and related systems involving alums and picromerites, it will be shown that all the picromerite systems so far studied are probably of Type II, showing to some degree a tendency toward positive deviations from ideality in the solid state. In this respect the picromerites of the present report, involving chromates and selenates besides sulfates, show, as expected, the most pronounced deviations and the greatest disagreement between the observed and the calculated distribution ratios.

Summary

1. The ternary systems $MgCrO_4$–$(NH_4)_2CrO_4$–H_2O and $MgSeO_4$–K_2SeO_4–H_2O, involving, respectively, the formation of the double salts $Mg(NH_4)_2(CrO_4)_2 \cdot 6H_2O$ and $MgK_2(SeO_4)_2 \cdot 6H_2O$, were studied at 25°.

2. The following ternary systems were also studied at 25°: $Mg(NH_4)_2(CrO_4)_2$–$Mg(NH_4)_2(SO_4)_2$–H_2O, $Mg(NH_4)_2(SO_4)_2$–$Mg(NH_4)_2(SeO_4)_2$–H_2O, $Mg(NH_4)_2(CrO_4)_2$–$Mg(NH_4)_2(SeO_4)_2$–H_2O, $Mg(NH_4)_2(SeO_4)_2$–$MgK_2(SeO_4)_2$–H_2O.

Continuous series of solid solutions were found in each case.

3. The results are considered from the point of view of the Roozeboom classification of solid solutions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NEW YORK UNIVERSITY]

Distribution of Isomorphous Salts in Solubility Equilibrium between Liquid and Solid Phases

BY ARTHUR E. HILL,[1] GEORGE S. DURHAM[2] AND JOHN E. RICCI

Several reports already have been published from this Laboratory on the experimental investigation of the equilibrium relations between solid solutions of isomorphous salts and their saturated aqueous solutions. The cases studied cover a number of pairs of alums,[3,4] in which one of the cations was varied, and a number of pairs of picromerites[5,6,7] (or schoenites), hexahydrated double sulfates, selenates or chromates of a univalent and a bivalent cation, in which again one of the ions was varied, to produce mixed crystals. The distribution of the isomorphous salts between liquid and solid phases in these systems was also studied for the purpose of assigning them to the proper type of solid solutions in the Roozeboom classification.[8] The present report is an attempt to account theoretically for the observed distribution, and to correlate this distribution quantitatively to some extent with the aqueous molar solubilities of the individual salts. The relations derived have been tested on what are believed to be probably the best data available on the equilibrium relations between solid solutions of isomorphous salts and their saturated aqueous solutions.[3–7] These measurements are in general quite reliable not only in respect to the precision and accuracy of the determinations, but also in respect to the question of the attainment of equilibrium, for which a special technique was used. It is felt therefore that whatever regularities can be shown to exist on the basis of these experimental observations, must have some significance which must be worth the attempt at interpretation.

The Roozeboom Classification

Roozeboom[8] classified systems of two isomorphous salts, A and B, varying in respect to only one ion so that with water they constitute ternary systems, and forming between themselves continuous solid solutions, into three types, depending on the relative distribution of the salts between liquid and solid phases. Calculating concentrations, whether in the liquid or in the solid phase, on the basis of the total salts present in the phase, disregarding the water, Roozeboom plotted the mole fraction of one salt, A, in the liquid phase, as y, against its mole fraction in the solid phase, as x, using the familiar type of rectangular diagram introduced by him. If the mole fraction of one of the salts, let us say A, is always greater in the liquid than in the solid phase, over the entire

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[1] This paper is being published, following the death of Professor Hill, by his collaborators; although originally submitted for publication March 18, 1940, it was rewritten to include the newer data of Ref. 7.

[2] The material of this article is taken (in part) from a thesis presented by G. S. Durham for the degree of Doctor of Philosophy at New York University, June, 1939.

[3] Hill and Kaplan, THIS JOURNAL, **60**, 550 (1938).

[4] Hill, Smith and Ricci, *ibid.*, **62**, 858 (1940).

[5] Hill and Taylor, *ibid.*, **60**, 1099 (1938).

[6] Hill, Durham and Ricci, *ibid.*, **62**, 1031 (1940).

[7] Hill, Soth and Ricci, *ibid.*, **62**, 2717 (1940).

[8] Roozeboom, *Z. physik. Chem.*, **8**, 521 (1891).

range of concentration of the system, the distribution is represented by curve I of Fig. 1, in which y is always greater than x; this is Roozeboom's Type I. If, the solid solution still remaining continuous, y for the salt A is greater than x over the lower range of concentrations (of A) and then becomes smaller than x for the range of concentrations approaching pure A, we have the distribution curve II of Fig. 1, or Type II of Roozeboom's classification. Finally, if the reverse is true, and with continuous solid solution, y begins as smaller than x at low concentrations of A, the curve crossing over as in Case III of Fig. 1, so that y is greater than x at high proportions of A, the system belongs to Type III of Roozeboom's classification.

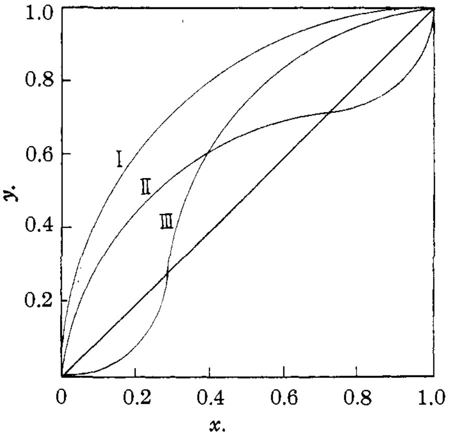

Fig. 1.—Distribution of two salts, A and B, forming continuous solid solution: x is mole fraction of A in solid phase; y is mole fraction of A in liquid phase (disregarding water).

The contrasting types, II and III, may also be distinguished, if the behavior underlying the phenomenon is sufficiently marked, by means of the ordinary mode of representation of ternary systems, on the Gibbs triangular diagram. This is possible on the basis of the disposition of the tie-lines connecting the compositions of the saturated liquid solution and the saturating solid phase. The tie-lines in systems of Type I would show no tendency to converge on either the liquid or the solid curve. Tie-lines of Type II would tend to converge on the liquid curve, leading, in extreme cases of Type II, to the formation of an isothermally invariant liquid phase in equilibrium with two solid phases, or discontinuous solid solution; this would result in Roozeboom's type IV, or possibly V. Tie-lines of Type III systems would tend to converge on the solid solution curve, leading finally to the formation of a definite solid compound between the two components.

On the basis of simple examination of such ternary tie-lines and of the kind of distribution curves illustrated in Fig. 1, all the systems studied with the exception of the systems involving the two picromerites $Mg(NH_4)_2(SeO_4)_2$ and $Mg(NH_4)_2(SO_4)_2$, appeared, as stated in the individual publications describing them, to fall in Type I of the Roozeboom classification. The number of experimental points obtained for any one system, however, is not sufficient to rule out the possibility at the extremities of the diagrams, of a crossing over of the y–x curve into Type II or III.

The Distribution Function

Two observations were made in the course of the preliminary work. The first is that the relation of y to x could in general be expressed with considerable accuracy by the equation, advanced empirically

$$y = x^m \qquad (1)$$

in which m is a positive constant, smaller than one. and characteristic for each system.[5] The second was that the distribution depended in some way on the ratio of the aqueous solubilities of the two salts involved in each system; since the systems studied belonged, almost without exception, apparently to Type I of the Roozeboom classification, it appeared that the salt with the higher aqueous solubility in molar units was generally present in higher proportion in the liquid than in the solid phase at equilibrium, over the whole range of concentration covered. We are here attempting therefore to derive some relation which will yield a distribution equation approximately of the form of equation (1), and in which the molar solubilities will be taken into account in the form of a distribution constant.

It is possible, with the aid of certain assumptions which appear reasonable, to derive from thermodynamic considerations a relation connecting the ratio of the activities of the two salts in the liquid phase, the same ratio in the solid phase and the solubilities of the pure salts.

In a system of two phases, the chemical potentials and hence the activities of each component must be the same at equilibrium, in the two phases. In the first place, inasmuch as we are dealing with strong electrolytes, the solid phase (mixed crystals) will be treated as though the electrolytes were completely ionized in the solid phase just as in the liquid solution. An infinitely dilute solution of each salt will be taken as the standard state for the liquid, and the pure salt for the solid phase.

We shall consider a system of water and two isomorphous salts, distinguished by the subscripts 1 and 2, the salt "1" being always that with the higher aqueous molar solubility. The general formula for the salts may be $\mathrm{B}_b\mathrm{C}_c\mathrm{D}_d \ldots$ for salt 1, and $\mathrm{B'}_b\mathrm{C}_c\mathrm{D}_d \ldots$ for salt 2, so that they can form a continuous series of solid solutions by the interchange of the ions B and B′.

Equilibrium between the solid phase and its aqueous solution requires, for either salt

$$a_l = ka_s \qquad (2)$$

where a is activity, k a proportionality constant necessary because of the choice of two standard states, and the subscripts l and s refer, here and throughout, to the liquid and solid phases, respectively.

From a consideration of the equilibrium between the pure salt and water, where $a_s = 1$, k can be evaluated and expressed as the activity product constant of the salt, or K_a.

Writing out equation (2) for each salt in terms of ionic activities, and substituting the value K_a for k, we have

$$(a_{\mathrm{B}}^b\ a_{\mathrm{C}}^c\ a_{\mathrm{D}}^d\ \ldots)_l = K_{a_1}\ (a_{\mathrm{B}}^b\ a_{\mathrm{C}}^c\ a_{\mathrm{D}}^d\ \ldots)_s \qquad (3)$$

and

$$(a_{\mathrm{B}'}\ a_{\mathrm{C}}^c\ a_{\mathrm{D}}^d\ \ldots)_l = K_{a_2}\ (a_{\mathrm{B}'}^b\ a_{\mathrm{C}}^c\ a_{\mathrm{D}}^d\ \ldots)_s \qquad (4)$$

If both salts are present together (as in mixed crystals in equilibrium with the aqueous solution), these relations are still valid. An expression involving the ratio of the activities of the two salts in the liquid phase and a similar ratio in the solid phase is then obtained by dividing equation (3) by equation (4). Since the two salts have been assumed to differ with respect to the ion B only, the activities of the other ions will cancel, leading to

$$\left(\frac{a_{\mathrm{B}}}{a_{\mathrm{B}'}}\right)_l^b = \frac{K_{a_1}}{K_{a_2}}\left(\frac{a_{\mathrm{B}}}{a_{\mathrm{B}'}}\right)_s^b \qquad (5)$$

Introducing concentrations and activity coefficients in place of activities, and setting R_l and R_s equal to the mole ratio of the ions, [B]/[B′], in the liquid and solid phases, respectively, then

$$R_l\left(\frac{f_{\mathrm{B}}}{f_{\mathrm{B}'}}\right)_l = \left(\frac{K_{a_1}}{K_{a_2}}\right)^{1/b} R_s\left(\frac{f_{\mathrm{B}}}{f_{\mathrm{B}'}}\right)_s \qquad (6)$$

where f is activity coefficient.

Since the ionic atmosphere in these equilibrium aqueous solutions will always be identical for the two ions B and B′, and since these ions are, moreover, for pairs of isomorphous alums or picromerites, of necessity closely similar to each other, having the same charge and approximately the same size, it will be assumed, for all the subsequent considerations, that the ratio $(f_{\mathrm{B}}/f_{\mathrm{B}'})_l = 1$. With this limitation in mind, we shall then speak of the following equation (7) as the "theoretical" equation for the distribution ratio, R_l/R_s

$$R_l/R_s = K(f_{\mathrm{B}}/f_{\mathrm{B}'})_s \qquad (7)$$

where K represents the function, $(K_{a_1}/K_{a_2})^{1/b}$, of the activity products.

This ratio R_l/R_s will be a constant, and equal to K itself, when the solid solution is sufficiently ideal so that $(f_{\mathrm{B}}/f_{\mathrm{B}'})_s$ may be taken as equal to 1, and independent of the composition of the mixed crystals. To test at least the constancy of the ratio immediately, Table I gives the values of log R_l, log R_s and log (R_l/R_s), for all the systems studied, together with the mole fraction, x, of the more soluble salt in the solid phase.

A substantial constancy of the distribution ratio, R_l/R_s, independent of the concentration, is observed for the alum systems as a group; but not for the picromerites. As already anticipated, therefore, on the basis of the Roozeboom plots, the alums are apparently very nearly ideal in their solid solutions, whereas the picromerites, as suggested by the curves of systems P-10 and P-11, are distinctly non-ideal.

The constancy in the case of the alums is rather poor for the system A-1, $\mathrm{NH_4Fe(SO_4)_2}$–$\mathrm{NH_4Al(SO_4)_2}$. This is the only alum system in which the tervalent cation is being interchanged, and was also one of the first systems to be studied, so that the experimental uncertainty involved may be somewhat greater than for those studied later. It must be realized in this connection that the criterion of constancy of the distribution ratio is a very severe one, and brings out irregularities which are not detectable in the usual ways of plotting such ternary equilibria.

The deviations from constancy in the case of the picromerite systems is not random, but suggests rather some regular change in the ratio R_l/R_s with composition; the distribution ratio, so expressed, falls off in every case as the proportion of the more soluble salt in the solid phase increases. This suggested that these systems, though not ideal, might be examples of "regular" solutions in the

TABLE I[a]

DEPENDENCE OF THE DISTRIBUTION RATIO, R_l/R_s, ON THE COMPOSITION OF THE SOLID PHASE

System[b]	Log R_l	Log R_s	Log (R_l/R_s)	x
		Alums		
A-1 $NH_4\frac{Fe}{Al}(SO_4)_2$	(+0.117)[c]	(−2.16)	2.277	0.007
	.542	−1.10	1.642	.073
	.877	−0.661	1.538	.179
	1.25	− .284	1.534	.342
	1.54	− .081	1.621	.453
	(1.92)[c]	(+ .053)	1.87	.531
A-2 $\frac{NH_4}{K}Al(SO_4)_2$	−0.445	− .429	−0.016	.264
	+ .020	+ .023	− .003	.512
	+ .471	+ .553	− .082	.781
A-3 $\frac{NH_4}{K}Cr(SO_4)_2$	− .380	− .585	.205	.233
	.106	− .110	.216	.474
	.364	.152	.212	.627
	.662	.465	.197	.774
	1.14	.960	.180	.914
A-4 $\frac{NH_4}{Tl}Al(SO_4)_2$	−0.656	−1.06	.404	.181
	− .107	−0.551	.444	.488
	.210	− .192	.402	.618
	.468	.068	.400	.747
	.743	.375	.368	.847
	1.14	.769	.371	.932
A-5 $\frac{K}{Tl}Al(SO_4)_2$	−0.008	− .411	.404	.276
	.403	.017	.386	.509
	.818	.447	.371	.737
	1.40	1.05	.35	.918
		Picromerites		
P-1 $\frac{Cu}{Zn}(NH_4)_2(SO_4)_2$	(−0.329)[c]	(−1.36)	1.03	0.042
	.066	−0.476	0.542	.225
	.238	− .281	.519	.344
	.465	.004	.461	.503
	.802	.377	.425	.704
P-2 $\frac{Zn}{Ni}(NH_4)_2(SO_4)_2$	− .470	−1.08	.610	.077
	.114	−0.638	.752	.187
	.408	− .205	.613	.384
	.575	− .003	.578	.498
	.778	.204	.574	.616
P-3 $\frac{Cu}{Ni}(NH_4)_2(SO_4)_2$	(− .035)[c]	(−1.15)	1.115	.066
	.553	−0.697	1.250	.159
	.950	− .267	1.207	.351
	1.20	− .016	1.216	.491
	1.40	.288	1.112	.660
P-4 $\frac{Mg}{Cu}(NH_4)_2(SO_4)_2$	−0.718	− .919	0.201	.108
	− .272	− .407	.135	.282
	.088	− .002	.090	.499
	.291	.234	.057	.632
	.661	.637	.024	.813
P-5 $\frac{Cu}{Ni}K_2(SO_4)_2$	− .170	− .782	.612	.142
	.210	− .385	.595	.292
	.464	− .112	.576	.436
	.709	.162	.547	.592
	1.109	.643	.466	.815
P-6 $\frac{Co}{Cu}K_2(SO_4)_2$	−0.443	− .807	.364	.136
	− .062	− .384	.322	.292
	.224	− .070	.294	.460
	.522	.261	.261	.646
	.955	.722	.233	.841

TABLE I[a] (*Concluded*)

System[b]	Log R_l	Log R_s	Log (R_l/R_s)	x
P-7 $\frac{Zn}{Cu}$ $K_2(SO_4)_2$	−0.499	−0.697	0.198	0.167
	− .134	− .280	.146	.344
	.144	.031	.113	.518
	.450	.365	.085	.699
	.898	.835	.053	.873
P-8 $\frac{Zn}{Ni}$ $K_2(SO_4)_2$	.015	− .664	.679	.178
	.345	− .327	.672	.320
	.660	− .007	.667	.496
	.949	.289	.660	.660
	1.359	.727	.632	.842
P-9 Cu $\frac{(NH_4)_2}{K_2}$ $(SO_4)_2$	−0.284	− .807	.523	.135
	.088	− .362	.450	.303
	.324	.073	.397	.458
	.673	.300	.373	.666
	.940	.601	.339	.800
P-10 $Mg(NH_4)_2$ $\frac{(SO_4)_2}{(CrO_4)_2}$	− .206	− .677	.471	.174
	.179	− .187	.366	.394
	.394	.107	.287	.561
	.708	.554	.154	.782
	.991	.903	.088	.889
P-11 $Mg(NH_4)_2$ $\frac{(SeO_4)_2}{(SO_4)_2}$	− .508	− .855	.347	.123
	− .137	− .415	.278	.278
	.182	.000	.182	.500
	.234	.064	.170	.537
	.465	.399	.066	.715
	.735	.772	− .037	.856
P-12 $Mg(NH_4)_2$ $\frac{(SeO_4)_2}{(CrO_4)_2}$	− .215	− .775	.560	.144
	.241	− .276	.517	.346
	.616	.121	.495	.569
	.904	.442	.462	.734
	1.227	.786	.441	.859
P-13 Mg $\frac{K_2}{(NH_4)_2}$ $(SeO_4)_2$	−0.554	− .970	.416	.097
	− .153	− .556	.403	.218
	.127	− .252	.379	.359
	.304	− .056	.360	.468
	.449	.133	.316	.576

[a] This table is taken in part from the doctorate thesis of G. C. Soth, New York University, June, 1940. [b] Systems A-1, 2: Ref. 3; A-3, 4, 5: Ref. 4; P-1, 2, 3: Ref. 5; P-4–9: Ref. 6; P-10–13: Ref. 7. [c] Omitted in plotting Figs. 4 and 5. In some of the first systems investigated, the straight line relationship brought out in Figs. 4 and 5 is not perfect, and the four isolated points here indicated have been omitted in preparing the diagrams.

sense of Hildebrand's definition.[9] The actual dependence of the ratio, R_l/R_s, on the composition of the solid phase, in these systems, however, is not what would be expected for "regular" solutions. The observed dependence is typified in Fig. 2, which represents the systems P-6 and P-10. Hildebrand's theory of "regular" solutions demands that the function log (R_l/R_s) should vary linearly with the mole fraction composition of the solid phase,[10] according to the equation[11]

$$\log (R_l/R_s) = \log K + \frac{0.4343}{RT} \frac{H}{N_1N_2} (2N_2 - 1) \quad (8)$$

where R and T have their usual significance and

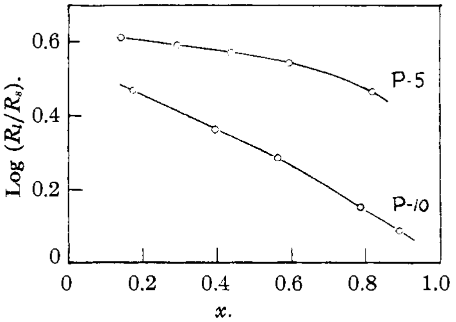

Fig. 2.—Dependence of log (R_l/R_s) on composition of solid phase, in picromerite systems: x is mole fraction of more soluble salt, in solid phase; systems: P-5, (Cu, Ni)$K_2(SO_4)_2$; P-10, $Mg(NH_2)_2(CrO_4,SO_4)_2$.

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[9] J. H. Hildebrand, "Solubility of Non-Electrolytes," A. C. S. Monograph, Second edition, Reinhold Publishing Company, New York, N. Y., 1936, p. 65.

[10] Flood and Bruun, *Z. anorg. allgem. Chem.*, **229**, 85 (1936).

[11] Yutzy and Kolthoff, THIS JOURNAL, **59**, 916 (1937).

H is the heat of mixing per mole, for the formation of the solid solution having the mole fractions N_1 and N_2, respectively, of the two salts.

Although it is possible that the curves of Fig. 2 might be considered linear, within the experimental errors of the functions plotted, the possibility was not pursued further in the present considerations, in the absence of data which could be used to verify the slope of the curves, and in view of the corresponding study, by others, of the system AgCl–AgBr–H_2O. For this system, involving very insoluble salts, Flood and Bruun[10] pointed out that the following equation (which is an approximate form of equation 7) should hold, assuming, in addition, ideal solid solution to be formed between silver chloride and silver bromide:

$$\frac{[\mathrm{Cl}^-]_l}{[\mathrm{Br}^-]_l} = K' \frac{[\mathrm{Cl}^-]_s}{[\mathrm{Br}^-]_s} \qquad (9)$$

In this expression K' should be the ratio of the ordinary solubility products of the two halides. At 98° the observed value of K' for this system was found to be approximately constant;[11] but at lower temperatures,[12] although still approximately equal to the solubility product ratio, K' varied more or less linearly with the mole fraction of silver bromide in the crystals, apparently because of the non-ideality of the solid solution. From the approximate linearity, Flood and Bruun concluded that the mixed crystals of silver chloride and silver bromide were probably an example of Hildebrand's "regular" solutions. Yutzy and Kolthoff however questioned this, and showed, by their more complete study of the system, that despite the approximate linearity of the observed relation, the slope did not agree with that calculated from known heats of solution of the solid phase,[13] so that the linearity was therefore probably accidental.

The data for all the present systems were therefore considered on the basis of the "theoretical" equation, no. 7, which has now to be examined further.

The constancy of the distribution ratio observed in the case of the alums is not sufficient as a verification of this equation, unless the value of the constant so obtained is compared with the values derived independently from the ratio $(K_{a_1}/K_{a_2})^{1/b}$. Although the actual mean ionic activity coefficients of these salts at saturation, f^0_1 and f^0_2, and hence the activity products themselves, are not known, it was found possible to estimate the desired ratio of these products.

$$K = \left(\frac{K_{a_1}}{K_{a_2}}\right)^{1/b} = \left(\frac{S_1 f^0_1}{S_2 f^0_2}\right)^{\nu/b} \qquad (10)$$

where S is aqueous solubility (molarity) and ν is total number of ions formed from one molecule of the electrolyte.

In the case of very insoluble substances, the ratio f^0_1/f^0_2 may be taken as 1, and a simplified constant, equal to the ratio of the solubility products, as in equation (9), should apply. Such an equation, as already stated, was tried, with only partial success, in the system AgCl–AgBr–H_2O. The same kind of approximate equation, ignoring all the activity coefficients, has been applied to the distribution of chromate ion between barium sulfate–chromate and aqueous solution,[14] and to the distribution of lead ion between barium–lead sulfate and aqueous solution[15]; in neither case, however, was the equation in satisfactory agreement with the experimental data, except over short, limited ranges of the ratio of the interchanging ions.

In the case of the picromerites and alums, with relatively high solubilities, the ratio f^0_1/f^0_2 will not in general equal 1, and therefore cannot be ignored. If we assume however that the activity coefficient of such complex sulfates depends in such a way upon the concentration of the solution that the simple type of substitution of a single ion such as is here being studied does not materially change the dependence of the activity coefficient on the ionic strength, then it should be possible to express the ratio f^0_1/f^0_2 in terms of the separate molar solubilities of the two salts concerned. An examination of the activity coefficients for a number of bivalent metal sulfates reveals, empirically, that the activity coefficients of these salts vary inversely as the square root of the ionic strength over the concentration range with which we are here concerned, namely, $\sqrt{\mu} = 1.5$ to $\sqrt{\mu} = 2.5$; thus if f is plotted against $1/\sqrt{\mu}$ in this range, a straight line results extrapolating roughly to $f = 0$ at $1/\sqrt{\mu} = 0$. Using the data for copper, zinc, nickel, cadmium, magnesium and manganese sulfates[16] listed in Table II and plotted in Fig. 3, the relation between f and μ in the range of concentration mentioned, is, approximately, the following

$$f = A + B/\sqrt{\mu} \qquad (11)$$

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[12] (a) Flood and Bruun, ref. 10, using the data of Küster, *Z. anorg. allgem. Chem.*, **19**, 81 (1899); (b) Yutzy and Kolthoff, ref. 11.

[13] Eastman and Milner, *J. Chem. Phys.*, **1**, 444 (1933).

[14] Kolthoff and Noponen, THIS JOURNAL, **60**, 39 (1938).

[15] Kolthoff and Noponen, *ibid.*, **60**, 197 (1938).

[16] Robinson and Jones, *ibid.*, **58**, 959 (1936).

TABLE II

MEAN ACTIVITY COEFFICIENT, f, FOR SOME SULFATES

$\sqrt{\mu}$	1.27	1.41	1.69	2.00	2.45	A	B
$CuSO_4$	0.077	0.068	0.056	0.047	0.040[a]	-0.003	0.103
$ZnSO_4$	.077	.068	.057	.047	.038	- .001	.103
$NiSO_4$	.086	.075	.062	.051	.041	- .006	.118
$CdSO_4$	.077	.067	.055	.046	.038	- .002	.103
$MgSO_4$	.099	.088	.075	.064	.056	+ .009	.113
$MnSO_4$	.120	.106	.088	.073	.061	- .002	.155

[a] At $\sqrt{\mu} = 2.33$.

in which A is very small, having the value 0.004 (±0.002), and in which B is approximately constant for at least the first five salts mentioned, having the value 0.108 (±0.006), manganese sulfate being exceptional, with $B = 0.155$. The individual values of A and B for the sulfates cited are included in Table II. Although no data are available for the tervalent metal sulfates and very few for the univalent, it will be assumed that a similar relation may hold at least approximately in all these cases. Ignoring A and small differences in B, it may be assumed, on the basis of this information, that for such cases $f^0_1/f^0_2 = \sqrt{\mu_2}/\sqrt{\mu_1}$. It is then possible to substitute $\sqrt{S_2}/\sqrt{S_1}$ (neglecting again small relative differences in transforming from the molal concentrations of Robinson and Jones[16] to molar solubilities) for the ratio f_1^0/f_2^0 in equation (10) with the following result

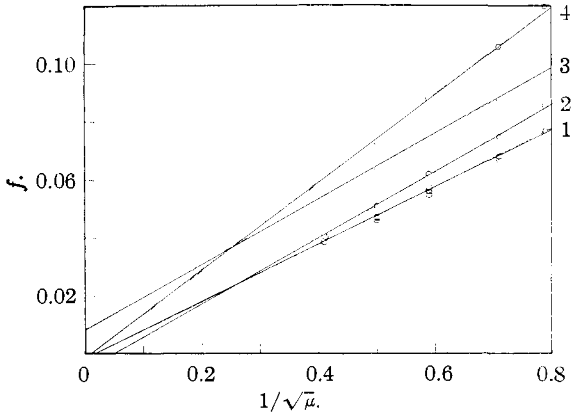

Fig. 3.—Activity coefficients of some sulfates: (1) Cu, Zn, Cd; (2) Ni; (3) Mg; (4) Mn.

$$K \cong \left(\frac{S_1}{S_2}\right)^{\nu/2b} \qquad (12)$$

Thus, the "calculated" value of the distribution constant for sulfate systems sufficiently ideal so that $(f_1/f_2)_s$ may be taken equal to 1 can then be compared with the observed constant. The observed may be determined either as the mean of the values of R_l/R_s in Table I, or graphically, from the plot of equation (7) in the useful logarithmic form

$$\log R_l = \log K + \log R_s + \log (f_1/f_2)_s \qquad (13)$$

With ideal solid solution, the last term equals zero, giving

$$\log R_l = \log K + \log R_s \qquad (14)$$

Log K is then given by the intercept of log R_l at log $R_s = 0$. The alum systems, plotted according to equation (14), are shown in Fig. 4, from which the "observed" values of log K, shown in Table III-A, are derived. In the same table the "calculated" value of log $K = (S_1/S_2)^2$, which is the value of the expression $(S_1/S_2)^{\nu/2b}$ for the alums when either of the cations is varied; the formula would be (S_1/S_2) for the variation of the anion.

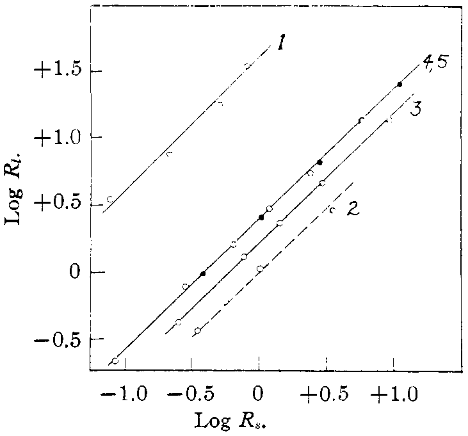

Fig. 4.—Distribution in alum systems (systems A, 1–5, of Table I).

The agreement between the observed and calculated values of log K is very close, considering the assumptions and approximations involved. The constancy of the distribution ratio, and the agreement of the observed value of the ratio with the value calculated as just explained, are results indicating that the alum solid solutions must evidently be very nearly ideal. Independent confirmation of this ideality, at least for one of these alum systems, has recently been obtained by Klug

TABLE III

APPLICATION OF EQUATION (15)

System	m	Log K Obsd.	Log K Calcd.	K, formula
		A. Alums		
A-1	0.98	1.58	1.51	$(S_1/S_2)^2$
A-2	1.00	0.00	0.02	
A-3	0.98	.20	.25	
A-4	1.00	.39	.38	
A-5	0.97	.39	.37	
		B. Picromerites		
P-1	0.87	0.47	0.52	$(S_1/S_2)^{5/2}$
P-2	.91	.60	.62	
P-3	.92	1.19	1.13	
P-4	.89	0.10	0.01	
P-5	.91	.55	.56	
P-6	.90	.31	.35	
P-7	.91	.13	.14	
P-8	.98	.68	.70	
P-9	.88	.41	.42	$(S_1/S_2)^{5/4}$
P-10	.74	.30	.30	
P-11	.78	.17	.06	
P-12	.91	.48	.36	
P-13	.94	.35	.15	

and Alexander,[17] through X-ray analysis of the mixed crystals. These investigators, who are now further examining a number of the solid solutions of alums we are here discussing, have found the mixed crystals of ammonium aluminum alum and potassium aluminum alum (system A-2) to obey Vegard's additivity law, in respect to lattice constant, almost perfectly.[18]

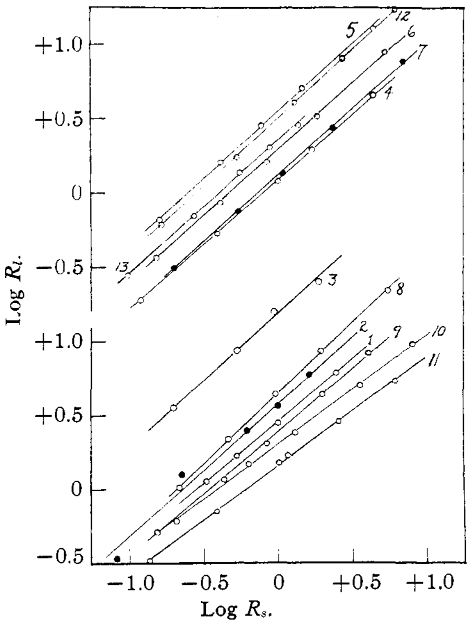

Fig. 5.—Distribution in picromerite systems (systems P, 1-13, of Table I).

As already indicated, the picromerites, on the other hand, cannot be considered ideal in their solid solutions; the value of the distribution ratio, in terms of concentrations, is not constant, and the ratio $(f_1/f_2)_s$ cannot be considered equal to 1. Nevertheless, ignoring for the moment the effect of this ratio of activity coefficients in the solid, and plotting simply log R_l against log R_s as shown in Fig. 5, a marked and significant regularity is revealed. All these systems give very good straight lines for the relation between log R_l and log R_s, but the slope is generally less than 1 rather than 1 as would be demanded by equation (14). Disregarding the very reasonable assumption that $(f_1/f_2)_l = 1$, equation (13), as stated above for the equation in another form, no. 7, is otherwise theoretically exact, and leads, in the ideal case, where $(f_1/f_2)_s = 1$, to equation (14), with a slope of 1 for log R_l or log R_s. As already shown, the alums form systems with distribution ratios which agree with this equation very well: the plots are straight lines, with a slope of 1, and log K, the intercept at $R_s = 1$, agrees with the constant calculated from the appropriate ratio of the activity products of the individual alums. In the case of the picromerites, which are not ideal in their solid solutions, we still obtain very good straight lines, but the slope is less than 1. Since the slope, however, is at least constant for any given system, we can introduce a specific constant, m, to modify equation 14, giving the empirical equation

$$\log R_l = \log K + m \log R_s \qquad (15)$$

It is interesting now to assume that the effect of the term log $(f_1/f_2)_s$ in equation (13), which was ignored in writing equation (14), is represented effectively by this constant m. If this should be true, then log K for these systems, derived graphically from equation (15) at $R_s = 1$, should still be the distribution constant, with the same significance as in the case of the alums. The values of m, of log K (observed, *i. e.*, derived graphically as just explained), and of log K calculated by the formula $K = (S_1/S_2)^{\nu/2b}$, are given for the picro-

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[17] Klug and Alexander, THIS JOURNAL, **62**, 1492 (1940).

[18] It therefore seems plausible to attribute to experimental error (possibly incomplete attainment of equilibrium) the deviations noticeable in the alum systems A-1 and A-2, in respect to constancy of log (R_l/R_s), in Table I, and in respect to the linearity expected in Fig. 4. These were among the first systems studied. The method of promoting the attainment of equilibrium by enclosing in each solubility tube two glass marbles to keep the crystals well ground, as stated in Ref. 4, a suggestion of Dr. C. M. Loucks, formerly of this Department, was then not yet in use.

merites in the second part of Table III. The particular formula for K is $(S_1/S_2)^{5/2}$ for the variation of the bivalent cation, and $(S_1/S_2)^{5/4}$ for the variation of the univalent cation or the anion. It is seen that m is generally less than 1, and that the agreement between the calculated and the observed log K is satisfactory in most cases.

The disagreement is most marked in systems P-11, 12, 13, which involve selenates. It is therefore to be recalled at this point that the empirical approximation used in deriving formula (12) is based on determinations of activity coefficients for sulfates only, and in ionic strengths somewhat lower than those corresponding to the higher solubilities of these selenates. In view of the rather close agreement therefore in the case of the majority of the systems studied, not involving selenates, one may conclude reasonably that the discrepancy in the case of the three systems just mentioned is probably due not to the form of the equation used, but to the approximate estimation of the dependence of the respective mean ionic activity coefficients at saturation for these salts (f^0) upon the ionic strength of the solutions. It may be ventured that if the necessary ratio of these coefficients could be more exactly calculated in terms of concentration ratios, better agreement would be obtained.

Conclusions

In view of the general agreement in log K observed and calculated for these systems in general, both the ideal alum solid solutions, and the non-ideal picromerite systems, the empirical equation (15) must be compared with the "theoretical" equation (13). It follows that

$$m \log R_s = \log R_s(f_1/f_2)_s \qquad (16)$$

and

$$(f_1/f_2)_s = R_s^{m-1} \qquad (17)$$

In these solid solutions, then

$$f_1 = kx_1^{m-1} \qquad (18)$$

where k is a proportionality factor, constant for both components, and x is mole fraction. Also

$$a_1 = kx_1^m \qquad (19)$$

or, the activity of a component is proportional to the m'th power of the concentration, or mole fraction, m being a constant. This relation apparently holds for all these systems over the entire range of concentrations studied, since the lines in Figs. 4 and 5 are quite straight throughout. For the alums, $m = 1$; for the picromerite systems, $m < 1$, being as small as 0.7.

The possible theoretical significance of this relation (19) is not evident. It is simply an experimental result. The constant m is evidently related to the relative attraction or repulsion between the two components in the solid phase. It can easily be shown that the three Roozeboom types of distribution in systems forming continuous solid solutions depend very simply on the value of m. With $m = 1$, the system belongs to Type I; with $m < 1$, the system is of Type II; and with $m > 1$, Type III. This is immediately evident from equation (19), describing the solid phase. With $m = 1$, the system is ideal, and of Type I. Since x is always < 1, then with $m < 1$, a is always $> x$, and the system shows positive deviations from ideality or from Raoult's law, *i. e.*, repulsion; the system then belongs to Type II. With $m > 1$, $a < x$, and the system involves negative deviations from ideality, or attraction, resulting in Type III distribution.

That the alums, with $m = 1$, belong to Type I, is of course evident from the Roozeboom diagrams for the systems (see refs. 3 and 4). The same diagrams for the picromerites (refs. 5–7), however, except in the case of system P-11, in which the experimental curve actually crosses the diagonal, and in the case of system P-10, where the curvature suggests crossing very clearly, would also apparently belong to Type I, and not to Type II as demanded by the values of m, < 1. It has been emphasized, however, in connection with these diagrams, that the experimental data are not sufficient to exclude the possibility of crossing near the extremities of the diagrams.

Writing the equation (15) in the form

$$R_l = KR_s^m \qquad (20)$$

and noting that $R_l = y/(1 - y)$ and $R_s = x/(1 - x)$, where x and y are the units, explained earlier, used in the Roozeboom diagrams, we have

$$\frac{y}{1 - y} = K\left(\frac{x}{1 - x}\right)^m \qquad (21)$$

Consideration of the limits of this equation leads actually to the following cases, depending on the value of m: when $m = 1$, the plot of y against x (Roozeboom diagram) results in a symmetrical curve of Type I of Roozeboom's classification; the initial slope of this curve is then K itself, and the final slope $1/K$. Thus the Roozeboom distribution curve for the system A-2, ammonium aluminum alum and potassium aluminum alum, in which the molar solubilities of the two individual salts are almost identical, is practically coincident with the 45° diagonal (see ref. 3). With $m < 1$, a curve of Type II results, apparently with limiting slopes of infinity at both extremities; with $m > 1$, the curve obtained is that of Type III, with limiting slopes of zero at both extremities. Now although the solid solutions between the picromerites appear, on superficial examination of the isothermal diagrams of the systems (Gibbs triangular phase diagrams and Roozeboom distribution curves) to belong to Type I of the Roozeboom classification, the present considerations, based on the relations of y and x through the parameter m, would demand that the curves, in all cases of $m < 1$, should cross the diagonal at some point near one of the extremities, giving actually therefore Type II. Thus if $K = 2$ and $m = 0.9$, it can be calculated that the curve will cross the 45° diagonal at $x = 0.9990$. Such behavior of course cannot be detected with the experimental data, which do not extend to such concentrations. In view of the fact that the curves of two of the systems do show definite characteristics of Type II, and on the basis of the mathematical considerations involved in the function of the parameter m, the picromerites studied must therefore be assigned as a group to Type II, systems involving repulsion between the components in the solid state. It is also conceivable that instead of a mere inflection point and a crossing of the diagonal, there may be an actual horizontal portion in the curve; there are not enough experimental points to rule out this possibility. The system then, with two incomplete series of solid solutions, would belong to Type IV of Roozeboom's classification. But in that case an equation such as (21) would not apply at all, since this equation presumes a continuous relation between y and x. The possibility, however, appears very unlikely in these systems, considering the close similarity between the salts making up the various solid solutions here studied.

It is to be noted that, if these considerations are valid, the Roozeboom distribution curve for a system of Type I must be symmetrical, theoretically, *i. e.*, if equation (21), with m a constant and equal to 1, for a particular system, describes the distribution between solid and aqueous phase. A system such as K_2SO_4–$(NH_4)_2SO_4$–H_2O, at 25°[19] would appear empirically to belong to Type I, since all the experimental points fall above the 45° diagonal in the Roozeboom diagram; but the asymmetry of the curve in this particular case clearly suggests the possibility (which theoretically is rather a necessity) that the curve must cross the diagonal, if enough experimental points were determined.

Summary

1. The distribution data for the equilibrium between solid solutions of alums or of picromerites and their aqueous solutions, are described by the empirical equation

$$\log R_l = \log K + m \log R_s$$

in which K is the true distribution constant in terms of activities, and in which m is a characteristic constant for each system, apparently related to the attraction or repulsion between the two components in the solid phase.

2. Comparison of this equation with the theoretical equation

$$\log R_l = \log K + \log R_s(f_1/f_2)_s$$

leads to the following relation, for the solid phase, between the activity, a, and the mole fraction, x, of a component

$$a_1 = kx_1{}^m$$

3. The three Roozeboom types of distribution for such ternary systems forming continuous solid solutions can be related to the value of the constant m: with $m = 1$, the solid solution is ideal, giving Type I; with $m < 1$, the system shows positive deviations from ideality, giving Type II; with $m > 1$, negative deviations result in Type III.

4. On this basis, the alums, giving $m = 1$, form ideal solid solutions with Type I distribution; the picromerites, for which $m < 1$, belong to Type II, with a tendency toward formation of incomplete series of solid solution.

5. The observed distribution constant, R_l/R_s, or better $R_l/R_s{}^m$, for all these systems, was found in general to be in good agreement with that calculated from the solubilities, using an empirical regularity observed for the activity coefficients of sulfates in the ionic strengths involved.

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[19] Weston, *J. Chem. Soc.*, **121**, 1231 (1922); see also W. C. Blasdale, "Equilibria in Saturated Salt Solutions," A. C. S. Monograph, Chemical Catalog Company, New York, N. Y., 1927, p. 93.