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THE STABILITY OF GASEOUS NICKEL OXIDE

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Berkeley, California

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The Stability of Gaseous Nickel Oxide

1. Introduction.

The apparent instability of FeO with respect to dissociation upon vaporization[1] leads one to suspect that NiO would behave in a similar fashion by virtue of the close similarity in the chemical properties of iron and nickel. However, Johnston and Marshall[2] report that gaseous NiO shows only a negligible tendency to dissociate between the temperatures 1438 and 1566° K. There are other reports in the literature which conflict with this,[3] indicating in some cases a high dissociation pressure at lower temperatures.

The stability of gaseous NiO has been investigated herein by a thermodynamic treatment of Johnston and Marshall's excellent data and experimental studies of the phase changes in solid NiO at high temperatures and the composition of the condensate resulting from effusion from a Knudsen cell containing NiO(s).

2. Thermodynamic Treatment.

Johnston and Marshall[2] determined the vapor pressure of NiO by measuring the rate of vaporization from a nickel ring which was slightly oxidized on its surface to NiO. The ring was supported in high vacuum and heated by induction. Extreme precautions were taken to assure accuracy in the experimental techniques. A determination of total weight loss per unit time was supplemented by a determination of the weight of oxygen lost during each run by subsequent reduction of the oxide film by hydrogen. Thus, assuming the only species which transported oxygen from the solid to the gas phase was NiO(g), the weight loss of Ni and NiO per unit time was determined. All weighings were carried out with an accuracy of $\pm$ 0.02 mg.

In the calculation of vapor pressures from these data, Johnston and Marshall used the expression

$$\log p + \log \alpha = \log m - \frac{1}{2} \log M + \frac{1}{2} \log T - 1.647$$

in which p is the pressure in atmospheres, α is the reflection coefficient, m is the weight loss in grams per cm^2 per second and T is the temperature in °K. In their treatment the reflection was assumed to be essentially zero which is in accord with other results in the literature.[4]

In the reference paper Johnston and Marshall give the free energy functions for Ni(s) as calculated by them from recent heat capacity data[5], and the same functions are given for NiO(g), as calculated from spectroscopic data. In the discussion of their results, they combine the functions for Ni(s) and NiO(s) with the free energy functions for O_2(g) given by Johnston and Walker[6] and the standard heat of formation of NiO(s) at 298.1°K as given by Roth[7] in order to calculate the dissociation pressure of oxygen to be expected under their experimental conditions. The pertinent results of their treatment of the NiO vapor pressure data and their calculated O_2 dissociation pressure are given in Table I.

By using the $\frac{F^o - H^o_o}{T}$ functions of NiO(s) and NiO(g) in conjuction with the ΔF^o values as calculated from the NiO(g) vapor pressures given in Table I, Johnston and Marshall calculated the ΔH^o_o for the sublimation of NiO(s). This value, $\Delta H^o_o = 117{,}055 \pm 1000$ cal, was found to be essentially constant over the temperature range investigated. This fact and the calculated low values for the oxygen dissociation pressures were taken as definite indication that the dissociation of NiO(s) was quite negligible at these temperatures.

Table I

T°K	Initial O_2, gms.	Evap. loss total, gms.	Residual O_2, gms.	Time, secs.	NiO evap. gms.	NiO v.p., atm	P_{O_2} atm
1438	0.01424	0.01732	0.01381	6930	0.00200	2.43×10^{-9}	
1441	.00759	.01160	.00722	7001	.00173	2.09×10^{-9}	7.76×10^{-10}
1495	.01840	.01803	.01770	2286	.00327	1.23×10^{-8}	3.29×10^{-9}
1511	.00917	.00465	.00877	609	.00187	2.66×10^{-8}	5.00×10^{-9}
1529	.00921	.01139	.00837	1340	.00392	2.72×10^{-8}	7.37×10^{-9}
1566	.0044	.01893	.00289	759	.0070	8.51×10^{-8}	1.84×10^{-8}

Now it was found that during their NiO vapor pressure runs the underlying Ni continued to vaporize essentially unimpeded through the NiO layer. Actually, their analyses show that the weight loss assumed to be due to NiO(g) varied from 12 to 46% of the total loss in their heatings. Thus, since the weight loss of oxygen is quite small relative to the total, it would be exceedingly difficult to fix the actual species responsible for the transference of the oxygen to the gas phase from their data alone.

In regard to their derivation of oxygen dissociation pressures it should be pointed out that the ratio of P_{NiO} to P_{O_2} is not actually as large as is indicated by their calculated pressures given in Table I. In the first place, it will be seen that the pressure which is obtained by the relation given above is a rather sensitive function of the molecular weight of species chosen for the calculation, this choice affecting the terms m and M. For instance, given the weight loss of oxygen per unit time one can assume that either the species NiO(g) or O_2(g) is responsible for the loss of oxygen from the solid NiO. The same oxygen weight loss then allows a calculated P_{NiO} <u>or</u> P_{O_2} which will have the following ratio:

$$P_{O_2} = \frac{0.214(m_{NiO})}{0.428(44.383)} \frac{\sqrt{T}}{\sqrt{M_{NiO}}} = 0.327\ P_{NiO}$$

The ratio of P_{O_2} to P_{NiO} as calculated by Johnston and Marshall (Table I) vary from 0.373 to 0.187. Thus, actually the oxygen pressures which they have calculated from thermodynamic data appear to agree reasonably well with those which they would have obtained if they had treated their experimental data for the species O_2(g) rather than NiO(g). In other words, the ΔH_0^0 of dissociation of NiO(s) which they used would agree very well with the average ΔH_0^0

which one would obtain by a treatment of their oxygen loss data assuming only dissociation to be occurring. By making use of the O_2 pressures they have calculated (Table I) and the free energy functions which they used one finds they use $\Delta H_0^0 = 59.5$ kcal. Again using the same functions and deriving the O_2 pressures from their data, we obtain $\Delta H_0^0 = 59.3$ kcal.

Now the second point to be made concerning the ratio of P_{NiO} to P_{O_2} given by Johnston and Marshall concerns the ΔH_0^0 which they have used in calculating their dissociation pressures. The National Bureau of Standards[8] gives $(\Delta H_{298}^0 - \Delta H_0^0) = 0.6$ for the reaction $NiO(s) = Ni(s) + \frac{1}{2} O_2(g)$. The heat of the reaction is greater at 298.1°K than at 0°K. However, Roth's value which they use as ΔH_{298}^0 is 58.9 kcal. The only explanation for the $\Delta H_0^0 = 59.5$ which they apparently use in calculating their O_2 pressures is that they added the $(\Delta H_{298}^0 - \Delta H_0^0)$ correction to Roth's heat rather than subtracting. This then introduces an error of about one kilocalorie in their ΔF^0 of dissociation and results in O_2 pressures which are roughly a factor of two lower than would result from the proper use of the $(\Delta H_{298}^0 - \Delta H_0^0)$ correction. With these two factors which normalize their P_{NiO} to P_{O_2} ratio, and indeed increase their O_2 pressures, one is no longer justified in concluding that dissociation is negligible relative to direct vaporization.

A recent evaluation by L. Brewer[9] of existing data on the heat of dissociation places the most probable value at $\Delta H_{298}^0 = 57.5$. If this were used instead of Roth's value, even higher dissociation pressures would result from such calculations. However, it will be recalled that the treatment of Johnston and Marshall's experimental data gave the still higher heat $\Delta H_{298}^0 = 59.9$, which of course means

that the oxygen pressures calculated from their data will be lower than those calculated by the use of Brewer's heat and the free energy functions used by Johnston and Marshall. While the reason for this discrepancy is not apparent, it is in the proper direction to support the dissociation mechanism. That this is so may be explained as follows: by assuming only the species $O_2(g)$ is responsible for the disappearance of O_2 during the heatings, we calculate from the weight loss and free energy functions a heat of formation of NiO(s) at 298.1°K which is higher than any heat given in the literature. If now, one assumes that any of the oxygen lost is in combination with nickel, then this will by virtue of introducing a lower oxygen pressure into the calculations necessarily give a calculated heat of dissociation still higher. Therefore, it appears that the dissociation mechanism is the only hypothesis by which Johnston and Marshall's data assumes the best fit to existing thermodynamic data.

With respect to the discrepancy between the heat of formation of NiO(s) which is derived from Johnston and Marshall's data and the free energy functions they give and the same heat which Brewer gives, it should be mentioned that there is apparently some error in the high temperature heat capacity data[5] which Johnston and Marshall used in calculating the free energy functions for NiO(s).[10] However, a still more serious factor may lie in the difference between the heat of formation of NiO(s) at a composition saturated with Ni (as in the experiments discussed herein) and the NiO(s) compositions used by the various experimentors who have reported this heat in the literature.

3. Experimental.

The NiO used in these high temperature heatings was obtained from a bottle of Baker's C.P. NiO and gave the following spectrochemical analysis: Be, Co, Fe, Ti, and V, not detected. The carbon content, determined by micro combustion, was 0.006%. No further purification was attempted. All samples were air dried at 140° C for 48 hours prior to use.

The heatings were effected by induction heating, the equipment and techniques being the same as those described in detail elsewhere.(11)

While in general it is desirable thermodynamically to use refractory metal containers for oxides at high temperatures, it was found that W was very unsatisfactory as rapid reduction of the NiO occured, forming the volatile tungsten oxides and the low melting W-Ni eutectic. By this, one could rule out Ta and Mo as the former was quite unstable towards FeO at 1600°C within one hour, and the latter has essentially the same electronegativity as W, oxides of high volatility at these temperatures and a low melting eutectic. Considering the high difference in the ionic radii of Be^{++} and Ni^{++} which would lead one to expect only slight solid formation between BeO(s) and NiO(s), and the fact that the minimum in the NiO-BeO liquidus curve occurs at 1890°C which is well above the temperature range investigated, this material was used as the container. The BeO crucible and effusion lid with an effusion hole $8.12 \times 10^{-2} cm^2$ in area were of the same dimensions as those used in the studies of the vapor-pressure of iron.(11)

Three effusion runs were made, two at 1816°K for 60 minutes each, and one at 1782°K for 100 minutes. After the first run tiny

globules of metallic Ni were found on the crucible walls as a result of condensation. Otherwise, the walls and lid were clean except for a continuous blue coloration. X-ray diffraction and spectrochemical analyses were made of the effusate which collected on a water-cooled Pt plate and of the solid remaining crucible.

The effusate, aside from large amounts of Ni, showed the following to spectrochemical analysis: Co, V, Ti, not detected; Be and Fe, $\sim$ 0.01%. X-ray diffraction showed the existence of two phases: Ni(s) and NiO(s). The same analyses carried out on the solid remaining in the crucible after heating for 220 minutes showed spectrochemically: Co, V, Ti, not detected; Be, Fe, $<$0.01%; by X-ray diffraction, two phases were present: Ni(s) and NiO(s). It is seen that BeO is a satisfactory container for NiO(s) at these temperatures.

Now at first inspection of these results it appears that dissociation is occurring in such a manner to bring about a continuous production of a Ni phase by virtue of the loss of oxygen. However, from Johnston and Marshall's data one calculates that at 1438°K, for example, the ratio of oxygen atoms to nickel atoms vaporizing from a surface mixture of nickel and nickel oxide or from an effusion chamber containing both nickel and nickel oxide phases should be about 0.1. Thus if one vaporizes such a mixture at constant temperature, the nickel phase will eventually disappear leaving a nickel oxide phase which will lose nickel. As the nickel content of the nickel oxide solid solution decreases, the nickel partial pressure will decrease and the oxygen partial pressure will rise until the composition of the solid is equal to the composition of the vapor. When this is reached, one will have a constant vaporizing mixture which will vaporize without change in composition. If one

starts well inside the nickel oxide solid solution range, the rate of escape of oxygen is higher than the rate of escape of nickel and the oxygen content of the solid solution decrease until the constant vaporizing mixture is reached.

Thus upon heating NiO, one should not form any Ni metal phase at the heating temperature. However, if the solubility of Ni in the nickel oxide phase or the extreme limit of the nickel oxide solid solution range decreases with decrease in temperature sufficiently and if the constant vaporizing composition is close enough to the Ni rich limit of the nickel oxide solid solution range, then one can obtain a nickel phase upon cooling the single phase constant vaporinzing nickel oxide solid solution due to disproportionation to metallic nickel and a nickel oxide solid solution higher in oxygen content. This appears to be the case for nickel oxide, since one obtains a mixture of nickel metal phase and nickel oxide phase upon cooling the constant vaporizing nickel oxide. Also one obtains nickel and nickel oxide phases in the sublimate due to the disproportionation of the same constant vaporizing composition.

No data are available in the literature on the Ni-NiO phase diagram, but these results indicate that study of this system will indicate a wide solid solution range for the nickel oxide cubic range with an increasing solubility of nickel in the oxide phase with increasing temperature.

In order to establish definitely the absence of reducing agents in the Baker's NiO which could account for the presence of nickel after heating, the nickel oxide was heated for 90 minutes at 1302°K. In a second run, the NiO was heated to 1629°K for 4 minutes, cooled to 1296°K over 12 minutes and held at 1296°K for 60 minutes. Under

these conditions, essentially no change in composition will result from volatilization and if a metallic nickel phase is found after the heating it must be due to a reducing impurity in the NiO. In both cases the X-ray diffraction pattern was exactly similar to that of the original nickel oxide with no metallic nickel lines being visible. These results exclude the possibility of reducing agents being responsible for the appearance of the metallic nickel phase in the effusion runs. Furthermore, the second heating to 1629°K and subsequent slow cooling shows that the NiO was not originally a metastable phase as no metallic nickel phase resulted from this treatment. Since analysis indicates the composition of the starting nickel oxide is $NiO_{0.995}$, the constant vaporizing composition at 1800°K must be richer in nickel than $NiO_{0.995}$ and the nickel rich solid solution limit at 1800°K must be even richer in nickel content.

From the results of these investigations one is led to the conclusion that nickel oxide must vaporize by dissociation since loss of the species NiO(g) would not result in nickel oxide solid solution which was unstable with respect to disproportionation into a metallic nickel phase and a solid solution nickel oxide phase at low temperatures since the original nickel oxide is not metastable in this respect.

4. Summary.

A thermodynamic treatment of Johnston and Marshall's data for the vapor pressure of nickel oxide indicates that the dissociation mechanism accounts for weight losses observed when nickel oxide is heated at high temperatures in vacuum. It is shown that their data actually affords a calculated heat of dissociation which is almost

exactly the heat which they chose in their calculations of the dissociation. The probable reasons that they concluded that dissociation was completely negligible are (1) the same data will give calculated oxygen pressures which are one third of the calculated nickel oxide pressures because of the difference in molecular weights, and (2) the oxygen pressures upon which they drew their conclusion were calculated from existing thermodynamic data in whose use an error was made which resulted a lowering of their results by a factor of two. Also, it is shown that the treatment of their data assuming dissociation yields a heat of dissociation which is higher than any heat in the literature and thus if the oxygen pressure were reduced by combination with nickel to form the NiO(g) species the calculated heat of dissociation only could diverge more from the literature values.

It is shown experimentally that nickel oxide changes in composition during heating at about 1800°K in an effusion cell such that upon cooling both a nickel oxide and metallic nickel phase are present. The same phases are found in the effusate which is collected on a water-cooled platinum collector. Since Johnston and Marshall's data show that from such a system containing both nickel and nickel oxide phase the initial ratio of oxygen to nickel atoms escaping must be about 0.1, it is concluded that the nickel phase must gradually disappear leaving a nickel oxide phase which will lose nickel until the composition of the solid is equal to the composition of the vapor, after which no further change in composition will occur. Since both the nickel oxide and metallic nickel phases appear upon cooling, it appears that the single oxide phase which is formed at the high temperature must disproportionate upon cooling; that is, the

nickel oxide must have a wide solid solution range with an increasing solubility of nickel in the oxide phase with increasing temperature.

Upon heating NiO to 1629°K for 4 minutes, gradually cooling to 1296°K and holding at the latter temperature for one hour it is found upon cooling that the X-ray diffraction pattern is sharp and unchanged from that of the unheated NiO, and that no metallic nickel lines are present. Therefore the original nickel oxide is not metastable with respect to disproportionation, and furthermore does not contain a reducing impurity which can account for the appearance of the nickel phase in the effusion experiments. If only the species NiO(g) were vaporizing from the effusion chamber the necessary change in composition for the disproportionation could not occur and thus dissociation is indicated as an important process in the vaporization.

In conclusion, one finds that Johnston and Marshall's data actually afford a better fit to the vaporization of nickel oxide by dissociation than to vaporization to the species NiO(g) as proposed by them. Experimental studies of the vaporization of nickel oxide from an effusion chamber further support the dissociation mechanism.

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