TABLE III

ENTROPY OF Cr_3C_2 AT 298.16°K. (CAL./MOLE DEG.)

K. K. Kelley, *et al.*	
0–50.12°K. (extrap.)	0.56
50.12–298.16°K. (graph.)	19.79
$S^0_{298.16}$	20.4 ± 0.2
This research	
0–12.90°K. (extrap.)	0.04
12.90–298.16°K. (graph.)	20.38
$S^0_{298.16}$	20.42 ± 0.05

probability, of the same order of magnitude, although Kelley does not report quantitatively the particle size in his work. The maximum deviation between the heat capacity data of this research and that of Kelley's amounts to less than 0.1%, which is below the experimental accuracy of both investigations. Therefore, there appears to be no size effect between the two studies.

The heat capacity of Cr_3C_2 can be described satisfactorily by three Debye functions, $3D\ (470/T)$ in the range 30 to 100°K. Below 30°K., the average characteristic temperature for the Cr_3C_2 lattice, calculated by employing three Debye functions, diminishes with decreasing temperature. At 13°K., $\theta_D = 294°$. The characteristic temperature, $\theta_D = 470°$, is approximately of the same order of magnitude as the characteristic temperature of the chromium lattice, calculated from the experimental data of Anderson[9] with one Debye function, in the liquid nitrogen temperature region. This Debye function is $1D\ (485/T)$. The variation of θ_D with temperature for chromium in the liquid hydrogen temperature region is not known. Estermann[10] has recently reported that the characteristic temperature of the chromium lattice has a constant value, $\theta_D = 418°$, in the liquid helium temperature range.

Acknowledgment.—The author is grateful to The Ohio State University Cryogenic Laboratory staff for the numerous discussions on high precision calorimetric techniques. It is a pleasure to mention the kind coöperation and helpfulness of Mr. E. B. Warner, Jr., and Mr. C. M. Moehle in the construction and installation of the apparatus. The author also wishes to thank Mr. A. J. Peat for his assistance in taking data and calculations, as well as Mrs. M. N. Doyle and Mrs. E. L. Fontanella who also assisted with the calculations.

[9] C. T. Anderson, THIS JOURNAL, **59**, 488 (1937).

[10] I. Estermann, S. A. Friedberg and J. E. Goldman, *Phys. Rev.*, **87**, 582 (1952).

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

Polarography of Tellurium(VI)[1a]

BY ELINOR NORTON, R. W. STOENNER AND A. I. MEDALIA[1b]

RECEIVED SEPTEMBER 15, 1952

The polarographic reduction of tellurium(VI) at the dropping mercury electrode has been investigated in a variety of media. Several media were found to be suitable for the analytical determination of this element. The half-wave potentials and diffusion current constants in these media have been obtained. The reduction of tellurium(VI) at the dropping electrode has been found coulometrically to proceed to the −2 state. It was found that selenium(VI) was not reduced at the dropping electrode in any of the media here reported.

Reduction of tellurium(VI) at the dropping mercury electrode has not previously been reported. At the conclusion of a thorough study of the polarography of tellurium and selenium in the +4 and −2 states,[2a] Lingane and Niedrach state[2b] that "The +6 states of selenium and tellurium are not reduced at the dropping electrode under any of the conditions investigated." However, it is shown in the present work that under a variety of conditions, samples of telluric acid prepared by several different procedures do exhibit well-defined (though irreversible) waves, suitable for the analytical determination of this element.

Experimental

Materials.—Three samples of telluric acid were used. Sample A was prepared by the method of Gilbertson[3] (H_2SO_4–H_2O_2) from elementary tellurium (Amend C.P.) in which only traces of other elements were detectable spectrographically. Sample B was prepared from this same lot of elementary tellurium by the procedure of Meyer and Franke[4] ($Ba(ClO_3)_2$), which was the procedure that had been employed by Lingane and Niedrach.[5] Sample C was telluric acid as received from Varlacoid Chemical Co.

Analyses were carried out by three different methods. (1) Reduction of a solution in 1 *N* hydrochloric acid at the boiling point to elementary tellurium by addition of hydrazine hydrochloride and sulfur dioxide.[6] Contrary to the statement of Lehner and Hornberger, reduction of telluric acid to the metal was not complete after the time of five minutes recommended by these authors, as established by the further formation of tellurium metal on treatment of the hot filtrate with sulfur dioxide or with metallic magnesium. In order to obtain complete reduction, it was found necessary to pass sulfur dioxide through the solution at the boiling point for a time of two hours, following the initial addition of hydrazine hydrochloride. A similar observation has been made by Niedrach.[7] (2) Reduction of tellurium(VI) to tellurium(IV) in concentrated hydrochloric acid, sweeping the chlorine gas thus formed into a solution of potassium iodide, and titrating the liberated iodine with thiosulfate. (3) Titration with alkali in the presence of glycerol (50%) with phenolphthalein as indicator. Since the end-point was not very sharp with 0.1 *N* reagent, the accuracy of this determination was limited to ±0.5%. Samples A and B were analyzed by all three methods; each determination

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[1] (a) Research carried out under the auspices of the U. S. Atomic Energy Commission; (b) Chem. Dept., Boston Univ., Boston, Mass.

[2] (a) J. J. Lingane and L. W. Niedrach, THIS JOURNAL, **70**, 4115 (1948); (b) **71**, 196 (1949).

[3] L. I. Gilbertson, *ibid.*, **55**, 1460 (1933).

[4] J. Meyer and W. Franke, *Z. anorg. Chem.*, **193**, 191 (1930).

[5] J. J. Lingane and L. W. Niedrach, THIS JOURNAL, **70**, 1997 (1948).

[6] V. Lehner and A. W. Hornberger, *ibid.*, **30**, 387 (1908).

[7] L. W. Niedrach, Ph.D. Thesis, Harvard University, 1948.

indicated a purity of 100 ± 0.8%. Sample C was analyzed by method (3) only, with the same result.

Most of the polarographic studies were carried out with sample A. However, identical polarograms were obtained with samples A, B and C in a few typical media (1 *M* NH_4Cl–NH_4OH, *p*H 8.1; 1 *M* NH_4 tartrate–NH_4OH, *p*H 8.4). Dilute solutions of tellurium(VI), prepared from stock solutions (telluric acid in water) of various ages up to as long as six months, gave identical polarograms.

Preparation of an allotropic modification of telluric acid, by heating in a sealed tube at 140° for 24 hours, has been described by Yost and Russell.[8] A sample of telluric acid was treated according to this procedure and polarograms were immediately run in five typical media (1 *M* NH_4Cl–NH_4OH, *p*H 8.0; 1 *M* NH_4 tartrate–NH_4OH, *p*H 8.2; saturated NH_4 oxalate–NH_4OH, *p*H 6.6; 0.5 *M* NH_4 citrate–NH_4OH, *p*H 6.2; 0.1 *M* NaOH). Results were identical with those obtained with ordinary telluric acid.

The gelatin used as maximum suppressor was J. T. Baker, U.S.P.

Apparatus.—All polarograms were determined with a Sargent Polarograph, Model XXI. The capillary had the following characteristics: *m*, 1.235 mg./sec.; *t*, 3.80 sec.; $m^{2/3}t^{1/6}$, 1.438 mg.$^{2/3}$ sec.$^{-1/2}$. An H-type cell was employed, but instead of a built-in calomel cell, the arm contained a salt bridge consisting of the supporting electrolyte used in the particular experiment being carried out; into this supporting electrolyte solution dipped the end of a flexible salt bridge of a calomel cell of the type devised by Harris and Hume.[9] The cell was immersed in a grounded water-bath thermostated at 25.0°. Before determining each polarogram, the solution was swept for five minutes with water-saturated nitrogen.

A Beckman Model G *p*H meter was used to measure and adjust the *p*H of the various media employed.

As a check on the over-all accuracy of the equipment, the half-wave potential of zinc in 1 *N* potassium nitrate, for which the accurate value of −1.012 v. *vs.* S.C.E. has been reported,[10] was determined; found, −1.018, −1.020, −1.020, −1.022 v. *vs.* S.C.E.

Results

Polarography of Tellurium(VI) in Ammonium Chloride Buffers.—Excellent waves are obtained in NH_4Cl–NH_4OH (*p*H 8.0) in the presence of a maximum suppressor. A typical wave found in this medium is included in Fig. 3.[11] Suitable suppressors include gelatin and gum ghatti, while the sodium salt of methyl red, thymol and basic fuchsin were found to be totally ineffective in suppressing the maximum. The gelatin in the solution must be present in a concentration between 0.003 and 0.0005%; with 0.01%, a significant decrease in i_d/c results; while with 0.0005% suppression is incomplete with the higher concentrations of tellurium.

With 0.0005% gelatin at *p*H 8.0, the diffusion current is strictly proportional to the concentration of tellurium over a wide range; thus, from 5.70 × 10^{-3} to 5.70 × 10^{-6} *M*, $E_{1/2}$ is −1.21 ± 0.01 v., and i_d/c is 25.1 ± 0.7 milliamp. l. mole^{-1}. Variation of the concentration of buffer over the range 2 to 0.1 *M*, keeping the *p*H constant at 8.0, causes no change in $E_{1/2}$ or in i_d/c. However, as the *p*H is increased, over the range 6.2 to 9.2, the half-wave potential shifts to more negative values (−1.17 to −1.34 v.), as is also found in other media (*v.i.*).

Polarography of Tellurium(VI) in Ammonium Citrate, Tartrate and Oxalate Buffers.—Excellent waves were obtained in 0.5 *M* ammonium citrate containing 0.003% gelatin, at *p*H of 6.1 to 8.9. At *p*H 5.7 the hydrogen wave begins after only a short measurable tellurium wave, while at *p*H 4.2 and 1.8, the tellurium and hydrogen waves merge (Fig. 1). At *p*H 6.2, the half-wave potential is constant over a 100-fold range in tellurium(VI) concentrations ($E_{1/2}$ = − 1.19 v. from 1.02 × 10^{-3} to 1.02 × 10^{-5} *M*). In ammonium tartrate at *p*H 8.4, an excellent wave is found with $E_{1/2}$ at −1.38 v. and i_d/c of 18.7. In saturated ammonium oxalate–ammonium hydroxide buffers of *p*H 5.2, 6.5, 8.0 and 9.0, respectively, $E_{1/2}$ is −1.18, −1.20, −1.23 and −1.32 v., respectively, with i_d/c constant at 23.5.

Polarography of Tellurium(VI) in Potassium Cyanide.—Satisfactory waves are also found in 0.1 *M* potassium cyanide (Fig. 2). The extremely negative half-wave potentials in cyanide media are probably associated with the high *p*H of these media; a similar shift of $E_{1/2}$ with increasing *p*H is observed with ammonium chloride and other media. With 1.3 × 10^{-3} *M* tellurium(VI) in 0.5 *M* and 1 *M* potassium cyanide, a maximum is found at −1.29 v. in the early part of the rising portion of the wave (Fig. 2); this maximum ceases before the diffusion current is reached. The presence of this maximum may obscure the true half-wave potential and thus be responsible for the apparent shift of $E_{1/2}$ to more negative values in polarograms exhibiting this maximum. A similar maximum has been found in a 1 *M* potassium cyanide–1 *M* sodium carbonate mixture; increase of gelatin concentration to as high as 0.03% was without effect on the maximum. The maximum is not observed in 0.1 *M* potassium cyanide, or in 1 *M* potassium cyanide–1 *M* sodium carbonate with a more dilute concentration of tellurium(VI) (0.39 × 10^{-3} *M* or less in 1 *M* KCN–1 *M* Na_2CO_3). The maximum occurs at nearly the same potential as the anodic wave of telluride ion (−1.2 v.),[2a] and may be ascribable to the formation of elementary tellurium at this potential, as has been reported[2b] for analogous maxima occurring with tellurium(IV).

Polarography of Tellurium(VI) in Various Media.—It was shown in Fig. 1 that the hydrogen wave coincides with the tellurium(VI) wave in an ammonium citrate buffer of *p*H 4.2 or lower. The same result was found with acetate buffers; at *p*H 4.6 the tellurium(VI) wave was barely separate from the hydrogen wave, while at *p*H 3.8, no separate tellurium(VI) wave is found. Satisfactory tellurium(VI) waves are found in acetate and carbonate buffers of *p*H 5.6 or higher. In an acetate buffer of *p*H 5.6, $E_{1/2}$ is −1.18 v. and i_d/c is 22.2. In carbonate buffers of *p*H 6.5, 8.3 and 9.1, respectively, $E_{1/2}$ is −1.34, −1.37 and −1.40, and i_d/c is constant at 23.9.

Polarograms of tellurium(VI) in various salt solutions are shown in Fig. 3. While waves are obtained in all these media (potassium chloride, perchlorate, and sulfate and sodium hydroxide) they are less well-defined, and more highly irreversible than in the other media studied. For com-

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[8] D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice–Hall, Inc., New York, N. Y., 1944, p. 350.

[9] D. N. Hume and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **15**, 465 (1943).

[10] J. J. Lingane, THIS JOURNAL, **61**, 2099 (1939).

[11] The tracings contained in the figures were made through the middle of the recorded wave.

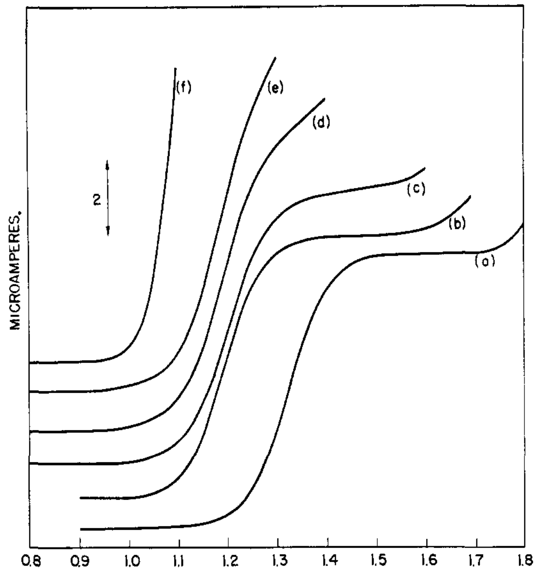

Fig. 1.—Tracings of polarograms of 0.34 millimolar tellurium(VI) in 0.5 *M* ammonium citrate buffers with 0.003% gelatin at: a, *p*H 8.9; b, *p*H 6.2; c, *p*H 5.8; d, *p*H 4.7; e. *p*H 4.2; f, *p*H 1.8.

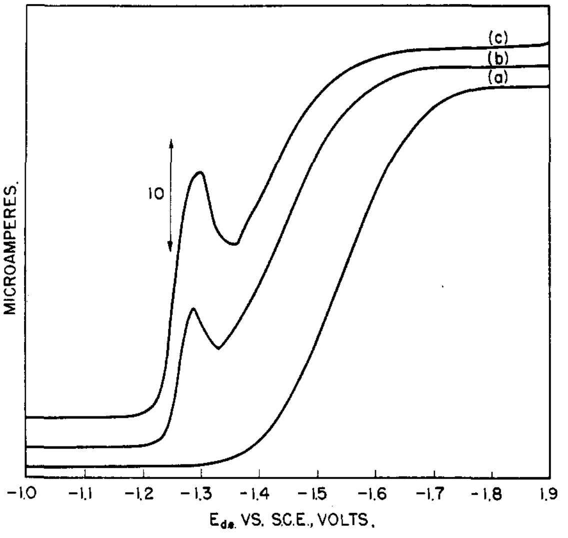

Fig. 2.—Tracings of polarograms of 1.3 millimolar tellurium(VI) in: a, 0.1 *M* KCN; b, 0.5 *M* KCN; c, 1 *M* KCN. All solutions contained 0.003% gelatin.

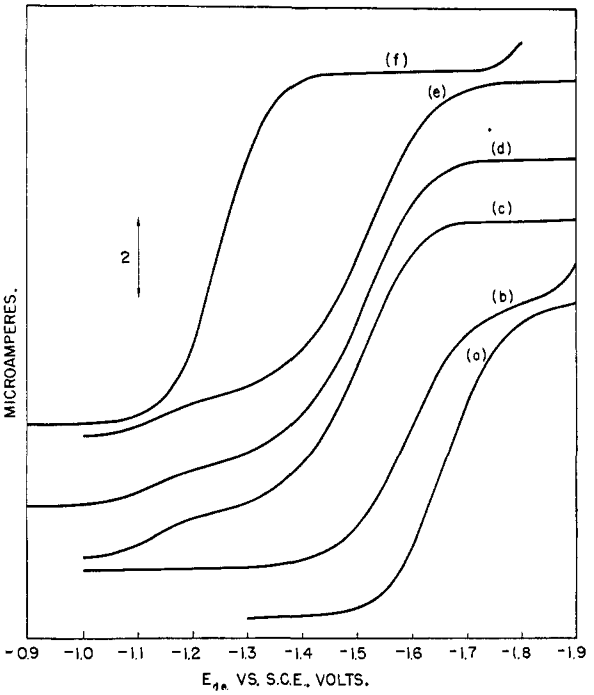

Fig. 3.—Tracings of polarograms of 0.3382 millimolar tellurium(VI) in: a, 0.1 *N* NaOH; b, 1 *N* NaOH; c, 0.1 *M* K_2SO_4: d, 0.1 *M* KCl; e, 0.1 *M* $KClO_4$; f, 1 *M* NH_4Cl-NH_4OH, *p*H 8.0. All solutions contained 0.003% gelatin.

parison, a wave in NH_4Cl-NH_4OH is included in Fig. 3. In general, media which are strong complexing agents for metallic ions give better waves with tellurium(VI) than do those which are not. It is not clear whether this is due to the formation of complexes between these complexing agents (NH_3, citrate, CN^-, etc.) and tellurium(VI) or possibly one of its reduction products. Formation of "telluryl citrate complexes" with tellurium(IV) was suggested by Lingane and Niedrach.[2b]

Determination of *n*.—An attempt was made to determine the number of electrons involved in the reduction of each molecule by analysis of a wave obtained in ammonium chloride media.[11a,12] Presumably owing to the irreversibility of the electrode reaction, the absurd result of $n = 0.5$ was found. The value of *n* was therefore determined coulometrically by the electrolysis of a 1.028 millimolar solution of tellurium(VI) in 1 *M* ammonium chloride, *p*H 8.0, contained in a cell with a large area mercury cathode, and a separate anode compartment. The potential was maintained constant at -1.30 v. *vs.* S.C.E. by means of an automatic potentiostat.[13] The quantity of electricity passed was measured by a hydrogen–oxygen coulometer containing a 0.5 *M* potassium sulfate solution as the electrolyte.[14] This coulometer has been thoroughly studied by Lingane, and was found to yield precise results which agree very well with the theoretical value of 0.1739 cc. gas per coulomb.

Four determinations of *n* in this manner resulted in values of 7.86, 8.11, 8.08 and 7.98 electrons per mole of tellurium(VI) reduced, indicating that the reduction proceeds to -2 tellurium. This is confirmed by observations of the electrolysis cell during the reduction. In the first stage elemental tellurium is produced, probably by reaction of the telluride ion with the remaining tellurium(VI). The elemental tellurium is later dissolved to form the violet polytelluride ion, which in turn is finally reduced to a completely colorless solution of the simple telluride ions.

Polarography of Tellurium(VI) in the Presence of Other Elements.—Lingane[2b] has found that the polarographic waves of tellurium(IV) were suppressed by any metal ion whose reduction wave preceded the tellurium wave, and which formed an insoluble telluride. In 1 *M* ammonium chloride–

(11a) J. Tomes, *Collection Czechoslov. Chem. Communs.*, **9**, 12, 81, 150 (1937).

(12) I. M. Kolthoff and J. J. Lingane, *Chem. Revs.*, **24**, 1 (1939).

(13) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **17**, 332 (1945).

(14) J. J. Lingane, THIS JOURNAL, **67**, 1916 (1945).

ammonium hydroxide, *p*H 8.1, copper and cadmium were found to suppress the reduction wave of tellurium(VI) in a manner analogous to that observed by Lingane, while nickel ion was found to have no effect, possibly because the nickel–ammonia complex is strong enough to prevent the precipitation of nickel telluride in this medium. Of the anions investigated, bromide was without effect in concentrations up to 0.1 *M;* fluoride at this same concentration depressed the apparent wave height by 20%; while tellurite at a concentration of 0.1 millimolar depressed the apparent wave height by 10%. No explanation is offered for the depressive effect of fluoride and tellurite ions on the reduction wave of tellurium(VI).

Polarography of Selenium(VI).—A solution of selenic acid was prepared by the method of Gilbertson and King.[15] Polarograms of this solution were obtained in the following media: 1 *M* NH_4Cl–NH_4OH, *p*H 7.7; 0.1 *M* NH_4Cl–NH_4OH, *p*H 9.0; 1 *M* NH_4 tartrate–NH_4OH, *p*H 8.2; 1 *M* KCl; 0.1 *M* NaOH; 0.5 *M* NH_4 citrate–NH_4OH, *p*H 6.2; saturated NH_4 oxalate–NH_4OH, *p*H 4.9. In no case was a selenium(VI) wave observed prior to the hydrogen wave, thus bearing out the statement of Lingane and Niedrach[2b] that the +6 state of selenium is not reduced at the dropping mercury electrode.

Acknowledgment.—We are grateful to Professor Lingane and Dr. Niedrach for consultation during the course of the present work.

(15) L. I. Gilbertson and G. B. King, THIS JOURNAL, **58**, 180 (1936).

UPTON, LONG ISLAND, N. Y.

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Vapor Pressures of Inorganic Substances. X. Dissociation Pressures of Lithium Hydroxide between 650° and 800°K.[1]

BY WALTER E. DITMARS AND HERRICK L. JOHNSTON

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By means of the dynamic effusion method the dissociation pressure of LiOH has been measured in the temperature range 648–795°K. The empirical equation, log $P = (-7635.1/T) + 5.6786$, was derived. The procedure is described, and an evaluation of results given.

Introduction

The dissociation pressure of LiOH has been measured by the dynamic effusion method in the temperature range 648–795°K. The study was made with the use of nickel Knudsen cells in a simple high vacuum apparatus. The only earlier work found in the literature was the research by J. Johnston[2] whose data were obtained in a completely different temperature range (823–1176°K.) than that of this research. Due to the experimental difficulties of handling the material at higher temperatures, these earlier values are believed to be somewhat uncertain.

Apparatus and Procedure

The procedure employed, to measure the dissociation pressure of LiOH, resembles that of the Knudsen method of vapor pressure measurements.[3] Details of the special apparatus are shown in Fig. 1, the heater and control circuits are shown in Fig. 2. The cell was pressed, in two sections, from sheet nickel 0.025 cm. in thickness. The main section is in the form of a cup 2.54 cm. in diameter by 2.54 cm. in height. This was closed by a cap pressed into position, and electrically welded in an atmosphere of hydrogen. The orifice was formed by drilling a hole through the center of the bottom of the cup, and producing a sharp edge by means of a lathe. The orifice diameter was measured by means of a travelling microscope and, since the hole was not quite round, the area was computed from the average of eight readings.

The LiOH, in the form of a fine powder, was introduced into the cell through the orifice, in a dry nitrogen atmosphere, and the filled cell was kept in a vacuum desiccator preliminary to measurements.

The cell was mounted, in an inverted position, on the end of a monel tube, as shown in the figure. Previous to heating, the system was evacuated from 3 to 18 hours to a pressure of 3×10^{-6} mm. Additional evacuation after this pressure was reached had no effect on the experimental results. A preliminary degassing run was then made to ensure decomposition of any $LiOH \cdot H_2O$. The pressure maintained in the cell during LiOH decomposition runs, was approximately 1×10^{-4} mm. Precautions were taken to avoid contact with air during cell weighings, and during introduction in or removal from the apparatus.

The iron–constantan thermocouple was calibrated by directly comparing a couple made from this same wire with a standardized Pt-10% Pt, Rh thermocouple.

Preliminary runs were made on relatively pure LiOH obtained from the Metalloy Corporation of Minneapolis. The experimental runs were made on material (approximately 99.9% pure) prepared by Dr. Thomas W. Bauer.[4]

The Knudsen cell on which the preliminary runs were made was subsequently cut open. No apparent reaction had occurred between the nickel and lithium compounds, nor between the nickel and the water vapor.

Experimental Results

Dissociation pressures were calculated from the formula

$$P = \frac{\Delta WC}{A_{\text{orifice}} t_{\text{eff}}} \sqrt{\frac{2\pi RT}{\text{M. W. } (H_2O)}} \qquad (1)$$

where ΔW, the weight loss was measured on an analytical balance; T, the absolute temperature was read directly from the calibrated pyrometer-controller dial; R is the universal gas constant = 8.3156×10^{-7} dyne/cm.^{2}; $C = 9.8692 \times 10^{-7}$ is the conversion factor to atm., A_{orifice} was directly measured at 25°, and coefficient of thermal expansion data from "The Metals Handbook, 1949" were

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[1] This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

[2] John Johnston, *Z. physik. Chem.*, **62**, 339 (1908).

[3] R. Speiser and H. L. Johnston, *Am. Soc. Metals*, **11**, 3 (1949).

[4] H. L. Johnston and T. W. Bauer, THIS JOURNAL, **73**, 1119 (1951).