position changes in the liquid phase. Thus the results on the distribution of europium in these systems are in accord with chemical evidence which indicates that europium(III) ions are reduced to the divalent state by sulfide and selenide ions and are thus incorporated into the strontium sulfide or selenide lattice. K_T decreases slightly with increasing temperature and is somewhat lower for higher europium concentrations.

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[CONTRIBUTION FROM EDWARD DAVIES CHEMICAL LABORATORIES, UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH]

The Conductances of Sodium, Potassium and Lanthanum Sulfates at 25°

BY I. L. JENKINS AND C. B. MONK

While the limiting ion conductances of most of the common anions have been measured with a high degree of precision at 25°, that of the sulfate ion does not appear to be known with the same degree of accuracy. In order to ascertain this value more closely, we have therefore made measurements on dilute solutions of sodium and potassium sulfates and obtained the conductances at zero concentration by the method of Owen.[1] This method, the merits of which have been discussed previously,[2] involves plotting the function $(\Lambda + b\mu^{1/2} - \Lambda_0)/C$ against log C, where b is the theoretical Onsager slope,[4] μ is the ionic strength, and C is in equivalents per liter. An approximate value of Λ_0 is first obtained by the usual method of plotting Λ against $C^{1/2}$, and slight variations of this are tried in the Owen function until a linear plot is obtained; this value of Λ_0 is then regarded as being the correct one. The experimental conductances obtained have been interpreted by the treatment of Davies,[3] in which deviations from the limiting Onsager equation[4] are interpreted in terms of ion-association. As a further contribution in this respect, the conductances of dilute lanthanum sulfate solutions have been measured and treated along similar lines.

Experimental

"AnalaR" grade sodium and potassium sulfates were recrystallized several times from conductance water. After a preliminary drying, the sodium sulfate was fused in a platinum crucible, and the potassium sulfate was heated until it sintered. Contrary to general belief, the sodium sulfate was found to be non-hygroscopic after fusion. The lanthanum sulfate was prepared from B.D.H. pure lanthanum nitrate by precipitation with "AnalaR" sulfuric acid. The sulfate was recrystallized three times from conductance water, then heated, recrystallized and dried by the method of Nathan.[5] By heating a sample at 650°, the composition of the crystals was confirmed as being $La_2(SO_4)_3 \cdot 9H_2O$ within ±0.02%. A 0.005 N solution in equilibrium with air had a pH of 5.5, so that hydrolysis corrections were considered to be negligible. Several cells were used, and these were calibrated from the data of Shedlovsky[6] for potassium chloride, using the empirical equation

$$\Lambda = 149.88 - 94.44\sqrt{C} - 22C \log C + 4100C^2$$

where C is expressed in equivalents per liter. In this expression the value of 149.88 for the limiting conductance of potassium chloride was derived by Owen's method,[1] and 94.44 is the theoretical limiting Onsager slope, using the latest values for the constants involved.[7] Satisfactory agreement up to 0.009 N is shown by the following table in which Δ represents observed less calculated conductances

10^4C	1	2	5	10	20	30
Δ	−0.01	0.01	0.01	−0.01	..	..
10^4C	40	50	60	70	80	90
Δ	..	0.01	0.02	0.01	..	−0.01

The apparatus and technique employed have been described elsewhere.[2,8] Tables I, II and III contain the data, and in Fig. 1 the conductances are plotted against the square root of C, together with the limiting Onsager slopes.

TABLE I

SODIUM SULFATE

Specific conductance of water, ohm^{-1} × 10^{-7} (a) 2.31, (b) 2.00.

Run	C	$\sqrt{C}$	Λ	K
a	0.00010384	0.01019	128.24	0.19
b	.00014380	.01196	127.90	.20
a	.00019427	.01394	127.51	.15
b	.00031898	.01786	126.78	.21
a	.00033736	.01837	126.61	.13
b	.00054671	.02338	125.68	.18
a	.00060919	.02468	125.42	.17
b	.00080013	.02829	124.73	.20
a	.00081186	.02849	124.73	.20
a	.0011901	.03450	123.57	.24

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[1] Owen, THIS JOURNAL, **61**, 1393 (1939).

[2] Monk, *ibid.*, **70**, 3281 (1948).

[3] Righellato and Davies, *Trans. Faraday Soc.*, **26**, 592 (1930).

[4] Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927).

[5] Nathan, Wallace and Robinson, THIS JOURNAL, **65**, 790 (1943).

[6] Shedlovsky, Brown and MacInnes, *Trans. Electrochem. Soc.*, **66**, 165 (1934).

[7] Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

[8] Davies, *J. Chem. Soc.*, 432 (1937).

TABLE II

POTASSIUM SULFATE

Specific conductance of water, ohm^{-1} × 10^{-7} (a) 2.26, (b) 2.17, (c) 2.00, (d) 2.08.

Run	C	$\sqrt{C}$	Λ	K
a	0.00011338	0.01065	151.35	0.07
b	.00014464	.01203	151.14	.15
c	.00015607	.01249	151.00	.10
a	.00022472	.01499	150.43	.08
b	.00023419	.01530	150.40	.10
c	.00027903	.01671	150.11	.10
b	.00033400	.01828	149.78	.10
a	.00035573	.01886	149.63	.10
c	.00044775	.02116	149.12	.10
b	.00045079	.02123	149.15	.11
a	.00063238	.02515	148.31	.11
d	.00064841	.02546	148.30	.13
c	.00066040	.02570	148.16	.16
d	.00091329	.03022	147.26	.12
c	.00099651	.03157	146.91	.13
d	.0011309	.03363	146.60	.16

TABLE III

LANTHANUM SULFATE

Specific conductance of water, ohm^{-1} × 10^{-7} (a) 2.68, (b) 3.01, (c) 2.15.

Run	C	$\sqrt{C}$	Λ	$10^5 x$	$10^4 K$
a	0.00039428	0.01986	103.81	4.43	2.49
b	.00059086	.02431	95.42	7.98	2.54
c	.00070563	.02656	91.77	10.2	2.52
c	.0010749	.03279	82.79	18.2	2.60
b	.0011994	.03463	80.81	21.0	2.61
a	.0012553	.03543	80.13	22.0	2.72
c	.0013661	.03696	78.07	24.8	2.68
b	.0015244	.03904	76.22	28.4	2.73
c	.0017139	.04130	73.75	33.1	2.72
b	.0018202	.04266	72.81	35.6	2.77

Discussion

Sodium Sulfate.—Extrapolation of the $\Lambda - \sqrt{C}$ curve gives $\Lambda_0 = 130.2 \pm 0.05$, and Owen's method[1] indicates that $\Lambda_0 = 130.15 \pm 0.05$. A slightly more consistent series of dissociation constants (discussed below) is obtained with $\Lambda_0 = 130.13$. Thus taking the mobility of the sodium ion as 50.11,[9] the limiting mobility of the sulfate ion is 80.02. MacInnes[10] has given the only other comparable measurements on sodium sulfate. These agree very closely with the present data, but his extrapolation of $\Lambda_0 = 129.9$ leads to 79.8 for the sulfate ion. Examination of his figures by the Owen method[1] shows that his value at $C = 0.0005$ is a little on the low side, and therefore leads to a slightly lower Λ_0 value than ours. The limiting Onsager equation based on the present data is

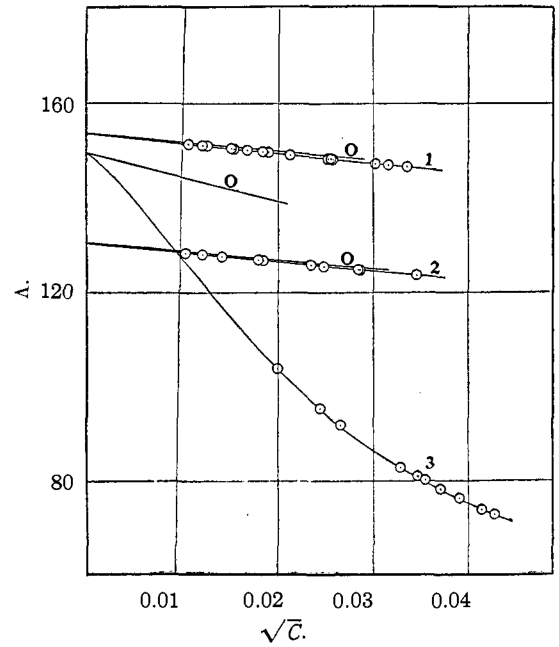

Fig. 1—Conductances of (1) potassium sulfate; (2) sodium sulfate; (3) lanthanam sulfate; O, corresponding Onsager slopes.

$$\Lambda_1 = 130.13 - 148.0\,\mu^{1/2} \qquad (1)$$

where μ is the ionic strength. The slight discrepancy between this and the experimental conductances has been interpreted by Davies[3] as due to the presence of $NaSO_4^-$ ions, and if α is the fraction of the sulfate in this form, we can apply the mixture rule to the fraction $1 - \alpha$ of the salt to which equation (1) applies, and the fraction α, for which we can write

$$\Lambda_2 = 98.0 - 88.4\,\mu^{1/2} \qquad (2)$$

Here the $NaSO_4^-$ ions are assumed to have a limiting mobility of 0.6 that of the sulfate ion,[3,11] *i. e.*, 47.9, giving 98.0 for the equivalent conductance of ($Na^+ + NaSO_4^-$) at zero ionic strength, and 88.4 for the corresponding Onsager slope. Substitution of equations (1) and (2) in the mixture rule

$$\Lambda = {}^1/_2\alpha\,\Lambda_2 + (1 - \alpha)\,\Lambda_1$$

gives

$$\Lambda = 130.13 - 148.0\,\mu^{1/2} - \alpha(81.13 - 103.8\,\mu^{1/2}) \qquad (3)$$

The values of α are easily evaluated from equation (3), and the dissociation constant K can be obtained, *i. e.*

$$K = \frac{[Na^+][SO_4^{2-}]f_1 f_2}{[NaSO_4^-]f_3} = \frac{(2 - \alpha)(1 - \alpha)Cf_1 f_2}{2\alpha f_3}$$

The ion activity coefficients f_1, f_2 and f_3 are obtained from the Debye–Hückel equation $-\log f_i = 0.509 z_i^2 \mu^{1/2}$, z_i being the valency of the ion, and $\mu = C(1.5 - \alpha)$. The values of K are listed in Table I, and the average value is 0.19, which is

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[9] Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943.

[10] Unpublished measurements of Shedlovsky and Longsworth, quoted by MacInnes in "Principles of Electrochemistry," Reinhold Publ. Corp., New York, N. Y., 1939.

[11] *Cf.* refs. 9, 10.

in agreement with the figure of 0.20 calculated by Davies[3] from the data of Noyes[12] at 18°.

Longsworth[13] has measured the transference numbers of sodium sulfate at 25°, and these may be compared with values calculated from the dissociation constant; a slightly modified treatment of the earlier method[3] has been used for this. The predicted anion transference numbers, T_-, are obtained from

$$T_- = (\alpha\Lambda_{\mathrm{NaSO_4^-}} + (1 - \alpha)\Lambda_{\mathrm{SO_4^{2-}}})/\Lambda$$

the values of α being calculated by approximations from the dissociation constant expression. Since the transference numbers were obtained at relatively high concentrations, a modified activity-coefficient expression was used.[14] In calculating the equivalent conductances involved, the corresponding Onsager equations have been used, namely

$$\Lambda_{\mathrm{SO_4^{2-}}} = 80.0 - 95.4\ \mu^{1/2}$$
$$\Lambda_{\mathrm{NaSO_4^-}} = 48.0 - 41.1\ \mu^{1/2}$$

These have been calculated by taking the mobilities at zero ionic strength for $\mathrm{Na^+}$, $\mathrm{SO_4^{2-}}$ and $\mathrm{NaSO_4^-}$, using the figures quoted earlier in this article. Equation (1) was used to calculate Λ in the denominator of the transference-number expression. The resultant calculations for T_- are given in Table IV. Above the concentrations cited, the discrepancies between the calculated and observed values increase; this is to be expected, since the Onsager treatment is essentially limited to dilute solutions.

TABLE IV

TRANSFERENCE NUMBERS

C	α	T_- (expt.)	T_- (calcd.)
	Sodium Sulfate		
0.01	0.031	0.615	0.614
.02	.051	.616	.616
.05	.095	.617	.619
	Potassium Sulfate		
.0025	.017	.480	.483
.005	.036	.482	.484
.01	.050	.483	.486
.02	.079	.485	.489

Potassium Sulfate.—The figures have been treated in a similar fashion to that described for the sodium salt. From the plot of Λ against $\sqrt{C}$, $\Lambda_0 = 153.6$, and the Owen method[1] gives $\Lambda_0 = 153.50 \pm 0.05$, which is also in agreement with consistent K values. The limiting conductance of the potassium ion, 73.52,[9] therefore gives 79.98 as the mobility of the sulfate ion. Hartley[15] measured the conductances of very dilute solutions of potassium sulfate at 25° and give 80.8 for the mobility; his data are about 0.7 unit higher than the present series. The Onsager equation, assuming the presence of $\mathrm{KSO_4^-}$ ions, by analogy with equation (3) is

$$\Lambda = 153.50 - 155.0\mu^{1/2} - \alpha(92.75 - 111.0\mu)^{1/2}$$

and the average dissociation constant (the values of which are given in Table II) is 0.11. This is comparable with the figure of 0.15 obtained by Davies[3] at 18°. Calculated transference numbers are compared with those obtained experimentally[15] in Table IV.

Lanthanum Sulfate.—With this salt, very marked ion-association probably occurs even in very dilute solutions. Using the data of LaMer[16] for the solubility of lanthanum iodate in potassium sulfate solutions at 25°, Davies[17] calculated a dissociation constant of 2.2×10^{-4} (averaging the three best results) for the equilibrium $\mathrm{LaSO_4^+} \rightleftarrows \mathrm{La^{3+}} + \mathrm{SO_4^{2-}}$, and showed that a rough check was obtained from the most dilute solution (0.002 N) used by Noyes[18] in conductance measurements on lanthanum sulfate at 18°; this latter gave a K of 1.8×10^{-4}. Another instance of the marked departure of lanthanum sulfate from the limiting laws of the interionic attraction theory has been noted by Robinson[5] in connection with heats of dilution. It is pointed out in the article referred to, that similar deviations are found with 2:2 valent salts; this has also been found to be the case with the conductances of such salts, and can be explained in terms of ion-association (see ref. 9, p. 147). It is hoped to show at a later date that a quantitative treatment of thermochemical properties can be evolved along similar lines.

In calculating dissociation constants for lanthanium sulfate from the conductance data, we have used the following treatment. Taking x as the concentration of $\mathrm{LaSO_4^+}$ ions, the concentration of sulfate ions is $1/2C - x$, and that of the lanthanum ions is $1/3C - x$. Application of the mixture rule gives

$$(\Lambda_{\mathrm{La^{3+}}} + \Lambda_{\mathrm{SO_4^{2-}}}) = (x/C)(3\Lambda_{\mathrm{La^{3+}}} + 2\Lambda_{\mathrm{SO_4^{2-}}} - \Lambda_{\mathrm{LaSO_4^+}})$$

where the equivalent conductances of the ions are calculated, at the ionic strength $\mu = 2.5C - 6x$, from the appropriate Onsager equations. These are, respectively

$$\Lambda_{\mathrm{La^{3+}}} = 69.5 - 181.5\ \mu^{1/2}$$

where 69.5 is the limiting conductance of the lanthanum ion[9]

$$\Lambda_{\mathrm{SO_4^{2-}}} = 80.0 - 166.4\ \mu^{1/2}$$

where 80.0 is the limiting conductance of the sulfate ion (present work), and

$$\Lambda_{\mathrm{LaSO_4^+}} = 23.2 - 60.5\ \mu^{1/2}$$

In the last equation, the limiting conductance of the $\mathrm{LaSO_4^+}$ ion has been taken as one third of that of the lanthanum ion, the time of relaxation effect has been calculated with respect to the lanthanum and sulfate ions (as in the other two

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[12] Noyes and Falk, THIS JOURNAL, **34**, 461 (1912).

[13] Longsworth, *ibid.*, **57**, 1185 (1935).

[14] Davies, *J. Chem. Soc.*, 2093 (1938).

[15] Hartley and Donaldson, *Trans. Faraday Soc.*, **33**, 457 (1937).

[16] LaMer and Goldman, THIS JOURNAL, **51**, 2632 (1929).

[17] Davies, *J. Chem. Soc.*, 2421 (1930).

[18] Noyes and Johnston, THIS JOURNAL, **31**, 987 (1909).

equations), and the electrophoretic effect has been based on the ion valencies. The assumptions involved here probably give rise to the greatest uncertainties in the calculations. Onsager[19] has shown that in solutions containing more than two ion species, the treatment is more complex than in the case of single electrolytes. However, in dilute solutions the modifications are small, and it is unlikely that the simpler treatment used in the present case is seriously in error. In calculating x, a first value is obtained by taking the ion conductances at zero concentration. Truer values are then quickly obtained by approximations. The final values are given in Table III. The values of the dissociation constant

$$K = \frac{[\mathrm{La}^{3+}][\mathrm{SO_4}^{2-}]f_1f_2}{[\mathrm{LaSO_4}^+]f_3} = \frac{({}^1/_3C - x)({}^1/_2C - x)f_1f_2}{xf_3}$$

where the activity coefficients are obtained from equation (4), are given in the last column of this table. A slight but systematic drift in the figures is probably the result of the approximations involved. Extrapolation to zero concentration indicates that the most probable value of K is 2.4×10^{-4}.

Summary

The conductances of sodium and potassium sulfate solutions at 25° have been measured over the range 0.0001 to 0.001 equivalents per liter. From the Owen method[1] of extrapolation, the zero conductance sulfate conductance averages 80.00 ± 0.05 unit. Dissociation constants of the ion-pairs $\mathrm{NaSO_4}^-$ and $\mathrm{KSO_4}^-$ are found by the method of Davies[3] to be 0.19 and 0.11, respectively, and these are shown to predict satisfactorily the transference numbers of these sulfates in dilute solutions.

Lanthanum sulfate conductances in the region 0.0004 to 0.0018 equivalent per liter have been measured at 25°, 'and the dissociation constant of the ion $\mathrm{LaSO_4}^+$ found to be 2.4×10^{-4}, in good agreement with 2.2×10^{-4} found previously from solubility studies.[17]

Aberystwyth, Wales

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(19) Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932

[Contribution from the Central Experiment Station, Bureau of Mines, Pittsburgh]

X-Ray Diffraction Studies of the Action of Carbon Monoxide on Cobalt–Thoria–Kieselguhr Catalysts. II

By L. J. E. Hofer,[1] W. C. Peebles[1] and E. H. Bean[1]

Below 235 ± 10° carbon monoxide reacts with finely divided cobalt to form only cobalt carbide[2]; above this temperature inert free carbon is also formed. This paper presents the results of a study of the reactions occurring above this critical temperature to permit more complete understanding of the problem of free-carbon formation in Fischer–Tropsch catalysts in the synthesis. The formation of such carbon leads to mechanical disintegration of the catalyst[3] and to a shift of product distribution toward lighter hydrocarbons, especially methane.[4] It should be emphasized that these effects are distinct from the inhibiting effect of cobalt carbide on the synthesis.[5]

Experimental

Preparation and Reduction of the Catalyst.—The catalyst, cobalt–thoria–kieselguhr (100:18:100) 108B,[2,6] the apparatus used for reduction and carburization,[2] the X-ray diffraction apparatus and its operating technique,[2] the preparation of the gases,[2] and the general operating procedure[2] were the same as those already described in the respective references. Before carburization, all the catalysts were reduced at 400 ± 2° (except that used in experiment 40, which was reduced at 383 ± 2°) for 44 to 159 hours to constant weight; the variation in reduction time did not materially affect the course of the subsequent carburization reaction.

Free Carbon and Carbidic Carbon Formation between 208 and 298°.—In experiments 23, 24, 27, 31, 33 and 37, the reduced catalyst was carburized with carbon monoxide at various temperatures. After a suitable carburizing period, one of the sample tubes was removed for X-ray diffraction analysis. The remaining sample tubes were then hydrogenated to constant weight at the temperature

Table I

Carbon Decomposition on Cobalt–Thoria–Kieselguhr Catalyst Reduced at 400° in Hydrogen

Expt.	Temp. carburization, °C.	Time of carburization, hr.	Diffraction analysis of product	C:Co ratio total	C:Co[a] ratio carbidic	C:Co[b] ratio of recarbided carbon
24	298	62	Dis. cobalt[c]	0.820	0.017	0.008
31	278	15	Dis. Co +	.435	.054	...
23	258	77.8	$\mathrm{Co_2C}$	.352	.063	.089
37	243	70.6	$\mathrm{Co_2C}$	.138	...	...
33	233	112	$\mathrm{Co_2C}$	.120	.099	...
27	208	120.8	$\mathrm{Co_2C}$	.104	.104	.099

[a] Amount of carbon which could be removed by treating with hydrogen at the temperature of carbon deposition. [b] Amount of carbidic carbon which could be added by carbon monoxide treatment at 220°. [c] Dis. = disordered.

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[1] Research and Development Branch, Office of Synthetic Liquid Fuels, Bureau of Mines, Bruceton, Pa.

[2] L. J. E. Hofer and W. C. Peebles, This Journal, **69**, 2497 (1947).

[3] Report of the Fuel Research Board for the Year Ended March 31, 1939, H. M. Stationery Office, London, p. 158.

[4] R. B. Anderson, W. Keith Hall, Abraham Krieg and Bernard Seligman, This Journal, **71**, 183 (1949).

[5] Sol Weller, L. J. E. Hofer and R. B. Anderson, This Journal, **70**, 799 (1949).

[6] H. H. Storch, *et al.*, Bureau of Mines Technical Paper 709, "Synthetic Liquid Fuels from the Hydrogenation of Carbon Monoxide, Part I."