	Ca+2NaF+2FeO→	1.5993	-20.42	4.0	843-911
	Na ₂ FeO ₂ +CaF ₂ +Fe	+0.0736	+8.38		
VI.	Na ₂ FeO ₂ +FeO+Cu ₂ O→	1.3559	-7.55	6.4	795-1048
	2NaFeO ₂ +2Cu	+0.0184	+1.95		
VII.	(Na ₂ O) ₂ ·FeO+3FeO +2Cu ₂ O→4NaFeO ₂ +4Cu	(Data erratic and unreliable)			

^aC is the root mean square deviation of the measured E values from the straight line. The other + values are the calculated standard deviation for the intercept and slope, respectively.

Table 8. Standard free energy of formation of double oxides,
 $x\text{Na}(\ell) + y\text{M}(\text{s}) + (z/2)\text{O}_2(\text{g}) \rightarrow \text{Na}_x\text{M}_y\text{O}_z(\text{s})$, in cal/mole,
 $\Delta G^\circ = (A + BT) + C$

Compound	-A	B	+C
$\text{NaCrO}_2^{\text{a}}$	211130	50.38	1900
$\text{NaCrO}_2^{\text{b}}$	206670	49.56	4000
Mean:	208900	49.97	3100
Na_2NiO_2	141360	44.03	2900
NaNiO_2	113350	34.40	1200
Na_2FeO_2	183060	51.34	3000
NaFeO_2	173410	43.66	1200
$\text{Na}_4\text{FeO}_3^{\text{c}}$	289180	82.69	

^aThe values were derived from measurements made with cell No. I.

^bThe values were obtained from measurements made with cell No. II.

^cEstimated value, see text.

enthalpy for the reaction

$$\Delta H(298^\circ\text{K}) = -25.07 \pm 0.55 \text{ Kcal.} \quad (62)$$

The entropy change for this reaction is probably within 0.0 ± 1.0 cal/mole- $^\circ\text{K}$. Therefore, from the data in Table 5, the standard free energy of formation was calculated according to the relation

$$\begin{aligned} \Delta G_f^\circ[(\text{Na}_2\text{O})_2 \cdot \text{FeO}] &= 2\Delta G_f^\circ[\text{Na}_2\text{O}] + \Delta G_f^\circ[\text{FeO}] - 25070 \\ &= -289180 + 82.69T. \end{aligned} \quad (63)$$

B. Critical Oxygen Concentration in Sodium for the Formation of Double Oxides

Oxygen saturated sodium is in equilibrium with Na_2O which is highly corrosive. The following equation is considered for the Na- Na_2O equilibrium:

It may be assumed that the activity of $\text{Na}(\ell)$ and Na_2O is unity, hence at equilibrium we have

$$\begin{aligned} \Delta G_{\text{Rxn}}^\circ &= \Delta G_f^\circ[\text{Na}_2\text{O}] = -RT \ln \frac{1}{a_{\text{O}}} = RT \ln \gamma_{\text{O}} N_{\text{O}} \\ &= RT \ln N_{\text{O}} + RT \ln \gamma_{\text{O}} \end{aligned} \quad (65)$$

$$\text{i.e. } \ln \gamma_{\text{O}} = \Delta G_f^\circ[\text{Na}_2\text{O}]/RT - \ln N_{\text{O}} \quad (66)$$

where a_{O} = activity of oxygen in sodium

γ_{O} = activity coefficient of oxygen in sodium

N_{O} = mole fraction of oxygen in sodium

The data in Table 5 permit calculation of γ_o . In subsequent calculations it is assumed that Henry's law is valid and γ_o remains constant at lower oxygen concentrations.

For the reaction of pure metal with oxygen contaminated sodium to form double oxide:

the following expression must be satisfied,

$$\Delta G^\circ [\text{Na}_x\text{M}_y\text{O}_z] = -RT \ln \frac{a_{\text{Na}_x\text{M}_y\text{O}_z}}{a_{\text{Na}}^x \cdot a_{\text{M}}^y \cdot a_{\text{O}}^z} \quad (68)$$

The activity for Na, M and $\text{Na}_x\text{M}_y\text{O}_z$ are assumed to be unity, hence

$$\Delta G^\circ (\text{Na}_x\text{M}_y\text{O}_z) = zRT \ln a_o = zRT \ln \gamma_o N'_o. \quad (69)$$

By using the calculated values for γ_o given in Table 9 and the standard free energy of formation of the double oxides given in Table 8, one can calculate the critical oxygen concentration, N'_o , for the formation of $\text{Na}_x\text{M}_y\text{O}_z$.

The free energy data in Tables 8 and 5 permit calculation of the free energy change for the reaction of the compounds with sodium to produce sodium oxide and the free base-metal. It is found that the free energy change is zero at the following temperatures for the given compound: Na_4FeO_3 - 693°K, NaFeO_2 - 1197°K, Na_2FeO_2 - 1141°K, NaNiO_2 - 2677°K, Na_2NiO_2 - 2581°K and for NaCrO_2 the free energy change is positive at all temperatures of interest. Therefore, only NaCrO_2 is

Table 9. Solubility data of oxygen in liquid sodium, the activity coefficient for oxygen in sodium and the derived critical oxygen concentration in sodium for the formation of double oxides

Temp. °K	N_O^b (ppm)	γ_O^c	Critical oxygen concentration for the formation of compounds ^a			
			NaCrO ₂ (ppm)	Na ₂ FeO ₂ (ppm)	(Na ₂ O) ₂ ·FeO (ppm)	Na ₂ NiO ₂ (ppm)
573	1.13x10 ²	4.55x10 ⁻²⁸	4.8x10 ⁻²	--d	--d	--d
673	5.99x10 ²	4.50x10 ⁻²³	4.2x10 ⁻¹	--d	--d	--d
773	2.07x10 ³	2.27x10 ⁻¹⁹	2.14	--d	1.81x10 ³	--d
873	5.38x10 ³	1.62x10 ⁻¹⁶	7.41	--d	3.53x10 ³	--d
973	1.15x10 ⁴	3.01x10 ⁻¹⁴	19.8	--d	5.71x10 ³	--d
1073	2.14x10 ⁴	2.11x10 ⁻¹²	37.7	--d	8.56x10 ³	--d

^aThe values are calculated from the ΔG° data given in Table 8. All the calculations are based on the assumption that liquid sodium is in equilibrium with pure metal. The activity of the metal is assumed to be unity.

^b N_O = solubility of oxygen in Na.

^c γ_O = activity coefficient of oxygen in Na.

^dConcentration exceeds the solubility limit.

stable in liquid sodium in the temperature range 400-1100°K, while Na_4FeO_3 is stable only at temperatures above 693°K (420°C). The latter compound will not be stable at temperatures and oxygen concentrations normally encountered in a sodium loop. The calculated critical concentrations of oxygen for the existence of these two compounds are summarized in Table 9.

It should be noted that these calculations assume the equilibrium activity is unity for the base metal component. In an iron-chromium-nickel alloy such as austenitic stainless steel or Inconel the activities will be less than unity. The activities have been measured by Slough, Spencer and Kubaschewski (61). They report the activity of chromium in a 20 mole % Cr, 16 mole % Ni, 64 mole % Fe alloy to be 0.29 at 1472°K. Assuming this value of the activity to be valid at lower temperatures, the critical oxygen concentrations for the formation of NaCrO_2 is calculated to be 0.09, 0.79, 4.0, 13.8, 37.0 and 70.5 ppm for temperatures of 573, 673, 773, 873, 973 and 1073°K respectively.

According to these calculations, the critical oxygen concentrations in sodium for the formation of NaCrO_2 with pure Cr as well as Cr in 18-8 austenitic stainless steels is much lower than the solubility of oxygen in liquid sodium for the temperature range up to 1073°K.

The critical oxygen concentration for formation of

Na_2FeO_2 based on the ΔG_f° values estimated by Wu (6) shows that Na_2FeO_2 can be stable at temperatures of 873°K or above, while the corresponding calculated values based on the ΔG_f° from measured emf data in this work shows that the compound Na_2FeO_2 is stable in oxygen-saturated sodium at temperatures at or above 1141°K.

The formation of $(\text{Na}_2\text{O})_2 \cdot \text{FeO}$ is possible at temperatures above 673°K, but the calculation based on the estimated values of ΔG° by Wu (6) shows the formation is possible only at 1073°K or above. Gross and Wilson (10) concluded that about 1000 ppm oxygen are needed for formation of $(\text{Na}_2\text{O})_2 \cdot \text{FeO}$ as a separate phase at 600°C (873°K). In our calculation, about 3500 ppm are needed at this same temperature. This oxygen level is lower than the solubility limit of oxygen in liquid sodium at this temperature.

For the reaction

Gross and Wilson (10) give

$$\Delta G^\circ = 22200 - 3.0T \text{ cal} \quad (71)$$

whereas data obtained in this investigation gives

$$\Delta G^\circ = 15190 - 5.43T \text{ cal.} \quad (72)$$

Although the agreement in the magnitude of the free energy change is not in close agreement, both observations show that $(\text{Na}_2\text{O})_2 \cdot \text{FeO}$ is stable relative to the compound NaFeO_2 in the temperature range of interest, 400-1100°K.

V. DISCUSSION

In theory, although electrochemical methods of determining thermodynamic quantities are most attractive, the practical difficulties of obtaining accurate results are very great. Immense precautions need to be taken during an experiment. Usually, the isolation of the two electrodes from each other by the electrolyte in a cell is essential without which the gas phase interaction makes the reversible emf measurement impossible. It is also noted by Markin et al. (62) that galvanic cell measurements with all fluoride cells require experimentally much more care than the corresponding solid oxide galvanic cell measurement. In addition, for the reference electrode containing Fe and FeO, such as cell V in this work, yttria doped thoria cannot be employed as electrolyte. It is generally known (63) that Wustite may react with the electrolyte and form YFe_2O_4 resulting in a mixed potential.

In this work, the thoria electrolyte was not employed and all cells were first heated in a vacuum at 10^{-2} Torr at 500°C or above for about 12 hrs before admitting high purity helium to the cells. This treatment presumably removed any moisture or extraneous gases absorbed on the electrode materials and the Inconel furnace tube which contained the cell. As a consequence of this pretreatment, the observed emf dependence on temperature was very small as expected for a cell reaction involving all condensed components. The temperature

dependence obtained by Wu (6) was in general much too large and led to very unrealistically low values for the entropy of formation for the double oxides. In this work, the same apparatus and procedure were employed, except for the vacuum treatment at 500-600°C prior to emf measurements. The reason for the resultant change in the temperature dependence is uncertain but is probably due to some extraneous gas phase reaction at the electrodes. It was noted by Bagshaw (64) that there is some difficulty with Ni,NiF₂ electrodes because of the evaporation of NiF₂ from the electrode at about 1060°K. In the present work, the Ni,NiF₂ mixture was contained in a nickel thimble, see Figure 4, which was fitted tightly to the single crystal CaF₂ electrolyte and any tendency toward vaporization was constrained.

The free energies of formation of the various compounds are summarized in Table 8. Both cell I and cell II were employed to measure emf data for calculating $\Delta G_f^\circ[\text{NaCrO}_2]$. The degree of consistency of the $\Delta G_f^\circ[\text{NaCrO}_2]$ calculation is considered very satisfactory. The comparison of the result of ΔG_f° for the compounds, NaCrO₂, Na₂NiO₂, Na₂FeO₂ and (Na₂O)₂·FeO, with those of other workers is given in Table 10. No data were found for the other compounds investigated.

The data for $\Delta G_f^\circ[\text{NaCrO}_2]$ in this investigation is found to be 3 Kcal/mole more negative than that reported by Clough (36) at 298°K and to be 1.4 Kcal/mole more negative than that

Table 10. Comparison of the free energies of formation of compounds obtained by different workers

Compound	Temp. °K	ΔH_f° -Kcal/mole	ΔS_f° cal/mole-K	ΔG_f° -Kcal/mole	Method	Ref.
NaCrO ₂	298			194.0	galvanic cell	This work
	298			191.5	estimated	(35)
	298	208.9			(see text)	(9)
	973	208.9	49.97	160.3	galvanic cell	This work
	973	202.4	44.80	158.9	estimated	(6)
Na ₂ FeO ₂	973	183.1	51.34	133.1	galvanic cell	This work
	973	182.2	48.2	135.3	estimated	(6)
(Na ₂ O) ₂	973	289.2	82.69	208.7	estimated	This work
FeO	973	276.4	80.6	198.0	estimated	(6)
Na ₂ NiO ₂	973	141.4	44.03	98.52	galvanic cell	This work
	973	167.5	53.0	115.9	estimated	(6)

estimated by Wu (6) at 973°K. Gross et al. (9) carried out measurements on the heat evolved in the reaction

by direct combination calorimetry and solution calorimetry.

They obtained a value of $\Delta H^\circ(298)$ of -24.24 ± 0.24 Kcal.

Combining our data for NaCrO_2 with data for Na_2O and Cr_2O_3 in Table 5 yields

$$\Delta G^\circ_{\text{Rxn}} = -24150 \pm 2.67T \quad (74)$$

which, neglecting ΔC_p , gives -24.15 ± 3.34 Kcal for ΔH . For the reaction,

We similarly obtain

$$\Delta G^\circ_{\text{Rxn}} = -7740 - 17.23T \quad (75)$$

Gross et al. (9) similarly estimated the free energy change for this reaction as

$$\Delta G^\circ_{\text{Rxn}} = -8300 - 19.6T \quad (76)$$

These data show that NaCrO_2 is sufficiently stable to exclude formation of Cr_2O_3 in liquid sodium contaminated with oxygen.

The free energy change based on various workers for some reactions of sodium oxide with iron and its oxides are summarized in Table 11. Oxide formation of the type

or

Table 11. Comparison of the ΔG° for the reactions of Na_2O with iron and its oxides

Reaction	Temp. °K	ΔG° Kcal	Method	Ref.
$\text{Na}_2\text{O} + \text{FeO} \rightarrow \text{Na}_2\text{FeO}_2$	298	-18.86	galvanic cell	This work (35)
	298	-18.0	estimated	
$2\text{Na}_2\text{O} + \text{Fe} \rightarrow \text{Na}_2\text{FeO}_2 + 2\text{Na}(\ell)$	298	+13.4	galvanic cell	This work
$2\text{Na}_2\text{O} + \text{Fe} + 1/2\text{O}_2 \rightarrow (\text{Na}_2\text{O})_2 \cdot \text{FeO}$	298	-83.4	estimated	This work (10)
	298	-88.8	estimated	
$2\text{Na}_2\text{O} + \text{FeO} \rightarrow (\text{Na}_2\text{C})_2 \cdot \text{FeO}$	298	-25.1	estimated	This work (10) (65)
	298	-25.07	calorimetry	
	298	-24.8	Knudsen effusion	
$3\text{Na}_2\text{O} + \text{Fe} \rightarrow (\text{Na}_2\text{C})_2 \cdot \text{FeO} + 2\text{Na}(\ell)$	298	+7.2	estimated	This work
	873	-3.2	estimated	This work
	873	-2.2	calorimetry	(10)
	873	-2.5	calorimetry	(18)
$\text{Na}_2\text{O} + \text{Fe} \rightarrow \text{FeO} + 2\text{Na}(\ell)$	298	+32.2	estimated	This work

is known to occur. However, in the presence of liquid sodium these compounds may be unstable and may be reduced to form elemental iron.

The estimated value of the free energy of formation of Na_2NiO_2 given by Wu (6) is -115.9 Kcal/mole at 973°K, whereas the value determined in this work is -98.52 ± 2.9 Kcal/mole. This agreement is somewhat less satisfactory than the data for NaCrO_2 . The discrepancies can be expected among sources of published values involved in the thermodynamic properties estimation.

An alternate method for determining the standard free energy of formation of the compound NaCrO_2 was tried by using the measurements of the equilibrium CO_2 pressure involved in the reaction

The details are given in Appendix B and the result gave -215 Kcal/mole for $\Delta H_f^\circ[\text{NaCrO}_2]$ and 58.95 e.u. for $\Delta S^\circ[\text{NaCrO}_2]$, while the corresponding values calculated from the measured emf data are -208.9 Kcal/mole and 49.97 e.u. The agreement is within 3% and 15% respectively. It was noted that the reaction 79 is not reversible on cooling, there was only a partial decrease of the gas pressure to the values obtained on heating. The reverse reaction is apparently very slow and equilibrium was not attained after 48 hours at a given temperature. These data which depend on a nonreversible reaction are considered unreliable and were discarded.

VI. CONCLUSIONS

1. Reliable thermodynamic data for compounds of NaCrO_2 , Na_2FeO_2 , NaFeO_2 , Na_2NiO_2 and NaNiO_2 at high temperature range from 500 to 800°C can be obtained by using emf measurements with solid electrolyte cells. The pretreatment of heating the cells in a vacuum of 10^{-2} Torr at 500°C or above for about 12 hours will make the observed emf dependence on temperature very small as expected for a cell reaction involving all condensed components.
2. The measurements in this work were carried out over the temperature range in which no phase transformations occurred, the ΔC_p for the compounds involved was reasonably considered as approximately zero. Linear emf-temperature plots were therefore expected for these cells and the equation of ΔG_f° was indeed valid for constant values of ΔH_f° and ΔS_f° .
3. The formation of compound NaCrO_2 is thermodynamically favorable in a sodium loop made of austenitic stainless steels. The critical oxygen concentration for the formation of NaCrO_2 shows that it will be stable in liquid sodium in temperature range from 400 to 1100°C and Cr_2O_3 will not exist with the double oxide in liquid sodium.
4. The existence temperature for $(\text{Na}_2\text{O})_2 \cdot \text{FeO}$ in equilibrium with oxygen saturated liquid sodium is 693°K or above, for Na_2FeO_2 it is 1141°K or above and for NaFeO_2 it is

1173°K or above. These existence temperatures show no iron double oxide is stable at temperature and oxygen concentration normally encountered in a sodium loop.

5. The double oxides of nickel with sodium oxide are much less stable than the iron double oxides and will therefore not exist in liquid sodium. The nickel in austenitic stainless steel will show the least attack by oxygen saturated liquid sodium.

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IX. APPENDIX A. EXPERIMENTAL X-RAY DIFFRACTION AND EMF
DATA

Table A1. X-ray data for double oxide of chromium and sodium

Compound	Intensity, I/I_1	Spacing, dÅ	hkl	Other constants
NaCrO ₂	90	5.311	003	hexagonal
	60	2.658	006	a=2.968Å
	50	2.531	101	c=15.94Å
	40	2.440	012	Density g/cm ³ =4.36
	100	2.156	104	Melting point = 1535±5°C
	20	1.703	107	Hygroscopic: No
	60	1.574	018	
	60	1.480	110	
	20	1.292	116	
	20	1.266	202	
	20	1.221	024	

Table A2. X-ray data for double oxides of nickel and sodium

Compound	Intensity, I/I_1	Spacing, $d\text{\AA}$	hkl	Other constants
NaNiO_2	90	5.250	001	Monoclinic: a=5.33 b=2.86 c=5.59 $\beta=110^\circ 30'$ Density $\text{g/cm}^3=4.72$ Hygroscopic: yes
	70	2.620	002	
	60	2.470	200	
	70	2.380	111	
	90	2.230	202	
	100	2.100	111	
	40	1.737	003	
	60	1.655	112	
	90	1.555	113	
	80	1.502	311	
	40	1.434	310	
	60	1.423	020	
	50	1.371	021	
	70	1.320	113	
	50	1.305	004	
	50	1.287	311	
	70	1.249	022	
Na_2NiO_2	90	4.3370	021	Orthorhombic: a=2.9 b=10.1 c=8.2 $\alpha=\beta=\gamma=90^\circ$ Density $\text{g/cm}^3=4.67$ Hygroscopic: yes Melting point: $800\pm 5^\circ\text{C}$
	90	4.1335	002	
	20	2.7177	110	
	50	2.5882	111	
	70	2.5261	040	
	100	2.4196	023	
	70	2.2726	112	
	90	2.1631	130	
	70	2.0933	131	
	30	1.9264	113	
	30	1.7040	133	
	50	1.6462	061	
	70	1.6167	151	
	20	1.5656	062	
	70	1.5301	152	
	5	1.5010	134	
	20	1.4413	063	
	50	1.4134	153	

Table A3. X-ray data for double oxides of iron and sodium

Compound	Intensity, I/I_1	Spacing, $d\text{\AA}$	hkl	Other constants
Na_2FeO_2	100	4.61299		Hygroscopic: yes No other information reported
	100	3.41531		
	60	2.66176		
	30	2.54041		
	30	2.46881		
	30	2.43013		
	30	2.35946		
	80	2.30428		
	100	2.22936		
	60	1.96688		
	30	1.84657		
	80	1.64772		
	30	1.59663		
	30	1.58262		
	30	1.53275		
	30	1.37113		
	30	1.35483		
	30	1.31674		
	60	1.27285		
	30	1.21971		
NaFeO_2	15	10.10		Hexagonal: $a=3.02$ (possible values)
	20	8.52	002	
	10	6.05		
	85	5.36	003	Density $\text{g/cm}^3=4.23$ Hygroscopic: yes
	60	2.67	100	
	50	2.58	101	
	70	2.48	102	
	100	2.19		
	40	2.03		
	30	1.76		
	60	1.72		
	80	1.59		
	90	1.51		
	50	1.45		
	50	1.37		
	50	1.34		
	60	1.31		
	45	1.29		
	45	1.28		
	80	1.24		

Table A3. (Continued)

Compound	Intensity, I/I_1	Spacing, $d\text{\AA}$	hkl	Other constants
$(\text{Na}_2\text{O})_2\text{FeO}$	60	5.02		No information has been reported
	60	4.64		
	80	3.83		
	40	3.72		
	60	3.35		
	40	3.08		
	20	2.88		
	40	2.74		
	60	2.62		
	80	2.54		
	100	2.43		
	20	2.33		
	20	2.25		
	50	1.94		
	60	1.91		
	40	1.88		
	20	1.807		
	20	1.772		
	20	1.675		
	60	1.647		
	40	1.562		

Table A4. Measured emf of electrochemical cells

Cell I		Cell II	
Ca/CaF ₂ /NaF, Cr ₂ O ₃ , Cr, NaCrO ₂		Ni, NiF ₂ /CaF ₂ /NaF, Cr ₂ O ₃ , Cr, NaCrO ₂	
Temp. °K	emf, mV	Temp. °K	emf, mV
824	1588.4	797	1349.0
838	1585.5	854	1344.0
846	1582.6	874	1347.0
850	1583.2	889	1342.0
874	1577.0	909	1339.0
875	1579.0	930	1348.0
894	1563.3	963	1334.0
896	1574.8	977	1343.0
918	1560.5	1001	1337.8
925	1560.8	1017	1338.6
932	1561.5	1041	1342.5
956	1558.0		
966	1563.7		
973	1569.3		
989	1555.8		
995	1557.4		
1020	1547.6		

Table A4. (Continued)

Cell III Ca/CaF ₂ /NaF, NiO, Ni, Na ₂ NiO ₂		Cell IV NaNiO ₂ , Na ₂ NiO ₂ , NiO/ZrO ₂ ·15 mole % CaO/ Cu ₂ O, Cu	
Temp. °K	emf, mV	Temp. °K	emf, mV
807	1180.4	826	35.60
852	1193.1	855	26.89
887	1207.2	868	26.50
888	1195.3	885	30.40
920	1210.0	907	33.20
928	1216.5	937	44.00
951	1217.2	949	46.80
965	1218.1	965	51.00
971	1220.0	990	55.00
982	1221.0	1014	81.50
1003	1226.0	1038	72.20
1014	1231.7	1044	90.70
1027	1230.0		
1067	1243.0		

Table A4. (Continued)

Cell V		Cell VI	
$\text{Na}_2\text{FeO}_2, \text{NaF}, \text{FeO}, \text{Fe}/\text{CaF}_2/\text{Ca}$		$\text{FeO}, \text{NaFeO}_2, \text{Na}_2\text{FeO}_2/\text{ZrO}_2 \cdot 15 \text{ mole } \% \text{ CaO}/$	
Temp. °K	emf, volt	Temp. °K	emf, volt
843	1.4248	795	1.3040
858	1.4220	820	1.2903
870	1.4246	835	1.2905
889	1.4249	850	1.2880
902	1.4149	867	1.2932
911	1.4080	879	1.2913
		896	1.2900
		904	1.2880
		920	1.2800
		937	1.2894
		948	1.2743
		970	1.2754
		974	1.2780
		989	1.2970
		993	1.2773
		1015	1.2930
		1029	1.2767
		1034	1.2777
		1040	1.2742
		1048	1.2743

X. APPENDIX B. THE DETERMINATION OF $\Delta G_f^\circ[\text{NaCrO}_2]$ BY USING
THE MEASUREMENTS OF THE EQUILIBRIUM CO_2 PRESSURE

On laboratory level, the compound NaCrO_2 is prepared by the reaction

or

in an open tantalum crucible under vacuum at 850°C in the induction furnace.

In Equation B1, the reaction involves the production of gas. Suppose that Na_2CO_3 , Cr_2O_3 and NaCrO_2 are placed in an isolated system excluding chemical reaction with their surroundings, the thermodynamic equilibrium constant, K , will be given by

$$K = \frac{a_{\text{NaCrO}_2} \cdot a_{\text{CO}_2}}{a_{\text{Na}_2\text{CO}_3} \cdot a_{\text{Cr}_2\text{O}_3}} \quad (\text{B3})$$

For pure solid, the activity, a , can be taken as unity, and also, in this case, as usual the gas CO_2 shall be assumed to behave ideally, hence the activity of CO_2 may be replaced by the partial pressure:

$$a_{\text{CO}_2} = \frac{f_{\text{CO}_2}}{f_{\text{CO}_2}^\circ} = \frac{p_{\text{CO}_2}}{p_{\text{CO}_2}^\circ} = \frac{p_{\text{CO}_2}}{1} = p_{\text{CO}_2} \quad (\text{B4})$$

where $f_{\text{CO}_2}^\circ$ and $p_{\text{CO}_2}^\circ$ are the fugacity and the reference pressure in the standard state for a pure substance respectively. The standard state of a substance is commonly chosen as the gas at 1 atm pressure and at the temperature under consideration.

Thus, the equilibrium constant, K , may be written in more convenient form as

$$K = p_{\text{CO}_2}, \quad (\text{B5})$$

and therefore

$$\Delta G_{\text{Rxn}}^{\circ} = -RT \ln p_{\text{CO}_2} \quad (\text{B6})$$

By applying this relation, $\Delta G_{\text{Rxn}}^{\circ}$ and hence $\Delta G_{\text{NaCrO}_2}^{\circ}$ may be determined from the measured CO_2 pressure.

The apparatus for measuring CO_2 pressure is presented schematically in Figure B1. Mixture of NaCrO_2 , Na_2CO_3 and Cr_2O_3 with a mole ratio of 1:1:1 was placed in an Al_2O_3 boat covered by silver foil, then the boat was put in the reaction tubing in the glove box in order to avoid the formation of $\text{Na}(\text{HCO}_3)_2$ by reaction of Na_2CO_3 with H_2O and CO_2 in the air. After the whole apparatus was made airtight and isolated from the atmosphere, the sample was initially heated under vacuum with both mercury columns at the same level. CO_2 pressures in mm Hg were recorded at each given temperature when the level of the mercury column no longer changed with time. Since the melting point of Na_2CO_3 is 850°C , the temperature range which can be employed is from 600°C to 840°C .

Both Vycor and stainless steel tubing were used to contain the reactants. The data obtained were plotted as $\Delta G_{\text{Rxn}}^{\circ}$ as a function of temperature, $^\circ\text{K}$, as shown in Figure B2. The line drawn is a least squares fit to the data. The equations

Figure B1. Schematic diagram of the apparatus for CO₂ pressure measurements

Figure B2. Calculated ΔG°_{RXN} from measured CO_2 pressure versus temperature

of $[A+BT(^{\circ}K)] + C$ are given in Table B1.

According to the Equation B1, the corresponding equations for the free energy of formation of NaCrO_2 can be obtained by the following relation:

$$\Delta G_f^{\circ}[\text{NaCrO}_2] = \frac{1}{2}\{\Delta G_{\text{Rxn}}^{\circ} - \Delta G_f^{\circ}[\text{CO}_2] + \Delta G_f^{\circ}[\text{Na}_2\text{CO}_3] + \Delta G_f^{\circ}[\text{Cr}_2\text{O}_3]\}. \quad (\text{B7})$$

The values of $\Delta G_f^{\circ}[\text{CO}_2]$, $\Delta G_f^{\circ}[\text{Na}_2\text{CO}_3]$ and $\Delta G_f^{\circ}[\text{Cr}_2\text{O}_3]$ are known as listed in Table 5 of this thesis, the values of $\Delta G_f^{\circ}[\text{NaCrO}_2]$ were hence obtained as summarized in Table B2.

The $\Delta S_{\text{NaCrO}_2}^{\circ}$ arises from the relation of $-\Delta S^{\circ} = dG^{\circ}/dT$ are given 0.05684 and 0.05895 in the unit of Kcal/mole- $^{\circ}K$, the values of $\Delta H_f^{\circ}[\text{NaCrO}_2]$ are given -213.2 and -215 in the unit of Kcal/mole.

Table B1. $\Delta G_{\text{Rxn}}^{\circ}$ versus temperature equations for the reaction of $\text{Na}_2\text{CO}_3 + \text{Cr}_2\text{O}_3 \rightarrow 2\text{NaCrO}_2 + \text{CO}_2$

Reactor	Temperature range $^{\circ}\text{K}$	Equation, $\Delta G_{\text{Rxn}}^{\circ} (\text{Kcal}) = [A + BT(^{\circ}\text{K})] \pm C$
Vycor tubing	809-1053	$\Delta G_{\text{Rxn}}^{\circ} = [16.150 - 1.329 \times 10^{-2}T] \pm 0.125$
Stainless steel tubing	770-1073	$\Delta G_{\text{Rxn}}^{\circ} = [12.517 - 9.08 \times 10^{-3}T] \pm 0.059$

Table B2. Free energies of formation of NaCrO_2 , Kcal/mole

Reactor	Temperature range $^{\circ}\text{K}$	Equation, $\Delta G_f^{\circ} [\text{NaCrO}_2] = [A + BT(^{\circ}\text{K})] \pm C$
Vycor tubing	809-1053	$\Delta G_f^{\circ} [\text{NaCrO}_2] = [-213.21 + 5.684 \times 10^{-2}T] \pm 0.978$
Stainless steel tubing	770-1073	$\Delta G_f^{\circ} [\text{NaCrO}_2] = [-215.02 + 5.895 \times 10^{-2}T] \pm 0.486$