dynamic formulation. The corresponding equilibrium constant, $K$, defined in terms of activities, then must be truly constant, independent of the variation of composition of the resin phase. In view of this fact, then, the relationship between $K_a$ and $K$, the true thermodynamic equilibrium constant, *i.e.*

$$K = K_m \left(\frac{\gamma_{HCl}}{\gamma_{NaCl}}\right)^2 \frac{f_{Na}}{f_H} = K_a \frac{f_{Na}}{f_H}$$

may be combined with the Gibbs-Duhem equation to yield the following results[6]

$$\ln K = \int_0^1 \ln K_a dN_{Na}$$

$$\ln f_{Na} = -(1 - N_{Na}) \ln K_a + \int_{N_{Na}}^1 \ln K_a dN_{Na}$$

$$\ln f_H = N_{Na} \ln K_a - \int_0^{N_{Na}} \ln K_a dN_{Na}$$

In these expressions $N_{Na}$ is the equilibrium mole fraction of sodium resin, and $f_{Na}$ and $f_H$ are the activity coefficients of sodium and hydrogen resins, respectively. The indicated integrations may be carried out graphically on plots of log $K_a$ *vs.* $N_{NaRes}$ like those in Fig. 5. The results of such graphical integration of the data for the $Na^+$–$H^+$ exchange at 1.0 $M$ and 0.3 $M$ ionic strengths at 25° are given in Table II.

TABLE II

EQUILIBRIUM CONSTANT AND RESIN ACTIVITY COEFFICIENTS IN $Na^+$–$H^+$ EXCHANGE

| | Ionic strength 1.0 $M$, $K$ = 1.73 | | Ionic strength 0.3 $M$, $K$ = 1.68 | |
|---|---|---|---|---|
| $N_{Na}$ | $f_{Na}$ | $f_H$ | $f_{Na}$ | $f_H$ |
| 0.0 | 0.865[a] | 1.000 | 0.879[a] | 1.000 |
| .1 | .867 | 0.999 | .879 | 1.000 |
| .2 | .870 | .999 | .879 | 1.000 |
| .3 | .876 | .996 | .883 | 0.997 |
| .4 | .884 | .992 | .887 | .995 |
| .5 | .894 | .983 | .899 | .984 |
| .6 | .909 | .963 | .917 | .960 |
| .7 | .933 | .916 | .940 | .917 |
| .8 | .964 | .836 | .966 | .847 |
| .9 | .986 | .720 | .989 | .735 |
| 1.0 | 1.000 | .532[a] | 1.000 | .583[a] |

[a] Extrapolated values.

The true exchange equilibrium constant, and the activity coefficients of the resin components at a given resin composition, should in theory be independent of the concentration of the solution, unless the nature of the resin is radically changed during the exchange process by some such means as excessive electrolyte adsorption. Experiments indicate very slight adsorption in the $Na^+$–$H^+$ system, and no other important complicating factors. The results for the equilibrium constant and the resin activity coefficients in the two series of experiments at different ionic strengths agree fairly well, the discrepancies being no greater than the uncertainty in the values used for the solution activity coefficients. Work now in progress in solutions at a constant ionic strength of 0.1 $M$ appears to offer further corroboration of this independence of solution concentration.

The method of calculation of resin activity coefficients and true exchange equilibrium constants here used may, as has been shown,[6] be extended to the general case of exchange of ions of any valence, provided solution activity coefficients are available. Although quite independently derived, the method is essentially the same as that of Ekedahl, Högfeldt and Sillén,[7] who have recently applied it to the computation of activity coefficients in the $Ag^+$–$H^+$ and $Ba^{++}$–$H^+$ systems.[9]

(9) E. Högfeldt, E. Ekedahl and L. G. Sillén, *Acta Chem. Scand.*, **4**, 828, 829 (1950).

LAWRENCE, KANSAS RECEIVED JULY 16, 1951

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

# Activity Coefficient Ratios of Nitric Acid and Silver Nitrate, and their Application to Ion Exchange Equilibria[1,2]

BY OSCAR D. BONNER,[3] ARTHUR W. DAVIDSON AND WILLIAM J. ARGERSINGER, JR.

Electromotive force measurements on cells of the type: Ag | AgCl | HCl (0.2 $M$) | glass | $HNO_3$ ($m_1$), $AgNO_3$ ($m_2$) | Ag were used for the calculation of the ratios of activity coefficients at 25° of nitric acid and silver nitrate in solutions of varying acid–salt ratio and of total ionic strengths ranging from 0.1 to 1.0 molal. These activity coefficient ratios were combined with ion exchange data for the $Ag^+$–$H^+$ equilibrium on Dowex 50. By means of graphical integration on a plot of the logarithm of the apparent equilibrium constant against the mole fraction of silver resin in the equilibrium mixed resin, the activity coefficients of the resin components and the true thermodynamic equilibrium constant for the exchange reaction were calculated. The activity coefficients in the mixed resins proved to be greater than unity. The value of the equilibrium constant at 25° was found to be 13.7.

## Introduction

In a previous paper from this Laboratory,[4] it has been shown that although the total interaction between a solution of an electrolyte and a resinous cation exchanger is more complex than has generally been supposed, the exchange process proper may nevertheless be regarded as a simple chemical reaction, subject to the law of chemical equilibrium.

An extensive investigation, from this viewpoint, of the $Ag^+$–$H^+$ exchange on Dowex 50 was made by Högfeldt, Ekedahl and Sillén,[5] and a study of this equilibrium has been reported also in our previous

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(1) From part of a thesis submitted by Oscar D. Bonner in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Kansas, 1951.

(2) Presented at the Cleveland Meeting of the American Chemical Society, April, 1951.

(3) du Pont Fellow, 1950–1951.

(4) O. D. Bonner, W. J. Argersinger, Jr., and A. W. Davidson, THIS JOURNAL, **74**, 1044 (1952).

(5) E. Högfeldt, E. Ekedahl and L. G. Sillén, *Acta Chem. Scand.*, **4**, 1471 (1950).

paper; the two sets of experimental results are in substantial agreement. However, because of lack of data on the activity coefficients in mixed aqueous solutions of the electrolytes used, it has not been possible hitherto to subject the equilibrium quotients, which vary widely with composition of the equilibrium resin, to rigorous thermodynamic interpretation.

When the hydrogen form of the resin is immersed in an aqueous solution of silver nitrate, the ensuing reaction may be represented by the equation

$$\mathrm{Ag^+ + H\ Res = H^+ + Ag\ Res}$$

Application of the law of chemical equilibrium to this process yields the equation

$$\frac{a_{\mathrm{H^+}}\,a_{\mathrm{AgRes}}}{a_{\mathrm{Ag^+}}\,a_{\mathrm{AgRes}}} = K \qquad (1)$$

in which $a$ denotes the activity of a particular species and $K$ is the thermodynamic equilibrium constant, the constancy of which at all solution and resin compositions is inherent in the definition of the term "activity." Representing the experimentally determined equilibrium molalities in the solution by $m_{\mathrm{H^+}}$ and $m_{\mathrm{Ag^+}}$, the experimentally determined equilibrium mole fractions of the two components in the resin by $N_{\mathrm{HRes}}$ and $N_{\mathrm{AgRes}}$, and the mean activity coefficients of nitric acid and silver nitrate by $\gamma_{\mathrm{HNO_3}}$ and $\gamma_{\mathrm{AgNO_3}}$, respectively, we have defined[4] the equilibrium quotient, $K_{\mathrm{m}}$, by means of the equation

$$K_{\mathrm{m}} = \frac{m_{\mathrm{H^+}}\,N_{\mathrm{AgRes}}}{m_{\mathrm{Ag^+}}\,N_{\mathrm{HRes}}}$$

and a quantity $K_{\mathrm{a}}$, which we have called the apparent equilibrium constant, by

$$K_{\mathrm{a}} = \frac{a_{\mathrm{H^+}}\,N_{\mathrm{AgRes}}}{a_{\mathrm{Ag^+}}\,N_{\mathrm{HRes}}} = K_{\mathrm{m}}\left(\frac{\gamma_{\mathrm{HNO_3}}}{\gamma_{\mathrm{AgNO_3}}}\right)^2 \qquad (2)$$

Furthermore, if the activity coefficients of the resin components (on the mole fraction basis) are represented by $f_{\mathrm{AgRes}}$ and $f_{\mathrm{HRes}}$, we may write

$$K = K_{\mathrm{a}} \times \frac{f_{\mathrm{AgRes}}}{f_{\mathrm{HRes}}} \qquad (3)$$

$K_{\mathrm{a}}$ would be expected to have a constant value only if the ratio of the activity coefficients of the resin components remained constant. If the values of $K_{\mathrm{a}}$ are known for a series of equilibrium states, however, it is possible by means of a relatively simple process of graphical integration[4] to determine the activity of both components of the solid phase, as well as the value of $K$.

The present work deals with the determination of the ratios of the activity coefficients of nitric acid and silver nitrate in mixed aqueous solutions at several constant total ionic strengths. These ratios for 1 molal solutions were then combined with previously determined exchange data for the calculation of the true equilibrium constant.

**General Method.**—In principle, it should be possible to determine the desired activity coefficient ratios from electromotive force measurements on cells of the type

$$\mathrm{Pt,\ H_2|HNO_3}(m_1),\ \mathrm{AgNO_3}(m_2)|\mathrm{Ag}$$

Practically, however, it is found that a hydrogen electrode cannot be used in silver nitrate solutions, since the silver ion undergoes direct reduction by hydrogen in the presence of platinum. This difficulty, however, may be overcome by the use of a glass electrode to indicate the hydrogen ion activity of the solution. Accordingly, the cells actually used were constituted as

$$\mathrm{Ag|AgCl|HCl\ (0.2\ \mathit{M})|glass|HNO_3}(m_1),\ \mathrm{AgNO_3}(m_2)|\mathrm{Ag}$$

For such a cell the equation

$$E = E^0 - \frac{RT}{F}\ln\frac{a_{\mathrm{HNO_3}}}{a_{\mathrm{AgNO_3}}} = E^0 - \frac{RT}{F}\ln\frac{m_1}{m_2} - \frac{2RT}{F}\ln\frac{\gamma_{\mathrm{HNO_3}}}{\gamma_{\mathrm{AgNO_3}}} \qquad (4)$$

is applicable, where $E^0$ is the electromotive force of the hypothetical cell in which both hydrogen ion and silver ion are at unit activity; that is

$$E^0 = E^0_{\mathrm{glass}} - E^0_{\mathrm{Ag,Ag^+}}$$

Thus, once the value of $E^0_{\mathrm{glass}}$ has been established, the value of the activity coefficient ratio for a solution of any desired composition may readily be calculated.

The standard potential of the glass electrode, which was found to vary slightly with the concentration of acid in which it was immersed, was determined from the measured e.m.f. values of cells of the type

$$\mathrm{Ag|AgCl|HCl(0.2\ \mathit{M})|glass|HCl}(m)|\mathrm{AgCl|Ag}$$

by means of the equation

$$E = E^0_{\mathrm{glass}} - E^0_{\mathrm{Ag,AgCl}} - \frac{2RT}{F}\ln(\gamma m) \qquad (5)$$

where $\gamma$ is the activity coefficient of the hydrochloric acid in the external solution.

## Experimental

**Silver Electrodes.**—The silver electrodes were prepared by the deposition of finely divided silver on a platinum wire, either by the decomposition at 400° of a paste of silver oxide, or by the rapid electrolysis of a slightly acid solution of silver nitrate. In either case, the electrodes were thoroughly washed first with dilute nitric acid and then with water.

The standard potential of each silver electrode was determined by extrapolation to infinite dilution ($m_1 = 0$) of e.m.f. measurements on cells of the type

$$\mathrm{Ag|AgCl|HCl\ (0.2\ \mathit{M})|glass|HNO_3}(m_1),\ \mathrm{AgNO_3}(m_1)|\mathrm{Ag}$$

in which $m_1$ had values ranging from 0.1 to 0.005 $M$. Any electrode whose standard potential at 25° differed by more than 0.4 mv. from the accepted value of −0.7995 volt was rejected.

**Silver Chloride Electrodes.**—The silver chloride electrodes used were of either the thermal or the electrolytic type. The former were prepared[6] by the decomposition at 650°, on a platinum wire, of a paste consisting of seven parts of silver oxide to one part of silver chlorate. For the preparation of electrodes of the latter type,[7,8] a coating of silver was deposited on a piece of silver foil by electrolysis of a solution of potassium silver cyanide for 24 hr. at 4 milliamperes. The electrode was rinsed with concentrated ammonia solution, then with water, chloridized as anode in 0.1 $M$ hydrochloric acid for one hr. at 5 milliamperes, and washed with water for 24 hr. All silver chloride electrodes were aged in 0.1 $M$ hydrochloric acid for several days before use, and were then found to be in agreement within 0.1 mv. The value of $E^0$ for the silver chloride electrode at 25° was taken to be −0.2224 volt.

**Glass Electrodes.**—The glass electrode bulbs were of the low resistance type furnished by Leeds and Northrup. Before use, each bulb was soaked in 6 $M$ hydrochloric acid and rinsed with dilute ammonia and then with distilled

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(6) C. K. Rule and V. K. LaMer, THIS JOURNAL, **58**, 2339 (1936).

(7) A. S. Brown, *ibid.*, **56**, 646 (1934).

(8) T. Shedlovsky and D. A. MacInnes, *ibid.*, **58**, 1970 (1936).

TABLE I

E.M.F. DATA FOR CELLS OF THE TYPE: GLASS | $HNO_3(m_1)$, $AgNO_3(m_2)$ | Ag AND CORRESPONDING ACTIVITY COEFFICIENT RATIOS

| $m_1 + m_2 =$ | 0.1 $M$ | | 0.2 $M$ | | 0.5 $M$ | | 1.0 $M$ | |
|---|---|---|---|---|---|---|---|---|
| $m_1/(m_1 + m_2)$ | $E^0 - E$ | $r$ | $E^0 - E$ | $r$ | $E^0 - E$ | $r$ | $E^0 - E$ | $r$ |
| 0.050 | −0.0725 | 1.062 | −0.0707 | 1.101 | −0.0661 | 1.203 | −0.0591 | 1.378 |
| .125 | − .0469 | 1.063 | − .0451 | 1.100 | − .0407 | 1.199 | − .0339 | 1.368 |
| .250 | − .0251 | 1.062 | − .0233 | 1.099 | − .0189 | 1.198 | − .0125 | 1.358 |
| .375 | − .0100 | 1.062 | − .0084 | 1.097 | − .0040 | 1.193 | + .0025 | 1.353 |
| .500 | + .0032 | 1.063 | + .0047 | 1.097 | + .0087 | 1.185 | .0153 | 1.346 |
| .625 | .0162 | 1.061 | .0178 | 1.097 | .0217 | 1.182 | .0282 | 1.341 |
| .750 | .0313 | 1.061 | .0329 | 1.095 | .0365 | 1.176 | .0432 | 1.338 |
| .875 | .0528 | 1.057 | .0545 | 1.092 | .0580 | 1.168 | .0646 | 1.328 |
| .950 | .0782 | 1.052 | .0800 | 1.088 | .0832 | 1.159 | .0893 | 1.305 |

water. The platinum inner element was converted to a silver–silver chloride electrode by the electrolytic method described in the preceding paragraph. The bulb was then filled with 0.2 $M$ hydrochloric acid, the silver chloride element was inserted, and the assembled electrode was stored in distilled water.

**Auxiliary Apparatus.**—A Leeds and Northrup Type K-2 potentiometer was used for e.m.f. measurements. The sensitivity of the galvanometer was $5 \times 10^{-4}$ microampere per mm. In order that a detectable deflection might be obtained when the potentiometer was off balance, a Leeds and Northrup thermionic amplifier with a practical limit of sensitivity of 0.1 mv. was used to amplify the very small currents which passed through cells containing a glass electrode. It was found necessary to allow the batteries which served as the source of power for the amplifier to discharge for at least an hour, before each series of determinations, in order to minimize the drift in the null point of the instrument.

During all e.m.f. measurements, the cells were immersed in a constant temperature bath maintained at 25.0 ± 0.1°.

**Calibration of Glass Electrodes.**—Since the standard potentials of the glass electrodes were found to change slowly with time, as well as to be somewhat dependent upon the concentration of the acid solution in which they were immersed, each glass electrode was calibrated against a silver chloride electrode twice daily, or before each period of continual use. in a series of hydrochloric acid solutions from 0.01 to 1 $M$. The $E^0$ values were calculated from the measured e.m.f. values by means of equation (5), with the aid of activity coefficient data for hydrochloric acid interpolated from those given by Harned and Owen.[9] The maximum increase in $E^0$ from very dilute to 1 $M$ acid was about 2 mv. It was assumed that the behavior of a given electrode would be the same in solutions of nitric acid, at concentrations up to 1 $M$, as in hydrochloric acid of the same concentration.

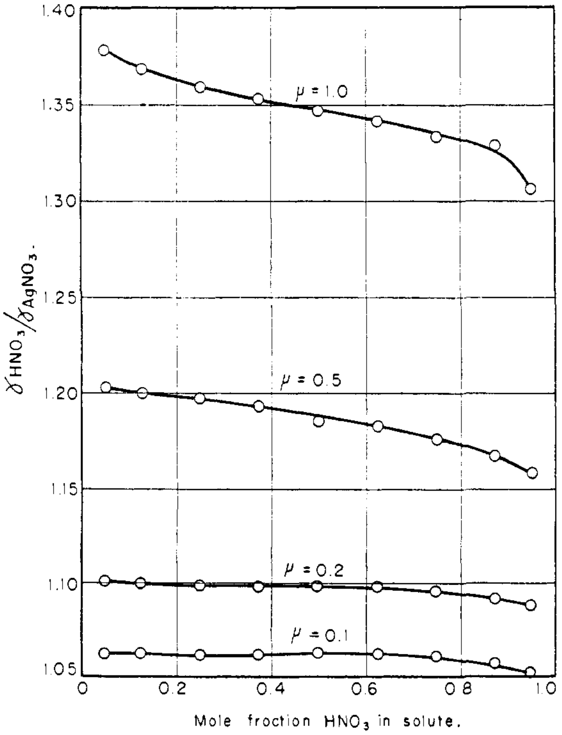

Fig. 1.—Variation of activity coefficient ratio with composition.

**Activity Coefficient Ratios.**—The results of e.m.f. measurements on cells of the type

Glass electrode | $HNO_3(m_1)$, $AgNO_3(m_2)$ | Ag

for various values of $m_1/(m_1 + m_2)$ at constant total ionic strengths of 0.1, 0.2, 0.5 and 1.0 molal, are shown in Table I. Each recorded value of $E^0 - E$ (in volts) is the mean of three independent determinations, and is believed to be correct to within 0.2 mv. The corresponding values of the activity coefficient ratio $\gamma_{HNO_3}/\gamma_{AgNO_3}$, denoted by $r$, as calculated from these measurements by means of equation (4), are included in the table also; and plots of these values against $m_1/(m_1 + m_2)$ for the several ionic strengths are shown in Fig. 1.

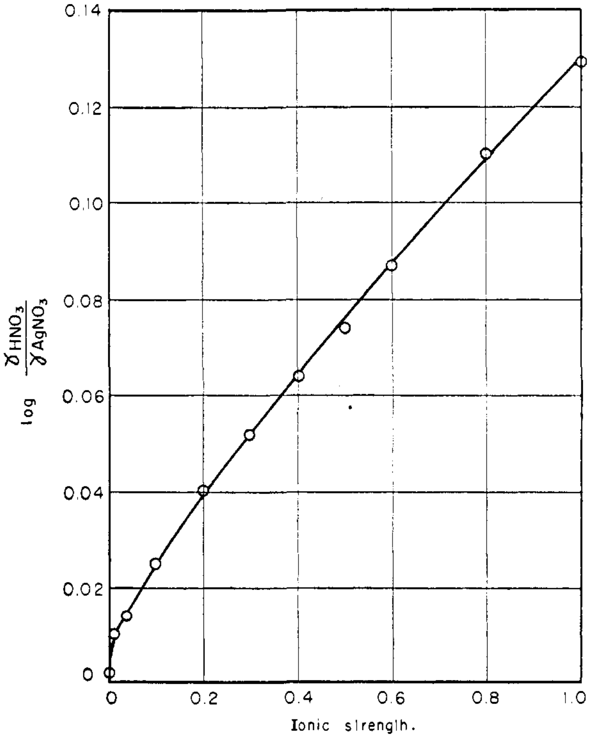

Fig. 2.—Variation of activity coefficient ratio with ionic strength.

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[9] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, p. 547.

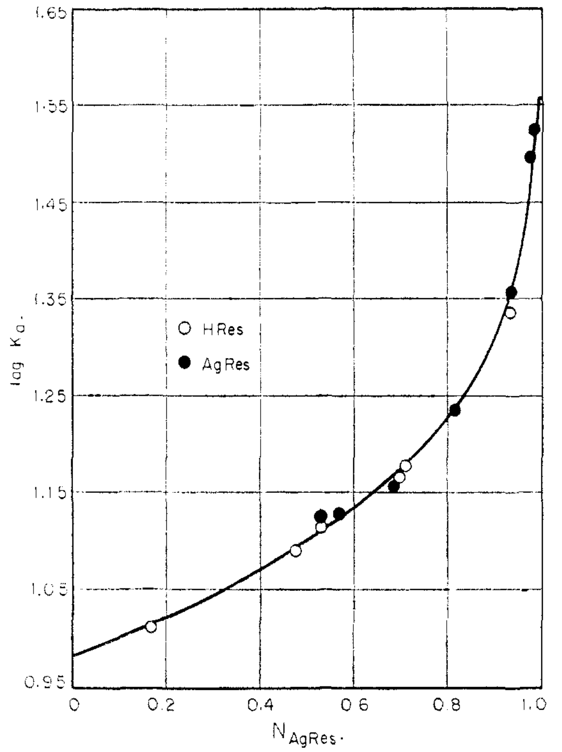

Fig. 3.—Silver-hydrogen exchange at unit ionic strength.

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

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[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).