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ENTHALPY OF FORMATION OF PO_2^-, PO_3^-, AND $NaPO_2$

UDC 541.51

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A mass-spectral study of the ionic and molecular composition of sodium metaphosphate vapor was carried out. The molecules and ions $NaPO_3$, $NaPO_2$, PO_2^-, PO_3^-, $NaP_2O_4^-$, $NaP_2O_5^-$, $NaP_2O_6^-$ were recorded. The measurements performed made it possible to find the following thermodynamic quantities: $\Delta_f H_0^0(PO_2^-) = -645 \pm 18$, $EA(PO_2) = 367 \pm 21$, $\Delta_f H_0^0(PO_3^-) = -943 \pm 16$, $EA(PO_3) = 433 \pm 51$, $\Delta_f H_0^0(NaPO_2) = -577 \pm 24$ kJ/mole. The published data are analyzed and the following values are recommended: $\Delta_f H_0^0(NaPO_3, g) = -860 \pm 13$, $\Delta_f H_0^0(KPO_3, g) = -900 \pm 13$ kJ/mole. The value $\Delta_f H_0^0(KPO_2) = -607 \pm 35$ kJ/mole is obtained based on an analysis of the heterolytic dissociation energies.

The formation of PO_2^- and PO_3^- ions in plasma setups lowers the electrical conductivity of the plasma [1]. For this reason, accurate data on the enthalpies of formation of these ions are necessary for engineering calculations. In [2], in a study of the ion-molecular equilibria in flames, the value $\Delta_f H_0^0(PO_2^-) = -601 \pm 25$ kJ/mole was obtained. In the handbook [3], based on an analysis of bond-breaking energies, the value $\Delta_f H_0^0(PO_2^-) = -588 \pm 30$ kJ/mole was predicted. In [4], in a study of the effect of additions of phosphorus compounds on the electron density, it was shown that the effect of phosphorus oxide ions is significantly smaller than expected from [2]. However, it was established in [5, 6] that the smaller effect of phosphorus compounds can be explained by the formation of KPO_2 and KPO_3 molecules in the gas phase.

Very little is known about the chemistry of phosphites of alkali metals, although there are obvious proofs of their appearance in the gas phase. In [7, 8] it was shown by the method of IR spectroscopy with matrix insulation that when the phosphates of alkali metals are evaporated from platinum crucibles the gas phase consists of MPO_3, and when they are evaporated from molybdenum crucibles the gas phase consists of MPO_2. In [9] the equilibrium constant of the reaction

$$NaPO_2 = Na + PO_2 \quad (1)$$

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was measured by the mass-spectrometric method and the value $\Delta_f H_0^0(NaPO_2) = -491 \pm 20$ kJ/mole was obtained. The previously measured equilibrium constant [10]

$$KAlF_4 + PO_3^- = KPO_3 + AlF_4^- \quad (2)$$

enabled determining $\Delta_f H_0^0(PO_3^-) = -980 \pm 23$ kJ/mole. An analysis of the literature showed (see Appendix), however, that the value $\Delta_f H_0^0(KPO_3, g) = -936 \pm 17$ kJ/mole used is inconsistent with the saturation vapor pressure. This made it necessary to change the enthalpy of formation of PO_3^-.

In this paper we studied the molecular and ionic composition of sodium metaphosphate vapor in order to obtain more accurate values of the enthalpies of formation of PO_2^-, PO_3^-, and $NaPO_2$.

Experiment. 1. Sodium Phosphite and Metaphosphate Pressure. The work was performed on an MS-1301 mass spectrometer by the method of high-temperature mass spectrometry with ionization by electron impact. The sodium phosphate with an addition of a small quantity of silver was placed into a molybdenum Knudsen chamber. The temperature was measured with a platinum–platinum-rhodium (10% Rh) thermocouple.

The ions Na^+ (300), PO^+ (27), PO_2^+ (3.7), $NaPO^+$ (3.3), $NaPO_2^+$ (10), $NaPO_3^+$ (1) were recorded at T = 1215°K and U_{ion} = 70 V (the relative intensity is shown in parentheses). This mass spectrum differed substantially from the mass spectrum of sodium metaphosphate, obtained by evaporation from a platinum crucible (the vapor contained only $NaPO_3$ [11]): Na^+ (143), PO^+ (6.1), $NaPO^+$ (0.9), $NaPO_2^+$ (0.7), $NaPO_3^+$ (1). This indicates the presence of $NaPO_2$ molecules in the molybdenum crucible. The sensitivity constant was determined from the Ag^+ ion current (the silver pressure is taken from [12], the atomic ionization cross sections are taken from [13], and the molecular ionization cross sections are calculated by the additive scheme).

The $NaPO_3$ and $NaPO_2$ pressures over liquid sodium metaphosphate accompanying evaporation from a molybdenum crucible with an addition of silver were determined in the temperature interval 1140-1300°K (in Pa): $\ln p(NaPO_3) = -23{,}800/T + 19.7$; $\ln p(NaPO_2) = -41{,}300/T + 33.8$.

The standard deviations of the equations presented can be calculated as a function of the temperature from the following formula:

$$s(\ln p) = \sigma_i \left\{ \frac{1}{47} + \left(\frac{T^{-1} - 1215^{-1}}{0{,}171 \cdot 10^{-3}} \right)^2 \right\}^{1/2}$$

where $\sigma_i = 0.41$ for $NaPO_3$ and $\delta_i = 0.55$ for $NaPO_2$.

2. Ion–Molecular Equilibria. The work was performed on an MKh-1303 mass spectrometer, reequipped for studying ion–molecular equilibria [14]. Platinum, nickel, and molybdenum crucibles were used. The ion currents were measured with a VÉU-6 electron multiplier. The multiplication factor for the PO_3^- ion is $\gamma = I_m/I_\ell \approx 10^5$, where I_m is the current measured by the multiplier and I_ℓ is the current measured by an electrometer. The transformation to the ratio of the ion pressures was performed using the formula [14]

$$\frac{p(A^-)}{p(B^-)} = \frac{I_m(A^-)}{I_m(B^-)} \frac{\gamma(B^-)}{\gamma(A^-)} \left(\frac{M(A)}{M(B)} \right)^{1/2} = \frac{I_m(A^-)}{I_m(B^-)} \frac{M(A)}{M(B)}.$$

The results of the experiments performed are presented in Table 1.

The ions PO_2^- (0.70), PO_3^- (6400), $NaP_2O_6^-$ (12) were recorded when sodium metaphosphate evaporated from a platinum crucible. For evaporation from a molybdenum crucible with the addition of silver the mass-spectrum of the negative ions changed substantially: PO_2^- (63), PO_3^- (400), $NaP_2O_4^-$ (0.036), $NaP_2O_5^-$ (0.099), $NaP_2O_6^-$ (0.100). The ion current measured by the multiplier ($\times 10^{11}$ A) at 1164°K is indicated in the parentheses. For evaporation from a platinum crucible $NaPO_3$ evaporates congruently and without decompositon [11] ($a(NaPO_3) = 1$). This made it possible to calculate the equilibrium reaction constant

$$[NaPO_3] + PO_3^- = NaP_2O_6^-. \quad (3)$$

The brackets indicate that the substance is in a condensed state.

To determine the enthalpies of formation of the ions PO_2^-, PO_3^- we studied the ion–molecular equilibria in the system Na_2SO_4–$NaPO_3$ in platinum and nickel crucibles. The equilibrium reaction constants were measured for the following reactions:

$$PO_3^- + [Na_2SO_4] = [NaPO_3] + NaSO_4^- \quad (4)$$

$$\left(\ln K_p(4) = \ln \frac{I(NaSO_4^-)\,I(NaP_2O_6^-)}{I^2(PO_3^-)} - \ln K_p(3) + \ln 3{,}63\right),$$

$$PO_2^- + {}^1/_2SO_4^- = PO_3^- + {}^1/_2SO_2^-, \quad (5)$$

$$PO_2^- + SO_3^- = PO_3^- + SO_2^-. \quad (6)$$

The activity of sodium sulphate in the equilibrium (4) was assumed to be equal to one, so that it is the main component of the system (>97 mole %).

Table 1 also shows the data obtained in studying the ion-molecular equilibrium in the system KPO_3–$KAlF_4$ [10]. Unlike [10], however, the equilibrium constant of (7) and not of (2) was calculated in Table 1:

$$PO_3^- + KAlF_4 = [KPO_3] + AlF_4^-, \quad (7)$$

$$\ln K_p(7) = \ln \frac{I^2(AlF_4^-)}{I(PO_3^-)\,I(KAl_2F_8^-)} - \ln K_p(8) + \ln 0{,}548,$$

where $K_p(8)$ is the ion-molecular equilibrium reaction constant of

$$KAl_2F_8^- = KAlF_4 + AlF_4^-. \quad (8)$$

The numerical values of $K_p(8)$ are taken from [14].

To determine the enthalpy of formation of $NaSO_4^-$ participating in the equilibrium (4), we studied the ion-molecular equilibria over pure sodium sulfate. The ions $^{32}SO_2^-$ (115), $^{32}SO_3^-$ (438), $^{32}SO_4^-$ (11.6), $Na^{32}SO_4^-$ (208), $Na_3{}^{32}S_2O_8^-$ (3.0) were recorded. The ion currents measured by the multiplier ($\times 10^{13}$ A) at 1344°K are indicated in the parentheses. The equilibrium reaction constants of the following reactions were determined:

$$SO_2^- + {}^1/_2O_2 = SO_3^-, \quad (9)$$

$$SO_2^- + O_2 = SO_4^-, \quad (10)$$

$$SO_2^- + Na + O_2 = NaSO_4^-. \quad (11)$$

The oxygen and sodium pressures were calculated from the condition of congruency of the evaporation of Na_2SO_4 [3] (for a more detailed discussion see [15]). As an example we present the pressure of the dissociation products over sodium sulphate at 1300°K (in Pa): $p(Na_2SO_4)$ 0.15, $p(Na) = 0.22$; $p(O_2) = 0.13$; $p(SO_2) = 0.18$.

The equilibrium reaction constants measured above make it possible to calculate K_p for the reaction

$$PO_2^- + {}^1/_2O_2 = PO_3^-. \quad (12)$$

Together with the measured ratios of the ion currents for PO_3^- and PO_2^- this makes it possible to determine the partial pressure of oxygen, established with the evaporation of sodium metaphosphate from platinum and molybdenum crucibles (Table 2).

Discussion. 1. Enthalpy of Formation of $NaSO_4^-$, PO_2^-, and PO_3^-. The reaction enthalpies were calculated from the third law of thermodynamics. The thermodynamic functions are taken from [3] for SO_2^-, O_2, Na, Na_2SO_4(c), $KAlF_4$, AlF_4^-, PO_2^- and from [15], for SO_3^-, SO_4^- and they are calculated in this work (see Appendix) for the remaining compounds. The error in the determination of the reaction enthalpies was calculated as in [15]; the random error, the possible systematic error in the measurement of the ion currents (coefficient 1.4), and the error in the calculation of the thermodynamic functions were taken into account.

The reaction enthalpies $\Delta H_0^\circ(9) = -206.3 \pm 7.2$ and $\Delta H_0^\circ(10) = -349.0 \pm 9.9$ kJ/mole are in good agreement with the corresponding values obtained in [15] in studying the ion-molecular equilibria over K_2SO_4: $\Delta H_0^\circ(9) = -201.0 \pm 6.5$, $\Delta H_0^\circ(10) = -344.0 \pm 9.5$ kJ/mole. The recommended values were taken as the average values $\Delta H_0^\circ(9) = -203.7 \pm 6.0$, $\Delta H_0^\circ(10) = -346.5 \pm 9.0$ kJ/mole, which gave a formation enthalpy of $\Delta_f H_0^\circ(SO_3^-) = -603.8 \pm 7.0$ and $\Delta_f H_0^\circ(SO_4^-) = -746.6 \pm 9.7$ kJ/mole ($\Delta_f H_0^\circ(SO_2^-) = -400.1 \pm 3.5$ kJ/mole [3]). With the use of $\Delta H_0^\circ(11) = -680 \pm 12$ kJ/mole, the formation enthalpy $\Delta_f H_0^\circ(NaSO^-) = -972 \pm 12$ kJ/mole ($\Delta_f H_0^\circ(Na) = 107.8 \pm 0.7$ kJ/mole [3]) was obtained. For the reaction (4), $\Delta H_0^\circ(4) = 142 \pm 14$ kJ/mole and,

TABLE 1. Equilibrium Reaction Constants

Conditions of expt.†	Reaction	T, K	$\ln K_i$	s_i	n_i	ΔH_i°, kJ/mole
$NaPO_3$ Pt crucible	(3)*	1070	−6,70	0,12	3	–
R=0,3 mm		1118	−6,10	0,12	4	–
E_1=160 V/mm						
E_2=0 V/mm		1164	−5,45	0,15	4	–
$NaPO_3$<5 mole% Na_2SO_4>95 mole%	(4)	1210	−14,99	0,68	3	142,1
Pt crucible		1255	−14,62	–	1	142,8
R=0,3 mm	(5)	1317	11,06	0,01	2	−128,3
E_1=90 V/mm		1344	10,93	0,42	5	−129,5
E_2=20 V/mm		1370	11,66	–	1	−140,3
$NaPO_3$<1 mole% Na_2SO_4>99 mole %	(6)	1210	7,75	–	1	−81,5
Ni crucible		1237	7,76	–	1	−83,4
R=0,35 mm		1300	8,51	0,09	2	−95,8
E_1=80 V/mm		1344	7,46	0,21	3	−87,3
E_2=40 V/mm						
KPO_3>97 mole % $KAlF_4$<3 mole%	(7)	987	19,12	0,15	4	−349,3
Pt crucible		1023	17,87	0,32	3	−350,6
Na_2SO_4	(9)	1300	8,92	0,06	2	−208,3
Pt crucible		1344	7,90	0,08	2	−205,9
R=0,3 mm		1370	7,43	0,01	2	−204,6
E_1=12 V/mm	(10)	1300	12,12	0,00	2	−351,8
E_2=25 V/mm		1344	10,78	0,24	2	−348,8
		1370	9,96	0,12	2	−346,2
	(11)	1300	28,12	0,05	2	−680,6
		1344	26,02	0,11	2	−680,2
		1370	24,76	0,06	2	−678,9

* $\ln K_p(3) = -16\,700/T + 8{,}90$; $s(\ln K) = 0{,}12\left[\frac{1}{11} + \left(\frac{T^{-1} - 1\,120^{-1}}{0{,}9\cdot 10^{-4}}\right)^2\right]^{1/2}$.

†R, radius of the effusion opening; E_1, intensity of the field between the crucible and the drawing electrode; E_2, intensity of the field after the drawing electrode; s_i, standard deviation of a separate measurement; n_i, number of points.

TABLE 2. Determination of the Oxygen Pressure

T, K	Crucible Pt				Crucible Mo+Ag						
	$\ln \frac{I(PO_3^-)}{I(PO_2^-)}$	s_i*	n_i†	$p(O_2)$, Pa	$\ln \frac{I(PO_3^-)}{I(PO_2^-)}$	s_i	n_i	$p(O_2)$, Pa	$\ln a_{(NaPO_3)}$‡	s_i	n_i
1070	9.88	–	1	$1{,}1\cdot 10^{-6}$	2,38	–	1	$3{,}3\cdot 10^{-13}$	−0,45	–	1
1118	9,78	0,28	4	$1{,}6\cdot 10^{-5}$	2,06	0,23	2	$3{,}1\cdot 10^{-12}$	–		
1164	9,18	0,13	3	$6{,}1\cdot 10^{-5}$	1,84	0,27	5	$2{,}6\cdot 10^{-11}$	−2,01	0,54	5
1210					1,56	0,20	5	$1{,}5\cdot 10^{-10}$	−1,92	0,61	5
1255					1,30	0,08	3	$7{,}7\cdot 10^{-9}$	−2,56	0,35	3
1300					1,42	0,18	2	$7{,}1\cdot 10^{-9}$	−2,78	0,19	2

*n_i is the number of points.
†s_i is the standard deviation of a separate measurement.
‡Determined from the ratio of the ion currents for $NaP_2O_6^-$ and PO_3^- and $K_p(3)$.

therefore, $\Delta_f H_0^\circ(PO_3^-) = -948 \pm 18$ kJ/mole, ($\Delta_f H_0^\circ(Na_2SO_4, c) = -1376.4 \pm 0.4$ kJ/mole [3]). For the reaction (7), $\Delta H_0^\circ(7) = -350 \pm 14$ and $\Delta_f H_0^\circ(PO_3^-) = -938 \pm 21$ kJ/mole ($\Delta_f H_0^\circ(AlF_4^-) = -1945 \pm 10$ [16], $\Delta_f H_0^\circ(KAlF_4, g) = -1894 \pm 11$ kJ/mole [17]). The agreement between the values obtained is entirely satisfactory, and the recommended value was taken as the average value $\Delta_f H_0^\circ(PO_3^-) = -943 \pm 16$ kJ/mole. This gives an electron affinity for the radical PO_3 of EA = 433 ± 51 kJ/mole ($\Delta_f H_0^\circ(PO_3) = -510 \pm 50$ kJ/mole [18]).

TABLE 3. Heterolytic Dissociation Energy (in kJ/mole)

Quantity	$D(A^+-B^-)$ (expt.)	E_C $(q(0)=0)$	E_C $(q(0)=-1)$	Quantity	$D(A^+-B^-)$ (expt.)	E_C $(q(0)=0)$	E_C $(q(0)=-1)$
$D(Na^+-NaSO_4^-)$	660	773	715	$D(K^+-PO_3^-)$	467	490	474
$D(K^+-KSO_4^-)$	599	696	662	$D(Na^+-PO_2^-)$	536	533	727
$D(Na^+-PO_3^-)$	522	548	511	$D(K^+-PO_2^-)$	471 *	476	655

* Estimated quantity.

TABLE 4. Enthalpy of Sublimation of $NaPO_3$ and KPO_3

Method, reference	$\Delta_s H_0^0(NaPO_3)$, kJ/mole		$\Delta_s H_0^0(KPO_3)$, kJ/mole	
	second law	third law	second law	third law
Mass spectral [11, 24]	1140–1345 K 347,5	342,5	1050–1200 K 314,8	335,4
Mass spectral [25]	1116–1316 K 338,3	350,4	1084–1293 K 326,9	332,2
"Flow" method [26]	1250–1350 K 340,6	357,0	1250–1350 K 303,5	340,1
"Boiling point" method [26]	–		1377–1474 K 343,2	341,0

The enthalpy of formation of PO_2^- was also obtained from the two equilibria (5) and (6): $\Delta H_0^0(5) = -130.5 \pm 8.3$ and $\Delta_f H_0^0(PO_2^-) = -639 \pm 20$ kJ/mole, $\Delta H_0^0(6) = -88.1 \pm 9.4$ and $\Delta_f H_0^0(PO_2^-) = -651 \pm 22$ kJ/mole. The recommended value was chosen as the average value $\Delta_f H_0^0(PO_2^-) = -645 \pm 18$ kJ/mole. The electron affinity of PO_2 was equal to 367 ± 21 kJ/mole ($\Delta_f H_0^0(PO_2^-) = -278 \pm 10$ kJ/mole [3]). It is difficult to determine the reason for the disagreement with the results of [2] ($\Delta_f H_0^0(PO_2^-) = -601 \pm 25$ kJ/mole), since the methods used to measure the equilibrium constants in this work differ substantially from those used in [2].

2. Enthalpy of Formation of $NaPO_2$. The results of the experiments performed in this work on the study of the evaporation of $NaPO_3$, obtained by the method of high-temperature mass spectrometry with ionization by electron impact and in complete agreement with the data from IR spectroscopy [7, 8], indicate that when $NaPO_3$ evaporates from different crucibles the composition of the vapor changes. With the transition from a platinum crucible to a molybdenum crucible, $NaPO_2$ appears in the vapor.

The ratio of the sodium phosphite and metaphosphate in the vapor can change only when the oxygen pressure changes:

$$NaPO_3 = NaPO_2 + {}^1/_2 O_2. \quad (13)$$

The data obtained by the method of ion–molecular equilibria confirmed this fact (see the mass spectrum and Table 2). The oxygen pressure determined from the equilibrium (12) through the ratio of the ion currents PO_3^-, PO_2^- decreased 10^6-fold with the transition from a platinum to a molybdenum crucible, which corresponds to an increase in the ratio $p(NaPO_2)/p(NaPO_3)$ by a factor of about 10^3.

The quantity $K_p(13)$ was calculated by combining the ratio of the pressures of $NaPO_2$, $NaPO_3$ (mass spectrometry with electron impact) and the oxygen pressure (method of ion–molecular equilibria), measured in a molybdenum crucible with an addition of silver. The error in $K_p(13)$ is estimated by the coefficient 10. From here, according to the third law, $\Delta H_0^0(13) = 283 \pm 20$ kJ/mole and $\Delta_f H_0^0(NaPO_2, g) = -577 \pm 24$ kJ/mole. According to [9], from the equilibrium (1), $k_{p,1200}(1) = 3.2 \cdot 10^{-9}$ and $K_{p,1200}(1) = 1.3 \cdot 10^{-13}$ according to our data. The difference is equal to four orders of magnitude. The data can be matched if it is assumed that the Na^+ ion in [9] is not a molecular ion, but was obtained as a result of the dissociative ionization of $NaPO_2$, $NaPO_3$.

3. Heterolytic Dissociation Energy. Salts of alkali metals have a high heterolytic dissociation energy. Table 3 shows the values of these energies calculated based on the data

TABLE 5. Thermodynamic Functions

T, K	PO_3^-	$NaSO_4^-$	$NaPO_2$	$NaPO_3$	KPO_3	$NaPO_3$* (c, 1)	KPO_3† (c, 2)
	$H^0_{298} - H^0_0$, kJ/mole						
	11,8	16,7	15,2	16,5	17,0	14,9	16,3
	$-(G^0_T - H^0_0)/T$, J/mole·K						
298	218,3	258,9	246,7	254,7	263,6	45,3	53,5
400	230,6	276,7	262,2	271,8	281,2	61,7	71,2
600	249,7	305,7	285,6	298,4	308,4	90,0	101,3
800	265,0	329,6	303,6	319,6	329,8	114,3	126,7
1000	277,9	350,0	318,3	337,2	347,6	137,8	149,2
1200	289,1	367,8	330,7	352,4	362,9	161,0	171,1
1400	298,9	383,6	341,5	365,7	376,3	181,7	192,1
1600	307,7	397,7	351,1	377,5	388,2	200,6	211,2
1800	315,7	410,4	359,7	388,2	398,9	217,7	228,7

*T_{melt} = 901°K, Φ_{901}^0 = 125.4 J/mole·°K.
†$T_{p.t}$ = 733°K, Φ_{733}^0 = 118.4 J/mole·°K; T_{melt} = 1086°K, Φ_{1086}^0 = 158.1 J/mole·°K.

obtained for sodium and potassium sulfates, metaphosphates, and phosphites. In order to give a theoretical interpretation the Coulomb interaction energy was calculated, since it is precisely this energy that makes the largest contribution to the heterolytic dissociation energy (80-95%):

$$E_c = 1391 \sum_{i>j} \frac{z_i z_j}{r_{ij}} \text{ kJ·Å/mole} ,$$

where z_i is the charge of an atom in units of the electron charge. In the calculation the following assumptions were used: for Na_2SO_4 and K_2SO_4 molecules the geometry from [3] was adopted, and for $NaPO_3$, KPO_3, $NaPO_2$, KPO_2 molecules the geometry was chosen by the authors (see Appendix); when the alkali metal is removed, the anion is not distorted; the alkali metal has a charge of +1; two variants of the charge distribution in the anion were chosen: the charge of the oxygen atom q(0) = 0 (point anion) and q(0) = −1. The results obtained are presented in Table 3. The experimental and theoretical values are in good agreement with one another. There is an especially good correlation for the difference of the heterolytic dissociation energies of the sodium and potassium salts. On this basis the values $D(K^+ - PO_2^-)$ = 471 kJ/mole and $\Delta_f H_0^c(KPO_2)$ = −607 ± 35 kJ/mole were obtained.

APPENDIX

PO_3^-. D_{3d} structure, R(P − O) = 0.148 nm (as in $NaPO_3$ [19]), $I_AI_BI_C = 1330 \cdot 10^{-117}$ $g^3 \cdot cm^6$. The frequencies of the normal vibrations 1008, 478, 1278(2), 512(2) cm^{-1} are chosen to be equal to the frequencies of the PO_3 anion in molecules of metaphosphates of alkali metals [8, 20].

$NaSO_4^-$. C_{2V} structure, R(Na − O) = 0.22 nm, R(S − O) = 0.147 nm, $I_AI_BI_C = 21{,}700 \cdot 10^{-117}$ $g^3 \cdot cm^6$. The frequencies are 1100, 961, 610, 550, 295, 470, 1100, 610, 75, 1157, 650, 320 cm^{-1}. The molecular constants were evaluated based on the corresponding values for the molecules Na_2SO_4 [3].

$NaPO_2$. C_{2V} structure, R(Na − O) = 0.22 nm, R(P − O) = 0.15 nm, ∠ OPO = 115°, $I_AI_BI_C = 3060 \cdot 10^{-117}$ $g^3 \cdot cm^6$. The frequencies 1060, 524, 307, 1155, 206, 70 cm^{-1} are taken from [7, 8]; the low frequencies, associated with the vibrations of Na^+, are set equal to the analogous frequencies in $NaNO_2$ [3].

$NaPO_3$, KPO_3. C_{2V} structure, R(Na − O) = 0.22 nm, P(K − O) = 0.245 nm, R(P − O) = 0.148 nm, ∠ OPO = 120°, $I_AI_BI_C = 8770 \cdot 10^{-117}$ and $19{,}800 \cdot 10^{-117}$ $g^3 \cdot cm^6$. The sets of frequencies are 1340, 1010, 533, 287, 1220, 533, 200, 478, 75 cm^{-1} and 1330, 1008, 515, 230, 1223, 515, 160, 480, 60 cm^{-1}. The molar constants were chosen based on [8, 19, 20]; the low frequencies, associated with the vibrations of the alkali metal, are set equal to the frequencies in the molecules $NaNO_3$ and KNO_3 [3].

The error in the computed thermodynamic functions was evaluated by the method proposed [3]. The error in the determination of IAIBIC was set equal to 15% for PO_3^-, and 30% for t remaining cases. The error of the estimated frequencies was $\Delta\nu = 100\ cm^{-1}$ ($\nu > 250\ cm^{-1}$), $\Delta\nu = 50\ cm^{-1}$ ($100 < \nu < 250$), $\Delta\nu = 20\ cm^{-1}$ ($\nu < 100$), the error in the experimental frequencies is $\Delta\nu = 15\ cm^{-1}$. As a result, the error in Φ_T^0 at 1200°K was equal to 2.8, 7.3, 6.0, 6.3, 6.5 J/mole·°K for PO_3^-, $NaSO_4^-$, $NaPO_2$, $NaPO_3$, and KPO_3, respectively.

KPO₃ (Condensed State, Liquid). The quantities S_{298}^0, $H_{298}^0 - H_0^0$ and data on the pha transitions are taken from [21], the data on the heat capacity in the interval 300-1200°K a taken from [22].

$NaPO_3$ (c, ℓ). The quantities S_{298}^0 and $H_{298}^0 - H_0^0$ and the data on phase transitions taken from [21]; the heat capacities $c_{p,500}^0 = 112$, $c_{p,900}^0 = 143$, $c_{p,\ell}^0 = 180$ J/mole·°K we evaluated from a comparison of the differences of the heat capacities between the sodium an potassium salts of the halides and nitrates. The thermodynamic functions were determined i terms of the values obtained and $c_{p,298}^0 = 86.6$ J/mole·°K [21] by drawing the parabola c_p^0 $85.7 + 0.0660T - 1.67\cdot10^6T^{-2}$ ($300 < T < 900.75$°K).

As a check, the high-temperature heat capacities were also calculated using an empiric equation with two parameters: $c_{p,298}^0$ and the melting temperatures [23]. This yielded the values $\Phi_{901}^0 = 126.0$ and $\Phi_{1086}^0 = 157.9$ J/mole·°K for $NaPO_3$ and KPO_3, respectively, in good agreement with the values calculated above: $\Phi_{901}^0 = 125.4$ and $\Phi_{1086}^0 = 158.1$ J/mole·°K. error in the calculation of Φ_T^0 at 1200°K was evaluated to be 4 and 6 J/mole·°K for KPO_3(c) and $NaPO_3$(c), respectively.

Table 4 includes the enthalpies of sublimation of sodium and potassium metaphosphate, obtained from the experimental data on the saturated vapor pressure with the computed value of the thermodynamic functions (Table 5). The recommended values were chosen to be the ave ages of the quantities obtained from the third law, $\Delta_S H_0^0(NaPO_3) = 350 \pm 13$, $\Delta_S H_0^0(KPO_3)$ 337 ± 12 kJ/mole. Using $\Delta_f H_0^0(NaPO_3, c) = -1210.2 \pm 1.7$ and $\Delta_f H_0^0(KPO_3, c) = -1236.8 \pm 4.2$ kJ/mole [21], the enthalpies of formation of the gaseous molecules were obtained: $\Delta_f H_0^0$ $(NaPO_3) = -860 \pm 13$, $\Delta_f H_0^0(KPO_3) = -900 \pm 13$ kJ/mole.

There is one more possibility for calculating $\Delta_f H_0^0(NaPO_3, g)$. In [27], the pressure of the dissociation products over sodium orthophosphate at 1478°K were measured. Based on this we calculated the enthalpy of the reaction

$$[Na_3PO_4] = NaPO_3 + 2Na + {}^1/_2O_2$$

from the third law: $\Delta H_0^0 = 1242 \pm 25$ kJ/mole. For solid Na_3PO_4 the values S_{298}^0 and $H_{298}^0 - H_0^0$ are taken from [21]. The high-temperature heat capacity was evaluated using an empiric equation [23]. From here, $\Phi_{1478}^0(Na_3PO_4, c) = 326.2$ J/mole·°K. Using the values $\Delta_f H_0^0(Na_3PO_4, c) = -1902.3 \pm 1.3$ [21] and $\Delta_f H_0^0(Na)$ [3], we obtained the value $\Delta_f H_0^0(NaPO_3, g) = -876 \pm 25$ kJ/mole, in good agreement with the enthalpy of formation calculated above.

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ADIABATIC COMPRESSION AND SOUND VELOCITY IN VAPOR–GAS–LIQUID SYSTEMS WITH SEPARATE VOLUMES OF VAPOR AND GAS

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Adiabatic compression of a special class of heterogeneous systems is considered. Differential equations are derived for adiabatic processes in such systems and a complete analytical solution is given. Formulas are also derived for the vapor content in adiabatic compression and the sound velocity. The asymptotic behavior of the expressions obtained at limitingly small content of the mixture components is investigated. The theoretical laws of adiabatic compression and variation in vapor content for a water–steam–air mixture, as well as the dependence of the sound velocity on the pressure and the content of the components, have qualitative and quantitative features that are significantly different from those of partial vapor–gas–liquid systems (for example, atmospheric clouds).

In [1], it was shown that vapor–gas–liquid systems may exist not only in the form of a continuum, the elementary structural cell of which is a liquid macroparticle with vapor and foreign gas molecules partially mixed in its vicinity (for example, an atmospheric cloud), but also in a form where the vapor and gas in the vicinity of the liquid particle are separated by some impermeable boundary (Fig. 1). Such systems may be realized in various technological processes, in ecological processes associated with environmental contamination, in complex biological systems, etc. It is obvious that they will also be realized in the absence of an impermeable boundary if the rate of particle evaporation is much larger than the rate of diffusion from vapor to gas and back.

In contrast to partial systems where the condition of phase equilibrium [2] relates the temperature of the mixture and the partial pressure of the vapor, in the present case this condition relates the temperature and the total pressure of the mixture. This means that heat and mass transfer in such systems is completely different, so that they may be interprete

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