[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Observations on the Rare Earths. XL. The Magnetic Susceptibilities of Europium and Ytterbium Salts

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The magnetic susceptibilities of the rare earths in anomalous valence states afford an interesting approach to a study of the electronic structures of the rare earth ions. The susceptibility determinations of praseodymium and cerium in the tetravalent state[2] and samarium in the divalent state[3] have been described. The purpose of this investigation was to determine the susceptibilities of europium and ytterbium in the di- and trivalent states.

Materials and Methods.—The europium material was of atomic weight purity. It was one of the intermediate fractions of a double magnesium nitrate crystallization series in which samarium and gadolinium had been removed in all but the end fractions. The arc spectrum of this material contained only the lines of europium, indicating the absence of the other rare earths above 0.1%. The ytterbium material was from a bromate fractionation series containing thulium, ytterbium and lutecium. The ytterbium was separated from the other earths by repeated precipitations as ytterbous sulfate. The sample of ytterbium used for this investigation contained spectroscopic traces of lutecium and thulium. The sample of gadolinium was of atomic weight purity. The arc spectrum showed this sample to be spectroscopically free of the other rare earths.

The trivalent europium sulfate was prepared by dissolving the oxide in dilute sulfuric acid and evaporating to dryness on the steam-bath. The salt after two recrystallizations from pure water was dried at 70°. The divalent europium sulfate was prepared by the electrolytic reduction of europium chloride in the presence of sulfuric acid.[4] This salt was found by analysis, consisting of europium and sulfate determinations, to be anhydrous $EuSO_4$. The ytterbic sulfate was prepared by heating the oxide with concentrated sulfuric acid until the excess acid had evaporated followed by recrystallization from water. The divalent sulfate was prepared by an electrolytic reduction similar to that used for the europium[5] and was found by analysis to be anhydrous $YbSO_4$.

The susceptibility determinations were made at room temperature on a modified Curie balance.[6] The balance was standardized against pure water using Pascal's value of 0.72×10^{-6} for water.

Results

The susceptibility per gram atom of rare earth for the salts measured is given in Table I.

The value of 25,710 obtained for gadolinium compares very favorably

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[1] Part of this paper will form a section of a thesis to be presented by D. W. Pearce to the Graduate School of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] St. Meyer, *Physik. Z.*, **26**, 51, 479 (1925).

[3] Klemm and Rockstroh, *Z. anorg. allgem. Chem.*, **176**, 181 (1928).

[4] Yntema, THIS JOURNAL, **52**, 2782 (1930).

[5] Ball and Yntema, *ibid.*, **52**, 4264 (1930).

[6] Curie and Chevenaux, *Phil. Mag.*, **236** [6], 357 (1910).

TABLE I

	$\chi \; 10^{-6}$		$\chi \; 10^{-6}$
$Eu_2(SO_4)_3 \cdot 8H_2O$	5,590	$Yb_2(SO_4)_3 \cdot 8H_2O$	7510
$EuSO_4$	21,900	$YbSO_4$	142
$Gd_2(SO_4)_3 \cdot 8H_2O$	25,710	Yb_2O_3	7260
		Lu^{+++}	Diamagnetic[7]

Klemm and Schuth, *Z. anorg. allgem. Chem.*, **184**, 352 (1929), from measurements made with $YbCl_2$ containing much Lu and small amounts of Tm and Er, have suggested that divalent ytterbium is diamagnetic.

with that of 25,860 obtained by Zernike and James[8] though it is low compared to the values of 28,200 and 27,900 as determined by Cabrera[9] and St. Meyer,[7] respectively. The value obtained for trivalent ytterbium sulfate is considerably lower than any published previously. The spectroscopic traces of thulium and of lutecium contained in this material would change the susceptibility but slightly. The higher values obtained by other investigators may be attributed to thulium they admit to have been present in their material.

It is to be noted, when a comparison is made of the susceptibility of a rare earth element in the divalent state with that in the trivalent state, that in the lower valence the susceptibility approaches that of the rare earth of next higher atomic number in the trivalent state. A similar phenomenon has been observed when the earth is in the tetravalent state except that the value approaches that of the earth of next lower atomic number. This change in susceptibility with valence may best be explained on the assumption that in the reduction from trivalence to divalence the added electron either enters the 4_4 electron orbital group or causes a general shift in the electron configuration such that the net effect is the same as the addition of an electron to this group. If the electronic structures of the europium and gadolinium atoms are compared it is seen that the only difference is in the 4_4 orbit, which contains an added electron in the case of gadolinium. It is this difference then which brings about the change of 20,120 in the susceptibility of the corresponding trivalent salts. The difference between europous sulfate and europic sulfate is of this same magnitude and may thus be ascribed as being due to electron shifts closely associated with the 4_4 orbital group. An electron shift in any single orbital group other than the 4_4 may be expected to give constant susceptibility differences for di- and trivalent salts for all the rare earths. Table I shows that this change in the susceptibility with change in valence is not constant with different earths. A change in the absorption spectrum of a rare earth would be expected with any change in the electronic constitution of the 4_4 orbit. Investigation on this phase of the subject is at present being carried out in this Laboratory.

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(7) St. Meyer, *Physik. Z.*, **26**, 53, 478 (1925).

(8) Zernike and James, THIS JOURNAL, **48**, 2827 (1926).

(9) Cabrera, *J. phys.*, **6**, 252 (1925).

Summary

The magnetic susceptibilities of europium and ytterbium in the form of the di- and trivalent sulfates have been determined. The values obtained check well with known values except in the case of ytterbic sulfate. The low value recorded is thought to be due to the absence of thulium in the material used.

The susceptibility of an earth in the divalent state is found to approach that of the earth of next higher atomic number in the trivalent state.

URBANA, ILLINOIS RECEIVED MAY 24, 1933
PUBLISHED AUGUST 5, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Activity Coefficient of Potassium Chloride in Aqueous Solutions at 0° from Electromotive Force and Freezing Point Data

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Since the electromotive forces of cells with flowing amalgams have been used extensively to determine activity coefficients, and since some question as to their applicability has arisen, it is of importance to have a direct comparison between such results and those obtained by some other accurate method. The recent values of the activity coefficients of potassium chloride calculated by Spencer[1] from freezing point measurements should serve as a good standard for comparison. While the activity coefficients of potassium chloride at 25° determined by Harned[2] from electromotive force measurements are in close agreement with those obtained from vapor pressure measurements, they are not in good agreement with the values obtained from freezing point measurements, corrected to 25° by the use of available calorimetric data. To make a fair comparison between the two methods, both determinations should be made at nearly the same temperature so that the temperature correction is either negligible or a very small quantity.

For this purpose the electromotive force of the cell

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{KCl}\ (m) \mid \mathrm{K_xHg} \mid \mathrm{KCl}\ (0.1) \mid \mathrm{AgCl} \mid \mathrm{Ag}$$

has been measured at 0°. The cells and the procedure were similar to those described by Harned[2] for type 2 electrodes. The temperature was maintained at less than 0.1° by a stirred ice-bath with a capacity of 300 lb. of cracked ice.

The relation between the electromotive force and the activity coefficient for this cell at 0° is given by the equation[3]

$$E = 0.10844 \log (\gamma \times m)/(\gamma_{0.1} \times 0.1) \qquad (1)$$

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[1] Spencer, THIS JOURNAL, **54**, 4490 (1932).

[2] Harned, *ibid.*, **51**, 416 (1929).

[3] The constants used are those given by Birge, *Phys. Rev. Suppl.*, I, **1**, 1929.