

Fig. 1.—Mass spectrometer curves obtained in the analysis of nitrogen samples before and after treatment with alkaline potassium permanganate: 1, unlabeled arginine; 2 and 3, N^{15} -glutamine containing different amounts of N^{15} ; Curves A, no further treatment; curves B, samples shaken in alkaline permanganate.

use of the former method resulted in consistently higher values. In the analysis of 48 samples of varying N^{15} content, the average deviation between results obtained by the two methods was 24%. It was brought to our attention that nitrogen samples from other institutions analyzed by the mass spectrometer also gave abnormally high mass 30 peaks.⁴

It appeared possible that some nitric oxide resulting from the combustion was escaping reduction and thus was contaminating the samples with a gas of mass 30. Since nitric oxide is easily removed from nitrogen samples by shaking in alkaline potassium permanganate, this principle was applied to the samples resulting from the Dumas method.

Experimental

Duplicate samples were oxidized in a Dumas combustion furnace. One sample of gas from each pair was analyzed by the mass spectrometer without further treatment, while the gas resulting from combustion of the other sample was drawn into a Van Slyke deamination apparatus and shaken for two minutes in a solution containing 40 g. of potassium permanganate and 18 g. of sodium hydroxide per liter of water. Care was taken during the transfer of the samples to exclude all air.

Results and Discussion

The difference in the volume of the gas before and after the permanganate treatment was too small to be detected in the gas buret.

Figure 1 shows typical mass spectrometer curves which resulted from the analysis of nitrogen from unlabeled arginine and from N^{15} -glutamine prepared in this Laboratory.⁵

From these curves it appears evident that nitric oxide is the source of the erratic mass 30 peaks. Values for the atom per cent. N^{15} in the samples calculated from the measured peaks of these curves, listed in Table I, confirm this.

It is apparent that for samples which contain a large atom per cent. of N^{15} this abnormality should not seriously influence the results. However, for samples which contain a low atom per cent. of N^{15} ,

(4) Private communication, Dr. Glen D. Hallmark.

(5) D. W. Hood and C. M. Lyman, *Arch. Biochem.*, **20**, 381 (1951).

TABLE I

Nitrogen source	ATOM PER CENT. N^{15} IN NITROGEN SAMPLES ANALYZED BY MASS SPECTROMETER CALCULATED BY BOTH METHODS			
	No treatment Direct method	Indirect method	KMnO ₄ treatment Direct method	Indirect method
Unlabeled arginine	0.52	0.37	0.38*	0.38
N^{15} -Glutamine	1.91	1.75	1.78	1.78
N^{15} -Glutamine	7.92	7.85	8.14	8.08

* Mass 30 peak value is zero.

traces of nitric oxide may seriously influence the results obtained in calculating the absolute concentration of N^{15} present in a labeled sample.

Acknowledgment.—We wish to thank Dr. Glen D. Hallmark of the Electrical Engineering Department, A. and M. College of Texas, for the mass spectrometer analyses of the nitrogen samples.

DEPT. OF BIOCHEMISTRY AND NUTRITION
TEXAS AGRICULTURAL EXPT. STATION
TEXAS AGRICULTURAL AND MECHANICAL COLLEGE SYSTEM
COLLEGE STATION, TEXAS

The Ternary System Na_2SO_4 - $Al_2(SO_4)_3$ - H_2O at 0°

BY J. A. SKARULIS, H. A. HORAN AND R. MALBENY

RECEIVED NOVEMBER 18, 1953

In the course of preliminary study of possible solid solution formation between lithium alum² and soda alum, it was found contrary to a previous report³ of the system Na_2SO_4 - $Al_2(SO_4)_3$ - H_2O at 0° that soda alum does exist as a solid phase in stable equilibrium with saturated solutions at this temperature. Partial reinvestigation of this system was undertaken to determine the compositions of the isothermally invariant solutions. It revealed that although incongruently soluble the alum exists as a stable saturating phase over a considerable range

(1) The work reported in this note was supported in part by a grant from the National Science Foundation, Grant G159.

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

(3) J. T. Dobbins and J. A. Addleston, *J. Phys. Chem.*, **39**, 837 (1935).

The experimental procedure was that described in a report⁴ on the ternary system $\text{Li}_2\text{SO}_4\text{-Al}_2(\text{SO}_4)_3\text{-H}_2\text{O}$ at 0° except that the $\text{Al}_2(\text{SO}_4)_3$ used was air-dried recrystallized hydrated material. The compositions of many different batches of this material were practically the same, varying over the narrow range 53.4–53.7% $\text{Al}_2(\text{SO}_4)_3$, based on aluminum determinations. The average analysis corresponds to the composition 1 mole $\text{Al}_2(\text{SO}_4)_3$ to 16.5 moles H_2O . This is in agreement with observation reported by other investigators.^{5,6} Mixtures of known composition were prepared from this analyzed material, anhydrous C.P. Na_2SO_4 and water, brought to equilibrium at 0° , analyzed for aluminum by the quinolate method⁷ and for sodium by the magnesium uranyl acetate method.⁸ Peculiar behavior was observed in mixtures made up to check the composition of the isothermally invariant saturated solution previously reported.³ The analysis of the saturated solution of the first mixture differed markedly from that expected. Mathematical extrapolation⁹ of the tie-line indicated that the solid phase was probably the pure alum. Four subsequent mixtures failed to yield a solid phase after stirring for 24 hours. The metastable condition of these mixtures was suspected. This led to the seeding of all the mixtures including the first one with a crystal of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Then the analysis of the saturated solution of the first mixture changed markedly and a solid phase appeared in the latter ones. All other mixtures were seeded after stirring for 24 hours at 0° . The mixtures were stirred for 1 week before analysis of the solution, and the attainment of equilibrium was proved by constancy of composition on reanalysis after further stirring for 1 week.

The results of the analyses are tabulated in weight % in Table I, and plotted in the usual manner in Fig. 1 together with that portion of the previously reported data³ which appears to be reliable. Also included in the table is the analysis

TABLE I

PARTIAL SYSTEM $\text{Na}_2\text{SO}_4(\text{A})\text{-Al}_2(\text{SO}_4)_3(\text{B})\text{-H}_2\text{O}(\text{W})$ at 0°

Complex		Solution		Solid phase
A, %	B, %	A, %	B, %	
10.69	25.35	7.37	17.62	A·B·24W ^c
7.89	20.05	3.71	21.58	A·B·24W + A·10W
6.07	21.45	3.74	21.58	A·B·24W + A·10W
4.00	23.01	3.35	22.16	A·B·24W
2.86	24.88	2.09	24.13	A·B·24W
... ^a	... ^a	1.93	24.68	A·B·24W
3.31	26.85	1.87	25.55	A·B·24W
13.39 ^b	37.99 ^b			
3.70	29.87	1.00	27.12	A·B·24W + B·17W
1.56	27.99	0.99	27.16	A·B·24W + B·17W
0.400	30.99	0.435	27.34	B·17W

^a Approximate complex. ^b Filtered wet residue. ^c Metastable.

- (4) H. A. Horan and J. A. Skarulis, *THIS JOURNAL*, **61**, 2689 (1939).
 (5) H. Bassett and T. Goodwin, *J. Chem. Soc.*, 2239 (1949).
 (6) D. Taylor and H. Bassett, *ibid.*, 4431 (1952).
 (7) I. M. Kolthoff and E. B. Sandell, *THIS JOURNAL*, **50**, 1900 (1928).
 (8) C. W. Foulk, H. V. Moyer and W. M. MacNevin, "Quantitative Chemical Analysis," McGraw-Hill Book Co., New York, N. Y., 1952, p. 436.
 (9) A. E. Hill and J. E. Ricci, *THIS JOURNAL*, **53**, 4305 (1931).

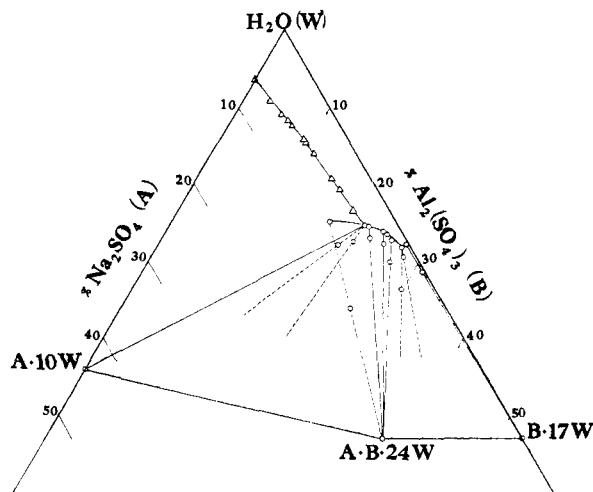


Fig. 1.—The ternary system $\text{Na}_2\text{SO}_4\text{-Al}_2(\text{SO}_4)_3\text{-H}_2\text{O}$ at 0° : O, this work; Δ , ref. 3.

of one filtered wet residue which differs somewhat from the theoretical composition of the alum, 15.50% Na_2SO_4 , 37.33% $\text{Al}_2(\text{SO}_4)_3$. This is attributed to the incomplete removal of mother liquor and some loss of water by evaporation when the residue was filtered by means of suction on a porous glass filter in air at room temperature.

Mathematical extrapolation⁹ of the tie-lines of the complexes where the alum is the solid phase (in the order in which they are listed in Table I) to % Na_2SO_4 at 47.17% H_2O , the theoretical % H_2O in the alum, gives values of 15.73, 15.19, 15.57 and 15.22 as compared with the theoretical value of 15.50%. The composition of the metastable saturated solution changed markedly to 3.77% Na_2SO_4 , 20.85% $\text{Al}_2(\text{SO}_4)_3$ on stirring for 48 hours after seeding. Reanalysis upon still further stirring was not possible because of the small amount of saturated solution remaining in the solubility tube. It is evident that the composition of the solution was still changing in the direction of that of the isothermally invariant solution saturated with respect to the alum and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. The congruent metastable solubility of soda alum at 0° can be estimated as 25.0% by weight on an anhydrous basis since the weight ratio $\text{Na}_2\text{SO}_4\text{:Al}_2(\text{SO}_4)_3$ in the metastable solution, 1:2.39, is close to that in the alum, 1:2.41.

DEPARTMENT OF CHEMISTRY
 ST. JOHN'S UNIVERSITY
 BROOKLYN 6, NEW YORK

Relative Basicities of Some Organic Nitrogen Bases

BY PHILLIP ROCHLIN, DANIEL B. MURPHY AND SAMUEL HELF

RECEIVED NOVEMBER 30, 1953

Although the 5-aminotetrazoles are generally represented, structurally, as primary amines I, their basicity appears never to have been determined quantitatively. It has been stated¹ that the basic nature of these compounds is masked in

- (1) R. M. Herbst, C. W. Roberts and E. J. Harvill, *J. Org. Chem.*, **16**, 139 (1951).