

bidity developed during the titration) the solutions at the end-point were always perfectly clear, and remained so on boiling. After considerable dilution, however, white precipitates of copper(I) thiocyanate formed: such precipitates could not be secured from copper(II) thiocyanate solutions even after long standing.

TABLE I
MILICOULOMETRIC ELECTROLYSIS OF COPPER(II) IN 1 *F* THIOCYANATE

The solution initially contained 0.500 micromole of copper(II) in 0.497 ml. of 1.00 *F* potassium thiocyanate. $E_{d.s.} = -0.90$ v. The blank counting rate of the millicoulometer was 0.2960 ± 0.0001 count/sec., including the contribution from the residual current, and the sensitivity was 4.53×10^{-4} microfaraday/count. Galvanometer deflections have been corrected for the residual current.

Time	Register	Counts	Counts, cor.	Micro-faraday	<i>d</i> , cm.	Micro-mole reduced	<i>n</i>	
0	11745	0	0	0	30.27	0	..	
1000	12178	433	137	0.062	28.40	0.0312	1.99	
2000	12602	857	265	.120	26.69	.0593	2.02	
3000	13019	1274	386	.175	25.08	.0859	2.04	
4000	13430	1685	501	.227	23.56	.111	2.05	
5000	13834	2089	609	.276	21.80	.140	1.97	
8000	14993	3248	880	.399	18.01	.203	1.97	
12000	16472	4727	1175	.533	14.36	.263	2.03	
Mean: 2.01 ± 0.03								

As it is not uncommon to find reducing impurities in ammonium thiocyanate preparations, it seems probable that the copper(II) in the solutions of Korshunov and Mal'yugina was reduced to the +1 state by some adventitious contaminant.

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Observations on the Rare Earths. LXI. Precipitation of Hydrus Oxides or Hydroxides from Perchlorate Solutions¹

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The utilities of data obtained from electrometric titrations of salt solutions with alkalis in establishing the relative basicities of the tripositive rare earth metal ions are well known.^{2,3} Both precipitation *pH* values and solubility product constants calculated for the hydrus hydroxides indicate basicity decreases paralleling decreases in ionic radii, but there are sufficient differences among data for nitrate, chloride, sulfate and acetate solutions of comparable concentrations³ to suggest that cation-anion interactions are of some importance. Although such interactions would probably be of least consequence in nitrate solutions, it was deemed advisable to carry out parallel

studies on solutions containing the non-complexing perchlorate ion.

Experimental

Materials Used.—The majority of the rare earths employed were either the same as those used previously² or of the same degrees of purity. With praseodymium (PR-43, 99% Pr₂O₃), europium (EU-5, 92.7% Eu₂O₃, 6.7% Sm₂O₃), and erbium (ER-1-2s, 98% Er₂O₃, 2% Y₂O₃), materials of slightly different compositions were used. Approximately 0.1 *M* (0.02 *M* with europium) perchlorate solutions were prepared by treating slight excesses of the oxides with 72% perchloric acid, filtering, and diluting to volume. Such solutions were standardized by the usual oxalate-oxide procedure. Carbonate-free sodium hydroxide solutions were standardized against potassium hydrogen phthalate.

Titration Procedure.—Titrations were carried out at $25 \pm 0.5^\circ$ exactly as previously described.² All solutions were stirred with nitrogen to minimize carbon dioxide interference. Measurements of *pH* were made immediately after each addition of alkali and at three-minute intervals until constant values were obtained.

Results

Numerical data characterizing these titrations are summarized in Table I. It is apparent that

TABLE I
ELECTROMETRIC TITRATION DATA FOR PERCHLORATE SOLUTIONS

Ion	Precipitation At pre- cipitation incidence	<i>pH</i> At OH ⁻ / R ⁺⁺⁺ = 0.4	Average solubility product constant	Average water solubility ($\times 10^6$) mole/liter
La ⁺⁺⁺	8.10	8.18	1.7×10^{-19}	8.8
Pr ⁺⁺⁺	7.40	7.43	6.7×10^{-22}	2.2
Nd ⁺⁺⁺	7.30	7.34	3.2×10^{-22}	1.9
Sm ⁺⁺⁺	7.13	7.17	8.4×10^{-23}	1.3
Eu ⁺⁺⁺	6.91	6.99	0.9×10^{-23}	0.8
Gd ⁺⁺⁺	6.84	6.90	1.8×10^{-23}	.9
Y ⁺⁺⁺	6.81	6.88	1.6×10^{-23}	.9
Er ⁺⁺⁺	6.61	6.68	4.1×10^{-24}	.6
Yb ⁺⁺⁺	6.45	6.55	2.5×10^{-24}	.5
Lu ⁺⁺⁺	6.45	6.55	1.9×10^{-24}	.5

data for perchlorate solutions are closely comparable with those already reported² for nitrate solutions. The differences in basicity between ions of adjacent elements are somewhat better defined, and the well-known excessively high basicity of the lanthanum ion is somewhat more apparent for perchlorate solutions. In addition the precipitation ranges for all of the cations were found to embrace smaller *pH* intervals than with the nitrate solutions. The apparently anomalous behavior of praseodymium shown in previous studies² was also resolved, and the titration curve for praseodymium perchlorate lay close to and above that for the neodymium salt and uniformly considerably below that for the lanthanum salt. Use of a more nearly pure praseodymium sample doubtless accounts for the difference.

Titration data for perchlorate solutions support the theoretical basicity order for these cations and place yttrium in its logical place between gadolinium and erbium. That precipitation was complete in all cases at OH⁻:R⁺⁺⁺ mole ratios of 2.60–2.75 suggests basic salt formation to be at a minimum in perchlorate solutions.

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(1) For the preceding communication in this series, see T. Moeller and F. A. J. Moss, *THIS JOURNAL*, **78**, 3149 (1951).

(2) T. Moeller and H. E. Kremers, *J. Phys. Chem.*, **48**, 395 (1944).

(3) T. Moeller and H. E. Kremers, *Chem. Revs.*, **37**, 97 (1945).