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March 1970

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ELECTROCHEMICAL STUDIES IN GLASS
I: THE SYSTEM $NiO-Na_2Si_2O_5$

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March 1970

ABSTRACT

A solid electrolyte electrochemical cell of the type $Pt|Ni:NiO_{a=1}||ZrO_2 + 7.5\%\ CaO||Ni:NiO_{a<1} + glass|Pt$ has been utilized to measure the activities of NiO in sodium disilicate glass over the temperature interval from 750 to 1100°C. The data indicates a solubility varying from 11 mole percent (5.0 wt%) at 800° to 20 mole percent (9.3 wt%) at 1100°C. From the variation in NiO activity, the activity of sodium disilicate in glass solution has been estimated; and from these combined data partial molar free energies and entropies of solution of NiO and $Na_2Si_2O_5$, and free energies and entropies of mixing have been calculated. A partial phase diagram for the system $NiO-Na_2Si_2O_5$ is proposed from solubility data indicating a eutectic at approximately 12 mole percent (5.3 wt%) NiO at 830°C.

This work was done under the auspices of the U. S. Atomic Energy Commission.

At the time this work was done the writers were, respectively, graduate research assistant and professor of ceramic engineering.

Based on part of the thesis submitted by Alton M. Lacy for the Ph.D. degree in ceramic science at the University of California, Berkeley, Sept. 1969.

I. INTRODUCTION

The ability to predict and understand reactions occurring between materials of any system requires a knowledge of the thermodynamic properties of the constituents. In the development of a chemical bond between glass and metal, Pask and co-workers[1-3] have shown that a necessary criterion for maximum bond strength is the establishment of a condition of saturation of the glass by the oxide of the metallic substrate. Equilibrium compositions can also develop at the interface by redox reactions between dissolved oxides in the glass and the metal substrate. The extent to which any reaction will occur is dependent upon the imbalance of chemical potentials of the constituents in the reacting phases. The stability of glasses in oxidizing or reducing atmospheres, as well as the kinetics of diffusion-controlled reactions are dependent upon the activities of constituents in glasses relative to activities of the same components elsewhere in the system of interest. This work has been undertaken to establish quantitatively the compositional dependence of activities of some "adherence oxides" in sodium disilicate glass (NS_2) in order that we may improve our understanding of this glass as a reactive constituent in bonding and wetting studies.

Those activity measurements on molten silicates reported in the literature have been made principally on binary metal oxide-silica systems and on multicomponent slags. Most of these have been carried out by gas equilibration techniques. An electrochemical method is often preferable because of the wider range of oxygen potentials capable of being measured accurately. The number of electrochemical studies of glasses reported is, however, relatively small.

Herring[4] and Didtshenko and Rochow[5] have used cells of the type O_2(Pt)/liq I::liq II/O_2(Pt) in order to determine the activities of Na_2O in soda-silica glasses and of Na_2O, K_2O and Li_2O in PbO-SiO_2 glasses respectively. This type of cell is not generally suitable for quantitative measurements because of the inherent possibilities for error arising from undefined thermoelectric emf's, liquid junction potentials, poorly defined cell reactions and indeterminant transferrence numbers of the conducting species. Esin[6] has utilized a simple formation cell of the type M/MO (in glass sol'n)/O_2 to measure activities of FeO in complex silicate melts. Unknown transference numbers and questionable reversibility also present problems in these measurements. Matsushita and Goto[7] and Charette and Flangas[8] have carried out studies of the oxide activities in the PbO-SiO system between 900-1100°C using a solid electrolyte cell of the type Ni/NiO//CSZ†//Pb/PbO + SiO_2. Their data corresponds well with that of Richardson and Webb[9] obtained by other methods.

We are presenting here the first part of a current series of electrochemical studies of the activities of the transition metal oxides NiO, $Fe_{0.47}$ and CoO in sodium disilicate glass.

II. EXPERIMENTAL

A schematic diagram of the experimental set-up is illustrated in Fig. 1. The cell arrangement was constructed by positioning a 6" calcia-stabilized zirconia tube* in a Coors CN-5 alumina crucible containing a tightly packed Ni/NiO mixture. The Ni powder was certified chemically

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† CSZ refers to 0.15 CaO·0.85 ZrO_2

* Obtained from Zirconium Corporation of America, Solon, Ohio.

pure by A. D. Mackay Co. Inc., and the NiO was a Baker's analyzed reagent. The electrodes were 20 mil Pt wire--the outer wire doubly wound around the lower portion of the zirconia electrolyte tube and twisted tightly to secure it, and the inner electrode was coiled on one end and pushed to the bottom of the tube. Approximately 1-1/2 grams of $xNiO \cdot Na_2O \cdot 2SiO_2$ glass was put into the tube with a small quantity of powdered Ni metal. A boron nitride plug with a 25 mil hole was placed over the upper end of the tube to prevent the Pt electrode from touching the tube walls at any point above the glass surface. In the latter stages of the experimental program, the outer electrode was contained in a short piece of mullite thermocouple protection tubing which penetrated the surface of the Ni/NiO mixture. The remaining exposed surface of the Ni/NiO powder was sealed off from the ambient atmosphere by covering it with a powdered sodium disilicate glass containing 7.55% NiO plus excess Ni metal. It was found that the e.m.f. output of a cell was not altered but that the cells were stabilized for longer periods of time, increasing the precision of the measurements.

The assembly shown in Fig. 1 was then seated in a Pt basket and suspended on a push rod containing a thermocouple and the electrodes leading to the recorder. After sealing in a resistance wound furnace, the system was pumped out to approximately 10^{-5} mm Hg. ($\sim 2 \times 10^{-8}$ atm O_2) and the cell was lowered in vacuo into the hot zone of the furnace. After one minute, argon was introduced into the furnace and the ambient pressure was brought up to 1 atm. After one hour, measurements of the generated e.m.f. were taken. Although a tendency existed for some of the residual oxygen in the system to be picked up by the Ni metal in the glass, this

presented no significant problem, since the quantity of oxygen was not large enough after evacuation to significantly alter the composition of the glass even if it were primarily absorbed into the glass; and secondly, the quantity of Ni metal exposed to the ambient atmosphere was substantially greater in the outer electrode compartment than inside the tube. Quantitative electron microprobe analysis after operation of the cell indicated no change in the glass composition due to Ni oxidation and subsequent solution.

The e.m.f. output was recorded by a Honeywell Electronik 19 high impedance potentiometric recorder. All cells were run for a minimum of 2 days. Over this time, the temperature was varied between 750-1100°C.

The reversibility of the cell was inferred from the reproducible behavior of several cells containing the same glass, and also by the tendency for the cell to return to the same e.m.f. value when disturbed by a temporary short circuit or by impressing a small voltage via a potentiometer.

III. RESULTS AND DISCUSSION

(1) Thermodynamic Data

Since measurements were made by using a cell of the type $Ni/NiO//CSZ//Ni/NiO_{a<1} + NS_2$, the overall cell reaction may be expressed as

$$NiO(solid)_{a=1} = NiO(glass)_{a<1} \qquad (1)$$

At equilibrium in a reversible cell, the free energy of this reaction may be related to the cell potential by the expression

$$\Delta F = -nFE = RT(2.303)\log(a_{NiO}). \qquad (2)$$

The activity of NiO in the glass (relative to pure solid NiO may therefore be directly calculated from (2) as

$$a_{NiO} = \exp(-nFE/2.303RT), \qquad (3)$$

where F = Faraday's constant (23,061 cal/volt), E = the cell output in volts, R = the gas constant (1.987 cal/°C), T = absolute temperature, and n = the number of electrons transferred in the cell reaction (in this case, two).

The isocompositional cell output vs. temperature is shown in Fig. 2. Each line represents the average of a minimum of two experimental determinations for each glass composition. The uncertainty is ±2 mv. The variation of a_{NiO} with temperature for each composition is shown in Fig. 3, and the [illegible] activity-composition curves are given in Fig. 4 for several temperatures.

The activity of NS_2 in the glass relative to pure liquid NS_2 may be found by calculating the activity coefficient, γ_{NS_2} (where $\gamma_{NS_2} \equiv a_{NS_2}/N_{NS_2}$), from integration of the Gibbs-Duhem equation

$$\ln \gamma_{NS_2} = \int_{N_{NS_2}=1}^{N_{NS_2}} \frac{N_{NiO}}{N_{NS_2}} \, d \ln \gamma_{NiO} \qquad (4)$$

The calculated activities of NS_2 are shown in Fig. 5. Over this small concentration range, the experimental uncertainty is too large to distinguish precisely the temperature variation of the activity of NS_2, hence a single line is drawn with an estimated uncertainty for all temperatures of 2%.

The partial molar quantities for the solution of pure solid NiO and pure liquid NS_2 in glass may be calculated from the following expressions:

$$\Delta\bar{F}_{oxide} = -RT \ln a_{oxide}, \tag{5}$$

$$\Delta\bar{S}_{oxide} = -\left(\frac{\partial\Delta\bar{F}}{\partial T}\right)_p, \text{ and} \tag{6}$$

$$\Delta\bar{H}_{oxide} = \Delta\bar{F}_{oxide} + T\Delta\bar{S}_{oxide} = -nF\left[E - T\left(\frac{\partial E}{\partial T}\right)_p\right] \tag{7}$$

where E is the cell output in volts. The partial molar data for the glass studied here is presented in Table 1. Free energies, entropies and enthalpies of mixing of pure NiO and NS_2 may be calculated from the general expression

$$N_1\bar{X}_1 + N_2\bar{X}_2 = \Delta X_{mix},$$

where N_1, N_2 are the mole fractions of each component, and X is the thermodynamic property of interest. Mixing data are presented in Table II.

(2) Solubility Limits

For any temperature, the composition in which the activity of NiO equals unity represents the saturation solubility of NiO. By extension of the isothermal activity-composition curves (Fig. 4) to $a_{NiO} = 1$, the

equilibrium solubility limits can be estimated. Similarly, extension of e.m.f.-temperature curves (Fig. 2) to E=0 will produce the same information.

The NS_2 liquidus was determined by the intersection of the experimentally calculated a_{NS_2} vs temperature plots, with the plot of the activity of pure solid NS_2 relative to the pure liquid standard state. The data for this determination was taken from the compilations of Kelley.[10] The graphical analysis is shown in Fig. 6.

Since no compounds along the join NiO-NS_2 are known to the authors, the solubility data determined from these data are presented in the tentative phase diagram of Fig. 7. Intersection of these two liquiduses indicates a eutectic at N_{NiO} = 0.12 (5.28 wt%) at a temperature of approximately 830°C. The broken curves in Fig. 7 are interpolated.

IV. SUMMARY

The solid electrolyte electrochemical method has been shown to be adaptable to studies on the solution of nickel oxide in sodium disilicate glass, providing numerical thermodynamic data as well as information concerning the phase diagram, in the absence of direct observation of crystalline products.

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Table I. Activity and partial molar free energy data for the solution of NiO in sodium disilicate glass

N_{NiO}	a_{NiO}				$\overline{\Delta F}_{NiO}$ (cal/mole)				N_{NS_2}	a_{NS_2}	$\overline{\Delta F}_{NS_2}$ (cal/mole)				$\overline{\Delta S}_{NiO}$*	$\overline{\Delta S}_{NS_2}$*
	800°	900°	1000°	1100°	800°	900°	1000°	1100°			800°	900°	1000°	1100°		
.015	.17	.11	.075	.050	-3780	-5150	-6550	-8170	.985	.99	- 20	- 20	- 25	- 30	15.2	.03
.027	.27	.17	.12	.080	-2790	-4130	-5360	-6890	.973	.98	- 40	- 50	- 55	- 60	13.3	.07
.053	.45	.29	.20	.14	-1700	-2890	-4070	-5360	.947	.96	- 60	- 70	- 80	- 90	10.8	.10
.076	.63	.42	.31	.22	- 990	-2020	-2960	-4130	.924	.93	-150	-170	-180	-200	9.7	.15
.099	.86	.59	.43	.32	- 320	-1230	-2130	-3110	.901	.90	-220	-250	-270	-290	9.0	.22
.109	1.00	.68	.50	.38	0	- 900	-1750	-2640	.891	.88	-270	-300	-320	-340	8.8	.25
.116	----	.74	.54	.42	-----	- 700	-1560	-2370	.884	.87	----	-330	-350	-380	8.5	.30
.127	----	.86	.62	.48	-----	- 350	-1210	-2000	.873	.85	----	-380	-410	-440	8.2	.40
.139	----	1.00	----	---	-----	0	-----	-----	.861	.83	----	-430	----	----	----	---
.149	----	----	.80	.62	-----	-----	- 560	-1300	.851	.82	----	----	-470	-510	----	---
.170	----	----	1.00	---	-----	-----	0	-----	.830	.77	----	----	-500	----	----	---
.200	----	----	----	1.00	-----	-----	-----	0	.800	---	----	----	----	-710	----	---

* Entropy data given in (cal/mole·°K).

Table II. Mixing data for the $NiO-Na_2Si_2O_5$ system

N_{NiO}	N_{NS_2}	ΔF_{mix} (cal/mole)				ΔS^*_{mix}
		800°	900°	1000°	1100°	
.015	.985	- 76	- 97	-123	-152	.26
.027	.973	-114	-160	-198	-244	.43
.053	.947	-147	-219	-291	-369	.67
.076	.924	-214	-311	-391	-499	.95
.099	.901	-230	-347	-454	-569	1.10
.109	.891	-241	-365	-476	-591	1.19
.116	.884	----	-373	-490	-611	1.25
.127	.873	----	-376	-512	-638	1.39
.139	.861	----	-370	----	----	----
.149	.851	----	----	-483	-628	----
.170	.830	----	----	-415	----	----
.200	.800	----	----	----	-568	----

* Entropy data given in (cal/mole·°K).

FIGURE CAPTIONS

Figure 1. Schematic diagram of the experimental cell assembly

Figure 2. Isocomposition cell output for $NiO-NS_2$ glasses as a function of temperature (±2 mv).

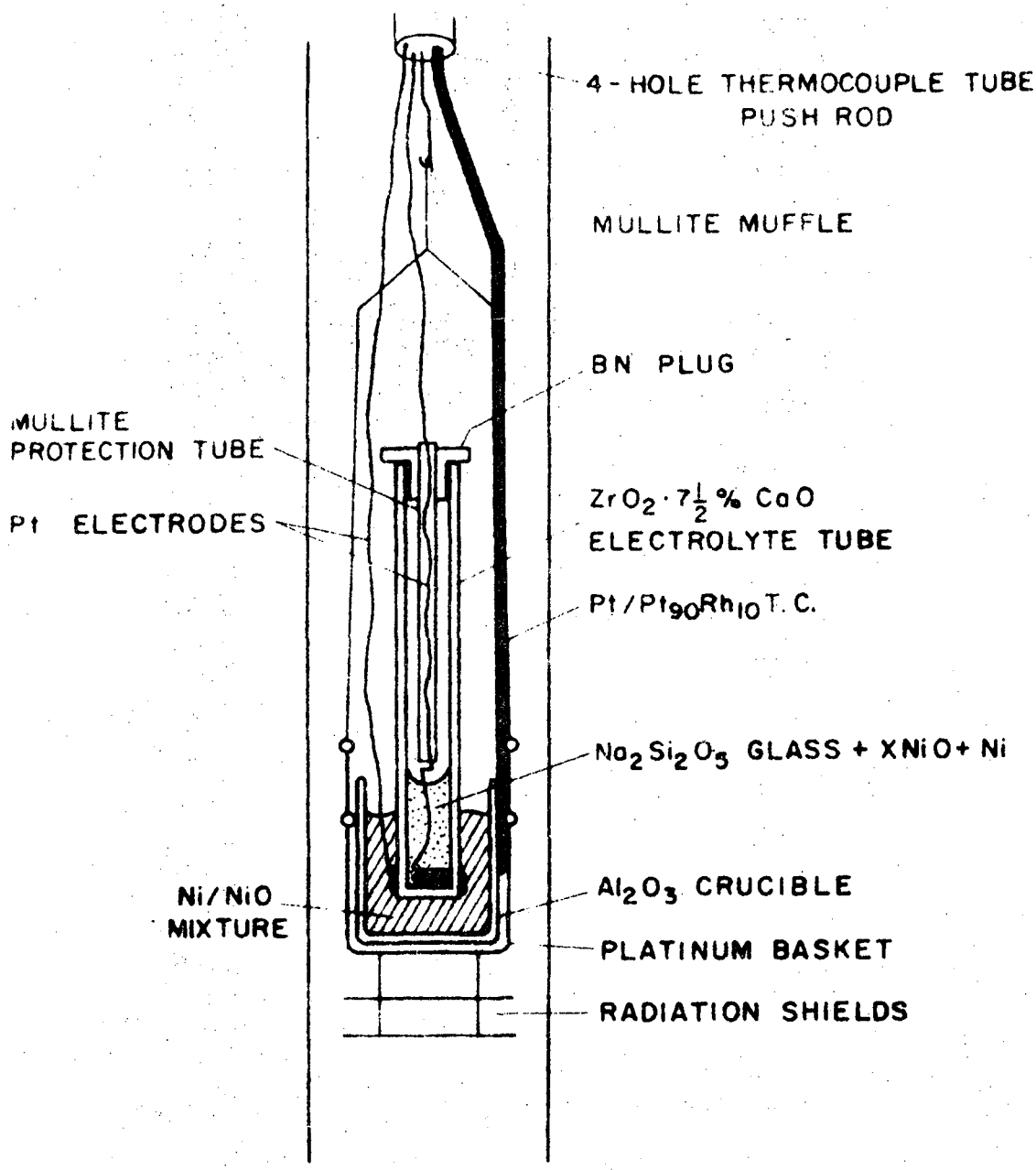
Figure 3. Variation in the activity of NiO (referred to the pure solid standard state) with temperature for each composition studied.

Figure 4. Isothermal dependence of NiO activity (referred to the pure solid standard state) on composition.

Figure 5. Activity of NS_2 (referred to the liquid standard state) calculated from integration of the modified Gibbs-Duhem equation. (One curve is drawn to represent all temperatures between 800° and 1100°C. Over this small range of concentration, the experimental uncertainty is too large to distinguish precisely the temperature variation on activity of NS_2). The estimated uncertainty in these data is 2%.

Figure 6. Isocompositional activity plots for NS_2 for determination of the NS_2 liquidus in the $NiO-NS_2$ system.

Figure 7. Proposed phase diagram for the $NiO-NS_2$ system.



XBL 692-225

Fig. 1

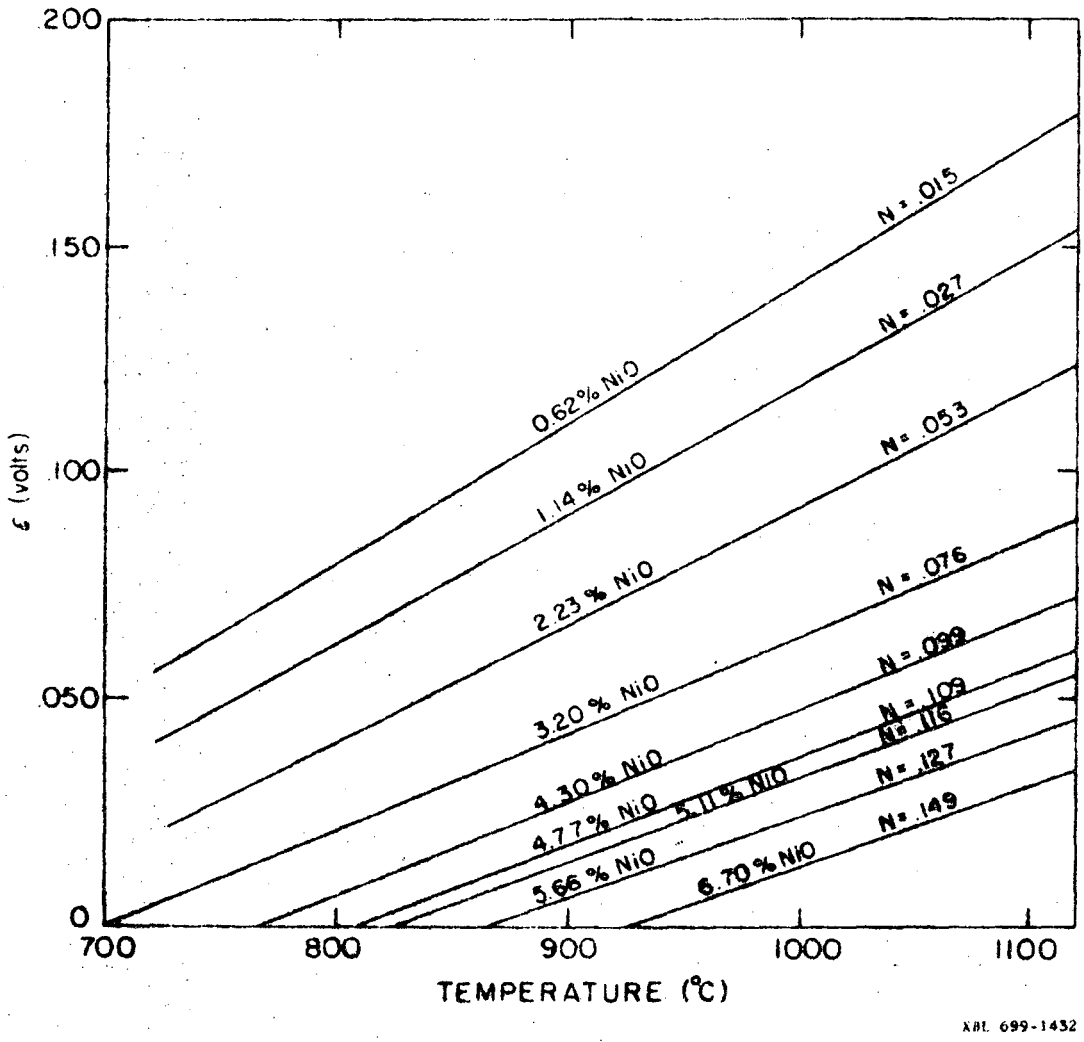

200
150
100
050
0
700
800
900
1000
1100
TEMPERATURE (°C)
ε (volts)
0.62% NiO
1.14% NiO
2.23% NiO
3.20% NiO
4.30% NiO
4.77% NiO
5.11% NiO
5.66% NiO
6.70% NiO
N = .015
N = .027
N = .053
N = .076
N = .099
N = .109
N = .116
N = .127
N = .149
XBL 699-1432

Fig. 2

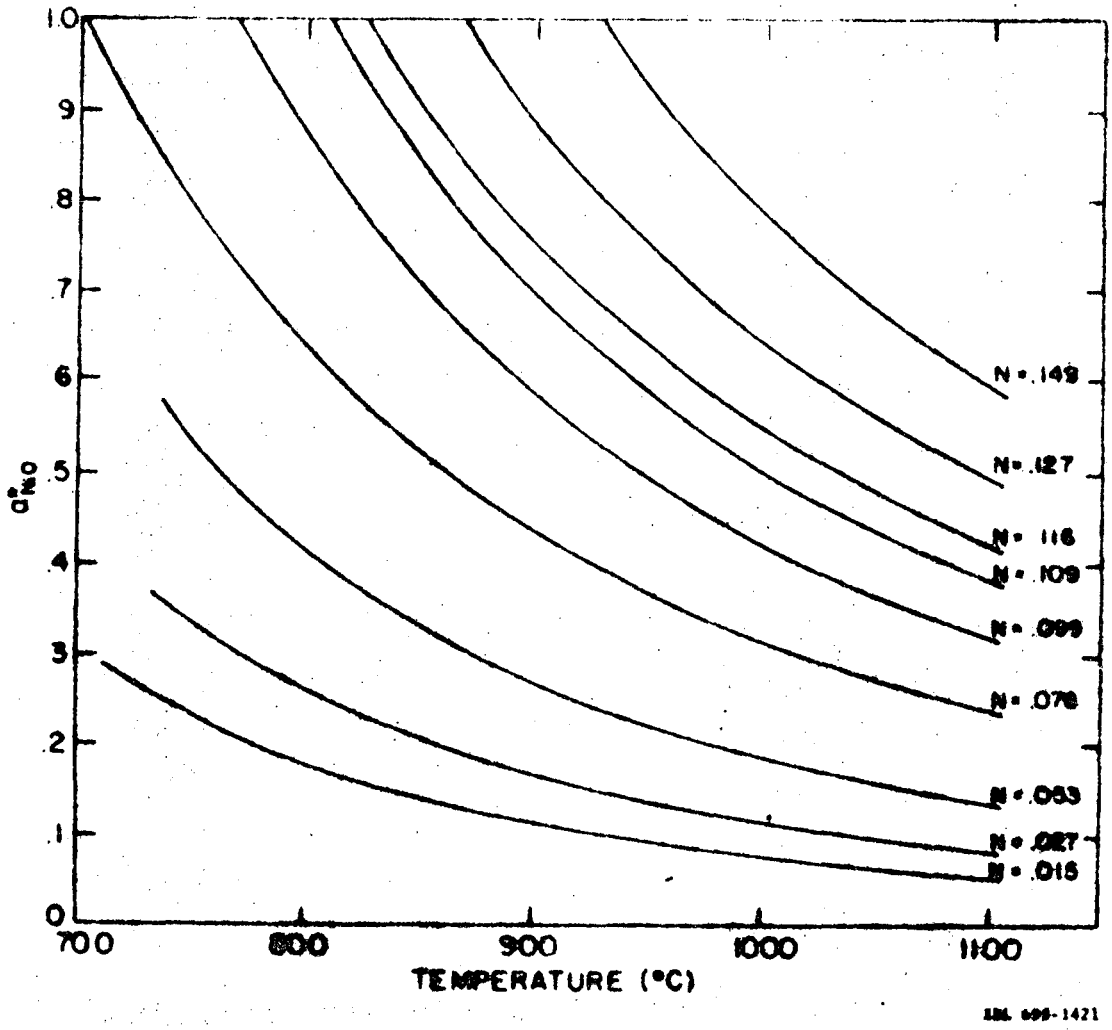

1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
a^{o}_{NiO}
700
800
900
1000
1100
TEMPERATURE (°C)
N = .149
N = .127
N = .116
N = .109
N = .099
N = .078
N = .053
N = .027
N = .015

Fig. 3

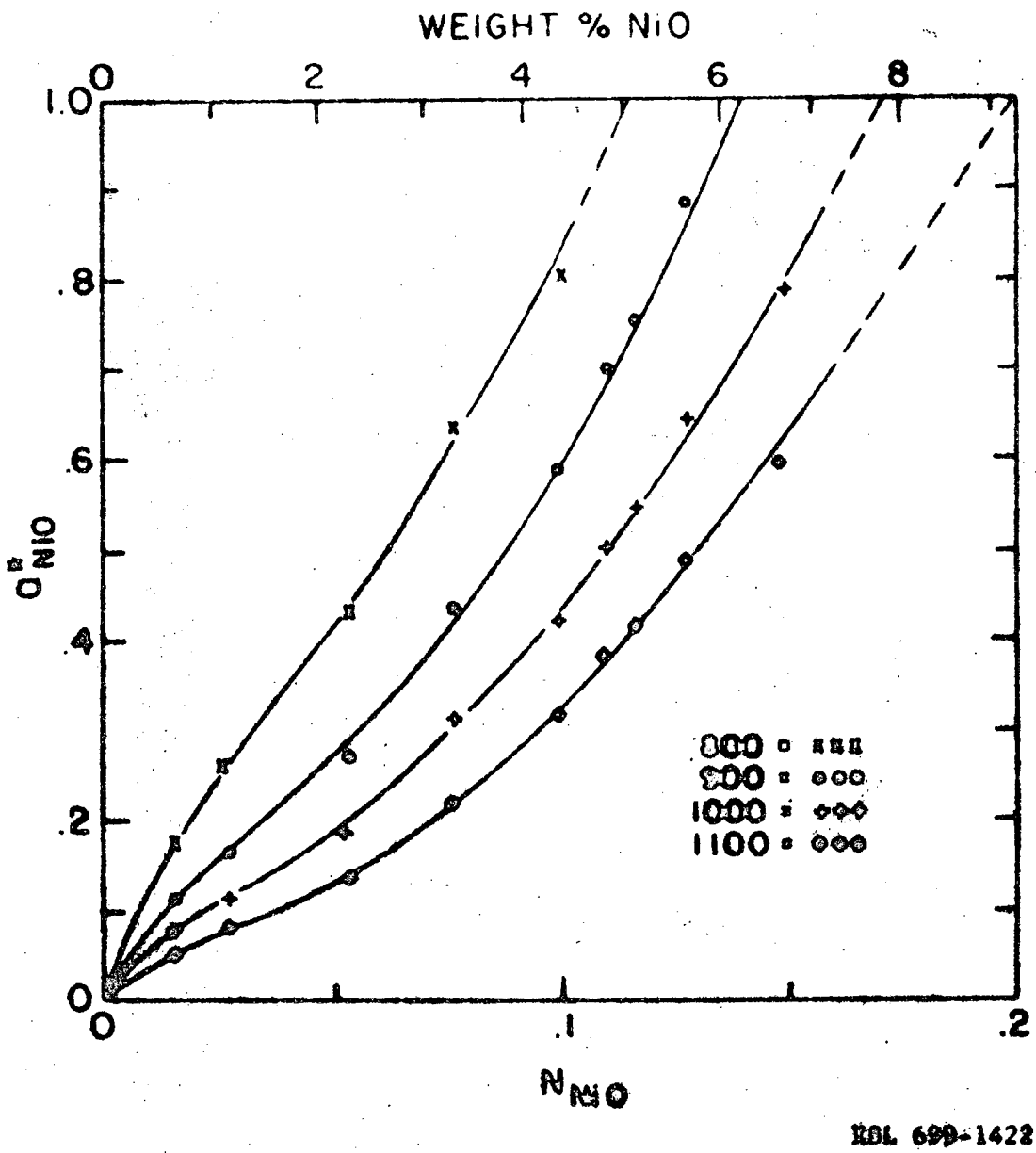


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Fig. 4

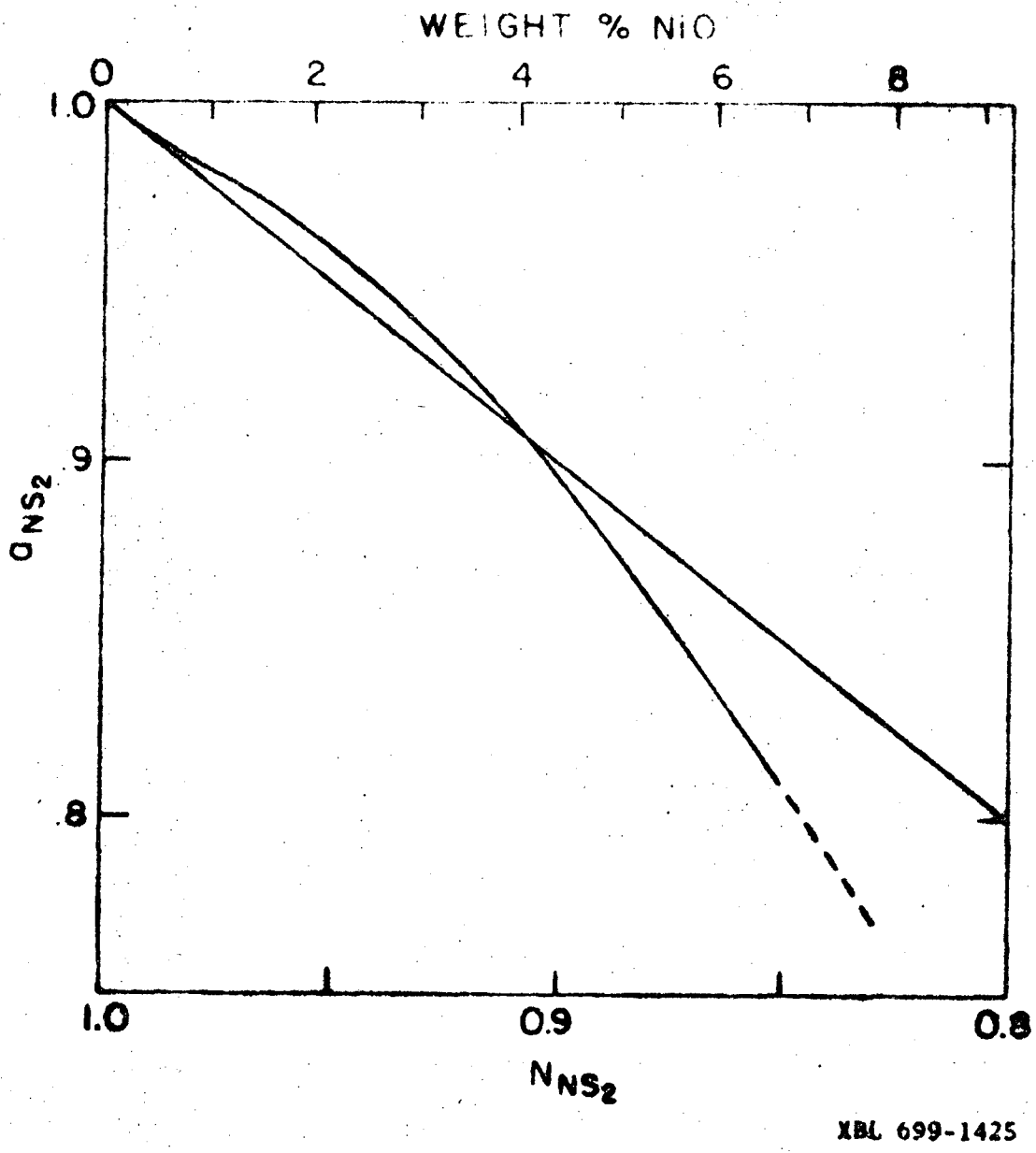

Fig. 5

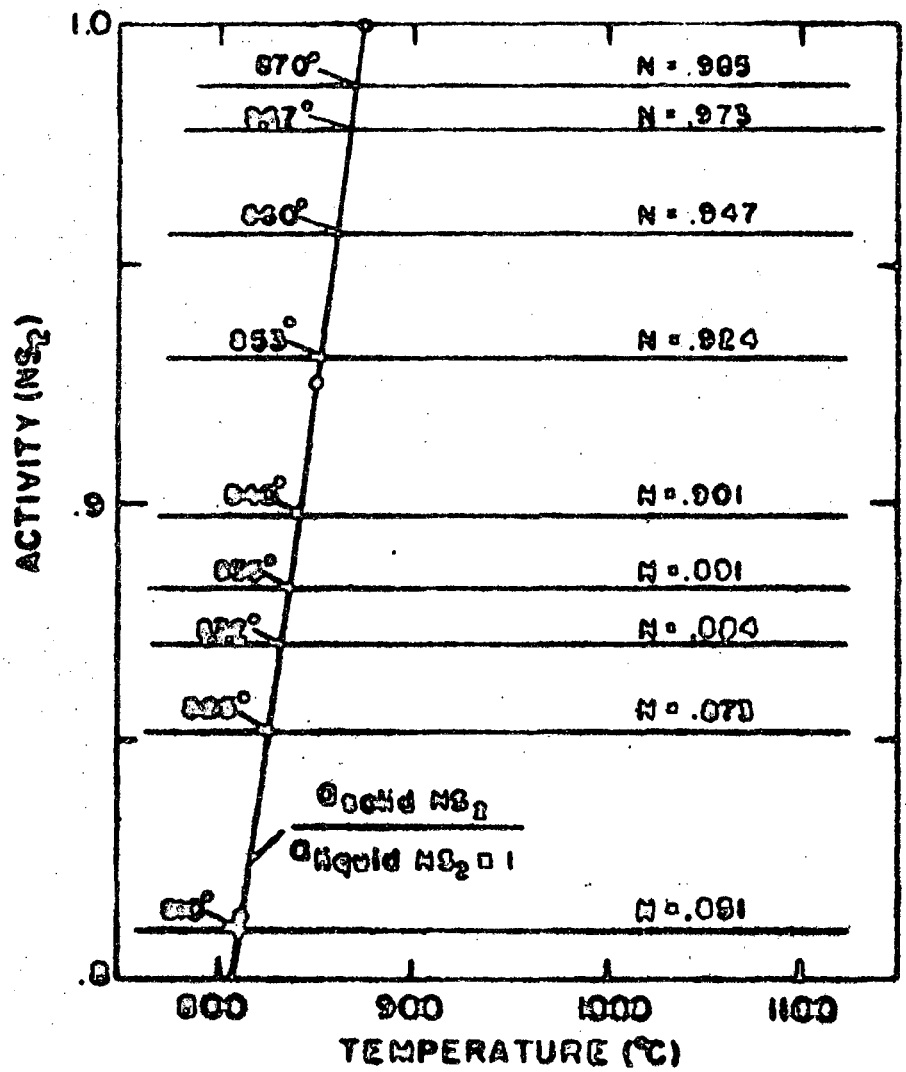

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Fig. 6

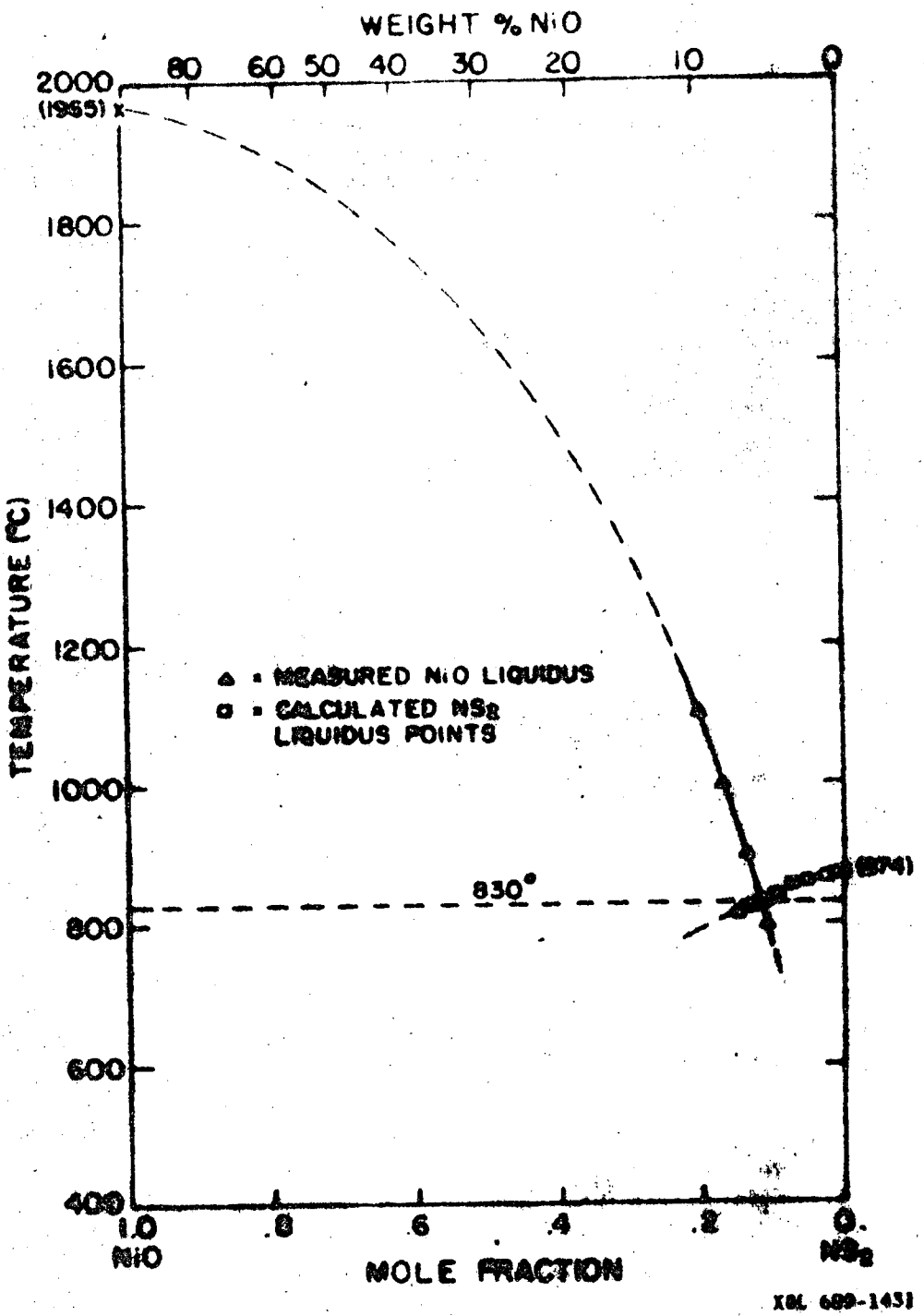
WEIGHT % NiO
80
60
50
40
30
20
10
0
2000
(1955)
1800
1600
1400
1200
1000
800
600
400
TEMPERATURE (°C)
△ = MEASURED NiO LIQUIDUS
□ = CALCULATED NiS LIQUIDUS POINTS
830°
1.0
NiO
.8
.6
.4
.2
0.
NiS
MOLE FRACTION
XBL 689-1431

Fig. 7

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