125. *The Dimethyl Phosphates of the Rare-earth Metals.*

By JOSEPH K. MARSH.

Solubility measurements of the dimethyl phosphates of certain rare-earth metals, $M[Me_2PO_4]_3$, are recorded. The great range, the higher rate of change in the yttrium group than in the cerium group, and the great decrease in solubility with rise in temperature are noteworthy features. Particulars are given of the purification of terbium, dysprosium, and holmium by fractional crystallisation of their dimethyl phosphates. Terbium can be completely purified, dysprosium retains a trace of gadolinium and terbium, and holmium is completely freed from yttrium but not from dysprosium. For purification of these three rare-earth metals, the dimethyl phosphates are of practical utility.

James and Morgan (*J. Amer. Chem. Soc.*, 1914, **36**, 10) first prepared representative rare-earth dimethyl phosphates and made solubility determinations. They believed the usefulness of the salt for separations to be seriously impaired by the extent to which it suffered hydrolysis, but showed that pure gadolinium was very rapidly prepared by the use of it. This was confirmed by Jordan and Hopkins (*ibid.*, 1917, **39**, 2614), who found that only a trace of terbium remained after 15 series of crystallisations on 6 fractions, 6 terbium head-fractions having been removed. The author (J., 1934, 1972) has shown that at temperatures below 50° hydrolysis of these salts of terbium and its neighbours is not serious, and has described methods of working which yielded pure terbium without difficulty.

New data for the solubilities of the rare-earth dimethyl phosphates are recorded in the table. The solubilities of yttrium, erbium, and ytterbium at 25° are respectively 26%, 89%, and 12·5% higher than those recorded by James and Morgan. The solubility of erbium has been determined by extrapolation from the experimental value for a sample containing erbium, 85; yttrium, 15%.

		Dimethyl phosphate, g. per 100 g. of H_2O.			Corresponding oxide.					
					G./l.			G.-mol./l.		
E.	*Z.*	0°.	25°.	50°.	0°.	25°.	50°.	0°.	25°.	50°.
Gd	64	37·0	24·2	15·7	126	82·3	53·4	0·348	0·227	0·148
Tb	65	24·2	12·6	8·07	83	43·2	27·7	0·227	0·118	0·076
Dy	66	15·0	8·24	4·83	52	28·5	16·7	0·139	0·076	0·045
Yt	39	6·44	3·53	1·90	15·8	6·9	4·7	0·069	0·038	0·025
Er	68	6·91	3·36	2·03	24·4	11·9	7·2	0·064	0·031	0·019
Yb	70	2·68	1·35	0·72	9·7	4·8	2·6	0·024	0·012	0·007

Solutions saturated at 0° were prepared by mechanically stirring excess of the salt with water for 3—4 hours. Cold saturated samples of solution were diluted somewhat, and kept at 25° or 50° for 3—4 hours with occasional stirring. Considerable salt crystallised. Samples of solution were withdrawn through a silk filter fitted to the end of a pipette, run into crystallising basins, and weighed. They were then evaporated to dryness at about 30°, and the residues desiccated all night over sulphuric acid. Duplicate samples of each solution were taken and always agreed to within 1%. The dimethyl phosphates easily attain equilibrium with the solvent. Initial high solubilities for erbium were found to be due to free acid. This was tested for by litmus paper pressed on the moistened salt at the conclusion of a determination. No analyses were made of the salts, James and Morgan's finding that except in the cases of lanthanum and cerium, they are anhydrous having been accepted. The fact that the solubilities as now determined constitute a geometrical progression is strong evidence of their substantial accuracy. The lower values found by James and Morgan may be due to the fact that they considered a solution saturated when by spontaneous evaporation a few crystals formed on the surface. Owing to the very rapid change in solubility, if any less soluble earth was present even in small amount, its crystals would form before the solution was really saturated with respect to the main earth present.

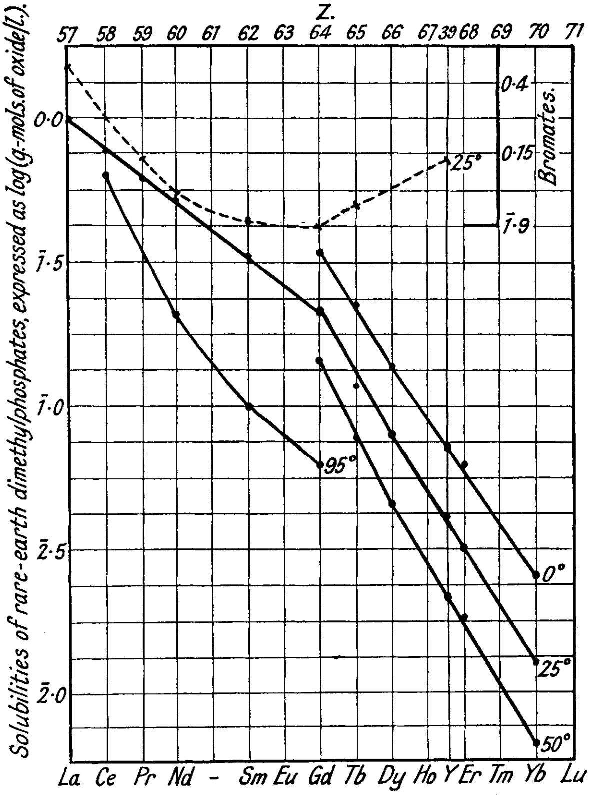
In the figure the logarithms of the concentrations (as g.-mols. of oxide per l.) are plotted against *Z*, the atomic number. The isotherms for 25° and 95° from lanthanum to gadolinium are based on the data of James and Morgan. For comparison, the solubilities of the bromates (James *et al.*, *J. Amer. Chem. Soc.*, 1909, **31**, 913; 1927, **49**, 132) have been similarly treated.

The following points will be noticed.

(1) The rapid change of solubility of the dimethyl phosphates from one metal to another. The bromates have been largely used as the most suitable salts for separating the yttrium group, but their much inferior efficiency on the basis of solubility differences may be gauged by the relative divergence of the 25° isotherms from the horizontal. For the metals from terbium to yttrium this shows a four-fold superiority for the dimethyl phosphates. The bromates, however, are advantageous on account of greater solubility, and therefore greater ease of handling in large quantity. Their crystals and mother-liquor are also more easily separated. The very small solubilities of the dimethyl phosphates of erbium or rare-earth metals of higher atomic number, coupled with a greater

ease of hydrolysis, render them unsuitable for fractional crystallisation, but it seems likely that a separation of the ytterbium earths from a crude mixture might be brought about by using an alkali dimethyl phosphate as a precipitating agent. A similar degree of efficiency to that of potassium sulphate as a reagent for separating the cerium earths from the yttrium earths might be expected.

(2) As is well known, the separation of the yttrium earths presents much greater difficulties than that of the cerium earths, because in general the solubility differences are much less marked. This is exemplified by the slope of the two arms of the solubility curve of the bromates. The dimethyl phosphates, however, show the opposite behaviour.



The cacodylates, $E[(CH_3)_2AsO_2]_3,8H_2O$, may resemble the dimethyl phosphates (James and Morgan, *loc. cit.*), but their solubilities are too low for practical purposes. The sulphate octahydrates may be similar, but they can be brought into equilibrium with their solvent only with great difficulty, and their utility is thereby destroyed.

(3) The dimethyl phosphates, and probably the cacodylates, appear to be the only known salts of the rare-earth metals which fall steadily in solubility from lanthanum to lutecium. Usually there is a rise in solubility with increasing atomic weight, or there is a minimum of solubility in the middle of the series, as in the case of the bromates.

(4) The negative temperature coefficient is remarkably high, especially among the less soluble dimethyl phosphates. There is a progressive proportional increase in this respect as the solubility falls; *e.g.*, the fall for neodymium between 25° and 95° is about 60%, but that for ytterbium between 25° and 50° is almost 50%. This means that the higher the final temperature of crystallisation the more rapid should be the fractionation, but in practice the temperature is kept low on account of hydrolysis.

(5) There is an almost constant factor of about 0·6 for the rate of decrease of solubility following the atomic number sequence from gadolinium to ytterbium: at 0°, $s_z = 1{\cdot}56s_{z+1}$; at 25°, $s_z = 1{\cdot}63s_{z+1}$; at 50°, $s_z = 1{\cdot}68s_{z+1}$.

(6) Yttrium takes its right place among the other rare-earth metals if assigned a hypothetical atomic number of 67·6.

Usually, yttrium and holmium are a more inseparable pair than erbium and yttrium, but the reverse appears to be the case with the dimethyl phosphates. Some crude erbium after 40 series of crystallisations on 12—15 fractions had yielded up its ytterbium and thulium at the insoluble end, but little progress could be detected in the separation of yttrium.

Fractional Crystallisation of the Dimethyl Phosphates.—Terbium, dysprosium, and holmium should be concentrated to a reasonable degree before use of the dimethyl phosphates is attempted. The elimination of yttrium especially should be aimed at, as its solubility (*ca.* 10 g. of oxide per l.) is inconveniently low. Driggs and Hopkins (*J. Amer. Chem. Soc.*, 1925, **47**, 363) have shown that holmium of apparent atomic weight of 150 can be prepared fairly easily by a series of partial thermal decompositions of the nitrate. It is for the further elimination of yttrium that the dimethyl phosphates are of use. Most of the gadolinium is best eliminated by crystallisation as double magnesium nitrate or as bromate.

Crude yttrium earths were fractionated as bromates until the bulk of the holmium and erbium had parted, and dysprosium and yttrium had largely separated (4000 crystallisations). The holmium–yttrium section was then submitted to basic nitrite precipitation, and the concentrated holmium together with the crude terbium and dysprosium bromates were ready for working as dimethyl phosphates.

Residues from monazite containing Sm_2O_3 (1 kg.), Gd_2O_3 (1 kg.), and yttrium earths (2 kg.) were crystallised as double magnesium nitrates with addition of bismuth magnesium nitrate with 35% nitric acid as solvent. Samarium, europium, and gadolinium were quickly removed, leaving the yttrium earths, but by careful seeded crystallisation and with the use of much bismuth it was found possible to separate most of the dysprosium and holmium (0·8 kg. of oxide) as double magnesium nitrates, leaving a yttrium residue (1·2 kg. of oxide).

Fractionation of the gadolinium magnesium nitrate was proceeded with till negligible amounts of dysprosium or terbium remained with it. The impure tail-fractions were heated to 220°, whereby the bismuth was converted into a basic salt and was precipitated when the melt was poured into water, the earths being recovered from solution as oxalates. These were next put through 100 crystallisations as bromate, whereby a considerable quantity of yttrium was eliminated.

Dimethyl hydrogen phosphate was made by Schiff's method from phosphorus oxychloride (1500 ml.), in a 5 l. flask fitted with a gas-tight stirrer, dropping-funnel and lead-off tube for hydrogen chloride and methyl chloride, by adding carefully dried methyl alcohol (2200 ml.) and keeping the mixture below 30° till near the end. The product was finally heated on a water-bath till free from hydrogen chloride fumes. It was found to contain very little phosphoric acid or methyl dihydrogen phosphate and was used without further purification.

A thin paste of rare earths was treated with dimethyl hydrogen phosphate, the reaction mass powdered and dissolved in 60 l. of water. Fractionation was done at the start generally 5 times weekly with cooling to autumn night temperature, and heating in a large water-bath to 40° or 50°. Quantities of yttrium were rapidly eliminated at the head so that the bulk was soon reduced. Any rare-earth phosphates which appeared were also removed. At first only about 20 fractions were employed, but as the purification proceeded this number was increased to 70. In the early stages when much yttrium was present the rather small crystals were collected on muslin on a Buchner funnel. After 55 series of crystallisations, yttrium had concentrated at the head (fraction 1), and holmium in fractions 15—27 with a trace down to 42; fractions 28—53 were mostly dysprosium, and 28—43 gave an oxide of uniform buff tint; fraction 70 was gadolinium. The bulk decreased from 800 ml. at the head to a few ml. at the tail. Some similar material, which had previously been obtained from 10 kg. of gadolinite and other rare-earth residues and partially fractionated, was added at what appeared to be the appropriate time and position in the series. Soon now it was possible to start to eliminate dysprosium. Decantation replaced filtration, about 70% of the mother-liquor being poured off. After 4 months nearly all the gadolinium had been removed; and in a further 3 months the greater part of the terbium (60 g. of oxide) had been obtained in a state of purity, and also most of the dysprosium (500 g. of oxide). The holmium fractions were reduced to a volume of about 150 ml. each, but they still held quantities of dysprosium. With the warmer weather, cooling in a refrigerator was resorted to, and in

14 months three-quarters of the holmium (30 g. of Ho_2O_3) had been obtained giving a spectrum free from any trace of the arc lines of yttrium. The head of the series was still almost colourless yttrium, yet 20 fractions down there was no trace of it. The next 24 fractions had identical arc spectra, but were not free from small quantities of dysprosium. This middle section was removed, and the heads and tails continued so as to increase the yield of holmium.

Purity of the Products Obtained.—(1) *Terbium.* Terbium of high purity is readily obtainable. A central terbium fraction was examined carefully for dysprosium and gadolinium. For detection of dysprosium use was made of the intense absorption band at λ 9090 (Freymann and Takvorien, *Compt. rend.*, 1932, **194**, 963), which was photographed on a prism spectrograph having a dispersion of 30 A./mm. in this region. A new band at λ 8070 was found, however, which is as strong as the other and, being more accessible photographically, is to be preferred for use in estimating dysprosium. 100 Mm. of 8·9N-terbium chloride showed the dysprosium band less intense than 16 mm. of N/20-dysprosium chloride in saturated gadolinium chloride solution; *i.e.*, the dysprosium content was less than 1 in 1100 and probably about 1 in 1500. An estimate of gadolinium in the terbium was made by comparing the strength of the gadolinium arc lines at λλ 3100—3000 with that in a lanthanum oxide base containing added quantities of gadolinium. Less than 1 part per 1000 of the latter was found.

(2) *Dysprosium.* This was readily freed from holmium, but the ignited oxide was not white. Prolonged fractionation did not alter the oxide tint, which resembled that of manilla paper and was presumably due to a faint trace of terbium oxide. The arc line of gadolinium, λ 3034, was also detectable in most samples of dysprosium, but a purity approximating to 99·9% has been readily achieved.

(3) *Holmium.* The effects of hydrolysis became more serious with the lower solubility of holmium than they were in the case of terbium or dysprosium. Dysprosium in the insoluble or slightly soluble hydrolysis product which forms in the fractions becomes distributed throughout the holmium fractions and is not eliminated; but the complete separation of yttrium from holmium is possible and it is doubtful if this has been achieved before. Driggs and Hopkins (*loc. cit.*), using gas heating for thermal decomposition of nitrates, found that the atomic weight of holmium fractions gave content values at 158·1, but with electric heating this rose to 163·5. This value has been accepted as the true atomic weight without the absence of yttrium having been proved, but is 1·4 units below that required if holmium has a single isotope 165 as found by Aston (*Proc. Roy. Soc.*, 1934, *A*, **146**, 46).

It was not possible to estimate dysprosium in holmium by means of infra-red absorption bands, for holmium itself absorbed at λλ 8050, 8900, 9090, and from 9400 upwards; but the product so far as ascertained approximates to holmium, 99; dysprosium 1%.

As a result of this study the author is of opinion that the dimethyl phosphates offer the easiest known means of purifying terbium, dysprosium, and holmium. For dysprosium of very high purity, the most suitable treatment will probably be a final repetition of the fractionation of the double magnesium nitrates in presence of much bismuth magnesium nitrate, whereupon the traces of gadolinium and terbium in dysprosium will crystallise with the bismuth salt.

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