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decompositions in N_2O, however, indicates that a stable, excited state of the ion does exist and that transitions from this excited state take place to a repulsive state. That all such transitions are not immediate may be due to a difference in multiplicity of the two states or a crossing of the potential curves at rather improbable interatomic distances requiring a tunneling effect for transition. The striking experimental fact about the mass spectra of all the species of N_2O is the appearance of ions produced by process (4). These ions were also reported for $N^{14}N^{15}O$ by Friedman and Bigeleisen,[5] who estimated a seven percent rearrangement in this molecule. In addition, our observations of the metastable peaks show this same association of nonbonded N and O atoms. A possible explanation of process 4 is the formation of triangular, activated ions which then decompose by the breaking of two bonds, yielding NO^+ ions which contain either of the nitrogen atoms from the N_2O. Thus it appears that in the case of the electron impact ionization and dissociation of N_2O, there are in operation simultaneously several processes as discussed above, and that no one picture exclusively explains the observed mass spectra.

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Thermodynamics of the Vaporization of Nickel Oxide*

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A mass spectrometric investigation of the vapor species in equilibrium with nickel oxide has shown the vapor phase to consist of Ni, O_2, NiO, and O, whereas the solid phase consists of a NiO solid solution and Ni(s). The dissociation energy of NiO(g) was found to be 86.5±5 kcal/mole.

INTRODUCTION

The vaporization of nickel oxide has been the subject of a number of investigations.[1] The most recent quantitative study is that of Johnston and Marshall[2] who performed a Langmuir type vaporization of a nickel oxide film which had previously been formed by oxidation of a nickel ring. Johnston and Marshall concluded that NiO vaporized without dissociation. They based this conclusion on the fact that the calculated $\Delta H_0{}^\circ{}_{\mathrm{vap}}(\mathrm{NiO})$ was constant as a function of temperature and, further, that they failed to detect the presence of oxygen in gases pumped off during one of their runs.

Brewer and Mastick[3] in a re-evaluation of Johnston and Marshall's data have cited evidence which indicates that the vaporization of NiO is primarily by dissociation to the elements. In addition, Brewer and Mastick performed several qualitative experiments in which x-ray examination revealed the presence of Ni and NiO in the vapor condensate and also in the residue which remained in the Knudsen cell after prolonged vaporization experiments. Brewer and Mastick believe that the Ni–O system possesses a wide solid solution range for NiO and that the solubility of nickel in the oxide phase increases with increasing temperature. Thus they feel that, in the case of the condensate, the nickel found in the x-ray pattern is due to disproportionation of the condensate from the constantly vaporizing NiO solid solution. And as the temperature is decreased, the decreased solubility of Ni in NiO at the lower temperatures results in precipitation of Ni in the residue.

Using the results of Johnston and Marshall, Brewer and Mastick have calculated a limiting dissociation energy for NiO of ≤ 99 kcal/mole. More recently, Huldt and Lagerqvist[4] attempted to determine the dissociation energy of NiO using the spectroscopic flame technique. The dissociation of NiO in the flame was so pronounced, however, that they were unable to determine an exact value, and a limiting value of ≤ 97 kcal/mole was estimated.

A spectrum which was attributed to NiO has been reported by Rosen.[5] The spectroscopic information on NiO is fragmentary and no value for the dissociation energy has been reported.

This mass spectrometric investigation was under-

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[1] (a) H. W. Foote and E. K. Smith, J. Am. Chem. Soc. **30,** 1344 (1908); (b) R. N. Pease and R. S. Cook, J. Am. Chem. Soc. **48,** 1199 (1926); (c) L. Wohler and O. Balz, Z. Elektrochem. **27,** 406 (1921); (d) A. Skapski and J. Dabrowski, Z. Elektrochem. **38,** 365 (1932); (d) A. F. Kapustinsky and L. Schamovsky, Z. anorg. u. allgem. Chem. **216,** 10 (1933).

[2] H. L. Johnston and A. L. Marshall, J. Am. Chem. Soc. **62,** 1383 (1940).

[3] L. Brewer and D. F. Mastick, J. Chem. Phys. **19,** 834 (1951).

[4] L. Huldt and A. Lagerqvist, Z. Naturforsch. **9a,** 358 (1954).

[5] B. Rosen, Nature **156,** 570 (1945).

TABLE I. Partial pressures of species in equilibrium with the Ni–O system.

T °K	P_{Ni} (atm)	P_{NiO} (atm)	P_{O_2} (atm)
1575	3.47×10^{-7}	4.46×10^{-9}	1.83×10^{-7}
1587	5.66×10^{-7}	8.98×10^{-9}	2.71×10^{-7}
1596	5.73×10^{-7}	8.34×10^{-9}	2.90×10^{-7}
1606	6.97×10^{-7}	1.33×10^{-8}	3.48×10^{-7}
1624	1.09×10^{-6}	1.70×10^{-8}	7.82×10^{-7}
1625	1.09×10^{-6}	1.77×10^{-8}	6.55×10^{-7}
1630	1.21×10^{-6}	2.17×10^{-8}	7.34×10^{-7}
1646	1.78×10^{-6}	3.23×10^{-8}	1.07×10^{-6}
1651	1.96×10^{-6}	3.67×10^{-8}	1.30×10^{-6}
1657	2.16×10^{-6}	3.85×10^{-8}	1.73×10^{-6}
1659	2.19×10^{-6}	4.45×10^{-8}	1.52×10^{-6}
1673	2.79×10^{-6}	5.90×10^{-8}	1.98×10^{-6}
1673	2.88×10^{-6}	5.65×10^{-8}	2.05×10^{-6}
1679	3.22×10^{-6}	6.58×10^{-8}	2.23×10^{-6}
1679	3.20×10^{-6}	7.31×10^{-8}	2.60×10^{-6}
1684	3.59×10^{-6}	7.06×10^{-8}	2.71×10^{-6}
1684	3.61×10^{-6}	7.43×10^{-8}	3.30×10^{-6}
1707	5.28×10^{-6}	1.20×10^{-7}	4.22×10^{-6}
1709	5.52×10^{-6}	8.10×10^{-8}	4.23×10^{-6}

taken in order to determine the vapor species over nickel oxide and also to determine the dissociation energies of these species.

EXPERIMENTAL PROCEDURE

The experimental details and techniques which are associated with the application of the mass spectrometer to high temperature vaporization processes have previously been reported.[6] For this study the outer Knudsen cell and lid were constructed of molybdenum, whereas the inner liner and lid were made of recrystallized morganite alumina. The knife-edged effusion hole in the alumina lid was 1 mm in diam.

Initially there was some question as to the suitability of Al_2O_3 as a container material, especially in view of the meager information available on the NiO–Al_2O_3 phase diagram.[7] However, no evidence of crucible reaction was found at the temperatures of this study other than a brilliant turquoise coloration on the walls of the crucible. This is apparently similar to the blue coloration observed by Brewer and Mastick[3] with their BeO cell. A calibrated Leeds and Northrup optical pyrometer was used to determine temperatures. Black body sighting holes were used and corrections were made for transmission of the windows. Fisher certified reagent grade NiO was used as a source of samples.

EXPERIMENTAL RESULTS

The mass spectrum was surprisingly simple and the only peaks observed in the temperature range 1575–1710°K were those corresponding to Ni^+, NiO^+, O_2^+, and O^+. The fact that the intensities of Ni^+ and O_2^+ were much greater than the NiO^+ intensity indicates that NiO vaporizes primarily by dissociation to the elements. Controlled atmosphere experiments were also used to establish the nature of the species present in the vaporization of NiO(s). Under conditions of increased oxygen partial pressure, no additional vapor species were detected. Ionization efficiency curves were measured as a means of distinguishing parent and fragment ions. The spectroscopic ionization potential of mercury was used to calibrate the electron energy scale. The corrected appearance potential of Ni^+ was 7.6±0.3 ev which is the spectroscopically observed value for the ionization potential of nickel.[8] The measured appearance potentials of NiO^+ and O_2^+ were 9.5±0.3 and 12.5±0.3 ev, respectively. The ionization efficiency curves gave no evidence which might suggest the formation of any of the ionic species by other than simple ionization. The results of both the ionization efficiency curves and the appearance potentials sub-

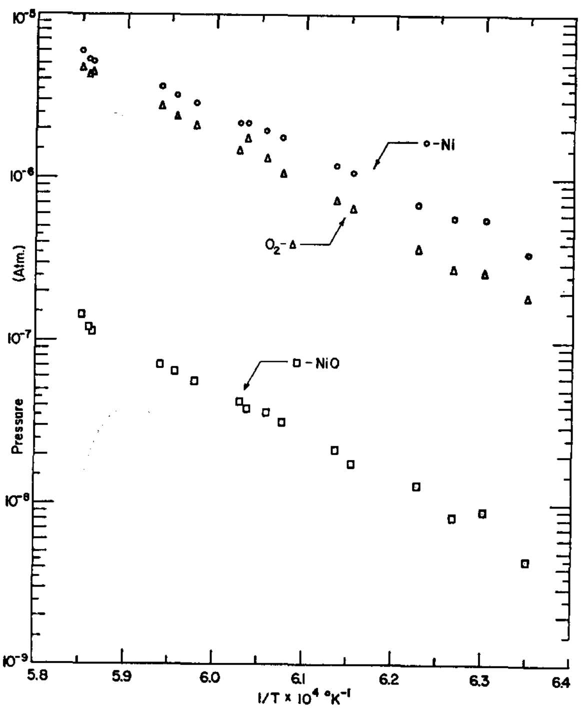

FIG. 1. Equilibrium partial pressures (atm) of the vapor species over NiO(s) as a function of $1/T\times10^4$ deg K^{-1}.

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[6] Mark G. Inghram and J. Drowart, in *International Symposium on High Temperature Chemistry at Asilomar, California* (McGraw-Hill Book Company, Inc., New York, 1960).

[7] E. M. Levin and H. F. McMurdie, *Phase Diagrams for Ceramists* (The American Ceramic Society, Columbus, Ohio, 1959).

[8] C. E. Moore, U.S. Natl. Bur. Standards Circ. No. 467.

stantiate the conclusion that the observed ions were formed by simple ionization.

The pressure calibration was obtained by quantitative vaporization of a known amount of silver. Furthermore, an independent calibration check was made by use of the O_2^+/O^+ ratios. The relative ionization cross sections used were Ag = 34.8, Ni = 24.4, NiO = 27.7, O_2 = 6.58 and 3.29.[9] Secondary electron efficiencies of the multiplier were corrected for molecular weight and structural effects where necessary. The pressure data for the vaporization of NiO(s) under neutral conditions are presented in Table I and Fig. 1.

DISCUSSION

The presence of nickel on the lid of the Knudsen cell in our experiments and those of Brewer and Mastick[3] suggest the possibility that some Ni(s) is present in the cell at the vaporization temperature. If metallic nickel is present under vaporizing conditions, then the reaction $NiO(s) \rightarrow Ni(s) + \frac{1}{2}O_2(g)$ should enable one to calculate the heat of formation of NiO(s) from the O_2 pressures. The free energy functions for Ni(s) were taken from Stull and Sinke.[10] The values for the heat of formation of NiO(s), $\Delta H_0{}^\circ{}_f$, are shown in Table II. The average third law heat of formation of NiO(s) is −56.5 kcal/mole. This shows good agreement with the value of −56.8 kcal/mole reported by Boyle, King, and Conway.[11]

Table II. Reaction energies.

T °K	$D_0{}^\circ$(NiO) kcal/mole	$\Delta H_0{}^\circ{}_f$(NiO) kcal/mole	$\Delta H_0{}^\circ{}_{\text{vap}}$(NiO) kcal/mole	$\Delta H_0{}^\circ{}_{\text{vap}}$(Ni) kcal/mole
1575	87.0	−57.0	130.3	101.3
1587	87.3	−56.8	129.0	100.6
1596	87.0	−57.0	130.0	101.1
1606	87.8	−57.0	129.3	101.1
1624	86.2	−56.4	129.9	101.7
1625	86.6	−56.7	129.8	100.8
1630	86.8	−56.7	129.5	102.0
1646	86.6	−56.6	129.4	100.5
1651	86.4	−56.4	129.4	100.5
1657	85.9	−56.2	129.7	100.5
1659	86.6	−56.5	129.4	100.6
1673	86.5	−56.5	129.5	100.6
1673	86.2	−56.4	129.6	100.5
1679	86.3	−56.5	129.6	100.5
1679	86.4	−56.2	129.2	100.5
1684	86.0	−56.3	129.7	100.4
1684	85.8	−56.0	129.5	100.4
1707	86.1	−56.3	129.6	100.4
1709	86.1	−56.2	129.1	100.1

Table III. Free energy functions, $-(F_T - H_0{}^\circ/T)$ in cal deg^{-1} mole^{-1}.

T °K	Ni(s)	Ni(g)	NiO(s)	NiO(g)	O_2(g)
1400	11.85	46.78	17.64	62.52	53.27
1500	12.33	47.16	18.44	63.10	53.81
1600	12.77	47.54	19.19	63.65	54.32
1700	13.22	47.89	19.92	64.18	54.80

In addition, the reaction $Ni(s) \rightarrow Ni(g)$ should allow one to calculate the heat of vaporization of nickel. The results of this calculation are presented in Table II and the average third law $\Delta H_0{}^\circ{}_{\text{vap}}$ (Ni) is found to be 100.7 kcal/mole. The most probable value for the heat of vaporization of nickel at 0°K as reported by Stull and Sinke is 100.8 kcal/mole. The presence of Ni(s) as well as NiO(s) in the the solid phase vaporization mixture is indicated by these results. One possible explanation of this behavior is that the solubility of nickel in NiO decreases as the temperature is increased such that precipitation of nickel occurs below the temperature range of our observations. The failure of Brewer and Mastick to detect nickel in samples which were heated for periods of short duration would appear to support the above explanation. However, it is equally possible that the nickel was not detected due to the insensitivity of the x-ray technique to small amounts of impurity. Moreover, the ratio of effusing oxygen to nickel atoms varied from approximately 1.7 at the lower temperatures to 2.2 at the higher temperatures. Due to some uncertainties in ionization cross section these ratios cannot be considered conclusive evidence in favor of another mechanism, but they do suggest another possibility. As the temperature is raised a preferential loss of O_2 from the NiO takes place until the Ni-rich solution limit of the NiO phase is reached. In either case, upon precipitation of nickel the system possesses zero degrees of freedom and the vapor composition is fixed at each temperature.

The agreement between the heat of formation of NiO obtained in this work and the value obtained by combustion calorimetry provides evidence of the over-all accuracy of the mass spectrometric measurements. Furthermore, the use of thermochemical cycles provides an opportunity to cross check direct calculations. For instance, the average third law heat of vaporization $\Delta H_0{}^\circ{}_{\text{vap}}$ of NiO is 129.5±5 kcal/mole. The free energy functions for NiO(s) were calculated from the heat

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[9] J. W. Otvos and D. P. Stevenson, J. Am. Chem. Soc. **78**, 546 (1956).

[10] D. R. Stull and G. C. Sinke, *Thermodynamic Properties of the Elements, Advances in Chem. Ser. No. 18* (American Chemical Society, Washington, D. C., 1956).

[11] B. J. Boyle, E. G. King, and K. C. Conway, J. Am. Chem. Soc. **76**, 3835 (1954).

content tabulations of Kelley[12] and the low temperature data of King.[13] The second law least-squares value is 134 kcal/mole. If one considers the following cycle:

$$\begin{tikzcd}
\mathrm{Ni(g)}+\mathrm{O(g)} & & \mathrm{NiO(g)} \arrow[ll, "D_0^\circ(\mathrm{NiO})"'] \\
\mathrm{Ni(s)}+\tfrac{1}{2}D_0^\circ\mathrm{O_2} \arrow[u, "\Delta H_0^\circ{}_{\mathrm{vap}}(\mathrm{Ni})"] & & \\
+\tfrac{1}{2}\mathrm{O_2(g)} \arrow[rr, "\Delta H_0^\circ{}_f"] & & \mathrm{NiO(s)} \arrow[uu, "\Delta H_0^\circ{}_{\mathrm{vap}}(\mathrm{NiO})"']
\end{tikzcd}$$

and uses the following values: heat of formation of NiO(s), −56.8 kcal/mole[11]; heat of vaporization of nickel, 100.8 kcal/mole[10]; dissociation energy of O_2, 117.9 kcal/mole[14]; and the experimentally determined heat of vaporization of NiO, 129.5 kcal/mole, then the heat of dissociation of NiO(g) which one calculates is 87.0 kcal/mole. The dissociation energy of NiO(g) was calculated from the sum of reactions 1 and 2:

$$\mathrm{NiO(g)}\rightarrow\mathrm{Ni(g)}+\tfrac{1}{2}\mathrm{O_2(g)} \tag{1}$$

$$\tfrac{1}{2}\mathrm{O_2(g)}\rightarrow\mathrm{O(g)} \tag{2}$$

$$\mathrm{NiO(g)}\rightarrow\mathrm{Ni(g)}+\mathrm{O(g)} \tag{3}$$

The ΔH_0° for reaction (1) was obtained from the experimentally determined K_{eq} and the free energy functions for NiO(g), Ni(g), and O_2(g) which are given in Table III. The tabulations of Stull and Sinke[10] were used for the free energy functions of Ni(g) and O_2(g), whereas the values of Brewer and Chandrasekharaiah[15] were used for NiO(g). Since the spectroscopic data for NiO(g) are quite fragmentary, the fundamental vibrational frequency and the interatomic distance are not well characterized. The values employed by Brewer and Chandrasekharaiah, $\omega=875$ cm^{-1} and $r_e=1.64$ A, are subject to some uncertainty since extrapolation procedures were used. For reaction (2) the dissociation energy of oxygen given by Brix and Herzberg[14] was employed. The third law dissociation energies D_0°(NiO) are shown in Table II and the average value is 86.5±5 kcal/mole as compared to the indirect calculation of 87.0 kcal/mole. These results are within the limiting values suggested by Brewer and Mastick, ≤ 99 kcal/mole, and by Huldt and Lagerqvist, ≤ 97 kcal/mole. However, a least squares treatment of the $\ln K_{\mathrm{eq}}$ data for reaction (1) when combined with the value for reaction (2) yielded a second law dissociation energy of 103±10 kcal/mole. Due to the excellent self-consistency of all other results and the acknowledged limitations of the second law method, the value of $D_0^\circ(\mathrm{NiO})=86.5$ kcal/mole is recommended.

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[12] K. K. Kelley, U. S. Bur. Mines Bull. No. 584 (1960).

[13] E. G. King, J. Am. Chem. Soc. **79,** 2399 (1957).

[14] P. Brix and G. Herzberg, Can. J. Phys. **32,** 110 (1954).

[15] L. Brewer and M. S. Chandrasekharaiah, UCRL-8713 (Rev) 1960.