[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Distribution of Europium(II) Ions between a Solid Phase and a Fused Salt Solution[1]

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The distribution of certain rare earth ions between solid strontium sulfide or selenide and fused salt solutions is of importance in the study of infrared-sensitive phosphors. In a previous paper[3] we presented the results of our investigation of the distribution of microamounts of the rare earth ions, europium, cerium and samarium between solid strontium sulfide or strontium selenide and a liquid phase consisting of a saturated solution of the strontium sulfide or selenide in a fused mixture of strontium chloride and strontium oxide. The results, at about 1000°, indicated that the equilibrium concentration of both cerium and samarium in the solid phase decreased rapidly and in about the same proportions as the oxide content of the liquid phase rose from zero to an amount almost sufficient to saturate the fused strontium chloride. The distribution of europium, however, was much less sensitive to the presence of strontium oxide in the liquid phase. These results offered a qualitative explanation of the peculiar effects of strontium oxide upon the brightness of the infrared stimulated emission of the Std. VI phosphors whose composition may be represented by

$$100\mathrm{SrS}(x\mathrm{Eu},y\mathrm{Sm})12\mathrm{SrCl_2},z\mathrm{SrO}$$

(the numbers represent parts by weight of the indicated substances[4]).

In the distribution studies of europium, samarium and cerium, the rare earths were introduced into the system in microquantities as the trivalent chlorides. Inasmuch as the sizes of these trivalent ions were almost identical we could only assume that the difference in the behavior of europium was due to its reduction to the divalent state by the sulfide or selenide ions present in these systems. There is sufficient chemical evidence to show that the stable valence state of both cerium and samarium in a sulfide lattice is the trivalent one whereas that of europium is the divalent one. E. Banks and H. Yakel[5] have studied the solid solutions of samarium(III) sulfide and cerium(III) sulfide in strontium sulfide at 1000° and have found that they are soluble to the extent of 37.0 mole per cent. and 5.26 mole per cent., respectively. A defect lattice results containing vacant cation positions. On the other hand, the only sulfide or selenide of europium reported is europium(II) sulfide or selenide.[6] This compound has a rock-salt structure and a lattice constant of 5.957 Å. compared to the lattice constant of strontium sulfide which is 6.007. Inasmuch as these unit cell dimensions differ by only 0.050 Å. we might expect europium(II) sulfide and strontium sulfide to form a complete series of solid solutions.

This paper presents the results of a further investigation of the distribution of divalent europium between the solid and liquid phases in the system SrS(Solid) ($\mathrm{SrCl_2}$,SrO, dissolved SrS) (Liquid) and SrSe (Solid) ($\mathrm{SrCl_2}$, SrO, dissolved SrSe) (Liquid). Only a few determinations were made with the second system.

Derivation of the Distribution Constant

The distribution of microamounts of salts between other salts and their saturated aqueous solutions has been studied both experimentally and theoretically.[7,8]

The fused salt solutions dealt with here are essentially similar. The macrocomponent salts are either strontium sulfide or strontium selenide and the microcomponent salts are the sulfides or selenides of cerium(III), samarium(III) or europium(II). The macrocomponent salt is designated by AB and the microcomponent salt by $\mathrm{R}_n\mathrm{B}_m$, where $n = 2$ and $m = 3$ for the trivalent sulfides and both n and m are 1 for europium(II) sulfide. Following the thermodynamic treatment of Schuliamkov[8] we can write a distribution constant

$$D = \left(\frac{a_\mathrm{R}^\nu}{a_\mathrm{A}}\right)_\mathrm{Solid}\left(\frac{a_\mathrm{A}}{a_\mathrm{R}^\nu}\right)_{\mathrm{Liquid}^a} \qquad (1)$$

where $\nu = n/m$ and a represents the activity of the indicated ions. The constant D is a function only of the temperature and pressure and is not in any way dependent upon changes that may occur in the composition of the liquid phase. Since we are dealing with extremely dilute solid solutions we may replace the activity of the ions in the solid phase by the corresponding ion fractions. The ion fraction is defined, in accordance with the concepts of the ideal salt solution as developed by Temkin,[9] as the number of gram ions of the given ion to the total number of gram ions of all ions of the same sign. The composition of the liquid phase, however, was not the same in all the runs

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[1] This work was carried out under Contract NObsr 39045 between the Polytechnic Institute of Brooklyn and the Bureau of Ships.

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[8] B. Schuliamkov, *J. Phys. Chem.* (*U. S. S. R.*), **21**, 975 (1947).

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but was changed by varying the ratio of strontium oxide to strontium chloride. We therefore write

$$(a_{\mathrm{R}})_{\mathrm{Liquid}} = (\mathrm{X}_{\mathrm{R}}\gamma_{\mathrm{R}})_{\mathrm{Liquid}} \qquad (2)$$

and

$$(a_{\mathrm{A}})_{\mathrm{Liquid}} = (\mathrm{X}_{\mathrm{A}}\gamma_{\mathrm{A}})_{\mathrm{Liquid}}$$

The X's are ion fractions and the γ's are ionic activity coefficients which will depend upon the properties of the ions and the composition of the liquid phase. Equation (1) can then be written

$$D = \left(\frac{\mathrm{X}_{\mathrm{R}}^{\nu}}{\mathrm{X}_{\mathrm{A}}}\right)_{\mathrm{Solid}} \left(\frac{\mathrm{X}_{\mathrm{A}}\gamma_{\mathrm{A}}}{\mathrm{X}_{\mathrm{R}}^{\nu}\gamma_{\mathrm{R}}^{\nu}}\right)_{\mathrm{Liquid}} \qquad (3)$$

The only positive ions in the systems were either those of strontium or the rare earths. Since the latter were present in amounts very much smaller than the former, we can set $\mathrm{X}_{\mathrm{A}} = 1$ in both phases and equation (3) becomes

$$D^{1/\nu} = \frac{(\mathrm{X}_{\mathrm{R}}^{\nu})_{\mathrm{Solid}}}{(\mathrm{X}_{\mathrm{R}})_{\mathrm{Liquid}}} \times \left(\frac{\gamma_{\mathrm{A}}^{1/\nu}}{\gamma_{\mathrm{R}}}\right)_{\mathrm{Liquid}} \qquad (4)$$

The first factor on the right-hand side of equation (4) is the quantity K_{T}, defined in the previous paper,[3] and is the quantity which can be determined experimentally. This may be written

$$K_{\mathrm{T}} = D^{1/\nu} \times \left(\frac{\gamma_{\mathrm{R}}}{\gamma_{\mathrm{A}}^{1/\nu}}\right)_{\mathrm{Liquid}} \qquad (5)$$

For the europium(II) sulfide–strontium sulfide systems, $\nu = 1$ and we can consider the ratio

$$(\gamma_{\mathrm{R}}/\gamma_{\mathrm{A}})_{\mathrm{Liquid}}$$

as being essentially independent of the composition of the liquid phase since the ions of the two components are of the same charge and are of almost identical dimensions.[6] The distribution of europium(II) should be little affected by the addition of strontium oxide to the liquid phase. For the systems involving the trivalent ions cerium and samarium, however, neither the charges nor the dimensions are the same as those of strontium ions. We have no reason, therefore, to expect K_{T} to remain constant as the composition of the liquid phase is changed by the addition of increasing amounts of strontium oxide.

Experimental

A procedure has been described for measuring the distribution of rare earth ions between liquid and solid phases at elevated temperatures using radioactive rare earths as tracers.[10] This involved equilibration of the solid–liquid system at elevated temperatures followed by the partial separation of the phases and their subsequent analysis.

(a) **Apparatus.**—The high temperature filtration method which yielded a partial separation of the solid and liquid phases, after equilibrium with respect to the distribution of the rare earth ions has been attained, was described in the previous paper.[3] The apparatus was modified slightly so that two runs could be made simultaneously. A calibrated chromel–alumel couple was placed directly beneath each set of nickel crucibles. The temperature during any run was constant to ±5° and the temperatures reported in the results are rounded off to the nearest 5°.

(b) **Materials.**—The radioactive europium used was the same as that previously described.[10] Europium(III) chloride solutions can be reduced by amalgamated zinc and the resulting divalent europium can be coprecipitated with strontium sulfate.[11] This procedure was followed using a solution of strontium chloride in 0.1 *N* hydrochloric acid to which had been added appropriate amounts of radio-europium chloride and non-radioactive europium chloride. This mixture was passed through a Jones reductor into a dilute solution of sulfuric acid. The low radioactivity of the supernatant liquid showed that the coprecipitation was essentially complete. The precipitated sulfate was washed with hot water until free of chloride, dried and reduced to the sulfide in a stream of purified hydrogen at 1000°. The product had a deep orange color and showed the orange fluorescence and phosphorescence, upon excitation with ultraviolet radiation, characteristic of the phosphor formed by heating together at 1000° strontium sulfide, strontium chloride and europium(III) chloride in microquantities. We thus have here additional evidence that the sulfide ion can reduce europium(III) at elevated temperatures.

The solid solutions (Sr,Eu)Se were prepared in a somewhat similar manner. $(\mathrm{Sr,Eu})\mathrm{SeO_3}$ was, in this case, precipitated from an alkaline solution of ammonium selenite. The selenite was reduced in a stream of ammonia at 830° followed by treatment with ammonia and selenium vapors at the same temperature. The resulting selenide was light yellow and had a yellow fluorescence and phosphorescence. Thus it also resembled the product resulting from heating together strontium selenide, strontium chloride and europium(III) chloride.

(c) **Analysis of Filtrate and Residue.**—The quantity K_{T} defined by the first factor in equation (4) can be expressed in terms of values obtained upon the analysis of the residue and filtrate resulting from the high temperature filtration as follows

$$K_{\mathrm{T}} = (C'/C) - (N'_{\mathrm{Cl}}/N_{\mathrm{Cl}})/(N'_{\mathrm{Sr}}/N_{\mathrm{Sr}}) - (N'_{\mathrm{Cl}}/N_{\mathrm{Cl}}) \qquad (6)$$

The primed quantities refer to the residue and the unprimed ones to the filtrate.

C = corrected counts per minute per 0.1 g. of filtrate
N_{Cl} = moles of chloride in 0.1 g. of filtrate
N_{Sr} = moles of strontium in 0.1 g. of filtrate

The method used for the determination of the necessary analytical quantities has been described.[3]

Results

In all experiments the amount of strontium sulfide or selenide was kept constant at 1.40 g. The total quantity of strontium chloride plus strontium oxide was also kept constant at 0.0340

TABLE I

TOTAL EUROPIUM PRESENT IN EACH SAMPLE = 1.44 × 10^{-4} G.

R	C'/C	$N'_{\mathrm{Cl}}/N_{\mathrm{Cl}}$	$N'_{\mathrm{Sr}}/N_{\mathrm{Sr}}$	Temp., °C.	K_{T}
0.000	1.810	0.662	1.072	1000	2.80
.000	2.077	.627	1.172	1000	2.68
.000	1.961	.641	1.133	1005	2.68
				Average	2.72 ± 0.03
.170	0.789	.613	1.141	985	2.23
.170	1.700	.624	1.126	1000	2.12
.170	1.934	.668	1.166	990	2.54
				Average	2.30 ± 0.09
.383	1.367	.695	1.042	1010	1.94
.383	1.385	.683	1.031	1010	2.02
.383	1.644	.643	1.111	1010	2.12
				Average	2.03 ± 0.04

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(10) R. W. Mason, C. F. Hiskey and R. Ward, THIS JOURNAL, **71**, 509 (1949).

(11) H. N. McCoy, *ibid.*, **61**, 2455 (1939).

mole, and only the ratio of the number of moles of oxide to chloride was varied.

These ratios are listed under the heading R in the tables. The duration of heating at the elevated temperatures was varied from 1.5 to 4.0 hours and since the values of K_T obtained were the same within the limits of precision of the method it is clear that equilibrium is established rapidly in these systems.

(a) The distribution of the europium(II) in the system $(\mathrm{SrS})_{\mathrm{Solid}}$–$(\mathrm{SrCl_2}$–SrO–dissolved $\mathrm{SrS})_{\mathrm{Liquid}}$ as a function of the composition of the liquid phase.

(b) The distribution of europium(II) in the system $(\mathrm{SrSe})_{\mathrm{Solid}}$–$(\mathrm{SrCl_2}$–SrO–dissolved $\mathrm{SrSe})_{\mathrm{Liquid}}$ as a function of the composition of the liquid phase.

TABLE II

TOTAL QUANTITY OF EUROPIUM PRESENT IN EACH SAMPLE = 1.44 × 10^{-4} G.

R	C'/C	$N'_{\mathrm{Cl}}/N_{\mathrm{Cl}}$	$N'_{\mathrm{Sr}}/N_{\mathrm{Sr}}$	Temp., °C.	K_T
0.000	1.727	0.514	0.977	1025	2.62
.170	1.567	.482	.993	1035	2.12
.383	1.122	.632	.982	1035	1.40
.383	1.330	.509	.926	1025	1.92
				Average	1.69 ± 0.02

(c) The distribution of europium(II) in the system $(\mathrm{SrS})_{\mathrm{Solid}}$–$(\mathrm{SrCl_2}$–SrO–dissolved $\mathrm{SrS})_{\mathrm{Liquid}}$ as a function of temperature.

TABLE III

TOTAL QUANTITY OF EUROPIUM PRESENT IN EACH SAMPLE = 1.44 × 10^{-4} G.

R	C'/C	$N'_{\mathrm{Cl}}/N_{\mathrm{Cl}}$	$N'_{\mathrm{Sr}}/N_{\mathrm{Sr}}$	Temp., °C.	K_T
0.000	1.899	0.706	1.122	905	2.85
.000	(From Table I)			1000–1005	2.72
.000	1.842	.667	1.095	1030	2.68
.000	1.862	.618	1.128	1095	2.44
.000	1.975	.538	1.167	1105	2.29
.383	(From Table I)			1010	2.03
.383	1.518	.605	1.093	1040	1.87
.383	1.159	.630	1.056	1050	1.24
.383	1.182	.538	1.130	1100	1.09
.383	1.178	.549	1.034	1115	1.30

(d) The distribution of europium(II) in the system $(\mathrm{SrS})_{\mathrm{Solid}}$–$(\mathrm{SrCl_2}$–SrO–dissolved $\mathrm{SrS})_{\mathrm{Liquid}}$ at a higher europium concentration.

TABLE IV

TOTAL QUANTITY OF EUROPIUM PRESENT IN EACH SAMPLE = 1.40 × 10^{-2} G.

R	C'/C	$N'_{\mathrm{Cl}}N/N_{\mathrm{Cl}}$	$N'_{\mathrm{Sr}}/N_{\mathrm{Sr}}$	Temp., °C.	K_T
0.000	1.318	0.860	1.052	1000	2.39
.383	1.405	.665	1.092	1005	1.74
.383	1.182	.769	1.019	1010	1.65
.383	1.401	.714	1.082	1005	1.86
				Average	1.75 ± 0.04

Discussion

The results listed in Table I indicate that the value of K_T decreased by about twenty-five per cent. as the oxide content rose from zero to a value almost sufficient to saturate the liquid phase. At 1000° saturation of fused strontium chloride by strontium oxide corresponds to a value of R equal to 0.47. It has been shown[3] that, at a value of R equal to only 0.170, K_T for both the SrS–$\mathrm{Ce_2S_3}$ and SrS–$\mathrm{Sm_2S_3}$ systems had fallen to extremely low values. A similar behavior is exhibited by the systems involving cerium and samarium with strontium selenide as a solid phase. From the results given in the previous paper for the distribution of europium we note an additional fact. When europium was introduced originally, either as a trivalent ion or as a divalent ion, the values of K_T for $R = 0$ were the same. As R increases to 0.383, however, the values of K_T seem to be slightly lower for those runs in which europium was introduced as the trivalent ion. This may be due to the stabilization of the europium (III) by oxide ion when it is present in the liquid phase. It may be that the one hour of heating was insufficient time to establish equilibrium. In general, the results of the distribution experiments confirm other evidence which indicates that europium is incorporated as a divalent ion in strontium sulfide or selenide phosphors.

The results on the temperature dependence of the distribution given in Table III show that K_T decreases slightly as the temperature increases. From the formulation of K_T it represents the equilibrium constant for the reaction $\mathrm{Sr^{+2}(l)} + \mathrm{Eu^{+2}(s)} \leftrightarrow \mathrm{Sr^{+2}(s)} + \mathrm{Eu^{+2}(l)}$, where (s) and (l) refer to the solid and liquid phases. Because of the similarity between the strontium(II) and europium(II) ions we would not expect K_T to vary much with temperature. The small range of temperatures over which determinations were possible did not permit the calculation of any heat of reaction. It would be of some interest to determine the temperature variation of the distribution of the trivalent ions, cerium and samarium.

At the higher europium concentrations the results given in Table IV indicate that the values of K_T are somewhat smaller for the same values of R than they are for the lower europium concentrations. Whether this is a real effect or is due to non-equilibrium conditions we cannot at present say.

Summary

The distribution of europium(II) between strontium sulfide or selenide and a liquid phase consisting of fused strontium chloride containing dissolved strontium sulfide or selenide and varying amounts of strontium oxide has been investigated. The distribution is less sensitive to strontium oxide than is the distribution of cerium and samarium. A thermodynamic treatment indicates that the distribution of a divalent ion similar in size to strontium should be independent of com-

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.

BROOKLYN, N. Y. RECEIVED NOVEMBER 23, 1949

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