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ELECTROCHEMICAL STUDIES IN GLASS

II: THE SYSTEM $Fe_{0.95}O$-$Na_2Si_2O_5$

Alton M. Lacy and Joseph A. Pask

Inorganic Materials Research Division, Lawrence Radiation Laboratory,
and Department of Materials Science and Engineering
College of Engineering, University of California
Berkeley, California

June 1970

ABSTRACT

A solid electrolyte electrochemical cell of the general type

$$Pt/Ni:NiO_{a=1} \| ZrO_2 + 7.5\% \ CaO \| Fe:FeO_{a<1} + glass/Pt$$

has been utilized to measure the activities of ferrous oxide in sodium disilicate glass over the temperature interval from 750-1050°C. The data indicate a solubility of ferrous oxide in sodium disilicate glass which is in good agreement with previous studies of the ternary system $Na\ O$-$Fe_{0.95}O$-SiO_2. From the variation in ferrous oxide activity, the activity of sodium disilicate in glass solution has been calculated; and from these combined data, partial molar free energies and entropies of solution of ferrous oxide and $Na_2Si_2O_5$, as well as free energies and

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This work was submitted in partial fulfillment of the requirements for the degree Doctor of Philosophy.

entropies of mixing have been calculated. Phase equilibria data determined from this investigation suggest some modification of both published phase diagrams of the system $Fe_{0.95}O$-$Na_2Si_2O_5$; and indicates the existence of a new compound in this system, as yet unidentified.

I. INTRODUCTION

In an attempt to better understand the nature of glass as a reactive component of a chemical system, and to further establish the criteria for the development of chemical glass-metal bonding, an electrochemical study of the thermodynamic activities of various oxides in a model glass solution has been undertaken. This report presents the results of the work on the thermodynamic properties of ferrous oxide in liquid sodium disilicate. Such data has particular value in the interpretation of physical and chemical behavior (e.g., bonding, mass transfer, wetting, environmental stability and structure) of glass and glass-metal system.

II. EXPERIMENTAL

Background information regarding the types of electrochemical cell constructions which have been used in the past for similar work on glass systems has been presented by Lacy and Pask[1] as Part I of this series. It contains a schematic diagram of the cell construction used and a description of the experimental procedure for obtaining data from this cell. In this study, however, the $Na_2Si_2O_5$ + NiO + Ni mixture in the inner electrode compartment was replaced with a mixture of $Na_2Si_2O_5$ + FeO* + Fe. In addition, another cell of the type Ni/NiO || calcia-stabilized zirconia** || FeO/Fe was constructed by replacing the glass-metal mixture in the inner electrode compartment with a mixture of Fe/FeO

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* The designation FeO will be used throughout this text to represent that iron oxide composition in thermodynamic equilibrium with Fe metal at the temperature of consideration. That is, over the temperature range 700-1050°C, FeO $\cong Fe_{0.95}O$.

** Obtained from Zircoa, Solon, Ohio

powder. The output of this cell over the temperature range from 700-1050°C was in good agreement (±1 mv) with that expected from theoretical calculations using the tabulated thermodynamic data for NiO and FeO of Elliott and Gleiser.[2] This procedure was followed to verify the proper operation of the experimental apparatus.

III. RESULTS AND DISCUSSION

(1) Thermodynamic Data

The overall cell reaction for the arrangement used in this work may be expressed as

$$NiO_{a=1}(s) + Fe(s) = Ni(s) + FeO_{a<1}(glass) \qquad (1)$$

The free energy for this reaction may then be written as

$$\Delta F = \Delta F^{o} + RT \ln a_{FeO}. \qquad (2)$$

Alternatively, using the equality $\Delta F = -n\mathcal{F}E$, where n = the number of electrons transferred in each half-cell reaction (in this case, 2); $\mathcal{F}$ = Faraday's Constant (23,061 cal volt); E = the cell output in volts; R = the gas constant (1.987 cal/°C); and T = the absolute temperature, Eq. (2) may be written as

$$-n\mathcal{F}E = n\mathcal{F}E^{o} + RT \ln a_{FeO}. \qquad (3)$$

(E^{o} is the cell output when all components are in their standard states.) The activity of FeO in the glass (relative to pure solid FeO) may therefore be calculated directly from (3) as

$$a_{FeO} = \exp(-n\mathcal{F}[E-E^{o}]/RT). \qquad (4)$$

The cell output for a number of compositions vs. temperature is shown in Fig. 1, along with the value of E^{o} determined from the cell containing Fe/FeO instead of glass + Fe + FeO. The uncertainty in each experimental curve is ±2 mv. The variation of a_{FeO} with temperature for

each composition is shown in Fig. 2 and the isothermal activity-composition curves are given in Fig. 3.

One activity value was unintentionally but positively confirmed by another series of experiments being conducted in this laboratory. The melting of NS_2* glasses containing 26.74 wt% FeO (N_{FeO}=0.491) and 29.80 wt% FeO (N_{FeO}=0.528) was attempted in an atmosphere of CO/CO_2 at a ratio of 10:1 at 1000°C. The results indicated that the 26.74% glass remained stable, but there was definite evidence of decomposition of the 29.80% glass. Calculation of the maximum activity of FeO which is stable according to the reaction

$$Fe + CO_2 = CO + FeO \tag{5}$$

under these conditions yielded a value of $a_{FeO} = 0.23$. The successful melting of the 26.74% glass without perceptible decomposition is indication that the activity of FeO in this composition is very near 0.23. This is in good agreement with the activity data derived from emf measurements (see Fig. 3).

The activity of NS_2 in the glass relative to pure liquid NS_2 may be calculated from the Gibbs-Duhem equation by performing the following integration:

$$\ln a_{NS_2} = -\int_{N_{NS_2} = 1}^{N_{NS_2}} \frac{N_{FeO}}{N_{NS_2}} \, d \ln a_{FeO} \tag{6}$$

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* NS_2 will be used throughout this article to designate $Na_2Si_2O_5$.

Activities calculated in this manner are shown in Fig. 4.

The partial molar quantities for the solution of pure solid FeO and pure liquid NS_2 together may be determined from the following expressions:

$$\Delta\overline{F}_{oxide} = -RT \ln a_{oxide} \tag{7}$$

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

$$\Delta\overline{H}_{oxide} = \Delta\overline{F}_{oxide} + T\Delta\overline{S}_{oxide} = -n\mathcal{F}\left[E-T\left(\frac{\partial E}{\partial T}\right)_p\right] \tag{9}$$

The partial molar free energies and entropies for the glass studied here are presented in Table I. Free energies, entropies and enthalpies of mixing of pure solid FeO and pure liquid NS_2 may be calculated from the general expression

$$N_1\overline{X}_1 + N_2\overline{X}_2 = \Delta X_{mix} \tag{10}$$

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

(2) Solubility Limits and Phase Equilibria

For any temperature, the composition at which the activity of FeO in the glass equals unity represents the saturation solubility of FeO. By extension of the isothermal activity-composition curves shown in Fig. 3 to $a_{FeO}=1$, the solubility limits of FeO in NS_2 can be estimated. (Extension of voltage-temperature curves of Fig. 1 to intersect the output curve for the test cell 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 activity of pure solid NS_2 relative to the pure liquid standard state. The data

for such a calculation was taken from the JANAF Tables of Thermochemical Data.[3] The graphical analysis is shown in Fig. 5, and the two liquiduses so determined are given in Fig. 6.

As can be seen from Fig. 6, the solubility data of FeO compares well with that of Ibrahim and Carter,[4] but the NS_2 solubility data is not consistent with their phase diagram. This discrepancy can be resolved by reconstruction of their diagram as shown in Fig. 7 by using all their data points, but postulating the existence of $Na_2O{\cdot}FeO{\cdot}2SiO_2$, a previously unreported compound. It is alternatively possible that the system $FeO\text{-}Na_2Si_2O_5$ is not a true binary system, but a pseudobinary with the join intersecting the primary phase field of some other ternary compound. Both alternatives are consistent with the data of Schairer et al.,[5] who through different experimental methods conclude that the region between $N_{FeO} = 0.32$ and $N_{FeO} = 0.59$ contained "several (phase) fields" which were not specified. At variance, however, is the indication that Schairer et al.'s 800° liquidus isotherm intersects the FeO-NS join at $N_{FeO} = 0.30$ (14 wt% FeO), while this work indicates an intersection at $N_{FeO} = 0.20$ (9 wt% FeO). No explanation for this difference is offered. If one accepts the eutectic of Schairer et al. at $N_{FeO} = 0.32$ (16 wt% FeO), this work indicates a eutectic temperature of 720°C.

Data from all three studies of the eutectic composition and temperature at $N_{FeO} = 0.59$ is in agreement.

IV. SUMMARY

A high temperature electrochemical cell utilizing a stabilized zirconia electrolyte has been successfully used for the acquisition of thermodynamic data on the solution of FeO in sodium disilicate glass.

From this data, the isothermal variations in activity with composition for FeO and NS_2 have been calculated, and the possible phase relations between these two compounds have been investigated. The results verify part of existing FeO-NS_2 phase diagrams and indicate the existence of at least one unreported compound within the ternary system Na_2O-FeO-SiO_2.

ACKNOWLEDGMENTS

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

	a_{FeO}			$\overline{\Delta F}_{FeO}$				a_{NS_2}			$\overline{\Delta F}_{NS_2}$				
N_{FeO}	800°	900°	1000°	800°	900°	1000°	N_{NS_2}	800°	900°	1000°	800°	900°	1000°	$\overline{\Delta S}_{FeO}$	$\overline{\Delta S}_{NS_2}$
.121	.021	.020	.020	-8240	-9120	-9895	.879	.87	.87	.87	- 310	- 330	- 360	7.4	.40
.127	1023	.022	.022	-8040	-8900	-9655	.873	.86	.86	.86	- 330	- 350	- 380	7.3	.40
.208	1045	.044	.043	-6610	-7280	-7960	.782	.75	.75	.75	- 620	- 680	- 720	6.0	.52
.284	1075	.075	.076	-5520	-6040	-6518	.716	.62	.63	.63	-1020	-1100	-1160	5.7	.55
.336	.12	.11	.10	-4610	-5190	-5701	.664	.52	.53	.54	-1400	-1480	-1550	5.7	.61
.388	.18	.16	.14	-3660	-4270	-4900	.612	.41	.43	.45	-1930	-1980	-2030	6.0	.61
.443	.28	.24	.20	-2710	-3380	-4060	.557	.30	.32	.35	-2600	-2630	-2660	6.5	.49
.491	.42	.33	.27	-1870	-2620	-3300	.509	.21	.24	.27	-3360	-3330	-3360	7.0	.12
.528	.56	.43	.35	-1260	-1980	-2660	.472	.15	.18	.20	-4000	-4020	-4020	7.2	.00
.568	.77	.58	.47	- 570	-1280	-1940	.432	.11	.13	.15	-4810	-4870	-4900	7.0	.29
.603	1.00	.75	.59	0	- 670	-1360	.397	.07	.09	.10	-5670	-5750	-5800	6.5	1.1
.638	---	1.00	---	----	0	----	.362	--	.05	--	----	-6800	----	---	---
.683	---	---	1.00	----	----	0	.317	--	--	.04	----	----	-8200	---	---

Table II. Mixing Data for the "FeO"-$Na_2Si_2O_5$ System

N_{FeO}	N_{NS_2}	ΔF_{mix} 800°	900°	1000°	ΔS_{mix}
.121	.879	-1270	-1400	-1520	1.25
.127	.873	-1310	-1440	-1560	1.27
.208	.792	-1810	-2050	-2230	1.81
.284	.716	-2300	-2500	-2680	2.00
.336	.664	-2480	-2730	-2940	2.32
.388	.612	-2600	-2870	-3120	2.70
.443	.557	-2650	-2960	-3280	3.15
.491	.509	-2630	-2980	-3330	3.50
.528	.472	-2550	-2950	-3300	3.75
.568	.432	-2400	-2830	-3220	4.10
.603	.397	-2250	-2690	-3120	4.35
.638	.362	----	-2460	----	----
.683	.317	----	----	-2600	----

FIGURE CAPTIONS

Fig. 1. Isocompositional cell output for $FeO-NS_2$ glasses as a function of temperature.

Fig. 2. Variation in the activity of FeO (referred to the pure solid standard state) with temperature for each composition studied.

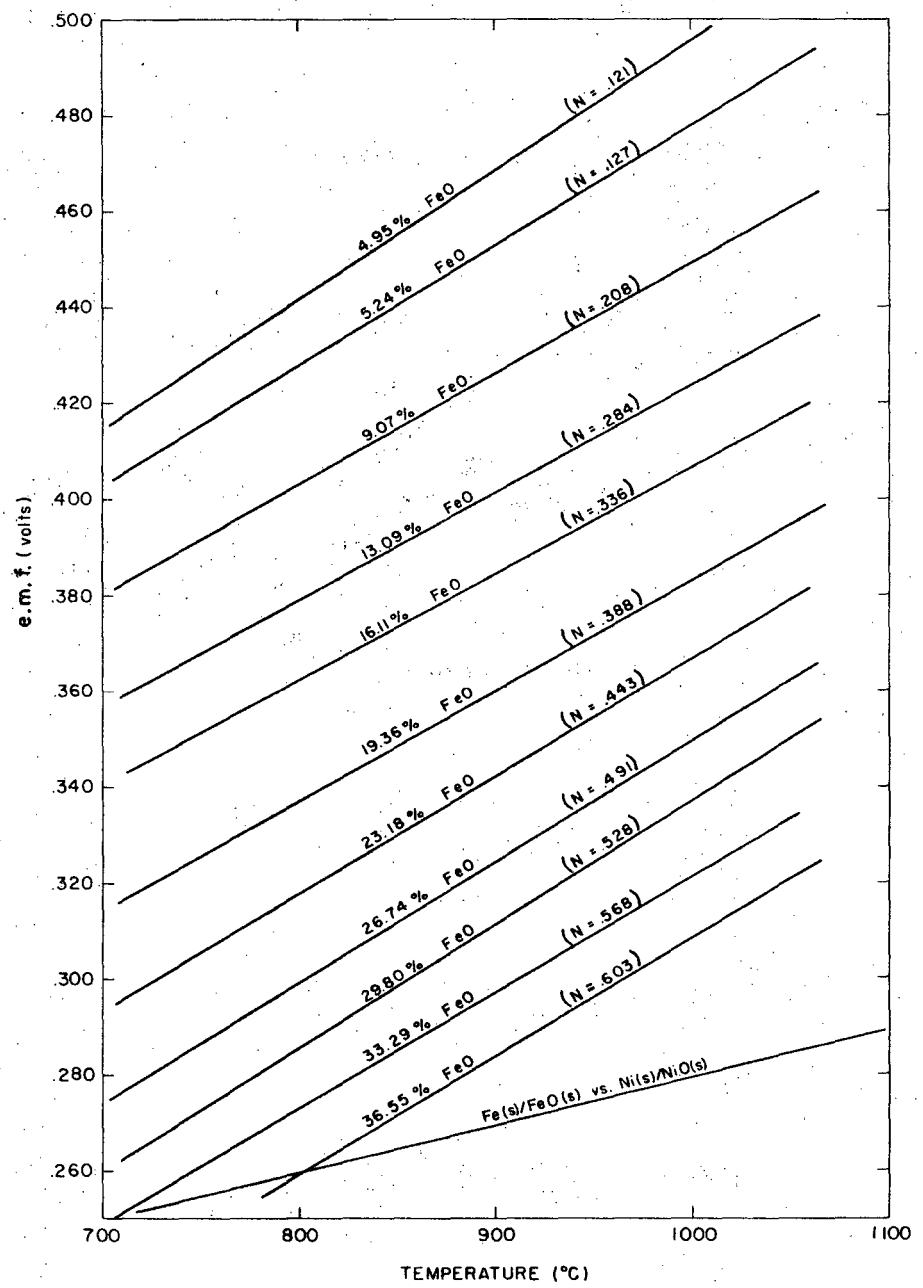
Fig. 3. Isothermal dependence of FeO activity (referred to the pure solid standard state) on composition.

Fig. 4. Isothermal activities of NS_2 (referred to liquid standard state) calculated from Gibbs-Duhem integration.

Fig. 5. Isocompositional activity plots for NS_2 for determination of the NS_2 liquidus in the $FeO-NS_2$ system.

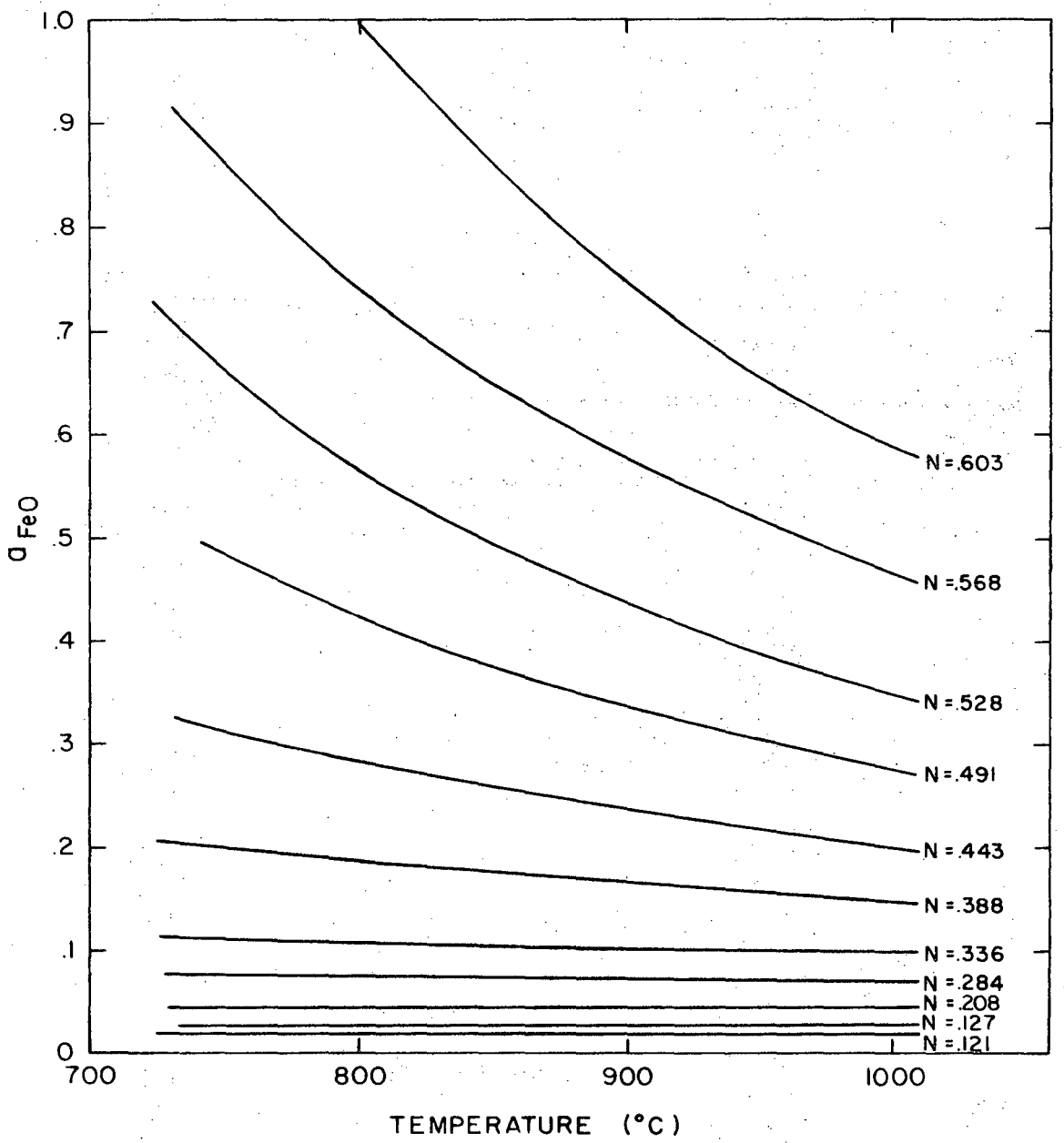
Fig. 6. Comparison of the calculated NS_2 and FeO liquiduses with the published phase diagram of Ibrahim and Carter.[11]

Fig. 7. Proposed phase diagram of the $FeO-NS_2$ system incorporating the postulated compound NFS_2.



XBL 699-1434

Fig. 1



XBL 699-1398

Fig. 2

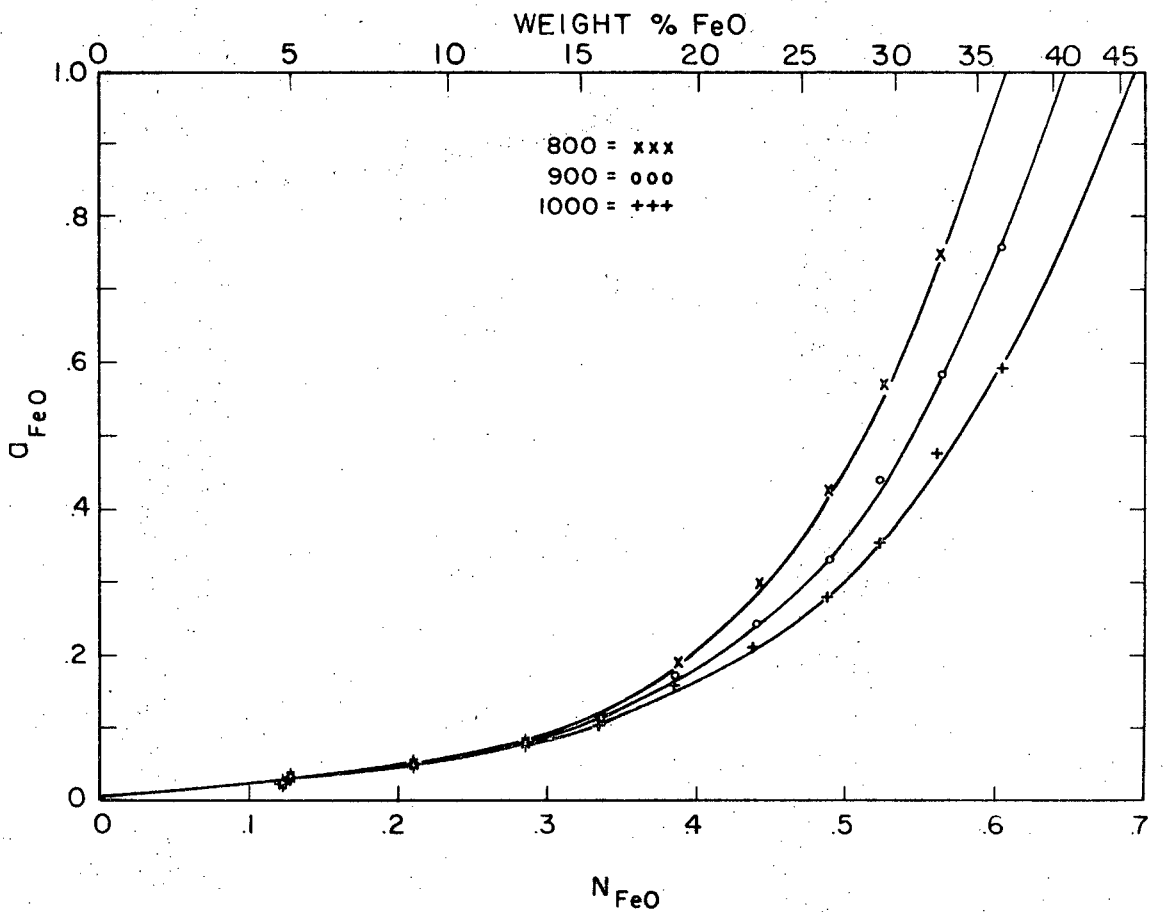


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Fig. 3

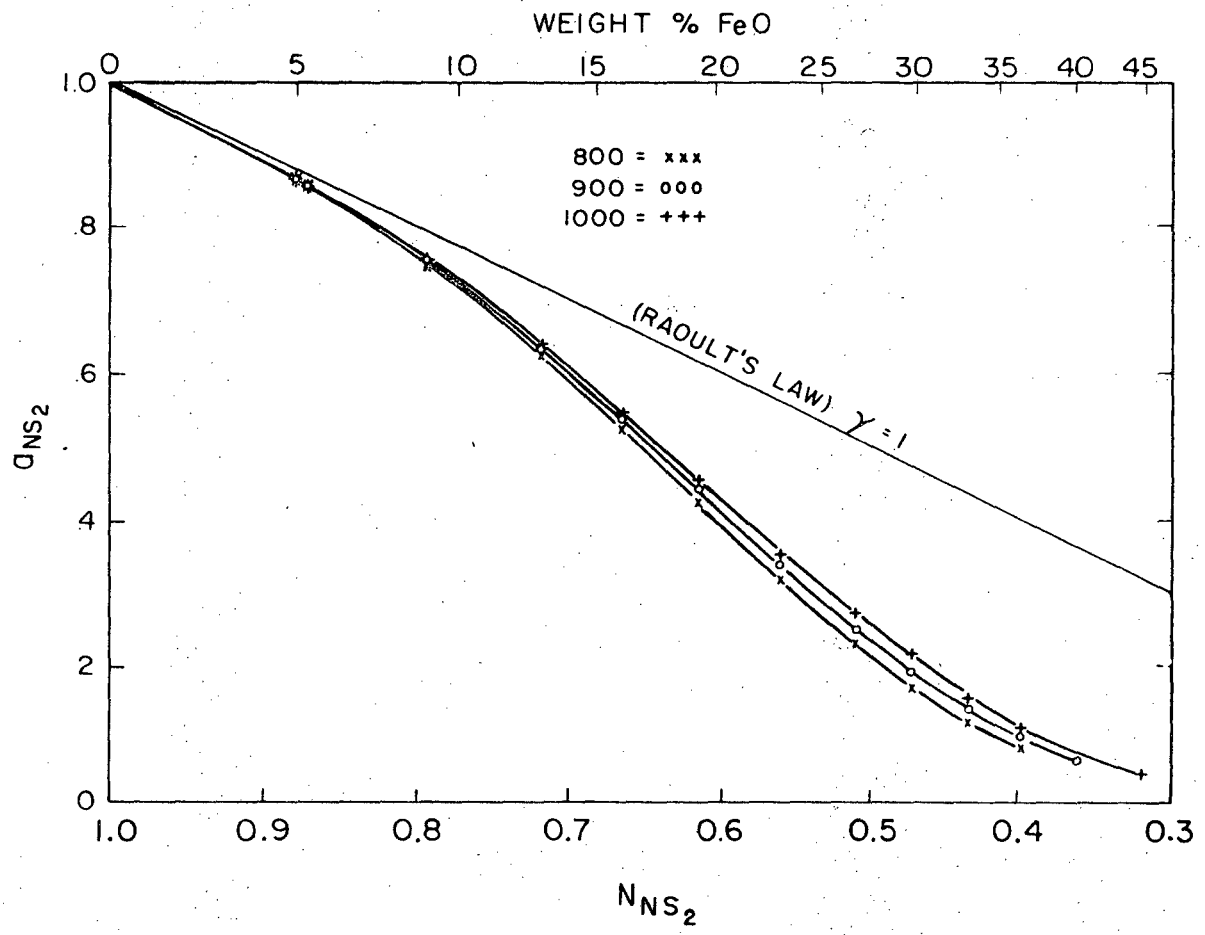

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Fig. 4

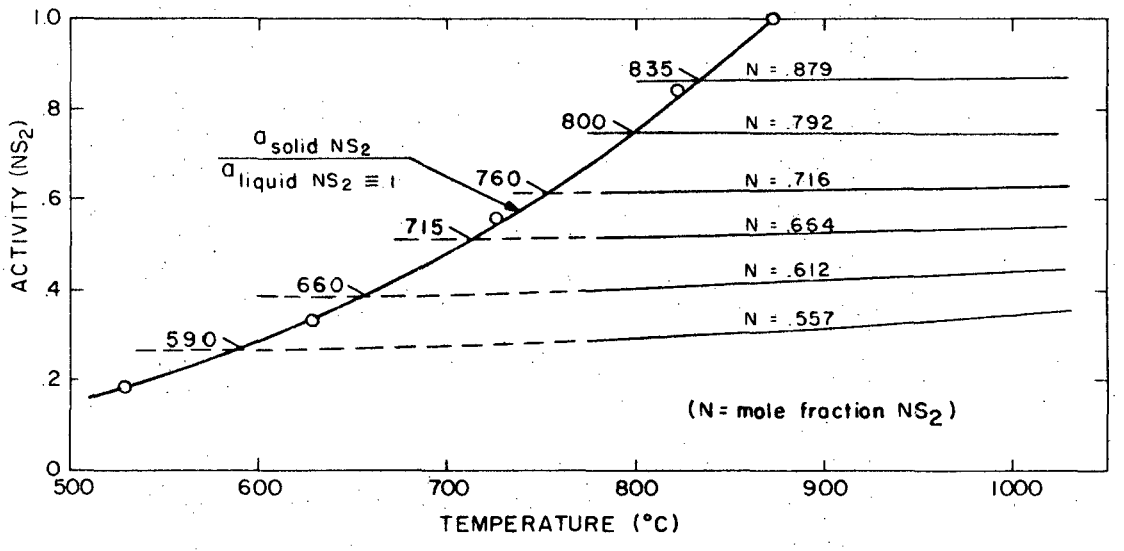

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Fig. 5

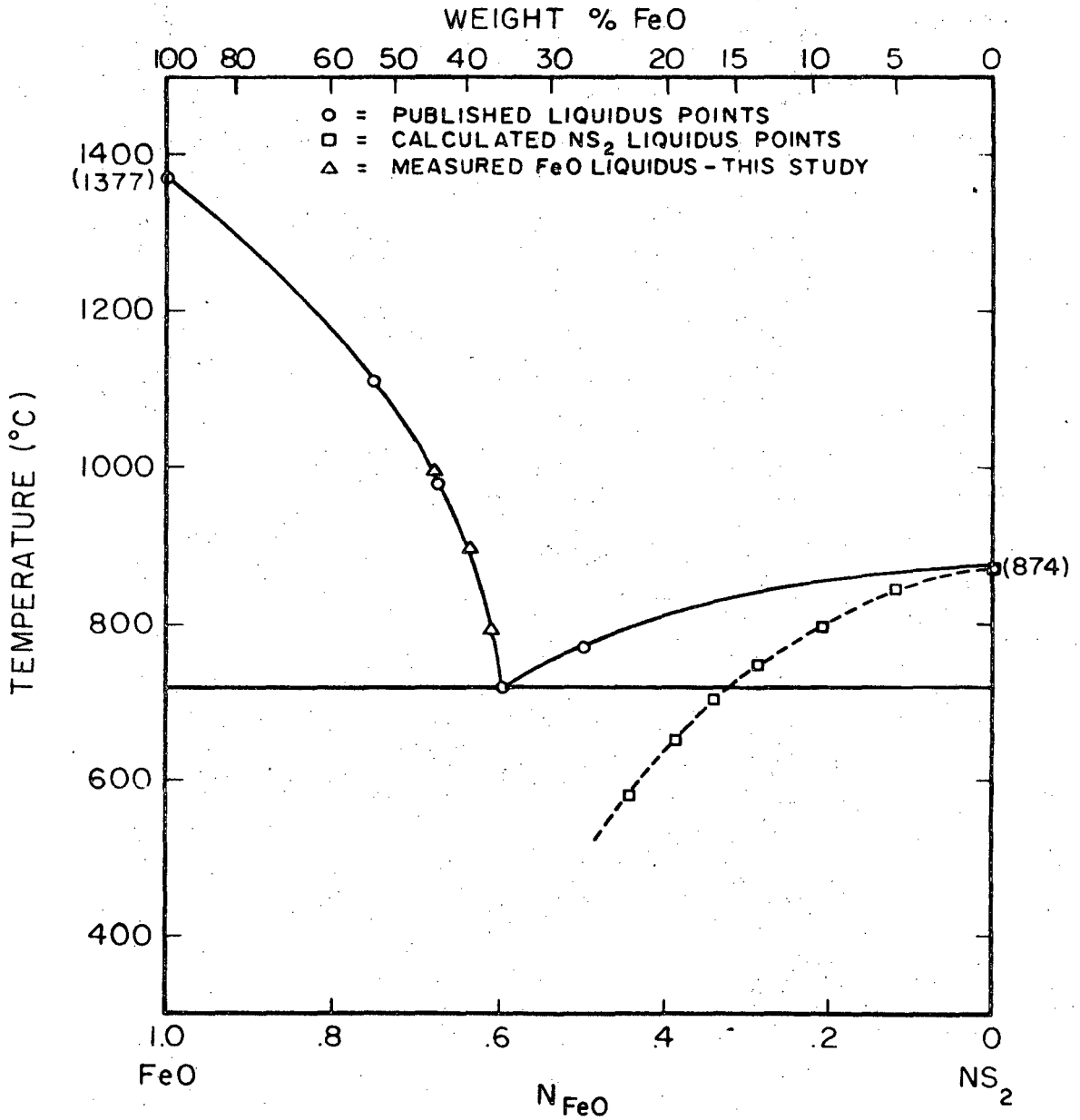

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Fig. 6

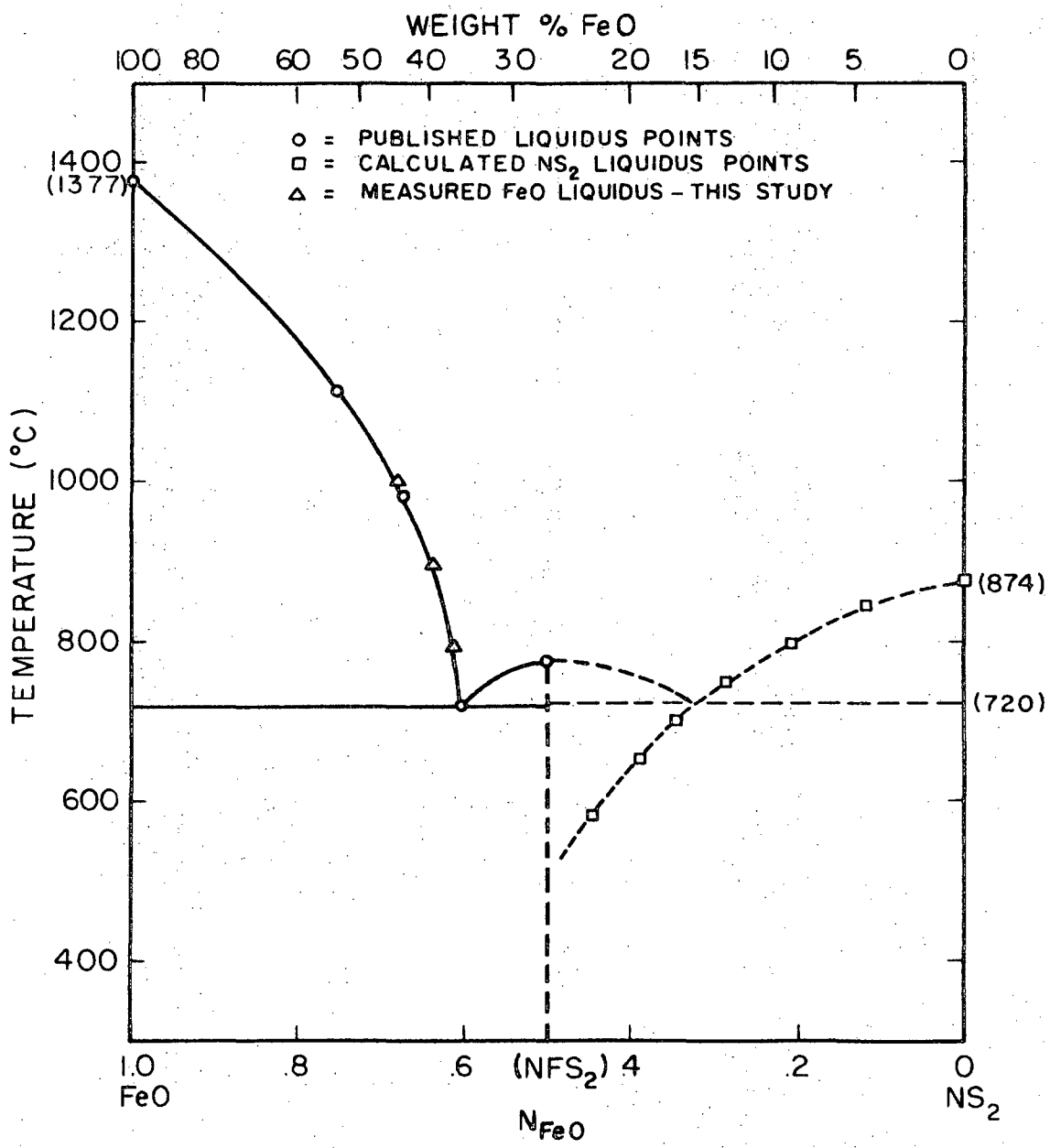

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Fig. 7

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