[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Heat Capacity of Nickel Oxide from 68–298°K. and the Thermodynamic Properties of the Oxide

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This paper describes the results of measurements of the heat capacity of nickel oxide, NiO, from 68–298.1°K., making use of the calorimeter described in a previous publication.[1] From these results the entropy has been evaluated at 298.1°K., and from published heats of formation and heat capacities at higher temperatures the complete thermodynamic properties of the oxide have been derived.

Material.—The nickel oxide used was a c. p. Baker analyzed grade containing less than 0.2% of impurities. Microscopic examination (×1000) showed the material to be made up of transparent cubic crystals of uniform size. This is the only form of the pure oxide which has been reported. The powder was dried for several days at 100°, and a sample then showed no ignition loss on heating to bright redness in a platinum crucible. The total charge of nickel oxide used in these measurements was 151.085 g. (*in vacuo*) or 2.0229 moles. Frequent checks of the calorimeter resistance against the calibrated thermocouple during the heat capacity measurements showed no significant changes in the calibration.

Experimental Results.—In Table I the experimental heat capacities for the oxide are given, and the results are plotted in Fig. 1. The over-all accuracy of these measurements is estimated at ±0.2%.

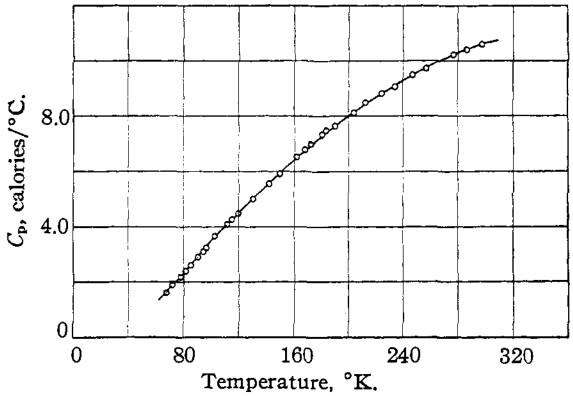

Fig. 1.—Molal heat capacity of NiO.

Calculations

The Entropy of NiO.—The method of Kelley[2] was used to extrapolate the heat capacity values from 68–0°K. It was found that

$$C_v = D\left(\frac{404}{T}\right) + E\left(\frac{620}{T}\right)$$

fitted the experimental curve very well up to 150°K. The contribution of the Debye function to the entropy was 0.648 e. u. at 68°K., while the contribution of the Einstein function was less than the experimental error. The entropy change from 68–298.1°K. was determined graphically and this amounted to 7.716 e. u. The rounded sum of the experimental and extrapolated entropies is 8.36 e. u. at 298.1°K. Since two moles of the oxide were used in these measurements, the accuracy of this value is estimated to be better than ±0.1 e. u.

TABLE I

Temp. °K.	C_p, cal./mole	Temp. °K.	C_p, cal./mole
68.05	1.607	151.86	6.02
71.96	1.909	162.37	6.54
78.19	2.185	168.09	6.80
82.07	2.403	172.61	7.02
85.89	2.625	181.32	7.36
86.70	2.644	183.01	7.50
91.08	2.927	190.75	7.64
94.42	3.094	204.20	8.12
96.32	3.298	213.13	8.54
103.13	3.693	225.34	8.84
111.70	4.094	235.37	9.09
115.71	4.242	247.81	9.52
120.33	4.464	257.49	9.75
131.10	5.00	277.20	10.27
141.72	5.58	286.32	10.43
150.08	5.93	296.68	10.56

Thermodynamic Properties of Nickel Oxide.—Using accepted[3] values for the entropies of nickel and oxygen, we calculate $\Delta S_{298 \cdot 1} = -18.00$ for the entropy of formation of the oxide. The heat of formation given by several investigators varies greatly, but the most acceptable value seems to be that given by Bichowsky and Rossini[4] $\Delta H_{298 \cdot 1} = -58{,}400$ cal. From this value and the entropy of formation we calculate $\Delta F^\circ_{298 \cdot 1} = -53{,}034$ for the free energy of formation. We thus write

$$\mathrm{Ni(s)} + {}^1/{}_2\mathrm{O_2(g)} = \mathrm{NiO(s)};\ \Delta S_{298.1} = -18.00;\ \Delta H_{298.1} = -58{,}400;\ \Delta F^\circ_{298.1} = -53{,}034$$

Watanabe[5] and Bogatskii[6] independently have studied the equilibrium

$$\mathrm{NiO(s)} + \mathrm{CO(g)} = \mathrm{Ni(s)} + \mathrm{CO_2(g)}$$

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[1] McDonald and Seltz, THIS JOURNAL, **61**, 2405 (1939).

[2] Kelley, "Bureau of Mines Bulletin 350," 1932, p. 8.

[3] Kelley, "Bureau of Mines Bulletin 394," 1935, p. 35.

[4] Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances." Reinhold Publishing Corp., New York, N. Y.

[5] M. Watanabe, *Science Repts. Tôhoku Imp. Univ.*, **22**, 436 (1933).

[6] D. P. Bogatskii, *Metallurg.*, **13**, No. 2, 18 (1938).

From his measurements Watanabe calculates the free energy of formation of NiO(s) as $\Delta F^\circ_{298\cdot 1} = -50{,}333$ cal., while Bogatskii's results lead to a value $\Delta F^\circ_{298\cdot 1} = -52{,}092$ cal. Pease and Cook[7] have studied the reduction equilibrium with hydrogen at two temperatures, 485 and 600°, and from these data calculate for the formation of the oxide, $\Delta F^\circ_{298} = -56{,}497$ cal. It will be noticed that the value obtained in this paper represents about the mean of the three previous determinations.

Kapustinskii and Novosel'tsev[8] have measured the heat capacity of NiO at temperatures from 373 to 1373°K. Their results can best be represented by the equation

$$C_p = 13.69 + 0.83 \times 10^{-3}T - 2.915 \times 10^5T^{-2}$$

Using Kelley's[9] equations for Ni(α) up to 626°K. and for Ni(β) above this temperature, and his equation for O_2, we obtain

$$\mathrm{Ni}(\alpha) + {}^1/_2\mathrm{O_2(g)} = \mathrm{NiO(s)}:\ \Delta F^\circ = -60{,}387 - 5.29T \ln T + 2.85 \times 10^{-3}T^2 + 0.988 \times 10^5T^{-1} + 52.84T$$

$$\mathrm{Ni}(\beta) + {}^1/_2\mathrm{O_2(g)} = \mathrm{NiO(s)}:\ \Delta F^\circ = -59{,}692 - 2.55T \ln T + 0.102 \times 10^{-3}T^2 + 0.988 \times 10^5T^{-1} + 35.80T$$

Summary

1. The heat capacity of nickel oxide, NiO, has been measured from 68-298°K.
2. The entropy of the oxide is found to be 8.36 e. u., with an estimated accuracy better than ±0.1 e. u.
3. The free energy of formation of the oxide has been calculated, $\Delta F^\circ_{298\cdot 1} = -53{,}034$ cal., and has been expressed as a function of the temperature.

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[7] Pease and Cook, THIS JOURNAL, **48**, 1199 (1926).

[8] A. F. Kapustinskii and K. A. Novosel'tsev, *J. Phys. Chem., U. S. S. R.*, **11**, 61 (1938).

[9] Kelley, "Bureau of Mines Bulletin 371," 1932.

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The Precision Conductivity Bridge Assembly

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I. Introduction

The papers of Jones and Josephs[1] and of Shedlovsky[2] marked the beginning of a new era in the investigation of various chemical phenomena by means of conductivity measurements. The precision which they obtained was, and still is, sufficient for most such investigations. However, the rapid development of communication engineering since the publication of their papers has now made it possible to effect several desirable improvements in the whole conductivity bridge assembly. Furthermore, by taking advantage of recent developments, the expense and difficulty of assembling a complete bridge can be greatly reduced.

At about the same time as the work of Jones and Josephs and Shedlovsky on the conductivity bridge, an increased interest in many other types of alternating current bridges was evident in the large number of papers which were published each year. According to Hague,[3] well over 250 papers on a. c. bridge methods must have appeared since 1928. There were 48 in 1932 alone. One of the most thorough of the recent papers is that of Astin.[4] Although his bridge is of the Schering type, Astin has used a Wagner ground, and certain conclusions reached by him are of value in conductivity bridge design. Following Ogawa,[5] Astin has brought a. c. bridge theory to a high degree of perfection. In surveying this large field, however, chemists will do well to keep in mind the fact that the requirements of such bridges as those of Astin and of Balsbaugh and Herzenberg[6] are considerably greater than similar requirements for a conductivity bridge. The conductivity bridge is one of the simpler alternating current bridges.

Communication engineering has more than kept pace with requirements of low frequency a. c. bridges. The application of inverse feedback to the problem of tuning an oscillator or an amplifier[7] probably will be of value in many cases. It is doubtful, however, whether much advantage is to be gained by using it with the ordinary conductivity bridge. This is especially true in

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[1] Jones and Josephs, THIS JOURNAL, **50**, 1049 (1928).

[2] T. Shedlovsky, *ibid.*, **52**, 1793 (1930).

[3] B. Hague, "A. C. Bridge Methods," Pitman, N. Y. (1938).

[4] A. V. Astin, *Bur. Standards J. Research*, **21**, 425 (1938).

[5] Kazukiyo Ogawa, *Researches Electrotech. Lab. Tokyo*, No. 254 (1929); No. 277 (1930).

[6] Balsbaugh and Herzenberg, *J. Franklin Inst.*, **218**, 49 (1934).

[7] H. H. Scott, *Proc. Inst. Radio Engrs.*, **26**, 226 (1938).