

204. *The Relation of Yttrium to the Lanthanons: A Study of Molecular Volumes.*

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When yttrium concentrates near samarium or neodymium in the lanthanon series, molecular and not ionic states are believed to be involved. The molecular volume of yttrium acetylacetone is found to approximate to that of neodymium, and to be larger than those of the lanthanons similar to yttrium in ionic size. Nevertheless, yttrium basic nitrate and ferricyanide were found to give molecular volumes indicating a polar crystalline state, though they accumulate at the position of No. 61 on fractionation. The basic nitrate will be un-ionised in nitrate solution, and triply ionised ferricyanide is unlikely to reach the solubility product with Y^{+++} or Ln^{+++} . The reaction to form these ferricyanides is therefore believed to be molecular in character, thus accounting for the behaviour of yttrium. This reasoning can be extended to other slightly soluble yttrium salts with multivalent anions (*e.g.*, phosphate, chromate, and ferrocyanide) showing similar behaviour.

In a previous communication (Marsh, this vol., p. 118) the suggestion was made that yttrium on passing from the ionic to the covalent state underwent a relatively larger increase in size on comparison with the lanthanon elements. For instance, yttrium and holmium ions are approximately of the same size, but sometimes yttrium shows behaviour indicating a resemblance to neodymium and samarium, which elements have larger ions than holmium. Certain sparingly soluble and basic salts incline to show yttrium associating with elements larger than holmium. A reason for this behaviour is now sought.

It is firmly established that a progressive fall in ionic radius with increasing atomic number occurs between lanthanum and lutecium. This is found by *X*-ray determination of the crystal-lattice size, and is confirmed by determination of the molecular volumes of the sulphate octahydrates (von Hevesy, *Z. anorg. Chem.*, 1925, 147, 217; 150, 68), though in both these instances the first two or three members of the rare-earth group lack isomorphism with the remainder. In the oxide series the yttrium ion falls in size between those of dysprosium and holmium, and in the sulphate series between holmium and erbium ions. The latter is the position usually taken by yttrium in a fractional crystallisation series, indicating an important correlation between ionic and molecular sizes and chemical properties in the lanthanon series. Generally, yttrium is isomorphous with holmium and erbium, but exceptions are known. For example, the 2-bromo-5-nitrobenzenesulphonates of yttrium crystallise with $10H_2O$ similarly to those of samarium and gadolinium and in contrast to the dodecahydrates of erbium and ytterbium. Direct evidence of yttrium having at times a larger volume than holmium is now sought by measurement of molecular volumes: it has already been reported in the case of the atomic volumes of the metals (Bommer and Hohmann, *Z. anorg. Chem.*, 1939, 241, 268). The crystalline basic nitrates and the ferricyanides have been examined throughout a representative series of earths. These are two good examples of salts by the formation of which rapid accumulation of yttrium with neodymium and samarium, and separation from the "yttrium earths", is brought about, but in both instances the molecular volume of the yttrium salt proved to have a value which placed yttrium in sequence in the usual ionic position among the other elements, *i.e.*, near to holmium. The crystals must therefore be regarded as polar in type. The acetylacetones, however, gave evidence that this covalent yttrium compound has in fact a larger molecular volume than that of the usual associates of yttrium in its ionic state.

The basic nitrates are obtained by crystallisation from hot concentrated nitrate solutions. They are decomposed by water, but in nitrate solution they appear to be stabilised by suppression of ionisation by a common-ion effect, on removal of which they hydrolyse. They may be regarded as existing in a non-ionising solvent only. If, then, they exist in solution in a non-ionised form, it is not surprising to find that the solubility of yttrium basic nitrate has a value interpolating in the lanthanon series at the position of No. 61, the same as is found in the case of the atomic volume, or the acetylacetone molecular volume. We must then postulate a transition from a non-ionic to an ionic state upon crystallisation, based on the evidence of the crystal molecular volumes. The precipitate produced by boiling a nitrate solution with sodium nitrite, being chiefly the basic nitrate $Y_8O_{14}(NO_3)_4 \cdot 17H_2O$ (Fogg and James, *J. Amer. Chem. Soc.*, 1922, 44, 397), appears to be a similar case to the basic nitrate $Y_6O_5(NO_3)_8 \cdot 20H_2O$ produced by crystallisation (James and Pratt, *ibid.*, 1910, 32, 873).

In the case of the ferricyanides, high concentrations of potassium ferricyanide and up to 200 g./l. of yttrium oxide in the form of chloride can be brought together in cold solution without any precipitate forming, yet the solubility of $YFe(CN)_6$ at 20° is represented by only

0.602 g./l. of Y_2O_3 (Prandtl and Mohr, *Z. anorg. Chem.*, 1938, **236**, 243). Seeding is ineffective in producing a precipitate. Indeed, the seed may dissolve, but on gentle warming a precipitate forms slowly, which has a molecular volume indicative of an ionic state of yttrium. An irreversible reaction takes place, since the precipitate will not redissolve appreciably on cooling. The formation of yttrium ferricyanide according to the simple equation $Y^{+++} + 3Cl^- + 3K^+ + Fe(CN)_6^{----} = YFe(CN)_6 + 3KCl$ cannot be expected to take place, since triple ionisation of ferricyanic acid is necessitated. Thus, in general, it will be seen that molecular reactions may be expected where the alternative involves the existence of a multivalent anion or the production of a series of unknown intermediates. Ferrocyanide, chromate, and phosphate are other examples of salts of yttrium showing closer resemblance to neodymium than to holmium in fractionations. All are compounds having low solubilities and are salts of multivalent acids incapable of complete ionisation.

A series of acetate molecular volumes have been measured, and as anticipated yttrium takes an ionic position in the series. The densities and molecular volumes of the four series of salts examined are presented in Table I. The values for the acetylacetones might be doubled, since the molecules are known to be double in solution. No high degree of accuracy for the molecular volume determinations can be claimed for these last compounds, but the results are sufficiently reliable to prove the point that the value for yttrium does not lie in the sequence close to those of the other yttrium earths, but is larger and more nearly equal to that of neodymium. The fused acetylacetone compounds were usually somewhat basic as indicated by high oxide contents on ignition. The densities found must therefore tend to be high and the molecular volumes low. For Table I, data have been selected from the italicised data of Table II,

TABLE I.

Densities.

	La.	Nd.	Sm.	Gd.	Dy.	Y.	Er.	Yb.
Acetates	—	1.885	1.942	1.990	2.042	1.689	2.075	2.142
Basic nitrates	—	—	2.940	3.045	3.159	2.431	3.223	3.326
Ferricyanides	2.044	2.110	2.179	2.243	—	1.937	2.348	2.410
Acetylacetones	1.542	1.618	1.651	1.678	1.709	1.403	—	1.748

Molecular volumes.

Acetates	—	208.7	205.8	205.0	201.6	200.4	199.9	197.1
Basic nitrates	—	—	634	617	605	605	602	594
Ferricyanides	207	203	199	197	—	193	192	190
Acetylacetones	283	273	271	271	269	275	—	269

TABLE II.

Acetylacetones.

	Density.			Oxide, %.			Calc.	Molecular volume.			Best.	Oxide, % in excess.
	1.	2.	3.	1.	2.	3.		1.	2.	3.		
La ...	1.536	1.549	—	36.75	35.82	—	37.34	284.0	281.6	—	283	—2.9
Nd ...	1.618	1.664	1.694	39.05	40.80	41.34	38.11	273.3	265.4	260.5	273	2.5
Sm ...	1.636	1.666	1.689	40.92	40.43	42.22	38.95	273.7	268.8	265.1	271	5.6
Gd ...	1.676	1.712	—	42.33	43.62	—	39.82	270.7	265.4	—	271	6.3
Dy ...	1.709	1.726	—	42.94	45.25	—	40.55	269.1	266.5	—	269	5.9
Y ...	1.393	1.400	1.416	30.83	29.85	31.47	29.23	277.1	275.2	272.7	275	5.1
Yb ...	1.740	1.746	1.759	43.58	43.60	41.23	41.90	270.5	269.5	267.5	269	2.2

sometimes by averaging, but more often by selection of the value relating to the acetylacetone sample which showed the nearest approach to theoretical oxide content. A fairly constant density increment of 0.03 between even-numbered elements from neodymium to dysprosium inclusive is found, and the excess oxide, except in the case of neodymium but with the addition of yttrium, is also fairly constant, so that this sequence of elements is comparable, and they lend mutual support. It was found that lanthanum acetylacetone was slightly volatile. Its true oxide content cannot therefore be determined by ignition and the low contents recorded in Table II are suspect. On the other hand, the low densities for the acetylacetone leading to an unexpectedly high value for the molecular volume are consistent with the presence of excess acetylacetone, but the melts were not gummy, as would be expected in that event, but quite vitreous. This in other instances accompanied deficient acetylacetone.

If we examine the molecular volumes of isomorphous compounds of neodymium and ytterbium, we find the values for the latter smaller than those of the former by the following percentages: sulphates 7.0, ferricyanides 6.5, acetates 5.6, ethyl sulphates 3.0. The fall in the case of the acetylacetonone compounds appears to be under 2%.

EXPERIMENTAL.

Densities.—In the case of the acetates, suspension of crystals in mixtures of chloroform and bromoform and determination of the density of the liquid by a Westphal balance proved very satisfactory. With basic nitrates and ferricyanides, determinations of the loss of weight in chloroform was more satisfactory, and the acetylacetones were weighed in water. A platinum bucket of 2 ml. capacity and about 0.5 g. of substance were used in these three cases. The accuracy of the method depended chiefly on the proper release of air bubbles before weighing in liquid.

Acetates, $E(C_2H_3O_2)_3, 4H_2O$.—The neodymium salt was prepared by evaporation of a solution in a desiccator. It is rather efflorescent, but large crystals may be grown. The other acetates crystallised readily from warm neutral solutions, and are stable.

Basic Nitrates, $E_2O_5(NO_3)_8, 20H_2O$ (James and Pratt, *loc. cit.*).—The normal slightly acid nitrates were boiled to dryness and heated till some decomposition had occurred. The vitreous melts were then poured into cold water and gave clear hot solutions which deposited crystals overnight. It was found possible to prepare the samarium basic nitrate if only slight decomposition of the melt was permitted, for its range of stability is small. The melt was vitreous like the others. Neodymium gave no vitreous melt or basic nitrate crystals. The nitrate creamed at once when decomposition began.

The density of the erbium salt as given in Table I is an extrapolation from the experimental value using material containing 2% of yttrium. Only a very small sample of dysprosium basic nitrate was available, and the single determination of the molecular volume appears low. Other values are believed to be correct within ± 2 . Three determinations for yttrium were within 1 part in 500.

Ferricyanides, $EFe(CN)_6, 4H_2O$.—Neutral chloride solutions containing 100 g./l. of oxide were treated at 40–50° dropwise with cold saturated potassium ferricyanide with mechanical stirring and the precipitate which formed was collected, washed, and dried. The precipitates of samarium and gadolinium could not be obtained as coarsely crystalline as in the other cases. Prandtl and Mohr (*Z. anorg. Chem.*, 1938, **236**, 243; **237**, 160) found some variation in the amount of water of crystallisation in the different salts but apparently without loss of isomorphism: *e.g.*, for the lanthanum salt they found 4.5H₂O, but the molecular volumes shown in Table I are calculated for 4H₂O in all cases.

Acetylacetonone Compounds, $E[CH(CO-CH_3)_2]_3$.—Acetylacetonone (3 g. in 10 ml. of alcohol) was added to an equivalent of lanthanon acetate in 50 ml. of cold water, and ammonia added dropwise with stirring, excess being avoided. The acetylacetonone compound soon separated and was collected with suction. Especially in the case of ytterbium, acetylacetonone washing appeared to decompose the precipitate. Washing was therefore omitted or kept to a minimum, but the products were well pressed on filter-paper and dried in a desiccator. Melting points were found to be close to known values without further purification.

Lanthanum acetylacetonone. The precipitate appeared to be basic and did not give a clear melt unless one or two drops of acetylacetonone were added before fusion; then clear melts giving a vitreous, pale amber solid were obtained.

Neodymium acetylacetonone. This, m. p. 150–152°, like the lanthanum compound, appeared basic (Found: Nd₂O₃, 39.04. Calc.: Nd₂O₃, 38.11%) and failed to give a clear melt without additional acetylacetonone.

Gadolinium acetylacetonone. This compound; m. p. 140°, was likewise basic (Found: Gd₂O₃, 40.53. Calc.: Gd₂O₃, 39.83%). Unlike preparations previously reported it did not appear to contain any water of crystallisation (1 and 2 H₂O, Jantsch and Meyer, *Ber.*, 1920, **53**, 1594; 3 H₂O, Sarkar, *Bull. Soc. chim.*, 1926, **39**, 1390). If damp acetylacetones were heated to their m. p. they reacted with water to form the hydroxides and failed to give satisfactory melts.

Ytterbium acetylacetonone. This had m. p. 114° but the melt was not clear. It did not gas at the m. p., as occurred with the higher-melting acetylacetones melting near the b. p. of free acetylacetonone. It was not considered likely that satisfactory density determinations by weighing the finely crystalline compounds in water could be made, nor could organic liquids be used, since they have solvent action. Quantities of about 1 g. were therefore fused in an oil-bath in thin 10-mm. specimen tubes with, when necessary, the addition of one or two drops of acetylacetonone to give clear melts. Loss of acetylacetonone occurred at the m. p. Unless a slight loss did occur, the fused mass cooled to a stiff gum which would quickly crystallise if kneaded. But when slightly basic, a vitreous resin was obtained in one or more large pieces on breaking the tubes, and the densities of these pieces could be obtained with a fair degree of accuracy by weighing in water. There was, however, always some devitrification or hydroxide formation on the surface in contact with water, with loss in weight. The surface deposit was removed so far as possible after determining the density, and the percentage of oxide contained in the material was obtained by ignition. In some cases burning the oxide free from carbon was difficult. The char required to be broken down with a glass rod in the silica crucible before final ignition. Particular care was taken to obtain reliable data for yttrium. The three analyses are in satisfactory agreement but the third shows a high density and high oxide content and low molecular volume. The final figure adopted in Table II for the molecular volume of yttrium acetylacetonone is therefore likely to be a little low.

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