before opening. The solid weighed 1762 g.; ignition loss under nitrogen was 8.1%, giving a corrected yield of 1619 g. (93.5%, based on zinc selenite).

Anal. Calcd. for ZnSe: Zn, 45.4; Se, 54.6. Found (after ignition): Zn, 45.9; Se, 54.2.

Zinc Selenide from Ammine Selenite Complex.—Wet zinc selenite filter cake prepared from 9 moles each of zinc acetate and selenious acid was suspended in 1150 ml. of deionized water, and ammonia gas was passed in to complete dissolution. This was added to 4 l. of 85% hydrazine hydrate and 50 g. of zinc acetate over 1.5 hours under conditions as previously described. The hydrazino selenide was decomposed in acetic acid; yield of zinc selenide, corrected for ignition loss, 1297 g. (quantitative).

Hydrazinocadmium Selenide.—To 150 ml. of 85% hydrazine hydrate, warmed on the steam cone, was added 23.94 g. (0.1 mole) of cadmium selenite; the originally white suspension was converted into bright orange, with a gradually accelerating evolution of nitrogen. The bulky, orange solid was collected on a filter, washed with deionized water and methanol, and dried; yield 21.50 g. (96.3% as $CdSe \cdot N_2H_4$).

Anal. Calcd. for $CdSe \cdot N_2H_4$: N, 12.56; ignition loss, 14.2. Found: N, 12.71; ignition loss 16.7 (some sublimation was noticed). The hydrazino selenide was nearly amorphous as judged by X-ray diffraction.

Cadmium Selenide.—Cadmium selenite wet filter cake prepared from 15 moles of selenious acid, was added to 6.5 l. of deionized water containing 1575 g. of ammonium carbonate and dissolved by passing in ammonia gas. This solution was fed into 8 kg. of 85% hydrazine hydrate in a 22-l. flask under continuous agitation and maintenance of temperature at 85–100°. The color of the suspension rapidly passed through the orange and maroon stages to brown-black with vigorous evolution of nitrogen; operation was completed in 3.5 hours. When the mixture had cooled, the solid was collected upon Whatman No. 50 paper in a 32 cm. funnel, slurried with 50% acetic acid to destroy any remaining hydrazino cadmium selenide, then washed with deionized water and methanol, and dried at 120° under carbon dioxide; yield 2815 g. (98%, based on selenious acid).

Anal. Calcd. for CdSe: Cd, 58.7; Se, 41.3. Found: Cd, 58.2; Se, 41.2.

Lead(II) Selenide.—Lead(II) selenite (334 g., 1 mole) was added gradually to a stirred and pre-heated mixture of 450 ml. of 85% hydrazine hydrate, 200 ml. of water and 5 ml. of glacial acetic acid. Reduction was vigorous; the product weighed 280 g. (98%, as PbSe). The solid was black, graphitic in texture, and gave a sharp X-ray diffraction pattern characteristic of cubic lead selenide.

Anal. Calcd. for PbSe: Pb, 72.4; Se, 27.6. Found: Pb, 72.1; Se, 27.9.

Mercury(II) Selenide.—Reduction of mercury(II) selenite, as described above, was violent, and care had to be taken during the addition. From 236 g. (0.72 mole) of selenite, there was obtained 190 g. (94.5%) of crystalline mercury(II) selenide.

Anal. Calcd. for HgSe: Hg, 71.7; Se, 28.3. Found: Hg, 70.7; Se, 29.2.

Copper(II) Selenide.—From 0.76 mole of copper(II) selenite there was obtained 109 g. of copper(II) selenide (quantitative).

Anal. Calcd. for CuSe: Cu, 44.4; Se, 55.6. Found: Cu, 44.4; Se, 55.8.

Copper(I) Selenide.—A mixture of 1 mole of copper(II) acetate and 0.5 mole of selenious acid was treated with ammonia gas until all solid dissolved. This solution was run dropwise into preheated hydrazine reduction mixture as described above; yield 104 g., ignition loss, 5.0% (95% as Cu_2Se).

Anal. Calcd. for Cu_2Se: Cu, 61.3; Se, 38.7. Found (after ignition): Cu, 60.7; Se, 39.3.

Acknowledgment.—The authors wish to thank R. N. Boos and associates for analytical data.

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[CONTRIBUTION FROM THE LOW TEMPERATURE LABORATORY, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

Perchloryl Fluoride. Vapor Pressure, Heat Capacity, Heats of Fusion and Vaporization Failure of the Crystal to Distinguish O and F[1]

BY J. K. KOEHLER AND W. F. GIAUQUE

RECEIVED DECEMBER 9, 1957

The heat capacity of perchloryl fluoride has been measured from 15 to 225°K. The heat of fusion was found to be 916.3 cal. mole^{-1} at the melting point which was determined as 125.41°K. The heat of vaporization was determined calorimetrically to be 4619 cal. mole^{-1} at the boiling point, 226.48°K. The $\int_0^{\text{b.p.}} C_p \, d \ln T$ gave 60.17 cal. deg.$^{-1}$ mole^{-1} for the ideal gas at 226.48°K. This is 2.42 cal. deg.$^{-1}$ mole^{-1} less than the entropy value 62.59 cal. deg.$^{-1}$ mole^{-1} based on gas molecular data at this temperature. This is in accordance with expectations that the crystal would largely fail to distinguish between O and F, which would lead to a maximum discrepancy of $R \ln 4 = 2.75$ cal. deg.$^{-1}$ mole^{-1}. The vapor pressure was measured and the data are represented by the equation $\log_{10} P(\text{int. cm.}) = -1652.37/T - 8.62625 \log_{10} T + 0.0046098T + 28.44780$.

In several previous investigations in this Laboratory $\int_0^T C_p \, d \ln T$ has been short of the known value of the entropy at ordinary temperatures by approximately $R \ln 2$. This has occurred in cases where molecules have contained carbon, oxygen and nitrogen atoms in positions which would otherwise be equivalent. Crystals do not distinguish, to any appreciable extent, between the several isotopes of an element and Clayton and Giauque[2] suggested that when substances solidify, crystals may also fail to order their systems with respect to different elements of similar size which occupy positions which would otherwise be nearly symmetrically equivalent. They explained the entropy discrepancy in their work on carbon monoxide in this way and predicted that it would occur in other cases when somewhat similar atoms or groups of atoms occupied two or more equivalent positions without producing much asymmetry.

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[1] This work was supported in part by the National Science Foundation and by the Office of Naval Research United States Navy. The U. S. Government may reproduce this article.

[2] J. O. Clayton and W. F. Giauque, THIS JOURNAL, **54**, 2610 (1932).

Blue and Giauque[3] tested this suggestion with the linear molecule NNO and found the expected discrepancy. They also used this idea to explain the discrepancy which had been found in the case of nitric oxide by Johnston and Giauque.[4] In this case the crystal consists of N_2O_2 units which reduces the expected discrepancy to $(R/2)$ ln 2 per mole of NO gas.

The present research considers the case of perchloryl fluoride which has three oxygen atoms and one fluorine located in an approximate tetrahedron about the centrally placed chlorine. The structural analysis of the gas molecule has been given by Lide and Mann[5,6] who have also calculated the thermodynamic properties from the molecular data. It seemed reasonable to expect that the crystal would fail to distinguish between the oxygen and fluorine in orienting this molecule in the solid state, thus leading to four possible positions for the fluorine and a discrepancy of approximately R ln 4 between the $\int_0^T C_p \, d \ln T$ and the known entropy. The experimental results given here have shown that the expected discrepancy occurs.

Calorimetric Apparatus.—A gold calorimeter with the laboratory designation IV A[7,8] was used for the measurements. A gold resistance thermometer–heater was used for high precision temperature measurements and energy input. A standard thermocouple with the laboratory designation "W" was attached to the calorimeter so that the calibration of the resistance thermometer was essentially continuous. The thermocouple was checked against the boiling (20.36°) point of normal hydrogen and the triple (63.15°) and boiling (77.34°) points of nitrogen. The thermocouple read 0.04° low at the boiling point of hydrogen and 0.05° low at both the triple and boiling points of nitrogen. Appropriate corrections were made. The triple point of water was taken as 273.16°K. (*i.e.*, 0°C. = 273.15°K.) and one defined calorie was taken equal to 4.1840 absolute joules.

The density of the liquid was represented by the equation[9] $d_{(l)} = 2.266 - 1.603 \times 10^{-3}T - 4.080 \times 10^{-6}T^2$.

Purification of Perchloryl Fluoride.—The perchloryl fluoride was supplied through the courtesy of Dr. J. F. Gall of the Pennsylvania Salt Manufacturing Company. After a simple distillation about 500 cc. of the material was condensed in a large glass bulb containing about 1000 g. of KOH pellets maintained at 196°K. by means of a solid carbon dioxide–isopropyl alcohol mixture for 24 hours. This was to remove any possible HF, CO_2 and H_2O. The perchloryl fluoride was then distilled in a vacuum jacketed and silvered glass low temperature fractionating column. Glass helices were used as packing. The column was 4 feet long and about 2 cm. in diameter. The vacuum jacketed boiler was heated electrically and the distilling pressure was maintained at 4 to 5 cm. of mercury. The glass condenser coils were contained in a vacuum jacketed cup filled with a mixture of cooled iso- and *n*-pentane. The desired temperature was maintained by an ethane vapor pressure thermometer which controlled liquid nitrogen fed through a copper coil immersed in the condenser cup. The reflux ratio of about 90 to 1 was accurately controlled by take-off through a capillary system and condensation in a receiver cooled with liquid nitrogen. The sample used in the calorimetric investigation was obtained by a redistillation of the middle fraction of a first distillation. The purified material was then transferred to a small stainless steel cylinder with a packless diaphragm type valve. The cylinder was small enough for convenient weighing on an ordinary balance.

Wet perchloryl fluoride at atmospheric pressure and room temperature reacted quite noticeably with mercury (whitish-grey deposit) and with Apiezen stopcock grease (brownish-black) after several hours contact. The reaction rate became negligible when the gas was extremely dry. The small premelting heat effect below the melting point was used to estimate the liquid soluble-solid insoluble impurity as 0.001 mole %.

Heat Capacity Measurements.—The heat capacity measurements are given in Table I. The measurements were continuous in the sense that each run began where the previous one ended, thus there were no unobserved regions.

The measurements were made in two series. Series I was terminated when a small leak developed in the bottom of the gold calorimeter. It later became evident that this was due to a welding defect which had remained tight during some twenty-three years of previous use. In order to complete the measurements before rebuilding the calorimeter the hole was plugged by means of some General Electric Resin No. 7031 after experiments which indicated that this material, after polymerization, would not react with or dissolve in cold, dry perchloryl fluoride. The expedient was successful and no further leak was observed. Series II on liquid ClO_3F followed. Corrections were made for vaporization into the gas volume. The values given for Series II, where the vapor pressure is increasing, are $C_{(sat)}$. C_p, the heat capacity at constant pressure, may be calculated from from the relation

$$C_p = C_{sat} + T\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial P}{\partial T}\right)_{sat} - \int_{sat}^{1 \text{ at.}}\left(\frac{\partial^2 V}{\partial T^2}\right)_p dP$$

The largest correction, which occurs at the highest temperature, is 0.027 cal. deg.$^{-1}$ mole^{-1}. It is more convenient to calculate the entropy directly from the values of C_{sat}.

TABLE I

HEAT CAPACITY OF PERCHLORYL FLUORIDE

0°C. = 273.15°K., mol. wt. ClO_3F = 102.457. Series I, 1.9467 moles; Series II, 2.0281 moles in the calorimeter. Cal. deg.$^{-1}$ mole^{-1}.

T_{av}	C_p	T_{av}	C_p	T_{av}	$C_{sat.}$
Series I				Series II	
14.98	1.73	56.95	10.62	130.51	21.02
16.55	2.47	60.14	11.17	136.41	21.03
18.10	2.72	64.42	11.76	142.92	21.06
19.63	3.23	69.08	12.18	149.31	21.15
21.75	3.88	73.31	12.48	155.38	21.26
24.08	4.65	78.84	12.90	162.14	21.32
26.21	5.25	88.39	13.69	169.26	21.45
28.48	5.87	93.06	14.12	176.16	21.58
30.90	6.50	97.91	14.65	183.24	21.76
33.45	7.10	102.48	15.17	190.35	21.91
36.62	7.74	107.67	15.79	197.27	22.12
40.13	8.36	113.25	16.78	204.40	22.28
43.59	8.89	118.88	18.04[a]	211.39	22.51
46.97	9.33	123.31	19.21[a]	218.22	22.73
50.20	9.68			223.34	22.90

[a] ΔT = 5.792° at 118.88°K. ΔT = 3.192° at 123.31°K.

The Melting Point and Heat of Fusion of Perchloryl Fluoride.—The melting point data are given in Table II. They were determined on a preliminary sample before the final purification was performed. Values were determined as a function of the fraction melted. A plot of the melting temperature against the reciprocal of the fraction melted, extrapolated to zero, gave a triple point of 125.41°K. The change in melting point with the fraction melted indicated a liquid soluble–solid insoluble impurity of 0.01 mole %.

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[3] R. W. Blue and W. F. Giauque, THIS JOURNAL, **57**, 991 (1935).

[4] H. L. Johnston and W. F. Giauque, *ibid.*, **51**, 3194 (1929).

[5] D. R. Lide, Jr., and D. E. Mann, Nat. Bur. Stds. Report No. 4399, 1 Nov. (1955).

[6] D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **25**, 1128 (1956).

[7] D. L. Hildenbrand and W. F. Giauque, THIS JOURNAL, **75**, 2811 (1953).

[8] R. H. Sherman and W. F. Giauque, *ibid.*, **77**, 2154 (1955).

[9] R. L. Jarry, *J. Phys. Chem.*, **61**, 498 (1957).

TABLE II

MELTING POINT OF PERCHLORYL FLUORIDE

% melted	Thermocouple °K.	Resist. therm. °K.
8.7	125.40	125.377
27.5	125.39	125.397
46.2	125.39	125.405

Accepted T.P. = 125.41°K.

The heat of fusion was determined in the usual manner of starting several degrees below the melting point and ending above it with appropriate corrections for $\int C_p dT$. The data are given in Table III.

TABLE III

HEAT OF FUSION OF PERCHLORYL FLUORIDE

Cal. mole^{-1}, triple point = 125.41°K.

T_1, °K.	T_2, °K.	Total heat input (cor.)	Cp d ln T	ΔH
123.992	129.278	1055.1	139.6	915.5
125.113	129.193	1036.7	119.7	917.0
			Av.	916.3 ± 1

The first determination in Table III was made on the preliminary sample used for the melting point determination mentioned above, with an impurity of 0.01 mole %. The impurity of the sample used for the second determination was 0.001 mole %. They are given equal weight.

Heat of Vaporization of Perchloryl Fluoride.—The method used was essentially that described by Giauque and Johnston[10] except that the 5-liter bulb which accepted the evolved gas at constant pressure was not thermostated or calibrated. The amount of perchloryl fluoride was determined by subsequent condensation and weighing in the stainless steel pressure vessel mentioned above. The 0.2 mole sample could be weighed within 0.01%. The weighings were corrected for buoyancy of the weights. The vaporizations were made within a few mm. of atmospheric pressure and appropriate correction applied. The results are given in Table IV.

TABLE IV

HEAT OF VAPORIZATION OF PERCHLORYL FLUORIDE

Cal. mole^{-1}, b.p. = 226.48°K.

Moles evap.	Time of heat input, min.	ΔH
0.19581	60	4617.6
.19369	60	4618.2
.19418	60	4619.9
	Av.	4619 ± 4

A less reliable value of the heat of vaporization, 4595 cal. mole^{-1}, was obtained from the vapor pressure data given below and the assumption that ClO_3F gas obeys Berthelot's equation with T_c = 368.3°K. and P_c = 53 atm.

The Vapor Pressure of Perchloryl Fluoride.—The vapor pressure was measured over the range 164 to 228°K. by means of a mercury manometer, 1.6 cm. diam. The measurements were made on a preliminary sample which was shown to contain 0.01 mole % of liquid soluble–solid insoluble impurity by means of several premelting heat capacity measurements made for that purpose. The line leading from the calorimeter was connected to the manometer, thus making the temperature stability of the calorimeter and its temperature scale available. Unfortunately some defect developed in the potentiometer and associated measuring system used for the resistance thermometer during these measurements, so that the high relative accuracy, desirable in a series of vapor pressure measurements, was not obtained. Thus the data given below were obtained only from thermocouple observations which somewhat limit the accuracy of calculations of dP/dT. A standard meter bar was compared with the manometer by means of a Société Généyoise cathetometer which could be read to 0.02 mm. and interpolated to 0.01 mm. The standard acceleration of gravity was taken as 980.665 cm. sec.$^{-2}$ and the value at this location as 979.973. The data are given in Table V.

TABLE V

VAPOR PRESSURE OF PERCHLORYL FLUORIDE

P = inter. cm., 0°C. = 273.15°K.

T, °K.	$P_{obsd.}$	($P_{obsd.} - P_{calcd.}$)	($T_{obsd.} - T_{calcd.}$)
164.11	1.057	−0.007	+0.067
167.63	1.502	+ .004	− .028
172.97	2.453	+ .016	− .074
176.59	3.324	.000	.000
181.88	5.097	− .006	+ .015
186.98	7.508	− .001	+ .002
191.99	10.723	+ .007	− .010
198.12	16.103	− .005	+ .005
204.47	23.833	+ .006	− .004
210.88	34.438	+ .023	− .012
217.86	49.846	− .027	+ .011
225.38	72.204	+ .014	− .004
(226.48)	(76.000)	.000	.000
228.67	84.083	.000	.000

Jarry[9] obtained 226.39°K. (corrected to scale 0°C. = 273.15°K.) for the boiling point.

The observations in Table V have been represented by the empirical equation

$$\log_{10} P_{(\text{int. cm.})} = \frac{-1652.37}{T} - 8.62625 \log_{10} T + 0.0046098T + 28.44780$$

The difference between the observed temperatures and pressures and those calculated from the above equation are given in columns 3 and 4. The accuracy is limited by the pressure observations at low pressures and by the temperature observations at the higher temperatures. The absolute values of the temperatures should be reliable to 0.05°.

TABLE VI

$\int_0^T C_p \, d \ln T$ FOR PERCHLORYL FLUORIDE, CAL. DEG.$^{-1}$ MOLE^{-1}

0–15°K., extrap.	0.62
15–125.41°K., $\int C_p \, d \ln T$	18.93
Fusion, 916.3/125.41	7.306
125.41–226.48°K., $\int C_p \, d \ln T$	12.781
Vaporization, 4619/226.48	20.395
$\int_0^{\text{b.p.}} C_p \, d \ln T$ of actual gas	60.03
Corrn. for gas imperfection	0.14
Ideal gas	60.17

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(10) W. F. Giauque and H. L. Johnston, THIS JOURNAL, 51, 2300 (1929).

The Entropy of Perchloryl Fluoride.—The entropy change between 0°K. and the boiling point is summarized in Table VI.

The correction for gas imperfection was made by assuming Berthelot's equation using $T_c = 368.3$°K. and $P_c = 53$ atm. $S_{\text{ideal}} - S_{\text{actual}} = 27RT_c^3P/32T^3P_c$.

The value 62.59 cal. deg.$^{-1}$ mole^{-1} for the entropy of ideal perchloryl fluoride gas at 226.48°K. may be found by interpolation in the table of thermodynamic properties given by Lide and Mann.[5] The value of $\int_0^{226.48°\text{K}} C_p \, d \ln T$ obtained from the measurements = 60.17 cal. deg.$^{-1}$ mole^{-1}.

If the crystal showed complete inability to order the oxygen and fluorine atoms to correspond to the equilibrium crystal perfection at 0°K., the expected difference would be $R \ln 4 = 2.75$ cal. deg.$^{-1}$ mole^{-1}. The fact that the observed discrepancy is a little less than this amount indicates a small amount of ordering of the O and F atoms.

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BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

The Synthesis of Ammonium Fluorometallates in Methanol[1a]

BY HELMUT M. HAENDLER, FREDERIC A. JOHNSON[1b] AND DAVID S. CROCKET

RECEIVED DECEMBER 9, 1957

A series of seventeen anhydrous ammonium fluorometallates has been prepared by reaction of methanol solutions of the metal bromides and ammonium fluoride. The products have been identified by X-ray and chemical analysis.

Introduction

The chemistry of reactions of simple inorganic compounds in organic solvents has been somewhat neglected, attention having been concentrated on organic systems containing water as one component. Comparisons of solubilities suggested to us the possibility of preparing anhydrous fluorides by metathesis in methanol, using ammonium fluoride and a metal halide. It was found, however, that in most cases an ammonium fluorometallate was produced.

Ammonium fluorometallates have long been of interest because of the structural problems they present, in themselves and in relation to fluorometallates of the alkali metals, and because of their potentialities as sources for anhydrous metal fluorides. Methods of preparation analogous to those used for the alkali complexes have not always been successful. Formation by fusion with ammonium fluoride is affected by the low decomposition temperatures of the ammonium complexes. Reactions in water or aqueous hydrogen fluoride solution often lead to hydrates, oxy- or hydroxy-compounds. The use of liquid hydrogen fluoride or bromine trifluoride as solvent and reactions with fluorine introduce obvious experimental difficulties.

Consequently, there have been some instances of failure to prepare specific compounds and other cases which appear to involve information based upon impure compounds. Cox and Sharpe,[2] for example, recently have pointed out that although several workers have reported different unit cell dimensions for ammonium hexafluoroferrate(III), $(NH_4)_3FeF_6$, none has reported analytical data. Their analyses indicate that all earlier studies, including their own, were actually made on $(NH_4)_{2.6}FeF_{5.6}\cdot 0.4H_2O$.

Experimental

Preparation of the Metal Bromides.—In each case the bromide was prepared by action of bromine on finely divided metal suspended in methanol. Excess bromine was used, except in the preparation of the iron(II) complex. The bromine was added in 1-ml. portions from a dropping funnel to a stirred suspension of 0.1 mole of metal in approximately 100 ml. of cooled "Absolute" methanol. The resultant solution was filtered to remove any insoluble residue and diluted to an approximately known molarity in a volumetric flask. The method is similar to that of Osthoff and West[3] and of Ducelliez and Raynaud.[4]

Preparation of the Complexes.—In all cases the reaction was carried out by the addition of metal bromide solution to a rapidly stirred saturated solution of ammonium fluoride in a polyethylene container. The volume of the bromide to be added was estimated from the approximate molarity of the metal bromide solution, the fluoride to metal ratio of the product expected, and the molarity (about 0.5 *M*) of the saturated ammonium fluoride solution. Generally a large excess of ammonium fluoride was used. Ammonium bromide is more soluble in methanol than is ammonium fluoride, the solubility of the latter being roughly 2 g./100 ml. of methanol.

In general the products were filtered with suction and washed on the filter with cold methanol until a test of the washings with aqueous silver nitrate showed them to be free from bromide. They were then washed with anhydrous ether, and dried in an oven at 60°. Digestion of a product was advisable to promote crystallization for better X-ray powder patterns, the samples being placed either in methanol or in a methanol solution of ammonium fluoride in a polyethylene container and kept at 40–50° for as long as a week. It was later found that running the initial reaction at about 60° greatly improved the quality of the powder patterns obtained. Negative tests for metal ions made with some filtrates indicate that precipitation is quantitative.

Analytical.—Ammonia was determined by distillation from strongly alkaline solution into cold boric acid solution, followed by titration with hydrochloric acid, using brom cresol green indicator.

Fluorine was determined by distillation from sulfuric or perchloric acid solution followed by titration of aliquots of the distillate with cerium(III) chloride, using murexide

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[1] (a) This work was supported in part by the Atomic Energy Commission. (b) National Science Foundation Predoctoral Fellow.

[2] B. Cox and A. C. Sharpe, *J. Chem. Soc.*, 1798 (1954).

[3] R. C. Osthoff and R. C. West, THIS JOURNAL, **76**, 4732 (1954).

[4] F. Ducelliez and A. Raynaud, *Compt. rend.*, **158**, 578, 2992 (1914); A. Raynaud, *ibid.*, **181**, 1069 (1925).