

<p>COMPONENTS:</p> <p>(1) Potassium dihydrogenphosphate; KH_2PO_4; [7778-77-0]</p> <p>(2) Water; H_2O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>J. Eysseltová Charles University Prague, Czechoslovakia</p> <p>May, 1985</p>
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CRITICAL EVALUATION:

THE BINARY SYSTEM

Several papers report solubility data for this system (1-6). Empirical smoothing equations describing the temperature dependence of this solubility have also been reported (6,7). Solubility data for this system have also been reported as part of a study of multicomponent systems having KH_2PO_4 as one component (8-24). Some of these values are clearly incorrect and were rejected immediately (8-10). The same is true for some of the solubility values reported for 323 K (11,12). In another report (13) the solubility of KH_2PO_4 at 298 K is given as 20.3% and also as 21.6%. The latter value is an obvious error. All the other data from the studies of multicomponent systems were evaluated together with the data in refs. (1-6).

The evaluation procedure was the same as that described in chapter 3. It was possible to use only one equation because no hydrate formation has been observed. The assumptions concerning the precision of the data were the same as those used in chapter 3. The general solubility equation [1] was used. Equation [2] was used for the

$$\ln x/x_0 = A \cdot (1/T - 1/T_0) + B \cdot \ln (T/T_0) + C \cdot (T - T_0) \quad [1]$$

selection of experimental points during the iterative procedure.

$$\left| \frac{x_j - x(T_j)}{x(T_j)} \right| \leq 0.015 \quad [2]$$

Table I is a summary of the solubility data used in the evaluation procedure. All the data from only two reports (22,24) were eliminated during the iteration procedure.

The results of this evaluation procedure are summarized in Table II, which gives the values obtained for the parameters in equation [1].

Table III is a list of the recommended solubility values calculated from equation [1]. The other smoothing equations that have been suggested (6,7) give values that are 8-10% larger than the recommended values (Table III) in the 273-288 K temperature interval. Above 288 K the one equation (6) gives values that agree with those in Table III while the other equation (7) gives values that have a constant error of about +10%.

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CRITICAL EVALUATION: (cont'd)

Table I. Solubility of KH_2PO_4 in water.

weight				weight			
T/K	mass%	ref.	init/final	T/K	mass%	ref.	init/final
273.2	10.48	1	1/0	298.2	20.30	13	1/0
273.2	12.48	2	1/0	298.2	19.92	4	1/1
273.2	12.68	4	1/0	298.2	19.93	19	1/1
273.2	12.88	6	1/0	298.2	20.3	21	1/0
273.2	12.15	15	1/0	298.2	20.21	23	1/1
273.2	11.8	5	1/1	298.2	20.42	12,13	2/0
273.2	12.2	3	1/0	299.2	20.00	3	1/0
273.2	12.7	4	1/0	300.2	20.00	5	1/0
273.2	12.41	19	1/0	303.2	21.90	6	1/1
273.2	12.30	24	1/0	303.2	21.0	3	1/0
274.0	12.00	5	1/1	305.0	22.00	5	1/0
278.2	14.00	6	1/0	305.4	22.00	3	1/0
283.2	15.50	6	1/0	308.2	23.65	6	1/1
283.2	14.95	15	1/1	308.2	22.90	15	1/0
283.2	15	5	1/1	313.2	25.10	6	1/1
283.2	14.9	3	1/1	313.2	25.00	20	1/1
283.2	15.20	24	1/0	313.2	27.15	22	1/0
286.8	16.00	5	1/1	313.2	27.12	22	1/0
287.3	16.00	3	1/1	318.2	26.90	6	1/1
288.2	16.78	2	1/0	323.2	29.26	1	1/1
293.0	18.00	5	1/1	323.2	29.15	4,16	2/2
293.2	18.45	6	1/1	323.2	29.00	6,21	2/2
293.2	18.20	15	1/1	323.2	29.42	14	1/0
293.2	18.2	5	1/1	323.2	29.1	4	1/1
293.2	18.50	18	1/0	323.2	28.70	19	1/1
293.2	17.8	3	1/0	333.2	33.40	6	1/0
293.2	17.73	2	1/0	333.2	32.37	20	1/0
293.2	18.04	20	1/0	343.2	36.68	1	1/1
293.2	18.00	24	1/0	343.2	36.65	1	1/1
293.8	18.00	3	1/0	343.2	37.05	6	1/1
298.2	19.87	1	1/1	348.2	39.20	21	1/1
298.2	20.15	1	1/1	348.2	38.61	19	1/1
298.2	19.90	4	1/1	353.2	41.30	6	1/1
298.2	20.04	6	1/1	353.2	40.75	20	1/1
298.2	19.80	15	1/1	356.2	41.38	1	1/0
298.2	20.07	2	1/1	356.2	41.92	1	1/1
298.2	20.49	16	1/0	363.2	45.5	6	1/1
				378.3	52.7	17	1/1

Table II. Values for the parameters of equation [1].

A		B		C		x_o	T_o
value	σ^a	value	σ^a	value	σ^a	value	value
-2.121×10^4	10	-1.224×10^2	0.5	0.1929	0.0005	0.031948	298.2

^a Standard deviation for the respective parameter.

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CRITICAL EVALUATION: (cont'd)

 Table III. Recommended values calculated from equation [1] for the solubility of KH_2PO_4 in water.

T/K	mole fraction	mol/kg	mass%
273.2	0.017287	0.98	11.74
278.2	0.019886	1.13	13.30
283.2	0.022653	1.29	14.91
288.2	0.025586	1.46	16.56
293.2	0.028684	1.64	18.25
298.2	0.031948	1.83	19.97
303.2	0.035385	2.04	21.71
308.2	0.039006	2.25	23.48
313.2	0.042825	2.48	25.28
318.2	0.046861	2.73	27.10
323.2	0.051139	2.99	28.95
328.2	0.055690	3.28	30.84
333.2	0.060548	3.58	32.76
338.2	0.065757	3.91	34.73
343.2	0.071367	4.27	36.75
348.2	0.077434	4.66	38.82
353.2	0.084028	5.10	40.96
358.2	0.091224	5.58	43.15
363.2	0.099113	6.11	45.41
368.2	0.10780	6.71	47.74
373.2	0.11740	7.39	50.14
378.2	0.12806	8.16	52.62

MULTICOMPONENT SYSTEMS

Solubility measurements have been made for a variety of multicomponent systems that include potassium dihydrogenphosphate as a component. However, an evaluation cannot be made of most of these studies because of a lack of corroborating results. The systems may be differentiated according to the type of solid phases that are in equilibrium with the saturated solutions.

The formation of compounds has been reported for two of these systems: the compounds $\text{KH}_2\text{PO}_4 \cdot \text{KHSeO}_4$ and $3\text{KH}_2\text{PO}_4 \cdot \text{KHSeO}_4$ were identified in the KH_2PO_4 - KHSeO_4 - H_2O system at 298 K (18); the compound $\text{Ca}_9\text{K}_4\text{H}_3(\text{PO}_4)_{18} \cdot 10\text{H}_2\text{O}$ was found to be present in the KH_2PO_4 - $\text{Ca}(\text{H}_2\text{PO}_4)_2$ - H_3PO_4 - H_2O system at 298 K (25).

Solid solutions were found to be present in several systems. A continuous series of solid solutions is present in the KH_2PO_4 - $\text{NH}_4\text{H}_2\text{PO}_4$ - H_2O system (10-13, 23, 26, 27). Some of the solubility data at 298 K (11-13, 23) are compared on Figure 1. All the values agree fairly well with each other and these are accepted as tentative values. However, the discontinuity around 2.9-3 molal $\text{NH}_4\text{H}_2\text{PO}_4$ and 1 molal KH_2PO_4 cannot be explained. Further work is needed in this part of the system. The solid solutions, which have been designated β -solid solutions (26), are also found in the K^+ , NH_4^+ | Cl^- , H_2PO_4^- - H_2O system at 273 K (10, 29). Two forms of solid solutions are said to exist in the KH_2PO_4 - $\text{NH}_4\text{H}_2\text{PO}_4$ - $\text{CO}(\text{NH}_2)_2$ - H_2O system (28). In addition, there are also the α -, β - and γ -modifications of urea. This is true also of the KH_2PO_4 - $\text{CO}(\text{NH}_2)_2$ - H_2O system (15).

A series of solid solutions was also observed in the KH_2PO_4 - KH_2AsO_4 - H_2O system at 280 K (9). These results cannot be evaluated, but it should be noted that the values reported for the solubility of KH_2PO_4 in water are in error by about 50%.

In all the other systems having two or more saturating components, no solid solutions or compounds were found to be present. These systems are referred to individually.

1. The KH_2PO_4 - $[(\text{C}_2\text{H}_5)_3\text{N}]\text{H}_2\text{PO}_4$ - H_2O system. Solubility measurements were made at 293, 313, 333 and 353 K (20).
2. The KH_2PO_4 - KBO_2 - H_2O system. Solubility values have been reported for 298 and 323 K (8). These values cannot be evaluated but mention should be made of the fact that the value given for the solubility of KH_2PO_4 in water is incorrect.
3. The KH_2PO_4 - KNO_3 - H_2O system. There are four reports of solubility values for this system (1, 5, 16, 17). The results are compared on Figure 2.

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[7778-77-0]
(2) Water; H_2O ; [7732-18-5]

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CRITICAL EVALUATION:

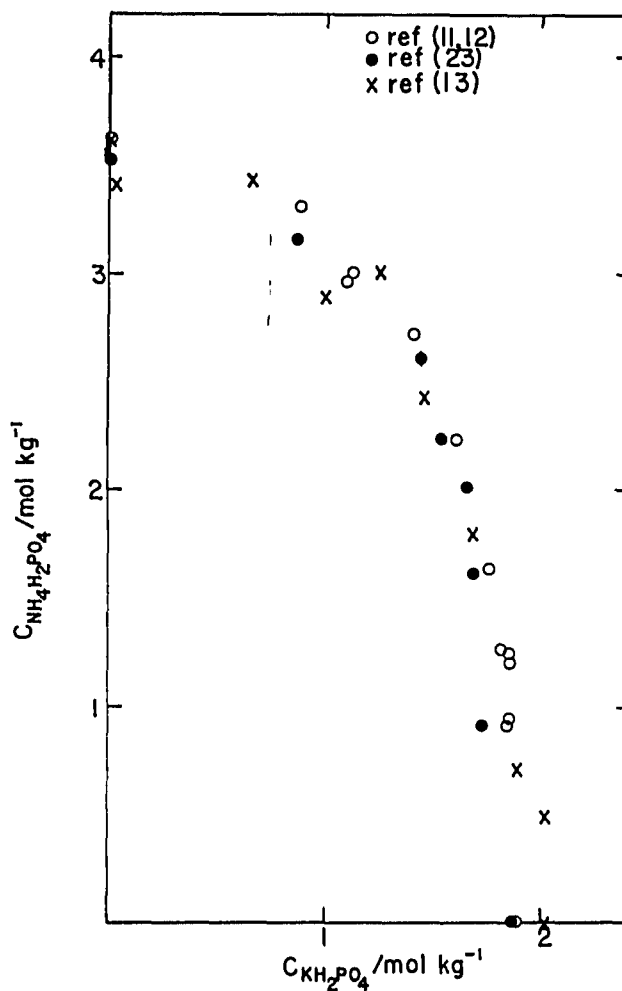
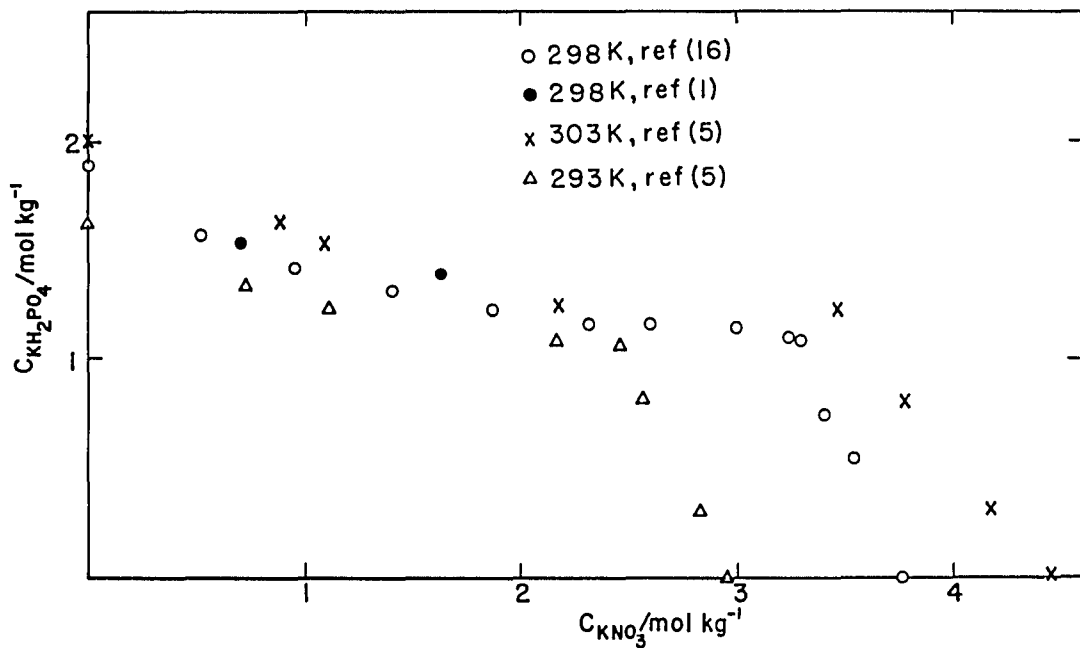
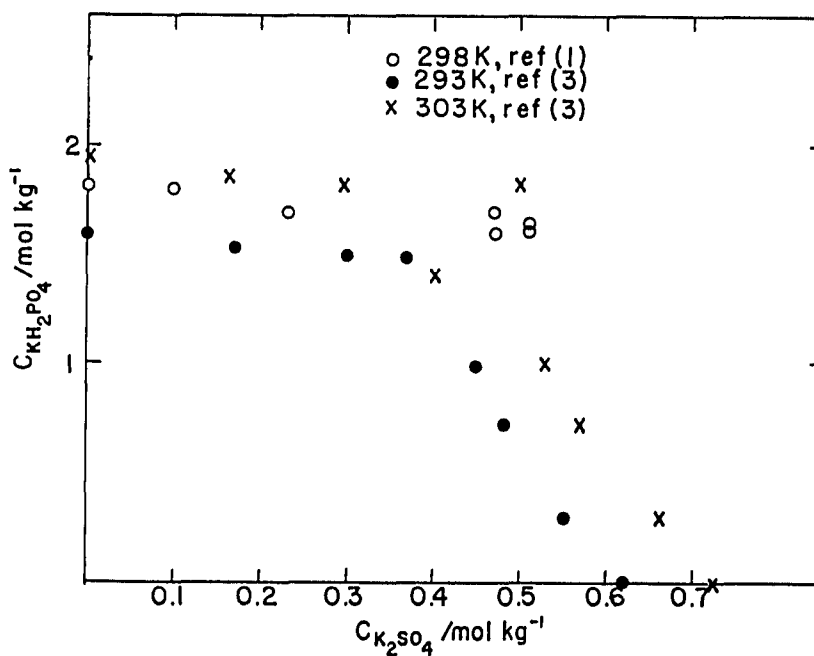


Figure 1. Solubility in the KH_2PO_4 - $\text{NH}_4\text{H}_2\text{PO}_4$ - H_2O system at 298 K.

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CRITICAL EVALUATION:

Figure 2. Solubility of KH_2PO_4 in aqueous KNO_3 .Figure 3. Solubility of KH_2PO_4 in aqueous K_2SO_4 .

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- (1) Potassium dihydrogenphosphate; KH_2PO_4 ; [7778-77-0]
 (2) Water; H_2O ; [7732-18-5]

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CRITICAL EVALUATION:

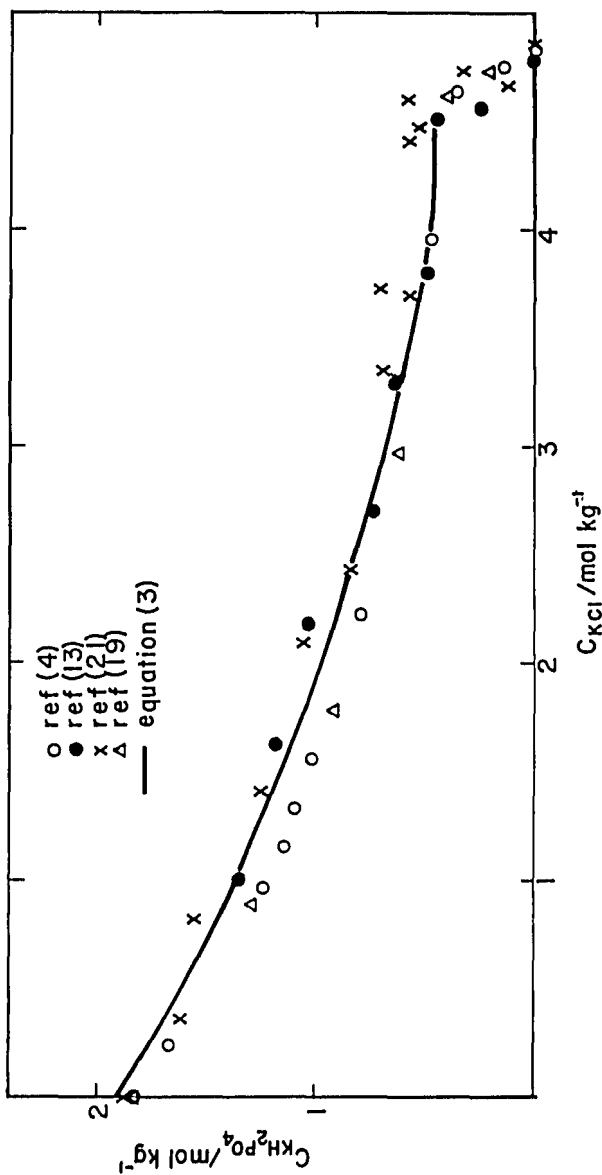


Figure 4. Solubility of KH_2PO_4 in aqueous KCl at 298 K.

<p>COMPONENTS:</p> <p>(1) Potassium dihydrogenphosphate; KH_2PO_4; [7778-77-0]</p> <p>(2) Water; H_2O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>J. Eysseltořá Charles University Prague, Czechoslovakia</p> <p>May 1985</p>
<p>CRITICAL EVALUATION: (cont'd)</p> <p>4. The $\text{KH}_2\text{PO}_4\text{-K}_2\text{SO}_4\text{-H}_2\text{O}$ system. The solubility values reported for this system (1, 3, 30) are compared on Figure 3.</p> <p>5. The $\text{KH}_2\text{PO}_4\text{-KCl-H}_2\text{O}$ system. Several investigators have published solubility values for this system (4, 10, 13, 19-22). The solubility of KH_2PO_4 at 298 K may be expressed by the smoothing equation of Kirgintsev (31) where m_1 is the molality of KH_2PO_4 and y_1 is its solute mole</p> $\log m_1 = \log 1.87 + (0.59 \pm 0.07) \log y_1 \quad [3]$ <p>fraction. The results calculated from equation [3] are compared with the experimental values on Figure 4.</p> <p>In addition to the solubility values reported above, there are values given for the $\text{KH}_2\text{PO}_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$ system at 273 K (2); some values for the $\text{KH}_2\text{PO}_4\text{-HCONH}_2\text{-H}_2\text{O}$ system at 298 K (32), at 323 K (14) and a polytherm in ref. (33); two values for the solubility of KH_2PO_4 in aqueous potassium acetate and in aqueous potassium carbonate at 298 K (1). The latter system cannot be treated as a ternary system because of the observed decomposition of the K_2CO_3.</p> <p>No solid solutions or compounds were observed in a study of the $2\text{K}^+, \text{Ca}^{2+} 2\text{Cl}^-$, $2\text{H}_2\text{PO}_4^- \text{-H}_2\text{O}$ system at 298 K (34).</p> <p style="text-align: center;">References</p> <ol style="list-style-type: none"> 1. Apfel, O. Dissertation, Technical University, Darmstadt 1911. 2. Menzel, H.; Gabler, C. Z. <i>Anorg. Chem.</i> 1929, 177, 187. 3. Bel'tschev, F.V. <i>Trudy Beloruss. S.-Kh. Akad.</i> 1953, 19, 145. 4. Krasil'shtschikov, A.I. <i>Izv. In-ta Fiz. Khim. Anal.</i> 1933, 6, 159. 5. Bergman, A.G.; Bochkarev, N.F. <i>Izv. Akad. Nauk SSSR</i> 1938, 237. 6. Kazantsev, A.A. <i>Zh. Obshch. Khim.</i> 1938, 13, 1230. 7. Punin, Yu. O.; Mirenkova, T.F.; Artamanova, O.I.; Ul'yanova, T.P. <i>Zh. Neorg. Khim.</i> 1975, 20, 2813. 8. Beremzhanov, B.A.; Voronina, L.V.; Savich, R.F. <i>Khim. Khim. Tekhnol. (Alma Ata)</i> 1978, 173. 9. Muthmann, F.; Kuntze, O. Z. <i>Kryst.</i> 1894, 23, 368. 10. Askenasy, P.; Nessler, F. Z. <i>Anorg. Chem.</i> 1930, 189, 305. 11. Dombrovskaya, N.S.; Zvorykin, A.Y. <i>Kaliy</i> 1937, 2, 24. 12. Zvorykin, A.Y.; Kuznetsov, V.G. <i>Izv. AN SSSR, Ser. Khim.</i> 1938, 195. 13. Solov'ev, A.P.; Balashova, E.F.; Verendyakina, N.A.; Zyuzina, L.F. <i>Vzaimodeistvie Khloridov Kaliya, Magniya, Ammoniya s ich Nitratami i Fosfatami</i>, 1977, 3. 14. Yugai, M.R.; Tukhtaev, S.; Beglov, B.M. <i>Uzb. Khim. Zh.</i> 1981, 6, 15. 15. Polosin, V.A.; Shakhparonov, M.I. <i>Zh. Obshch. Khim.</i> 1947, 17, 397. 16. Girich, T.E.; Gulyamov, Yu. M.; Ganz, S.N. <i>Zh. Neorg. Khim.</i> 1979, 24, 1084. 17. Shenkin, Ya. S.; Gorozhankin, E.V. <i>Zh. Neorg. Khim.</i> 1976, 21, 2293. 18. Zbořilovř, L.; Krejřil, J. <i>Scripta Fac. Sci. Nat. UJEP Brunensis, Chemia 1</i> 1972, 77. 19. Brunisholz, G.; Bodmer, M. <i>Helv. Chim. Acta</i> 1963, 46, 288, 2566. 20. Filipescu, L. <i>Rev. Chim. (Bucharest)</i> 1971, 22, 533. 21. Mrřz, R.; Srb, V.; Tichy, S.; Vosolsobě, J. <i>Chem. Prřm.</i> 1976, 26, 511. 22. Khalieva, Sh. D.; <i>Izv. AN Turkmen.-SSR, Ser. Khim.</i> 1978, 3, 125. 23. Kuznetsov, D.I.; Kozhukhovskij, A.A.; Borovaya, F.E. <i>Zh. Prikl. Khim.</i> 1948, 21, 1278. 24. Babenko, A.M.; Vorob'eva, T.A. <i>Zh. Prikl. Khim. (Leningrad)</i> 1975, 48, 2437. 25. Flatt, R.; Brunisholz, G.; Bourgeois, J. <i>Helv. Chim. Acta</i> 1956, 39, 841. 26. Bergman, A.G.; Gladkovskaya, A.A.; Galushkina, R.A. <i>Zh. Neorg. Khim.</i> 1972, 17, 2055. 27. Shenkin, Ya. S.; Ruchnova, S.A.; Rodionova, N.A.; <i>Zh. Neorg. Khim.</i> 1972, 17, 3368. 28. Bergman, A.G.; Gladkovskaya, A.A.; Galushkina, N.A. <i>Zh. Neorg. Khim.</i> 1973, 18, 1978. 29. Iovi, A.; Haiduc, C. <i>Rev. Roum. Chim.</i> 1971, 16, 1743. 30. Gladkovskaya, A.A.; Bergman, A.G. <i>Tr. Kuban. S.-Kh. In-ta</i> 1975, 102, 31, 130. 31. Kirgintsev, A.N. <i>Izv. Akad. Nauk SSSR, Ser. Khim.</i> 1965, 8, 1591. 32. Becker, B. J. <i>Chem. Eng. Data</i> 1969, 14, 431. 33. Beglov, B.M.; Tukhtaev, S.; Yugai, M.R. <i>Zh. Neorg. Khim.</i> 1980, 25, 2283. 34. Timoshenko, Yu. M.; Gilyazova, G.N. <i>Zh. Neorg. Khim.</i> 1981, 26, 1104. 	