the stability of excited states. Thus in the case of the alkaline earths, it appears likely that the ground state is a triplet electronic state and the spectroscopic data involving singlet electronic states give misleading results. In the case of AlO, the spectroscopic data appear to indicate a $^2\Sigma$ electronic state for the ground state of gaseous AlO. The results obtained in this paper indicate either that the true ground state is a quartet electronic state or a doublet state lower in energy than those observed to date. However, there is also the possibility that Al_2O_2 is the chemical species rather than AlO as noted above.

Acknowledgments.—The X-ray diffraction work for this paper was performed by Prof. David H. Templeton, Mrs. Carol H. Dauben and Mrs. Lee Jackson. The spectroscopic analyses were performed by Mr. John Conway and Mr. Milton F. Moore.

BERKELEY, CALIF. RECEIVED AUGUST 9, 1950

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

High-Temperature Heat Content of Nickel Chloride

BY J. P. COUGHLIN

High temperature heat content measurements of nickel chloride were conducted over the temperature range from 298.16 to 1336°K. The temperature and heat of fusion were evaluated. A table of heat content and matching entropy increments above 298.16°K. is included.

Introduction

The need for reliable high temperature heat content values for nickel chloride was made imperative by research conducted by W. F. Giauque and R. H. Busey[1] of the Chemistry Department of the University of California, who requested that the present investigation be undertaken. The only previous data are those of Krestovnikov and Karetnikov[2] (extending to 1073°K.), the average accuracy of which has been estimated by Kelley[3] as about ± 5%. The present paper reports measurements to 1336°K., which cover the entire crystalline range above 298.16°K. and a portion of the liquid range, so that the heat of fusion is obtained.

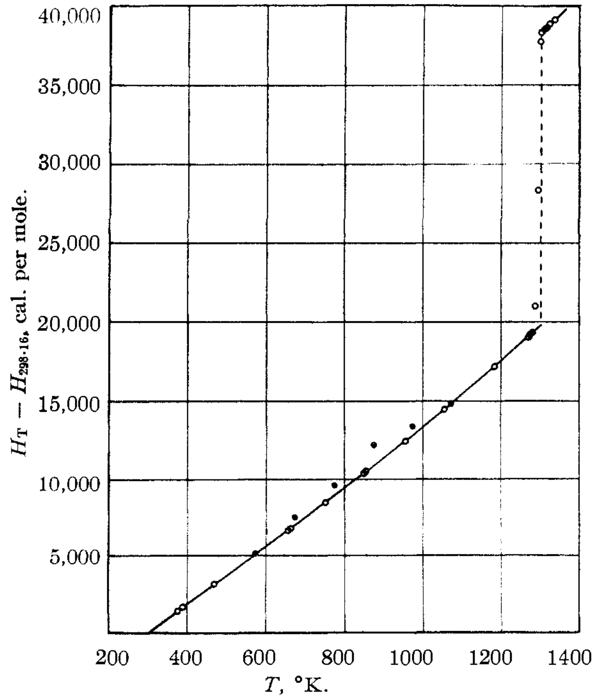

Fig. 1.—Heat content of $NiCl_2$: open circles, this research; dark circles, Krestovnikov and Karetnikov.

Material and Method

The nickel chloride was furnished by Giauque and Busey.[1] It was a portion of the material prepared, purified and used in their low temperature heat capacity and hydrogen reduction equilibrium measurements. Their analysis gave 45.29% Ni and 54.71% Cl, as compared with the theoretical 45.28 and 54.72%, respectively.

The substance was sealed in platinum-rhodium capsules preparatory to the measurements. The capsules were filled in an inert atmosphere in a dry-box, temporarily closed by tightly fitting rubber caps to permit weighing, and finally sealed gas-tight by pinching shut the capsule necks and welding with platinum.

The heat content measurements were made by the "dropping" method, using apparatus and techniques previously described.[4]

TABLE I

MEASURED HEAT CONTENTS OF $NiCl_2$

T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole
376.3	1,395	1183.4	17,150
389.4	1,635	1269.7	19,070
468.8	3,140	1276.1	19,210
568.3	4,940	1281.1	19,360
568.6	4,950	1286.6	20,980[a]
654.1	6,575	1295.4	28,330[a]
657.3	6,670	1300.8	37,730[a]
662.8	6,750	1303.9	38,310
752.2	8,475	1311.3	38,560
847.5	10,370	1319.1	38,610
853.2	10,420	1320.1	38,640
954.9	12,420	1324.8	38,830
1054.6	14,460	1336.0	39,120

[a] Includes premelting.

---

[1] W. F. Giauque and R. H. Busey, unpublished measurements.

[2] A. N. Krestovnikov and G. A. Karetnikov, *J. Gen. Chem.* (*U. S. S. R.*), **6**, 955 (1936).

[3] K. K. Kelley, U. S. Bureau of Mines Bull., 476 (1949).

[4] K. K. Kelley, B. F. Naylor and C. H. Shomate, *Bureau of Mines Tech. Paper* 686, 1946.

Results

The measured heat contents above 298.16°K., expressed in defined cal. per mole of nickel chloride (129.60 g.), are listed in Table I and plotted in Fig. 1. Correction for condensation of nickel chloride vapor was applied as necessary, using the equation of Kelley.[5] This correction was negligible below 1100°K. and it never exceeded 0.2% at higher temperatures.

The trend in the heat content of the crystals is regular to 1281.1°K. Premelting became evident at 1286.6°K., and most of the substance was melted at 1300.8°K. (results labeled (a) in Table I). The adopted melting point is 1303°K., the temperature at which all the substance became molten. The heat of fusion was obtained as 18,470 cal./mole, yielding an entropy of fusion of 14.18 cal./deg./mole.

Measurements beyond 1336°K. were precluded by failure of the platinum–rhodium capsules, caused by the high vapor pressure of nickel chloride. From Kelley's[5] equations, in conjunction with the present results, it is estimated that the vapor pressure is about 3.5 atm. at this temperature.

The measured heat content of the crystals is represented to within an average deviation of 0.5% by the equation

$$H_T - H_{298.16} = 17.50T + 1.58 \times 10^{-3}T^2 + 1.19 \times 10^5T^{-1} - 5{,}757$$

For the short portion of the liquid range covered, the heat capacity is 24.00 cal./deg./mole, and the heat content is reproduced to within 0.2% by

$$H_T - H_{298.16} = 24.00T + 7{,}020$$

The previous data of Krestovnikov and Karetnikov[2] are mutually inconsistent to the extent of more than 10%, and they are 6% higher on the average than the present results.

Table II contains values of the molal heat content and entropy increments above 298.16°K. at even temperatures and at the melting point. The latter have been calculated to match the former by use of the method of Kelley.[3]

TABLE II

MOLAL HEAT CONTENT AND ENTROPY INCREMENTS ABOVE 298.16°K.

T, °K.	$H_T - H_{298.16}$	$S_T - S_{298.16}$	T, °K.	$H_T - H_{298.16}$	$S_T - S_{298.16}$
400	1,800	5.18	1100	15,390	24.65
500	3,650	9.31	1200	17,510	26.50
600	5,545	12.76	1300	19,750	28.29
700	7,465	15.72	1303	19,820^{c}	28.34
800	9,400	18.30	1303	38,290^{l}	42.52
900	11,360	20.61	1350	39,420	43.37
1000	13,350	22.71			

BERKELEY 4, CALIFORNIA RECEIVED MAY 7, 1951

---

[5] K. K. Kelley, *U. S. Bureau of Mines Bull.* 383, 1935.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Catalytic Polarographic Waves of Hydrogen Peroxide. II. Kinetic Waves for the Peroxy Compounds of Molybdenum(VI), Tungsten(VI) and Vanadium(V)[1]

BY I. M. KOLTHOFF AND E. P. PARRY

Kinetic polarographic waves are observed in the systems molybdate or tungstate or vanadate with hydrogen peroxide. These kinetic waves are characterized by a pronounced maximum at about +0.15 to 0.3 volt *vs.* S.C.E. The maximum is not due to stirring or adsorption effects. The kinetic waves are observed at *p*H smaller than 6 where the active species are polymerized. The rate determining step is the reaction between some polymerized form with hydrogen peroxide to give the peroxy compound which is reduced instantaneously at the electrode. The kinetic currents have been studied as a function of concentration and kind of mineral acid, of *p*H and kind of buffer, of concentrations of hydrogen peroxide and of molybdate (W(VI) and V(V), respectively), of temperature and of height of mercury in the reservoir. In dilute mineral acids Mo, W and V give measurable kinetic currents even at concentrations as small as 10^{-6} *M*. In a phosphate buffer of *p*H about 5 molybdate can be detected (kinetic current) at a concentration of 10^{-7} *M* and vanadate of 10^{-8} *M*.

In a previous paper[2] the kinetic current observed in the ferric iron–hydrogen peroxide system was discussed. The ferrous iron formed at the electrode reacts with hydrogen peroxide to regenerate ferric iron which is again reduced at the electrode.

It has been found that molybdate in acid medium reacts with hydrogen peroxide with the formation of a peroxy compound which is reduced at positive potentials *versus* the saturated calomel electrode (S.C.E.). The rate of reaction of molybdate with hydrogen peroxide under proper conditions is so great that this ion, even at high dilutions, gives a measurable kinetic current produced by the reduction of the peroxy compound which is continuously reformed at the surface of the electrode

$$MoO_4^{=} + H_2O_2 \longrightarrow MoO_5^{=} + H_2O \qquad (1)$$

$$MoO_5^{=} + 2H^+ + 2e \longrightarrow MoO_4^{=} + H_2O \qquad (2)$$

For the sake of convenience, $MoO_4^{=}$ and $MoO_5^{=}$ are written in equations (1) and (2) although the molybdenum is undoubtedly present in different degrees of polymerization. Vanadate and tungstate with hydrogen peroxide give similar kinetic waves as molybdate.

This paper presents a study of the characteristics of the kinetic waves observed with these systems. The kinetic waves observed with mixtures of molybdate or vanadate and hydrogen peroxide in a phosphate buffer of *p*H about 5 are especially interesting. As little as 10^{-8} *M* molybdate or vanadate gives a measurable kinetic current, alluding to the use of this method for the trace detection of these ions. Analytical applications of kinetic currents will be described in subsequent papers.

Experimental

Apparatus and Materials.—The apparatus, including the capillary and most of the chemicals, were described previously.[2] As a source of molybdate, both sodium molybdate

---

[1] From a Ph.D. Thesis submitted by E. P. Parry to the Graduate School of the University of Minnesota, 1950.

[2] I. M. Kolthoff and E. P. Parry, THIS JOURNAL, **73**, 3718 (1951).