running several spectral analyses during the course of this investigation. The author also wishes to thank S. E. J. Johnsen and K. M. Taylor for their assistance in the purification of *cis*-1-cyano-1,3-butadiene.

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Solid Solutions in the System Li_2SO_4–$(NH_4)_2SO_4$–H_2O[1]

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Although the alums generally belong to the cubic system there are three distinct internal arrangements of the structural units: α-, β- and γ-structures.[2] However, lithium aluminum alum is not cubic.[3] It would be interesting to determine whether it forms solid solutions with alums having the various internal structures. The acquisition of several well-formed ammonium aluminum alum crystals which contained significant amounts of lithium had led to the speculation that perhaps they contained lithium alum in solid solution.[4] A systematic study of the quaternary system Li_2SO_4–$Al_2(SO_4)_3$–$(NH_4)_2SO_4$–H_2O at 0° was therefore undertaken in connection with this and with the general question of whether lithium alum formed solid solutions with alums possessing the different internal structures. Since the ternary system Li_2SO_4–$(NH_4)_2SO_4$–H_2O at 0° had not been previously reported, a partial study of it was also necessary to determine the compositions of the isothermally invariant saturated solutions. A more detailed study of the system was made as a result of the discovery of solid solutions. Experimental evidence is presented below which indicates that the solid solutions are discontinuous and are actually between $Li_2SO_4{\cdot}H_2O$ and $LiNH_4SO_4$. A few results of a study of the same system at 25° which substantiate the occurrence of solid solutions at a higher temperature also are given.

It appears that the occurrence of solid solutions in the system Li_2SO_4–$(NH_4)_2SO_4$–H_2O at various temperatures has been overlooked because of the limited data and the absence of any indication of solid solutions in the graphical representations. The diagram of the system at 30° reproduced in Mellor[5] is taken from an earlier report by Schreinemakers and Cocheret.[6] It shows four solid phases: $Li_2SO_4{\cdot}H_2O$, Li_2SO_4, $LiNH_4SO_4$ and $(NH_4)_2SO_4$. The diagram commonly used as an illustration of a classical ternary isotherm,[7–9] is taken from a later report by the same investigators.[10] It indicates only three solid phases: $Li_2SO_4{\cdot}H_2O$, $LiNH_4SO_4$ and $(NH_4)_2SO_4$. The two diagrams are based on the same table of data appearing in both of the above-mentioned reports. However, algebraic extrapolation[11] of the figures lends little support to the conclusion that $Li_2SO_4{\cdot}H_2O$ is a solid phase in equilibrium with saturated solutions. In the later report[10] which also contains results of a study of the system at 50° there appears a brief mention by the authors that Li_2SO_4 does not exist as a pure solid phase at 30 and 50° but in solid solutions, the nature of which they did not investigate further. Two other references[12,13] to the ternary system at 20, 57 and 97° contain no mention of solid solutions. The presentation of results in these reports is fragmentary and pertains to the double salt $LiNH_4SO_4$.

Experimental Procedure

Anhydrous Li_2SO_4 was prepared from J. T. Baker reagent Li_2CO_3 which had been recrystallized by the method of Kraus and Burgess.[14] The final product was heated in platinum in a muffle furnace at 550–600° to remove the last traces of acid and water. Merck reagent $(NH_4)_2SO_4$ was used without further purification. It was pulverized and then dried for several hours at 105°.

Complexes of known compositions, totaling 50–60 g., were prepared in capped solubility tubes which contained two glass marbles to produce a grinding action during mixing. They were brought to equilibrium at 0° in a completely enclosed, well-insulated ice-water bath. The tubes were rotated end over end on a completely submerged wheel turned by a horizontal, motor-driven shaft which entered the bath through one of the sides.

The complexes were mixed 14–21 days before final analysis. In most cases the saturated solutions were first analyzed after 7 days, the mixtures rotated for an additional 48 hours, and the solutions then reanalyzed. Constancy of composition upon repetition of this process was used as a criterion of attainment of equilibrium. The procedure followed in the work at 25° was the same.

The saturated solutions were sampled by means of pipets fitted with filter paper, and analyzed by one of two methods. Complexes 1–7 inclusive of Table I were analyzed for ammonia by distillation into excess standard sulfuric acid,[15] and for lithium sulfate on separate samples by volatilization of ammonium sulfate after evaporation to dryness. Complexes 8–32 were analyzed for total sulfates by evaporation and drying, and for lithium sulfate by ignition of the residues. The first method was adopted for part of the work at 0° to shorten the time of analysis. The procedure of the second method was that employed in a similar study of solid solutions between ammonium sulfate and other alkali metal sulfates.[16] It gave slightly higher ammonium sulfate values, about 5 parts per 1000, than the first method presumably because the last traces of entrapped water were removed very slowly in the drying process. A tracer tech-

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[1] This work was supported in part by the National Science Foundation Grant G159.

[2] Primary references and a discussion of the criteria of isomorphism appear in Therald Moeller's "Inorganic Chemistry," John Wiley and Sons, New York, N. Y., 1952, p. 541.

[3] An X-ray study of the structure of lithium alum is in progress. It appears to be monoclinic.

[4] J. A. N. Friend, private communication to H. A. Horan. The limited amount of material permitted an aluminum analysis only; calcd. % $Al_2(SO_4)_3$ in $NH_4Al(SO_4)_2{\cdot}12H_2O$: 37.7, found 37.0. The determined value should be higher than the calculated if solid solutions of lithium alum were involved.

[5] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, Longmans, Green and Co., New York, N. Y., 1922, p. 706.

[6] F. A. H. Schreinemakers and D. H. Cocheret, *Chem. Weekblad*, **2**, 771 (1905).

[7] Farrington Daniels, "Outlines of Physical Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 335.

[8] Louis Hammett, "Introduction to the Study of Physical Chemistry," McGraw-Hill Book Co., New York, N. Y., 1952, p. 282.

[9] "International Critical Tables," Vol. IV, McGraw-Hill Book Co., New York, N. Y., 1928, p. 388.

[10] F. A. H. Schreinemakers and Cocheret, *Z. physik. Chem.*, **59**, 645 (1907).

[11] A. E. Hill and J. E. Ricci, THIS JOURNAL, **53**, 4306 (1931).

[12] C. Spielrein, *Compt. rend.*, **155**, 347 (1912).

[13] C. Spielrein, *ibid.*, **157**, 46 (1913).

[14] C. A. Kraus and W. B. Burgess, THIS JOURNAL, **49**, 1227 (1927).

[15] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Third Ed., The Macmillan Co., New York, N. Y. 1952, p. 537.

[16] C. Calvo and E. Simons, THIS JOURNAL, **74**, 1202 (1952).

nique was applied in complexes 1, 3 and 6 of Table I, in an attempt to ascertain the nature of the solid solutions. This was necessary because the solid phase could not be adequately separated from the adhering saturated solution by filtration at 0° but retained as much as 50–60% by wt. of the latter. Instead of pure water, 0.15% aqueous ammonium thiocyanate was employed as the solvent. The thiocyanate analyses of the saturated solution and the corresponding wet residue were used to calculate the composition of the solid phase in equilibrium with the saturated solution. The thiocyanate was determined by titration with standard silver nitrate solution. The end-point was located potentiometrically by means of a Beckman *p*H meter with a silver electrode and saturated calomel reference electrode, the two electrodes being separated by an agar–KNO_3 salt bridge. All analyses were run in duplicate.

Results and Discussion

The results together with figures obtained at 25° are summarized in Table I. The results at 0° except for the filtered wet residues are plotted in the usual manner in Fig. 1.

TABLE I

THE SYSTEM Li_2SO_4–$(NH_4)_2SO_4$–H_2O

A = Li_2SO_4, B = $(NH_4)_2SO_4$, W = H_2O, s = solid soln. A·B in A·W

	Complex		Solution		Solid	
	A, %	B, %	A, %	B, %	A, %[a]	B, %[a]
			0°			
1	36.64	1.01	26.13	1.13	s85.6	0.5
	52.47[b]	0.80			s90.9	0.3
2	36.11	2.00	25.82	2.31	s85.5	0.5
3	30.61	3.07	25.56	3.30	s85.5	0.6
	51.95[b]	2.17			s89.7	0.6
4	30.75	4.08	25.32	4.35	s84.9	1.4
5	29.06	6.61	24.66	7.04	s85.1	1.2
6	28.64	7.40	24.34	7.82	s84.5	2.0
	53.58[b]	5.23			s87.3	2.2
7	27.98	8.26	24.20	8.62	s83.7	3.0
8	34.00	8.60	24.10	9.13	s81.4	6.1
9	35.04	8.62	24.20	9.29	s81.7	5.8
10	28.02	10.00	23.72	9.94	s + A·B	
11	27.95	11.46	23.67	9.91	s + A·B	
12	27.01	17.01	23.74	10.05	A·B	
13	22.94	22.94	18.39	16.39	A·B	
14	14.99	30.00	11.57	27.56	A·B	
15	15.00	40.02	7.59	36.52	A·B	
16	9.98	45.05	7.62	36.54	A·B + B	
17	7.01	44.01	7.60	36.54	A·B + B	
18	3.03	46.00	3.48	39.42	B	
			25°			
19	30.01	5.01	24.45	5.50	85.9	0.1
20	28.93	7.99	23.53	8.29	82.2	5.0
21	35.03	10.31	23.13	10.98	80.2	7.8
22	28.02	10.51	22.87	10.82	80.5	7.4
23	26.96	11.98	22.37	12.38	80.5	7.3
24	27.06	12.00	22.37	12.45	80.8	6.9
25	26.42	13.45	22.31	12.51	s + A·B	
26	29.20	21.15	22.29	12.55	s + A·B	
27	21.51	21.52	18.37	17.07	A·B	
28	18.69	24.95	15.39	21.31	A·B	
29	12.95	33.97	9.61	32.11	A·B	
30	16.69	50.06	6.71	39.58	A·B + B	
31	5.95	44.67	6.69	39.56	A·B + B	
32	2.00	46.02	2.21	42.12	B	

[a] Calcd. [b] Filtered wet residue; solid calcd. from tracer analysis.

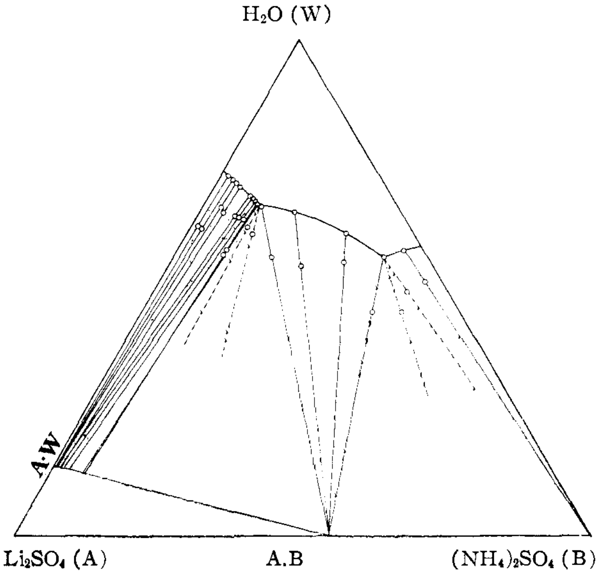

Fig. 1.—The system Li_2SO_4–$(NH_4)_2SO_4$–H_2O at 0°.

The tie-lines in Fig. 1 fail to converge at the point representing $Li_2SO_4 \cdot H_2O$. Algebraic extrapolation[11] of the tie-lines of complexes 1–7 inclusive to % Li_2SO_4 at 0% H_2O gives values of 99.71, 99.92, 99.33, 100.36, 99.53 and 98.45, respectively. One might conclude from these that the solid phase is anhydrous Li_2SO_4. However, an examination of other ternary systems involving Li_2SO_4 indicates that this convergence of tie-lines is fortuitous. For example, $Li_2SO_4 \cdot H_2O$ is the only solid phase in equilibrium with saturated solutions containing up to 16.65% $(Al_2SO_4)_3$ in the system Li_2SO_4–$Al(SO_4)_3$–H_2O at 0°.[17,18] It is therefore very unlikely that anhydrous Li_2SO_4 would be a solid phase in equilibrium with solutions containing only several % $(NH_4)_2SO_4$. At 30°, the anhydrous salt is not a solid phase in the system Li_2SO_4–H_2SO_4–H_2O[19] until the saturated solution contains 55% H_2SO_4. There is no doubt that solid solutions are formed between $Li_2SO_4 \cdot H_2O$ and $LiNH_4SO_4$.[20] The compositions of the solid phases in complexes 1, 3 and 6 calculated from the tracer analyses support this conclusion. However, the points representing these compositions, if plotted, would fall somewhat below the line connecting the points representing $Li_2SO_4 \cdot H_2O$ and $LiNH_4SO_4$ in Fig. 1. This discrepancy is largely the result of the inability to free the solid phases sufficiently from the adhering saturated solutions and the experimental difficulties in carrying out the slow filtrations at 0° in humid summer weather. The figures at 25° when plotted give a diagram similar to Fig. 1. They also indicate solid solutions as do the previously reported figures at 30 and 50°.[10]

The behavior of Li_2SO_4 with $(NH_4)_2SO_4$ is interesting in the light of the behavior of the other alkali sulfates with the latter. The sulfates of K, Cs and Rb form continuous solid solutions[16] while that of Na only a double salt.[21] Li_2SO_4 in addition to a

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(17) H. A. Horan and J. J. Duane, THIS JOURNAL, **63**, 3533 (1941).

(18) H. A. Horan and J. A. Skarulis, *ibid.*, **61**, 2689 (1939).

(19) Reference 9, p. 353.

(20) For a discussion of the type of solid solution and a similar hypothetical system see J. E. Ricci's "The Phase Rule and Heterogeneous Equilibrium," D. Van Nostrand Co., Inc., New York, N. Y., 1951, pp. 340–341.

(21) Reference 9, p. 222.

double salt also forms solid solutions. Although the internal structure of $Li_2SO_4 \cdot H_2O$ has been determined,[22] it is unfortunate that the structure of $LiNH_4SO_4$ has not. It would be interesting to see whether the role of NH_4^+ ion in $LiNH_4SO_4$ is the same as that of the combination $Li^+–H_2O$ in $Li_2SO_4 \cdot H_2O$.

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[22] G. E. Ziegler, *Z. Krist.*, **89**, 456 (1934).

COMMUNICATIONS TO THE EDITOR

MECHANISM OF THE REACTION OF NITROMETHANE WITH BASES

Sir:

We wish to report a mechanism for the reaction of nitromethane with bases in aqueous solutions which accounts for both the initial reaction to form the salt of the aci form of nitromethane, and the subsequent slower reaction to form the salt of methazonic acid.

$$CH_3NO_2 + OH^- \rightleftarrows CH_2NO_2^- + H_2O \quad (1)$$

$$2\ CH_2NO_2^- \xrightarrow{k_2} O_2NCH_2CHNO^- + OH^- \quad (2)$$

We have found that basic solutions containing methazonate ion show very strong absorption of light at 2,980 Å. while acid solutions show none. We have also observed that freshly prepared mixtures of dilute solutions of nitromethane and bases react at relatively slow rates to form the methazonate ion which we can follow by observing the increasing absorption at 2,980 Å. with time. The identification of the absorption peak with the methazonate ion has been made by preparing ammonium methazonate by a well established procedure (3) and establishing the absorption spectra pattern of this material.[3]

Our studies at 25.6° show that the initial rate of formation of methazonate ion is second order with respect to the initial concentration of nitromethane over the range of pH from 9.5 to 12.5. The order with respect to hydroxide ion concentration is second order at pH 9.5, and decreases asymptotically to almost zero order as we increase the pH to 12.5. It should be noted that the pH remains constant during the course of any single experiment.

On the assumption that the equilibrium in reaction (1) is established very rapidly relative to the velocity of reaction (2), an expression can be derived for the over-all rate from equations (1) and (2) as shown

$$r = \frac{k_2K^2X^2(OH^-)^2}{[1 + K(OH^-)]^2} \quad (3)$$

where

r = rate of formation of methazonate ion
k_2 = specific rate constant for reaction (2)
K = equilibrium constant for reaction (1)
X = concentration of nitromethane plus aci nitromethane.

The kinetic data obtained are in complete agreement with equation (3).

This relation enables us to estimate K at higher temperatures than has been heretofore possible, and we will also be able to obtain the ΔH for reaction (1) and the activation energy for reaction (2). It should be noted that the evaluation of K is not our primary purpose. Rather we wish to show that known values of K_N are entirely consistent with our proposed mechanism.

This work supports the Pedersen mechanism[1] for pseudo acid behavior of nitro paraffins and gives good agreement with published data[2,3] on the ionization constant of nitromethane, K_N. This constant is related through the water equilibrium constant K_W to our equilibrium constant K in the following way

$$K = K_N/K_W$$

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[1] J. K. Pedersen, *Det. Kgl. Videnak. Selskab., Math-fys. Medd.*, **12**, 1–16 (1932) (in English).

[2] D. Turnbull and S. H. Maron, THIS JOURNAL, **65**, 212 (1943).

[3] W. R. Dunstan and E. Goulding, *J. Chem. Soc. Trans.*, **2**, 1262 (1900).

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RECEIVED MARCH 18, 1954

CARBON DIOXIDE FIXATION IN HEART EXTRACTS BY β-HYDROXYISOVALERYL COENZYME A[1]

Sir:

Previous isotopic studies have indicated that isovaleric acid, an intermediate in leucine metabolism, yields acetoacetate in liver tissue.[2,3,4,5,6] Carbons 1 and 2 furnish "acetate" for the well-recognized acetoacetate condensation, and the carbons of the isopropyl group yield acetoacetate by a carbon dioxide-fixing reaction. The intermediate steps in this metabolic pathway have recently been investigated in heart and liver extracts in this laboratory, and the following series of reactions is proposed to account for the results obtained

$$\text{Isovaleryl CoA} \longrightarrow \text{Senecioyl CoA}^{7} \quad (1)$$

$$\text{Senecioyl CoA} + H_2O \longrightarrow \text{HIV CoA} \quad (2)$$

$$\text{HIV CoA} + CO_2 \xrightarrow{\text{ATP}} \text{HMG CoA} \quad (3)$$

$$\text{HMG CoA} \longrightarrow \text{Acetoacetate} + \text{Acetyl CoA} \quad (4)$$

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[1] Supported by grants from the National Science Foundation and the United States Public Health Service.

[2] K. Bloch, *J. Biol. Chem.*, **155**, 255 (1944).

[3] M. J. Coon and S. Gurin, *ibid.*, **180**, 1159 (1949).

[4] I. Zabin and K. Bloch, *ibid.*, **185**, 117 (1950).

[5] M. J. Coon, *ibid.*, **187**, 71 (1950).

[6] G. W. E. Plaut and H. A. Lardy, *ibid.*, **192**, 435 (1951).

[7] Abbreviations: acyl Coenzyme A derivatives, acyl CoA; β-hydroxyisovaleryl CoA, HIV CoA; β-hydroxy-β-methylglutaryl CoA, HMG CoA; adenosine triphosphate, ATP; tris-(hydroxymethyl)-aminomethane, Tris.