

## PHASE DIAGRAM OF THE CONVERSION SYSTEM

$2 \text{NH}_4^+, 2 \text{Na}^+, \text{SO}_4^{2-}, \text{S}_2\text{O}_8^{2-} - \text{H}_2\text{O}$  AT  $20^\circ\text{C}$

J. BALEJ, M. ČÍŽEK and M. THUMOVÁ

*Institute of Inorganic Chemistry,*

*Czechoslovak Academy of Sciences, 160 00, Prague 6*

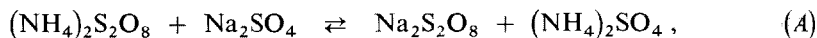
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In order to complete the investigation of the phase diagram of the conversion system  $2 \text{NH}_4^+, 2 \text{Na}^+, \text{SO}_4^{2-}, \text{S}_2\text{O}_8^{2-} - \text{H}_2\text{O}$  at  $20^\circ\text{C}$ , at first the solubilities were measured in the quasiternary sections passing through the apex of pure water and further a detailed measurement of the solubilities along the binary eutonics and of three ternary eutonics was carried out. The final phase diagram revealed, however, that at  $20^\circ\text{C}$  no reciprocal pair of salts without a common ion forms a pair of mutually compatible salts in this system, since in both cases the crystallization regions of these pairs of salts are separated by a relatively wide region of crystallization of the double salt  $\text{NaNH}_4 \cdot \text{SO}_4 \cdot 2 \text{H}_2\text{O}$ .

When studying the phase diagram of the system  $(\text{NH}_4)_2\text{S}_2\text{O}_8 - \text{Na}_2\text{S}_2\text{O}_8 - \text{H}_2\text{O}$  it was found<sup>1</sup> that eutonic solutions contain, in the temperature interval  $10 - 30^\circ\text{C}$ , more peroxydisulphate anions than saturated solutions of pure ammonium or sodium peroxydisulphate at the same temperature. This finding led to the conclusion that mixed solutions of ammonium and sodium sulphate with the necessary excess of sulphuric acid might be used for the preparation of concentrated solutions of peroxydisulphates as intermediates in the electrolytic production of hydrogen peroxide. In this way, a higher concentration of peroxydisulphate ions will probably be attained in the final electrolyte which could positively affect further technical and economic parameters of the whole process. In order to verify thoroughly the above considerations, it is necessary to know at least the respective part of the phase diagram of the multicomponent system  $(\text{NH}_4)_2\text{S}_2\text{O}_8 - (\text{NH}_4)_2\text{SO}_4 - \text{Na}_2\text{S}_2\text{O}_8 - \text{Na}_2\text{SO}_4 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$  at the temperature of electrolysis which lies in the interval  $15 - 30^\circ\text{C}$ . Up to now, however, only the less complicated partial phase diagrams of three- or four-component systems are known in which no conversion reaction takes place, leading to the formation of reciprocal pairs of salts. These are the following ternary systems:  $(\text{NH}_4)_2\text{S}_2\text{O}_8 - \text{Na}_2\text{S}_2\text{O}_8 - \text{H}_2\text{O}$  (ref.<sup>1</sup>),  $(\text{NH}_4)_2\text{S}_2\text{O}_8 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$  (ref.<sup>2</sup>),  $\text{Na}_2\text{S}_2\text{O}_8 - \text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$  (ref.<sup>3</sup>),  $\text{Na}_2\text{SO}_4 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$  (ref.<sup>4</sup>),  $(\text{NH}_4)_2\text{S}_2\text{O}_8 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$  (ref.<sup>5</sup>),  $\text{Na}_2\text{S}_2\text{O}_8 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$  (ref.<sup>6</sup>),  $(\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$  (ref.<sup>7,8</sup>),  $\text{Na}_2\text{SO}_4 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$  (ref.<sup>9</sup>) and quaternary systems:  $(\text{NH}_4)_2\text{S}_2\text{O}_8 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$  (ref.<sup>8</sup>),  $\text{Na}_2\text{S}_2\text{O}_8 - \text{Na}_2\text{SO}_4 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$  (ref.<sup>10</sup>) and  $(\text{NH}_4)_2\text{S}_2\text{O}_8 - \text{Na}_2\text{S}_2\text{O}_8 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$  (ref.<sup>11</sup>). In most cases isothermic phase diagrams of the

systems which do not contain sulphuric acid exhibit a simple eutonics in which both pure components coexist in the solid phase with saturated solution, in other cases one or the other pure component crystallizes from the saturated solutions. Only in the system  $(\text{NH}_4)_2\text{SO}_4\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$  double sodium ammonium sulphate  $\text{NaNH}_4 \cdot \text{SO}_4 \cdot 2 \text{H}_2\text{O}$  is formed under certain concentration conditions. The systems, containing sulphuric acid, are also characterized, in the case of sodium or ammonium sulphate, by the formation of double salts with sulphuric acid in various molar ratios. In systems, containing sulphuric acid and sodium or ammonium peroxydisulphate whose solubility diagram has been measured in a limited region of sulphuric acid concentrations, the solid phase, coexisting with saturated solutions of the respective composition, was found to contain only the corresponding pure peroxydisulphate.

The subject of the present communication are the results of measurements of the solubility data of a further partial system, belonging to the above-mentioned poly-component system, namely of the system in which the principal components are ammonium peroxydisulphate and sodium sulphate, at 20°C. This represents a pair of salts without common ions, so that it can be theoretically expected that, under certain concentration conditions and at a given temperature, the following conversion reaction may proceed between the two salts



yielding a reciprocal pair of salts in the solid phase.

## EXPERIMENTAL

The solubility data were measured over the whole concentration range, using the method which had been found suitable earlier<sup>9</sup>. It consists in stirring the appropriate amounts of starting components up to the equilibrium which was attained in 24 h. After this time samples of the saturated solution and of the coexisting solid phase were taken off. In order to guarantee the attaining of equilibrium in the chosen time, the systems were always prepared from solid salts whose existence was supposed in the solid phases. It turned out that spontaneous chemical decomposition of peroxydisulphate ion was practically negligible under the reaction conditions used.

*Analytical methods.* Samples of saturated solutions as well as of the coexisting solid phases with the adhering residuals of mother liquor (the so-called wet residue) were analyzed in respect of the content of their individual components. The content of ammonium ions was determined titrimetrically according to Hanuš<sup>13</sup>, peroxydisulphate anions were determined by permanganometry according to Le Blanc and Eckardt<sup>14</sup>, sulphates were determined by titration with chromate<sup>15</sup>. The content of sodium ions was calculated on the basis of equality of the sums of equivalents of anions and cations. The content of water was finally calculated from the determined contents of the individual ions and the total weight of the sample to be analyzed. Simultaneously, the density of saturated solutions was also determined, within the accuracy of three decades (*i.e.* 0.1% rel.)

*Chemicals used.* Solubility measurements were performed using chemicals of the reagent grade purity which were several times recrystallized. Sodium peroxydisulphate was prepared from ammo-

mium peroxydisulphate, purified as described above, by its conversion by concentrated solution of sodium hydroxide<sup>16</sup>. Double sodium ammonium sulphate was prepared as dihydrate by cooling the warm saturated solution of the appropriate composition, determined from the respective phase polythermal diagram of the system  $(\text{NH}_4)_2\text{SO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$  (ref.<sup>4</sup>).

## RESULTS AND DISCUSSION

Isothermic solubility diagram of a conversion system consisting of a pair of reciprocal salts is represented by a regular tetrahedral pyramid whose faces, equilateral triangles, are the phase diagrams of the partial ternary systems (in our case  $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-(NH}_4)_2\text{SO}_4\text{-H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-Na}_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$ ,  $\text{Na}_2\text{S}_2\text{O}_8\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4\text{-(NH}_4)_2\text{SO}_4\text{-H}_2\text{O}$ ) at the given temperature and whose square base illustrates the content on the respective dry salts in the system. The planar representation of this spatial isothermal diagram was performed using the clinogonal projection on its square bases according to Jänecke<sup>17</sup>. Composition of the system was expressed in equivalent per cents of individual ions, both cations and anions, so that  $\sum \text{val}_{\text{cat}}\% = \sum \text{val}_{\text{an}}\% = 100\%$ .

The shape of phase diagrams of partial ternary systems, forming the faces of the space diagram of the conversion system showed that only in the system  $(\text{NH}_4)_2\text{SO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$  a double compound is formed from the starting components, *i.e.*  $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ . Consequently, four vertical sections can be drawn through the spatial diagram, cutting the apex of pure water. In these sections the corresponding equilibrium compositions of the system can also be expressed in the form of triangles for the following quasiternary systems (schematically shown in Fig. 1):  $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{SO}_4\text{-Na}_2\text{S}_2\text{O}_8\text{-H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-NaNH}_4\text{SO}_4\text{-H}_2\text{O}$  and  $\text{Na}_2\text{S}_2\text{O}_8\text{-NaNH}_4\text{SO}_4\text{-H}_2\text{O}$ . Phase diagrams of these quasiternary systems together with the diagrams of the peripheral ternary systems form then a basis for the construction of the resulting spatial diagram of the studied conversion system, over the whole concentration range. The solubility data of the peripheral ternary systems were taken from the cited literature, with the exception of the system  $(\text{NH}_4)_2\text{SO}_4\text{-NaSO}_4\text{-H}_2\text{O}$ .

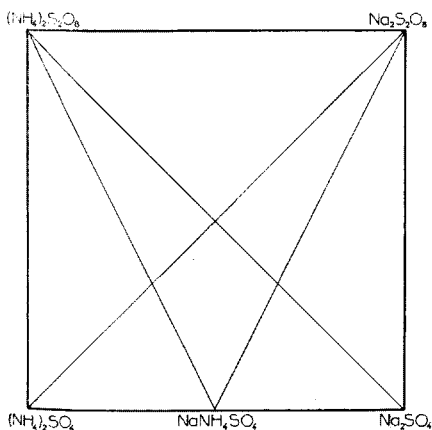


FIG. 1

Schematic Illustration of the Sections through Spatial Isothermic Phase Diagram of the Reciprocal Conversion System  $2\text{NH}_4^+$ ,  $2\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_8^{2-}\text{-H}_2\text{O}$  in Clinogonal Projection According to Jänecke

TABLE I

Solubility Data in Partial Ternary and Quasiternary Systems of the Conversion System  $2 \text{NH}_4^+$ ,  $2 \text{Na}^+$ ,  $\text{SO}_4^{4-}$ ,  $\text{S}_2\text{O}_8^{8-}$ - $\text{H}_2\text{O}$  at  $20^\circ\text{C}$

A. Ternary System  $(\text{NH}_4)_2\text{SO}_4$ - $\text{Na}_2\text{SO}_4$ - $\text{H}_2\text{O}$ .

Saturated solution				density	Solid phase
$(\text{NH}_4)_2\text{SO}_4$ mass %	$\text{Na}_2\text{SO}_4$	$(\text{NH}_4)_2\text{SO}_4$ mol. % in dry subst.	$\text{Na}_2\text{SO}_4$		
43.00	0.00	100.00	0.00	1.244	} $(\text{NH}_4)_2\text{SO}_4$
41.57	2.22	95.27	4.73	1.257	
40.03	4.60	90.34	9.66	1.271	
38.86	6.65	86.78	13.22	1.285	} $(\text{NH}_4)_2\text{SO}_4 +$ + $\text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O}$
38.4 <sup>a</sup>	7.2 <sup>a</sup>	85.15	14.85	—	
31.65	9.19	78.73	21.27	1.280	} $\text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O}$
28.22	11.57	72.39	27.61	1.279	
27.90	11.38	72.49	27.51	1.279	
26.27	12.37	69.54	30.46	1.278	
21.70	15.69	59.79	40.21	1.285	
17.69	19.56	49.30	50.70	1.302	} $\text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O} +$ + $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$
18.0 <sup>a</sup>	19.6 <sup>a</sup>	49.68	50.32	—	
8.57	17.80	34.12	65.88	1.224	} $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$
0.00	16.15	0.00	100.00	1.151	

<sup>a</sup> Determined by interpolation of data<sup>4</sup> for other temperatures.

B. Quasiternary System of the Diagonal Section  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ - $\text{Na}_2\text{SO}_4$ - $\text{H}_2\text{O}$ .

Saturated solution				density	Solid phase
$(\text{NH}_4)_2\text{S}_2\text{O}_8$ mass %	$\text{Na}_2\text{SO}_4$	$(\text{NH}_4)_2\text{S}_2\text{O}_8$ mol. % in dry subst.	$\text{Na}_2\text{SO}_4$		
44.75	0.00	100.00	0.00	1.265	} $(\text{NH}_4)_2\text{S}_2\text{O}_8$
44.00	2.71	91.00	9.00	—	
43.60	4.30	86.33	13.67	1.310	
42.10	6.90	79.16	20.84	1.336	
41.20	9.70	72.56	27.44	1.358	
41.54	10.26	71.60	28.40	1.367	
40.55	10.63	70.37	29.63	—	
39.42	13.03	65.32	34.68	1.386	
38.53	15.46	60.81	39.19	1.406	} $(\text{NH}_4)_2\text{S}_2\text{O}_8 +$ + $\text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O}$ $\text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O} +$ + $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$
26.38	20.62	44.34	55.66	1.381	

TABLE I  
(Continued)

Saturated solution				density	Solid phase
$(\text{NH}_4)_2\text{S}_2\text{O}_8$ mass %	$\text{Na}_2\text{SO}_4$	$(\text{NH}_4)_2\text{S}_2\text{O}_8$ mol % in dry subst.	$\text{Na}_2\text{SO}_4$		
24.84	20.52	42.98	57.02	1.365	} $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$
24.89	20.50	43.05	56.95	—	
23.71	20.72	41.61	58.39	1.354	
20.27	19.72	39.03	60.97	—	
14.66	18.97	32.49	67.51	1.274	
13.27	19.04	30.27	69.73	—	
8.12	18.04	21.89	78.11	1.218	
0.00	16.15	0.00	100.00	1.151	

C. Quasiternary System of the Diagonal Section  $\text{Na}_2\text{S}_2\text{O}_8$ – $(\text{NH}_4)_2\text{SO}_4$ – $\text{H}_2\text{O}$ .

Saturated solution				density	Solid phase
$\text{Na}_2\text{S}_2\text{O}_8$ mass %	$(\text{NH}_4)_2\text{SO}_4$	$\text{Na}_2\text{S}_2\text{O}_8$ mol. % in dry subst.	$(\text{NH}_4)_2\text{SO}_4$		
41.33	0.00	100.00	0.00	1.355	} $\text{Na}_2\text{S}_2\text{O}_8$
39.80	4.76	82.27	17.73	1.379	
37.74	10.48	66.65	33.35	1.406	
36.88	13.99	59.40	40.60	1.442	$\text{Na}_2\text{S}_2\text{O}_8$ + $+\text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O}$
11.76	39.37	14.22	85.78	1.316	$(\text{NH}_4)_2\text{SO}_4$ + $+\text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O}$
6.02	41.05	7.53	92.47	1.282	} $(\text{NH}_4)_2\text{SO}_4$
0.00	43.00	0.00	100.00	1.244	

D. Quasiternary System of the Section  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ – $\text{NaNH}_4\text{SO}_4$ – $\text{H}_2\text{O}$

Saturated solution				density	Solid phase
$(\text{NH}_4)_2\text{S}_2\text{O}_8$ mass %	$\text{NaNH}_4\text{SO}_4$	$(\text{NH}_4)_2\text{S}_2\text{O}_8$ mol. % in dry subst.	$\text{NaNH}_4\text{SO}_4$		
44.75	0.00	100.00	0.00	1.265	} $(\text{NH}_4)_2\text{S}_2\text{O}_8$
37.38	10.73	67.67	32.33	1.322	
28.69	22.18	43.73	56.27	1.349	$(\text{NH}_4)_2\text{S}_2\text{O}_8$ + $+\text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O}$
10.35	32.04	16.25	83.75	1.318	} $\text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O}$
0.00	37.5	0.00	100.00	1.304	

TABLE I

(Continued)

E. Quasiternary System of the Section  $\text{Na}_2\text{S}_2\text{O}_8\text{-NaNH}_4\text{SO}_4\text{-H}_2\text{O}$ 

Saturated solution				density	Solid phase
$\text{Na}_2\text{S}_2\text{O}_8$ mass %	$\text{NaNH}_4\text{SO}_4$ mass %	$\text{Na}_2\text{S}_2\text{O}_8$ mol % in dry subst.	$\text{NaNH}_4\text{SO}_4$ mol % in dry subst.		
41.33	0.00	100.00	0.00	1.355	$\text{Na}_2\text{S}_2\text{O}_8$
38.63	4.68	82.50	17.50	1.370	
37.04	7.11	75.00	25.00	1.377	$\text{Na}_2\text{S}_2\text{O}_8 +$ $+ \text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$

$\text{-H}_2\text{O}$ , for which the data had to be determined both by graphical interpolation of data from ref.<sup>4</sup>, published for other temperatures, and by our own measurements. The thus obtained data on this ternary system together with other experimental solubility data in the mentioned quasiternary systems of the studied conversion system are presented in Table I as well as in Figs 2–6. However, the Tables represent only the necessary restricted number of chosen samples of the total of 180 measured samples of saturated solutions and the coexisting solid phases. To make possible further calculations on the basis of the given phase diagram, the empirical correlation equations are also given, describing the course of the solubility lines of the components coexisting in the solid phase, in dependence on the content of further components in the saturated solution.

From the presented results it follows that in the system  $(\text{NH}_4)_2\text{SO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$

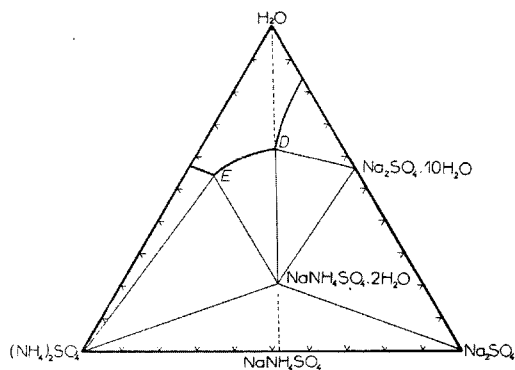


FIG. 2

Solubility Diagram of the System  $(\text{NH}_4)_2\text{SO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$  at 20°C in mass %

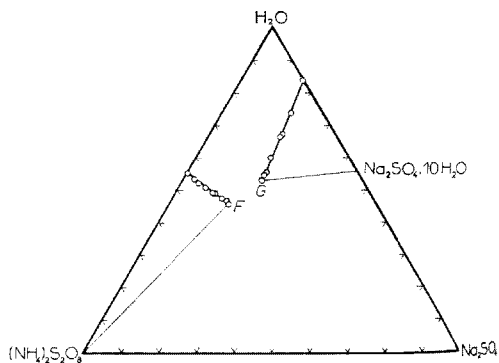


FIG. 3

Solubility Diagram of the Quasiternary Section  $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$  at 20°C in mass %

the formed double sulphate  $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$  dissolves still congruently at this temperature, but comparison with the solubility data for other temperatures<sup>4</sup> indicates that 20°C is a transition temperature below which this double sulphate dissolves already incongruently. Consequently, the eutonic point *D* at 20°C (Fig. 2), in which both dihydrate of the double sodium ammonium sulphate and sodium sulphate decahydrate can coexist with this saturated solution, gives actually the solubility of this double sulphate at the mentioned temperature.

The quasiternary system in the section  $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$  appears to be stable only in partial regions. In the region from the solubility point of pure ammonium peroxydisulphate up to point *F* (Fig. 3) solid ammonium peroxydisulphate coexists with the saturated solution, on the other side, from the solubility point of pure sodium sulphate up to point *G* sodium sulphate decahydrate coexists with the saturated solution. In the concentration region between points *F* and *G* the system cannot be synthesized from the two initial components, since the saturated solutions lying on the diagonal  $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{--Na}_2\text{SO}_4$  coexist with solid sodium ammonium sulphate dihydrate. Thus, point *F* represents the eutonic point in which ammonium peroxydisulphate and sodium ammonium sulphate (dihydrate) coexist in the solid phase with this saturated solution, point *G* is the eutonic point, characterized by the coexistence of sodium ammonium sulphate dihydrate and sodium sulphate decahydrate in the solid phases with saturated solution. From Fig. 3 it can be seen that the course of solubility lines in both stable regions is linear (when the composition of the system is expressed in mass per cent), so that up to point *F* the dependence of the solubility of ammonium peroxydisulphate on the content of sodium sulphate in saturated solutions can be expressed by a simple relation

$$a = 44.75 - 0.4023b \quad (\text{mass } \% (\text{NH}_4)_2\text{S}_2\text{O}_8) \quad (1)$$

and analogously, up to point *G*, the dependence of the solubility of sodium sulphate

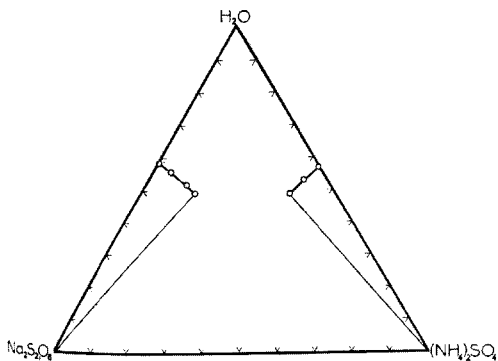


FIG. 4  
Solubility Diagram of the Quasiternary Section  $\text{Na}_2\text{S}_2\text{O}_8\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$  at 20°C in mass % (left eutonic point *H*; right eutonic point *I*).

on the content of ammonium peroxydisulphate in saturated solution can be described by the relation

$$b = 16.15 + 0.1706a \quad (\text{mass } \% \text{ Na}_2\text{SO}_4). \quad (2)$$

Eq. (1) is valid for  $b \leq 15.46 \text{ mass } \% \text{ Na}_2\text{SO}_4$ , Eq. (2) is valid for  $a \leq 26.20 \text{ mass } \% (\text{NH}_4)_2\text{S}_2\text{O}_8$ .

The quasiternary system in the diagonal section  $\text{Na}_2\text{S}_2\text{O}_8$ – $(\text{NH}_4)_2\text{SO}_4$ – $\text{H}_2\text{O}$  is at  $20^\circ\text{C}$  stable in the restricted concentration range (Fig. 4), too. In the region from the solubility point of pure sodium peroxydisulphate up to point *H*, pure sodium peroxydisulphate coexists with saturated solutions, in the region from the solubility point of pure ammonium sulphate up to point *H* pure ammonium sulphate coexists with saturated solutions. The region between points *H* and *I* is not stable with respect to initial pure components, because of the coexistence of sodium ammonium dihydrate in the solid phase with saturated solutions, lying on the mentioned diagonal. Therefore, point *H* represents an eutonic point, in which the saturated solution of this composition coexists with sodium peroxydisulphate and sodium ammonium sulphate (dihydrate) in the solid phase, whereas eutonic point *I* is characterized by the coexistence of solid sodium-ammonium sulphate dihydrate and ammonium sulphate with the saturated solution. The effect of ammonium sulphate on the solubility of sodium peroxydisulphate can be expressed, according to the data in Table I, by the relation (for  $20^\circ\text{C}$ )

$$c = 41.33 - 0.3225d + 0.0025d^2 \quad (\text{mass } \% \text{ Na}_2\text{S}_2\text{O}_8). \quad (3)$$

Analogously, the effect of sodium peroxydisulphate on the solubility of ammonium sulphate (in the crystallization region of ammonium sulphate) can be described by

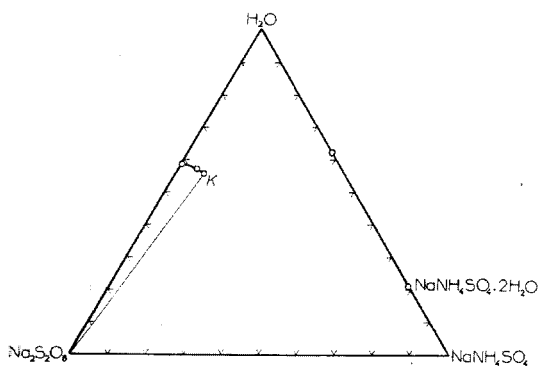


FIG. 5

Solubility Diagram of the Quasiternary Section  $\text{Na}_2\text{S}_2\text{O}_8$ – $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ – $\text{H}_2\text{O}$  at  $20^\circ\text{C}$  in mass %

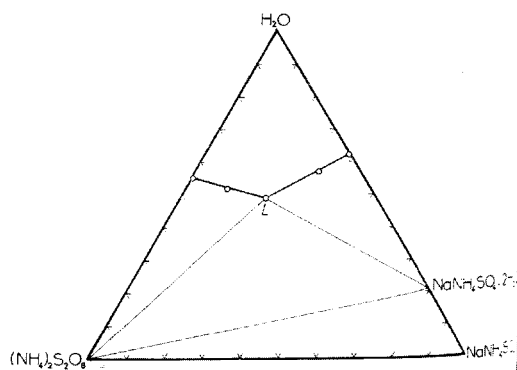


FIG. 6

Solubility Diagram of the Quasiternary Section  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ – $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ – $\text{H}_2\text{O}$  at  $20^\circ\text{C}$  in mass %



the relation

$$d = 43.00 - 0.359c + 0.0043c^2 \text{ (mass \% } (\text{NH}_4)_2\text{SO}_4 \text{)}. \quad (4)$$

Eq. (3) is valid for  $d \leq 13.99$  mass %  $(\text{NH}_4)_2\text{SO}_4$ , Eq. (4) for  $c \leq 11.76$  mass %  $\text{Na}_2\text{S}_2\text{O}_8$ .

The quasiternary system in the section  $\text{Na}_2\text{S}_2\text{O}_8$ - $\text{NaNH}_4\text{SO}_4$ - $\text{H}_2\text{O}$  is also stable only in a limited concentration range. The stable crystallization region is found only with sodium peroxydisulphate (Fig. 5), ranging from the point of solubility of this salt in pure water up to point K which represents the eutonic point in which sodium peroxydisulphate and sodium sulphate decahydrate coexist in the solid phase with the saturated solution of this composition. The effect of sodium ammonium sulphate on the solubility of sodium peroxydisulphate can be, accordingly, described by the relation

$$c = 41.33 - 0.5322f - 0.01f^2 \text{ (mass \% } \text{Na}_2\text{S}_2\text{O}_8 \text{)}, \quad (5)$$

valid in the interval  $f \leq 7.11$  mass %  $\text{NaNH}_4\text{SO}_4$ . Further region up to saturated solution of double sodium ammonium sulphate in pure water is not stable in the given quasiternary system due to the fact that the solubility point of this double sulphate in pure water at 20°C is at the same time the eutonic point in which  $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$  coexist in the solid phase with the saturated solution.

The quasiternary system in the section  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ - $\text{NaNH}_4\text{SO}_4$ - $\text{H}_2\text{O}$  at 20°C appears to be the only one really stable system over the whole concentration range, with a simple eutonic point (point L in Fig. 6), characterized by the coexistence of both initial components of this system with the saturated solution. As can be seen from the diagram, the solubility lines in both solubility branches show a linear course (when the composition is expressed in mass %), and therefore the effect of double sodium ammonium sulphate on the solubility of ammonium peroxydisulphate can be expressed by the relation

$$a = 44.75 - 0.7241f \text{ (mass \% } (\text{NH}_4)_2\text{S}_2\text{O}_8 \text{)}. \quad (6)$$

Analogously the dependence of the solubility of sodium ammonium sulphate on the presence of ammonium peroxydisulphate in the saturated solution, can be described by the equation

$$f = 37.60 - 0.5375a \text{ (mass \% } \text{NaNH}_4\text{SO}_4 \text{)}. \quad (7)$$

Eq. (6) holds for  $f \leq 22.18$  mass %  $\text{NaNH}_4\text{SO}_4$  and Eq. (7) for  $a \leq 28.69$  mass %  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ .

For a reliable construction of the total phase diagram of the studied conversion system at the given temperature it was further necessary to measure the solubility data in a series of systems whose composition lay outside the mentioned sections, either in regions of crystallization of one single solid phase, or represented binary or ternary eutonics. In view of the fact that the existence of one stable binary compound,

TABLE II

Composition of Binary and Ternary Eutonics in the Reciprocal Conversion System  $2\text{NH}_4^+$ ,  $2\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{H}_2\text{O}$  at  $20^\circ\text{C}$ A. Binary Eutonics Coexisting with  $(\text{NH}_4)_2\text{S}_2\text{O}_8 + (\text{NH}_4)_2\text{SO}_4$  in the Solid Phase (line AM in Fig. 8).

Saturated solution							Solid phase		
$\text{Na}^+$	$\text{NH}_4^+$	$\text{S}_2\text{O}_8^{2-}$ mass %	$\text{SO}_4^{2-}$	$\text{Na}^+$	$\text{NH}_4^+$	$\text{S}_2\text{O}_8^{2-}$ equiv. %		$\text{SO}_4^{2-}$	density
0.00	11.24	12.48	23.68	0.00	100.00	20.85	79.15	1.277	$(\text{NH}_4)_2\text{S}_2\text{O}_8 + (\text{NH}_4)_2\text{SO}_4$
1.21	10.61	12.49	24.54	8.25	91.75	20.27	79.73	1.301	
2.27	10.08	12.25	25.46	15.02	84.98	19.39	80.61	1.323	$(\text{NH}_4)_2\text{S}_2\text{O}_8 + (\text{NH}_4)_2\text{SO}_4 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$

B. Binary Eutonics Coexisting with  $\text{Na}_2\text{S}_2\text{O}_8 + (\text{NH}_4)_2\text{S}_2\text{O}_8$  in the Solid Phase (line BO in Fig. 8).

5.11	4.80	46.97	0.00	45.43	54.57	100.00	0.00	1.449	
5.45	4.91	44.63	2.28	46.54	53.46	91.24	8.76	1.450	$(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{Na}_2\text{S}_2\text{O}_8$
5.52	5.05	44.36	2.82	46.99	53.01	88.72	11.28	1.451	
5.97	5.20	38.47	7.06	47.37	52.63	73.15	25.85	1.455	$(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{Na}_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$

C. Binary Eutonics Coexisting with  $\text{Na}_2\text{S}_2\text{O}_8 + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  in the Solid Phase (line CN in Fig. 8).

8.86	0.00	28.55	4.20	100.00	0.00	77.24	22.76	1.364	
8.75	0.27	29.13	4.40	96.16	3.84	76.84	23.16	1.367	
7.97	1.77	30.70	6.01	77.92	22.08	71.85	28.15	1.390	$\text{Na}_2\text{S}_2\text{O}_8 + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
7.93	1.82	30.89	5.97	77.79	22.21	72.10	27.90	1.390	
7.72	2.47	31.07	7.18	71.03	28.97	68.37	31.63	1.400	
7.63	2.79	30.93	7.92	68.20	31.80	66.13	33.87	1.404	
7.45	3.80	29.90	10.67	60.63	39.37	58.25	41.75	1.422	$\text{Na}_2\text{S}_2\text{O}_8 + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$

TABLE II  
(Continued)G. Binary Eutonics Coexisting with  $\text{Na}_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O}$  in the Solid Phase (line NO in Fig. 8).

Saturated solution							Solid phase		
$\text{Na}^+$	$\text{NH}_4^+$	$\text{S}_2\text{O}_8^{2-}$ mass %	$\text{SO}_4^{2-}$	$\text{Na}^+$	$\text{NH}_4^+$	$\text{S}_2\text{O}_8^{2-}$ equiv. %			
							density		
7.45	3.80	29.90	10.67	60.63	39.37	58.25	41.75	1.422	$\text{Na}_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O} +$ $+ \text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$
72.0	3.82	29.72	10.66	59.68	40.32	58.92	41.08	1.422	$\text{Na}_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O}$
6.84	4.27	32.38	9.48	55.68	44.32	63.05	36.95	1.427	
6.36	5.21	37.89	8.21	48.95	51.05	69.74	30.26	1.439	
6.10	5.07	37.52	7.50	48.56	51.44	71.42	28.58	1.440	
6.06	5.15	38.11	7.32	47.98	52.02	72.33	27.67	1.447	
5.97	5.20	38.47	7.06	47.37	52.63	73.15	26.85	1.455	$\text{Na}_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O} +$ $+ (\text{NH}_4)_2\text{S}_2\text{O}_8$
H. Ternary Eutonics in the System $2 \text{NH}_4^+$ , $2 \text{Na}^+$ , $\text{SO}_4^{2-}$ , $\text{S}_2\text{O}_8^{2-} - \text{H}_2\text{O}$ at $20^\circ\text{C}$ .									
2.27	10.08	12.25	25.46	15.02	84.98	19.39	80.61	1.323	$(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O} +$ $+ (\text{NH}_4)_2\text{SO}_4$ (point M in Fig. 8)
7.45	3.80	29.90	10.67	60.63	39.37	58.25	41.75	1.422	$\text{Na}_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O} + \text{Na}_2\text{SO}_4 \cdot$ $10 \text{H}_2\text{O}$ (point N in Fig. 8)
5.97	5.20	38.47	7.06	47.37	52.63	73.15	26.85	1.455	$(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{Na}_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot$ $2 \text{H}_2\text{O}$ (point O in Fig. 8)

D. Binary Eutectics Coexisting with  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$  in the Solid Phase (line DN in Fig. 8).

6-30	4-93	0-00	26-27	50-05	49-95	0-00	100-00	1-304	
6-33	4-54	8-23	21-18	52-28	47-72	16-26	83-74	1-320	
6-41	4-22	18-97	15-14	54-39	45-61	38-50	61-50	1-366	
6-73	4-31	18-15	16-45	55-07	44-93	35-53	64-47	1-360	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$
6-54	4-13	22-80	13-20	55-51	44-49	46-34	53-66	1-384	
6-92	3-98	26-84	11-62	57-70	42-30	53-58	46-42	1-407	
7-13	3-89	28-39	11-28	59-30	40-70	55-70	44-30	1-412	
7-33	3-84	29-06	10-79	59-91	40-09	56-94	43-04	1-417	
7-45	3-80	29-72	10-66	59-68	40-32	58-92	41-08	1-422	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O} +$ $+ \text{Na}_2\text{S}_2\text{O}_8$

E. Binary Eutectics Coexisting with  $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O} + (\text{NH}_4)_2\text{SO}_4$  in the Solid Phase (line EM in Fig. 8).

2-23	10-52	0-00	32-75	14-03	85-97	0-00	100-00	1-284	$\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O} + (\text{NH}_4)_2\text{SO}_4$
2-40	10-20	8-49	27-92	15-61	84-39	13-19	86-81	1-308	
2-27	10-08	12-25	25-46	15-02	84-98	19-39	80-61	1-323	$\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O} + (\text{NH}_4)_2\text{SO}_4 +$ $+ (\text{NH}_4)_2\text{S}_2\text{O}_8$

F. Binary Eutectics Coexisting with  $(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$  in the Solid Phase (line MO in Fig. 8).

2-27	10-08	12-25	25-46	15-02	84-98	19-39	80-61	1-323	$(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O} + (\text{NH}_4)_2\text{SO}_4$
2-77	8-86	17-40	20-69	19-74	80-26	29-59	70-41	1-330	
3-72	7-49	24-14	15-52	28-14	71-86	43-73	56-27	1-349	
4-20	6-70	28-78	12-21	32-98	67-02	54-08	45-92	1-373	
4-74	6-23	32-23	10-41	37-31	62-69	60-74	39-26	1-392	$(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$
4-94	6-00	33-19	9-72	39-20	60-80	63-06	36-94	1-410	
5-35	5-75	35-41	8-80	42-10	57-90	66-85	33-15	1-420	
5-59	5-53	36-82	8-03	44-16	55-84	69-63	30-37	1-431	
5-13	4-61	38-34	6-33	46-63	53-37	72-46	27-54	1-454	
5-97	5-20	38-47	7-06	47-37	52-63	73-15	26-85	1-455	$(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{S}_2\text{O}_8$

formed from the initial components of the conversion system (*i.e.* sodium ammonium sulphate dihydrate) has already been proved, we can expect that the number of ternary eutonics, in which simultaneously three solid phases coexist with the saturated solution will be three. The results of this series of measurements are summarized in Table II.

The resulting two-dimensional projection of the spatial phase diagram of the studied system of reciprocal pair of salts according to Jänecke<sup>17</sup> is shown in Fig. 7. In this diagram where the compositions are plotted in val % of the proper salts, heavy full lines denote the courses of binary eutonics for the coexistence of two solid phases with the saturated solution of the given composition. Their three intersections (points *M*, *N* and *O*) represent the mentioned ternary eutonics of this system, the remaining areas delimited by heavy full lines represent the regions where one solid phase coexists with the saturated solution of the given composition. Since this two-dimensional projection of a space diagram of the conversion system does not allow to express directly the content of water in saturated solutions, thin lines were used in this diagram to denote the course of isohydors, *i.e.* of lines with constant content of water in saturated solutions of different composition. Numbers on these isohydors denote the content of water in mass %. The numbers at several outstanding points of this system, marked by letters, have the same meaning. Points *A*, *B*, *C*, *D* and *E* represent the composition of binary eutonics in phase diagrams of ternary systems

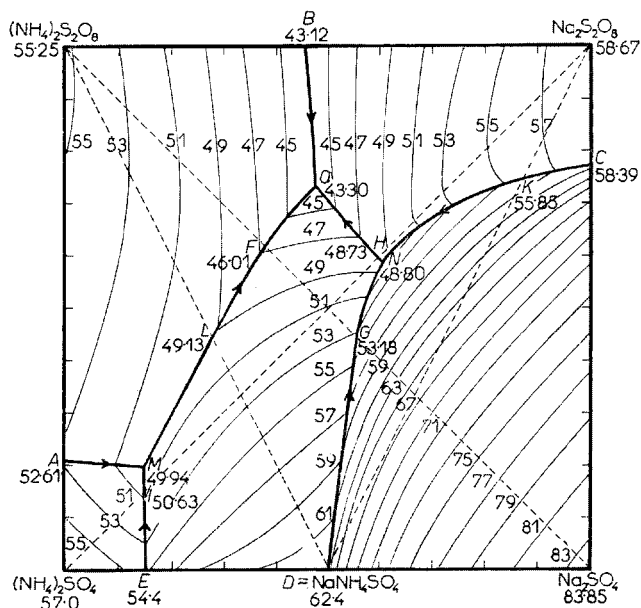


FIG. 7

Solubility Diagram of the Reciprocal Conversion System  $2 \text{NH}_4^+$ ,  $2 \text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_8^{2-} - \text{H}_2\text{O}$  at  $20^\circ\text{C}$  in Clinogonal Projection according to Jänecke with Marked Course of Isohydors

which form the sides of the spatial phase diagram of the studied conversion system (the figurative point *D* of the eutonic point for the coexistence of solid sodium ammonium sulphate dihydrate and ammonium sulphate decahydrate, in Fig. 2, coincides in this projection with the figurative point of pure sodium ammonium sulphate, according to the above mentioned findings). The meaning of points *F*, *G*, *H*, *I*, *K* and *L* was already explained in discussing the results of solubility measurements in the sections of quasiternary systems (Figs 3–6). The ternary eutonic point *M* gives the composition of the saturated solution, coexisting with solid ammonium peroxydisulphate, ammonium sulphate and sodium ammonium sulphate dihydrate, the ternary eutonic point *N* gives the composition of the saturated solution coexisting with solid ammonium peroxydisulphate, sodium peroxydisulphate and sodium ammonium sulphate dihydrate and the ternary eutonic point *O* denotes the composition of the saturated solutions, coexisting with sodium peroxydisulphate, sodium sulphate decahydrate and sodium ammonium sulphate dihydrate in the solid phase. No further ternary eutonics were found to exist in this system at 20°C which indicates that also in systems lying outside the discussed quasiternary sections, no further double salts are formed nor any change in the number of crystalline water molecules in the hydrates occurs.

The arrows on the lines of binary eutonics denote the direction in which the composition of saturated solutions gradually changes during drying up of the system.

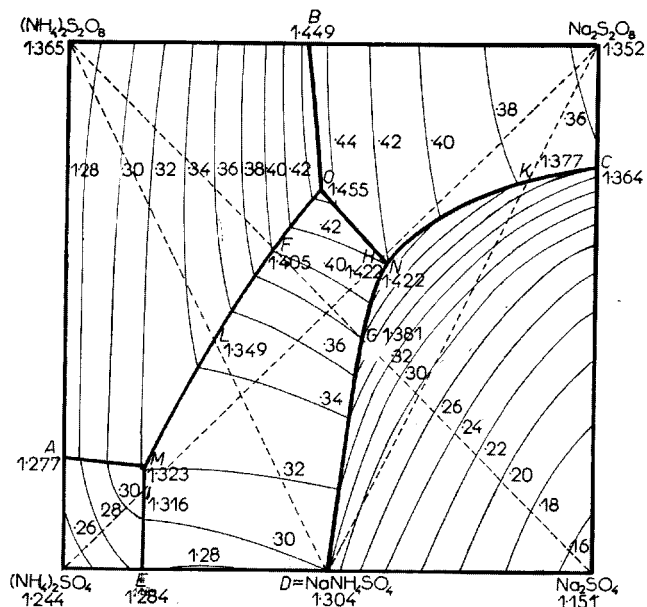


FIG. 8

Solubility Diagram of the Reciprocal Conversion System  $2 \text{NH}_4^+$ ,  $2 \text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_8^{2-} - \text{H}_2\text{O}$  at 20°C with Marked Course of the Curves Connecting the Compositions of Saturated Solutions of the Same Density

Their course as well as the values indicating the content of water in outstanding points of the system show that the lowest water content is attained in the ternary eutonic point *O*, which represents thus a congruent ternary eutonic solution of this system at 20°C. Similarly, also point *N* appears to be a congruent ternary eutonic solution. The binary eutonic solutions connecting point *N* with point *O*, however, exhibit in their water content a difficultly distinguishable maximum at point *H* having only very slightly higher content of water than that found in point *N*. Consequently, within the limits of experimental errors, a continuous, at the beginning very slow decrease of water content in the direction *NO* cannot be excluded. The ternary eutonic point *M* evidently corresponds to an incongruently saturated solution, because by gradual drying up of the system the composition of saturated solutions is shifted from point *M* to point *O*.

Fig. 8 illustrates the same phase diagram of the studied system in which thin lines connect the points with constant density of saturated solutions of different compositions. The data in this phase diagram, together with the data in Fig. 7, make it possible to express the composition of saturated solutions of the system in arbitrary concentration units.

The presented phase diagram of the studied system of reciprocal salts demonstrates an interesting finding that in this case no reciprocal pair of salts without a common ion forms a pair of mutually compatible salts at 20°C, since both in the case of the pair  $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-Na}_2\text{SO}_4$  and  $\text{Na}_2\text{S}_2\text{O}_8\text{-(NH}_4)_2\text{SO}_4$  their crystallization regions are always separated by a relatively large crystallization region of the double salt  $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , extending far outside both diagonals of the conversion system (Fig. 7).

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