

CONDITIONS OF FORMATION OF ALKALI HYDROGENPHOSPHITES*

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Received June 1st, 1978

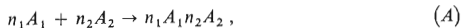
The Filippov's eutonic method was applied to the study of $M_2HPO_3-H_3PO_3-H_2O$ heterogeneous systems ($M = Li, Na, K$) at 25°C. The values of the standard Gibbs energy changes for the reactions occurring in these systems were obtained. The highest changes in the Gibbs energy accompany the formation of hydrogenphosphites $M(H_2PO_3)$, the energy increases from Li to K and decreases from hydrogenphosphite to tris(orthophosphite) and bis(orthophosphite).

During the study of the heterogeneous $M_2HPO_3-H_3PO_3-H_2O$ systems ($M = Li, Na, K$), we have not as yet paid attention to the energy conditions under which compounds are formed. A method by which these conditions can be determined based on thermodynamic data is the Filippov's eutonic method¹⁻³, making it possible to calculate the change in the standard Gibbs energy for a phase reaction of two components in a starting heterogeneous system leading to the formation of a compound as the third component, based on the chemical potential values of the components and the solvent in saturated solutions. For this purpose, the chemical potential of the solvent is determined by measuring its vapour pressure above the saturated solution.

In the present work, the change in the standard Gibbs energy is examined for phase reactions that give rise to alkali hydrogenphosphites in saturated aqueous solutions.

THEORETICAL

The Filippov's method for the calculation of the standard Gibbs energy change for the formation of a new compound in a ternary system is based on the following concept. For the formation of a binary compound in a ternary system (Fig. 1) according to the equation



* Part V in the series Heterogeneous Inorganic Systems; Part IV: This Journal 45, 2283 (1980). The results of this work are discussed also in Part IV.

where n_1 and n_2 are the stoichiometric coefficients of the components A_1 and A_2 , respectively, the change in the standard Gibbs energy ΔG^0 can be expressed as

$$\Delta G^0 = G^0[n_1, n_2] - n_1\mu_1^0 - n_2\mu_2^0, \quad (1)$$

where $G^0[n_1, n_2]$ is the Gibbs energy of the compound $n_1A_1n_2A_2$ and μ_i^0 is the chemical potential of the i -th component; the superscript 0 refers to the component in the standard state. The Gibbs energy of the compound $n_1A_1n_2A_2$ in the eutonic point D (Fig. 1) can be expressed as

$$G^0[n_1, n_2] = n_1\mu_1^D + n_2\mu_2^D. \quad (2)$$

For equilibrium in the eutonic point D we have

$$\mu_1^D = \mu_1^0. \quad (3)$$

Inserting the relations (2) and (3) in Eq. (1) we obtain

$$\Delta G^0 = n_2(\mu_2^D - \mu_2^0). \quad (4)$$

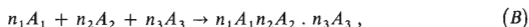
Analogously for the eutonic point E ,

$$\Delta G^0 = n_1(\mu_1^E - \mu_1^0) = n_1(\mu_1^E - \mu_1^D) = n_2(\mu_2^D - \mu_2^E). \quad (5)$$

In case that the resulting substance is a solvate (a hydrate in the case of water), the relation

$$\Delta G^0 = n_2(\mu_2^D - \mu_2^0) + n_3(\mu_3^D - \mu_3^0) \quad (6)$$

can be derived analogously for the reaction



where the subscript 3 refers to the solvent.

It is convenient to replace the chemical potentials of the components A_1 and A_2 by the chemical potential of the solvent, as the latter can be readily determined by measuring the vapour pressure. The substitution can be performed on solving a system of equations determined by the Gibbs–Duhem relations for the two phases of the three-component system.

In any point of the region of existence of the solid phase, given by the points $D, E, n_1A_1n_2A_2$ (Fig. 1), the relations

$$x_1 d\mu + x_2 d\mu_2 + x_3 d\mu_3 = 0 \quad (7)$$

and

$$n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 = 0 \quad (8)$$

hold true for the liquid and solid phases, respectively; here x_i is the mole fraction of the i -th component in the liquid phase and n_i the corresponding stoichiometric coefficient in the solid phase. Combining the two equations, we can express the dependences of the chemical potentials of the two components on the chemical potential of the solvent:

$$d\mu_1 = [(x_2n_3 - x_3n_2)/(x_1n_2 - x_2n_1)] d\mu_3, \quad (9)$$

$$d\mu_2 = [(x_1n_3 - x_3n_1)/(x_1n_2 - x_2n_1)] d\mu_3. \quad (10)$$

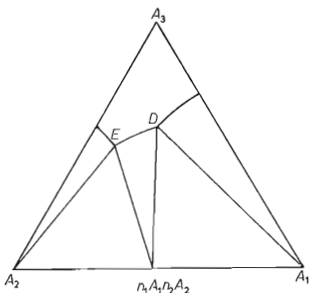
In the simplest case – formation of the compound A_1A_2 – we have

$$d\mu_1 = [x_3/(x_2 - x_1)] d\mu_3. \quad (11)$$

The change in the standard Gibbs energy ΔG^0 for the formation of the compound A_1A_2 from the components A_1 and A_2 in a heterogeneous system can be written as

$$\Delta G^0 = (\mu_1^E - \mu_1^D) = \int_D^E [x_3/(x_2 - x_1)] d\mu_3. \quad (12)$$

FIG. 1
The Ternary Diagram A_1 - A_2 - A_3 of the Heterogeneous Systems where One Compound is Formed



If the compound A_1A_2 is incongruently soluble, hence if in the region $\langle D, E \rangle$ x_1 is different from x_2 in any point, the change in the standard Gibbs energy can be calculated by integration of Eq. (12). Knowing the solvent vapour pressure or activity, we can calculate its chemical potential using the relation $\mu_3 = RT \ln a_w$, where a_w is the solvent activity in the solution.

If the compound A_1A_2 formed is congruently soluble, *i.e.* if in one point of the interval $\langle D, E \rangle$ x_1 equals x_2 , Eq. (12) cannot be directly applied to the calculation. The equation can be, however, transformed to

$$\Delta G^0 = (\mu_1^E - \mu_1^0) = \int_D^E [x_3/(x_2 - x_1)] (\partial\mu_3/\partial x_1) dx_1. \quad (13)$$

For calculation of the ΔG^0 values for congruently soluble substances according to this equation, the dependence $\mu_3 = f(x_1)$ must be first differentiated, the derivatives in the points x_1 are multiplied by the $x_3/(x_2 - x_1)$ value for the same x_1 , and the function is integrated with respect to x_1 .

EXPERIMENTAL

Chemicals and Methods

The chemicals used were commercial preparations of Lachema, reagent or CP grade. Phosphorous acid was prepared by hydrolysis of phosphorus trichloride⁴, the phosphites $\text{Li}_2\text{HPO}_3 \cdot \text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_3 \cdot 5 \text{H}_2\text{O}$, and K_2HPO_3 were obtained by neutralization of the acid with the corresponding hydroxides in ethanol.

In the substances prepared, phosphorus was determined as $\text{Mg}_2\text{P}_2\text{O}_7$, lithium as Li_3PO_4 , sodium as $\text{NaZn}(\text{UO}_2)_3 \cdot (\text{CH}_3\text{COO})_9 \cdot 6 \text{H}_2\text{O}$, and potassium as KClO_4 .

During the study of the heterogeneous systems, the metals were determined also gravimetrically, phosphorous acid by alkalimetric titration with 0.1M-NaOH using phenolphthalein as the indicator.

The measurement procedure comprises preparation of a suitable heterogeneous mixture of phosphorous acid, the phosphite under study, and water, checking of the establishing of the equilibrium, and analysis of the liquid and solid phases, and also measurement of the water vapour pressure above the system.

The heterogeneous systems were mixed in wide-necked Erlenmeyer flasks so that the composition of the liquid phase in the equilibrium corresponded to the pertinent eutonic points or to uniformly spaced mapping points on the solubility curve. In the case of incongruently soluble substances, there were five to seven points, in the case of congruently soluble substances, eight to ten points. The amount of the heterogeneous mixture was chosen such that it contained at least 40 ml of the liquid phase in systems where the content of phosphorous acid in the liquid phase was below 50%, and at least 15 ml in cases where the acid content was higher. The establishing of the equilibrium was monitored analytically, by determining phosphorous acid in the liquid phase. In order to shorten the time necessary for the equilibrium to establish, the heterogeneous mixtures were stirred with mechanical stirrer or shaken on a shaking machine.

The water vapour pressure above the heterogeneous system was measured by the dynamic⁵ and the isopiestic⁶ methods. In case that a pressure exceeding 1.6 kPa was expected, the liquid phase was separated and the pressure was measured by the dynamic method, whereas the isopiestic method was employed for mixtures displaying water vapour pressure below 1.6 kPa; the liquid phase was not separated — mixture of both phases was sampled.

The standard Gibbs energy change for the formation of incongruently soluble compounds was calculated according to Filippov: the ratios of the mole fractions, found from the Gibbs–Duhem equations for the compound under study, were plotted against the chemical potential values of water; the integration was performed graphically.

For the calculation of the standard Gibbs energy change for the formation of congruently soluble compounds, the dependence of the saturated vapour pressure of water on the mole percentage of one component was first found and expressed analytically in the form of a polynomial of the fourth or fifth degree by employing a Hewlett–Packard 983A computer. The values of the $\partial\mu_3/\partial x_1$ derivatives, where μ_3 is the chemical potential of water and x_1 the mole per cent H_3PO_3 , were then calculated from the analytical expression.

The values of the derivative for the x_1 's were multiplied by the mole fraction values, found from the Gibbs–Duhem equations, and plotted against the x_1 values. The integration was again graphical.

The relative error of determination of the water vapour pressure did not exceed 0.2% (refs^{5,6}). In addition to the water vapour pressure for the pertinent points on the solubility curve, the contents of the components in the solution have to be known as well for the calculation of the change in the standard Gibbs energy. They were determined by various analytical methods as described in the Experimental. The relative errors of the various analyses did not exceed 0.5%. For the calculation of the standard Gibbs energy change for congruently soluble substances, the experimentally found dependence of μ_3 on x_1 had first to be differentiated. The dependence was described in the form of a polynomial function; the fit was expressed through the R^2 value, the square of the total correlation coefficient for multi-linear regression⁷. The R^2 values for the various functions lay in the range of 0.981 to 0.998 thus indicating very good fit to the dependences observed.

The main source of error was the graphical integration. The integral areas below curves constructed in different ways were compared, and the error of calculation of the standard Gibbs energy change was found to be below 5%.

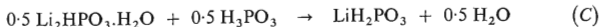
RESULTS

The measured values of the water vapour pressure along with the results of analyses of the corresponding saturated solutions are given in Tables I–III. The capital letters denote the eutonic and peritonic points.

$\text{Li}_2\text{HPO}_3\text{—H}_3\text{PO}_3\text{—H}_2\text{O}$ System

In this system only lithium hydrogenphosphite LiH_2PO_3 is formed. The results of analyses and the water vapour pressure values are given in Table I.

The change in the standard Gibbs energy for the reaction



is

$$\Delta G(C) = 0.5(\mu_1^B - \mu_1^A) - 0.5(\mu_3^B - \mu_3^0). \quad (14)$$

The term $(\mu_1^B - \mu_1^A)$ is

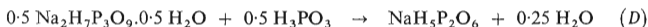
$$\mu_1^B - \mu_1^A = 0.5 \int_A^B [x_3/(x_2 - x_1)] d\mu_3. \quad (15)$$

From the graphical integration (15) and insertion in Eq. (14) the change in the standard Gibbs energy $\Delta G(C) = -9.21 \text{ kJ mol}^{-1}$ was obtained.

$\text{Na}_2\text{HPO}_3\text{—H}_3\text{PO}_3\text{—H}_2\text{O}$ System

In this system, disodium tetrahydrogentris(orthophosphite) $\text{Na}_2\text{H}_7\text{P}_3\text{O}_9 \cdot 0.5 \text{ H}_2\text{O}$ and sodium trihydrogenbis(orthophosphite) $\text{NaH}_3\text{P}_2\text{O}_6$ are formed in addition to the hydrogenphosphite $\text{NaH}_2\text{PO}_3 \cdot 2.5 \text{ H}_2\text{O}$. The results of analyses along with the values of the water vapour pressure are given in Table II.

The change in the standard Gibbs energy for the reaction



is

$$\Delta G^0(D) = 0.5(\mu_1^B - \mu_1^A) - 0.25(\mu_3^B - \mu_3^0), \quad (16)$$

TABLE I

Physical Data of $\text{Li}_2\text{HPO}_3\text{—H}_3\text{PO}_3\text{—H}_2\text{O}$ System

Content of the liquid phase mol. %			Water vapour pressure kPa	Chemical potential of water kJ/mol	Condition of the solid phase ^a
H_3PO_3	Li_2HPO_3	H_2O			
7.08	6.90	86.0	2.330	— 761.1	<i>B</i> $\text{Li}_2\text{HPO}_3 \cdot \text{H}_2\text{O} + \text{LiH}_2\text{PO}_3$
9.71	5.76	84.5	2.302	— 790.8	
18.2	5.25	76.6	2.013	—1 124.9	
25.1	5.11	69.8	1.528	—1 807.9	
36.7	4.84	58.5	1.135	—2 545.1	
55.4	4.70	39.9	0.437	—4 909.9	<i>A</i> $\text{LiH}_2\text{PO}_3 + \text{H}_3\text{PO}_3$

^a Symbols *A*, *B* denote the corresponding eutonic points.

where for the term $(\mu_1^B - \mu_1^A)$ we have

$$\mu_1^B - \mu_1^A = \int_A^B [x_3/(3x_2 - x_1)] d\mu_3. \quad (17)$$

On the integration (17) and substitution in the relation (16) we found $\Delta G(D) = -2.43 \text{ kJ mol}^{-1}$.

For the reaction

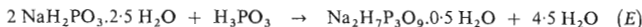


TABLE II

Physical Data of $\text{Na}_2\text{HPO}_3\text{-H}_3\text{PO}_3\text{-H}_2\text{O}$ System

Content in the liquid phase mol.%			Water vapour pressure kPa	Chemical potential of water kJ/mol	Composition of the solid phase ^a
H_3PO_3	Na_2HPO_3	H_2O			
5.08	15.1	79.8	1.463	-1 700	<i>D</i> $\text{Na}_2\text{HPO}_3 \cdot 5 \text{H}_2\text{O} + \text{NaH}_2\text{PO}_3 \cdot 2.5 \text{H}_2\text{O}$
5.89	13.9	80.2	1.845	-1 322	$\text{NaH}_2\text{PO}_3 \cdot 2.5 \text{H}_2\text{O}$
6.94	12.0	81.1	2.048	-1 082	$\text{NaH}_2\text{PO}_3 \cdot 2.5 \text{H}_2\text{O}$
7.99	10.5	81.5	2.180	- 926.8	$\text{NaH}_2\text{PO}_3 \cdot 2.5 \text{H}_2\text{O}$
10.9	10.1	79.0	2.229	- 871.1	$\text{NaH}_2\text{PO}_3 \cdot 2.5 \text{H}_2\text{O}$
11.5	10.1	78.4	2.216	- 885.8	$\text{NaH}_2\text{PO}_3 \cdot 2.5 \text{H}_2\text{O}$
11.9	10.1	78.0	2.160	- 949.3	$\text{NaH}_2\text{PO}_3 \cdot 2.5 \text{H}_2\text{O}$
12.2	9.96	77.8	2.089	-1 032	<i>C</i> $\text{NaH}_2\text{PO}_3 \cdot 2.5 \text{H}_2\text{O} + \text{Na}_2\text{H}_7\text{P}_3\text{O}_9 \cdot 0.5 \text{H}_2\text{O}$
12.3	9.88	77.8	2.121	- 994.5	$\text{Na}_2\text{H}_7\text{P}_3\text{O}_9 \cdot 0.5 \text{H}_2\text{O}$
13.4	8.70	77.9	2.258	- 838.5	$\text{Na}_2\text{H}_7\text{P}_3\text{O}_9 \cdot 0.5 \text{H}_2\text{O}$
16.0	5.91	78.1	2.722	- 824.2	$\text{Na}_2\text{H}_7\text{P}_3\text{O}_9 \cdot 0.5 \text{H}_2\text{O}$
17.0	5.15	77.9	2.249	- 848.9	$\text{Na}_2\text{H}_7\text{P}_3\text{O}_9 \cdot 0.5 \text{H}_2\text{O}$
18.2	4.65	77.2	2.193	- 911.7	$\text{Na}_2\text{H}_7\text{P}_3\text{O}_9 \cdot 0.5 \text{H}_2\text{O}$
19.0	4.06	76.9	2.168	- 940.1	$\text{Na}_2\text{H}_7\text{P}_3\text{O}_9 \cdot 0.5 \text{H}_2\text{O}$
20.2	3.40	76.4	2.141	- 971.1	<i>B</i> $\text{Na}_2\text{H}_7\text{P}_3\text{O}_9 \cdot 0.5 \text{H}_2\text{O} + \text{NaH}_5\text{P}_2\text{O}_6$
22.3	3.12	74.6	2.037	-1 095	$\text{NaH}_5\text{P}_2\text{O}_6$
24.7	2.15	73.1	1.886	-1 285	$\text{NaH}_5\text{P}_2\text{O}_6$
36.1	2.13	61.8	1.437	-1 959	$\text{NaH}_5\text{P}_2\text{O}_6$
60.2	2.11	37.7	0.624	-4 028	<i>A</i> $\text{NaH}_5\text{P}_2\text{O}_6 + \text{H}_3\text{PO}_3$

^a Symbols *A*, *B*, *C*, *D* denote the corresponding eutonic points.

the change in the standard Gibbs energy is

$$\Delta G^0(E) = (\mu_1^C - \mu_1^A) - 4.5(\mu_3^C - \mu_3^0) \quad (18)$$

which can be rearranged to

$$\Delta G^0(E) = (\mu_1^C - \mu_1^B) + (\mu_1^B - \mu_1^A) - 4.5(\mu_3^C - \mu_3^0) \quad (19)$$

and the difference $\mu_1^B - \mu_1^A$ can be evaluated according to Eq. (17).

Since disodium tetrahydrogentris(orthophosphite) is a compound congruently soluble in one valid point $2x_2 = x_1$, the difference $\mu_1^C - \mu_1^B$ can be written as

$$\mu_1^C - \mu_1^B = \int_B^C [(x_3 - 0.5x_2)/(2x_2 - x_1)] (\partial\mu_3/\partial x_1) dx_1. \quad (20)$$

TABLE III
Physical Data of $K_2HPO_3-H_3PO_3-H_2O$ System

Content in the liquid phase mol.%			Water vapour pressure kPa	Chemical potential of water kJ/mol	Composition of the solid phase ^a
H_3PO_3	K_2HPO_3	H_2O			
4.60	15.3	80.1	1.517	-1 825	<i>D</i> $K_2HPO_3 + KH_2PO_3$
6.18	13.3	80.5	1.660	-1 602	KH_2PO_3
7.24	12.1	80.7	1.717	-1 518	KH_2PO_3
14.3	10.8	74.9	1.762	-1 454	KH_2PO_3
14.3	10.5	74.6	1.738	-1 487	KH_2PO_3
15.4	10.5	74.1	1.686	-1 556	KH_2PO_3
16.1	10.5	73.4	1.599	-1 695	<i>C</i> $KH_2PO_3 + K_2H_7P_3O_9$
16.2	9.59	74.2	1.811	-1 385	$K_2H_7P_3O_9$
17.6	6.66	75.8	1.805	-1 394	$K_2H_7P_3O_9$
22.6	6.73	70.7	1.661	-1 600	$K_2H_7P_3O_9$
28.6	7.38	64.0	1.473	-1 898	$K_2H_7P_3O_9$
31.5	7.84	60.7	1.331	-2 151	$K_2H_7P_3O_9$
36.2	8.62	55.2	1.113	-2 593	$K_2H_7P_3O_9$
41.8	10.0	48.2	1.024	-2 800	$K_2H_7P_3O_9$
47.4	11.3	41.3	0.867	-3 213	<i>B</i> $K_2H_7P_3O_9 + KH_5P_2O_6$
48.3	10.9	40.8	0.857	-3 241	$KH_5P_2O_6$
53.0	10.4	36.6	0.752	-3 607	$KH_5P_2O_6$
59.5	7.72	30.8	0.579	-4 215	$KH_5P_2O_6$
86.2	9.64	4.24	0.337	-6 074	<i>A</i> $KH_5P_2O_6 + H_3PO_3$

^a Symbols *A*, *B*, *C*, *D* denote the corresponding eutonic points.

The dependence of μ_3 on x_1 could be expressed in the polynomial form

$$\mu_3 = 40394.283 - 8896.6969x_1 + 740.4349x_1^2 - 27.1040x_1^3 + 0.3699x_1^4. \quad (21)$$

The variance characterized by the R^2 value was 0.991.

The difference $\mu_1^C - \mu_1^B$ was found to be $-6.98 \text{ kJ mol}^{-1}$, which inserted in Eq. (19) gave $\Delta G^0(E) = -8.08 \text{ kJ mol}^{-1}$.

For the reaction



we have

$$\Delta G^0(F) = 0.5(\mu_1^D - \mu_1^C) + (\mu_1^C - \mu_1^B) + (\mu_1^B - \mu_1^A). \quad (22)$$

The two last terms are known, the term $(\mu_1^D - \mu_1^C)$ can be expressed, with regard to the congruent solubility of $\text{NaH}_2\text{PO}_3 \cdot 2.5 \text{ H}_2\text{O}$, as

$$\mu_1^D - \mu_1^C = \int_C^D [(x_3 - 5x_2)/(x_2 - x_1)] (\partial\mu_3/\partial x_1) dx_1. \quad (23)$$

The relation between μ_3 and x_1 was expressed in the polynomial form

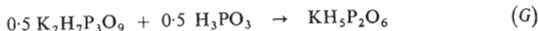
$$\begin{aligned} \mu_3 = & 7614.5569 - 1266.3763x_1 - 188.4591x_1^2 + 67.0227x_1^3 - \\ & - 6.0354x_1^4 - 0.1807x_1^5. \end{aligned} \quad (24)$$

The fit of this polynomial to the experimental dependence is expressed by the value $R^2 = 0.998$. The value of the integral (23) is $-7.88 \text{ kJ mol}^{-1}$, from which $\Delta G^0(F) = -10.1 \text{ kJ mol}^{-1}$.

$\text{K}_2\text{HPO}_3\text{—H}_3\text{PO}_3\text{—H}_2\text{O}$ System

In this system, potassium hydrogenphosphite KH_2PO_3 , dipotassium tetrahydrogen-tris(orthophosphite) $\text{K}_2\text{H}_7\text{P}_3\text{O}_9$, and potassium trihydrogenbis(orthophosphite) $\text{KH}_5\text{P}_2\text{O}_6$ were found. The results of analyses as well as the water vapour pressure values are given in Table III.

For the formation of potassium trihydrogenbis(orthosphosphite) according to the equation



we have

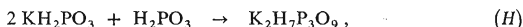
$$\Delta G^0(G) = 0.5(\mu_1^B - \mu_1^A), \quad (25)$$

where the term in parentheses can be written as

$$\mu_1^B - \mu_1^A = \int_A^B [x_3/(3x_2 - x_1)] d\mu_3. \quad (26)$$

The integration afforded the value $(\mu_1^B - \mu_1^A) = -2.70 \text{ kJ mol}^{-1}$, and $\Delta G^0(G) = -1.35 \text{ kJ mol}^{-1}$.

For the reaction



we have

$$\Delta G^0(H) = (\mu_1^C - \mu_1^0) = (\mu_1^C - \mu_1^B) + (\mu_1^B - \mu_1^A). \quad (27)$$

The term $(\mu_1^B - \mu_1^A)$ is known from the calculation according to Eq. (26), the difference $(\mu_1^C - \mu_1^B)$ can be expressed as

$$\mu_1^C - \mu_1^B = \int_A^B [x_3/(2x_2 - x_1)] (\partial\mu_3/\partial x_1) dx_1 \quad (28)$$

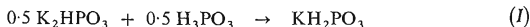
with regard to the fact that dipotassium tetrahydrogentris(orthophosphite) is a congruently soluble compound.

The dependence of μ_3 on x_1 was expressed as the polynomial

$$\mu_3 = 9469.6413 - 1127.1988x_1 + 54.7393x_1^2 - 1.0782x_1^3 + 0.0077x_1^4 \quad (29)$$

with the R^2 value 0.981. The polynomial was differentiated with respect to x_1 and the value $(\mu_1^C - \mu_1^B) = -11.1 \text{ kJ mol}^{-1}$ was calculated; from this, $\Delta G^0(H) = -13.8 \text{ kJ mol}^{-1}$.

For the change in the standard Gibbs energy of the reaction



we have

$$\Delta G^0(I) = 0.5(\mu_1^D - \mu_1^A) = 0.5[(\mu_1^D - \mu_1^C) + (\mu_1^C - \mu_1^B) + (\mu_1^B - \mu_1^A)]. \quad (30)$$

The difference ($\mu_1^D - \mu_1^C$) was calculated as in the preceding case, as sodium hydrogenphosphite is a congruently soluble substance:

$$\mu_1^D - \mu_1^C = \int_A^D [x_3/(x_2 - x_1)] (\partial\mu_3/\partial x_1) dx_1. \quad (31)$$

The polynomial

$$\begin{aligned} \mu_3 = & 1586.6715 + 595.5012x_1 - 221.6035x_1^2 + 29.7277x_1^3 \\ & - 1.7564x_1^4 + 0.0389x_1^5 \end{aligned} \quad (32)$$

was used to express the dependence of μ_3 on x_1 ; $R^2 = 0.998$. After differentiation of the polynomial and integration with respect to x_1 , $(\mu_1^D - \mu_1^C) = -18.3 \text{ kJ mol}^{-1}$; after insertion in Eq. (30) we obtain $\Delta G^0(I) = -16.0 \text{ kJ mol}^{-1}$.

DISCUSSION

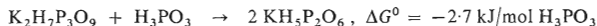
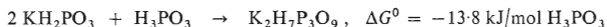
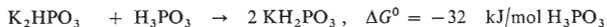
The existence of alkali hydrogenphosphites and poly(orthophosphites) in the $M_2\text{HPO}_3\text{—H}_3\text{PO}_3\text{—H}_2\text{O}$ systems was confirmed. The values measured can be used to evaluate the effect of the cation on the hydrogen bond formation and the degree of polymerization or linking of the H_2PO_3^- groups by hydrogen bonds as the basic bonding motive⁸.

The highest changes in the standard Gibbs energy occur on the transition from phosphite to hydrogenphosphite and increase in the series from lithium to potassium. In the sodium and potassium phosphite systems, disodium or dipotassium tetrahydrogen tris(orthophosphite) form in addition. The changes in the standard Gibbs energy for the formation of those substances increase again from sodium to potassium. The changes in the standard Gibbs energy for the formation of trihydrogen bis(orthophosphites) by reaction of the acid with the tris(orthophosphites) decrease on going from sodium to potassium, but the overall change ΔG^0 for the formation of those compounds from the phosphites and the acid increases again in this direction.

As mentioned above, the highest changes in the standard Gibbs energy accompany reactions associated with the formation of hydrogen bonds and also with the greatest structural changes, hence reactions of phosphites with phosphorous acid resulting in formation of hydrogenphosphites. The additional changes in the standard Gibbs energy occurring during the formation of tetrahydrogentris(orthophosphites) indicate further changes in structure, but minor ones, so that the hydrogen bonding system must have been established.

During the formation of trihydrogenbis(orthophosphites) the hydrogen bonding system changes only slightly, and these phosphites can be expected to approach

most the hydrogen bonding system of phosphorous acid as compared with the other phosphites. This is apparent from the system of equations for potassium phosphite,



The ΔG^0 values are related to one mol of phosphorous acid, hence to the incorporation of two hydrogen bonds into the system. Generally, the hydrogen bonding system stabilizes on going from lithium to potassium, its stability lowers as the phosphorus-to-metal ratio increases.

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Translated by P. Adámek.