TABLE IX

ENTROPY OF CARBONYL SULFIDE FROM MOLECULAR DATA

		222.87°K.	298.1°K.
Translation		36.761	38.206
Rotation		15.19	15.77
Vibration		0.711	1.389
Calculated entropy		52.66 E. U.	55.37 E. U.
Experimental entropy	Actual gas	52.43 E. U.	......
	Ideal gas	52.56 E. U.	55.27 E. U.

Cross[13] has also calculated the entropy at 298.1° K. His value is 0.03 E. U. higher than the calculated value given above. The difference is due to his use of slightly different vibrational constants.

The good agreement between the entropy value obtained from the third law of thermodynamics and that calculated from molecular data and quantum statistics proves that no random molecular orientation exists in carbonyl sulfide at low temperatures.

Summary

The heat capacity of liquid and solid carbonyl sulfide has been determined from 15°K. to the boiling point.

The melting point is 134.31°K., the boiling point, 222.87°K. (0°C. = 273.1°K.). The heat of fusion is 1129.8 cal. per mole and the heat of vaporization at the boiling point, 4423 cal. per mole.

The vapor pressure of liquid carbonyl sulfide has been measured and the data are represented very closely by the equation: liquid carbonyl sulfide 161.8 to 223.8°K.

$$\log_{10}P(\text{int. cm. Hg}) = -(1318.260/T) + 10.15309 - 0.0147784T + 0.0000188838T^2$$

The density of carbonyl sulfide gas at 25°C. and 1 atm. is 2.4849 ± 0.0005 g./l.

From the experimental data the entropy of the ideal gas at the boiling point was found to be 52.56 cal./deg. per mole. This may be compared with the value 52.66 cal./deg. per mole, calculated from electron diffraction measurements and spectroscopic data.

The good agreement between the experimental and calculated values of the entropy indicates that the difference in size between the oxygen and sulfur ends of the carbonyl sulfide molecule suffices to prevent random orientation of the type found in carbon monoxide and nitrous and nitric oxides at low temperatures.

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(13) Cross, *J. Chem. Phys.*, **3**, 825 (1935).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, AUCKLAND UNIVERSITY COLLEGE]

The Osmotic and Activity Coefficient Data of Some Aqueous Salt Solutions from Vapor Pressure Measurements

BY ROBERT A. ROBINSON

The isopiestic vapor pressure method has been[1] applied to the determination of the activity coefficients of some alkali halides, nitrates, acetates and *p*-toluenesulfonates and of some bivalent metal sulfates. The object of this communication is to describe: (1) the determination of the activity coefficients of some thallous salts; (2) the completion of the data for the nitrates and acetates by the inclusion of figures for the rubidium and cesium salts; (3) a redetermination on some rubidium and cesium halides and (4) the extension of measurements to polyvalent electrolytes, namely, barium chloride, lanthanum chloride, aluminum sulfate and potassium ferrocyanide.

All data in this paper refer to 25°.

I. Thallous Salts.—Thallous nitrate, perchlorate and acetate were prepared by interaction between the carbonate and the corresponding acid, the first salt being recrystallized five times and the other two salts four times. They were balanced against isopiestic solutions of potassium chloride and thence the osmotic and activity coefficients calculated in the manner described previously.[1c] The densities of aqueous solutions of the perchlorate and acetate, not hitherto recorded, have also been measured. Table I gives the data relevant to these salts, γ(D. H.) being the activity coefficient calculated on the limiting Debye–Hückel equation. Eleven determinations were made on the nitrate and twelve on the perchlorate. Twenty-nine measure-

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(1) (a) Robinson and Sinclair, THIS JOURNAL, **56**, 1830 (1934), (b) Robinson, *ibid.*, **57**, 1161, 1165 (1935); (c) Robinson and Jones, *ibid.*, **58**, 959 (1936).

ments on the acetate were necessary to cover the concentration range up to 6 *M*, this being one of the few thallous salts which gives concentrated solutions. The activity coefficients are plotted against $\sqrt{m}$ in Fig. 1.

TABLE I

PROPERTIES OF AQUEOUS SOLUTIONS OF THALLOUS SALTS

	$TlNO_3$			$TlClO_4$		
m	φ	γ	γ(D. H.)	φ	γ	d^{25}_4
0.025	0.940	0.834	0.832	0.945	0.844	1.0033
.05	.915	.774	.770	.926	.791	1.0094
.1	.881	.698	.692	.900	.727	1.0217
.2	.833	.603	.593	.867	.649	1.0460
.3	.800	.542	.527	.842	.597	1.0699
.4	.775	.497	.477	.822	.551	1.0935
.5	..	..	..	.806	.525	1.1167

	$TlC_2H_3O_2$					
m	0.05	0.1	0.2	0.3	0.5	0.7
φ	.932	.913	.891	.877	.857	.844
γ	.801	.745	.681	.640	.586	.550
d^{25}_4	1.0077	1.0180	1.0387	1.0590	1.0989	1.1378
m		1.0	1.5	2.0	2.5	3.0
φ		.829	.816	.809	.802	.797
γ		.511	.470	.442	.420	.403
d^{25}_4		1.1940	1.2831	1.3671	1.4457	1.5193
m	3.5	4.0	4.5	5.0	5.5	6.0
φ	0.791	0.785	0.780	0.775	0.769	0.763
γ	.388	.375	.364	.353	.344	.335

From the density determinations, together with the data for thallous nitrate in the "International Critical Tables,"[2] the apparent molal volumes, Φ have been calculated. If Φ is plotted against $\sqrt{m}$, the points lie on a straight line within the limit of experimental error and consequently Φ can be represented by the equation[3]

$$\Phi = a\sqrt{m} + b$$

using the following values of the constants

$TlNO_3$	$a = 5.9$	$b = 39.5$
$TlClO_4$	$a = 5.3$	$b = 53.55$
$TlC_2H_3O_2$	$a = 4.3$	$b = 50.9$

The partial molal volume of salt will be given by

$$\overline{V}_s = (3a\sqrt{m}/2) + b$$

and the partial molal volume of water by

$$55.51\overline{V}_w = 18.07 - (am^{1/2}/2)$$

These formulas reproduce the experimental data for the nitrate and perchlorate within approximately 0.1 cc. The equation for the acetate is valid up to 3 *M* within approximately the same limit; there is no trend in the observations from the calculated curve, so that any error is probably experimental.

Thallous nitrate is remarkable in that it has a lower activity coefficient than any other uniunivalent salt at the same concentration; the values of the activity coefficient are so low that the limiting Debye–Hückel equation reproduces the experimental data at concentrations at which it would be expected that the finite radius and the variation of the dielectric constant would invalidate the limiting law. The Gronwall–La Mer–Sandved equation[4] is no more satisfactory, because in order to reproduce the experimental data it is necessary to choose a value of a = 1.3 Å., which is a most improbable figure.

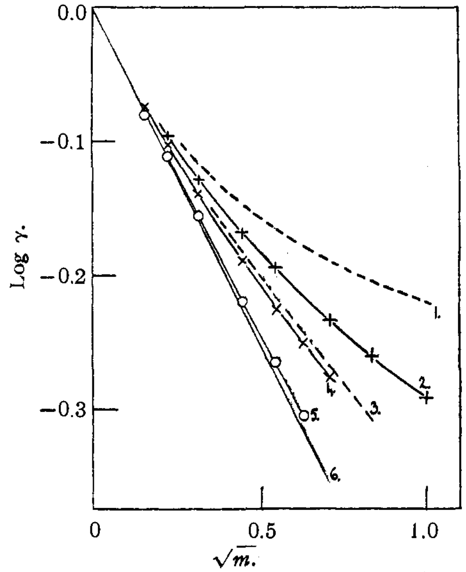

Fig. 1.—Activity coefficients of thallous salts: 1, KCl; 2, $TlC_2H_3O_2$; 3, KNO_3; 4, $TlClO_4$; 5, $TlNO_3$; 6, limiting Debye–Hückel slope.

The activity coefficient of thallous perchlorate is slightly less than that of rubidium nitrate at the same concentration and comparable with that of cesium nitrate. The data for the acetate lie between those for sodium and potassium nitrate. Thus the analogy with the heavier alkali metals exhibited by thallous nitrate and perchlorate does not extend to the acetate, for the alkali acetates are characterized by the very high values of their activity coefficients.

II. The Nitrate and Acetate of Rubidium and Cesium.—Rubidium carbonate of good quality was converted into the dichloroiodide and recrystallized twice in this form.[5] It was then converted into carbonate and the nitrate, acetate,

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[2] "International Critical Tables," Vol. III, p. 64.

[3] Masson, *Phil. Mag.*, **8**, 218 (1929).

[4] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

[5] Archibald, *J. Chem. Soc.*, **85**, 776 (1904).

TABLE II

OSMOTIC AND ACTIVITY COEFFICIENTS OF RUBIDIUM AND CESIUM NITRATE AND ACETATE

	$RbNO_3$		$CsNO_3$		$RbC_2H_3O_2$		$CsC_2H_3O_2$	
m	φ	γ	φ	γ	φ	γ	φ	γ
0.1	0.903	0.727	0.902	0.726	0.943	0.794	0.945	0.795
.2	.871	.653	.869	.648	.948	.768	.950	.770
.3	.848	.601	.843	.596	.953	.756	.956	.760
.5	.811	.532	.804	.524	.973	.757	.977	.762
.7	.782	.482	.775	.473	.992	.766	.997	.774
1.0	.745	.427	.730	.417	1.023	.792	1.026	.799
1.5	.698	.364	.685	.353	1.080	.856	1.084	.865
2.0	.656	.318	..	..	1.139	.936	1.144	.948
2.5	.620	.283	..	..	1.196	1.030	1.200	1.042
3.0	.588	.255	..	..	1.253	1.134	1.256	1.148
3.5	.562	.234	..	..	1.307	1.250	1.311	1.272
4.0	.539	.215	..	..	...	...	...	...
4.5	.517	.199	..	..	...	...	...	...

bromide and iodide prepared. Halogen analysis gave concordant values of the equivalent weight of the metal, namely, 85.38 (Rb = 85.44). Similarly cesium chloride was purified by the method described by Harned and Schupp.[6] It gave an equivalent weight of 132.75 (Cs = 132.91). From the purified material the nitrate, acetate, bromide and iodide were prepared.

The solutions of the nitrate and acetate were balanced against isopiestic solutions of potassium chloride, the number of determinations being: $RbNO_3$, 20; $RbC_2H_3O_2$, 22; $CsNO_3$ 18; $CsC_2H_3O_2$, 26. The osmotic and activity coefficients recorded in Table II were calculated. The activity coefficients of these four salts are of the magnitude which would be expected from an inspection of the data for the salts of the other alkali metals, the curves for rubidium and cesium nitrate lying close below that for potassium nitrate, while cesium acetate gives a curve above that for rubidium acetate which in turn lies above that for potassium acetate. The order of acetates, Cs > Rb > K > Na > Li is, therefore, the reverse of that which holds for alkali nitrates, chlorides, bromides and iodides.

Densities of solutions of the two acetates were also measured, but as only small quantities of material were available, small pycnometers had to be used, with a larger margin of error. The determinations should, however, be sufficient to transfer molality data to volume concentrations and to give approximate values of the coefficients in Masson's equation for the apparent molal volume. They are recorded in this manner, together with the corresponding figures for the nitrates and the remaining acetates, using data in the "International Critical Tables."[7] Similar data for the alkali halides have already been calculated by Scott.[8]

TABLE III

VALUES OF THE a AND b COEFFICIENTS

Nitrates	Li	Na	K	Rb	Cs
a	0.84	2.18	2.31	2.65	2.1
b	28.75	28.0	38.0	42.85	50.8
Acetates	**Li**	**Na**	**K**	**Rb**	**Cs**
a	...	2.22	2.48	2.4	2.0
b	...	39.8	47.2	53.5	61.3

III. **Halides of Rubidium and Cesium.**—As few measurements have been made on rubidium chloride, it was felt desirable to make another determination of the activity coefficient of this salt, using a purer specimen than was available in the previous investigation.[1a] In this work, moreover, trouble was experienced by the decomposition of the iodides of rubidium and cesium[1b] and by corrosion of the silver dishes by the more concentrated solutions. Better results have now been obtained by using chromium plated boxes of "staybrite" steel. These boxes were also used to redetermine the data for the bromides. As far as can be judged, corrosion has been eliminated, for the full amount of halogen was recoverable and there was no detectable loss in weight of the dishes even after a lengthy run. Nevertheless, a minute error assumes importance in the case of such salts whose coefficients are so close together and it is still desirable that an independent determination by another method should be made. The redetermined data are not substantially different, except in the case of rubidium iodide whose activity coefficient is slightly higher

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(6) Harned and Schupp, THIS JOURNAL, 52, 3886 (1930).

(7) "International Critical Tables," Vol. III, pp. 78 *et seq.*

(8) Scott, *J. Phys. Chem.*, 35, 2315 (1931).

TABLE IV

ACTIVITY COEFFICIENTS OF RUBIDIUM AND CESIUM HALIDES

	RbCl		RbBr		RbI		CsBr		CsI	
m	φ	γ	φ	γ	φ	γ	φ	γ	φ	γ
0.1	0.923	0.761	0.922	0.760	0.921	0.759	0.917	0.751	0.916	0.750
.2	.907	.706	.905	.703	.904	.702	.896	.689	.895	.688
.3	.899	.672	.898	.671	.897	.670	.883	.650	.881	.648
.5	.891	.631	.890	.631	.888	.628	.867	.600	.865	.597
.7	.887	.605	.885	.604	.882	.600	.858	.568	.856	.564
1.0	.885	.581	.881	.577	.878	.573	.850	.535	.846	.530
1.5	.889	.557	.882	.550	.879	.546	.848	.502	.838	.493
2.0	.896	.545	.887	.535	.886	.531	.852	.484	.832	.468
2.5	.906	.538	.894	.525	.894	.523	.860	.472	.827	.448
3.0	.918	.536	.901	.519	.903	.517	.868	.464	.824	.432
3.5	.931	.537	.910	.516	.914	.516	.877	.460	..	..
4.0	.944	.539	.919	.515	.924	.515	.887	.458	..	..
4.5	.956	.542	.928	.515	.935	.517	.896	.457	..	..
5.0	.970	.545	.938	.516	.944	.518	.905	.458	..	..

TABLE V

OSMOTIC AND ACTIVITY COEFFICIENTS OF POLYVALENT ELECTROLYTES

	$BaCl_2$		$LaCl_3$		$Al_2(SO_4)_3$	$K_4Fe(CN)_6$	
m	φ	γ	φ	γ	φ	φ	γ
0.05	0.861	(0.561)	0.810	(0.380)	..	0.635	(0.189)
.1	.843	.497	.793	.325	0.420	.595	.138
.2	.835	.440	.788	.279	.390	.557	.107
.3	.836	.412	.818	.265	.391	.536	.088
.4	.842	.395	.859	.264	.422	.519	.076
.5	.8565	.388	.906	.269	.477	.507	.067
.6	.873	.384	.962	.278	.545	.498	.061
.7	.888	.383	1.010	.292	.625	.494	.055
.8	.904	.384	1.059	.317	.718	.494	.052
.9	.919	.385	1.107	.336	.810	.501	.050
1.0	.9345	.389	1.157	.358	.923	..	..
1.1	.950	.392	1.212	.385	1.037	..	..
1.2	.966	.398	1.270	.417	..	..	..
1.3	.983	.403	1.330	.454	..	..	..
1.4	1.000	.410	1.392	.495	..	..	..
1.5	1.017	.417	1.441	.535	..	..	..
1.6	1.033	.425	...	..	..	..	..
1.7	1.049	.433	...	..	..	..	..
1.8	1.064	.441	...	..	..	..	..

than that of the bromide in concentrated solutions and in the case of cesium iodide, the previous data for which differ considerably from the redetermined values. The latter are considered more reliable. This redetermination does not alter the order of the curves of γ against $\sqrt{m}$.

IV. **Polyvalent Electrolytes.**—Barium chloride of A. R. purity was used, analysis showing it to be of good quality. Lanthanum chloride was recrystallized three times; aluminum sulfate was prepared from A. R. potash alum and potassium ferrocyanide recrystallized once from Kahlbaum material. Table V gives the osmotic and activity coefficients derived from measurements on these four salts, numbering 36, 33, 36 and 24, respectively.

The activity coefficient of barium chloride at 0.05 M has been put equal to the value at this concentration calculated by Scatchard;[9] the present values at high concentrations are about 2% lower than those calculated by Scatchard and somewhat lower still than those derived from the measurements of Lucasse.[10] The agreement with the determinations of Pearce and Gelbach[11] is not good. For lanthanum chloride it is more difficult to select an initial value; as a temporary expedient, the activity coefficient at 0.05 M was taken as 0.380, the value for lanthanum nitrate at this concentration.[12] Similarly the value at 0.05 M for potassium ferrocyanide was taken from freezing point data.[12]

[9] Scatchard, THIS JOURNAL, **52**, 2272 (1930).

[10] Lucasse, *ibid.*, **47**, 743 (1925).

[11] Pearce and Gelbach, *J. Phys. Chem.*, **29**, 1021 (1925).

[12] Landolt-Börnstein, "Tabellen," Fifth Edition, Zweiter Ergänzungsband.

The osmotic coefficients of these salts are shown in Fig. 2 in the form of a plot of $(1 - \varphi)/z_1z_2\sqrt{\mu}$ against $\sqrt{\mu}$, z_1, z_2 being the ionic valences and μ the ionic strength. The limiting value of this function is 0.387 at 25°.

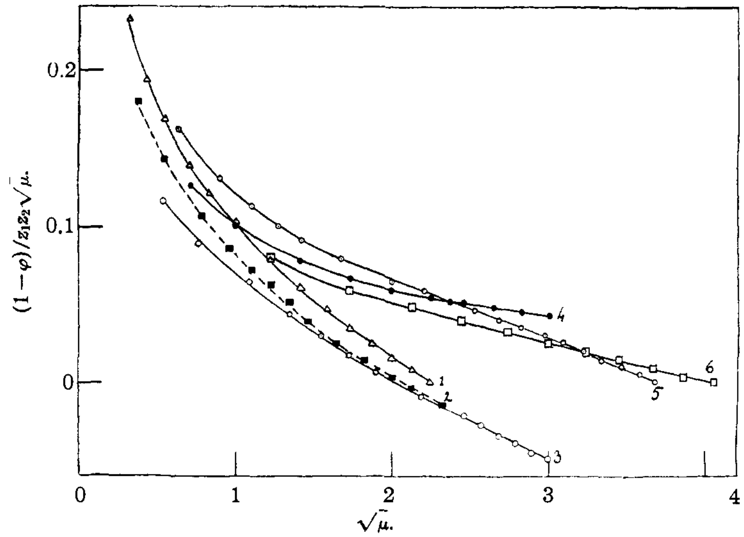

Fig. 2.—Deviation of osmotic coefficient of salt solutions from the limiting Debye–Hückel value: 1, KCl; 2, $BaCl_2$; 3, $LaCl_3$; 4, $K_4Fe(CN)_6$; 5. $ZnSO_4$; 6. $Al_2(SO_4)_3$.

Discussion

The experimental results which have been described in this and the previous papers, may be summarized qualitatively as follows. (1) The curves of γ against $\sqrt{m}$ lie in the order of I > Br > Cl for the lithium, sodium and potassium salts. This order is reversed for the rubidium and cesium salts. (2) All lithium salts have high activity coefficients, the lowest recorded being those of the *p*-toluenesulfonate. (3) With the exception of lithium nitrate, the alkali nitrates are characterized by very low activity coefficients. This is also true of sodium and potassium *p*-toluenesulfonate. (4) The alkali acetates are characterized by a reversal of the order Li > Na > K > Rb > Cs, which holds for other alkali salts. In addition, the values are all high and comparable with those of lithium salts in general. (5) Thallous salts have low activity coefficients, the nitrate having the lowest activity coefficient of any uni-univalent salt; another characteristic is to be found in the acetate which does not reproduce the behavior of the alkali acetates but has a low activity coefficient.

In another publication Professor Scatchard will discuss on the basis of his equation[13] the osmotic coefficients of the alkali halides and he will show that this equation will not only predict the magnitude of the activity coefficients within the limits anticipated but will also explain the reversal of the order I > Br > Cl for the cesium salts. Consequently I shall not enter into a discussion of these halides. It is important, however, to point out that both the constants in Scatchard's equation, which determine the variation of polarization with concentration and the non-ionic effect, respectively, are related to the molal volume of the salts.

Turning now to the thallous salts, it has been shown that the activity coefficient of the nitrate cannot be reconciled either with the limiting Debye–Hückel equation or with the Gronwall–La Mer–Sandved equation. The molal volume of thallous nitrate lies between those of rubidium chloride and bromide (39.5, 25.2 and 41.8, respectively) and its ionic radii are probably comparable with those of rubidium bromide. The disparity between the osmotic coefficients (0.800 for thallous nitrate and 0.898 for rubidium bromide at 0.3 *M*) is therefore remarkable. While an explanation in terms of a physical difference between the nitrate and halogen ions, such as the increased possibility of polarization of the latter by oppositely charged ions, cannot be excluded, it seems improbable since a like disparity between lithium nitrate and lithium bromide with osmotic coefficients of 0.941 and 0.951 at 0.3 *M*, is not found. This leaves the possibility of the incomplete dissociation of thallous nitrate to be considered. Onsager[14] has already shown that conductivity data in very dilute solutions agree with the hypothesis of incomplete dissociation in the case of potassium nitrate, thallous nitrate and thallous chloride, with dissociation constants of 1.3, 0.55 and 0.31, respectively. Similarly Redlich and Rosenfeld[15] assign a dissociation constant of 1.2 to nitric acid and Cowperthwaite, La Mer and Barksdale[16] have also used this hypothesis to account for some anomalous e. m. f. data for thallous chloride, which otherwise lead to impossibly

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[13] Scatchard, *Physik. Z.*, **33**, 22 (1932).

[14] Onsager, *ibid.*, **28**, 277 (1927).

[15] Redlich and Rosenfeld, *Monatsh.*, **67**, 223 (1936).

[16] Cowperthwaite, La Mer and Barksdale, This Journal, **56**, 544 (1934).

low values for the ionic radii. Unfortunately the data for thallous nitrate apply to concentrations too high to be dealt with by Onsager's method but Davies[17] has devised an extension of the conductivity equation to which many uni-univalent salts conform up to molar concentration, *viz.*

$$\lambda_{\text{calcd.}} \sqrt{\eta} = \lambda_0 - (0.2238\, \lambda_0 + 50.49) f(c)$$

where η is the viscosity and $f(c)$ is an empirical function of the concentration. This equation applies at 18° but it can be used at 25° if suitable alteration is made in the numerical magnitude of the constants. In spite of its empirical nature, this theory deserves consideration for it satisfies the available data for all the alkali chlorides, bromides and iodides using the same values of $f(c)$ for each salt and indeed can be extended to even higher concentrations than were originally considered by Davies. In the case of an incompletely dissociated salt Davies assumes that the degree of dissociation is given by $\alpha = \lambda_{\text{obsd.}}/\lambda_{\text{calcd.}}$ and thence the dissociation constant by

$$K = \gamma^2\alpha^2c/(1 - \alpha)$$

The conductivity data for thallous nitrate are not as extensive as could be desired but they give the following values of the dissociation constant.

m	0.01	0.02	0.05	0.1	0.2	0.25
α	.983	.972	.946	.911	.870	.848
K	.45	.48	.48	.44	.38	.36

The values of K are as constant as can be expected in view of the large variation in $(1 - \alpha)$ caused by a slight error in α. It remains now to be shown that such incomplete dissociation accords with the anomalous osmotic coefficients. The vapor pressure lowering, from which the osmotic coefficient was calculated, may be assumed to be due to two factors, one due to the ions and the other to the undissociated molecules. The relative lowering of the vapor pressure due to the latter may be taken as 0.018 m_u, m_u being the molality of the undissociated molecules, provided they can be assumed to act as a perfect solute. The osmotic coefficient of the solution in the absence of these undissociated molecules would therefore be given by

$$\varphi' = -55.51/2m_{\pm} \ln\left[(p + 0.018 m_u p_0)/p_0\right]$$

where $m_{\pm}$ is the ionic molality. Calculating φ' in this manner we obtain the following values

m	0.01	0.02	0.05	0.1	0.2	0.25
φ'	.969	.959	.938	.918	.882	.871

These values are of the right order; they can not be regarded as quantitatively reliable but it is nevertheless significant that Davies' method of computing the degree of dissociation leads to osmotic coefficients which correspond to reasonable ionic dimensions.

In the case of cesium, rubidium, potassium and sodium nitrate, although their activity coefficients are not as low as in the case of thallous nitrate, yet it would be anticipated from a comparison of their molal volumes with the data for the bromides that their activity coefficients would be of the same order as those of the corresponding bromides. From this point of view the anomalies are most pronounced, especially as lithium nitrate has an activity coefficient not greatly different from that of lithium bromide. The ratios of the activity coefficient of the bromide to that of the corresponding nitrate at 1 *M* concentration are as follows

Li	Na	K	Rb	Cs
1.09	1.27	1.40	1.35	1.28

Moreover, it may be significant that conductivity data, interpreted on the basis of Davies' equation, correspond to complete dissociation of lithium nitrate; on the other hand, incomplete dissociation is indicated in the case of the nitrates of sodium, potassium and cesium (the necessary data for the rubidium salt are lacking). It is therefore tempting to ascribe the anomalous activity coefficients of these nitrates to incomplete dissociation, the most powerful argument against this hypothesis being found in the work of Rao[18] who showed that the Raman spectrum from a solution of sodium nitrate showed no lines which could be ascribed to the undissociated molecule. The argument, however, cannot be held to be conclusive until much further work has been done, for Woodward[19] has found an example in hydrofluoric acid of an electrolyte which is certainly incompletely dissociated but gives no Raman lines for the undissociated molecule. Applying Davies' equation to these three nitrates, the following results are obtained.

Molality	0.01	0.05	0.1	0.5	1
			$NaNO_3$		
α	0.996	0.985	0.982	0.947	0.913
K	2.0	2.0	3.0	3.2	2.9
φ'	0.978	0.943	0.912	0.898	0.880

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[17] Davies, *Trans. Faraday Soc.*, **23**, 354 (1927).

[18] Rao, *Proc. Roy. Soc.* (London), **144**, 159 (1934).

[19] Woodward, *Physik. Z.*, **32**, 777 (1931).

Molality	0.01	0.05	0.1	0.5	1
			KNO_3		
α	0.991	0.973	0.959	0.895	0.845
K	.87	1.09	1.19	1.11	.91
φ'	.978	0.947	0.919	0.855	.803
			$CsNO_3$		
α	0.991	0.966	0.948	0.877	0.821
K	.87	.85	.91	.86	.66
φ'	.978	.950	.924	.839	.784

Whilst these osmotic coefficients can have little quantitative significance, especially for more concentrated solutions, the purpose of the calculation is achieved by showing that the effect of incomplete dissociation is such as to lead to osmotic coefficients of a more reasonable order.

The osmotic coefficients of the alkali acetates are much higher than one would expect from a consideration of their molal volumes. Davies' equation, however, gives no indication of incomplete dissociation and it is probable that the abnormally high values for all but the lithium salt as well as the reversal in the normal order Li > Na > K > Rb > Cs will find an explanation in the asymmetrical distribution of charge in the acetate ion.

There seems to be no purpose at present in attempting a theoretical explanation of the coefficients of the polyvalent salts. It may, however, be pointed out that, as Fig. 2 shows, the departure from the limiting Debye–Hückel equation at high concentrations is no more marked for polyvalent electrolytes in general than it is for a typical uni-univalent salt such as potassium chloride.

Finally I wish to record my thanks to Professor G. Scatchard, who has helped me with much information regarding his theory and to the Chemical Society for a grant which assisted in the purchase of rubidium and cesium salts.

Summary

1. Osmotic and activity coefficients have been determined by the isopiestic vapor pressure method for thallous nitrate, perchlorate and acetate, rubidium and cesium nitrate and acetate, barium chloride, lanthanum chloride, potassium ferrocyanide and aluminum sulfate. The data for rubidium chloride, bromide and iodide and cesium bromide and iodide have been redetermined.

2. The possibility of incomplete dissociation of sodium, potassium, cesium and thallous nitrate has been discussed and it is shown that not only is this hypothesis consistent with Davies' extension of the conductivity equation but it also explains the abnormally low values found for the osmotic and activity coefficients of these salts.

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The Use of Crotonaldehyde to Reduce the Postprecipitation of Zinc on Copper Sulfide

BY JOHN R. CALDWELL[1] AND HARVEY V. MOYER

It has been known for many years that copper sulfide, precipitated in the presence of zinc, will carry down appreciable quantities of zinc even when the precipitation is made in a normal acid solution. Various theories of mixed crystal formation, of solid solution and of coprecipitation have been proposed as explanations. Comparatively recent studies have been made by Kolthoff and Pearson,[2] Knowles and Martin,[3] Balarew[4] and Kolthoff and Moltzau.[5] Kolthoff has presented evidence which seems to indicate that an adsorbed layer of hydrogen sulfide on the surface of the copper sulfide causes the postprecipitation of the zinc as sulfide.

Recently we have found that certain organic compounds may be used to alter the nature of analytical precipitates.[6–9] In a study of the separation of zinc and cobalt, it was found that if zinc sulfide was precipitated in the presence of a small amount of certain aldehydes, acrolein in particular, the quantity of cobalt carried down is

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(2) Kolthoff and Pearson, *J. Phys. Chem.*, **36**, 549 (1932).

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