[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OBSERVATIONS ON THE RARE EARTHS. XXIX. THE PREPARATION AND PROPERTIES OF SOME ANHYDROUS RARE EARTH CHLORIDES

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I. Introduction

Very little work has been done recently to determine the properties of the anhydrous chlorides of some of the rare earths. The literature reports several such determinations, many of which vary considerably. As early as 1853 Marignac,[2] working with didymium, prepared the anhydrous chloride but did not determine its properties. In 1905, Matignon[3] published a rather complete work on the dehydration of the chlorides of neodymium, praseodymium, lanthanum, samarium and yttrium, and determined such properties as melting point, density and heat of solution. In 1910, Bourion[4] completed his work on the dehydration of some rare earth chlorides, having used sulfur monochloride to convert the oxides to the anhydrous chlorides. More recently Baxter and Chapin[5] with several other workers have made a rather extensive study of methods of obtaining the anhydrous rare earth chlorides.

Since very pure salts of most of the rare earth metals were available in this Laboratory, it was the purpose of this investigation further to study the preparation of the anhydrous chlorides of the rare earths and to determine several physical properties.

II. Rare Earths Used

With the exception of thulium all of the rare earths studied were available in a high state of purity. Several of these salts were formerly prepared in this Laboratory for atomic weight work, as described elsewhere in THIS JOURNAL.[6]

The lanthanum, cerium, praseodymium, samarium and yttrium salts were entirely free from other earths. The dysprosium material con-

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[1] An abstract of a thesis submitted by J. H. Kleinheksel in partial fulfilment of the requirements of the degree of Doctor of Philosophy in Chemistry in the Graduate School of the University of Illinois.

[2] Marignac, *Ann. chim. phys.*, [III] **38,** 148 (1853).

[3] Matignon, *Compt. rend.*, **140,** 1340 (1905).

[4] Bourion, *Ann. chim. phys.*, **21,** 49 (1910).

[5] (a) Baxter and Chapin, THIS JOURNAL, **33,** 1 (1911); (b) **37,** 526 (1915); (c) **43,** 1086 (1921); (d) **44,** 307 (1922).

[6] (a) Kremers and Balke, THIS JOURNAL, **40,** 593 (1918); (b) Kremers and Hopkins, *ibid.*, **41,** 718 (1919); (c) Owens, Balke and Kremers, *ibid.*, **42,** 518 (1920); (d) Driggs with Hopkins, *ibid.*, **47,** 363 (1924).

tained only small traces of terbium. This material was the same as that supplied to the Bureau of Standards for their arc spectrum work.[7]

The holmium salt was part of Fraction 22 prepared and used by Driggs and Hopkins in the determination of the atomic weight of holmium. The thulium salt, by spectrum analysis, indicated the presence of small traces of erbium and presumably also contained very small quantities of ytterbium and lutecium.

III. Dehydration of Rare Earth Chlorides

Dehydration of the chlorides was carried out in the presence of dry hydrogen chloride both at ordinary and reduced pressures.

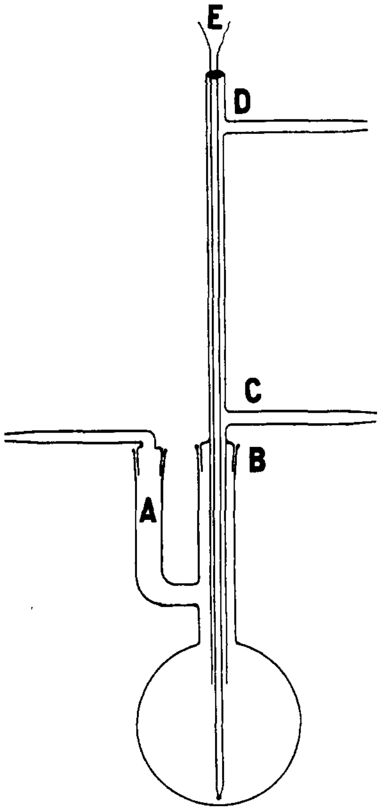

Fig. 1.

The method used at ordinary pressures was essentially the same as that employed in other researches in this Laboratory for atomic weight work.[6]

The 25cc. quartz reaction flask shown in Fig. 1 was a modification of those used in the above-mentioned researches on atomic weights of the rare earths. The extra vertical quartz tube with side arm D was provided to accommodate the platinum-platinum rhodium thermocouple E. A wax seal-in at E was used. The melting points of the rare earth chlorides, described later, were determined in this flask. The flask was heated by a carefully controlled electric furnace. Complete dehydration of the hydrated chloride was carried out in this flask with the thermocouple in position as shown. Dry hydrogen chloride was passed into the flask through side arm A and the exit gases passed out through outlets C and D. At the completion of dehydration the salt was fused and the melting point taken by the ordinary time-temperature cooling curve method.

Since the first five molecules of water of hydration are removed at temperatures from 85 to 120°, depending upon the rare earth in question, there is considerable tendency for the salt to fuse during the early stages of dehydration if the temperature is allowed to rise too fast. This usually results in the formation of basic salt. Thus with the necessity of keeping the temperature well below 100° during the removal of the first five molecules of water of hydration, dehydration is very slow and usually several days were spent in carrying out one complete dehydration. Dehydration at reduced pressures overcame this difficulty completely.

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[7] *Scientific Papers*, No. 421, Oct. 14, 1921.

Dehydration at Reduced Pressures

Dehydration of the hexahydrated rare earth chlorides at reduced pressures was carried out in a horizontal tube furnace shown in Fig. 3. The chlorides were placed in the quartz boats A contained in a Pyrex tube B with ground glass joint at D. Pure, dry hydrochloric acid gas first passed through a pressure reduction device illustrated in Fig. 2. Inside of a glass tube A was a smaller tube B, closed at the top with a stopcock through which varying amounts of mercury were admitted, depending upon the reduction in pressure necessary. The bottom end of tube B terminated in a small, round ball of glass. This was ground in to fit perfectly on the upper end of tube C, thus acting as a valve. When the pressure in A was sufficiently reduced, tube B was raised and gas allowed to enter at E. During operation the exit D of the furnace was attached to a water suction pump. Exit D of the pressure regulator was attached to B of the furnace. Dry hydrogen chloride from the generator was allowed to enter E of the pressure regulator.

With this reduced pressure dehydration apparatus the complete dehydration of all or any of the hydrated chlorides was accomplished within twelve hours. A gas flow through the tube at the rate of about one cc. per second at a pressure of about 25 cm. of mercury was maintained. For the first three or four hours the temperature was maintained at 70°, then was gradually raised to 160° to remove the last molecule of water, held at that temperature for one or two hours and then raised slowly to 250°. At this point all of the water of hydration was removed. While still hot the furnace was opened, the boats quickly removed to a desiccator over sulfuric acid and allowed to cool. The samples were then transferred to hot, dry glass tubes and quickly sealed. This method gave a perfectly anhydrous product. These samples of anhydrous rare earth chlorides were used in the density and heat of solution determinations as well as those samples obtained from the melting point determinations.

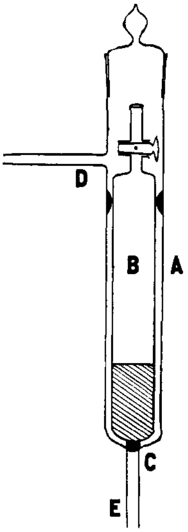

Fig. 2.

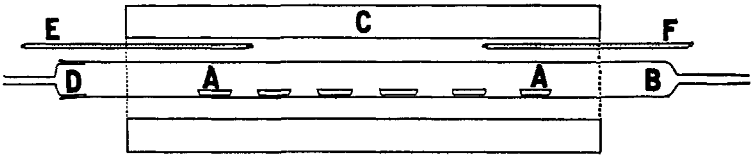

Fig. 3.

IV. Melting Points of the Anhydrous Chlorides

In the melting point determinations the anhydrous chlorides were prepared both at normal and at reduced pressures. When prepared in the quartz reaction flask the thermocouple was in position during dehydration. In cases where the salt was prepared at reduced pressures, the anhydrous salt was transferred to the quartz reaction flask at a temperature of 200° or above.

The platinum to platinum-rhodium thermocouple with potentiometer indicator was previously calibrated in the usual manner by determining the melting points of Bureau of Standards metallic zinc and metallic aluminum and of pure metallic silver[8] prepared in this Laboratory. Finally, to insure the calibration under actual working conditions, the pyrometer was calibrated against the melting points of especially purified sodium chloride and potassium chloride. The sodium and potassium chlorides were fused under the exact conditions that were present during the fusion of the anhydrous rare earth chlorides, thus eliminating any possibility of a constant source of error.

After the dehydration, the temperature was rapidly raised until fusion of the salt occurred. Immediately upon fusion the temperature was gradually lowered and the usual time-temperature cooling curve taken. To insure check results, at least two series of dehydrations and melting point determinations were carried out on each rare earth reported. Results are tabulated.

TABLE I

DATA ON ANHYDROUS RARE EARTH CHLORIDES

Chloride	Color of fused salt	Temp. range of removal of water of hydration,[a] °C.	Values for melting point previously obtained, °C.	Values for melting point obtained by authors, °C.
$LaCl_3$	White	85 to 90	907 (1)[b]	872
		125 to 135	890 (2)[c]	872
$CeCl_3$	White	90 to 110	848 (2)	822
		165 to 190	...	822
$PrCl_3$	Light green	110 to 115	818 (1)	823
		180 to 195	810 (2)	823
$NdCl_3$	Wine red	120 to 125	785 (1)	761
		155 to 165	784 (2)	761
$SmCl_3$	Pale yellow	100 to 110	686 (1)	682
		180 to 200	686 (2)	682
$DyCl_3$	Pale olive green	110 to 130	680 (2)	655
		200 to 230	...	655
$YtCl_3$	White	110 to 120	686 (1)	624
		190 to 210	...	624
$HoCl_3$	Slight yellow tint	95 to 105	...	696
		195 to 225	...	696
$TmCl_3$	Pale yellow-green	100 to 115	...	866
		190 to 205	...	866

[a] The first value shows the temperature range in which the first five molecules of water of hydration are removed and the second value that of the removal of the last molecule of water of hydration.

[b] (1), melting point values given by Matignon.

[c] (2), melting point values given by Bourion.

Discussion

No definite explanation can be given at the present time for the variation of melting points from those given by Matignon and Bourion.

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[8] Kremers, THIS JOURNAL, **40**, 593, 598 (1918).

Bourion reports abnormal supercooling in the case of fused lanthanum chloride. He states that in the first reading the temperature dropped to 830° and then rose to 878°. In the second reading the temperature dropped to 836° and then rose to 880°. After heating the anhydrous chloride again, the crystallization took place between 887 and 893° and he therefore adopts 890° as the melting point of the chloride.

It was observed in the present work on the melting point of lanthanum chloride, especially, that abnormal supercooling occurred when relatively large amounts of basic salt were present. When the chloride was found to be perfectly anhydrous, supercooling in many cases was absent and never in excess of four or five degrees. The presence of small amounts of basic salt lowered the melting point of the anhydrous chloride. On the other hand, the presence of a large amount of basic chloride raised the melting point of the mixture. In the present work only those determinations in which the chlorides were perfectly anhydrous are listed.

Matignon and Bourion prepared their anhydrous chlorides by passing a mixture of chlorine and sulfur monochloride over the heated oxide. It has been suggested that there may be some sulfate formed in this manner. The presence of a small amount of sulfate would alter the melting point of the anhydrous chloride considerably.

Lack of time prevented the preparation of anhydrous chloride by the use of chlorine and sulfur monochloride.

V. Density of the Anhydrous Chlorides

The density of some of the anhydrous rare earth chlorides has been determined, usually by the pycnometer method. Due to the extremely hygroscopic properties of the anhydrous rare earth chlorides, it seemed advisable to use a method in which no liquid is necessary to contact with the anhydrous salt. The apparatus used was that described by Karns,[9] in which the displacement of a small amount of dry air from a calibrated glass chamber is recorded by the height of a column of mercury. By reference to mercury and a correction for a change in barometric pressure, it is possible to determine very accurately the density of the anhydrous chloride under fairly anhydrous conditions. This method is especially applicable when only small quantities are available, as was the case in some of the anhydrous chloride density determinations.

The mercury in the apparatus was first purified by running it through a column of nitric acid in a fine spray; it was then twice distilled under reduced pressure and finally boiled to remove all the moisture. The mercury in the apparatus, as well as that in the density chamber, was protected from the moisture of the air by drying tubes filled with anhydrous calcium chloride.

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[9] Karns, This Journal, **48**, 1176 (1926).

The values obtained for the density of the anhydrous chlorides at 25° are represented in Table II.

TABLE II

DENSITIES OF ANHYDROUS CHLORIDES AT 25°

Chloride	Previous value given	Density, found	Chloride	Previous value given	Density, found
$LaCl_3$	3.79[a]	3.82	$SmCl_3$	4.27[a]	4.30
	3.94[b]			4.465[b]	
$CeCl_3$	3.92[a]	3.97	$DyCl_3$	3.67[a]	3.60
$PrCl_3$	4.07[a]	4.15	$YtCl_3$	..	2.81
	4.017[b]			2.80[b]	
$NdCl_3$	4.14[a]	4.17	$HoCl_3$	3.80[c]	4.25
	4.195[b]		$TmCl_3$	..	4.34
	4.134[d]				

[a] Values as given by Matignon, ref. 3.

[b] Values as given by Bourion, ref. 4.

[c] Values given by Hopkins and Driggs, ref. 6 d.

[d] Values given by Baxter and Chapin, ref. 5 a.

The values for the density of the anhydrous chlorides as obtained by this method agree fairly well with those given by Matignon[3] and Bourion.[4] There are indications that the density of the powdered, anhydrous, fused chloride may vary slightly with that of the crystalline fused anhydrous chloride. In general, it seems that the density of the fused mass is somewhat lower than that of the powdered anhydrous chloride. Such a difference might occur if the fused mass contained voids and the density were determined by the liquid displacement method. The determinations here given were made by the use of coarsely powdered material.

VI. Hydrogen Ion Concentration of the Aqueous Solutions

The hydrogen ion concentrations of the aqueous solutions prepared by dissolving the anhydrous chlorides of the rare earth salts in water are of interest because of the marked degree of hydrolysis exhibited by these salts when dissolved in water.

A Leeds and Northrup Students' Potentiometer, as described in their bulletin No. 765, was used in the determination of the hydrogen ion concentration. The calomel half-cell was made from mercury thrice distilled in a vacuum, while the calomel was prepared electrolytically in the manner described by Ewing.[10] The calomel half-cell contained a saturated potassium chloride solution and was connected to the aqueous rare earth chloride solution by a salt bridge. A hydrogen electrode prepared by depositing platinum black over a gold plated platinum electrode dipped into the beaker containing the solution of anhydrous rare earth chloride. The hydrogen passed over the hydrogen electrode was obtained from a cylinder, bubbled through an alkaline pyrogallic

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[10] Ewing, THIS JOURNAL, **47**, 301 (1925).

acid solution and then through a solution of the same vapor pressure as the solution whose hydrogen ion concentration was to be determined. After the hydrogen electrode had come to normal the electromotive force maintained between the hydrogen electrode and the calomel half-cell was measured by the potentiometer adjusted by a Weston standard cell. The hydrogen electrode was always carefully washed when a change of solutions took place to prevent any dilution of the standard rare earth chloride solution. After the hydrogen electrode had come to constant value, the electromotive force maintained between the hydrogen electrode and the calomel half-cell was determined by the potentiometer adjusted against a Weston standard cell. From this value of the electromotive force maintained in the aqueous solution of the rare earth chloride the hydrogen ion concentration expressed in *P*H units may be calculated by the following formula

$$P_{\mathrm{H}} = 16.9\ (V = 0.246)$$

where V is the electromotive force as measured and 0.246 is the electrode potential of the calomel half-cell.

The *P*H values for the solutions of the anhydrous rare earth chlorides as calculated are given in Table III.

Table III

Values of Hydrogen Ion Concentration

Chloride	Normality	E.m.f., volts	*P*H values	Chlorine	Normality	E.m.f., volts	*P*H values
$LaCl_3$	0.4950	0.4457	3.375	$DyCl_3$	0.3204	0.4910	4.140
	.0495	.4992	4.279		.03204	.5170	4.580
	.00495	.5714	5.497		.003204	.5370	5.180
$CeCl_3$	.5780	.3225	1.293	$YtCl_3$	.2635	.3050	0.9971
	.0578	.3570	1.876		.02635	.3085	1.056
	.00578	.4033	2.659		.002635	.3450	1.673
$PrCl_3$	.3330	.4072	2.662	$HoCl_3$	.0209	.2990	0.8957
	.0333	.4756	3.880		.00209	.3280	1.386
	.00333	.5666	5.417		.000209	.3793	2.253
$NdCl_3$	.4333	.3832	2.319	$TmCl_3$	.1108	.3108	1.095
	.04333	.4138	2.835		.01108	.3492	1.638
	.004333	.4664	3.724		.001108	.4045	2.679
$SmCl_3$	.4188	.3083	1.053				
	.04188	.3396	1.582				
	.004188	.3912	2.453				

In order that the relative values determined for the hydrogen ion concentration of the various rare earth chlorides may have a greater comprehensive value, they are plotted in the following graph shown in Fig. 4. In order that the curves may be of significance, the logarithm of the *P*H value multiplied by the normality is plotted against the logarithm of the normality. Under these conditions, it is evident from the curves that the anhydrous chlorides of the rare earths will be completely hydrolyzed at infinite dilution.

Hopkins[11] gives the following order of decreasing basicity of the rare earths: lanthanum, cerous cerium, praseodymium, neodymium, gadolinium, samarium, yttrium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutecium and ceric cerium. It is evident from the curves that the results obtained follow this order rather closely with the exception of dysprosium which, from the hydrogen ion concentration values in aqueous solutions, seems to be far more basic than heretofore represented.

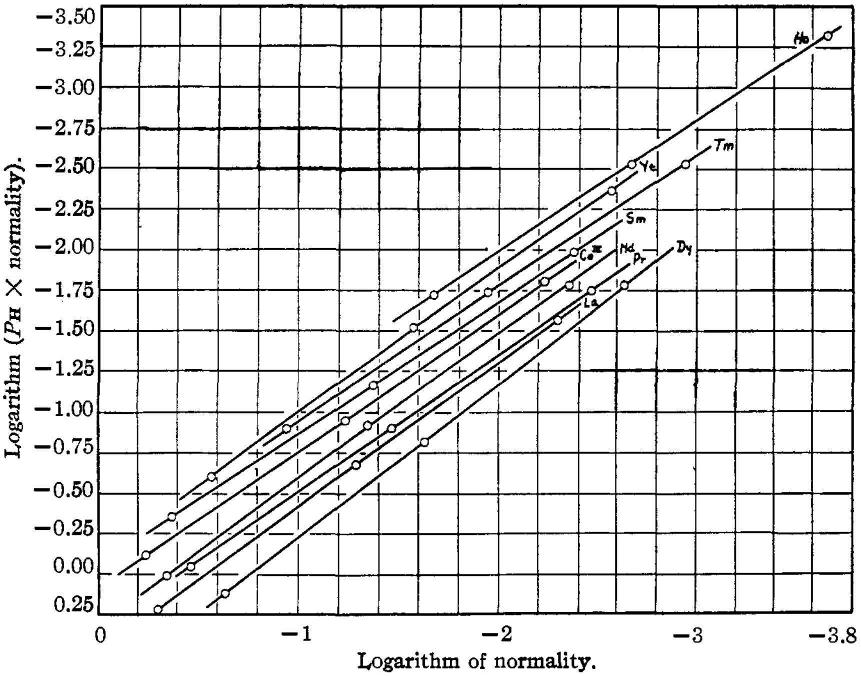

Fig. 4.—Hydrogen ion concentration of aqueous solutions of some anhydrous rare earth chlorides at 25°.

It is at this time impossible to give any explanation of this fact. The results were thrice checked and there seems to be no error which can account for the peculiarity. The values obtained are not sufficiently accurate to be taken as absolute values but show very definitely the relative hydrogen ion concentration of the aqueous anhydrous rare earth chloride solution.

VII. Summary

The anhydrous chlorides of lanthanum, cerous cerium, praseodymium, neodymium, samarium, dysprosium, yttrium, holmium and thulium were prepared by heating their hexahydrates in an atmosphere of dry hydrochloric acid gas until all of the water of hydration was expelled.

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[11] Hopkins, "Chemistry of the Rarer Elements," D. C. Heath and Co., Boston, **1923**, p. 101.

The dehydration of the hydrated rare earth chlorides was accomplished first at ordinary pressures, when the process is slow; and second at reduced pressures, when the dehydration is rapid.

The melting points of some of the anhydrous rare earth chlorides were determined in an atmosphere of dry hydrochloric acid gas by use of the cooling curve method.

The densities of some of the anhydrous chlorides of the rare earths were determined by an air displacement method.

The hydrogen ion concentration of the aqueous solutions of some of the anhydrous rare earth chlorides was determined by electrometric measurement with a hydrogen electrode.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

GASEOUS SOLUTIONS

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There are two types of formulation of the properties of systems involving gaseous solutions, corresponding to the two types of formulation of the properties of liquid solutions. The one, recently used by Keyes,[1] requires, aside from a knowledge of the empirical constants of a selected equation of state, a knowledge of the change in the heat capacity and heat content of the gas or gases in the mixture with temperature and pressure. The other, used by Lewis and Randall,[2] determines the ratio of the fugacity of each gas in the mixture to the fugacity in a selected standard state at each temperature, and needs then only the change in the heat content of the gas in its standard state, with the temperature, to complete the ordinary thermodynamic formulation of the system.

Either type of formulation, if supplied with sufficient empirical constants, will give accurate results, but we believe that the second type leads to greater accuracy with fewer constants[3] and less labor. In this paper we shall elaborate the method of the latter authors and present the values of the fugacity of the constituents of gaseous mixtures in so far as they can be determined from the existing data. The rough regularities exhibited by these functions should be useful for estimating the values of similar functions in other undetermined systems.

In the absence of experimental information, Lewis and Randall[4] in

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[1] Keyes, THIS JOURNAL, **49**, 1393 (1927).

[2] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, Chap. XVII.

[3] See Randall, *Trans. Faraday Soc.*, **23**, 498 (1927), for a discussion of the significance of the activity coefficient.

[4] Ref. 2, p. 225.