

The precipitates were removed and washed five times by centrifuging with diluted hydrochloric acid containing sodium nitrate to prevent peptization. After being dried, the precipitates were counted, using a thin-wall beta counting tube. Inasmuch as activities in the precipitates (*ca.* 0–100 counts per minute) were negligible in comparison with the activity of the standards (4500–4600 counts per minute per milliliter) the absence of exchange is indicated. Extreme washing reduced activities in the precipitates still further, showing that observed activities were probably due only to adsorption and occlusion. Neither alteration of *pH* nor of temperature gave any evidences of exchange.

Attempted Pyrophosphate-Hypophosphate Exchange.—Radiophosphoric acid was converted to pyrophosphate by evaporating with disodium hydrogen orthophosphate solution and igniting the residue for 2 hr. at 600°. The active pyrophosphate was dissolved in water and diluted appropriately with tetrasodium pyrophosphate solution. The exchange procedure was identical with that described above except that concentrations were reduced to 0.01 *M* to avoid precipitation of thorium pyrophosphate.⁸ Results exactly comparable with those mentioned above are again interpreted as indicating no exchange. Again some adsorption and occlusion effects were noted.

It should be pointed out that the counting rates noted for the solids were not absolutely correct because the weights of the precipitates used were not determined and because the layers counted were not of uniform thickness, but the values obtained were of the correct orders of magnitude and the interpretations logical.

Acknowledgment.—Support received from the Office of Naval Research is gratefully acknowledged.

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Radiometric Determination of the Solubilities of Thorium and Certain Rare Earth Metal Hypophosphates

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RECEIVED JUNE 20, 1952

Although the extremely small acid solubility of thorium hypophosphate has been used to advantage for the efficient removal of thorium from its admixtures with the rare earth elements,^{1–6} no quantitative comparisons of hypophosphate solubilities which might lend support to the method have appeared. The availability of radiohypophosphate⁷ provided a tool for solubility determinations. Neodymium and yttrium were selected as representative members of the cerium and yttrium sub-groups, respectively, for comparison with thorium.

Data summarized in Table I indicate that thorium hypophosphate remains essentially quantitatively insoluble in at least 4 *N* hydrochloric acid, whereas under comparable conditions the rare earth metal hypophosphates are sufficiently soluble to permit separations. Thorium hypophosphate is markedly less soluble than the pyrophosphate.⁸

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TABLE I

SOLUBILITIES OF HYPOPHOSPHATES IN HYDROCHLORIC ACID SOLUTIONS

Sample	Hydrochloric acid concentration, <i>N</i>	Solubility, mole/liter × 10 ⁴
ThP ₂ O ₆	1.00	0.25
	2.00	.47
	4.00	1.65
	6.00	2.10
Nd ₄ (P ₂ O ₆) ₃	0.05	0.11
	.10	.48
	.20	1.60
	.30	2.00
	1.00	14.46
	2.00	34.70
Y ₄ (P ₂ O ₆) ₃	0.20	3.02
	0.30	5.52
	1.00	26.90

Experimental

Solubilities were determined by essentially the same procedure previously described for pyrophosphates.⁸ Thorium, neodymium and yttrium hypophosphates were precipitated by adding suitable volumes of a standard sodium hypophosphate solution (26.4 mg. P₂O₆⁻⁴ per ml.) of known radioactivity (*ca.* 4500 counts per minute per milliliter)⁷ to excesses of the metal salt solutions. The precipitates were washed thoroughly, air-dried, and suspended in 50-ml. volumes of hydrochloric acid solutions of varying normalities. These suspensions were equilibrated for 5 days in a thermostat at 25 ± 0.1°, studies having shown that longer periods produced no significant changes. The suspensions were then filtered and the activities of the filtrates measured using an annular volume tube.⁸ Comparisons of these activities with that of the standard indicated the solubilities. These are expressed in terms of anhydrous hypophosphates in Table I, the compositions of the precipitates having been determined by independent means.⁹

Although statistical errors at some of the low counting rates encountered and the probable presence of low activities of thorium decay products render these results not absolutely quantitative, the values are of the correct orders of magnitude and especially useful on comparative bases. The rare earth metal hypophosphates are too soluble at acidities above 1–2 *N* to permit accurate evaluations by this procedure.

Acknowledgment.—Support received from the Office of Naval Research is gratefully acknowledged.

(9) G. H. Quinty, Doctoral Dissertation, University of Illinois, 1951.

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The Solid State Reaction between Magnesium and Chromium Oxides

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RECEIVED JUNE 30, 1952

Chemical reactivity of inorganic materials is known to be structure-sensitive, being dependent on a variety of variables which are involved in the history and preparation of the reacting substances. Thus, ill-defined phase boundary effects are responsible for the empirical relations often deduced for the kinetics of solid state changes. These relations cannot be used for the direct establishment of a reaction mechanism.

It has been realized that in order to minimize the conditions under which phase boundary processes