merize seriously during a ten-hour period until 275° was reached.

The constants of an equation of state of gaseous isobutene were determined from the data up to the critical density; and the values of the second virial coefficients determined from the experimental data are given from 150 to 275°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Activity Coefficients of Rubidium and Cesium Sulfates in Aqueous Solution at 25°[1]

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Introduction

In a previous paper[3] an experimental modification of the isopiestic method of determining activities of electrolytes was presented. In order to test the apparatus and technique still further and to gain information on the activity coefficients of two of the rarer alkali sulfates, rubidium and cesium, this investigation was undertaken.

No data on the activity coefficients for these salts were found in the literature.

Experimental

Method and Apparatus.—The method employed was the familiar isopiestic method, using the apparatus described by Phillips, Watson and Felsing.[3] The procedure in this investigation differed only in the simultaneous use of 12 solution cups instead of the usual nine; this lengthened considerably the time required for vapor pressure equilibration.

Sodium sulfate was selected as the reference salt.

Purification of Materials. Sodium Sulfate.—The salt was crystallized four times as the decahydrate and was dehydrated according to the procedure of Ephraim.[4] The mass was finally dried at 140°, ground to a fine powder, and re-dried in a vacuum oven at 140° for seventy-two hours. It was stored in a desiccator over Anhydrone. **Rubidium and Cesium Sulfates.**—C. P. samples of these salts were purified according to the directions of Archibald.[5] In addition, each salt was recrystallized twice from conductivity water, dried, and stored over Anhydrone. **Water.**—All water used had a specific conductance of 0.6–0.7 $\times 10^{-6}$ reciprocal ohms as delivered from the still; as used, its conductance was approximately 1×10^{-6} mhos.

Preparation of Solutions.—The dry salts were weighed directly from weighing bottles into weight burets by difference. To the weight buret and its contents was added a calculated amount of water.

The solutions were weighed from the weight burets directly into the tared solution cups; the weights were checked by weighing the cups and their contents. The precision in weighing was better than one part in 5000, varying with the size of sample; samples ranged from 1.5 to 6.0 g.

The Data Obtained

The isopiestic solutions investigated extended over the concentration range of approximately 0.4 to 1.9 molal. The upper limit was determined by the solubility of rubidium sulfate; the lower limit, as a practical matter, was determined by the times required for the attainment of equilibrium. The data are listed in Table I. The columns M(obs.) − M(calcd.) are the differences between observed values and values calculated from the smoothed curve.

TABLE I

MOLALITIES OF SOLUTIONS OF RUBIDIUM AND CESIUM SULFATES ISOPIESTIC WITH SOLUTIONS OF SODIUM SULFATE AT 25°

Sodium sulfate	Rubidium sulfate M(obs.)	Rubidium sulfate M(obs.) − M(calcd.)	Cesium sulfate M (obs.)	Cesium sulfate M(obs.) − M (calcd.)
0.433	0.422	+0.002	0.418	+0.006
.612	.601	+ .017	.565	± .000
.780	.748	+ .008	.715	+ .003
.916	.858	− .005	.811	− .016
1.031	.968	± .000	.923	± .000
1.198	1.118	± .000	1.068	+ .007
1.488	1.383	+ .014	1.303	± .000
1.610	1.486	+ .010	1.412	+ .008
1.715	1.570	+ .003	1.488	− .002
1.800	1.640	− .002	1.563	+ .003
1.875	1.707	± .000	1.631	+ .008

Treatment of Results

From the observed isopiestic molalities there was determined for each salt the isopiestic ratio, $M(Na_2SO_4)/M(Rb_2SO_4)$ and $M(Na_2SO_4)/M(Cs_2SO_4)$. These ratios were then plotted against the observed molalities of rubidium and cesium sulfate. From the smooth curve (passing to the origin), there were read off values of the isopiestic ratio at rounded values of the molalities

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(3) Phillips, Watson and Felsing, THIS JOURNAL, **64**, 244 (1942).

(4) Ephraim, "Textbook of Inorganic Chemistry" (translated by Thorne), Gurney and Jackson, London, 1934.

(5) Archibald, "Preparation of Pure Inorganic Substances," John Wiley and Sons, New York, N. Y., 1932.

of the two salts. These ratios are presented in Table II.

TABLE II

ISOPIESTIC RATIOS AT ROUNDED CONCENTRATIONS
M_x denotes $M(Rb_2SO_4)$ and $M(Cs_2SO_4)$

Molality, M_x	$\frac{M(Na_2SO_4)}{M(Rb_2SO_4)}$	$\frac{M(Na_2SO_4)}{M(Cs_2SO_4)}$
0.1	1.008	1.015
.2	1.016	1.027
.3	1.024	1.040
.4	1.030	1.053
.5	1.038	1.066
.6	1.044	1.078
.7	1.051	1.090
.8	1.057	1.102
.9	1.063	1.112
1.0	1.069	1.122
1.2	1.079	1.137
1.4	1.089	1.148
1.6	1.095	1.155
1.8	1.102	1.160

From these ratios were calculated the concentrations of sodium sulfate isopiestic with each rounded concentration of the two salts. From a plot of the activity coefficient, γ, *versus* molality for sodium sulfate, based upon the data of Robinson, Wilson, and Stokes,[6] activity coefficients for each of these molalities were determined.

The method for calculating the activity coefficients of the two salts investigated is the method of Robinson and Sinclair,[7] using the relation

$$\log \gamma = \log \gamma_r + \log(M_r/M_x) + \frac{2}{2.3026}\int_0^{a_r^{1/2}} \frac{\left(\frac{M_r}{M_x} - 1\right) da_r^{1/2}}{a_r^{1/2}}$$

where the subscript r denotes the reference salt, sodium sulfate, and the subscript x refers to either rubidium or cesium sulfate. The value of the integral was determined graphically. Table III presents the values of the activity coefficients thus calculated. The values in parentheses are included in the table for the sake of completeness; this investigation actually did not cover such low concentrations. For the same reason the activity coefficients for the reference salt, sodium sulfate, are included. Values of the osmotic coefficient for sodium sulfate were taken from the data of Robinson, Wilson and Stokes[6]; ϕ-values for rubidium and cesium sulfates were based upon these sodium sulfate ϕ-values by means of the relation

$$\phi_x = \frac{\phi(Na_2SO_4)M(Na_2SO_4)}{M_x}$$

TABLE III

CALCULATED OSMOTIC AND ACTIVITY COEFFICIENTS FOR RUBIDIUM AND CESIUM SULFATES AT 25°

Molality	(Na_2SO_4) ϕ	(Na_2SO_4) γ	(Rb_2SO_4) ϕ	(Rb_2SO_4) γ	(Cs_2SO_4) ϕ	(Cs_2SO_4) γ
0.1	0.792	0.445	(0.798)	(0.452)	(0.804)	(0.456)
.2	.754	.365	(.765)	(.373)	(.772)	(.380)
.3	.726	.320	(.741)	(.331)	(.753)	(.339)
.4	.708	.2895	.728	.302	.741	.312
.5	.693	.267	.711	.281	.733	.292
.6	.681	.249	.707	.264	.724	.276
.7	.671	.234	.701	.261	.722	.263
.8	.661	.222	.694	.241	.720	.253
.9	.653	.2115	.690	.229	.718	.244
1.0	.646	.202	.686	.221	.717	.237
1.2	.636	.187	.681	.207	.716	.223
1.4	.629	.175	.680	.197	.717	.215
1.6	.625	.171	.683	.191	.720	.210
1.8	.623	.159	.687	.187	.725	.206

Summary

1. The isopiestic ratios for sodium sulfate–rubidium sulfate and sodium sulfate–cesium sulfate were determined experimentally over a range of concentrations of approximately 0.4 to 1.8 molal.

2. From the observed molalities and ratios were calculated the activity coefficients of rubidium and cesium sulfates by comparison with those of sodium sulfate.

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(6) Robinson, Wilson and Stokes, THIS JOURNAL, **63**, 1011 (1941).
(7) Robinson and Sinclair, *ibid.*, **56**, 1830 (1934).