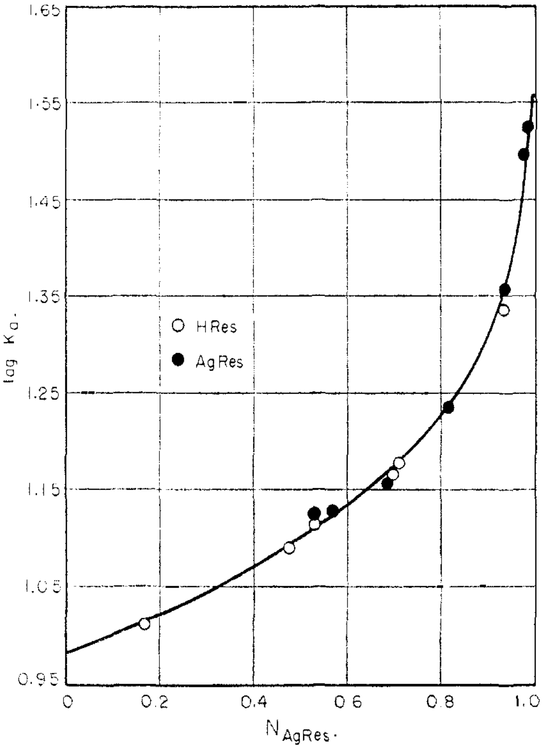

Fig. 3.—Silver-hydrogen exchange at unit ionic strength.

These data were supplemented, in the case of solutions containing equimolar quantities of nitric acid and silver nitrate ($m_1/(m_1 + m_2) = 0.500$), by measurements at additional ionic strengths from 0.005 to 1.0 molal. The variation of log r with ionic strength, as calculated from these data, is shown in Fig. 2.

Application of Activity Coefficient Ratios to Ion Exchange Data.—In Fig. 3, the values of log K_a as calculated from our ion exchange equilibrium data for solutions of ionic strength approximately equal to unity are plotted against the mole fraction of silver resin in the equilibrium mixture. From this plot, the activity coefficients of the resin components at various concentrations, shown in Table II, and the true equilibrium constant, K (equations (1) and (3)), have been determined by graphical integration. The slope of the curve of Fig. 3 being positive throughout its length, the activity coefficients of both components (in contrast to those of sodium–hydrogen resins)[4] are found to have values greater than unity. The value of the equilibrium constant is found to be 13.7.

Table II

Activity Coefficients of Resin Components

N_{AgRes}	f_{AgRes}	f_{HRes}
0.0	1.417[a]	1.000
.1	1.350	1.003
.2	1.293	1.012
.3	1.240	1.023
.4	1.193	1.045
.5	1.155	1.074
.6	1.117	1.116
.7	1.087	1.177
.8	1.054	1.291
.9	1.024	1.531
1.0	1.000	3.05[a]

[a] Extrapolated values.

These results are similar to those of Högfeldt, Ekedahl and Sillén,[10] with which, however, they are not exactly comparable because these authors did not take solution activity coefficients into account in their calculations.

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[10] E. Högfeldt, E. Ekedahl and L. G. Sillén, *Acta Chem. Scand.*, **4**, 828 (1950).

Lawrence, Kansas Received July 16, 1951

[Contribution from the Department of Chemistry, the Royal Institute of Science]

The Preparation of the Double Sulfates of Antimony and Bivalent Metal

By S. R. Patel

A procedure for the preparation of the compounds $RSO_4 \cdot Sb_2(SO_4)_3$ where R = magnesium, zinc, cadmium, cobalt and manganese has been worked out and from the conductivity data it is shown that these compounds appear to be double sulfates. The compounds $RSO_4 \cdot Sb_2(SO_4)_3 \cdot 6H_2O$ where R = alkaline earth metal described by Kühl could not be obtained.

A series of new compounds of the type $RSO_4 \cdot Sb_2(SO_4)_3$ where R = magnesium, zinc, cadmium, cobalt and manganese has been prepared (Table I). For the preparation of these compounds the sulfate of bivalent metal (0.5 g.) was heated to fumes in sulfuric acid (sp. gr. 1.8, 50 cc.) in presence of different amounts of antimony trioxide (0.25 to 0.50 g.). When the clear solution so obtained was cooled (28–29°) a precipitate separated out which was filtered in a sintered glass crucible (1 G 3) and washed first with sulfuric acid (sp. gr. 1.8) and then with absolute alcohol till the filtrate was free from sulfate ions. It was then dried at about 200–230°. This precipitate when analyzed agreed with the formula $RSO_4 \cdot Sb_2(SO_4)_3$. The analytical data obtained are given in Table I.

Table I

R	Calcd. R	Calcd. Sb	Calcd. SO_4	Found R	Found Sb	Found SO_4
Mg	3.73	37.36	58.91	4.22	37.11	59.42
Zu	9.43	35.14	55.42	9.81	35.45	55.73
Cd	15.19	32.92	51.90	14.92	33.02	52.31
Co	8.59	35.47	55.94	8.88	35.21	56.04
Mn	8.0	35.7	56.3	7.70	35.83	56.50

The only compounds of antimony sulfate in combination with a sulfate of bivalent metal described in the literature are those with alkaline earth sulfates.[1] When attempts were made to prepare these compounds, *viz.*, $CaSO_4 \cdot Sb_2(SO_4)_3 \cdot 6H_2O$, $SrSO_4 \cdot Sb_2(SO_4)_3 \cdot 6H_2O$ and $BaSO_4 \cdot Sb_2(SO_4)_3 \cdot 6H_2O$ it was noticed that only $Sb_2(SO_4)_3$ was obtained which contained 1.5 to 0.5% of alkaline earth metal.

The compounds $RSO_4 \cdot Sb_2(SO_4)_3$ are white in color except the compound containing cobalt which is pink. The yield of these compounds varies between 50 to 60%. These compounds are hygroscopic and are hydrolyzed by water.

If the compounds $RSO_4 \cdot Sb_2(SO_4)_3$ behave as

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[1] Kühl, *Z. anorg. Chem.*, **54**, 256 (1907).

double sulfates, each mole of the same will liberate one mole of the sulfate of bivalent metal and three moles of sulfuric acid. The electrical conductivity measurements were made of the solutions obtained after hydrolysis and these values were compared with similar values obtained from artificial solutions prepared on the above assumption.

TABLE II

SPECIFIC CONDUCTIVITY OF HYDROLYZED SOLUTIONS AND SYNTHETIC SOLUTIONS OF SAME CONCENTRATION

Solution	Wt. of $RSO_4 \cdot Sb_2(SO_4)_3$, g.	Sp. conductivity, mhos × 10^{-3}				
$MgSO_4Sb_2(SO_4)_3$	3.9	10.92	5.65	3.06	1.65	0.89
$MgSO_4 + H_2SO_4$		10.51	5.49	3.01	1.63	.88
$ZnSO_4 \cdot Sb_2(SO_4)_3$	3.88	8.61	4.82	2.61	1.39	.75
$ZnSO_4 + H_2SO_4$		8.32	4.63	2.55	1.36	.73
$CdSO_4 \cdot Sb_2(SO_4)_3$	3.7	7.52	4.35	2.45	1.32	.72
$CdSO_4 + H_2SO_4$		7.25	4.21	2.39	1.28	.69
$CoSO_4 \cdot Sb_2(SO_4)_3$	3.78	10.55	5.46	2.92	1.56	.81
$CoSO_4 + H_2SO_4$		10.28	5.30	2.85	1.51	.79
$MnSO_4 \cdot Sb_2(SO_4)_3$	3.9	9.51	5.11	2.94	1.55	1.82
$MnSO_4 + H_2SO_4$		9.36	5.01	2.87	1.51	0.79

A weighed amount (3.9 to 3.7 g.) of $RSO_4 \cdot Sb_2(SO_4)_3$ was boiled with distilled water (400 cc.), the hydrated antimony oxide was filtered off and the filtrate was made to 100 cc. The sp. conductivity of this solution was determined by the method of Kohlrausch; 50 cc. of this filtrate was made to 100 cc. with distilled water and the sp. conductivity was measured once again. This operation was repeated thrice. Similar measurements were made for the solutions containing the exact amount of sulfuric acid and the sulfate of bivalent metal calculated on the assumption that each mole of $RSO_4 \cdot Sb_2(SO_4)_3$ liberates on hydrolysis one mole of the sulfate of bivalent metal and three molecules of sulfuric acid. The data obtained are given in Table II.

From the above Table II it is observed that the values of sp. conductivity of hydrolyzed solutions and synthetic solutions of same concentration are very close to each other. This indicates that the compounds $RSO_4 \cdot Sb_2(SO_4)_3$ appear to be double sulfates.

BOMBAY, INDIA RECEIVED AUGUST 21, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Supported Oxides of Manganese: Influence of Support Modification[1]

BY P. W. SELWOOD AND LORRAINE LYON

The susceptibility isotherm method has been extended to a series of modified alumina supports—the supported oxides being those of manganese. It has been found that support phase modification has a negligible effect on the oxidation state or dispersion of the supported manganese, provided that the specific surface area is maintained large, and that no appreciable amounts of alkali are present. The presence of alkali in the support causes a large change in the susceptibility isotherm, reflecting substantial changes in oxidation state and degree of dispersion of the manganese.

Earlier papers from this Laboratory have been concerned with the possible influence of substrate modification on the susceptibility isotherm only to the extent of comparing low specific surface α-alumina with high area so-called γ-alumina, and with magnesia, rutile, anatase and silica as compared with alumina. The object of the present work was to examine the effect of phase modifications in alumina on the susceptibility isotherm. Supported oxides of manganese[2] were chosen for this study because this system has been shown to be sensitive to structural changes and to show large variations of magnetic susceptibility for relatively slight changes in oxidation state and degree of dispersion. Interest in this system was further stimulated by the appearance of a communication by Rodier and Rodier[3] in which it is stated that a major change takes place in the form of the susceptibility isotherm for supported manganese oxides on an alumina characterized only as "très actif."

The procedure adopted was to obtain magnetic susceptibility data for supported oxides of manganese on all the known phases of alumina, on alumina to which some alkali had been added and for samples obtained by various modifications of the preparation method.

Experimental Part

There will first be described the preparation of the several different substrates. Some of the starting materials were obtained from the Aluminum Company of America, Research Laboratories, through the courtesy of Dr. A. S. Russell. Several of the preparations were made by the methods described by Stumpf, Russell, Newsome and Tucker.[4]

α-$Al_2O_3 \cdot H_2O$ was made from Alcoa α-trihydrate by digestion in water at 200° at about 30 atmospheres pressure for 2.5 hours in a glass-lined nickel bomb. The X-ray pattern agreed in detail with that accepted. The magnetic susceptibility at room temperature was about 0.2×10^{-6}. This high susceptibility was doubtless due to a trace of impurity.

β-$Al_2O_3 \cdot 3H_2O$ was made by precipitation from "sodium aluminate" with carbon dioxide at 40°. The X-ray pattern agreed with the ASTM Index.

χ-Al_2O_3 was made from α-trihydrate by heating in dry air at 800° for one hour. The X-ray pattern agreed with Stumpf, *et al.* The susceptibility at −125° was -0.1×10^{-6}.

κ-Al_2O_3 was made by heating α-trihydrate in air at 1000° for one hour. The X-ray pattern agreed with Stumpf, *et al.*, and the susceptibility showed some temperature dependence, being 0.6 ($\times 10^{-6}$) at 28°, 1.2 at −125°, and 1.3 at −187°.

γ-Al_2O_3 was prepared from α-monohydrate by heating for one hour at 600° in a stream of dry air. The X-ray pattern

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[1] This is the tenth paper on the susceptibility isotherm from this Laboratory. The ninth, by Selwood, Lyon and Ellis appeared in THIS JOURNAL, **73**, 2310 (1951).

[2] P. W. Selwood, T. E. Moore, M. Ellis and K. Wethington, *ibid.*, **71**, 693 (1949).

[3] G. Rodier and G. Rodier, *Compt. rend.*, **230**, 93 (1950).

[4] H. C. Stumpf, A. S. Russell, J. W. Newsome and C. M. Tucker, *Ind. Eng. Chem.*, **42**, 1398 (1950).