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ACTIVITY MEASUREMENTS IN OXIDE SOLID SOLUTIONS: THE SYSTEMS NiO–MgO AND NiO–MnO IN THE TEMPERATURE INTERVAL 1100–1300°C*

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Abstract—Activities of NiO in NiO–MgO and NiO–MnO solid solutions have been measured by equilibrating oxide samples with pure metallic Ni in atmospheres of known oxygen partial pressures. The system NiO–MgO is ideal, within limits of experimental error, whereas the system NiO–MnO shows considerable positive deviation from ideality in the temperature interval studied in the present investigation, 1100–1300°C.

I. INTRODUCTION

MANY activity measurements of components in liquid oxides have been reported, as demonstrated by the voluminous literature in the field of slag chemistry. In constrast, very little is known about the thermodynamic behavior of components in oxide solid solutions.

The present paper deals with activity measurements in two such solutions, NiO–MgO and NiO–MnO, both with sodium chloride structure. Complete solubility has been shown to exist between NiO and MgO at 900°C,(1) whereas the system NiO–MnO exhibits only partial solid solubility at 350°C.(2) It will be shown in the present investigation that the latter system exhibits complete solid solubility above 1100°C.

Consider the reaction

$$2\text{NiO}_{\text{solid solution}} = 2\,\text{Ni}_{\text{metal}} + \text{O}_{2\text{gas}}$$

in which NiO dissolved in another oxide dissociates to metal and gas. The activity of NiO in the solid solution, relative to pure NiO as a standard state, is then expressed as

$$a_{\text{NiO}} = \left(\frac{P_{\text{O}_2}}{P_{\text{O}_2}{}^*}\right)^{1/2}$$

Here P_{O_2} and $P_{\text{O}_2}{}^*$ are the partial pressures of oxygen of the gas phase in equilibrium with metallic iron and the oxide solid solution or the pure NiO, respectively. The equation holds only if the metal phase is essentially pure Ni. The oxide combinations used in the present investigation were chosen with this consideration in mind. Both MgO and MnO are so much more stable than NiO that for all practical purposes $a_{\text{Ni}} = 1$ in the metal phase present in all mixtures used in this investigation.

II. EXPERIMENTAL METHOD

1. *General procedure*

The experimental method used was analogous to that developed by FOSTER and WELCH(3). It consisted of four steps:

(*a*) Determination of K_T for the reduction of NiO to Ni.

(*b*) Determination of *d*-spacing change with composition in oxide solid solutions.

(*c*) Equilibration of various members of the solid solution series with a metal phase and gas phase of known O_2 partial pressure.

(*d*) Determination of compositions of solid solutions resulting from step (*c*) by means of data obtained in step (*b*).

2. *Starting materials*

"Baker Analyzed" reagent grade NiO was the

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source of nickelous oxide used in the present investigation. Its reported analysis was as follows: NiO, 99·5 per cent; nitrogen compounds (as N), 0·003 per cent; chloride, 0·003 per cent; sulfate, 0·005 per cent; lead, 0·001 per cent; copper, 0·005 per cent; cobalt, 0·005 per cent; iron, 0·004 per cent; zinc, 0·005 per cent, alkalies and earths (as SO_4), 0·13 per cent. The reagent was heated in a drying oven at approximately 100°C prior to its use as a constituent in mixtures for the samples.

The source of magnesium oxide was "Baker Analyzed" reagent grade MgO of reported analysis as follows: insoluble in HCl, 0·020 per cent; soluble in water, 0·020 per cent; loss on ignition, 0·62 per cent; silica, 0·010 per cent; ammonium hydroxide precipitate, 0·020 per cent; chloride, 0·005 per cent; nitrate, 0·005 per cent; sulfate and sulfite (as SO_4), 0·005 per cent; barium, 0·002 per cent; calcium, 0·030 per cent; heavy metals as lead, 0·002 per cent; iron, 0·003 per cent. The MgO was prepared for use by igniting it at 1200°C for 24 hr, cooling over P_2O_5 and immediate weighing.

Manganous oxide was prepared from "Baker Analyzed" reagent grade MnO_2 of reported analysis as follows: MnO_2, 100·0 per cent; insoluble in HCl, 0·015 per cent; chloride, 0·002 per cent; nitrate, 0·025 per cent; sulfate, 0·025 per cent; iron, 0·03 per cent; earths and alkalies (as SO_4), 0·10 per cent. The MnO_2 was first heated at 1100°C in air for 24 hr to produce Mn_3O_4. The resulting Mn_3O_4 was then heated in commercial tank H_2 for two hours at 1100°C to produce manganous oxide of composition $MnO_{1.005}$, as determined by the method described below. (It is to be noted that the partial pressure of oxygen in the H_2 used in this investigation was high enough to prevent reduction of manganese oxide to metallic manganese.) Reduction of MnO_2 in two steps was employed in order to avoid the "spattering" produced by the violent decomposition of MnO_2 directly to manganous oxide at high temperatures.

The manganous oxide was analyzed by methods developed during the course of a previous investigation in this laboratory.(4) The sample, weighing approximately 0·1 g, was placed along with approximately 0·75 g of $Fe(NH_4)_2(SO_4)_2 . 6H_2O$ in 25 ml of distilled water and 10 ml of 1:4 H_2SO_4; 3 ml of 49 per cent HF was added. The solution was boiled for 10 min to dissolve all the sample. Upon cooling to room temperature, 25 ml of distilled water and 15 ml of 2 per cent H_3BO_3 were added and the solution was titrated with 0·05 N $KMnO_4$.

The nickel used was premium grade powder of representative analysis as follows: nickel, 99·9 per cent min.; carbon, 0·20 per cent max.; sulfur, 0·001 per cent max.; iron, 0·03 per cent max.; others, 0·01 per cent max.

3. *Control of atmosphere*

The method used for controlling oxygen pressures was similar to that used by DARKEN and GURRY(5) and later by MUAN(6). The atmospheres were obtained by mixing CO_2 and H_2 at room temperature; the partial pressures of oxygen at the temperatures of the experiments were then calculated from the data compiled by COUGHLIN(7). The gases used were of reported compositions 99·98 per cent CO_2 and 99·5 per cent H_2. The rate of flow of each of the two gases was measured separately by means of two capillary flow meters with bleeder tubes inserted on both ends of the capillaries to maintain a constant pressure drop. A series of mutually interchangeable capillaries of different openings was at hand so that a wide range of mixing ratios could be obtained with manometer readings of convenient magnitude. A third manometer was inserted in the line to measure the rate of flow of gas through the furnace tube. The flow meters were calibrated individually with the various capillaries, using a standard wet test meter.

4. *Furnaces and temperature control*

A vertical tube furnace with an 80 per cent Pt–20 per cent Rh resistance winding was used in this investigation. The furnace was equipped with ground glass joints fused to the top and bottom of the mullite furnace tube. The upper ground glass attachment was drawn out to a long, relatively narrow tube to prevent air from diffusing into the furnace tube. The gas from the mixer passed through the furnace tube from bottom to top.

Furnace temperatures were regulated by means of a Celectray controller. The thermal gradient at the hot spot did not exceed 2°C over one inch at 1400°C.

5. *Method of equilibration*

Equilibrium was approached from both sides in all runs carried out in the present investigation. In the case of the Ni–O system, one sample of metallic Ni and one sample of NiO were kept side by side in the furnace at chosen temperature and chosen oxygen partial pressure for 3–5 hr. After quenching the samples rapidly to room temperature, the phases present were determined by visual examination, supplemented in preliminary experiments by X-ray examination.

In the case of oxide solid solutions, one sample with NiO content above the equilibrium value and one sample with metallic nickel and oxide of NiO content below the equilibrium value were equilibrated side by side at chosen temperature and oxygen partial pressure for approximately 22 hr. It was found important to use starting oxide materials whose NiO contents were reasonably close to those at equilibrium, in order to avoid the presence of large quantities of metal phase which had a tendency to impair attainment of equilibrium.

Contamination of samples by crucible materials was avoided by pressing powders into discs which were then drilled to permit their suspension in the furnace from wires of pure nickel. The discs weighed approximately 0·2 gm; they were 1·0 cm in diameter and approximately 1 mm thick. The oxide samples were pressed at 25,000 p.s.i. and the pure metal samples at 6000 p.s.i.

That the method described above did in fact eliminate contamination was shown by the following observations. Samples of mixtures containing NiO, when run under conditions such that no metal phase was produced, exhibited the same d-spacing whether suspended from a nickel or a platinum wire and in atmospheres which were very reducing or slightly oxidizing with respect to the Ni–NiO equilibrium.

The samples used to establish variations of d-spacing with compositions in the oxide solutions were run in the furnace in much the same manner

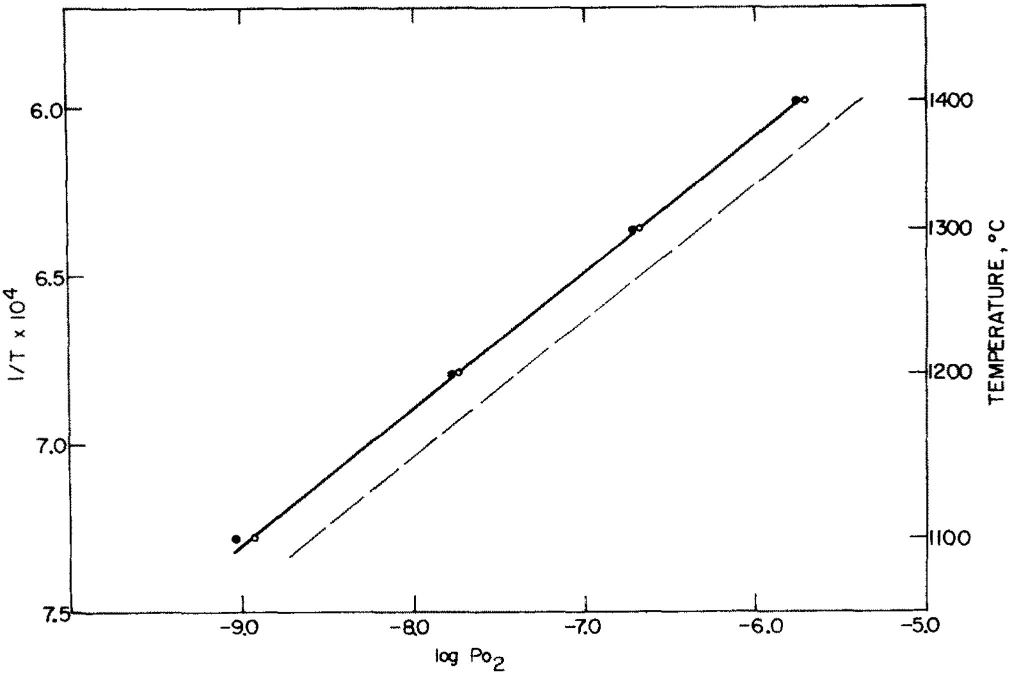

FIG. 1. Stabilities of the phases Ni and NiO as a function of oxygen partial pressure (log scale in atmospheres) and temperature (inverse °K scale). Solid and open circles represent observed stable occurrences of Ni and NiO, respectively. The solid line is drawn to fit the experimental data by the method of least squares. The dashed line is drawn to represent the same equilibrium based on data tabulated by COUGHLIN(7).

as described above. However, in these cases it was necessary to prevent the formation of a metal phase in order that the final composition would be the same as initially. In view of the above observation of negligible variation of *d*-spacing within a range of oxygen partial pressure, it was possible to prepare all of these samples in atmospheres which were slightly oxidizing with respect to the Ni–NiO equilibrium.

6. *X-ray analysis*

Compositions of oxide solid solutions were determined by accurate *d*-spacing (200) measurements and comparison with known standards. A General Electric XRD-3 diffractometer unit with scanning speed of 0·2° per minute and unfiltered iron radiation was used in these experiments. Metallic Ni served as an internal standard, based on the unit cell dimensions reported by SWANSON and co-workers.(8)

The (200)-reflections of the oxide solid solutions of interest in the present study occur at a value of 2θ in the neighborhood of 50° when iron radiation is used. This reflection was chosen rather than a higher angle reflection because the lower intensities and broadness of the latter reflections introduced difficulties in the determination of their position which more than vitiated the attendant advantages.

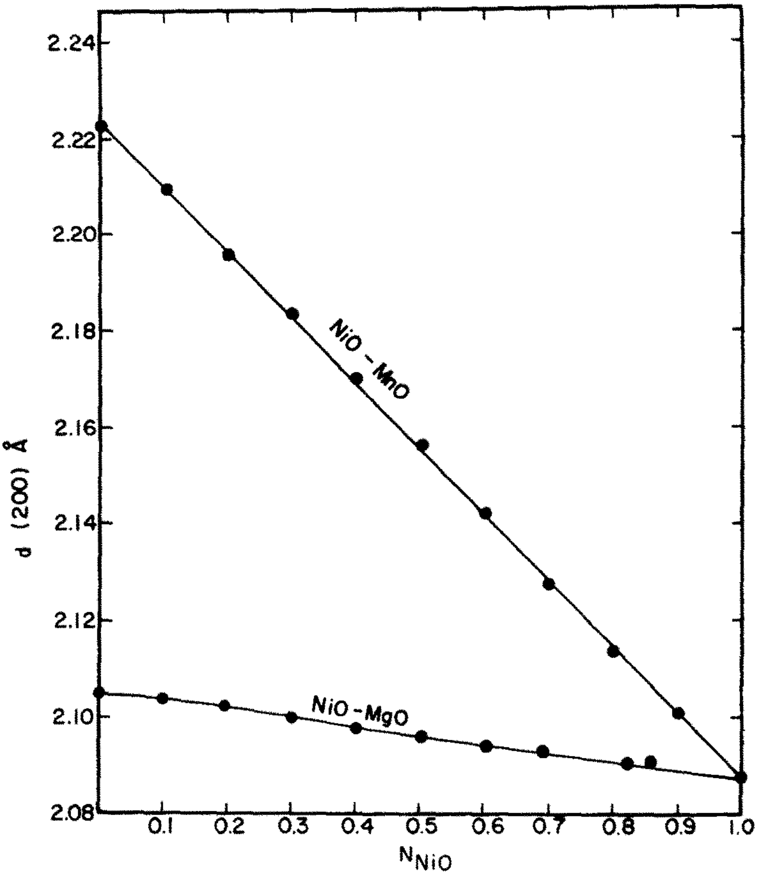

FIG. 2. Changes in *d*-spacing with composition in the systems NiO–MgO and NiO–MnO. Dots represent experimentally determined values, and straight lines connect points for *d*-spacings of the pure end numbers.

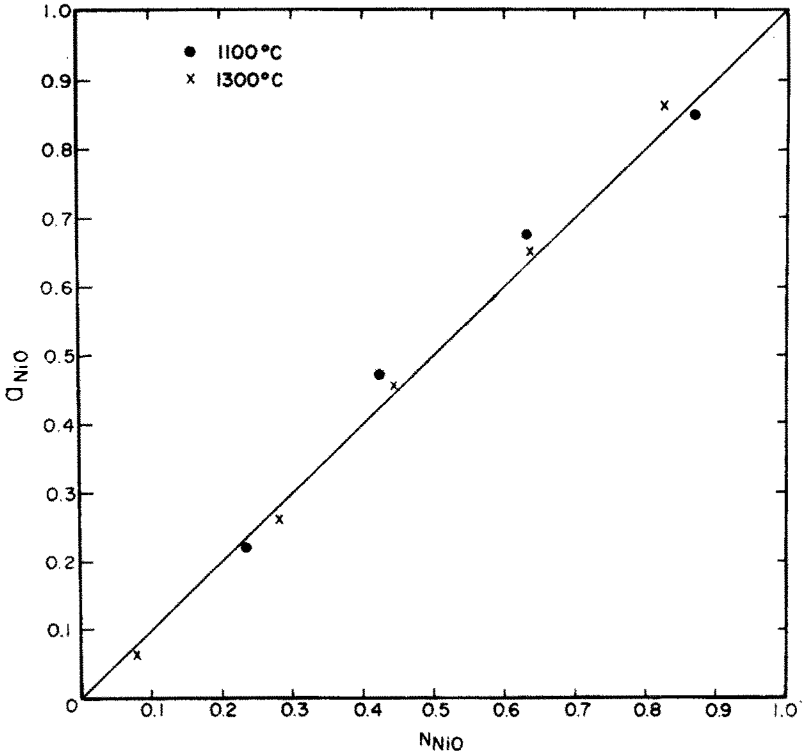

FIG. 3. Activity of NiO as a function of composition in the system NiO–MgO at 1100 and 1300°C. Symbols used are explained in upper left corner of diagram.

Table 1. *Critical runs for determination of the equilibrium* $2NiO = 2Ni + O_2$

Temperature, °C	$1/T \times 10^4$, °K^{-1}	$-\log P_{O_2}$	Duration of run, hr	Observed stable phase
1100	7·28	8·920	5	NiO
1100	7·28	9·034	5	Ni
1200	6·79	7·721	3	NiO
1200	6·79	7·763	3	Ni
1300	6·36	6·671	4	NiO
1300	6·36	6·705	5	Ni
1400	5·98	5·718	4	NiO
1400	5·98	5·758	4	Ni

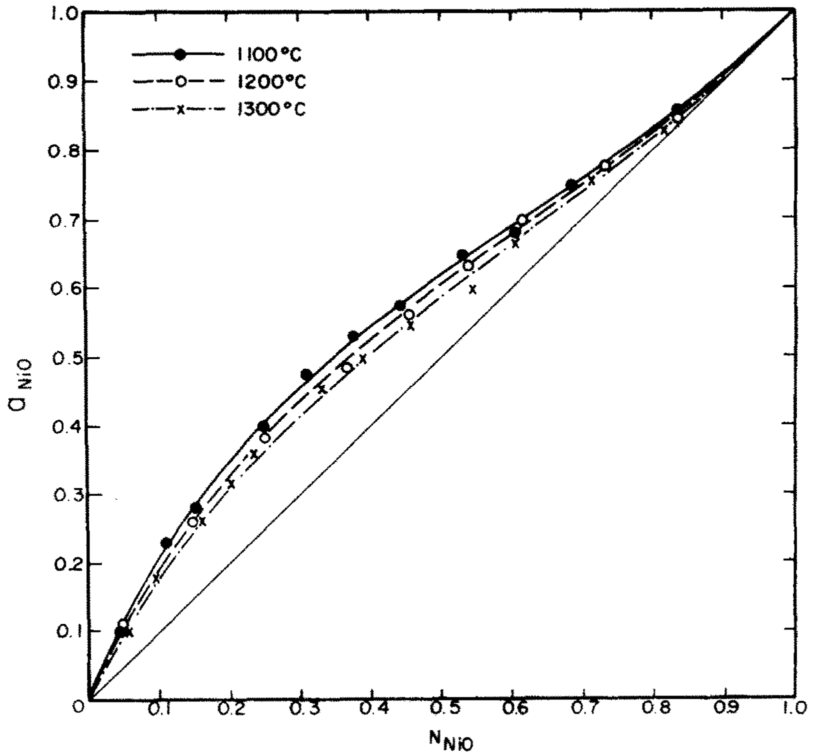

Fig. 4. Activity of NiO as a function of composition in the system NiO–MnO at 1100, 1200 and 1300°C. The symbols used are explained in upper left corner of diagram.

Table 2. d(200) *as a function of composition in the systems* NiO–MgO *and* NiO–MnO *as measured on samples heated at* 1300°C *for* 22 *hr in an atmosphere with* $P_{O_2} = 10^{-6.650}$ *atm. and quenched to room temperature*

The system NiO–MgO			The system NiO–MnO		
N_{NiO}	2θ	$d(200)$, Å	N_{NiO}	2θ	$d(200)$, Å
0·000	54·77	2·1045	0·000	51·65	2·2221
0·099	54·79	2·1038	0·100	51·97	2·2094
0·195	54·82	2·1027	0·200	52·31	2·1960
0·301	54·90	2·0999	0·301	52·64	2·1832
0·399	54·96	2·0977	0·400	52·98	2·1702
0·499	55·01	2·0960	0·504	53·35	2·1562
0·604	55·06	2·0942	0·600	53·73	2·1421
0·691	55·09	2·0932	0·700	54·13	2·1275
0·824	55·16	2·0907	0·800	54·51	2·1138
0·868	55·16	2·0907	0·900	54·87	2·1010
1·000	55·22	2·0886	1·000	55·22	2·0886

Table 3. *Activity measurements in the system* NiO–MgO

$-\log P_{O_2}$	N_{NiO} in starting mixture	End of run		N_{NiO} of solution, end of run	Calculated activity of NiO
		2θ	$d(200)$, Å		
1100°C					
10·297	0·195*	54·84	2·1020	0·22	0·22
	0·301	54·86	2·1013	0·25	
9·625	0·399*	54·96	2·0977	0·41	0·47
	0·499	54·97	2·0970	0·44	
9·317	0·604*	55·06	2·0942	0·61	0·68
	0·691	55·08	2·0935	0·65	
9·118	0·824*	55·16	2·0907	0·85	0·85
	0·868	55·18	2·0900	0·90	
1300°C					
9·081	0·000*	54·78	2·1041	0·06	0·06
	0·099	54·79	2·1038	0·10	
7·857	0·195*	54·88	2·1006	0·28	0·26
	0·301	54·88	2·1006	0·28	
7·366	0·399*	54·98	2·0970	0·44	0·46
	0·499	54·99	2·0967	0·45	
7·058	0·604*	55·07	2·0939	0·63	0·65
	0·691	55·08	2·0935	0·65	
6·825	0·824*	55·15	2·0911	0·82	0·85
	0·868	55·16	2·0907	0·85	

* Metallic nickel added to starting mixture.

The 2θ values were measured with an accuracy of approximately ± 0·01°, corresponding to an accuracy in d-spacing of ± 0·0004 Å.

III. RESULTS AND DISCUSSION

The equilibrium

$$2\text{NiO} = 2\text{Ni}+\text{O}_2$$

was investigated in the temperature interval 1100 to 1400°C and at oxygen partial pressures ranging from $10^{-8\cdot920}$ to $10^{-5\cdot758}$ atm. Data obtained in critical runs appear in Table 1 and are shown graphically in Fig. 1. Conditions for coexistence of Ni and NiO are expressed by the equation

$$\log P_{O_2} = 9{\cdot}043-24{,}730[1/T]$$

and the standard heat of reaction, ΔH^0, as determined (by method of least squares) from the slope of the curve in Fig. 1, is 113,140 ± 2300 cal. This agrees adequately with the value of 112,520 ± 650 cal as tabulated by COUGHLIN(7) for the same temperature interval.

Changes in d-spacing with composition for the (200)-reflection in the systems NiO–MgO and NiO–MnO are shown in Table 2 and Fig. 2.

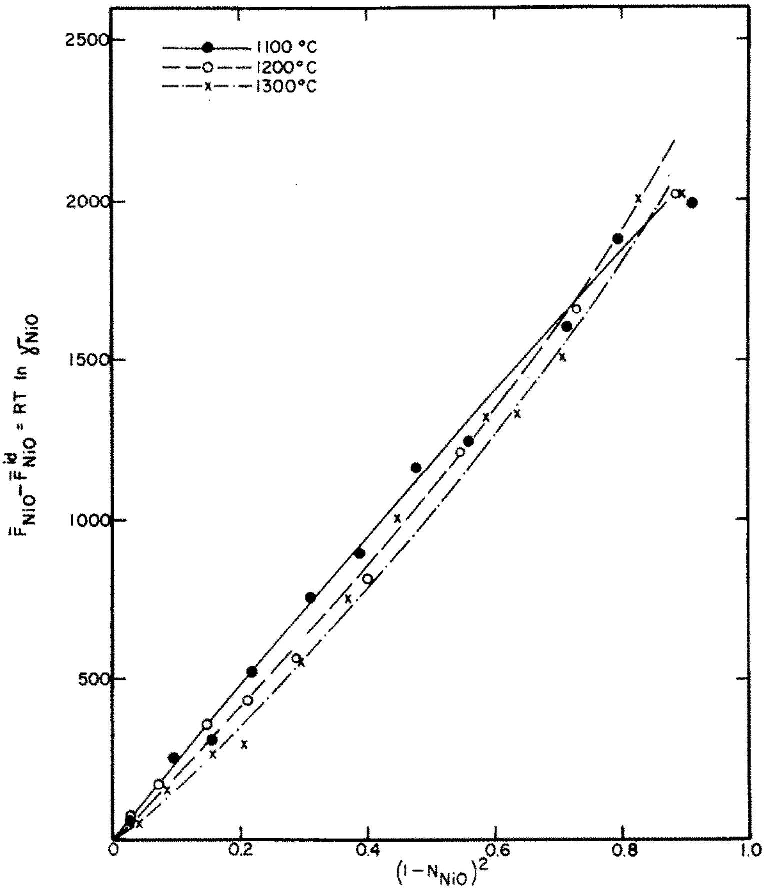

FIG. 5. Excess partial molal free energy of NiO dissolved in MnO at 1100, 1200 and 1300°C. Symbols used are explained in upper left corner of diagram.

Results of activity measurements are summarized in Tables 3 and 4 and shown graphically in Figs. 3 and 4.

The activity values listed in these tables have estimated accuracies increasing from approximately ± 0·02 at the highest NiO contents to approximately ± 0·01 at the lowest NiO contents of the oxide solid solutions.

Compositions (N_{NiO}) of solid solution crystals in the NiO–MgO series are accurate to approximately ± 0·03. This relatively wide limit is imposed by the flatness of the *d*-spacing vs. composition curve (Fig. 2). In the NiO–MnO system the *d*-spacing vs. composition curve is much steeper, and compositions (N_{NiO}) can be determined to approximately ± 0·003. The limiting factor in this solid solution series in most instances is the degree of attainment of equilibrium. This is shown (Table 4) by the spread in N_{NiO} values obtained by approaching the equilibrium from different directions. It is seen that the over-all accuracy of N_{NiO} in the system NiO–MnO varies in the range from approximately ± 0·003 to ± 0·035.

Excess partial molal free energy of NiO dissolved in MnO at 1100, 1200 and 1300°C is shown as a function of $(1-N_{\text{NiO}})^2$ in Fig. 5 (for a discussion of the significance of this function, the reader is referred to the book by DARKEN and GURRY(9)).

It is concluded from the data presented in the

Table 4. Activity measurements in the system NiO–MnO

$-\log P_{O_2}$	N_{NiO} in starting mixture	End of run		N_{NiO} of solution, end of run	Calculated activity of NiO
		2θ	$d(200)$ Å		
1100°C					
10·996	0·000*	51·78	2·2169	0·045	0·10
	0·100	51·79	2·2166	0·047	
10·297	0·100*	52·00	2·2081	0·112	0·22
	0·200	52·01	2·2078	0·114	
10·088	0·100*	52·12	2·2034	0·145	0·28
	0·200	52·16	2·2018	0·159	
9·781	0·200*	52·48	2·1893	0·250	0·40
	0·301	52·48	2·1893	0·250	
9·625	0·301*	52·63	2·1836	0·294	0·47
	0·400	52·73	2·1798	0·321	
9·533	0·301*	52·90	2·1732	0·370	0·53
	0·400	52·96	2·1709	0·387	
9·462	0·400*	53·15	2·1638	0·440	0·57
	0·504	53·18	2·1626	0·447	
9·358	0·504*	53·41	2·1540	0·512	0·64
	0·600	53·56	2·1484	0·550	
9·317	0·600*	53·74	2·1417	0·601	0·68
	0·700	63·77	2·1407	0·608	
9·233	0·700*	54·00	2·1322	0·668	0·74
	0·800	54·04	2·1307	0·680	
9·118	0·800*	54·53	2·1131	0·808	0·85
	0·900	54·69	2·1074	0·853	
1200°C					
9·677	0·000*	51·81	2·2158	0·052	0·11
	0·100	51·82	2·2153	0·056	
8·904	0·100*	52·13	2·2031	0·148	0·26
	0·200	52·13	2·2031	0·148	
8·581	0·200*	52·48	2·1893	0·250	0·38
	0·301	52·49	2·1890	0·252	
8·370	0·301*	52·88	2·1740	0·364	0·49
	0·400	52·92	2·1724	0·375	
8·242	0·400*	53·22	2·1611	0·458	0·56
	0·504	53·25	2·1600	0·466	

* Metallic nickel added to starting mixture.

Table 4 (Contd.)

$-\log P_{O_2}$	N_{NiO} in starting mixture	End of run		N_{NiO} of solution, end of run	Calculated activity of NiO
		2θ	$d(200)$, Å		
1200°C					
8·143	0·504*	53·52	2·1499	0·540	0·63
	0·600	53·53	2·1497	0·542	
8·055	0·600*	53·77	2·1407	0·608	0·70
	0·700	53·82	2·1388	0·620	
7·961	0·700*	54·15	2·1268	0·710	0·78
	0·800	54·31	2·1210	0·753	
7·885	0·800*	54·52	2·1134	0·807	0·85
	0·900	54·74	2·1056	0·868	
1300°C					
8·661	0·000*	51·81	2·2158	0·050	0·10
	0·100	51·83	2·2149	0·057	
8·207	0·000*	51·93	2·2110	0·088	0·17
	0·100	51·95	2·2102	0·094	
7·860	0·200*	52·16	2·2018	0·159	0·26
	0·301	52·19	2·2008	0·167	
7·701	0·200*	52·31	2·1961	0·200	0·31
	0·301	52·33	2·1953	0·205	
7·582	0·200*	52·43	2·1914	0·236	0·36
	0·301	52·44	2·1909	0·240	
7·369	0·301*	52·75	2·1790	0·327	0·46
	0·400	52·82	2·1763	0·347	
7·296	0·400*	52·96	2·1709	0·388	0·50
	0·504	52·97	2·1706	0·390	
7·218	0·400*	53·19	2·1623	0·449	0·54
	0·504	53·22	2·1611	0·457	
7·139	0·504*	53·53	2·1496	0·542	0·59
	0·600	53·53	2·1496	0·542	
7·046	0·600*	53·73	2·1421	0·600	0·66
	0·700	53·80	2·1395	0·616	
6·936	0·700*	54·11	2·1282	0·700	0·75
	0·800	54·20	2·1249	0·724	
6·848	0·800*	54·54	2·1126	0·815	0·83
	0·900	54·55	2·1123	0·817	

* Metallic nickel added to starting mixture.

tables and diagrams that the system NiO–MgO behaves ideally, whereas the system NiO–MnO shows considerable positive deviation from linear relationship. The latter system approaches the behavior of a regular solution, as the excess partial molal free energy is approximately proportional to $(1-N_{\text{NiO}})^2$ and is very little dependent on temperature.

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