CCXXI.—*The Solubilities of the Octahydrates of the Rare-earth Sulphates.*

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THE series of isomorphous octahydrates of the rare-earth sulphates have already been accurately investigated with regard to their molecular volumes (von Hevesy, *Z. anorg. Chem.*, 1925, **147**, 217; **150**, 68); an almost steady contraction in the latter takes place from praseodymium to lutecium, with a corresponding decrease in the ionic radii of the kations. Such a series should be exceptionally suitable for the study of the influence of alteration in the radius of an ion on the solubility. As the total contraction in molecular volume over the whole of this range only amounts to 7·5%, we have to deal in this case with a specially fine gradation of properties, whereas other series of isomorphous salts contain only a few members and show also a greater alteration in the ionic radius.

In the present work the solubilities were determined, at 20° and 40°, of the whole series of octahydrates mentioned above, with the exception of illinium and thulium, and, in addition, that of yttrium; the heats of solution were then calculated from the solubility data. The very valuable collection of pure sulphates was placed at the disposal of Professor von Hevesy through the generosity of Dr. Auer von Welsbach.

The saturated solution was obtained by shaking an excess of the substance in a thermostat, constant to $\pm$ 0·01°, for at least 24 hours. In each case we ascertained that a longer time of shaking had no effect on the amount dissolved. The original substances, used by Auer von Welsbach for atomic-weight determinations, were dissolved and again evaporated to dryness. It was found that the original water content remained unchanged so long as the temperature of 70° was not exceeded, except in the case of ytterbium and lutecium, where it was found essential to evaporate at a lower temperature. In the latter cases, therefore, we dried the substance in a desiccator at 20°. The method used was to weigh out a certain quantity of the saturated solution, evaporate this to dryness at 70°, or in a desiccator at 20°, and weigh the residue as $M_2(SO_4)_3,8H_2O$. From the weight of the latter, and the weight of the water lost in evaporation, the solubility can be calculated.

The heats of solution of the sulphates have been calculated from the equation $\log_e K_2 - \log_e K_1 = Q/R\,.\,(1/T_1 - 1/T_2)$, the integrated form of $d \log K/dT = Q/RT^2$; R is assumed to be 1·998 cals., and the temperatures are 20° and 40°. In the table are shown the solubilities (S) determined at these temperatures and the values of Q calculated therefrom.

The abnormally high value for the solubility of ytterbium sulphate at 40° was confirmed by repeated experiments by both authors; it was determined, not only by weighing the evaporated solution, but also by precipitation with ammonia, heating to redness, and weighing as Yb_2O_3.

Solubility of $M_2(SO_4)_3,8H_2O$ (*g. per* 100 *g. of water*).

Element.	$S_{20°}$.	$S_{40°}$.	Q, g.-cals.	Element.	$S_{20°}$.	$S_{40°}$.	Q, g.-cals.
Pr	12·74	7·64	−4690	Dy	5·072	3·34	−3830
Nd	7·00	4·51	−4030	Ho	8·181	4·52	−5440
Sm	2·67	1·99	−2690	Y	9·764	4·90	−6320
Eu	2·563	1·93	−2500	Er	16·00	6·53	−8220
Gd	2·886	2·19	−2520	Yb	34·78	22·9	−3816
Tb	3·561	2·51	−3207	Lu	47·27	16·93	−9420

Neither the solubilities at 20° and at 40° nor the heats of solution show any proportionality with the molecular volumes of the sulphates or with the ionic radii of the kations, but all these quantities show a minimum at europium, while the values for yttrium lie very near those of holmium. Analogous relationships occur in the solubilities of the nonahydrates of the rare-earth bromates (James, *J. Amer. Chem., Soc.*, 1908, **30**, 182; 1912, **34**, 757; Jordan and Hopkins, *ibid.*, 1917, **39**, 2214; Kremers and Balke, *ibid.*, 1918, **40**, 593; Harris and Hopkins, *ibid.*, 1926, **48**, 1588; Zernicke and James, *ibid.*, p. 2871; James, Fogg, McIntire, Evans, and Donovan, *ibid.*, 1927, **49**, 132); here we find a minimum at europium, while the value for yttrium lies between those of holmium and erbium. The solubility curves of the oxalates (with 10 H_2O) (Rimbach and Schubert, *Z. physikal. Chem.*, 1909, **64**, 184; Schohren, Diss., Berlin, 1913; Wirth, *Z. anorg. Chem.*, 1912, **76**, 199; Bodländer, Diss., Berlin, 1915), glycollates (Jantsch and Grünkraut, *Z. anorg. Chem.*, 1913, **79**, 305; James, Hoben, and Robinson, *J. Amer. Chem. Soc.*, 1912, **34**, 276; Pratt and James, *ibid.*, 1911, **33**, 1330), and lactates (Jantsch, *Z. anorg. Chem.*, 1926, **153**, 9) are also known, though not completely; here we find that the oxalates have a solubility minimum at gadolinium (europium was not measured). The rather scanty data on the glycollates and lactates do not allow any definite conclusion to be drawn, as the solid phase is not always the same, but the solubilities of the glycollates rise from lanthanum to gadolinium, whereas those of the lactates decrease in the same series.

In considering the minimum in our solubility curve, as well as in that of the bromates, it must be remembered that several analogous cases are known. The series NaCl, KCl, RbCl, and also RbCl, RbBr, RbI, exhibit a minimum solubility at KCl and RbBr respectively, although the ionic radius of the changing ion alters in the same direction each time, and Fajans (*Naturwiss.*, 1921, **9**, 731) has called attention to the fact that these minima are associated with a certain ratio of the ionic radii, which in the above cases is approximately 3 : 4. The minimum in our solubility curve is presumably due to the same cause, and it is to be expected that it will be displaced on introduction of a different anion. That the minimum in the case of the bromates lies in essentially the same place, is doubtless due to the fact that the size of the hydrated bromate ion cannot be very different from that of the hydrated sulphate ion.

Another point of interest is the close similarity between the solubilities of yttrium and holmium; the former does not belong to the group of elements having an incomplete electron group, which, according to the quantum theory of atomic structure, characterises the rare-earth elements, but its ionic radius is very little different from that of holmium (the molecular volumes of the sulphates differ only by 0·8%), so that the closely related solubilities are clearly due to the great similarity of the ionic radii, as indicated in the explanation given above.

The question arises whether the minimum in our solubility values has any connexion with a possible sub-grouping of the rare earths; it has often been suggested that these extraordinarily similar elements can be split up into a number of series, on the same lines as the division into cerium and yttrium earths which is at present used from the point of view of their preparation. A sub-division of this kind would mean that a quite definite intermediate structure occurred in filling up the 4_4-electron group from lanthanum to lutecium, leading to a sharp sub-division of the 4_4-electrons. The Stoner–Main Smith theory (compare, *e.g.*, von Hevesy, " Die seltenen Erden vom Standpunkte des Atombaus," Berlin, 1927, p. 36) provides for such a sub-division; according to this, the first group would extend from cerium to europium, and the second from gadolinium to lutecium. It is well known that a periodicity exists in the magnetic properties of the rare-earth group (St. Meyer, *Physikal. Z.*, 1925, **26**, 51, 479; Cabrera, *J. Physique*, 1925, **6**, 252; Wedekind, *Ber.*, 1921, **54**, 253; compare also von Hevesy, *op. cit.*, pp. 38—46), for a minimum occurs in the magnetic susceptibility curve at samarium, and Main Smith, in particular (*Nature*, 1927, **120**, 583), emphasises the periodic nature of the optical properties of the ions and the minimum in colour which occurs at gadolinium; he attaches special importance to the sequence of colour in the elements from cerium onwards, which is again repeated from gadolinium onwards. Moreover, Klemm (*Z. anorg. Chem.*, 1929, **184**, 345; **187**, 29; Klemm and Rockstroh, *ibid.*, 1928, **176**, 181; Klemm and Schütt, *ibid.*, 1929, **184**, 352) has recently concluded, from a systematic investigation of the bi- and quadri-valent compounds of the rare earths, that a division into sub-groups actually does exist, and that it is reflected in the chemical properties. According to him, gadolinium has a specially stable electron grouping, indicating the termination of a sub-group.

On the other hand, it must be pointed out that *X*-ray spectroscopic investigations by van der Tuuk (*Z. Physik*, 1927, **44**, 737), Jönsson (*ibid.*, 1928, **46**, 391), and Lindberg (*ibid.*, 1928, **50**, 82) have as yet given no indication of any sub-grouping of the 4_4-electrons. Moreover, neither the molecular volumes of the sesquioxides, as determined by Goldschmidt (Goldschmidt, Ulrich, and Barth, *Vidensk. Skrifter Mat. Nat. Kl. Akad. Oslo*, 1925, No. 5; Goldschmidt, Barth, and Lunde, *ibid.*, 1925, No. 6; Goldschmidt, *ibid.*, 1926, No. 2), nor those of the octahydrated sulphates, determined by von Hevesy (*op. cit.*), nor, again, the ionisation potentials of the rare-earth elements, measured by Rolla and Piccardi (*Phil.

Mag., 1929, **7**, 286), indicate any appreciable irregularities in the rare-earth series; on the contrary, there is a practically constant increase in the ionisation potentials with increasing atomic number, accompanied by a corresponding decrease in the ionic radius.

In any case, the minimum in our solubility curve is in no way connected with irregularities of this kind, but depends solely on the ratio of the ionic radii.

Summary.

The solubilities of the octahydrates of the rare-earth sulphates have been determined at 20° and at 40°. The values show a minimum at europium. The connexion between this minimum and a possible division of the rare earths into sub-groups is discussed.

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