COMPONENTS:	EVALUATOR:
(1) Rubidium dihydrogen phosphate; RbH_2PO_4; [13774-16-8] (2) Water; H_2O; [7732-18-5]	J. Eysseltová Charles University Prague, Czechoslovakia December, 1983

CRITICAL EVALUATION:

Qualitative solubility studies were made of three rubidium orthophosphates (1): $Rb_3PO_4 \cdot 4H_2O$ [101056-52-4]; $Rb_2HPO_4 \cdot H_2O$ [79832-54-5]; and RbH_2PO_4 [13774-16-8]. It was estimated that all these compounds are highly soluble. There is also a reference to $Rb_3PO_4 \cdot 3H_2O$ [10156-51-3] but no solubility data are reported (2). When it was discovered that the crystals of rubidium dihydrogen phosphate had some desirable electrical characteristics, further solubility studies were made.

The binary system RbH_2PO_4-H_2O was studied by Bykova, et al. (3). All other solubility studies (4, 5) were for ternary systems. The solubility values were determined by a direct analytical method in all the studies, but some of the analytical procedures are questionable. One group (4) used a potentiometric titration with aqueous KOH and report an accuracy of ± 0.2 mass%. The others (3, 5) used gravimetric procedures. Bykova, et al. (3) weighed rubidium as the tetraphenylborate and discuss the problem of analyzing for phosphorus in the presence of rubidium. Literature data for the solubility of rubidium phosphomolybdate (6, 7) are cited (8.1×10^{-6} mol dm^{-3} in 0.1 mol dm^{-3} HNO_3 at 293 K) and the possible formation of $RbMgPO_4$ is discussed (8). Because of these facts the gravimetric determination of phosphorus in systems containing rubidium must be carried out under carefully defined and controlled conditions. Zvorykin, et al. (5) precipitated phosphorus as $(NH_4)_3PMO_{12}O_{40}$, reprecipitated it as NH_4MgPO_4 and then calcined the latter to form $Mg_2P_2O_7$. They made no comment about the consistency of their determinations of NH_3, Rb and P. The compiler found these values to be inconsistent with each other.

THE BINARY SYSTEM

The solubility of RbH_2PO_4 in water has been determined over the temperature range of 273 to 353 K (3). The temperature coefficient of solubility was also determined and the authors split the temperature interval in two parts: 273-313 and 323-353 K. The evaluator treated these data by the linear regression method. The results are summarized in Table I where the coefficients for equation [1] are given for concentrations expressed as mass% and as mol/kg. The results in Table I suggest that there is no

$$c_{RbH_2PO_4} = a(T-273) + b \qquad [1]$$

need to split the temperature interval.

Table I. Coefficients for equation [1]

temp. range	a	b	R
	c as mass%		
273 - 313 K	0.52 ± 0.01	30.4 ± 0.4	0.9988
273 - 323 K	0.50 ± 0.01	30.6 ± 0.5	0.9983
273 - 333 K	0.47 ± 0.02	31.2 ± 0.9	0.9939
273 - 353 K	0.40 ± 0.03	32.9 ± 1.7	0.9788
	c as mol/kg		
273 - 313 K	0.082 ± 0.002	2.33 ± 0.06	0.9990
273 - 323 K	0.087 ± 0.003	2.28 ± 0.10	0.9974
273 - 333 K	0.087 ± 0.002	2.28 ± 0.08	0.9983
273 - 353 K	0.084 ± 0.002	2.3 ± 0.1	0.9981

MULTICOMPONENT SYSTEMS

The solubility of RbH_2PO_4 has been measured in three ternary systems.

1. The RbH_2PO_4-RbCl-H_2O system. The solubility in this system was measured only at 298 K (3). The system is an eutonic one with the invariant solution having a composition of 4.34 mass% (0.47 mol/kg) RbH_2PO_4 and 45.12 mass% (7.41 mol/kg) RbCl.

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CRITICAL EVALUATION: (continued)

2. The RbH_2PO_4-$NH_4H_2PO_4$-H_2O system. The solubility in this system has been measured only at 298 K (5). There are legitimate questions about the analytical procedures used in this work and the results must be considered to be questionable. There is considerable scatter in the data, which are plotted on Figure 1. It appears that one series of solid solutions is formed. Figure 1 shows that they belong to Type I in the Roozeboom classification (9).

3. The RbH_2PO_4-Rb_2O-H_3PO_4-H_2O system. Solubilities in this system have been measured at 298 and 323 K (4). The authors considered it as the ternary system Rb_2O-P_2O_5-H_2O. The compiler transformed the values to those for the quaternary system, Figure 2. In the RbH_2PO_4-Rb_2O-H_2O part of the system the solubility of RbH_2PO_4 is only slightly affected by change in concentration of the solutions, especially at 323 K. However, in the RbH_2PO_4-H_3PO_4-H_2O part of the system the solubility of the rubidium dihydrogenphosphate increases with increasing H_3PO_4 content until the invariant point is reached. Beyond this, the acid salt $RbH_5(PO_4)_2$ appears in the solid phase. Such acid phosphates are reported for most systems involving the alkaline metals (10-14).

The solubility of RbH_2PO_4 in aqueous H_3PO_4 may be described by equation [2] where c is the concentration expressed as

$$c_{RbH_2PO_4} = a \cdot c_{H_3PO_4} + b \qquad [2]$$

mass% or as mol/kg. The value of the coefficients, calculated by linear regression, are given in Table II.

Table II. Values of coefficients for equation [2].

	c as mass%			c as mol/kg		
T/K	a	b	R	a	b	R
298	0.55 ± 0.02	44.1 ± 0.3	0.9950	0.93 ± 0.02	4.38 ± 0.07	0.9991
323	0.280 ± 0.007	54.8 ± 0.1	0.9979	0.983 ± 0.004	6.65 ± 0.03	1.0000

The authors (4) also linearized their data using equation [3].

$$w_{Rb_2O} = a + b \cdot w_{P_2O_5} \qquad [3]$$

However, they gave no details for the method they used. The compiler recalculated their values to give the following results:
for P/Rb > 1
T = 298 K a = 17.6 ± 0.7 mass%; b = 0.30 ± 0.02; R = 0.9825
T = 323 K a = 25.2 ± 0.5 mass%; b = 0.15 ± 0.02; R = 0.9647
for P/Rb < 1
T = 298 K a = -41 ± 5 mass%; b = 3.9 ± 0.3; R = 0.9832
T = 323 K a = -132 ± 35 mass%; b = 7.7 ± 1.7; R = 0.8688.

CONCLUSIONS

The results of two studies (3, 4) agree well with each other. Therefore, the tentative solubility values for RbH_2PO_4 in water in the temperature range 273-353 K can be described by equation [1]. There are insufficient data to use the method that was described in the Critical Evaluation for the solubility of NaH_2PO_4 (chap. 3).

More work is needed to describe the solubility of other rubidium phosphates.

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CRITICAL EVALUATION:

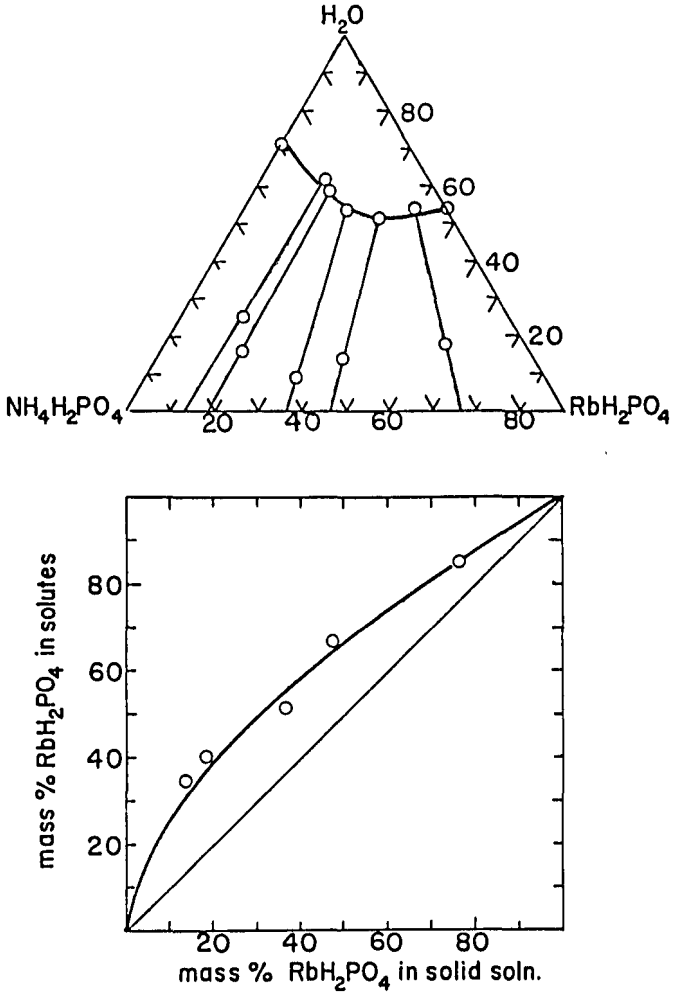

Figure 1. Phase diagram and distribution curve for the RbH_2PO_4-$NH_4H_2PO_4$-H_2O system at 298 K.

The data are from ref. (5). The distribution curve was constructed by the evaluator.

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CRITICAL EVALUATION:

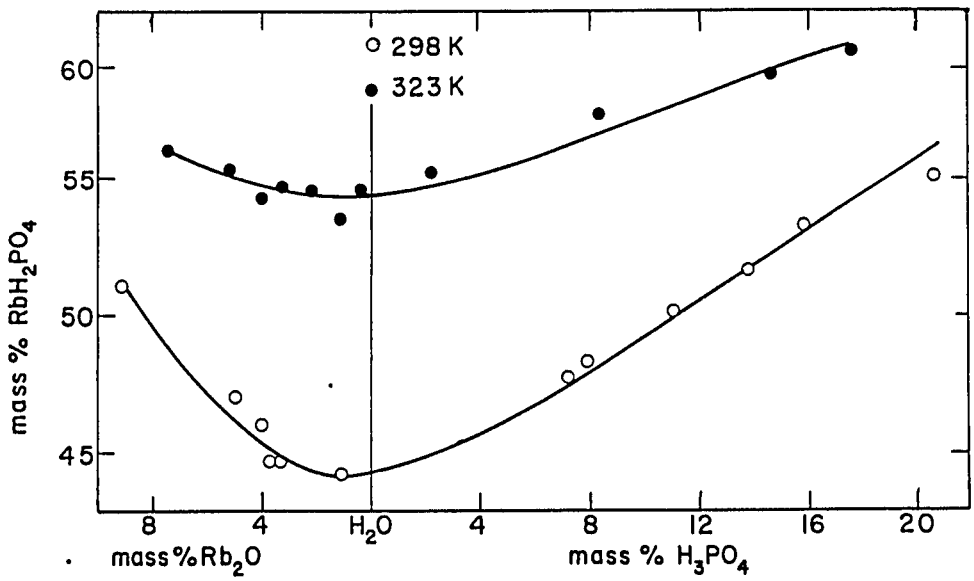

Figure 2. Solubility in the Rb_2O-P_2O_5-H_2O system. The data have been recalculated from ref. (4) by the compiler.

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CRITICAL EVALUATION: (continued)

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