COMPONENTS:

(1) Sodium dihydrogenphosphate; NaH_2PO_4; [7558-80-7]

(2) 2-Propanone (acetone); C_3H_6O; [67-64-1]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ferroni, G.; Galea, J.; Antonetti, G.

Bull. Soc. Chim. Fr. 1974, *12*, (Pt. 1), 273-81.

VARIABLES:

Composition at 25°C.

PREPARED BY:

J. Eysseltová

EXPERIMENTAL VALUES:

A miscibility gap was found in the NaH_2PO_4-C_3H_6O-H_2O system.

The results for the isothermal binodal curve at 25°C are:

upper layer				lower layer				
	NaH_2PO_4	C_3H_6O	H_2O		NaH_2PO_4	C_3H_6O	H_2O	
ρ/g cm^{-3}	mass%	mass%	mass%	ρ/g cm^{-3}	mass%	mass%	mass%	solid phase[α]
0.7940	∿0	100	∿0	----	----	----	----	A
0.8032	0.10	92.99	6.91	1.5317	54.81	0.98	44.21	
0.8343	0.23	75.74	24.03	1.4930	52.24	1.18	46.58	
0.8941	1.10	51.85	47.05	1.4684	50.51	1.25	48.24	
0.9066	1.38	41.16	57.45	1.4125	46.44	1.66	51.89	
0.9304	2.42	34.12	63.47	1.2694	34.17	2.19	63.64	
0.9807	5.75	21.35	72.90	1.1344	21.53	7.15	71.32	
1.1022	18.44	9.44	72.22		critical solution			B
1.5576	56.10	0	43.90					C

[a] The solid phases are: A = NaH_2PO_4; B = $NaH_2PO_4 \cdot H_2O$; C = $NaH_2PO_4 \cdot 2H_2O$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The mixtures were equilibrated by stirring in a thermostat for 48 hours. This was done in the dark to prevent photodecomposition. The dihydrogenphosphate ion content was determined by an automatic potentiometric pH titration after evaporating the solution to dryness and dissolving the residue in bidistilled water. The 2-propanone content was determined iodometrically using a potentiometric titration.

SOURCE AND PURITY OF MATERIALS:

Reagent grade 2-propanone was used. Reagent grade NaH_2PO_4 was dehydrated at 100°C and then stored in a vacuum over NaOH. The water was twice distilled and deaerated.

ESTIMATED ERROR:

The temperature was held to within ±0.1 K. The precision of the analyses was 0.5%.

REFERENCES:

COMPONENTS:

(1) Sodium dihydrogenphosphate; NaH_2PO_4; [7558-80-7]

(2) Sodium perchlorate; $NaClO_4$; [7601-89-0]

(3) 2-Propanone (acetone); C_3H_6O; [67-64-1]

(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ferroni, G.; Galea, J.; Antonetti, G.

Bull. Soc. Chim. Fr. 1974, *12*, (Pt. 1), 273-81.

VARIABLES:

Concentration of $NaClO_4$ at 25°C.

PREPARED BY:

J. Eysseltová

EXPERIMENTAL VALUES:

Composition of the saturated solutions at 25°C.

	1 mol $NaClO_4/dm^3$		3 mols $NaClO_4/dm^3$	
H_2O c^a	NaH_2PO_4 mol/dm^3	solid phase	NaH_2PO_4 mol/dm^3	solid phase
100	4.912	$NaH_2PO_4\cdot 2H_2O$	2.400	$NaH_2PO_4\cdot 2H_2O$
90.9	1.089	binodal curve	0.741	binodal curve
83.3	0.241	" "	0.029	" "
66.7	0.026	" "	0.0052	" "
50.0	0.0061	" "	0.0024	$NaH_2PO_4\cdot H_2O$
33.3	$\sim 7.5 \times 10^{-4}$	" "	4.2×10^{-4}	"
9.1	$\sim 6 \times 10^{-6}$	" "	5×10^{-6}	"
0.0	10^{-6}	NaH_2PO_4	10^{-7}	NaH_2PO_4

[a] The concentration units are: mol/100 mols of solvent.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The mixtures were equilibrated by stirring in a thermostat for 48 hours. This was done in the dark to prevent photo-decomposition. The dihydrogenphosphate ion content was determined by an automatic potentiometric pH titration after evaporating the solution to dryness and then dissolving the residue in bidistilled water. The 2-propanone content was determined iodometrically using a potentiometric titration.

SOURCE AND PURITY OF MATERIALS:

Reagent grade materials were used. The NaH_2PO_4 was dehydrated at 100°C and stored in a vacuum over NaOH. The water was bidistilled and deaerated.

ESTIMATED ERROR:

The temperature was constant to within ±0.1 K. The analyses had a precision of ±0.5%.

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Disodium hydrogenphosphate; Na_2HPO_4; [7558-79-4] (2) Water; H_2O; [7732-18-5]	J. Eysseltová Charles University Prague, Czechoslovakia May 1985

CRITICAL EVALUATION:

THE BINARY SYSTEM

Solubility data have been reported for the temperature interval 273-373 K (1), for the 272-313 K interval (2), and at 273, 291 and 298 K (3). Wendrow and Kobe (4) report their own extrapolated data as well as data obtained by others (5). Older data (7-13) are cited in the article by D'Ans and Schreiner (6). But these data appear to have a systematic error and were eliminated from consideration during the first graphical examination of the material. On the other hand, some data from studies of multicomponent systems (14-19) were consistent with those reported by others (1-3) and were included in the evaluation procedure.

Several hydrates of disodium hydrogenphosphate have been reported. Wendrow and Kobe (4) stated that the transition temperatures of the dodecahydrate to the heptahydrate and of the heptahydrate to the dihydrate were 308.7 and 321.2 K, respectively. A more precise determination of these values (6) gives transition temperatures of 308.55 and 321.55 K, respectively. There is also a report of the existence of two forms of the dodecahydrate with a transition temperature of 302.8 K (2), but this has not been confirmed by any other investigators. The transition temperature of the dihydrate to the anhydrous salt was said to be 368.2 K (4).

All the experimental data that were not eliminated in the first graphical examination were evaluated by the method described in chapter 3. The data were fitted to equation [1]. The precision of the published data was estimated to be about the same as

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

that for sodium dihydrogenphosphate and hence, the criteria for the selection of relevant points were the same as those used in chapter 3. However, these criteria could be applied completely only to the data for the dodecahydrate. For the heptahydrate and the dihydrate the data in the different reports were not in sufficiently good agreement and the selection of values for x_o was based on the results of only one report (1). Table I is a summary of the solubility data.

During the iteration procedure practically all the data except those of Shiomi (1) were eliminated. Therefore, the results of this procedure are considered to be tentative.

The values for the parameters of equation [1] are given in Table II while in Table III the solubility values calculated from equation [1] are given.

MULTICOMPONENT SYSTEMS

Solubility data have been reported for several ternary and quaternary systems but in only a few instances have data for a given system been reported by more than one investigator(s). In three of the systems solid phases other than the components or their hydrates have been reported.

Two reports (3,15) give data for the Na_2HPO_4-H_2O_2-H_2O system at 273 K but a comparison of the two reports cannot be made because the concentration range studied in one report (3) is too narrow. The other article (15) reports the presence of the two compounds $Na_2HPO_4\cdot1.5H_2O_2$ [13769-82-9] and $Na_2HPO_4\cdot2.5H_2O_2$ [13769-83-0] at H_2O_2 concentrations greater than 27 mass% for this system.

Data for the Na_2HPO_4-H_3BO_3-H_2O system at 298 K have been reported by Beremzhanov, et al. (20). The results are analogous to those for the NaH_2PO_4-$NaBO_2$-H_2O system reported by the same authors (21) and discussed in chapter 4. The appearance of $Na_2B_4O_7\cdot10H_2O$ [61028-24-8] as a solid phase suggests that the system should be treated as part of the Na_2O-B_2O_3-P_2O_5-H_2O system.

A similar situation exists with respect to the Na_2HPO_4-Na_2SiO_3-H_2O system. Data for this system at 293 K were reported by Manvelyan, et al. (22). The formation of $Na_3PO_4\cdot12H_2O$ [10101-89-0] in this system is an indication of its pseudo-ternary character.

There is no evidence for the formation of solid solutions and/or ternary compounds in the other multicomponent systems for which data are available.

There is only one report giving data for the systems Na_2HPO_4-Na_2H_2EDTA-H_2O (17), Na_2HPO_4-$NaNO_3$-H_2O (23) and Na_2HPO_4-NaCl-H_2O (24). All these data were obtained at 298 K.

Makin and his co-workers have reported data for several systems containing Na_2HPO_4 as a component. There are two reports for the Na_2HPO_4-Na_2SO_4-H_2O system at 298 K (18, 19). This group has also published data for two quaternary systems: the Na_2HPO_4-$NaNO_3$-Na_2SO_4-H_2O system (25); and the Na_2HPO_4-$NaNO_3$-NaCl-H_2O system (26), both at

(continued next page)

COMPONENTS:

(1) Disodium hydrogenphosphate; Na_2HPO_4; [7558-79-4]

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

EVALUATOR:

J. Eysseltová
Charles University
Prague, Czechoslovakia

May 1985

CRITICAL EVALUATION:

Table I. Solubility of Na_2HPO_4 in water.

T/K	mass%	ref.	weight init/final	T/K	mass%	ref.	weight init/final
			$Na_2HPO_4 \cdot 12H_2O$				
268.5	1.43	2	1/1	298.30	10.74	1	1/1
273.2	1.605	3	2/0	298.30	10.72	1	2/2
273.2	1.6	15	2/0	298.60	10.97	1	1/1
273.8	1.71	1	2/0	298.60	10.98	1	1/1
279.7	2.66	2	1/1	298.60	10.96	1	1/1
283.41	3.43	1	1/0	298.70	11.05	1	1/1
283.41	3.42	1	1/0	298.70	11.04	1	1/1
283.51	3.46	1	4/0	298.70	11.09	1	1/1
288.26	4.97	1	1/1	301.0	12.40	2	1/0
288.26	4.96	1	1/1	301.8	13.70	2	1/0
291.2	5.985	3	1/0	302.2	13.82	2	1/0
293.10	6.77	2	1/0	302.7	14.66	2	1/0
293.39	7.30	1	1/0	303.3	16.28	2	1/0
293.39	7.32	1	1/0	303.36	17.22	1	1/1
293.39	7.31	1	2/0	303.36	17.27	1	1/1
295.92	8.20	2	1/0	303.41	17.76	1	3/0
297.30	8.70	2	1/0	303.41	17.78	1	1/0
298.2	10.829	3	1/0	303.41	17.74	1	1/0
298.2	10.59	17	1/1	303.41	17.44	1	1/0
298.2	10.32	18, 19	2/0	303.41	17.77	1	1/0
298.2	10.80	16	1/0	303.91	18.98	1	1/0
298.2	10.4	14	1/0	303.91	18.96	1	1/0
298.2	10.60	17	1/1	303.91	18.97	1	1/0
				306.19	23.59	1	2/2
				306.29	23.89	1	1/1
				306.29	23.88	1	1/1
			$Na_2HPO_4 \cdot 7H_2O$				
309.42	31.20	1	7/7	313.44	35.42	1	2/0
309.42	31.21	1	1/1	313.44	35.41	1	1/0
309.42	31.22	1	1/1	318.29	40.68	1	1/1
309.42	31.23	1	1/1	318.29	40.69	1	1/1
310.42	32.23	1	3/3	318.29	40.71	1	1/1
310.42	32.19	1	2/2	318.29	40.72	1	1/1
310.42	32.18	1	1/1	320.5	43.37	1	1/1
310.42	32.22	1	1/1	320.5	43.36	1	1/1
313.44	35.46	1	2/0	321.3	44.45	1	2/2
313.44	35.43	1	1/0	321.3	44.48	1	1/1
			$Na_2HPO_4 \cdot 2H_2O$				
323.37	44.57	1	1/1	343.41	46.83	1	1/1
323.37	44.55	1	1/1	353.54	48.65	1	2/0
323.37	44.54	1	1/1	353.54	48.67	1	1/0
323.37	44.56	1	1/1	362.89	50.70	1	1/1
328.32	44.86	1	1/1	362.89	50.71	1	1/1
328.32	44.88	1	1/1	367.90	51.76	1	1/0
328.42	44.94	1	1/1	367.90	51.78	1	1/0
328.42	44.95	1	1/1	367.90	51.77	1	1/0
333.38	45.36	1	2/2	369.01	51.71	1	2/0
333.38	45.35	1	1/1	370.01	51.20	1	1/1
343.41	46.84	1	1/1	370.01	51.22	1	1/1
343.41	46.86	1	1/1	372.92	50.52	1	1/0
				372.92	50.53	1	2/0

(Table continued on next page)

COMPONENTS:	EVALUATOR:
(1) Disodium hydrogenphosphate; Na_2HPO_4; [7558-79-4] (2) Water; H_2O; [7732-18-5]	J. Eysseltová Charles University Prague, Czechoslovakia May 1985

CRITICAL EVALUATION:

Table II. Parameters for equation [1].

	$Na_2HPO_4 \cdot 12H_2O$		$Na_2HPO_4 \cdot 7H_2O$		$Na_2HPO_4 \cdot 2H_2O$	
Parameter	value	σ^a	value	σ^a	value	σ^a
A	-1.989×10^6	5000	-7.56×10^5	300	-1.546×10^5	500
B	-1.379×10^4	50	-4.79×10^3	20	887	5
C	24.0	0.1	7.63	0.03	-1.264	0.005
x_o	0.014714		0.064963		0.10040	
T_o	298.2		313.4		343.4	

[a]The standard deviation for the parameter.

Table III. Tentative values, calculated from equation [1], for the solubility of Na_2HPO_4 in water.

T/K	mole fraction	mole/kg	mass%
	$Na_2HPO_4 \cdot 12H_2O$		
273.2	0.0021371	0.12	1.66
278.2	0.0037242	0.21	2.87
283.2	0.0055018	0.31	4.19
288.2	0.0074979	0.42	5.63
293.2	0.010172	0.57	7.51
298.2	0.014714	0.83	10.55
303.2	0.024149	1.37	16.34
308.2	0.047504	2.77	28.25
309.45[a]	0.058234	3.43	32.80
	$Na_2HPO_4 \cdot 7H_2O$		
309.45	0.058234	3.43	32.80
311.2	0.058862	3.47	33.06
313.2	0.064287	3.82	35.17
315.2	0.070110	4.19	37.32
317.2	0.076443	4.60	39.53
319.2	0.083431	5.06	41.82
321.2	0.091254	5.58	44.23
321.6[b]	0.092892	5.69	44.71

[a]The dodecahydrate to heptahydrate transition temperature.

[b]The heptahydrate to dihydrate transition temperature.

Both transition temperatures were found graphically by the evaluator.

(continued next page)

COMPONENTS:

(1) Disodium hydrogenphosphate; Na_2HPO_4; [7558-79-4]

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

EVALUATOR:

J. Eysseltová
Charles University
Prague, Czechoslovakia

May 1985

CRITICAL EVALUATION:

Table III, contd.

$Na_2HPO_4 \cdot 2H_2O$

T/K	mole fraction	mole/kg	mass%
321.6	0.092892	5.69	44.71
323.2	0.092657	5.67	44.64
328.2	0.093014	5.70	44.75
333.2	0.094587	5.80	45.20
338.2	0.097088	5.97	45.92
343.2	0.10026	6.19	46.81
348.2	0.10386	6.44	47.78
353.2	0.10762	6.70	48.78
358.2	0.11126	6.95	49.72
363.2	0.11451	7.18	50.52
368.2	0.11707	7.36	51.15
373.2	0.11865	7.48	51.53

298 K. In the articles by Makin and his co-workers (18, 19, 23-26), data for the solubility of Na_2HPO_4 in water are also included and these form a consistent set of data. Furthermore, the data in these articles may be compared with respect to the composition of solutions saturated with respect to two salts, but in one of these reports (26) the headings "$NaNO_3$" and "NaCl" for two of the columns appear to have been interchanged. It appears also that some incorrect constants have been used in calculating the mol% values in this paper. The evaluator was unable to reproduce these calculations.

No solid solutions or ternary compounds were found in the Na_2HPO_4-$MgHPO_4$-H_2O system at 298 K (17) but potassium sodium hydrogen phosphate, $NaKHPO_4 \cdot 5H_2O$ [14518-27-5] was observed in the Na_2HPO_4-K_2HPO_4-H_2O system at 273 and 298 K (16), and sodium ammonium hydrogenphosphate, $NaNH_4HPO_4$ [13011-54-6] was found to be present in the Na_2HPO_4-$(NH_4)_2HPO_4$-H_2O system at 298 K (14). The latter compound was also observed in the quaternary system $2Na^+$, $2NH_4^+$||HPO_4^{2-}, Cl^--H_2O at 273 and 298 K (27). However, the data in this report (27) are at variance with those of Platford (14) with respect to the composition of solutions saturated with both $NaNH_4HPO_4$ and $Na_2HPO_4 \cdot 12H_2O$ as well as with those saturated with both $NaNH_4HPO_4$ and $(NH_4)_2HPO_4$. The data in (27) also disagree with those of Makin (24) with respect to the composition of the eutonic solution of the Na_2HPO_4-NaCl-H_2O system at 298 K. The values for the Na_2HPO_4 content in the work of Lauffenburger and Brodsky (27) seem to have a large negative systemtic error.

Values have been reported for three systems having an organic component. Ferroni, et al. (28) report values for the Na_2HPO_4-CH_3COCH_3-H_2O system and for two sections through the Na_2HPO_4-$NaClO_4$-CH_3COCH_3-H_2O system at 298 K. Bruder, et al. (29) report solubility data for the Na_2HPO_4-CH_3OH-H_2O system at 333 K. All three systems are characterized by limited miscibility.

(continued next page)

COMPONENTS:	EVALUATOR:
(1) Disodium hydrogenphosphate; Na_2HPO_4; [7558-79-4] (2) Water; H_2O; [7732-18-5]	J. Eysseltová Charles University Prague, Czechoslovakia May 1985

CRITICAL EVALUATION:

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