m. p. 5°, was fractionally distilled and the middle fraction boiling close to 80° was used. Six determinations were made at varying bubble rates with an average deviation from the mean of less than one part in a thousand. Saturating the nitrogen gas with benzene vapor before entering the capillaries had no effect whatever on the values. Values given by the original unpurified benzene differed but slightly from those given by the purified product.

The chloroform used was prepared from the C. P. analyzed grade by washing with water, drying over calcium chloride, and finally fractionally distilling. The portion boiling close to 61° was used.

The surface tension values obtained at 25.0° using dried nitrogen were: 26.47, 26.49, 26.52, 26.57, 26.56, 26.54; average 26.53 dynes per cm., average deviation from the mean <1/1000.

At 25.0°, using dried nitrogen saturated with chloroform vapor, the following values were obtained: 26.37, 26.47, 26.47, 26.52; average 26.46 dynes per cm., average deviation, <3/2000.

The above values show that saturating the inlet gas with chloroform vapor has little effect upon the surface tension values obtained by using the dried gas alone in Sugden's apparatus.

The values obtained at 20.0° using dried nitrogen were: 27.20, 27.15, 27.16, 27.14, 27.17, 27.14; average, 27.16 dynes per cm., average deviation, <1/1000. These values are very close to Richards and Carver's[3] and with those obtained at 25° fall squarely on the upper curve.

Like benzene, the unpurified chloroform gave essentially the same values as the purified liquid. This confirms Sugden's observation that the normal impurities in water and benzene have but slight effect on their respective surface tension values when the maximum bubble pressure method is used.

Summary

The surface tension of chloroform has been determined at 20 and 25° using Sugden's form of maximum bubble pressure apparatus. The values obtained check Richards and Carver's[3] results very closely.

Using Sugden's apparatus, saturation of the inlet gas with chloroform vapor before entering the capillaries has very little effect on the surface tension values. This confirms Whatmough's[10] observation, contrary to Cupples' findings. The probable explanation for the low values of Ramsay and Aston is reiterated.

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

The Systems Chromic Ammonium Sulfate–Ferric Ammonium Sulfate–Water and Chromic Ammonium Sulfate–Aluminum Ammonium Sulfate–Water at 25°

BY NORMAN O. SMITH AND CHARLES S. LENNOX

In a summary of the results of a series of isothermal investigations of ternary systems consisting of pairs of isomorphous salts and water Hill, Durham and Ricci[1] showed that the distribution of the salts between liquid and solid solutions obeys the semi-empirical relation

$$\log R_1 = \log K + m \log R_s \qquad (1)$$

where R_1 is the mole ratio of the salts in the liquid, R_s that in the coexisting solid solution, and m and K are constants for a particular system. The distribution constant K was shown to equal $(S_1\gamma_1^0/S_2\gamma_2^0)^{\nu/b}$, where S_1 and S_2 are the aqueous molal solubilities of the component salts, γ_1^0 and γ_2^0 the respective mean ion activity coefficients at these concentrations, ν the total number of ions per molecule of salt and b the number of ions per molecule of the ion which is being interchanged. Originally applied to alums and picromerites equation (1) has since been found to hold also for other isomorphous salt pairs.[2] In the case of alums m, in general, is unity, implying that solid solutions of alums are ideal. Of the five alum pairs reported, however, the ferric ammonium–aluminum ammonium pair did not obey the above relation satisfactorily. It was concluded[1] that this was the result of experimental error, but at the same time it was pointed out that this pair differed fundamentally from the other four in involving an interchange of the trivalent instead of the univalent cation. In order to examine further the effect of interchanging the trivalent cation the distribution studies of the present paper were undertaken.

Experimental

The technique employed was that of the previous alum studies: Complexes of known composition were made up in duplicate from the two alums and water in glass-stoppered test-tubes, glass marbles were added and the tubes rotated in a thermostat at 25 ± 0.03° for many weeks, at the end of which time both the liquid and solid phases were analyzed, the latter after being filtered from the liquid, centrifuged and air-dried for a few minutes. In the chromium–iron system two marbles were used but in the chromium–aluminum system one marble. In most cases the tubes contained about 35 g. of material but in regions of low chromium this was increased to 60 g. The members of each duplicate pair differed only in the order of addition of the components, one alum being dissolved in the water (by slight warming where necessary) before the other was added. In this way each point in the system was approached from two directions thereby establishing the attainment of equilibrium. The fact that a chrome alum was a component of both systems suggested that no less than three months of rotation would be required as it had been shown[3] that well over two months of time is required merely to attain the simple solubility equilibrium of a chrome alum in water. It was found, however, that for the chromium–iron system only nine weeks gave agreement of the duplicates. In

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(1) Hill, Durham and Ricci, THIS JOURNAL, **62**, 2723 (1940).

(2) See, for example, Ricci and Smiley, *ibid.*, **66**, 1011 (1944), and Simons and Ricci, *ibid.*, **68**, 2194 (1946).

(3) Hill, Smith and Ricci, *ibid.*, **62**, 858 (1940).

TABLE I

SYSTEM $NH_4Cr(SO_4)_2$–$NH_4Fe(SO_4)_2$–H_2O AT 25°

	Complex, wt. %		Liquid solution, wt. %		Solid solution, wt. %		Log R_1 (mean of A & B)	Log R_s (mean of A & B)	Log (R_1/R_s)
	$NH_4Cr(SO_4)_2$	$NH_4Fe(SO_4)_2$	$NH_4Cr(SO_4)_2$	$NH_4Fe(SO_4)_2$	$NH_4Cr(SO_4)_2$	$NH_4Fe(SO_4)_2$			
1	0.000	....	0.000	31.20	0.000	55.17			
2A	1.000	34.00	.332	29.53	3.799	50.43			
B	1.000	34.00	.332	29.56	3.778	50.49	1.943	1.181	0.762
3A	2.000	32.00	.743	28.76	8.019	47.16			
B	2.000	32.00	.747	28.66	7.964	47.11	1.580	0.764	.816
4A	3.000	30.00	1.151	27.58	11.97	41.95			
B	3.000	30.00	1.154	27.57	10.93	40.46	1.373	.550	.823
5A	5.000	28.00	1.785	25.64	17.07	37.56			
B	5.000	28.00	1.790	25.60	17.45	36.84	1.150	.327	.823
6A	7.50	25.00	2.713	23.29	23.58	31.29			
B	7.50	25.00	2.671	23.29	23.52	31.39	0.931	.118	.813
7A	9.00	19.00	4.555	19.03	33.26	21.36			
B	9.00	19.00	4.537	19.00	33.51	19.00[a]	.615	− .225	.840
8A	11.00	12.00	7.401	12.08	44.25	10.47			
B	11.00	12.00	7.403	12.10	44.26	10.31	.207	− .636	.843
9A	12.40	6.000	10.29	6.086	49.09	4.655			
B	12.40	6.000	10.30	6.075	50.27	4.469	− .235	−1.043	.808
10	....	0.000	13.66	0.000	54.81	0.000			

[a] By algebraic extrapolation.

TABLE II

SYSTEM $NH_4Cr(SO_4)_2$–$NH_4Al(SO_4)_2$–H_2O AT 25°

	Complex, wt. %		Liquid solution, wt. %		Solid solution, wt. %		Log R_1 (mean of A & B)	Log R_s (mean of A & B)	Log (R_1/R_s)
	$NH_4Cr(SO_4)_2$	$NH_4Al(SO_4)_2$	$NH_4Cr(SO_4)_2$	$NH_4Al(SO_4)_2$	$NH_4Cr(SO_4)_2$	$NH_4Al(SO_4)_2$			
1	0.000	...	0.000	6.15	0.00	52.31			
2A	3.000	8.000	2.760	4.821	6.54	46.24			
B	3.000	8.000	2.762	4.830	6.34	46.29	−0.286	−0.900	0.614
3A	6.000	5.500	5.389	3.333	15.13[a]	37.87[a]			
B	6.000	5.500	5.246	3.622	16.20	36.23	+ .141	− .417	.558
4A	10.00	5.000	8.04	2.308	25.83	27.15			
B	10.00	5.000	7.95	2.440	26.05	27.46	+ .484	− .066	.550
5A	12.90	3.000	10.19	0.967	37.14	19.61	+ .979	+ .234	.745
6A	17.00	2.000	11.94	.659	44.02	9.29			
B	17.00	2.000	12.01	.560	43.96	8.69	+1.249	+ .646	.603
7	....	0.000	13.66	.000	54.81	0.00			

[a] By algebraic extrapolation.

the chromium-aluminum system about three months of rotation was allowed.

Materials.—The aluminum ammonium and chromic ammonium alums were recrystallized Baker Analyzed chemicals and the ferric ammonium alum was recrystallized British Drug Houses Analar product. These three alums will henceforth be referred to as the aluminum, chrome and iron alums, respectively. The first-mentioned retained its theoretical composition indefinitely; the other two effloresced slightly so that their analytical composition at the time of using was employed in calculating the compositions of the complexes.

Analysis.—In both systems the liquids and solids were analyzed for total ammonium and chromium. Ammonium was determined by alkaline distillation in steam of the ammonia into excess boric acid and titration of the excess of the latter with standard hydrochloric acid.[4] Chromium was determined by oxidation with persulfate in the presence of silver nitrate, precipitation of silver with hydrochloric acid, addition of a measured excess of standard ferrous sulfate and titration of the excess of the latter with standard dichromate in the presence of phosphoric acid using barium diphenylamine sulfonate as internal indicator. By preliminary trials these analytical methods were found to give an accuracy of better than 0.2% even for low proportions of chromium.

Results and Discussion

Tables I and II give the analytical compositions of the liquid and solid phases for the chrome–iron and chrome–aluminum systems, respectively. In Table I the A data are for those tubes in which the chrome alum, and the B data the iron alum, was present as the initial solid phase. In Table II chrome alum was the initial solid for the A data and aluminum alum for the B data. The single solubilities of the alums are those of a previous paper.[3]

The agreement of the duplicates indicates satisfactory approach to equilibrium. To test the consistency of the analyses the per cent. of chromic ammonium sulfate in each solid was calculated by algebraic extrapolation from the compositions of

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[4] Wagner, *Ind. Eng. Chem., Anal. Ed.*, **12**, 771 (1940).

the liquid and complex to the analytical water content of the solid and compared with the observed per cent. In the first system the average absolute deviation for all the tubes was only 0.48% and in the second 0.71%.

The plots of the data are shown in Figs. 1 and 2. It is seen that in both systems there is a complete series of solid solutions as found (with one exception[5]) in all previous alum studies. The points for the liquid lie on a smoother curve for the first than for the second system suggesting a less complete attainment of equilibrium in the latter in spite of the longer period of rotation—the result, doubtless, of a less effective grinding of the solids during rotation (only one marble used).

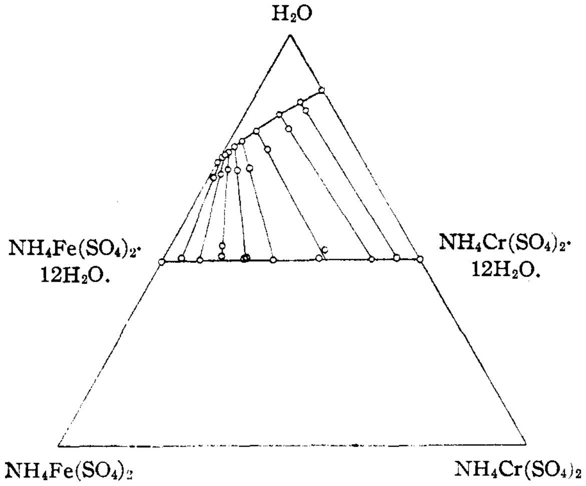

Fig. 1.—The system $NH_4Cr(SO_4)_2$–$NH_4Fe(SO_4)_2$–H_2O at 25°.

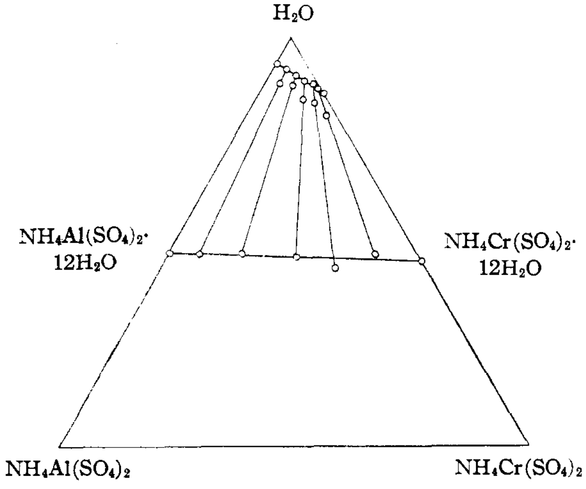

Fig. 2.—The system $NH_4Cr(SO_4)_2$–$NH_4Al(SO_4)_2$–H_2O at 25°.

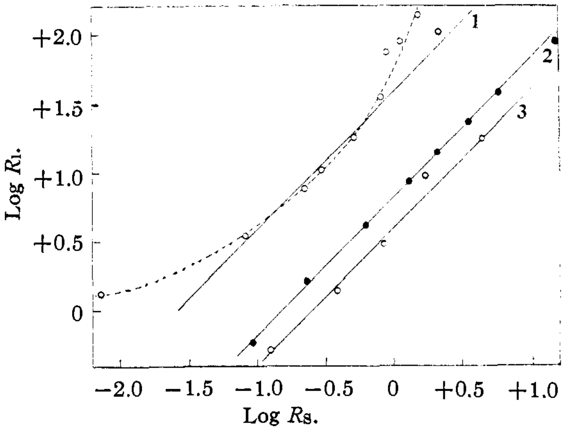

Fig. 3.—Distribution in alum systems: (1) $NH_4Fe(SO_4)_2$–$NH_4Al(SO_4)_2$–H_2O, (2) $NH_4Fe(SO_4)_2$–$NH_4Cr(SO_4)_2$–H_2O, (3) $NH_4Cr(SO_4)_2$–$NH_4Al(SO_4)_2$–H_2O.

In order to test the applicability of the distribution relation (1) log R_l is plotted against log R_s in Fig. 3 from the values listed in Tables I and II. These are the logarithms of the ratios, in liquid and coexisting solid, respectively, of the molal concentration of the alum with the greater molal solubility to that of the alum with the lower. It is evident that the present systems, particularly the chrome–iron pair where more complete equilibrium was attained, give, within the limits of experimental error, a linear relation between log R_l and log R_s and furthermore that the slope is unity. The data, therefore, obey equation (1) where m is unity, and the intercepts on the vertical axis, namely, 0.82 for the chrome–iron and 0.59 for the chrome–aluminum pair, should give the value of log K defined earlier. Because of lack of data on activity coefficients of alums these intercepts can, as yet, only be tested by the approximation[1]

$$K = (S_1/S_2)^{\nu/2b} \qquad (2)$$

based on the observation that for bi-bivalent sulfates $\gamma \cong A + B/\sqrt{\mu}$ over a limited concentration range, where μ is ionic strength, A is a very small constant and B a constant for most of the sulfates for which data were then available. It may be noted here that recent measurements in this Laboratory[6] show that this is also nearly true for chromic potassium and chromic ammonium sulfates from $\sqrt{\mu} = 0.9$ to $\sqrt{\mu} = 2.3$. Similarly, available data on chromic,[7] aluminum[7] and indium[8] sulfates suggest that these too satisfy the relation approximately, except that B is half as large. Thus the assumed applicability[1] of the relation to higher valence types is to some extent confirmed. Calculation of log K from (2) for the chrome–iron system gives 0.90 and for the chrome–aluminum system 0.68 in satisfactory agreement with the observed intercepts.

Another consequence of the linear relationships of Fig. 3 is that both systems can be assigned to Type I of the Roozeboom classification,[9] for the slope of each line is unity.

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(5) Hill and Kaplan, THIS JOURNAL, **60**, 550 (1938).

(6) Smith, *ibid.*, **69**, 91 (1947).

(7) Robinson, *ibid.*, **59**, 84 (1937).

(8) Hattox and DeVries, *ibid.*, **58**, 2126 (1936).

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

Included in Fig. 3 for purposes of comparison are the data of Hill and Kaplan[5] for the ferric ammonium–aluminum ammonium system. The suggestion of Hill, Durham and Ricci that the distribution in this system is also a linear one in spite of the fact that the points tend to lie on a curve is therefore further supported by the two analogous systems here reported.

The relation

$$\log R_l = \text{constant} + \log R_s \qquad (3)$$

thus found valid in all alum systems so far studied has been shown[1] to have a theoretical basis as a special case of

$$\log R_l = \log K + \log (f_B/f_{B'}) - \log (\gamma_B/\gamma_{B'}) + \log R_s \qquad (4)$$

where f_B and $f_{B'}$ are the rational activity coefficients of the interchanging ions in the solid solution and γ_B and $\gamma_{B'}$ their practical activity coefficients in the coexisting liquid solution. To reduce this to (3) requires that $f_B/f_{B'}$ and $\gamma_B/\gamma_{B'}$ shall be constant at all points across the diagram and Hill, Durham and Ricci propose that in systems where *m* is unity both ratios are not only constant but unity. This assumption is, of course, necessary if the intercepts of Fig. 3 are to be identified with log *K*.

It is possible to raise an objection to the identification of the intercepts with log *K* in the light of data of ref. 6 as applied to the chromic potassium–chromic ammonium alum pair.[3] The values of the molal solubilities of these alums are 0.817 and 0.603, respectively, in which solutions the respective mean ion activity coefficients are 0.0358 and 0.0465. This gives $\log K = \log (0.817 \times 0.0358/0.603 \times 0.0465)^4 = 0.07$. The intercept on the $\log R_l$ *vs.* $\log R_s$ plot is given[1] as 0.20 which equals the sum of the first three terms on the right side of (4). This means that $\log (f_K/f_{NH_4}) - \log (\gamma_K/\gamma_{NH_4}) = 0.13$, a finite constant for all proportions of the two alums. It is very unlikely that as one passes across the diagram the *f* and γ ratios both alter in such a way that the difference of their logarithms is constant; it is more reasonable to suppose that they are both constant, but then both could not be unity. It is interesting to note that if f_K/f_{NH_4} is regarded as unity then $\log (\gamma_K/\gamma_{NH_4})$, becomes -0.13 which may be compared with that estimated as follows: The ratio of the mean ion activity coefficient of chromic potassium sulfate to that of chromic ammonium sulfate is reasonably constant (about 0.88) over the range of ionic strengths of the isotherm. If the activity coefficients of chromic and sulfate ions are assumed to be the same in solutions of single alums as they are in mixed alums of the same ionic strength then $\log (\gamma_K/\gamma_{NH_4})$ should be given roughly by $\log (0.88)^4 = -0.22$. On the other hand, the uncertainties involved in the evaluation of the activity coefficients of the alums may have combined to produce a large error in log *K* thus invalidating the above argument.

Summary

1. The systems chromic ammonium sulfate–ferric ammonium sulfate–water and chromic ammonium sulfate–aluminum ammonium sulfate–water have been investigated at 25°.
2. Both systems exhibit a complete series of solid solutions at this temperature, and, as the distribution of the components follows the relation $\log R_l = \text{constant} + \log R_s$, they are assigned to Type I of the Roozeboom classification. The values of the constant for each system compare favorably with the values estimated from the individual solubilities of the component alums.
3. A possible objection is raised to the assumption of a value of unity for the ratio of the activity coefficients of the interchanging ions in the liquid.

WINNIPEG, CANADA RECEIVED NOVEMBER 12, 1947

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

The System Ammonium Nitrate–Ammonium Sulfamate[1]

BY JACK H. THELIN[2] AND P. A. VAN DER MEULEN

The present research represents the initial investigation of the phase equilibria in the reciprocal salt pair system sodium nitrate–ammonium sulfamate. This included the phase diagram of the binary system ammonium nitrate–ammonium sulfamate.

Ammonium nitrate is known to exist in five crystalline modifications. Early and Lowry[3] have re-examined the transition temperatures of the various modifications and have summarized the results. Two of the transition points are of importance in the present investigation. They are the transition temperatures of 125.2° at which the cubic changes to the tetragonal and 84.2° at which the tetragonal changes to the monoclinic modification. There are no published records concerning possible polymorphism of ammonium sulfamate.

Experimental Method

Purification of Materials.—Merck ammonium nitrate was crystallized twice from distilled water and dried under

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(1) Based on a thesis submitted by Jack H. Thelin to the graduate faculty of Rutgers University in partial fullfillment of the requirements for the degree of Doctor of Philosophy.

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(3) R. G. Early and T. M. Lowry, *J. Chem. Soc.*, **115**, 1387 (1919).