

## 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  $30^\circ\text{C}$ 

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Phase diagram of the given conversion system was determined on the basis of individual quasi-ternary sections passing through the apex of pure water, further from the courses of binary eutonics between the coexisting pairs of solid phases and of ternary eutonics. At the same time the phase diagrams of partial systems  $(\text{NH}_4)_2\text{SO}_4$ - $\text{Na}_2\text{SO}_4$ - $\text{H}_2\text{O}$  and  $\text{Na}_2\text{S}_2\text{O}_8$ - $\text{Na}_2\text{SO}_4$ - $\text{H}_2\text{O}$  at the given temperature were precisified. From the resulting phase diagram of the conversion system it followed that, similarly as at  $20^\circ\text{C}$ , no pair of reciprocal salts without a common ion forms a pair of mutually compatible salts in this system, since in both cases the crystallization regions of these reciprocal salts are separated by a relatively wide region of crystallization of the double salt  $\text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O}$ .

The results of the investigation of 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  $20^\circ\text{C}$  were reported in the preceding publication<sup>1</sup>. This diagram can be, *inter alia*, used for determining the maximum admissible concentration of the initial solution for electrolytic preparation of highly concentrated solutions of peroxydisulphate ions, *via* anodic oxidation of mixed solutions of ammonium and sodium sulphate with a suitable excess of sulphuric acid. Since the temperature of this electrolytic process lies between  $15$ - $30^\circ\text{C}$ , it was of interest to investigate the course of phase diagram of this system also at  $30^\circ\text{C}$ . The results of these measurements form the subject of the present communication.

Phase diagrams of ternary systems which form the faces of the spatial diagram of the mentioned conversion system, are mostly known for the mentioned temperature:  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ - $(\text{NH}_4)_2\text{SO}_4$ - $\text{H}_2\text{O}$  (see ref.<sup>2</sup>),  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ - $\text{Na}_2\text{S}_2\text{O}_8$ - $\text{H}_2\text{O}$  (see ref.<sup>3</sup>). In the system  $(\text{NH}_4)_2\text{SO}_4$ - $\text{Na}_2\text{SO}_4$ - $\text{H}_2\text{O}$  only the positions of binary eutonics are known for  $30^\circ\text{C}$  (see ref.<sup>4</sup>) so that it was necessary to measure the course of solubility curves over the whole range of compositions. Moreover, it was found in the course of measurements that the earlier published data<sup>5</sup> on the system  $\text{Na}_2\text{S}_2\text{O}_8$ - $\text{Na}_2\text{SO}_4$ - $\text{H}_2\text{O}$  for  $30^\circ\text{C}$  in the eutonic region correspond to a metastable coexistence of saturated solution with sodium sulphate decahydrate and thus it was necessary to precisify the course of stable solubility data at the mentioned temperature also in this system.

Working procedure, purity of chemicals used and methods of analytical determination of the composition of saturated aqueous solutions and the coexisting solid phases as well as the determination of the densities of saturated solutions were the same as in the preceding work<sup>1</sup>.

## RESULTS AND DISCUSSION

Solubility data in the system  $(\text{NH}_4)_2\text{SO}_4$ - $\text{Na}_2\text{SO}_4$ - $\text{H}_2\text{O}$  are presented in Table I and the corresponding phase diagram is shown in Fig. 1. From the diagram it follows that the region of coexistence of crystals of sodium sulphate decahydrate with saturated solution is markedly diminished when compared with the isotherm for  $20^\circ\text{C}$ , since the increase in the content of ammonium sulphate in the solution over a limiting value leads to the dehydration of the solid phase to anhydrous sulphate, coexisting with saturated solutions in the region *ED*. Contrary to this, the crystallization region of double sodium ammonium sulphate has become somewhat wider in comparison with that at  $20^\circ\text{C}$  so that at  $30^\circ\text{C}$  this salt, crystallizing as  $\text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O}$ , dissolves distinctly congruently. At this temperature its solubility was found to be 40.19 mass%  $\text{NaNH}_4\text{SO}_4$ , the density of saturated solution being  $1.313 \text{ g cm}^{-3}$ .

Precise solubility data in the system  $\text{Na}_2\text{S}_2\text{O}_8$ - $\text{Na}_2\text{SO}_4$ - $\text{H}_2\text{O}$  are summarized in Table II and the corresponding part of the phase diagram (up to 50 mass% of both salts) is illustrated in Fig. 2. The diagram shows that, in contradiction to the earlier published data<sup>5</sup> which were obtained in the course of shorter equilibration time (see Fig. 2, full points), in the present case the course of solubility in the crystallization

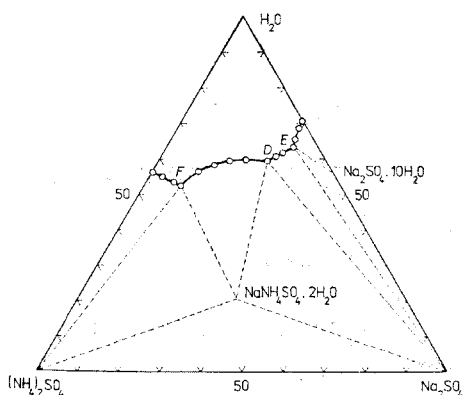


FIG. 1

Solubility Diagram (in mass%) of the System  $(\text{NH}_4)_2\text{SO}_4$ - $\text{Na}_2\text{SO}_4$ - $\text{H}_2\text{O}$  at  $30^\circ\text{C}$

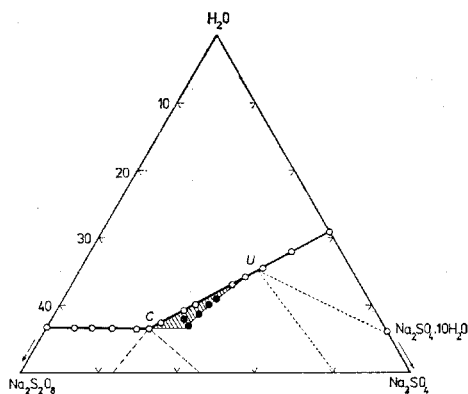


FIG. 2

Solubility Diagram (in mass%) of the System  $\text{Na}_2\text{S}_2\text{O}_8$ - $\text{Na}_2\text{SO}_4$ - $\text{H}_2\text{O}$  at  $30^\circ\text{C}$   
Hatched area metastable region.

region of sodium sulphate shows practically a single linear dependence on the content of sodium peroxydisulphate in saturated solution. At the same time, however, a decahydrate coexists in the solid phase with the saturated solutions containing lower amounts of peroxydisulphate and only anhydrous sodium sulphate coexists with saturated solutions with higher content of peroxydisulphate. Consequently, the composition of saturated solution at which dehydration of sodium sulphate decahydrate occurs at 30°C, cannot be determined from the continuous course of the solubility dependence in the crystallization region of sodium sulphate. Also the dependence of densities of saturated solutions on their composition is expressed over the whole stable crystallization region by a single line and thus even these data cannot help in determining the mentioned transition point.

The hatched area in Fig. 2 denotes the metastable region, corresponding to the coexistence of saturated (or oversaturated) solution with sodium sulphate decahydrate which, at these concentration conditions, exists already as the unstable solid phase. These metastable solubility data are obtained when a shorter time of mixing the excess solid sulphate decahydrate with the solution of the respective composition is used (as it was the case in the determination of solubility in this system in the previous publication<sup>5</sup>). When anhydrous sodium sulphate is used as the excess solid phase

TABLE I  
Solubility Data in the System  $(\text{NH}_4)_2\text{SO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$  at 30°C

| Saturated solution                     |                          |  |                          | density | Solid phase   |
|--|--------------------------|--|--------------------------|---------|---|
| $(\text{NH}_4)_2\text{SO}_4$<br>mass % | $\text{Na}_2\text{SO}_4$ | $(\text{NH}_4)_2\text{SO}_4$<br>mol. % in dry subst. | $\text{Na}_2\text{SO}_4$ |         |   |
| 43.90                                  | 0.00                     | 100.00   | 0.00                     | 1.247   | } $(\text{NH}_4)_2\text{SO}_4$  |
| 41.98                                  | 3.01                     | 93.75  | 6.25                     | 1.266   |   |
| 39.89                                  | 6.73                     | 86.43  | 13.57                    | 1.290   |   |
| 38.67                                  | 8.31                     | 83.34  | 16.66                    | 1.300   | } $(\text{NH}_4)_2\text{SO}_4 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ |
| 32.60                                  | 11.01                    | 76.09  | 23.91                    | 1.301   |   |
| 27.60                                  | 14.03                    | 67.89  | 32.11                    | 1.302   | } $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$                              |
| 23.44                                  | 17.06                    | 59.63  | 40.37                    | 1.305   |   |
| 19.37                                  | 20.82                    | 50.00  | 50.00                    | 1.313   |   |
| 14.40                                  | 26.11                    | 37.22  | 62.78                    | 1.350   | } $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$     |
| 11.61                                  | 27.70                    | 31.05  | 68.95                    | 1.349   |   |
| 9.37                                   | 28.87                    | 25.86  | 74.14                    | 1.348   | } $\text{Na}_2\text{SO}_4$  |
| 5.83                                   | 30.64                    | 16.97  | 83.08                    | 1.345   |   |
| 4.55                                   | 29.98                    | 14.02  | 85.98                    | 1.335   | } $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$                               |
| 1.85                                   | 29.28                    | 6.35   | 93.65                    | 1.308   |   |
| 0.00                                   | 29.05                    | 0.00   | 100.00                   | 1.284   |   |

or when a sufficiently long time is allowed for dehydration of decahydrate in contact with saturated solutions of the respective composition (minimum 20 h), stable solubility data are obtained. Of course, even this time lag is not long enough for a complete transformation of the initial charge of the solid phase in its bulk to the corresponding stable state which is formed only in the surface layer which evidently is sufficient for obtaining a stable value of solubility. This may also serve as an explanation why a precise transition point of decahydrate to anhydrous sodium sulphate could not be determined within the time of solubility equilibration which could not be prolonged any more because of the possible decomposition of peroxydisulphates. However, the possibility cannot be excluded that this point might roughly correspond to the composition of the saturated solution at which the metastable region begins, *i.e.* c. 12 mass%  $\text{Na}_2\text{S}_2\text{O}_8$  and 23 mass%  $\text{Na}_2\text{SO}_4$ .

TABLE II  
Solubility Data in the System  $\text{Na}_2\text{S}_2\text{O}_8 - \text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$  at  $30^\circ\text{C}$

| Saturated solution                          |                          |  |                          |         | Solid phase   |
|---|--------------------------|--|--------------------------|---------|---|
| $\text{Na}_2\text{S}_2\text{O}_8$<br>mass % | $\text{Na}_2\text{SO}_4$ | $\text{Na}_2\text{S}_2\text{O}_8$<br>mol % in dry subst. | $\text{Na}_2\text{SO}_4$ | density |   |
| stable region                               |                          |  |                          |         |   |
| 43.19                                       | 0.00                     | 100.00   | 0.00                     | 1.367   | } $\text{Na}_2\text{S}_2\text{O}_8$   |
| 39.76                                       | 3.49                     | 87.17  | 12.83                    | 1.370   |   |
| 37.54                                       | 5.81                     | 79.40  | 20.60                    | 1.376   |   |
| 35.06                                       | 8.42                     | 71.30  | 28.70                    | 1.382   |   |
| 32.02                                       | 11.71                    | 62.00  | 38.00                    | 1.388   |   |
| 30.42                                       | 13.13                    | 58.02  | 41.98                    | 1.391   | } $\text{Na}_2\text{S}_2\text{O}_8 + \text{Na}_2\text{SO}_4$                        |
| 28.28                                       | 14.44                    | 53.88  | 46.12                    | 1.383   |   |
| 24.52                                       | 16.17                    | 47.50  | 52.50                    | 1.370   | } $\text{Na}_2\text{SO}_4$  |
| 24.42                                       | 16.57                    | 46.79  | 53.21                    | 1.370   |   |
| 22.70                                       | 17.37                    | 43.81  | 56.19                    | 1.364   |   |
| 16.34                                       | 20.59                    | 32.17  | 67.87                    | 1.341   |   |
| 14.18                                       | 21.69                    | 28.06  | 71.94                    | 1.334   |   |
| 11.28                                       | 23.20                    | 22.48  | 77.51                    | 1.323   | } $\text{Na}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O} (?)$ |
| 6.84  | 25.58                    | 13.76  | 86.24                    | 1.308   |   |
| 0.00  | 29.05                    | 0.00   | 100.00                   | 1.284   | } $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$                              |
| metastable region                           |                          |  |                          |         |   |
| 19.45                                       | 19.47                    | 37.34  | 62.66                    | 1.364   | } $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$                              |
| 20.80                                       | 19.07                    | 39.42  | 60.58                    | 1.372   |   |
| 22.92                                       | 18.60                    | 42.37  | 57.63                    | 1.387   |   |
| 25.06                                       | 16.83                    | 47.04  | 52.96                    | 1.389   |   |

Also the dependence of densities of stable and metastable saturated solutions on composition shows a similar course to that of the stable and metastable solubility curves.

TABLE III

Solubility Data in Partial Quasiternary Systems 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  $30^\circ\text{C}$

Quasiternary system of the 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   |
|---|---|--------|--------|---------|---|
| $\text{Na}_2\text{S}_2\text{O}_8$ (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub><br>mass % | $\text{Na}_2\text{S}_2\text{O}_8$ (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub><br>mol. % in dry subst. |        |        |         |   |
| 43.19   | 0.00  | 100.00 | 0.00   | 1.367   | Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>   |
| 42.54   | 2.77  | 89.50  | 10.50  | 1.385   |   |
| 41.79   | 6.74  | 77.47  | 22.53  | 1.404   |   |
| 40.59   | 12.03   | 65.19  | 34.81  | 1.424   |   |
| 39.93   | 14.46   | 60.50  | 39.50  | 1.432   | Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> + Na <sub>2</sub> SO <sub>4</sub>                         |
| 13.65   | 37.05   | 16.58  | 83.42  | 1.329   | NaNH <sub>4</sub> SO <sub>4</sub> .2 H <sub>2</sub> O + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> |
| 12.51   | 37.49   | 15.62  | 84.38  | 1.319   | (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>   |
| 8.63  | 39.56   | 10.80  | 89.20  | 1.297   |   |
| 5.35  | 41.27   | 7.02   | 92.98  | 1.279   |   |
| 0.00  | 43.90   | 0.00   | 100.00 | 1.247   |   |

Quasiternary system of the section  $(\text{NH}_4)_2\text{S}_2\text{O}_8-\text{Na}_2\text{SO}_4-\text{H}_2\text{O}$

| $(\text{NH}_4)_2\text{S}_2\text{O}_8$ Na <sub>2</sub> SO <sub>4</sub><br>mass % | $(\text{NH}_4)_2\text{S}_2\text{O}_8$ Na <sub>2</sub> SO <sub>4</sub><br>mol % in dry subst. |        |        | density |   |
|---|--|--------|--------|---------|---|
| 48.40   | 0.00   | 100.00 | 0.00   | 1.287   | (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>   |
| 46.13   | 4.87   | 85.51  | 14.49  | 1.338   |   |
| 44.07   | 9.13   | 75.02  | 24.98  | 1.367   |   |
| 42.60   | 12.44  | 68.06  | 31.94  | 1.390   |   |
| 41.25   | 15.40  | 62.50  | 37.50  | 1.417   | (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> + NaNH <sub>4</sub> SO <sub>4</sub> .2 H <sub>2</sub> O |
| 26.60   | 22.40  | 42.50  | 57.50  | 1.391   | NaNH <sub>4</sub> SO <sub>4</sub> .2 H <sub>2</sub> O + Na <sub>2</sub> SO <sub>4</sub>                               |
| 24.27   | 23.53  | 39.11  | 60.89  | 1.386   | Na <sub>2</sub> SO <sub>4</sub>   |
| 16.78   | 26.74  | 28.10  | 71.90  | 1.368   |   |
| 10.99   | 28.87  | 19.26  | 80.74  | 1.355   |   |
| 9.22  | 29.03  | 16.65  | 83.35  | 1.349   |   |
| 5.42  | 30.11  | 10.04  | 89.96  | 1.340   | Na <sub>2</sub> SO <sub>4</sub> .10 H <sub>2</sub> O(?)   |
| 2.03  | 29.35  | 4.11   | 95.89  | 1.307   |   |
| 0.00  | 29.05  | 0.00   | 100.00 | 1.284   | Na <sub>2</sub> SO <sub>4</sub> .10 H <sub>2</sub> O  |

TABLE III

(Continued)

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   |
|--|---|--------|--------|---------|---|
| $(\text{NH}_4)_2\text{S}_2\text{O}_8$<br>NaNH <sub>4</sub> SO <sub>4</sub><br>mass % | $(\text{NH}_4)_2\text{S}_2\text{O}_8$<br>NaNH <sub>4</sub> SO <sub>4</sub><br>mol % in dry subst. |        |        |         |   |
| 48.40  | 0.00  | 100.00 | 0.00   | 1.287   | $(\text{NH}_4)_2\text{S}_2\text{O}_8$   |
| 43.90  | 6.08  | 81.25  | 18.75  | 1.315   |   |
| 40.79  | 10.50   | 70.00  | 30.00  | 1.332   |   |
| 36.49  | 16.05   | 57.73  | 42.27  | 1.351   |   |
| 31.71  | 22.19   | 46.20  | 53.80  | 1.369   | $(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O}$ |
| 25.88  | 25.92   | 37.50  | 62.50  | 1.359   | $\text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O}$                                       |
| 18.89  | 29.96   | 27.48  | 72.52  | 1.347   |   |
| 9.84   | 35.26   | 14.36  | 85.64  | 1.331   |   |
| 0.00   | 40.19   | 0.00   | 100.00 | 1.313   |   |

Quasiternary system of the section  $\text{Na}_2\text{S}_2\text{O}_8 - \text{NaNH}_4\text{SO}_4 - \text{H}_2\text{O}$ 

| $\text{Na}_2\text{S}_2\text{O}_8$<br>NaNH <sub>4</sub> SO <sub>4</sub><br>mass % | $\text{Na}_2\text{S}_2\text{O}_8$<br>NaNH <sub>4</sub> SO <sub>4</sub><br>mol. % in dry subst. |        |        | density |  |
|--|--|--------|--------|---------|--|
| 43.19  | 0.00   | 100.00 | 0.00   | 1.367   | $\text{Na}_2\text{S}_2\text{O}_8$  |
| 41.36  | 2.64   | 90.01  | 9.99   | 1.379   |  |
| 38.20  | 7.80   | 73.82  | 26.18  | 1.396   |  |
| 35.34  | 12.03  | 62.85  | 37.15  | 1.404   |  |
| 34.77  | 12.73  | 61.13  | 38.87  | 1.405   | $\text{Na}_2\text{S}_2\text{O}_8 + \text{Na}_2\text{SO}_4$                     |
| 34.10  | 13.42  | 59.41  | 40.59  | 1.406   |  |
| 15.01  | 30.07  | 22.32  | 77.68  | 1.369   | $\text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O} + \text{Na}_2\text{SO}_4$ |
| 12.73  | 31.62  | 18.81  | 81.19  | 1.359   | $\text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O}$                          |
| 9.40   | 34.02  | 13.73  | 86.27  | 1.347   |  |
| 3.31   | 38.09  | 4.77   | 95.23  | 1.324   |  |
| 0.00   | 40.19  | 0.00   | 100.00 | 1.313   |  |

On the basis of the present results it is also necessary to make corrections in the earlier correlation equations of the dependence of solubility of the crystallizing component on the content of the second component in the saturated solution for  $30^\circ\text{C}$ . The dependence of the solubility of sodium peroxydisulphate ( $c$ , mass%) on the con-

tent of sodium sulphate ( $b$ , mass%) is described by the relation

$$c = 43.19 - 0.9726b \quad (1)$$

and *vice versa*, the dependence of the solubility of sodium sulphate on the content of sodium peroxydisulphate can be expressed as follows

$$b = 29.05 - 0.5333c \quad (2)$$

Comparison of these results with those published earlier<sup>5</sup> for temperatures 10° and 20°C gives a practically constant value of the slope of the dependence of sodium peroxydisulphate solubility on the content of sodium sulphate and therefore this dependence can be described for the whole temperature interval 10°–30°C by a common equation

$$c_t = c_t^0 - 0.9726b \quad (3)$$

Similar relations can also be derived for the dependence of densities of saturated solutions on their composition for the individual crystallization branches of this system.

Solubility data, pertaining to the internal compositions of the studied conversion system, are presented in Table III for individual quasiternary sections and in Table IV for binary and ternary eutonics. The results for individual quasiternary sections are graphically illustrated in Figs 3–6, the clinogonal projection of the resulting spatial phase diagram of the studied conversion system onto a square basis according to Jänecke with indicated course of isohydors is shown in Fig. 7, and the same projection

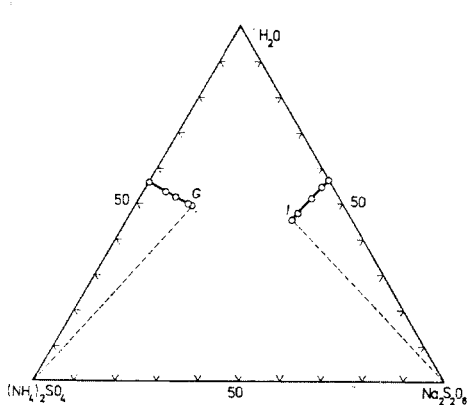


FIG. 3

Solubility Diagram (in mass%) of the Quasiternary Section  $\text{Na}_2\text{S}_2\text{O}_8$ – $(\text{NH}_4)_2\text{SO}_4$ – $\text{H}_2\text{O}$  at 30°C

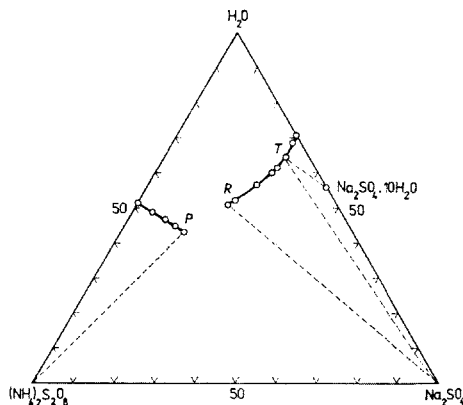


FIG. 4

Solubility Diagram (in mass%) 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 30°C

in which the lines connecting sites of the same density is presented in Fig. 8. These data are fully sufficient to describe any point of the system which lies on solubility lines or planes, in any commonly used weight or volume scale.

The results obtained with quasiternary sections are mostly similar to those reported for  $20^\circ\text{C}$  (see ref.<sup>1</sup>). The course of the section  $(\text{NH}_4)_2\text{SO}_4 - \text{Na}_2\text{S}_2\text{O}_8 - \text{H}_2\text{O}$  is completely analogous. This system is stable only in a limited range of compositions (see Fig. 3); *G* represents the eutonic point where ammonium sulphate and double sulphate  $\text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O}$  coexist in the solid phase with a saturated solution of the given composition and on the other hand, *I* denotes the eutonic point where sodium peroxydisulphate and anhydrous sodium sulphate coexist in the solid phase with saturated solution of the corresponding composition. Solubility lines in the crystallization region of both pure ammonium sulphate and sodium peroxydisulphate are practically linear and thus the effect of ammonium sulphate on the solubility of sodium peroxydisulphate can be expressed for  $30^\circ\text{C}$  as follows

$$c = 43.19 - 0.22545d \quad (\text{mass}\% \text{Na}_2\text{S}_2\text{O}_8) \quad (4)$$

and analogously

$$d = 43.90 - 0.5018c \quad (\text{mass}\% (\text{NH}_4)_2\text{SO}_4). \quad (5)$$

Eq. (4) holds for the interval  $d \leq 14.46 \text{ mass}\% (\text{NH}_4)_2\text{SO}_4$  and Eq. (5) for  $c \leq 13.65 \text{ mass}\% \text{Na}_2\text{S}_2\text{O}_8$ . Point *H* (see Fig. 7), which lies also on the mentioned diagonal section and which represents the eutonic solution coexisting with solid anhydrous sodium sulphate and double sulphate  $\text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O}$ , falls already, like the other points between eutonics *G* and *I*, into the unstable region, since these systems cannot be

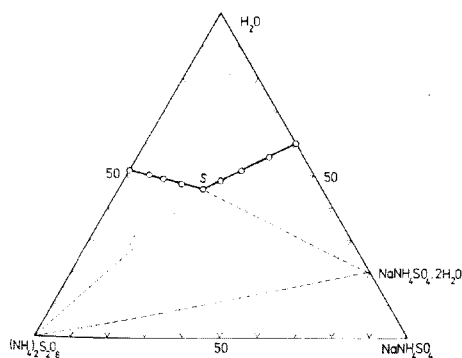


FIG. 5

Solubility Diagram (in mass%) of the Quasiternary Section  $(\text{NH}_4)_2\text{S}_2\text{O}_8 - \text{NaNH}_4\text{SO}_4 - \text{H}_2\text{O}$  at  $30^\circ\text{C}$

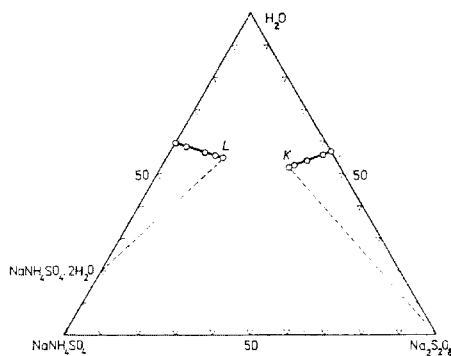


FIG. 6

Solubility Diagram (in mass%) of the Quasiternary Section  $\text{Na}_2\text{S}_2\text{O}_8 - \text{NaNH}_4\text{SO}_4 - \text{H}_2\text{O}$  at  $30^\circ\text{C}$



TABLE IV  
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  $30^\circ\text{C}$  (see Fig. 7)

| Saturated solution  |                 |                             |                    |               |                 |                             | Solid phases           |                    |  |
|---|-----------------|-----------------------------|--------------------|---------------|-----------------|-----------------------------|------------------------|--------------------|--|
| $\text{Na}^+$   | $\text{NH}_4^+$ | $\text{S}_2\text{O}_8^{2-}$ | $\text{SO}_4^{2-}$ | $\text{Na}^+$ | $\text{NH}_4^+$ | $\text{S}_2\text{O}_8^{2-}$ |                        | $\text{SO}_4^{2-}$ | density  |
| mass %  |                 |                             |                    |               |                 |                             | equiv. % in dry subst. |                    |  |
| Binary eutonics with coexistence of $(\text{NH}_4)_2\text{S}_2\text{O}_8 + (\text{NH}_4)_2\text{SO}_4$ in the solid phase (line AM)             |                 |                             |                    |               |                 |                             |                        |                    |  |
| 0.00  | 11.25           | 17.44                       | 21.24              | 0.00          | 100.00          | 29.12                       | 70.82                  | 1.292              | $(\text{NH}_4)_2\text{S}_2\text{O}_8 + (\text{NH}_4)_2\text{SO}_4$             |
| 0.41  | 11.10           | 17.14                       | 21.85              | 2.84          | 97.16           | 28.18                       | 71.82                  | 1.300              |  |
| 1.33  | 10.63           | 16.97                       | 22.60              | 8.93          | 91.07           | 27.29                       | 72.71                  | 1.321              |  |
| 2.55  | 10.05           | 16.68                       | 23.75              | 16.60         | 83.40           | 26.00                       | 74.00                  | 1.346              |  |
| Binary eutonics with coexistence of $(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{Na}_2\text{S}_2\text{O}_8$ in the solid phase (line BO)        |                 |                             |                    |               |                 |                             |                        |                    |  |
| 5.10  | 5.47            | 48.60                       | 0.00               | 43.57         | 56.43           | 100.00                      | 0.00                   | 1.463              | $(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{Na}_2\text{S}_2\text{O}_8$        |
| 5.66  | 5.40            | 45.85                       | 3.27               | 45.08         | 54.92           | 87.53                       | 12.47                  | 1.464              |  |
| 6.00  | 5.61            | 41.89                       | 6.53               | 45.61         | 54.39           | 76.14                       | 23.86                  | 1.465              |  |
| 5.85  | 5.78            | 39.25                       | 8.00               | 44.24         | 55.76           | 71.05                       | 28.95                  | 1.465              |  |
| Binary eutonics with coexistence of $\text{Na}_2\text{S}_2\text{O}_8 + \text{Na}_2\text{SO}_4$ in the solid phase (line CN)                     |                 |                             |                    |               |                 |                             |                        |                    |  |
| 10.12   | 0.00            | 24.55                       | 8.88               | 100.00        | 0.00            | 58.02                       | 41.98                  | 1.391              | $\text{Na}_2\text{S}_2\text{O}_8 + \text{Na}_2\text{SO}_4$                     |
| 9.62  | 0.55            | 25.34                       | 8.89               | 93.23         | 6.77            | 58.77                       | 41.23                  | 1.396              |  |
| 9.18  | 1.47            | 27.19                       | 9.50               | 83.06         | 16.94           | 58.88                       | 41.12                  | 1.402              |  |
| 8.83  | 1.76            | 27.50                       | 9.39               | 79.70         | 20.30           | 59.41                       | 40.59                  | 1.406              |  |
| 8.13  | 2.97            | 29.88                       | 9.97               | 68.24         | 31.76           | 59.98                       | 40.02                  | 1.420              |  |
| 7.71  | 3.95            | 32.33                       | 10.51              | 60.50         | 39.50           | 60.50                       | 39.50                  | 1.423              |  |
| 6.84  | 4.83            | 35.15                       | 9.70               | 53.04         | 46.96           | 64.17                       | 35.83                  | 1.450              |  |
| 8.45  | 3.93            | 0.00                        | 28.13              | 62.78         | 37.22           | 0.00                        | 100.00                 | 1.350              |  |
| 7.94  | 3.96            | 12.11                       | 21.07              | 61.16         | 38.84           | 22.32                       | 77.68                  | 1.369              |  |
| Binary eutonics with coexistence of $\text{Na}_2\text{SO}_4 + \text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O}$ in the solid phase (line DN) |                 |                             |                    |               |                 |                             |                        |                    |  |
| 8.45  | 3.93            | 0.00                        | 28.13              | 62.78         | 37.22           | 0.00                        | 100.00                 | 1.350              | $\text{Na}_2\text{SO}_4 + \text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O}$ |
| 7.94  | 3.96            | 12.11                       | 21.07              | 61.16         | 38.84           | 22.32                       | 77.68                  | 1.369              |  |

|   |       |       |       |       |       |       |        |       |  |
|---|-------|-------|-------|-------|-------|-------|--------|-------|--|
| 7-69  | 4-02  | 16-60 | 18-45 | 60-01 | 39-99 | 30-03 | 69-97  | 1-378 | } $\text{Na}_2\text{SO}_4 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$  |
| 8-10  | 4-54  | 18-62 | 20-78 | 58-28 | 41-72 | 35-83 | 64-17  | 1-386 |  |
| 7-25  | 4-20  | 22-40 | 15-15 | 57-50 | 42-50 | 42-50 | 57-50  | 1-391 |  |
| 7-09  | 4-61  | 29-18 | 12-51 | 45-67 | 45-33 | 53-84 | 46-16  | 1-420 |  |
| 7-01  | 4-58  | 30-31 | 11-70 | 54-56 | 45-44 | 56-43 | 43-57  | 1-427 |  |
| 6-84  | 4-83  | 35-15 | 9-70  | 53-04 | 46-96 | 64-17 | 35-83  | 1-450 | $\text{Na}_2\text{SO}_4 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{S}_2\text{O}_8$                        |
| Binary eutonics with coexistence of $(\text{NH}_4)_2\text{SO}_4 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ in the solid phase (line FM)          |       |       |       |       |       |       |        |       |  |
| 2-69  | 10-56 | 0-00  | 33-73 | 16-66 | 83-34 | 0-00  | 100-00 | 1-300 | } $(\text{NH}_4)_2\text{SO}_4 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$  |
| 2-63  | 10-35 | 4-96  | 30-58 | 16-64 | 83-36 | 7-50  | 92-50  | 1-313 |  |
| 2-57  | 10-15 | 10-73 | 27-05 | 16-57 | 83-43 | 16-56 | 83-44  | 1-326 |  |
| 2-55  | 10-05 | 16-68 | 23-75 | 16-60 | 83-40 | 26-00 | 74-00  | 1-346 | $(\text{NH}_4)_2\text{SO}_4 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O} + (\text{NH}_4)_2\text{S}_2\text{O}_8$                |
| Binary eutonics with coexistence of $(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ in the solid phase (line MO) |       |       |       |       |       |       |        |       |  |
| 2-55  | 10-05 | 16-68 | 23-75 | 16-60 | 83-40 | 26-00 | 74-00  | 1-346 | } $(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O} + (\text{NH}_4)_2\text{SO}_4$              |
| 3-01  | 9-15  | 20-94 | 20-15 | 20-50 | 79-50 | 34-18 | 65-82  | 1-353 |  |
| 3-72  | 7-93  | 26-70 | 15-55 | 23-90 | 76-10 | 46-20 | 53-80  | 1-369 |  |
| 4-28  | 7-18  | 30-92 | 12-60 | 31-90 | 68-10 | 55-10 | 44-90  | 1-388 | } $(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$   |
| 4-99  | 6-52  | 34-73 | 10-41 | 37-50 | 62-50 | 62-50 | 37-50  | 1-417 |  |
| 5-13  | 6-32  | 35-77 | 9-64  | 38-91 | 61-09 | 64-96 | 35-04  | 1-431 |  |
| 5-85  | 5-78  | 39-35 | 8-00  | 44-24 | 55-76 | 71-05 | 28-95  | 1-465 | $(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{S}_2\text{O}_8$           |
| Binary eutonics with coexistence of $\text{Na}_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ in the solid phase (line NO)     |       |       |       |       |       |       |        |       |  |
| 6-84  | 4-83  | 35-15 | 9-70  | 53-04 | 46-96 | 64-17 | 35-83  | 1-450 | } $\text{Na}_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$                      |
| 6-60  | 5-08  | 36-20 | 9-22  | 50-51 | 49-49 | 66-26 | 33-74  | 1-454 |  |
| 6-27  | 5-39  | 37-68 | 8-61  | 47-71 | 52-29 | 68-64 | 31-36  | 1-458 |  |
| 5-85  | 5-78  | 39-25 | 8-00  | 44-24 | 55-76 | 71-05 | 28-95  | 1-465 | $\text{Na}_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O} + (\text{NH}_4)_2\text{S}_2\text{O}_8$           |
| Ternary eutonics  |       |       |       |       |       |       |        |       |  |
| 2-55  | 10-05 | 16-68 | 23-75 | 16-60 | 83-40 | 26-00 | 74-00  | 1-346 | $(\text{NH}_4)_2\text{S}_2\text{O}_8 + (\text{NH}_4)_2\text{SO}_4 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (point M)      |
| 6-84  | 4-83  | 35-15 | 9-70  | 53-04 | 46-96 | 64-17 | 35-83  | 1-450 | $\text{Na}_2\text{S}_2\text{O}_8 + \text{Na}_2\text{SO}_4 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (point N)              |
| 5-85  | 5-78  | 39-25 | 8-00  | 44-24 | 55-76 | 71-05 | 28-95  | 1-465 | $\text{Na}_2\text{S}_2\text{O}_8 + \text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O} + (\text{NH}_4)_2\text{S}_2\text{O}_8$ (point O) |

prepared by simple mixing of the basic components of the system of the studied quasiternary section, *i.e.*  $\text{Na}_2\text{S}_2\text{O}_8$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{H}_2\text{O}$ .

A similar course was also found in the section  $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$  (Fig. 4) in which this quasiternary system is also stable only in a limited range of composition. Ammonium peroxydisulphate coexists with saturated solution up to concentration  $b = 15.40$  mass%  $\text{Na}_2\text{SO}_4$  and its solubility is a linear function of the content of sodium sulphate in the solution, so that the corresponding solubility dependence can again be described by a simple relation

$$a = 48.40 - 0.4643b \quad (\text{mass}\% (\text{NH}_4)_2\text{S}_2\text{O}_8). \quad (6)$$

Point *P* represents the eutonic solution coexisting with ammonium peroxydisulphate and double sulphate  $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$  in the solid phase. Sodium sulphate coexists with saturated solutions up to the content of ammonium peroxydisulphate  $a = 26.60$  mass%. Contrary to the results for isotherm at  $20^\circ\text{C}$ , the solubility of this sulphate does not show a linear dependence on the content of ammonium peroxydisulphate in the solution. It is probable that this nonlinear dependence is caused by the transition between the region of crystallization of decahydrate and of anhydrous sodium sulphate. This assumption is also supported by a marked break on the dependence of densities of saturated solutions of this quasiternary system on the content of ammonium peroxydisulphate, appearing at  $a = 5.4$  mass%  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in the solution (*i.e.* *c.* 10 mol%  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in the total dry substance of salts present in the saturated solution). The presence of ammonium ion seems thus to contribute to the dehydration of sodium sulphate in the solid phase, since without its presence, *viz.* in the system  $\text{Na}_2\text{S}_2\text{O}_8\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$  the beginning of dehydration is observed, judging from the beginning of the visibly metastable region (see Fig. 2), probably at *c.* 10–12 mass%  $\text{Na}_2\text{S}_2\text{O}_8$  in the saturated solution which corresponds to *c.* 20–24 mol% of this component in the dry substance of dissolved salts. In this connection it is also worth mentioning that in the measurement of the shift of compositions of binary eutonic points, denoting the coexistence of saturated solutions with solid sodium peroxydisulphate and sulphate in dependence on the content of ammonium ions in the solution, the metastable region could not be attained even for the lowest chosen contents of this ion and even using sodium sulphate as the starting substance. Anyhow, these results led us to the conclusion that the earlier solubility data in the system  $\text{Na}_2\text{S}_2\text{O}_8\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$  at  $30^\circ\text{C}$  need revision. It should be also mentioned that similar phenomena were never found in the determination of isotherm at  $20^\circ\text{C}$  and the position of eutonic point in the ternary system  $\text{Na}_2\text{S}_2\text{O}_8\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$  coincides, according to earlier measurements<sup>5</sup>, with the further course of binary eutonics between solid sodium peroxydisulphate and sodium sulphate decahydrate, even in the presence of ammonium ions<sup>1</sup>, since at this temperature sodium sulphate coexists with saturated solution in the whole crystallization region only in the form of decahydrate.

Also the course of the section through the quasiternary system  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ - $\text{NaNH}_4\text{SO}_4$ - $\text{H}_2\text{O}$ , the only stable one over the whole composition region (see Fig. 5) is quite analogous to the course found at  $20^\circ\text{C}$ . Both basic components crystallize in the respective crystallization regions in the form of pure salts and only in the eutonic solution (point S in Figs 5 and 7) both solid phases coexist with this solution simultaneously. The effect of the presence of the second component in saturated solutions on the solubility of the solid component is in both cases linear, so that the dependence of solubility of ammonium peroxydisulphate on the content of double sodium ammonium sulphate in the solution can be expressed by the relation

$$a = 48.40 - 0.7521e \quad (\text{mass}\% (\text{NH}_4)_2\text{S}_2\text{O}_8), \quad (7)$$

valid for  $e \leq 22.19$  mass%  $\text{NaNH}_4\text{SO}_4$ . *Vice versa*, the dependence of solubility of sodium ammonium sulphate on the content of ammonium peroxydisulphate

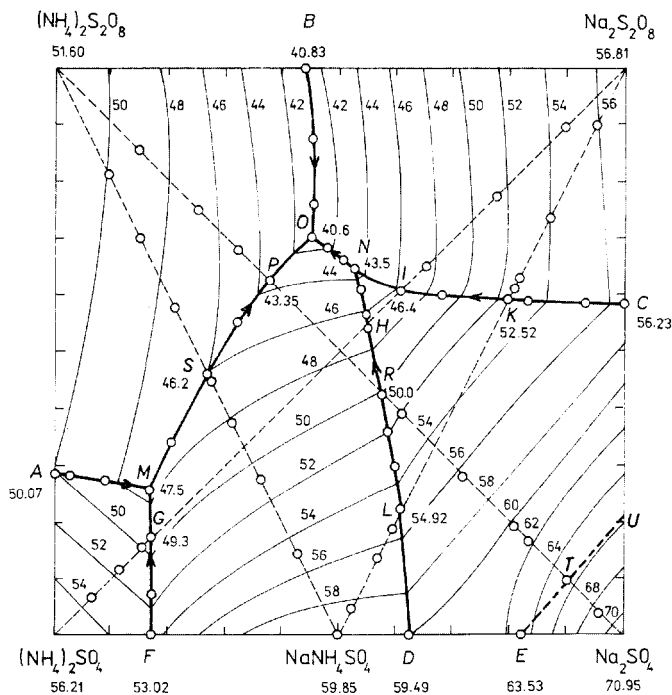


FIG. 7

Solubility Diagram (in equiv.%) 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  $30^\circ\text{C}$  in Clinogonal Projection onto the Square Basis of Pure Salts with Marked Course of Isohydors (g  $\text{H}_2\text{O}/100$  g of saturated solution)

in the solution can be described by Eq. (8)

$$e = 40.19 - 0.5676a \quad (\text{mass}\% \text{NaNH}_4\text{SO}_4), \quad (8)$$

valid for  $a \leq 31.71 \text{ mass}\% (\text{NH}_4)_2\text{S}_2\text{O}_8$ .

Finally, the section through the quasiternary system  $\text{Na}_2\text{S}_2\text{O}_8\text{-NaNH}_4\text{SO}_4\text{-H}_2\text{O}$  (see Fig. 6) is similar to the corresponding section for  $20^\circ\text{C}$  only as to the crystallization region of sodium peroxydisulphate, whose solubility decreases directly proportionally to the content of the double sulphate in the solution, according to the relation

$$c = 43.19 - 0.6773e \quad (\text{mass}\% \text{Na}_2\text{S}_2\text{O}_8) \quad (9)$$

which holds for  $e \leq 13.42 \text{ mass}\% \text{NaNH}_4\text{SO}_4$ . Contrary to the isotherm for  $20^\circ\text{C}$ , in this case also the region of crystallization of double sodium ammonium sulphate can be found, due to the widened crystallization region of this salt in the partial ternary system  $(\text{NH}_4)_2\text{SO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$  at  $30^\circ\text{C}$  (see Fig. 1). This salt separates from saturated solutions up to the value of  $c = 15.01 \text{ mass}\% \text{Na}_2\text{S}_2\text{O}_8$  and its solubil-

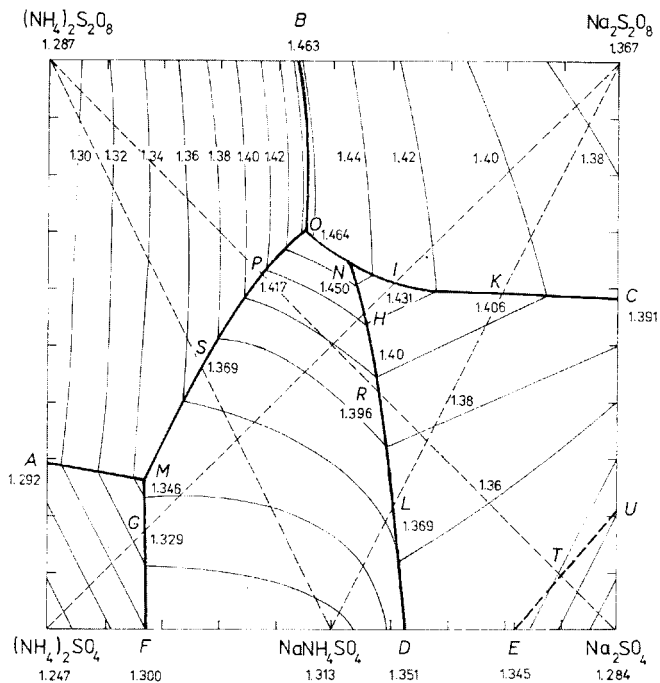


FIG. 8

Solubility Diagram (in equiv.%) 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  $30^\circ\text{C}$  with Marked Course of the Curves Connecting the Compositions of Saturated Solutions of the Same Density

ity is also directly proportional to the content of sodium peroxydisulphate in the solution, according to the relation

$$e = 40.19 - 0.6742c \quad (\text{mass}\% \text{NaNH}_4\text{SO}_4). \quad (10)$$

Point *K* represents the eutonic saturated solution coexisting with solid sodium peroxydisulphate and with anhydrous sodium sulphate and *L* denotes the eutonic point where double sulphate and anhydrous sodium sulphate coexist in the solid phase with the saturated solution of the given composition. Between point *K* and *L* this quasiternary system is unstable.

The resulting phase diagram of the studied conversion system as shown in Figs 7 and 8 in the form of clinogonal projection onto the basis of dry salts, leads practically to the same qualitative conclusions as were stated in the preceding publication<sup>1</sup> for this system at  $20^\circ\text{C}$ . Even at  $30^\circ\text{C}$ , neither pair of the salts of this conversion system forms a mutually compatible pair of salts, because in both cases their crystallization regions are separated by a crystallization region of the double sulphate  $\text{NaNH}_4\text{SO}_4 \cdot 2 \text{H}_2\text{O}$ . From the three ternary eutonics, the only stable one is the eutonic point *O*, as it has the lowest content of water of the whole system, so that during drying out any arbitrary initial composition of the system, the saturated solutions change gradually their composition up to the final stable ternary eutonic point *O*, as it is also indicated by arrows in the lines of binary eutonics in Fig. 7.

With respect to the fact that the times used for equilibration did not allow to determine with sufficient accuracy the point of transition of sodium sulphate decahydrate to the anhydrous salt in the whole corresponding concentration region and particularly in the partial ternary system  $\text{Na}_2\text{S}_2\text{O}_8 - \text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$ , the assumed boundary of this transition is marked in Figs 7 and 8 in a bold dashed line. On the diagonal  $\text{Na}_2\text{SO}_4 - (\text{NH}_4)_2\text{S}_2\text{O}_8$  there are only the eutonic points *P* and *R* and also point *T* relatively precisely placed. The point *T* results from the observed break on the dependence of densities of saturated solutions on composition along this diagonal, whereas the position of point *U* is only approximately estimated from the beginning of the appearance of metastable region of  $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ .

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