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산화철계의 비화학양론에 관한 연구

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A Study on the Nonstoichiometry of the Iron Oxide System

Jae Shi Choi, Chul Hyun Yo and **Sung Nack Choi**
Department of Chemistry, Yonsei University, Seoul, Korea

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요 약. 0 °C～1200 °C 온도범위와 10^{-4}～10^2 mmHg 산소압력하에 산화철계의 무게감소를 석영마이크로 천평을 사용하여 측정하므로서 산화철계의 비화학양론에 대한 연구를 실시하였다. 이를 측정하기 위한 종래의 방법으로 시료를 급냉시킨후 분석을 하는 방법을 피하고 직접측정하여 FeO_{1+Y}의 Y값을 구하였다. $\log Y$ 대 $\log P_{O_2}$(혹은 $\log Y=n \log P_{O_2}$)의 Plot은 직선관계가 성립된다. 이의기울기에서 n값을 구한결과 1000°C에서는 $n=\frac{1}{10}$을 얻을 수 있고 이로부터 산화반응기구와 비화학양론적반응기구의 차이를 설명하였다. 화학양론적 FeO(Fe : O=1 : 1)를 형성하는 기준조건을 1200 °C와 10^{-3} mmHg 산소압력으로 하였으며 표준조건에서의 이산화철계의 조성은 $FeO_{1.11185}$로 표시된다. 일반적으로 낮은온도와 높은산소압력하에서 더많은 산소가 산화물계에 용해되어 화학양론적 FeO로 부터 편기가 크다. 산화철계의 전기전도도를 Y값과 비교해보면 전기전도의 전이점이 산화철계의 완전한 상전이를 동반하지 않음을 알 수 있었다.

Abstract. The nonstoichiometry of the iron oxide system has been studied by analyzing the weight loss of a sample, measured by using a quartz microbalance, in a temperature range from 0 °C to 1200 °C under oxygen pressures from 10^2 mmHg to 10^{-4} mmHg. The Y values of the formula, FeO_{1+Y}, that have been obtained by this means for various conditions of temperature and pressure in this range are considered to be more accurate than values obtained by methods requiring the quenching of the sample before measurements are made. The plots of $\log Y$ *vs* $\log P_{O_2}$ (or $\log Y = n \log P_{O_2}$) show linearity and n calculated from the slope of the plot is about 1/10 at 1000 °C, indicating a difference between the nonstoichiometric and oxidation mechanisms. The condition for the formation of stoichiometric FeO was determined to be 1200 °C under 10^{-3} mmHg of O_2 and the composition of the oxide under standard conditions was $FeO_{1.11185}$. As in general more oxygen dissolves into the oxide system at lower temperatures and higher oxygen pressures, the deviation from stoichiometric FeO is greater under those conditions. A comparison of the change in conductivity of the sample indicates that full phase transition does not take place with conductivity transition.

Introduction

At high temperature, iron develops a three layer[1] surface composed roughly of ferrous oxide (FeO), magnetite (Fe_3O_4) and ferric oxide (Fe_2O_3), the composition changing gradually in passing from one layer to the next as first emphasized by Pheil.[2] The composition of this iron oxide system varies with temperature and oxygen pressure and a clearer understanding of that variation is needed.

The decomposition reaction $4FeO \rightarrow Fe_3O_4 + Fe$ was studied by R. Collongues[3] at temperatures above 570 °C. He pointed out that a study of the properties of solid solutions containing iron oxides and ferrites (order-disorder transformations) revealed an analogy between the properties of nonstoichiometric compounds and intermetallic phases. V. A. Shushunov and M. M. Blagina[4] attempted to explain the phase transition of the two reactants when Fe_3O_4 and Fe (I) or Fe_2O_3 and Fe (II) are heated to various fixed temperatures in an evacuated quartz tube. When the mixtures were heated to 900 °C, reaction mixture (I) was practically complete in 15 minutes with the concentration of the bivalent ion at 95 %. The rate of formation of FeO for the reaction in mixture (II) depended on temperature to a greater degree and was faster than that of mixture (I). In both cases heat was applied for 45 minutes. In each case the reaction products consisted of FeO and the bivalent Fe content were determined by dissolving the oxide in 2 N-H_2SO_4 and titrating with 0.1 N-$KMnO_4$. Phase equilibrium for iron oxide has also been studied by B. Philips and A. Muan[5] in the 1194-1588 °C temperature range.

All of the earlier studies were carried out by means of titration[4] or X-ray[6] or electron diffraction of the quenched samples. Therefore the results were necessarily determined at room temperature and atmospheric pressure rather than under the temperature and pressure conditions before quenching. This change in conditions can not help but have introduced some error in the determination of the nonstoichiometry of the iron oxide system.

In this study the weight changes have been measured directly under the given conditions by a quartz microbalance[7] and the nonstoichiometric chemical formula of the iron oxide system interpreted from this data. While the measurement of the weight change of the oxide is very difficult due to the extra-fine handling required for the microbalance and the possible error due to bouyancy and thermomolecular flow[8] which modify the reading of this sensitive balance, an experimental procedure was devised to determine and compensate for this possible error. Measurements were made for various combinations of temperature and pressure ranging from 0 °C to 1200 °C and 10^{-4} to 10^2 mmHg of O_2 and the Y values for the composition formula[9], FeO_{1+Y}, calculated for each condition. The results indicate that partial phase changes[10] take place in the iron oxide system and they form solid oxide mixtures. The formula of the iron oxide system and the physical view of the reaction are discussed later in this paper.

Experimental Section

Preparation of polycrystalline iron oxide

Iron metal supplied by Johnson-Mathey and Company, "Specpure" iron rod, was used in the preparation of the polycrystalline iron oxide. The iron rod was cut into a rectangular shape and then oxidized according to the following steps; (i) the iron plate was etched with a saturated $FeCl_3$ solution and then with a 20 % $(NH_4)_2S_2O_8$ solution for 5 minutes each; (ii) the material was then oxidized in air at 1200 °C for 96 hours and cooled slowly; (iii) the oxide layers which formed were separated from the inner non-oxidized metal iron for use as the sample; (iv) the oxide sample was then again subjected to step (ii) mentioned above for 24 hours to ensure complete oxidation of any iron still remaining in the sample.

After the annealing process was completed the iron oxide sample was washed with distilled water and stored in a vacuum desicator. The weight of the sample used in this experiment was 0.037030 gram, and its composition under standard conditions, as determined in the investigation, was $FeO_{1.11185}$.

Apparatus

The oxide sample prepared as indicated above was placed in the sample basket of the microbalance in the atmosphere and temperature control system shown in *Fig.* 1. The microbalance, constructed of quartz fiber and in all essential details like a previous design of our own,[11] is located in its support tube with the sample suspended in the maximum temperature region of the furnance by the sample basket and hanger also made of quartz fiber. A centering device makes it possible to keep the specimen from touching the side walls. The temperature controller, with its thermocouple located in the sample region, controls the temperature of the sample in steps of 100 °C from 0 °C to 1200 °C. The oxygen gas is generated by heating potassium chlorate[12] at 600 °C in the oxygen generator and stored in the oxygen storage tank from which it is supplied to the sample chamber at the appropriate pressure.

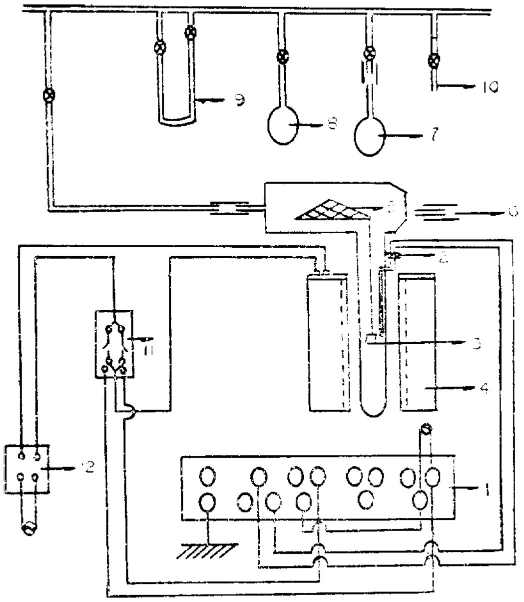

Fig. 1. Schematic drawing of measurement assembly. (1) Temperature controller, (2) Thermocouple, (3) Sample (Iron Oxide), (4) Furnace, (5) Microbalance, (6) Reading microscope, (7) Oxygen generator, (8) Oxygen tank, (9) Manometer, (10) Mcleod gauge and Ionization Gauge, (11) Relay, (12) Powerstat.

To calibrate the microbalance, the right arm of the balance beam is loaded with the sample in the sample basket and then the left arm of the beam is loaded with suitable riders made of platinum wire until the balance beam is approximately level. A point at the end of the horizontal beam is taken as a zero point for the balance height changes. Standard weights, cut from gold wire to give 100, 200, 300, 400 and 500 micro-grams and verified on a Cahn electrobalance, are then placed in turn on the left pan of the balance. The data shows that the balance height changes are proportional to the weight changes in this range and for this balance the following relation was obtained; $W=0.125\,h \pm 5\times10^{-4}$, where W is the weight change in milligrams and h is the balance height change in mm.

Experimental Procedure.

Due to the great sensitivity of the microbalance, which is about micro-gram, a serious problem arose in connection with effects due to buoyancy and thermomolecular flow.[8] The magnitude of these effects was directly measured in this experiment by the following procedure. Before measuring the weight change of the sample under various conditions, a pseudo-sample, of equal size and weight to that of the real sample and not susceptible to weight changes under the experimental condition, was put in the sample basket in place of the sample. The balance height change for this pseudo-sample made of quartz stick and platinum wire was measured under all the disired conditions, and then similar measurements were made with sample itself under the same conditions. The effective balance height change for the sample was the difference between the balance height change due to the sample and that due to the pseudo sample. For each condition of temperature and oxygen pressure the movement of the microbalance was observed through the reading microscope until there was no further change in position for at least several hours before the reading was made. The system can therefore be assumed to have reached thermodynamic equilibrium at each stage. The weight change of the sample was calculated from the relationship; $W=0.125\,h\pm5\times10^{-4}$. Where h is the balance height change and W is the weight change of the sample.

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Table 1. Effective balance height changes, weight changes of the sample and Y values at various temperatures under fixed air pressure of one atmosphere (inc. temp. -dec. temp. full cycle)

Temp. (°C)	Balance height change(mm)	Weight change		Y
		ΔW_1 (gm)	ΔW_2 (gm)	
0	0	0	9.0×10^{-4}	0.11185
100	0	0	9.0×10^{-4}	0.11185
200	0.20	3.0×10^{-5}	8.7×10^{-4}	0.10812
300	0.37	5.0×10^{-5}	8.5×10^{-4}	0.10563
400	0.55	7.0×10^{-5}	8.3×10^{-4}	0.10315
500	0.75	9.0×10^{-5}	8.1×10^{-4}	0.10066
600	0.80	1.0×10^{-4}	8.0×10^{-4}	0.09942
700	1.10	1.4×10^{-4}	7.6×10^{-4}	0.09445
800	1.90	2.4×10^{-4}	6.6×10^{-4}	0.08202
900	2.40	3.0×10^{-4}	6.0×10^{-4}	0.07456
1,000	3.20	4.0×10^{-4}	5.0×10^{-4}	0.06214
1,100	4.00	5.0×10^{-4}	4.0×10^{-4}	0.04971
1,200	4.80	6.0×10^{-4}	3.0×10^{-4}	0.03728
1,100	4.32	5.4×10^{-4}	3.6×10^{-4}	0.04474
1,000	4.00	5.0×10^{-4}	4.0×10^{-4}	0.04971
900	3.20	4.0×10^{-4}	5.0×10^{-4}	0.06214
800	2.90	3.6×10^{-4}	5.4×10^{-4}	0.06711
700	2.70	3.4×10^{-4}	5.6×10^{-4}	0.06959
600	2.55	3.2×10^{-4}	5.8×10^{-4}	0.07208
500	2.48	3.0×10^{-4}	6.0×10^{-4}	0.07456
400	2.25	2.8×10^{-4}	6.2×10^{-4}	0.07705
300	1.90	2.4×10^{-4}	6.6×10^{-4}	0.08202
200	1.60	2.0×10^{-4}	7.0×10^{-4}	0.08699
100	0.80	1.0×10^{-4}	8.0×10^{-4}	0.09942
0	0	0	9.0×10^{-4}	0.11185

stoichiometric FeO has been determined (see below), a thin film of the original spec-pure iron was placed in air at one atmosphere and 1200 °C and allowed to oxidize. Then the pressure was reduced to 10^{-3} mmHg for sintering. The final weight change of the thin film gave further check on the stoichiometric FeO.[6,13]

The conductivity[14] of the sample was measured for the full temperature range at a pressure of 10^{-4} mmHg of O_2.

Results

As shown in *Table* 1, the first series of experiments was designed to establish the temperature dependence of nonstoichiometry from 0 °C to 1200°C at intervals of 100 °C under a fixed air pressure of one atomsphere. After the increase-decrease full temperature cycle was completed, the microbalance returned to the original zero point. This shows that there was no nondissociated evaportion of the sample. However, some nondissociated evaporation of the sample was detected at an oxygen pressure of 10^{-4} mmHg and 1200 °C. If we correct for this evaporation, the nonstoichiometric quantity at 1200 °C under 10^{-4} mmHg of O_2 is the same as that at 1200 °C under 10^{-3} mmHg of O_2. We decided therefore that 1200 °C and 10^{-3} mmHg is the condition for the formation of stoichiometric ferrous oxide. Thus, for clarity, the real weight loss of the polycrystalline iron oxide starting from 0 °C under one atomosphere of air pressure, ΔW_1, has been converted to ΔW_2, the weight change based on the weight of the stoichiometric FeO formed at 1200 °C and 10^{-3} mmHg of O_2. For the various conditions, the weight changes of the sample from stoichiometric FeO formed at 1200 °C under 10^{-3} mmHg oxygen pressure can also be converted to the number of gram atoms of oxygen in excess per mole of FeO by the relationship:

$$Y=\frac{\Delta W_2}{W}\times\frac{M_{FeO}}{A_{WO}}=\frac{\Delta W_2}{0.03613}\times\frac{71.8464}{15.9994}$$

where W is the weight of the sample, ΔW_2 is the weight change from the stoichiometric sample weight, M_{FeO} is the molecular weight of ferrous oxide, A_{WO} is the atomic weight of oxygen and Y is the number of gram atoms of oxygen in excess per mole of FeO.

The Y values under various conditions are listed in *Table* 2 and *Table* 3. Plots of log Y *vs.* $1000/T$ are shown in *Fig.* 2 and *Fig.* 3 for

Table 2. The number of gram atoms of oxygen per mole of FeO or Y values as a function of oxygen pressure and temperature (increasing temperature)

O_2 press. (mmHg) / Temp. (°C)	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}
0	0. 11185	0. 11185	0. 11185	0. 11185	0. 11185	0. 11185	0. 11185
100	0. 10563	0. 10563	0. 10812	0. 10863	0. 11185	0. 11185	0. 11185
200	0. 09693	0. 09942	0. 10060	0. 10190	0. 10812	0. 11060	0. 11080
300	0. 09196	0. 09445	0. 09942	0. 09942	0. 10563	0. 10936	0. 11025
400	0. 08699	0. 09196	0. 09445	0. 09445	0. 10190	0. 10812	0. 11010
500	0. 07456	0. 08699	0. 08699	0. 08699	0. 09942	0. 10563	0. 10936
600	0. 06214	0. 07456	0. 07953	0. 08202	0. 09445	0. 09942	0. 10812
700	0. 05468	0. 06214	0. 07456	0. 07456	0. 08699	0. 09445	0. 10563
800	0. 03977	0. 04474	0. 06214	0. 06214	0. 07456	0. 08699	0. 09445
900	0. 03728	0. 03728	0. 04971	0. 05468	0. 06711	0. 07456	0. 08948
1, 000	0. 02485	0. 02485	0. 04474	0. 04971	0. 05219	0. 06959	0. 07705
1, 100	0. 01243	0. 01243	0. 02983	0. 03728	0. 04971	0. 06214	0. 07208
1, 200	0. 00000	0. 00000	0. 01243	0. 02485	0. 03728	0. 04971	0. 06074

Table 3. The number of gram atoms of oxygen per mole of FeO or *Y* values as a function of oxygen pressure and temperature (decreasingt emperature)

Temp. (°C) \ O_2 press. (mmHg)	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}
0	0. 11185	0. 11185	0. 11185	0. 11185	0. 11185	0. 11185	0. 11185
100	0. 09942	0. 09942	0. 10439	0. 10563	0. 10562	0. 10563	0. 10563
200	0. 08699	0. 08699	0. 09445	0. 09942	0. 09942	0. 09942	0. 09942
300	0. 07456	0. 07953	0. 08451	0. 08699	0. 09445	0. 09693	0. 09693
400	0. 06462	0. 07456	0. 07953	0. 08202	0. 08699	0. 09196	0. 09445
500	0. 05468	0. 06214	0. 07456	0. 07456	0. 07953	0. 08699	0. 09196
600	0. 04722	0. 05717	0. 06214	0. 06711	0. 07456	0. 08451	0. 08948
700	0. 03977	0. 04971	0. 05468	0. 06214	0. 07208	0. 07953	0. 08699
800	0. 02983	0. 03728	0. 04972	0. 05468	0. 06711	0. 07456	0. 08451
900	0. 01988	0. 02983	0. 04474	0. 04971	0. 06214	0. 06959	0. 07953
1, 000	0. 01243	0. 01740	0. 03480	0. 03977	0. 05717	0. 06214	0. 07456
1, 100	0. 00497	0. 01243	0. 01988	0. 03231	0. 04971	0. 05717	0. 06214
1, 200	0. 00000	0. 00000	0. 01243	0. 02485	0. 03728	0. 04971	0. 06074

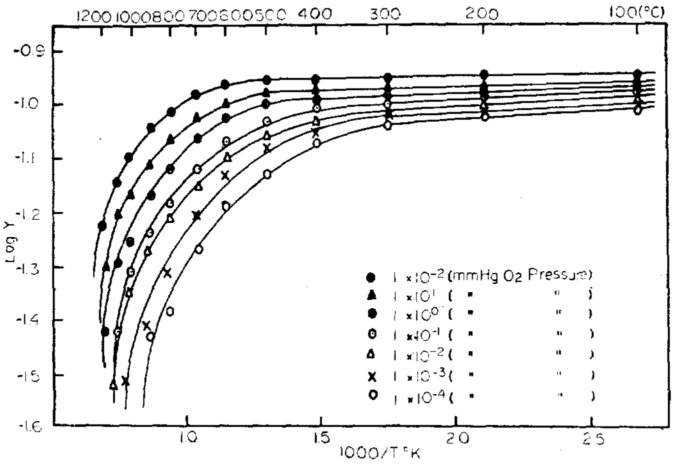

Fig. 2. Log *Y* *vs.* 1000/*T* (increasing temperature)

increasing and decreasing temperature respectively. Plots of log *Y* *vs.* log P_{O_2} are shown in *Fig.* 4 and *Fig.* 5 for each temperature. The plots are linear. And also a plot of log conductivity *vs.* 1000/*T* is shown in *Fig.* 6.

Discussion

We may classify nonstoichiometric compounds into the four principal types.[15] They are compounds with excess metal due to the existence of anion vacancies (type I), compounds with excess metal due to interstitial cations (type II), compounds with excess electronegative constituents due to the presence of interstitial anions (type III), and compounds with excess electronegative constituents due to cation vacancies (type IV). The iron oxide system is classified as type IV and cation vacancies or excess of the electronegative oxygen will form partly trivalent iron oxide. *Table* 1 lists the balance height change, weight change (ΔW_1, ΔW_2) and *Y* values at various temperatures for increasing and decreasing full cycle under one atmosphere of air pressure. Under the conditions covered in *Table* 1 no stoichiometric FeO was obtained; the formula was $FeO_{1.03728}$ at 1200 °C. The most likely explanation is that excess oxygen is dissolved in the substitutional sites of the oxide and this decreases with increasing temperature. There was still some dissolved oxygen at the maximum temperature reached at one atmosphere of pressure.

In *Table* 2, the nonstoichiometric quantities are listed for various conditions under increasing temperature, and in *Table* 3 they are listed for various conditions under decreasing temperatures. These values are not the same for identical conditions in the two cases.

When we measured the electrical conductivity of the iron oxide system[14] under increasing and then decreasing temperatures we found that it was not the same. This fact concerning the p-type semiconductor can be explained by the differencies in nonstoichiometric quantities between the two cases.

The Y values were calculated based on weight deviations from that of stoichiometric FeO for the various conditions. The Y values clearly show that the iron oxide has a nonstoichiometric form under these various conditions.

As shown in ***Fig.*** 2 and ***Fig.*** 3, the plots of log Y *vs.* $1000/T$ are not linear curves but nearly hyperbolas. Under a given oxygen pressure, more oxygen is dissolved into the oxide system at lower temperature and therefore the deviation from stoichiometric quantities is larger in the lower temperature region.

The plots of log Y *vs.* P_{O_2} are linear as shown in ***Fig.*** 4 and ***Fig.*** 5. The n values calculated from the slopes of the plot for $\log Y = n \log P_{O_2}$ are about 1/40 at 400 °C and about **1/10** at 1000 °C. It can be seen that the nonstoichiometric me-

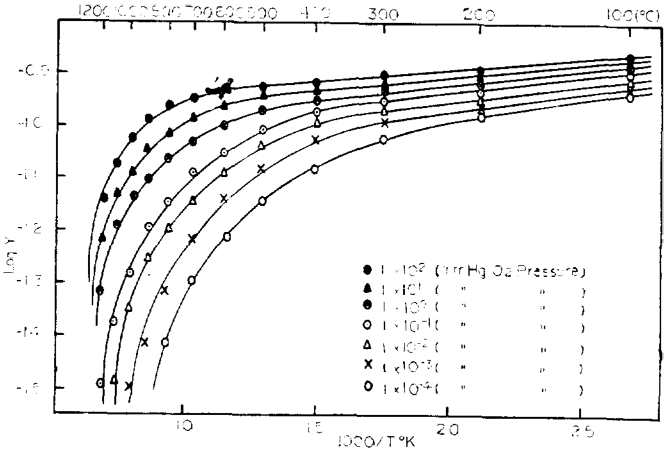

Fig. 3. Log Y *vs.* $1000/T$(decreasing temperature)

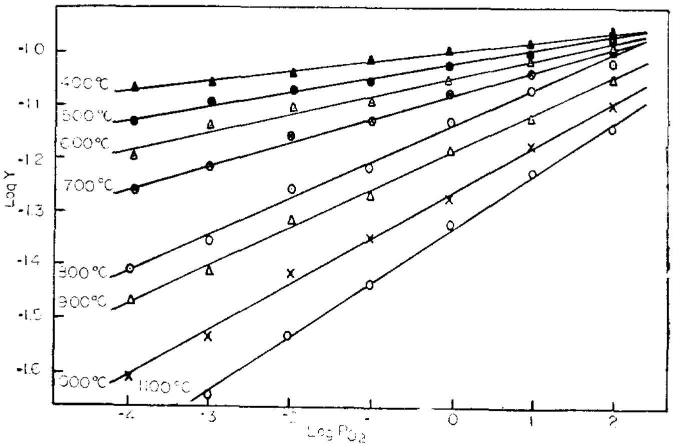

Fig. 4. Log$Y$ *vs.* log P_{O_2} (Increasing temperature)

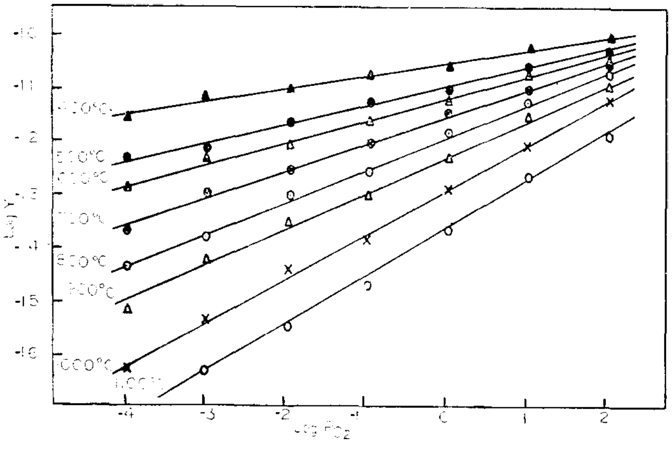

Fig. 5. Log Y *vs.* log P_{O_2} (Decreasing temperature)

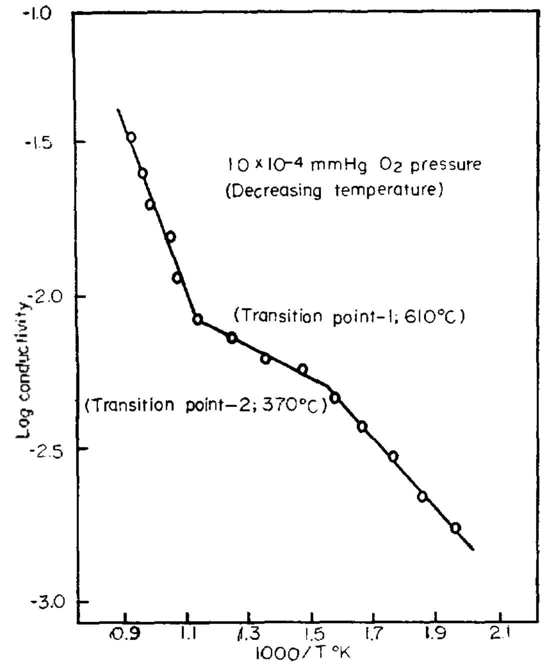

Fig. 6. Log conductivity *vs* 1000/*T*

chanism is different from the oxidation mechanism which has in general larger *n* values than the above values. The slope of the curve is steeper at higher temperatures than at lower temperatures. This also shows that the nonstoichiometry of the iron oxide system depends increasingly on the oxygen pressure at high temperatures. The *Y* values are larger in the low temperature and high oxygen pressure region. Inversely, at lower oxygen pressure and higher temperatures, more stoichiometric ferrous oxide is formed.

These *Y* values of the formula, FeO_{1+Y}, are more accurate than the values obtained from the titration analysis method[4,16] or X-ray diffraction method with quenched[5,6] samples because a quench sufficiently drastic to preserve the structure or the composition is extremely difficult. Indeed it is doubtful whether a method depending upon a quench has ever revealed correctly the high temperature boundaries of the wustite field.

It is to be expected that most of the physical properties of the oxide such as the electrical conductivity, thermal electrical power, Hall effect, catalytic effect, together with their mechanisms can be explained by the nonstoichiometry of the sample. For example, the electrical conductivity of the iron oxide system changes at a uniform rate within a phase area, but there is a definite change at the transition points. The *Y* values, on the other hand, do not show this radical change at the transition points of conductivity[14,17] (*Fig*. 6). It can be seen that a small deviation from stoichiometry will make a radical change in conductivity. The transition point of the plot of log conductivity *vs* 1000/*T* is therefore, not accompanied by a full phase transition of the iron oxide system.

These *Y* values can now be used as basic data for the interpretation of the physical properties of the iron oxide system.

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