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SOLUBILITIES OF RARE-EARTH SALTS
PART I

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It has been shown that the fractional crystallization of the chlorides of yttrium and holmium from 1:1 hydrochloric acid causes the holmium to concentrate rather rapidly in the least soluble portions.[1] Because the separation of these elements from each other is very difficult, it was considered that a careful study of the solubility of the chlorides might reveal some striking characteristic available for the separation of certain members of the rare-earth series.

Preparation of Chlorides.—The chlorides were prepared by dissolving the highly purified oxides in hydrochloric acid, evaporating the solutions to the point of crystallization, cooling in ice and saturating with hydrogen chloride. The crystals were separated as much as possible from adhering mother liquor by suction and washed with hydrochloric acid previously saturated with hydrogen chloride. Whenever necessary, the chlorides were submitted to a second crystallization.

In order to obtain the most efficient drying, it was found that the vacuum desiccator should contain both sulfuric acid and sodium hydroxide and that the crystals should be stirred at frequent intervals to prevent caking. The greatest care was taken in this procedure to dry the salt thoroughly and yet prevent dehydration. When the process was considered complete, a careful analysis was employed as a check. Determinations were made of the solubilities of the hexahydrated trichlorides of yttrium, samarium and neodymium in water and in hydrochloric acid of d. 1.1051, and of

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[1] THIS JOURNAL, 43, 1398 (1921).

ytterbium in the latter solvent. In order to obtain fairly representative curves, determinations were made at 10°, 20°, 30°, 40° and 50°. The samples for the thermostat were made up in the usual manner. Before the bottles were sealed, they were brought to either slightly above, or slightly below, the temperature at which the determination was to be made

TABLE I

SOLUBILITIES

Temp. °C.	% of oxide M_2O_3	% of MCl_3	Parts of MCl_3 per 100 parts of solvent	% $MCl_3.6H_2O$	Parts of MCl_3.-$6H_2O$ per 100 parts of solvent
		$NdCl_3$ IN WATER[a]			
10	33.01	49.16	96.70	70.37	237.5
20	33.23	49.49	97.97	70.84	243.0
30	33.52	49.91	99.63	71.45	250.2
40	33.85	50.41	101.60	72.16	259.2
50	34.32	51.11	107.00	73.16	272.6
		$NdCl_3$ IN HCl (d., 1.1051)			
10	17.57	26.16	35.43	37.42	59.73
20	17.84	26.57	36.18	38.02	61.34
30	18.74	27.92	38.74	39.96	66.55
40	20.03	29.83	42.51	42.69	74.46
50	21.45	31.94	46.99	45.71	84.20
		$SaCl_3$ IN WATER			
10	32.62	48.02	92.35	68.22	214.7
20	32.79	48.29	93.37	68.59	218.4
30	33.00	48.60	94.53	69.02	
40	33.41	49.20	96.84	69.88	
50	33.94	49.98	99.91	70.99	[illegible]
		$SaCl_3$ IN HCl (d., 1.1051)			
10	14.83	21.84	27.95	31.02	
20	15.22	22.42	28.90	31.84	
30	16.28	23.97	31.54	34.05	
40	17.33	25.52	34.26	36	
	18.66	27.49	37.91		
		YCl_3 IN WATER			
10	25.37	43.85	78.07		
20	25.50	44.08	78.82	6[illegible]	
30	25.64	44.33	79.62	68.[illegible]	
40	25.86	44.70	80.81	69.41	
50	26.07	45.07	82.03	69.99	
		YCl_3 IN HCl (d., 1.1051)			
10	14.09	24.35	32.19	37.81	60.80
15	14.12	24.41	32.28	37.90	61.03
20	14.25	24.63	32.68	38.23	61.87
30	14.74	25.48	34.19	39.57	65.48
40	15.34	26.52	36.08	41.18	70.00
50	15.94	27.55	38.02	42.78	74.76

TABLE I (*Concluded*)

$YbCl_3$ IN HCl (*d.*, 1.1051)

Temp. °C.	% of oxide M_2O_3	% of MCl_3	Parts of MCl_3 per 100 parts of solvent	% $MCl_3.6H_2O$	Parts of $MCl_3.6H_2O$ per 100 parts of solvent
10	22.58	32.00	47.04	44.35	79.70
20	22.85	32.38	47.89	44.89	81.45
30	23.31	33.03	49.32	45.78	84.45
40	23.88	33.84	51.15	46.91	88.33
50	24.62	34.88	53.56	48.35	93.59

[a] These results were obtained by R. M. Wiggin, to whom the writers wish to express their thanks.

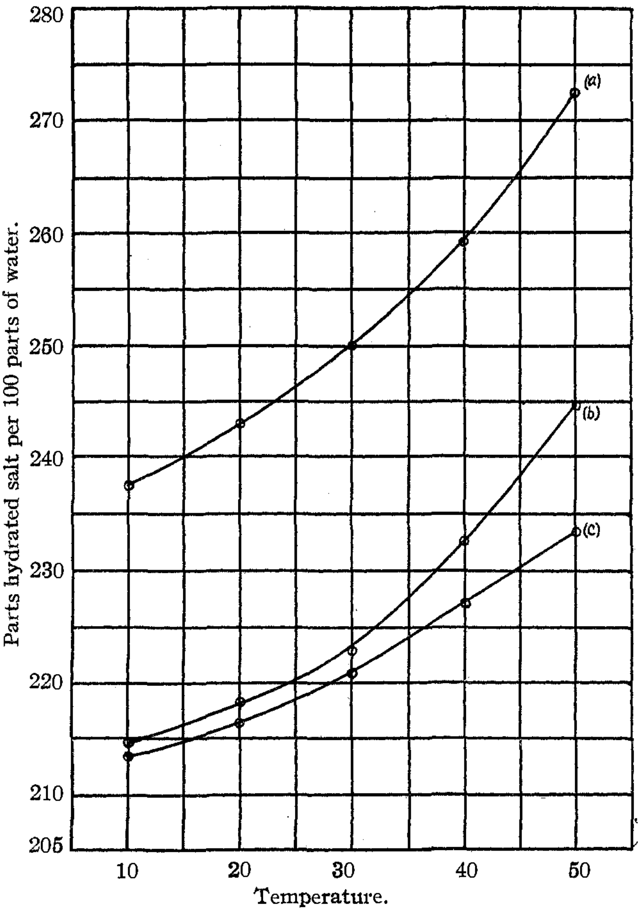

Fig. 1.

(a) $NdCl_3.6H_2O$
(b) $SaCl_3.6H_2O$
(c) $YCl_3.6H_2O$

in order to avoid difference in pressure. All analyses, excepting those pertaining to ytterbium chloride, were made in duplicate, the samples coming from two separate bottles. In the case of ytterbium chloride, the analyses were made in duplicate but the samples were taken from the same bottle.

After the solutions had been rotated in the thermostat for nine hours or more, which time was found to give checking results, approximately 1 cc. of the solution was withdrawn, weighed, diluted to 150 cc., precipitated with oxalic acid solution, the mixture allowed to stand for 12 hours or more, filtered, the precipitate washed, ignited to oxide and weighed. All results were calculated from weights obtained in air.

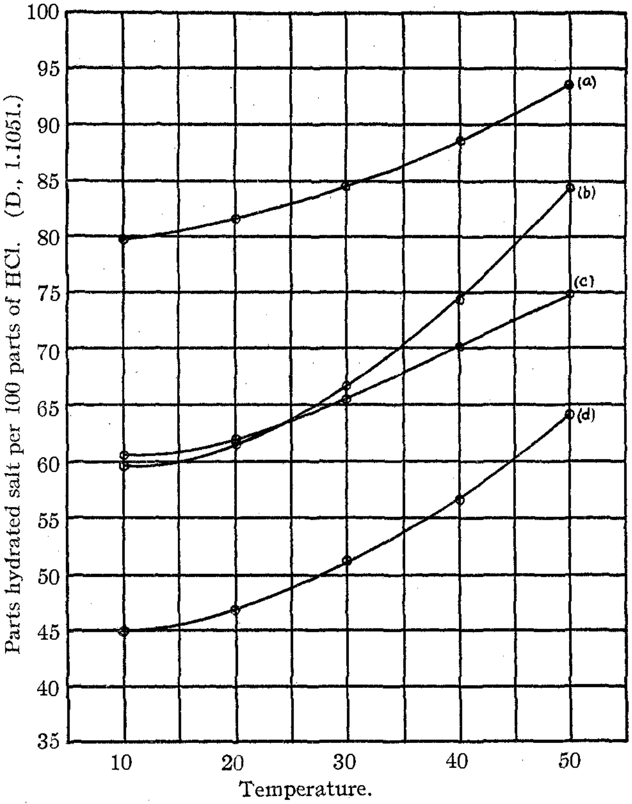

Fig. 2.

(a) $YbCl_3.6H_2O$
(b) $NdCl_3.6H_2O$
(c) $YCl_3.6H_2O$
(d) $SaCl_3.6H_2O$

Figs. 1 and 2 give the curves obtained by plotting parts of hydrated chloride per 100 parts of water and per 100 parts of hydrochloric acid, respectively.

The following melting points were found for the salts.

$MCl_3.6H_2O$	Nd	Sa	Y	Yb
M. p., °C.	124	142–142.5	161–163	153–155

Summary

The solubilities of the hexahydrated trichlorides of yttrium, samarium and neodymium in water and in hydrochloric acid (d., 1.1051), and that of ytterbium in the latter solvent have been determined.

This work is being continued with other salts and solvents.

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[CONTRIBUTION FROM THE WM. H. CHANDLER CHEMICAL LABORATORY OF LEHIGH UNIVERSITY]

THE PREPARATION OF ELECTROLYTIC MERCUROUS CHLORIDE IN SATURATED POTASSIUM CHLORIDE FOR USE IN THE CALOMEL ELECTRODE

BY WARREN W. EWING

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The use of single electrode potentials is becoming more and more important. This is especially true of the use of the hydrogen electrode potential in acidimetric titrations and in determinations of the hydrogen-ion concentration, as well as of the use of oxidation-reduction potentials in various electrometric determinations. The measurement of single electrode potentials involves the use of some standard half-cell of known potential. The calomel electrode in 0.1 *N*, in 1 *N* and in saturated potassium chloride solutions are the standard half-cells generally used. This article offers an electrolytic method of preparing calomel directly in a saturated potassium chloride solution. It eliminates the preparation of pure hydrochloric and nitric acids and the tedious washing and shaking processes involved in the other methods. It offers a reliable and dependable standard which is comparatively easy to prepare.

Preparation of Calomel

The calomel used in the electrodes described in this article was made electrolytically and directly in saturated potassium chloride solutions employing the apparatus shown in the figure.

A and B were battery jars 10 cm. in diameter. They were connected by means of salt bridges E 1 cm. in diameter. The ends of the bridges were covered with collodion membranes G which were made in the following manner. The ends were first covered with strong filter paper which was held in place by means of rubber bands. They were then dipped in a 4% collodion solution in a mixture of alcohol and ether. After a few