

FORMATION OF HYDROGEN PHOSPHITES OF ALKALINE EARTH METALS⁺

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In this paper a study of heterogeneous systems $M\text{HPO}_3\text{-H}_3\text{PO}_3\text{-H}_2\text{O}$ ($M = \text{Mg, Ca, Sr}$) at a temperature of 25°C using the Filippov's eutonic method has been described. Values of change in standard Gibbs energy for reactions of the studied systems have been found. Effect of the cation on hydrogen bond between the $\text{H}_2\text{PO}_3^{2-}$ groups is discussed.

In an earlier paper¹ we paid attention to the calculation of change in the standard Gibbs energy for the formation of hydrogenphosphites of alkali metals. In this paper we intend, using the same procedure, and the Filippov's eutonic method, to determine changes in the standard Gibbs energy in the formation of magnesium, calcium, and strontium hydrogenphosphites, and to compare values thus obtained with those achieved for hydrogenphosphites of alkali metals.

EXPERIMENTAL

The reagents used were all A.R. grade and chemically pure products of firm Lachema. Phosphorous acid H_3PO_3 was prepared by hydrolysis of phosphorus trichloride² and magnesium ($\text{MgHPO}_3 \cdot 6\text{H}_2\text{O}$), calcium ($\text{CaHPO}_3 \cdot \text{H}_2\text{O}$), and strontium ($\text{SrHPO}_3 \cdot 2.5\text{H}_2\text{O}$) phosphites were prepared by precipitation of ammonium phosphite solution with appropriate chlorides. In the prepared reagents, phosphorus, calcium, and strontium were determined gravimetrically as $\text{Mg}_2\text{P}_2\text{O}_7$, CaO , and SrSO_4 , respectively.

Within the study of individual heterogeneous systems the metals were determined complexometrically: magnesium, calcium, and strontium by titration using eriochrome black T, murexide, and thymolphthalein³, respectively. The experimental procedure is described in paper¹.

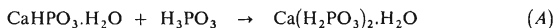
RESULTS

System $\text{CaHPO}_3\text{-H}_3\text{PO}_3\text{-H}_2\text{O}$

In this system only incongruently soluble calcium hydrogenphosphite $\text{Ca}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$ was found. The obtained values of analysis along with the measured values of water vapour pressure and chemical potential of water are given in Table I.

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For the change in standard Gibbs energy ΔG^0 of reaction



$$\Delta G^0 = (\mu_1^B - \mu_1^A) \quad (1)$$

and for difference

$$(\mu_1^B - \mu_1^A) = \int_c^B (x_3 - x_2)/(x_2 - x_1) d\mu_3 \quad (2)$$

where μ_i^0 denotes chemical potential of pure i -numbered component, $\mu_i^{A,B}$ is chemical potential of the i -numbered component at eutonic point A or B; x_i denotes mole fraction of i -numbered component. $i = 1$ holds for phosphorous acid, $i = 2$ for appropriate phosphite, and $i = 3$ for water.

On integration of (2), we obtain $\Delta G^0 = -15.6$ kJ/mol.

System $\text{SrHPO}_3\text{-H}_3\text{PO}_3\text{-H}_2\text{O}$

In this system, strontium hydrogenphosphite $\text{Sr}(\text{H}_2\text{PO}_3)_2$ and distrontium hexahydrogenpentakisorthophosphite $\text{Sr}_2\text{H}_{11}\text{P}_5\text{O}_{15} \cdot 2 \text{H}_2\text{O}$ were found.

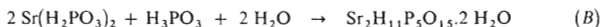
TABLE I

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

Content in liquid phase mol. %			Water vapour pressure kPa	Chemical potential of water J/mol	Solid phase composition
H_3PO_3	CaHPO_3	H_2O			
2.80	2.25	95.0	2.860	- 253.6	B $\text{CaHPO}_3 \cdot \text{H}_2\text{O} +$ $+ \text{Ca}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$
6.50	2.19	91.3	2.849	- 262.8	$\text{Ca}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$
10.7	2.14	87.1	2.541	- 546.8	$\text{Ca}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$
16.7	2.13	81.1	2.385	- 703.7	$\text{Ca}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$
23.2	2.12	74.7	1.913	- 1 250	$\text{Ca}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$
28.9	2.09	69.0	1.460	- 1 920	$\text{Ca}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$
34.4	1.95	63.7	1.309	- 2 191	$\text{Ca}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$
37.5	1.82	60.7	1.123	- 2 572	$\text{Ca}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$
45.4	1.64	53.0	0.792	- 3 437	$\text{Ca}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$
50.0	1.33	48.7	0.561	- 4 290	A $\text{Ca}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O} +$ $+ \text{H}_3\text{PO}_3$

Letters A, B denote appropriate eutonic points.

Analytical values as well as measured values of water vapour pressure are summarized in Table II. For the change in standard Gibbs energy ΔG^0 of reaction



$$\Delta G^0 = (\mu_1^B - \mu_1^A) + 2(\mu_2^B - \mu_2^A) \quad (3)$$

and for difference

$$(\mu_1^B - \mu_1^A) = \int_A^B \frac{x_3 - x_2}{(3/2)(x_2 - x_1)} d\mu_3 \quad (4)$$

On integration, we obtain $(\mu_1^B - \mu_1^A) = -6.79 \text{ kJ/mol}$ and on introducing into relationship (3), $\Delta G^0 = -8.16 \text{ kJ/mol}$.

For the change in standard Gibbs energy of reaction

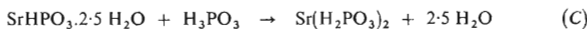


TABLE II
Physical Data of System $\text{SrHPO}_3\text{-H}_3\text{PO}_3\text{-H}_2\text{O}$
Letters A, B, C denote appropriate eutonic points.

Content in liquid phase mol. %			Water vapour pressure	Chemical potential of water	Solid phase composition
H_3PO_3	SrHPO_3	H_2O	kPa	J/mol	
1.85	1.67	96.5	2.926	- 196.6	C $\text{SrHPO}_3 \cdot 2.5 \text{H}_2\text{O} + \text{Sr}(\text{H}_2\text{PO}_3)_2$
4.51	1.59	93.9	2.902	- 217.1	$\text{Sr}(\text{H}_2\text{PO}_3)_2$
6.29	1.58	92.1	2.820	- 288.7	$\text{Sr}(\text{H}_2\text{PO}_3)_2$
10.4	1.54	88.1	2.676	- 418.4	$\text{Sr}(\text{H}_2\text{PO}_3)_2$
15.8	1.54	82.6	2.396	- 692.5	B $\text{Sr}(\text{H}_2\text{PO}_3)_2 + \text{Sr}_2\text{H}_{11}\text{P}_5\text{O}_{15} \cdot 2 \text{H}_2\text{O}$
21.0	1.42	77.5	2.098	-1 021	$\text{Sr}_2\text{H}_{11}\text{P}_5\text{O}_{15} \cdot 2 \text{H}_2\text{O}$
29.8	1.12	69.1	1.607	-1 683	$\text{Sr}_2\text{H}_{11}\text{P}_5\text{O}_{15} \cdot 2 \text{H}_2\text{O}$
37.0	0.98	65.0	1.240	-2 325	$\text{Sr}_2\text{H}_{11}\text{P}_5\text{O}_{15} \cdot 2 \text{H}_2\text{O}$
52.8	0.97	46.2	0.736	-3 619	A $\text{Sr}_2\text{H}_{11}\text{P}_5\text{O}_{15} \cdot 2 \text{H}_2\text{O} + \text{H}_3\text{PO}_3$

it can be derived analogously as in previous cases that

$$\Delta G^0 = (\mu_1^C - \mu_1^A) - 2 \cdot 5(\mu_3^C - \mu_3^0). \quad (5)$$

Difference $(\mu_1^C - \mu_1^A)$ in equation (5) can be decomposed into

$$\Delta G^0 = (\mu_1^C - \mu_1^B) + (\mu_1^B - \mu_1^A) - 2 \cdot 5(\mu_3^C - \mu_3^0) \quad (6)$$

Difference $(\mu_1^B - \mu_1^A)$ is known from relationship (4), and for $(\mu_1^C - \mu_1^B)$ we obtain

$$(\mu_1^C - \mu_1^B) = \int_B^C x_3 / (x_2 - x_1) d\mu_3 \quad (7)$$

On integration, we obtain $(\mu_1^C - \mu_1^B) = -11.8 \text{ kJ/mol}$ or $\Delta G^0 = -18.6 \text{ kJ/mol}$.

System $\text{MgHPO}_3\text{-H}_3\text{PO}_3\text{-H}_2\text{O}$

In this system, magnesium hydrogen phosphite $\text{Mg}(\text{H}_2\text{PO}_3)_2$, dimagnesium hexahydrogenpentakis(orthophosphite) $\text{Mg}_2\text{H}_{11}\text{P}_5\text{O}_{15}$, and magnesium hexahydrogen-tetrakis(orthophosphite) $\text{MgH}_{10}\text{P}_4\text{O}_{12}$ were found. Analytical results as well as values of water vapour pressure and chemical potential of water are given in Table III. For the change in standard Gibbs energy of reaction



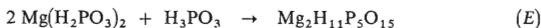
$$\Delta G^0 = 3/2(\mu_1^B - \mu_1^A) \quad (8)$$

and

$$(\mu_1^B - \mu_1^A) = \int_B^A x_3 / (3x_2 - x_1) d\mu_3. \quad (9)$$

On integration, we obtain $(\mu_1^B - \mu_1^A) = -1.77 \text{ kJ/mol}$ and $\Delta G^0 = -2.65 \text{ kJ/mol}$.

For the change in standard Gibbs energy of reaction



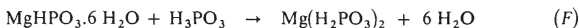
$$\Delta G^0 = (\mu_1^C - \mu_1^A) = (\mu_1^C - \mu_1^B) + (\mu_1^B - \mu_1^A). \quad (10)$$

Difference $(\mu_1^B - \mu_1^A)$ is known from relationship (8) and for $(\mu_1^C - \mu_1^B)_B$, we obtain

$$(\mu_1^C - \mu_1^B) = \int_A^B \frac{x_3}{(3/2)(x_2 - x_1)} d\mu_4. \quad (11)$$

By integration, difference $(\mu_1^C - \mu_1^B) = -20.3$ kJ/mol was established. The change in standard Gibbs energy is for the above given reaction $\Delta G^0 = -22.1$ kJ/mol.

For the change in standard Gibbs energy of reaction



$$\Delta G^0 = (\mu_1^D - \mu_1^A) - 6(\mu_3^D - \mu_3^0) = (\mu_1^D - \mu_1^C) + (\mu_1^C - \mu_1^B) + (\mu_1^B - \mu_1^A) - 6(\mu_3^D - \mu_3^0) \quad (12)$$

Differences $(\mu_1^B - \mu_1^A)$ and $(\mu_1^C - \mu_1^B)$ are known from equations (11) and (9).

TABLE III

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

Letters A, B, C, D denote appropriate eutonic points.

Content in liquid phase mol. %			Water vapour pressure	Chemical potential of water	Solid phase composition
H_3PO_3	MgPO_3	H_2O	kPa	kJ/mol	
4.54	9.02	87.0	2.344	- 746.8	D $\text{MgHPO}_3 \cdot 6 \text{H}_2\text{O} + \text{Mg}(\text{H}_2\text{PO}_3)_2$
5.21	8.24	85.5	2.380	- 708.8	$\text{Mg}(\text{H}_2\text{PO}_3)_2$
6.25	7.49	86.2	2.401	- 693.3	$\text{Mg}(\text{H}_2\text{PO}_3)_2$
9.71	8.12	82.2	2.342	- 748.1	$\text{Mg}(\text{H}_2\text{PO}_3)_2$
12.3	8.74	78.0	2.200	- 879.1	$\text{Mg}(\text{H}_2\text{PO}_3)_2$
14.1	8.97	76.9	2.120	- 995.8	$\text{Mg}(\text{H}_2\text{PO}_3)_2$
16.2	9.87	73.9	2.008	-1 131	C $\text{Mg}(\text{H}_2\text{PO}_3)_2 + \text{Mg}_2\text{H}_{11}\text{P}_5\text{O}_{15}$
18.8	8.91	72.3	1.793	-1 411	$\text{Mg}_2\text{H}_{11}\text{P}_5\text{O}_{15}$
20.8	8.44	70.8	1.632	-1 644	$\text{Mg}_2\text{H}_{11}\text{P}_5\text{O}_{15}$
25.8	8.41	65.8	1.363	-2 092	$\text{Mg}_2\text{H}_{11}\text{P}_5\text{O}_{15}$
32.3	8.36	59.3	0.987	-2 901	$\text{Mg}_2\text{H}_{11}\text{P}_5\text{O}_{15}$
39.2	8.18	52.6	0.780	-3 475	B $\text{Mg}_2\text{H}_{11}\text{P}_5\text{O}_{15} + \text{MgH}_{10}\text{P}_4\text{O}_{12}$
43.0	7.59	49.4	0.713	-3 696	$\text{MgH}_{10}\text{P}_4\text{O}_{12}$
45.3	6.85	47.9	0.643	-3 954	$\text{MgH}_{10}\text{P}_4\text{O}_{12}$
47.2	6.60	46.2	0.600	-4 125	$\text{MgH}_{10}\text{P}_4\text{O}_{12}$
50.7	6.03	43.3	0.564	-4 363	A $\text{MgH}_{10}\text{P}_4\text{O}_{12} + \text{H}_3\text{PO}_3$

Owing to congruent solubility it holds for $(\mu_1^D - \mu_1^C)$ that

$$(\mu_1^D - \mu_1^C) = \int_c^D x_3 / (x_2 - x_1) \cdot \partial \mu_3 / \partial x_1 \cdot dx_1 \quad (13)$$

The dependence of μ_3 on x_1 was expressed by a polynomial

$$\mu_3 = 1866.8522 - 466.8403x_1 + 57.6292x_1^2 - 2.9765x_1^3 + 0.0586x_1^4.$$

Scatter of experimental points from the calculated curve is characterized by $R^2 = 0.9959$. On calculation and integration, value $(\mu_1^D - \mu_1^C) = -15.8$ kJ/mol was obtained. From equation (11) $\Delta G^0 = -35.6$ kJ/mol may be calculated.

DISCUSSION

In the study of heterogeneous systems $MHPO_3-H_3PO_3-H_2O$ ($M = Ca, Sr, Mg$) on the basis of water vapour pressure, existence of hydrogenphosphites $Ca(H_2PO_3)_2 \cdot H_2O$, $Sr(H_2PO_3)_2$, $Mg(H_2PO_3)_2$, $Sr_2H_{11}P_5O_{15} \cdot 2H_2O$, $Mg_2H_{11}P_5O_{15}$, $MgH_{10} \cdot P_4O_{12}$ has been confirmed and change in standard Gibbs energy of heterogeneous reactions, leading to their formation, established. A comparison of ΔG^0 values shows that greatest change takes place, analogously to alkali hydrogenphosphites [1], in the formation of hydrogenphosphites of the $M(H_2PO_3)_2$ type; ($M = Ca, Sr, Mg$). At the same time values of the change also increase with rising cation radius, from

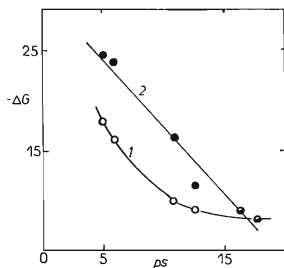


FIG. 1

$-\Delta G^0$ (kJ/mol of hydrogen bond) as Function of the Polarization Strength of Cation ($ps = n/r^2$ (nm^{-2}) $n =$ Charge of Ion, $r =$ Ionic Radius by Goldschmidt)

Curve 1 indicates ΔG^0 of reactions $0.5 M_2HPO_3 + 0.5 H_3PO_3 \rightarrow MH_2PO_3$, $M = Li, Na, K$; $0.5 Mg, 0.5 Ca, 0.5 Sr$. Curve 2 indicates ΔG^0 of reactions in which phosphite reacts with phosphorous acid to form a hydrogen salt of highest ratio of phosphorus to metal. ΔG^0 for $Ca(H_2PO_3)_2 \cdot H_2O$ and LiH_2PO_3 are common for both curves. The polarization strength values for individual ions are $Li^+ = 164$, $Na^+ = 104$, $K^+ = 56$, $Mg(H_2O)_6^{2+} = 45$, $Ca^{2+} = 180$, $Sr^{2+} = 124$ (nm^{-2}).

calcium over strontium to the magnesium ion, if the magnesium cation is understood as $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ particle of radius 210 pm (ref.⁴).

Effect of the other cations on vicinal water molecules is no more so great that an analogous compact particle could be formed. In order to compare the effect of the Ca^{2+} , Sr^{2+} , and Mg^{2+} cations with the Li^+ , Na^+ , and K^+ ones, we mathematically convert ΔG^0 values for bivalent cations to one positive charge. For the reaction of phosphite with phosphorous acid to form hydrogen phosphites of ratio $\text{M}/\text{P} = 1$, we then obtain for the increasing change in ΔG^0 a series $\text{Ca} < \text{Li} \approx \text{Sr} < \text{Na} < \text{K} \approx \text{Mg}$. Sequence of this series corresponds to that of decreasing polarization ionic strength ($ps = n/2$, $n =$ charge of ion, $r =$ radius of ion Goldschmidt). This dependence of ΔG^0 on ps is expressed by curve 1 in Fig. 1.

If we consider the reaction of phosphites with phosphorous acid to form $\text{Ca}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$, LiH_2PO_3 , $\text{Sr}_2\text{H}_{11}\text{P}_5\text{O}_{15} \cdot 2\text{H}_2\text{O}$, $\text{NaH}_5\text{P}_2\text{O}_6$, $\text{KH}_5\text{P}_2\text{O}_6$, and $\text{MgH}_{10}\text{P}_4\text{O}_{12}$, *i.e.* hydrogenphosphites of the highest ratio of phosphorus to metal, then the $-\Delta G^0$ values of this reaction again follow the above given sequence, but dependence of $-\Delta G^0$ on the polarization strength is linear (Fig. 1, curve 2).

In the systems, where cations possess a great polarizing effect (Li^+ , Ca^{2+}), the formation of hydrogen salts is limited, and only one, incongruently soluble hydrogen phosphite is being formed. The reaction of its formation is accompanied by merely a small change in $-\Delta G^0$. In the Na^+ , K^+ , and Mg^{2+} systems, where cation has a small polarization strength, several mostly congruently soluble hydrogen phosphites are produced and the reactions are accompanied by high $-\Delta G^0$ values.

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