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ELECTROCHEMICAL STUDIES IN GLASS:

III, THE SYSTEM $\text{CoO-Na}_2\text{Si}_2\text{O}_5$

Alton M. Lacy and Joseph A. Pask

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ABSTRACT

December 1970

A solid electrolyte electrochemical cell of the type $\text{Pt}|\text{Ni:NiO}_{a=1}||\text{ZrO}_2 + 7.5\% \text{CaO}||\text{Co:CoO}_{a<1} + \text{Na}_2\text{Si}_2\text{O}_5 \text{ glass}|\text{Pt}$ has been used to measure the activities of cobalt(ous) oxide in $\text{Na}_2\text{Si}_2\text{O}_5$ glass over the temperature interval $700^\circ\text{-}1100^\circ\text{C}$. From the variation in CoO activity, the activity of NS_2 glass in solution has been calculated. Partial molar free energies and entropies of solution, as well as free energies and entropies of mixing of these components have been calculated from activity data. A partial phase diagram for the $\text{CoO-Na}_2\text{Si}_2\text{O}_5$ system has been proposed from solubility data acquired in this study. The solubility of CoO in $\text{Na}_2\text{Si}_2\text{O}_5$ glass varies from 44 to 52 mole % (~ 24 to 31 wt%) over this temperature range. Comparison of partial molar entropies of $\text{Fe}_{.95}\text{O}$, CoO and NiO in glass solution suggests that the structure is basically the same for a given O/Si ratio. Solubility limits are determined by the relative strengths of the -cation-O-cation- and -Si-O-cation- bond assemblages.

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

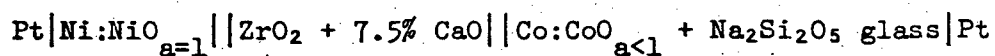
Based on part of a thesis submitted by Alton M. Lacy for the Ph.D. degree in ceramic science at the University of California, Berkeley, Sept. 1969.

I. INTRODUCTION

It is well known that the presence of cobalt oxide in the glass at the interface of enameled iron promotes adherence of the glass to the metal. This phenomenon is due to the redox reaction of the oxide with the base metal to form iron oxide in the glass at the interface which contributes to the development and maintenance of a chemical bond; the corresponding roughening of the metal and growth of cobalt-iron alloy dendrites into the glass contribute to adherence by some mechanical anchoring of the glass to the base metal. Since the strength of the glass-metal bond depends upon the nature of the reactions, the rate of these interfacial reactions, and the degree to which they proceed to completion, it is necessary to have thermodynamic activity data available in order to quantitatively assess the extent to which reactions will occur between metal oxides in glass solution and the base metal. In parts I and II of this series, the authors have presented thermodynamic data for NiO- and $\text{Fe}_{0.95}\text{O}-\text{Na}_2\text{Si}_2\text{O}_5$ solutions at elevated temperatures.^{1,2} In this paper, we present similar data for the system $\text{CoO}-\text{Na}_2\text{Si}_2\text{O}_5$ and discuss some structural implications.

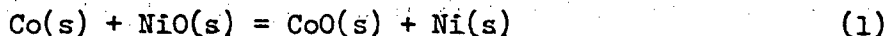
II. EXPERIMENTAL

Experimental measurements were made using an electrochemical cell with a solid electrolyte of the type



over the temperature interval from 700-1100°C. Details of cell construction and operation have been given in part I of this series.¹ In

addition, a cell of similar design was constructed but which contained a mixture of Co/CoO in the inner electrode compartment in place of the glass mixture. The overall cell reaction for this cell can be written as

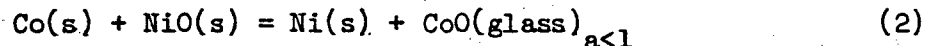


Its e.m.f. output was compared with that calculated from tabulated thermodynamic data of Elliott and Gleiser³ in order to verify the proper operation of the cell as constructed; the agreement was ± 1 mv. Furthermore, the cell output established the reference e.m.f. which corresponded to unit activity of CoO in the glass.

III. RESULTS AND DISCUSSION

(1) Thermodynamic Data

The total cell reaction for the experimental arrangement may be expressed as



The free energy of this reaction may then be written as

$$\Delta F = \Delta F^\circ + RT \ln (a_{\text{CoO}}) \quad (3)$$

if we define pure solid Ni, Co and NiO as the standard states. From the equality

$$\Delta F = -nFE \quad (4)$$

where n = the number of electrons transferred in each half-cell reaction (in this case, 2), \mathcal{F} = Faraday's constant (23,061 cal/V), and E = the cell output (V), Eq. (3) may be rewritten as

$$- n\mathcal{F}E = - n\mathcal{F}E^{\circ} + RT \ln (a_{\text{CoO}}) \quad (3a)$$

where E° is the output from the cell described by Eq. (1). From Eq. (3a) the activity of CoO dissolved in the glass solution (relative to the pure solid oxide standard state) may then be expressed as

$$a_{\text{CoO}} = \exp (- n\mathcal{F}[E-E^{\circ}]/RT). \quad (5)$$

The e.m.f. output for all cells vs temperature is presented in Fig. 1. The experimental uncertainty in each curve is ± 2 mv. The isothermal variation in activity of CoO with composition is given in Table I and Fig. 2. The activity of NS_2^* in solution relative to pure liquid NS_2 (Fig. 3) was calculated by applying the activity-composition data to the integral form of the Gibbs-Duhem equation as follows:

$$\ln \gamma_{\text{NS}_2} = - \int_{N_{\text{NS}_2}=1}^{N_{\text{NS}_2}} \frac{N_{\text{CoO}}}{N_{\text{NS}_2}} d \ln \gamma_{\text{CoO}} \quad (6)$$

where γ = activity coefficient.

* NS_2 is used throughout to designate $\text{Na}_2\text{Si}_2\text{O}_5$.

Partial molar thermodynamic quantities for the solution of solid CoO and liquid NS₂ may be evaluated from the following expressions:

$$\Delta\bar{F}_{\text{oxide}} = -RT \ln (a_{\text{oxide}}) = -RT \ln N\gamma_{\text{oxide}} \quad (7)$$

$$\Delta\bar{S}_{\text{oxide}} = - \left(\frac{\partial \Delta\bar{F}}{\partial T} \right)_p, \text{ and} \quad (8)$$

$$\Delta\bar{H}_{\text{oxide}} = \Delta\bar{F}_{\text{oxide}} + T\Delta\bar{S}_{\text{oxide}} = -n \int \left[E - T \left(\frac{dE}{dT} \right)_p \right]. \quad (9)$$

The partial molar free energies and entropies for the solution of CoO and NS₂ are presented in Table I. The partial molar entropy values for CoO solutions are illustrated in Fig. 4 along with similar values for the solutions of NiO and Fe_{0.95}O in NS₂ as calculated from data in parts I and II.

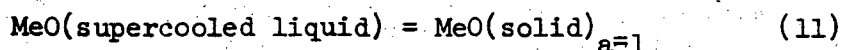
Free energies, entropies and enthalpies of mixing may be calculated from partial molar data from the general expression

$$N_1\bar{X}_1 + N_2\bar{X}_2 = \Delta X_{\text{mix}} \quad (10)$$

where N_1 and N_2 are the mole fractions of each component, and X is the thermodynamic property of interest. Free energies and entropies of mixing of CoO and NS₂ are given in Table II.

For purposes of structural interpretation of deviations from ideal solution behavior, the activity of the oxides may be referred to a

hypothetical supercooled liquid standard state by consideration of the reaction



at some temperature of interest below the normal melting point (T_f) where Me represents Fe, Co, or Ni. The free energy of this reaction may be expressed as

$$\Delta F_{\text{reaction}} = RT \ln \frac{a_{\text{solid}}}{a_{\text{liquid}}} = RT \ln K \quad (12)$$

Since heat capacity data for such hypothetical supercooled liquids are not available, it is necessary to assume their equality at temperatures below T_f . As a first approximation, the value K may be related to the heat of fusion (ΔH_f) of these oxides by the relation

$$\ln K = - \frac{\Delta H_f}{RT} \left(1 - \frac{T}{T_f} \right). \quad (13)$$

Data pertinent to this calculation is presented in Table III.

Activities of the oxides relative to the pure solid standard state may be simply converted to those relative to the pure supercooled liquid standard state by multiplication of the former by K.

(2) Solubility Limits and Phase Equilibria

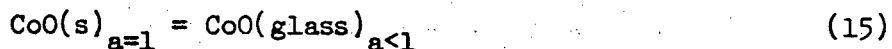
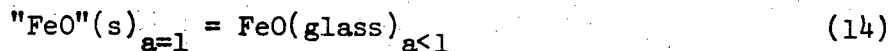
The saturation solubility of CoO in NS_2 ($a_{\text{CoO}} = 1$) may be determined by noting the composition of CoO in solution at which the cell output is equal at the same temperature to the e.m.f. of the cell containing the

mixture of solid Co/CoO. As can be seen from Fig. 2, the values of saturation of CoO at 800, 900, 1000, and 1100°C were 24, 26, 28 and 31 wt%, respectively. These values correspond to mole fractions of CoO of 0.44, 0.46, 0.48 and 0.52.

The solubility of NS₂ may be determined by plotting the calculated activities of NS₂ relative to the pure liquid standard state and the activity of liquid NS₂ relative to pure solid NS₂ (as determined from tabulated data of Kelley.⁴) The points of intersection of the experimental curves and the calculated curve indicate solubility compositions and temperatures for NS₂. This plot is shown in Fig. 5. The solubility data, presented in terms of a proposed phase diagram, for both CoO and NS₂ are given in Fig. 6. The intersection of the two liquidus lines indicates a eutectic at 21.5 wt% CoO ($N_{\text{CoO}} = 0.40$) and 630°C. Although a simple eutectic diagram appears to be the most probable, in the absence of a phase diagram for the CoO-Na₂O-SiO₂ system the possibility of an unidentified ternary compound analogous to that postulated for the "FeO"-Na₂O-SiO₂ system² should be recognized.

(3) Partial Molar Entropy and Structural Considerations

Comparison of the plots of partial molar entropy of dissolution of Fe_{0.95}O, CoO, and NiO as functions of composition (Fig. 4) reveals similar behavior, in that the curves within corresponding composition ranges are essentially parallel to each other. If no basic structural change were occurring in the glass with an increase of the amount of the modifying oxide, then the probability for any one modifying cation site being available for an equivalent cation would decrease, and a continuous decrease in the entropy for the reactions



would be expected. The upswing in the curves for "FeO" and CoO at a mole fraction of about 0.3, O/Si ratio about 2.75, is indicative of significant structural changes beginning to occur in the glass with further increase of the O/Si ratio. At this point, the average number of silicon tetrahedra sharing 2 corners (bridging oxygens) with other tetrahedra is becoming greater than the number sharing 3 corners. The subsequent decrease in entropy with additions of "FeO" beyond a mole fraction of about 0.5, O/Si ratio of 3.0, again indicates no further major change in the structure of the glass. At this point, the three-dimensional silica network has broken down since the structure corresponds to one wherein, on an average, each silicon tetrahedron is sharing only 2 corners.

The parallel behavior of these curves suggests that the structure is basically the same for a given O/Si ratio and that the atomic structure may be considered to be isomorphous for a given mole fraction of transition metal oxide. Consequently, the solubility range for the different oxides is not determined by the atomic structure of the glass but by the relative strengths of the -Si-O-Si-, -Si-O-cation-, and

-cation-O-cation- bonds. The descending magnitude of \bar{S}_{oxide} in solution in the series "FeO", CoO, NiO suggests a corresponding increasing tightness or strength of the -cation-O-cation- relative to the -Si-O-cation- bond in the glass which is consistent with respective increases in heats of fusion and melting points for these three oxides.

The decreasing tightness of the -cation-O-cation- bonds in the order NiO, CoO, "FeO", respectively, is also indicated by the comparative deviations from Raoult's Law, when the activity of the oxide in glass solution (relative to a pure supercooled liquid standard state) is plotted against mole fraction of the oxide as seen in Fig. 7. The deviations exhibited by the metal oxides are interpreted as a competition between Me^{2+} and Si^{4+} for the oxygen introduced by the metal oxide. The most negative deviation (and largest solubility) exhibited by "FeO" is indicative of the largest degree of dissociation of the -Fe-O-Fe- structure by the -Si-O-Si- of the glass to form -Si-O-cation- bonds. The near ideality and low solubility of NiO in solution, correspondingly, indicates relatively strong -Ni-O-Ni- bonds which cannot be so easily dissociated by the sodium disilicate solvent.

IV. SUMMARY

A high temperature electrochemical cell utilizing a stabilized zirconia electrolyte has been used to obtain thermodynamic data on the solution of CoO in NS_2 glass over the temperature interval $700^\circ\text{--}1100^\circ\text{C}$. From this data, the authors have calculated the activities of both CoO and NS_2 in a mixed solution. From solubility data for these components, a binary phase diagram for the CoO- NS_2 system has been proposed. Partial molar entropy data suggests similarities in atomic structure for the three

systems "FeO"-, CoO-, and NiO-NS₂, with a respectively increasing strength of the -cation-O-cation- relative to the -Si-O-cation- bond. The latter conclusion is consistent with melting point and heat of fusion data for the pure oxides.

V. ACKNOWLEDGMENTS

The authors wish to express their appreciation to Prodyot Roy, Leo Brewer, Ralph Hultgren, and John Chipman for helpful comments.

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3. J. F. Elliott and Molly Gleiser, Thermochemistry for Steelmaking, Vol. 1, Addison-Wesley Publishing Co., Inc., Reading, Mass. (1960).
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Table I. Activity and partial molar thermodynamic data for solution of CoO in sodium disilicate glass

N_{CoO}	a_{CoO}				$\Delta\bar{F}_{\text{CoO}}$				N_{NS_2}	a_{NS_2}				$\Delta\bar{F}_{\text{NS}_2}$				$\Delta\bar{S}_{\text{CoO}}$	$\Delta\bar{S}_{\text{NS}_2}$
	800°	900°	1000°	1100°	800°	900°	1000°	1100°		800°	900°	1000°	1100°	800°	900°	1000°	1100°		
.054	.020	.020	.020	.020	-8340	-9120	-9890	-10700	.946	.945	.945	.946	.946	-120	-130	-140	-150	7.8	.05
.120	.056	.056	.056	.056	-6140	-6720	-7290	-7860	.880	.885	.86	.87	.88	-330	-350	-350	-360	5.8	.14
.182	.120	.115	.110	.107	-4520	-5040	-5580	-6100	.818	.760	.77	.78	.79	-580	-600	-630	-640	4.7	.32
.221	.17	.16	.155	.147	-3780	-4390	-4710	-5230	.779	.69	.71	.72	.73	-790	-800	-830	-860	4.3	.41
.277	.26	.24	.225	.21	-2910	-3330	-3770	-4260	.723	.59	.61	.63	.65	-1130	-1150	-1170	-1200	4.1	.52
.321	.35	.33	.29	.27	-2270	-2620	-3130	-3570	.679	.52	.53	.56	.57	-1420	-1480	-1490	-1520	4.1	.53
.367	.49	.44	.39	.36	-1540	-2910	-2380	-2830	.633	.43	.45	.47	.50	-1820	-1880	-1910	-1950	4.2	.48
.407	.72	.59	.51	.46	-710	-1230	-1730	-2120	.593	.34	.37	.40	.43	-2290	-2320	-2340	-2340	4.4	.36
.437	1.00				0				.563	.28				-2710				4.7	.10
.454		.89	.73	.63		-280	-800	-1280	.546		.27	.31	.34		-3050	-2960	-2940		
.462		1.00				0			.538		.25	.24		-3210					
.488			1.00				0		.512				.22			-3660			
.517				1.00				0	.483								-4190		

Table II. Mixing Data for CoO-Na₂Si₂O₅ System

N _{CoO}	N _{NS₂}	ΔF_{mix}				ΔS_{mix}
		800°C	900°C	1000°C	1100°C	
.054	.946	- 560	- 620	- 670	- 720	0.40
.120	.880	-1030	-1110	-1180	-1250	0.82
.182	.818	-1300	-1410	-1530	-1640	1.12
.221	.779	-1450	-1570	-1690	-1830	1.28
.277	.723	-1620	-1750	-1890	-2050	1.50
.321	.679	-1690	-1850	-2020	-2180	1.66
.367	.633	-1720	-1890	-2080	-2260	1.81
.407	.593	-1660	-1880	-2090	-2250	1.92
.437	.563	-1530				2.00
.454	.546		-1800	-1980	-2190	
.462	.538		-1730			
.488	.512			-1880		
.517	.483				-2030	

Table III. Estimation of Entropies, Heats and Free Energies of Fusion of Pure Supercooled Liquid Oxides at 1173°K (900°C)

Oxide	T_f (°K)	ΔH_f (cal/mole)	ΔS_f (e.u.)	ΔF_f (cal/mole)	K
Fe _{0.95} O	1650	7490*	4.54	-2170	.395
CoO	2078	9430**	4.54†	-4110	.171
NiO	2238	10160**	4.54†	-4836	.125

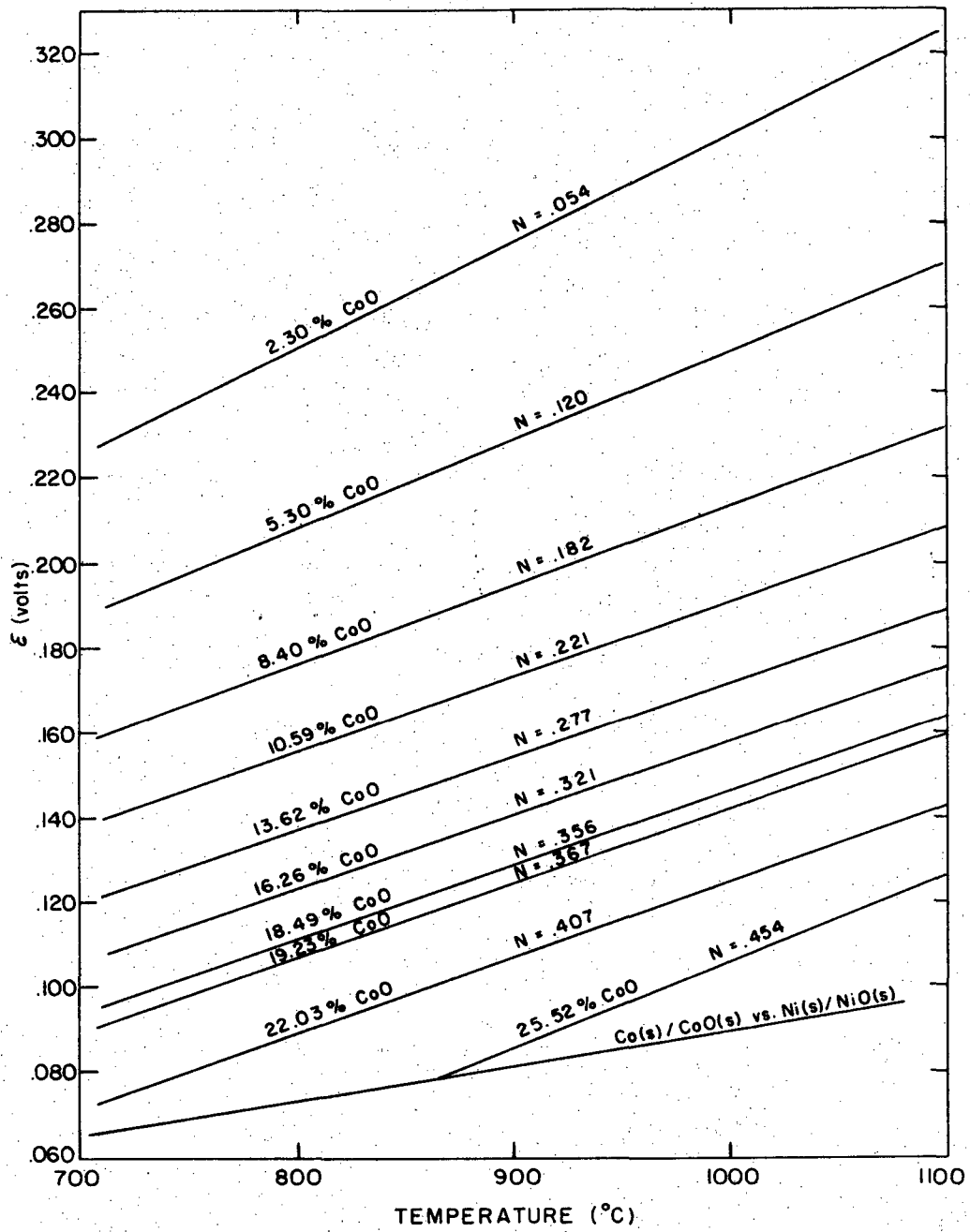
* reference 4

** calculated assuming $\Delta S_f = 4.54$ e.u.

† estimated

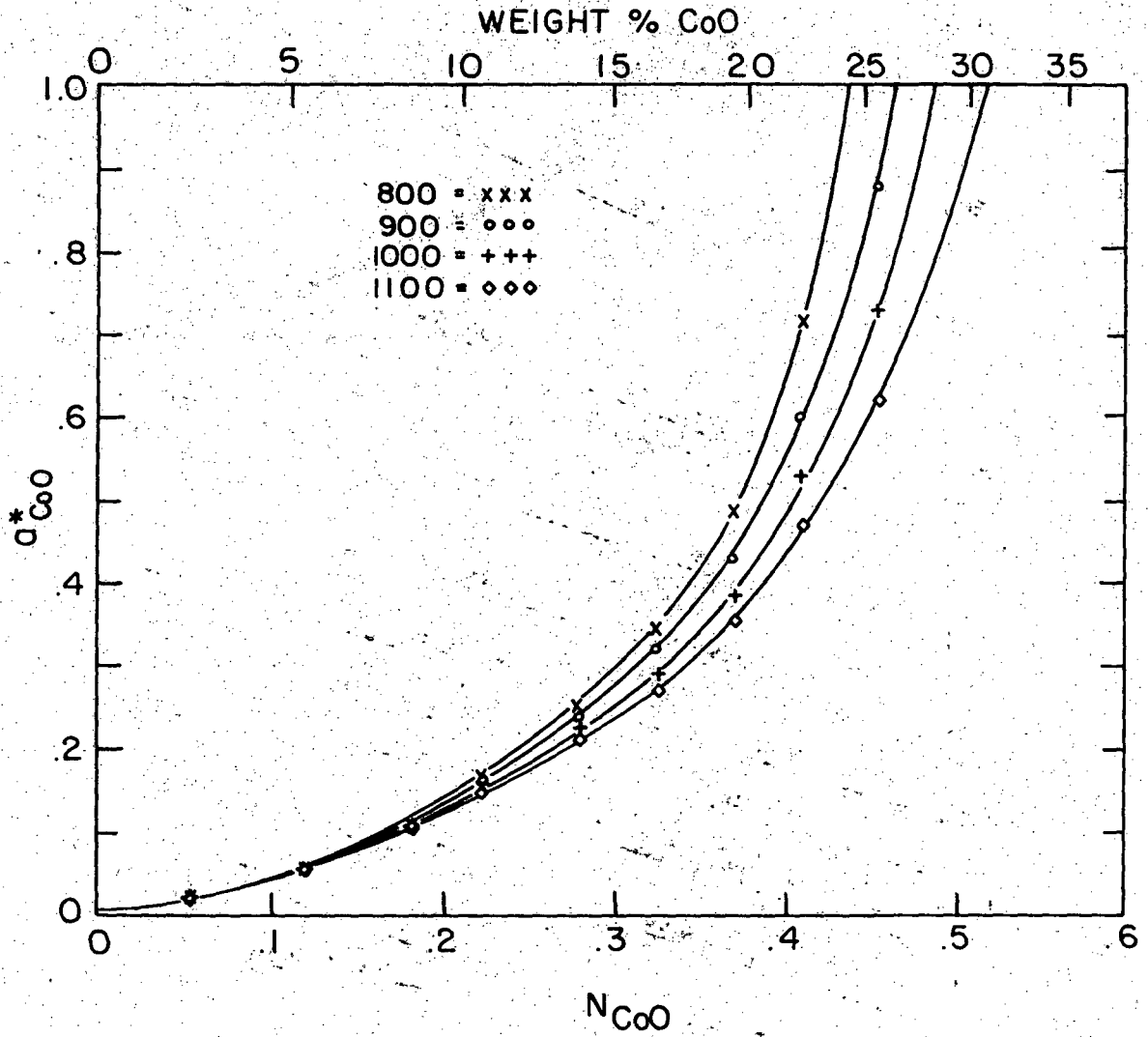
FIGURES

- Fig. 1. Isocompositional cell output for CoO-NS_2 glasses as a function of temperature (± 2 mv.).
- Fig. 2. Isothermal dependence of CoO activity (referred to pure solid standard state) on composition.
- Fig. 3. Isothermal activities of NS_2 (referred to pure liquid standard state) calculated from Gibbs-Duhem integration.
- Fig. 4. Variation of \bar{S}_{oxide} in NS_2 solution at 900°C (1173°K).
- Fig. 5. Isocompositional activity plots for NS_2 for determination of NS_2 liquidus in the CoO-NS_2 system.
- Fig. 6. Proposed partial phase diagram for the CoO-NS_2 system.
- Fig. 7. Estimated activities of metal oxides in NS_2 glass solution relative to the pure supercooled liquid standard state.



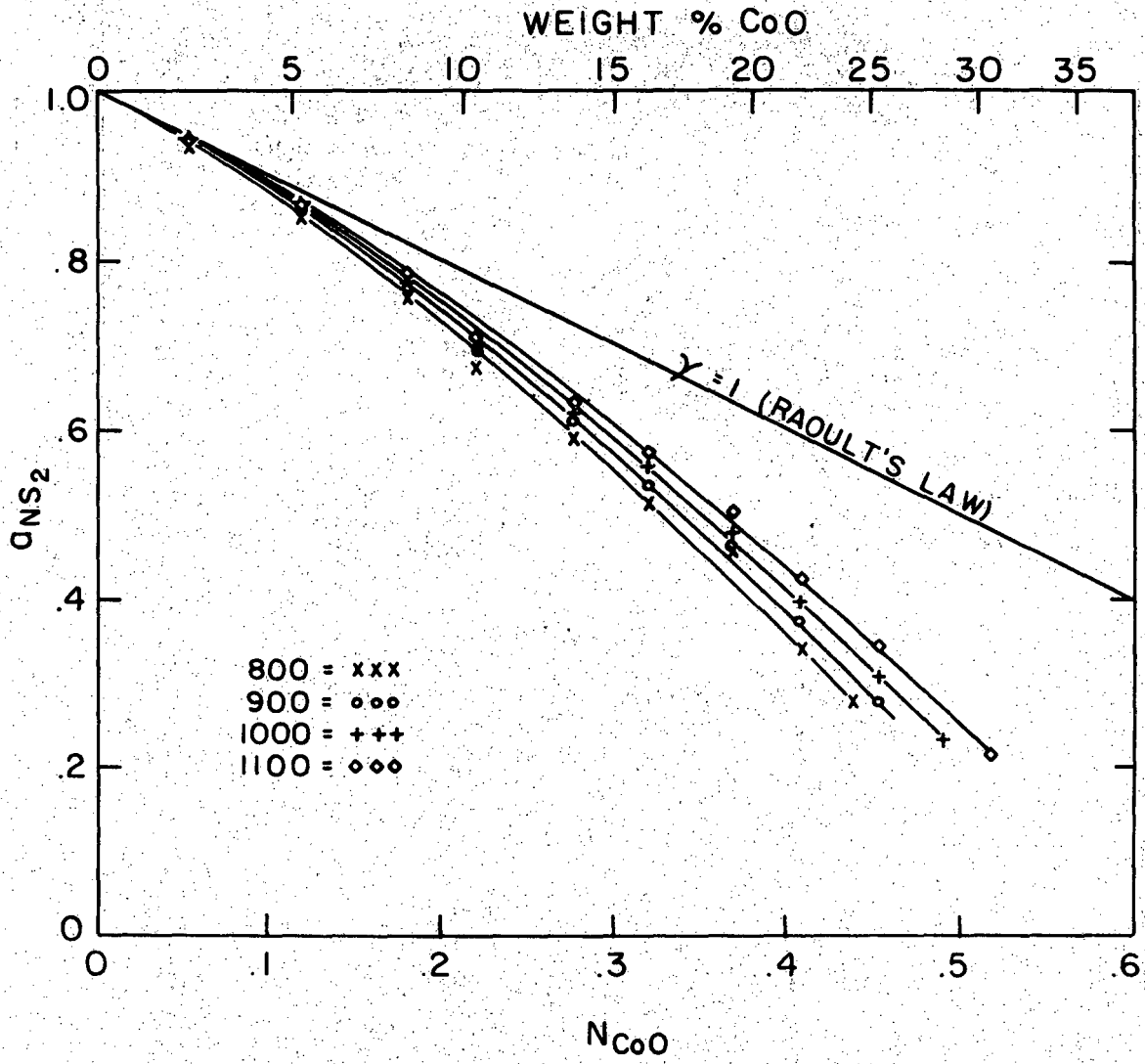
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Fig. 1.



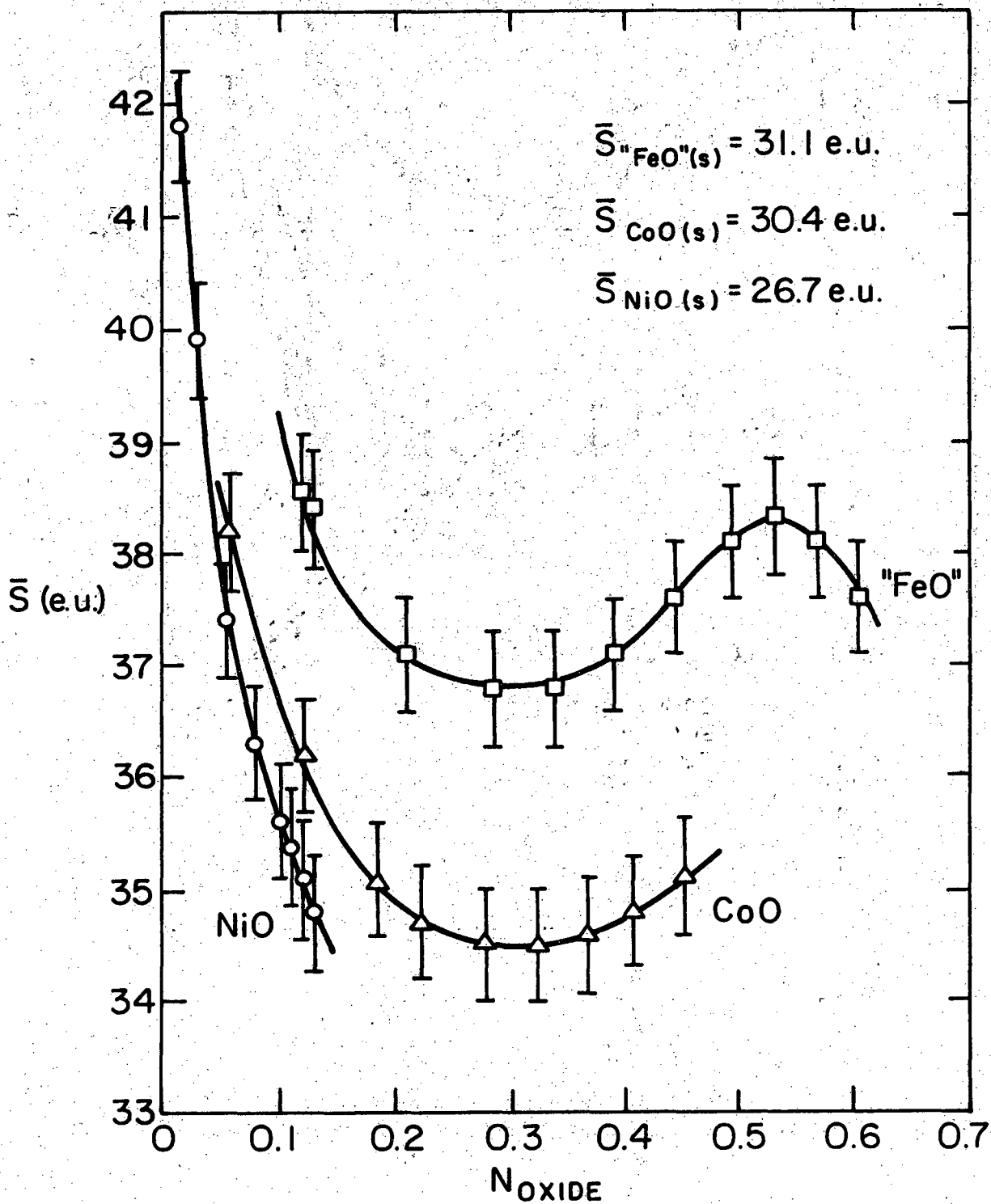
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Fig. 2.



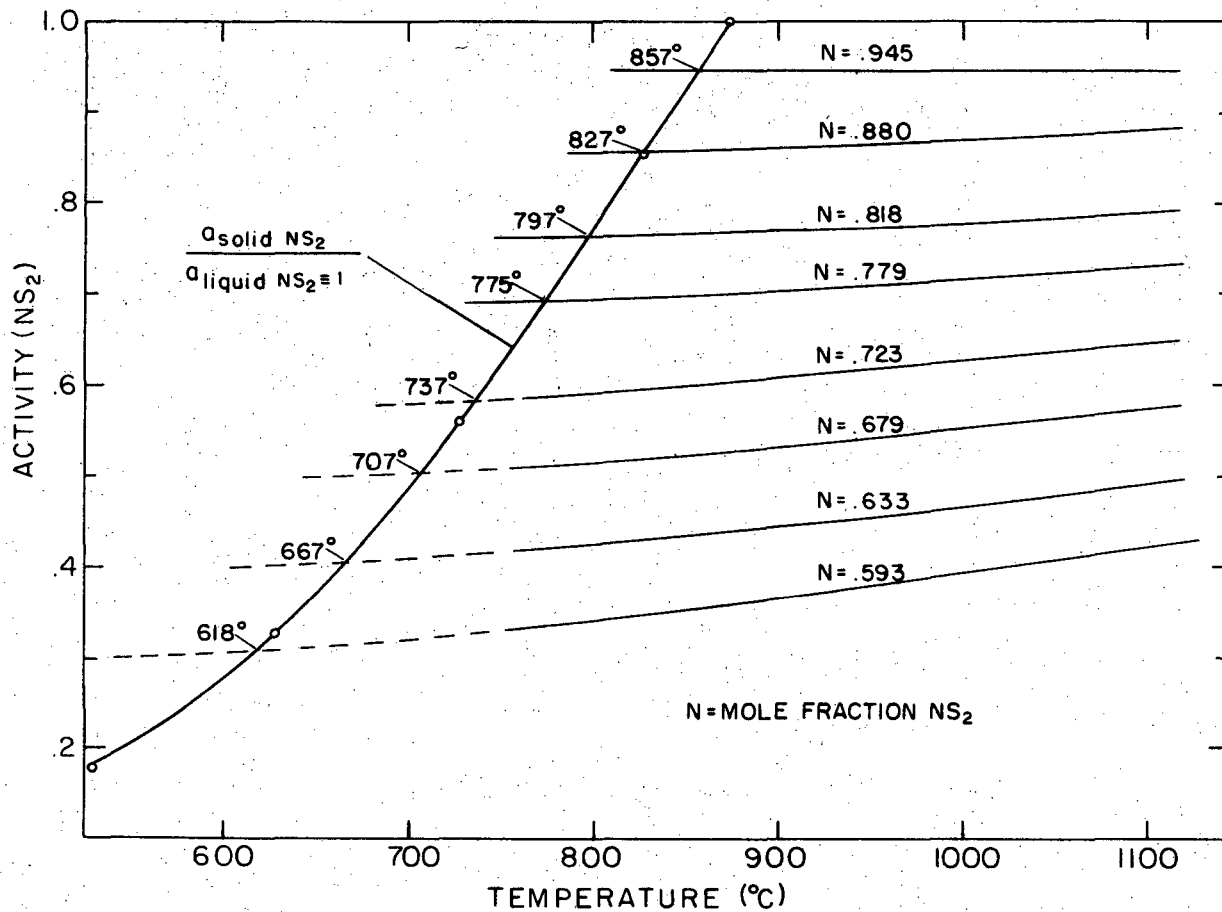
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Fig. 3.



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Fig. 4.



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Fig. 5

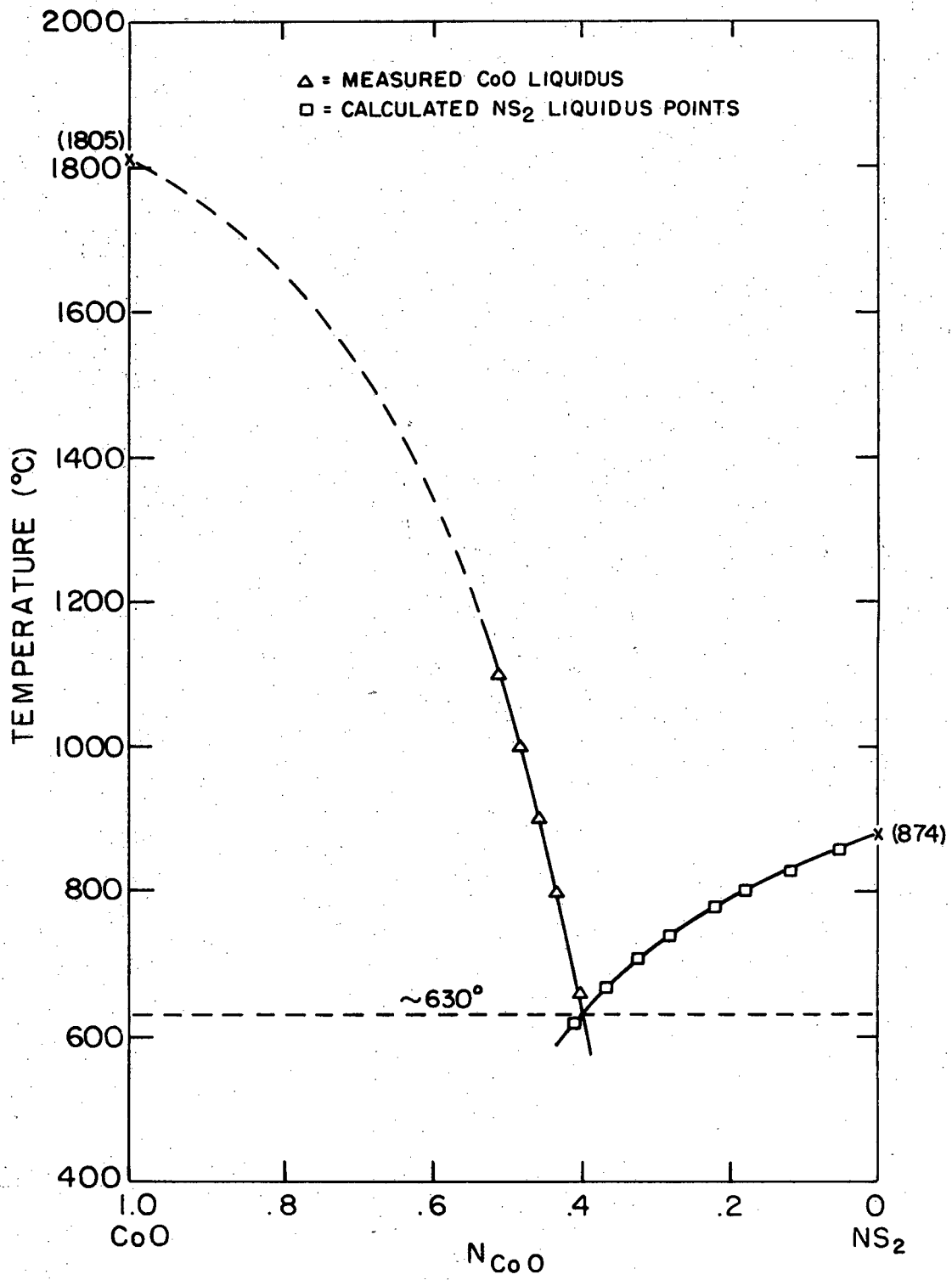
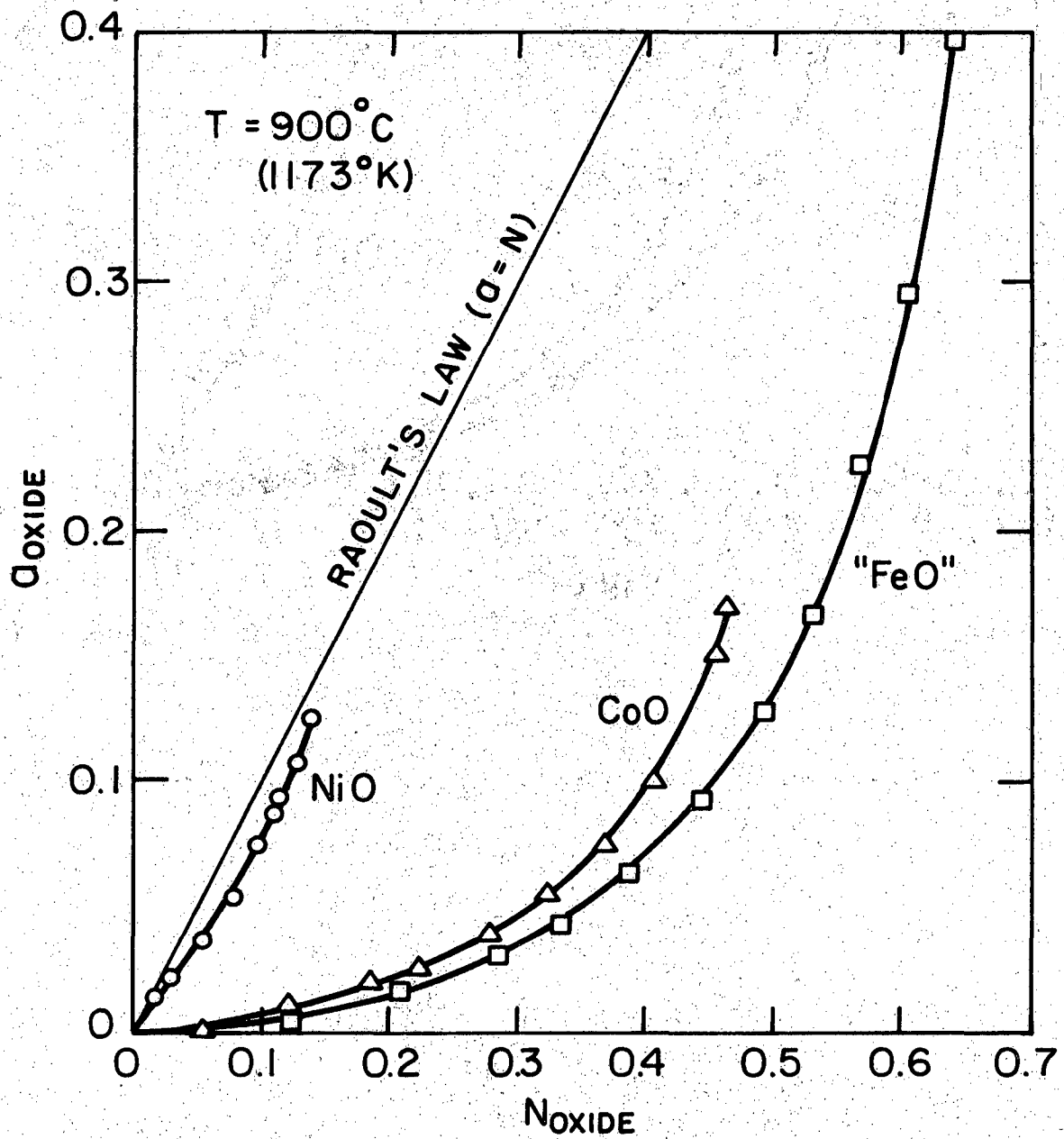


Fig. 6

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Fig. 7

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