ACTION OF CARBON DIOXIDE

Molarity of trisodium citrate	pH						
	In CO ₂ -free solutions	After saturation with CO ₂	After bubbling nitrogen through solutions				
			1 hr.	2 hr.	3 hr.	4 hr.	5 hr.
0.1	8.97	6.20-6.35*	6.91	7.43	7.82	7.86	7.84
1	10.30	6.90-7.03*	7.65	8.20	8.76	8.72	8.70

* pH not constant: rises at a rate of about 0.15 per 15 min.

are reached, after the lapse of three to four weeks. The same final pH may be obtained within a few hours (see table) by bubbling successively carbon dioxide and nitrogen through the solutions.

Citrate solutions ought, therefore, to be stored in paraffin-coated flasks if it is desired to keep their pH constant; furthermore, contamination by carbon dioxide must be avoided.

We have pleasure in thanking Miss T. Rayss for examining the *Penicillium* moulds.

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¹ *J. Amer. Chem. Soc.*, **67**, 1824 (1945).

² *J. Amer. Chem. Soc.*, in the press.

Preparation of Rare-Earth Chlorides

THE preparation of chlorides of the rare-earth elements directly from monazite by chlorination in the presence of carbon possesses certain advantages over conventional methods. (1) Phosphorus is volatilized as oxychloride in a single operation and the chlorides may be obtained phosphate-free. Conventional methods involve lengthy operations for its complete removal, particularly from thorium. (2) Impurities present in the mineral (as well as those in the added carbon) are largely eliminated as volatile chlorides; for example, as the chlorides of iron, silicon, titanium, aluminium, zirconium and tin. (3) The anhydrous chlorides produced may be extracted either in water or non-aqueous solvents or recovered in a molten state.

The reaction has been studied by briquetting the powdered phosphate with wood charcoal, using rare-earth chlorides as a binding agent. The dried briquettes were heated to reaction temperature in a vertical tube, and a known weight of chlorine passed. Nitrogen was passed through the charge before and after reaction to remove moisture and oxygen and to displace residual volatiles. Condensation of phosphorus oxychloride served as a guide to the progress of reaction. The chlorinated briquettes were extracted with dilute nitric acid (pH 2), and the yield estimated by analysis of this solution.

Reaction proceeded smoothly when the phosphate and charcoal were finely ground and when the temperature was as close as possible to the sintering temperature of the briquettes (700-750° C.). The consumption of carbon indicated that the approximate course of the reaction was

(*R* stands for rare-earth elements: a similar expression holds for thorium.) Some results are given in the accompanying table. The conditions were as follows. Temperature, 700° C.; dimensions of charge: height, 7 cm., cross-section, 2.6 cm.², weight, 50 gm.;

weight-ratio monazite/carbon, 6.7; particle sizes, Tyler screens: phosphate, 100%-325, charcoal, 100%-200, briquettes, - 6 + 10; *RCl*₃, 1 gm. per 50 gm. of charge; monazite analysis: rare-earth oxides, 59.7 per cent; ThO₂, 6.8 per cent; P₂O₅, 27.4 per cent; insoluble in sulphuric acid, 2.0 per cent; ash in charcoal, 7.8 per cent.

Chlorine passed††		Yield*, %		Overall chlorine efficiency**
(gm./min.)	total (gm.)	R ₂ O ₃	ThO ₂	
0.19	20	41	0.1	64†
	30	63	2.9	70†
	40	90	14	75†
	50	91	17	61
0.50	20	49	trace	79†
	31	62	0.40	67
	41	73	0.65	58
	95	89	9.2	31
0.70	20	34	Nil	56
	30	47	trace	52
	40	54	0.10	45
	145	90	9.1	21

* Corrected for *RCl*₃ used as binder.

** Calculated from data in columns 2, 3 and 4.

† No free chlorine evolved.

†† Theoretical consumption of chlorine, 33 gm.

No phosphate was detected in the extracts, which contained only small quantities of impurities, chiefly calcium and magnesium chlorides.

Under optimum conditions, it is therefore possible to obtain a 90 per cent yield of rare-earth chlorides of very satisfactory purity for an overall chlorine efficiency of 75 per cent. The real efficiency is undoubtedly greater than this, because several grams of chlorine are consumed by impurities. The time required to produce a 90 per cent yield is almost independent of the flow-rate; but the rate of reaction falls off very markedly after a 90 per cent yield has been attained.

Thorium is not chlorinated until approximately 50 per cent of the rare earths has been attacked, and thereafter reacts much more slowly than the latter. After extraction of soluble chlorides and separation of unconsumed carbon, a residue is obtained which corresponds in composition to a rare-earth phosphate in which the weight ratio ThO₂/(ThO₂ + R₂O₃) has been increased from an initial value of 0.10 to 0.45.

At 800° C. the reaction becomes rapid, but the chlorides melt and a considerable amount of thorium chloride volatilizes. The reaction at high temperatures is under further investigation. A fuller account of results and experimental procedures will be published elsewhere.

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Mechanism of Conductance by Hydrogen and Hydroxyl Ions in Aqueous Solutions

It has been suggested¹⁻⁵ that the process of electrolytic conduction by hydrogen and hydroxyl ion in water involves, in addition to the mass transport of the hydrated ions, a proton transmission mechanism. This mechanism yields by means of a relatively small motion (*c.* 0.4 Å.) of a proton as great a charge transport as would result from a much larger (*c.* 3 Å.) motion of the entire ion.