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Thermochemical Studies of Liquid Alkali Metaphosphates

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The enthalpies of mixing in the liquid mixtures of $LiPO_3$ with $NaPO_3$, KPO_3, $RbPO_3$, and $CsPO_3$ and of $NaPO_3$ with KPO_3, $RbPO_3$, and $CsPO_3$ have been measured at 843 ± 2°. The experimental results show analogies with enthalpy data previously reported for the binary alkali halides and nitrates and can be represented by the approximate semiempirical relation: $\Delta H^M \cong N_1N_2(U_0^{++} - 478\delta_{12}^2)$ kcal/mol. In this expression N_1 and N_2 are the mole fractions of the two salts, U_0^{++} is the estimated contribution to the enthalpy of mixing which arises from the London dispersion interaction between the cations, while δ_{12} is a size parameter, $(d_1 - d_2)/d_1d_2$, where $d = r_{\text{cation}} + r_{\text{anion}}$. Since the metaphosphate is a chain anion consisting of connected PO_4 groups and does not have a simple geometry, we have set the "effective ionic radius" of this ion equal to 2.0 Å. This choice is justified by means of structural and other information. Some new data are also reported for the partial enthalpies of solution of solid WO_3 in $NaPO_3$–$Na_4P_2O_7$ melts with Na_2O contents below 61 mol %. The results are discussed briefly in terms of the Lux–Flood concepts of the acid–base chemistry of oxide melts.

Introduction

During the past 10 years we have in this laboratory carried out thermochemical investigations of a significant number of different types of simple fused-salt mixtures involving the salts of the alkali metals. This work started with the study by Kleppa and Hersh of the binary alkali nitrates,[1] was extended by Hersh and Kleppa to the corresponding chlorides and bromides,[2] by Holm and Kleppa to the alkali fluorides,[3] and by Melnichak and Kleppa to the binary alkali iodides.[4] Most recently Østvold and Kleppa have carried out a similar study of the binary alkali sulfates.[5] A characteristic feature of all these mixed systems has been the presence in the melts of common anions of spherical or other well-understood geometry. In the present communication our work on fused-salt mixtures is extended to systems in which the common anions are no longer small, well-defined, discrete entities but consist instead of fragments of metaphosphate chains. It is expected that the results reported below may be indicative of the behavior of other fused-salt systems which contain complex common anions such as one would find, *e.g.*, among some of the binary alkali borates, germanates, and silicates.

While the emphasis of the present investigation has been placed on the study of the binary alkali metaphosphates, we report also some new calorimetric information relating to mixtures of sodium metaphosphate with sodium pyrophosphate. This information consists of data on the partial heats of solution of the strong oxidic acid WO_3 in $NaPO_3$–$Na_4P_2O_7$ melts. These melts ranged in composition from 50 mol % Na_2O to 61 mol % Na_2O.

Experimental Section

Apparatus.—All calorimetric experiments were performed at 843 ± 2° in a single-unit microcalorimeter designed for work at temperatures up to 1100°. Apart from its single-unit, rather than twin, construction, this calorimeter is similar to that used by Hersh and Kleppa at temperatures up to 800°.[2] Since metaphosphate melts dissolve quartz at an appreciable rate, platinum crucibles and "dippers" were used to contain the salts. The internal arrangements in the calorimeter were similar to those adopted for fluoride melts by Holm and Kleppa.[3]

In the calorimeter proper mixing and stirring was initiated by lowering the "dipper" into the platinum crucible. At the same time the platinum-covered plunger was moved up and down inside the dipper, which has the effect of displacing the liquid and stirring the melt. The whole stirring operation was repeated a certain number of times within a short time interval. After the conclusion of each mixing experiment, the heat effect associated with mixing and stirring was determined in a blank experiment and applied as a correction to the total observed heat.

Calibration of the calorimeter was by the platinum-drop method, based on the heat content equation for platinum given by Kelley.[6] Since we found no systematic difference in calibration between 1- and 2-mm diameter Pt wires, no correction has been applied for the small pickup of heat by the falling platinum wires. Integration of the emf *vs.* time curves was by means of an Ott precision planimeter.

Materials.—$LiPO_3$ and KPO_3 were prepared by heating LiH_2PO_4 (from Lithcoa) and KH_2PO_4 (analytical reagent grade, from Fisher), respectively, in a platinum crucible over a Bunsen burner until evolution of water stopped. The platinum crucible was then placed in a small furnace at 920° and kept there for a period of about 2 hr. It had been established in separate experiments that this was the approximate time required for the sample to reach a constant weight. The melt was then cast onto a cold silver plate, ground in a mortar to small chunks, and stored in a desiccator. $NaPO_3$ was analytical reagent grade from Baker and Adamson and was dried for 24 hr at 200° before use. $RbPO_3$ and $CsPO_3$ were prepared by us in the following manner. Equimolar amounts of RbCl (or CsCl) (99.9% from Kawecki) and $NH_4H_2PO_4$ (analytical reagent grade from Baker and Aamson) were thoroughly mixed and placed in a platinum crucible, which was then heated with a Bunsen burner until the evolution of fumes ceased. The crucible was then transferred to the small furnance at 920° and kept there until constant weight was registered.

The salts prepared were analyzed for metallic impurities by semiquantitative (visual estimate) emission spectrography and for phosphorus by gravimetric determination as magnesium pyrophosphate. The results of the analyses are given in Table I. In each mixing experiment we used 0.065–0.13 mol of mixture. The actual heat effects observed ranged from about 6 to about 100 cal.

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[1] O. J. Kleppa and L. S. Hersh, *J. Chem. Phys.*, **34**, 351 (1961).

[2] L. S. Hersh and O. J. Kleppa, *ibid.*, **42**, 1309 (1965).

[3] J. L. Holm and O. J. Kleppa, *ibid.*, **49**, 2425 (1968).

[4] M. E. Melnichak and O. J. Kleppa, *ibid.*, **52**, 1790 (1970).

[5] T. Østvold and O. J. Kleppa, *Acta Chem. Scand.*, in press.

[6] K. K. Kelley, *U. S., Bur. Mines, Bull.*, **No. 584** (1960).

Table I

Analysis of Alkali Metaphosphates

Salt	Wt % P Calcd	Wt % P Found	Metallic impurities (spectrographic)
$LiPO_3$	36.05	35.90	Na, 0.01; other metals, <0.01
$NaPO_3$	30.38	29.81	Other metals, <0.01
KPO_3	26.23	26.09	Na, 0.01; other metals, <0.01
$RbPO_3$	18.83	18.67	Cs, 0.07; Sr, Ba, K, Li, Na, Mg, Al, <0.1
$CsPO_3$	14.62	14.83	Rb, 0.06; K, Na, Al, Mg, Li, <0.1

For use in the metaphosphate–pyrophosphate experiments $Na_4P_2O_7$ was prepared by heating Na_2HPO_4 (Baker's Analyzed reagent) in a muffle furnace at about 370° overnight. Different phosphate compositions were then prepared from weighed out mixtures of solid $NaPO_3$ and $Na_4P_2O_7$, which were melted together in a small furnace at 860°. The melts were quenched by pouring them out on a cold silver plate, ground to small chunks, and stored in a desiccator until use. The heats of solution of pure WO_3 (Baker's Analyzed reagent) in these melts were determined at 50, 51, 52, 54, 56, 58, 60, and 61 mol % Na_2O.

In each of these experiments we used 60–80 mmol of phosphate melt and added about 0.4 mmol of WO_3. The actually observed heat effects were of the order of ±1.5 cal or less.

Results

Seven of the ten possible binary systems formed among the alkali metaphosphates were studied. The exceptions were (K–Rb)PO_3, (K–Cs)PO_3, and (Rb–Cs)PO_3, for which the heats of mixing are very small.

The experimental results are presented in Figures 1 and 2. In these figures we plot the enthalpy interaction parameter, $\Delta H^M/N_1N_2$, against the mole fraction of the salt with the smaller cation. In each case this plot is represented by a straight line

$$\Delta H^M/N_1N_2 = a + bN_2 \qquad (1)$$

A least-squares treatment of the data yields the values of a and b listed in Table II. In this table we give also the value of the interaction parameter at the 50:50 composition, $(\Delta H^M/N_1N_2)_{0.5}$, and the standard deviation of the experimentally determined points from the analytical curves.

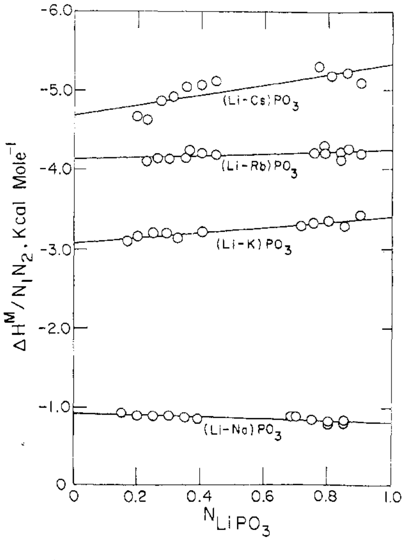

Figure 1.—$\Delta H^M/N_1N_2$ for liquid mixtures of $LiPO_3$ with $NaPO_3$, KPO_3, $RbPO_3$, and $CsPO_3$.

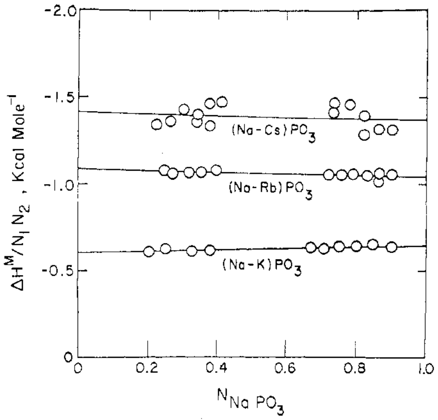

Figure 2.—$\Delta H^M/N_1N_2$ for liquid mixtures of $NaPO_3$ with KPO_3, $RbPO_3$, and $CsPO_3$.

Table II

Enthalpies of Mixing of Binary Alkali Metaphosphates at 843 ± 2°[a]

	a	b	$(\Delta H^M/N_1N_2)_{0.5}$	SD
Li–Na	−918	+104	−866	24
Li–K	−3067	−339	−3236	36
Li–Rb	−4125	−105	−4178	49
Li–Cs	−4679	−656	−5007	125
Na–K	−605	−39	−624	9
Na–Rb	−1088	+49	−1064	12
Na–Cs	−1415	+50	−1390	60

[a] $\Delta H^M = N_1N_2(a + bN_2)$ cal/mol; N_2 is the mole fraction of the component with the smaller cation.

The results of the experiments on the heat of solution of WO_3 in $NaPO_3$–$Na_4P_2O_7$ mixtures are given in Table III and are plotted against composition (N_{Na_2O}) in Figure 3.

Table III

Enthalpies of Solution of Solid WO_3 in $NaPO_3$–$Na_4P_2O_7$ Melts[a]

Solvent compn, N_{Na_2O}	ΔH_{soln}, kcal/mol	Solvent compn, N_{Na_2O}	ΔH_{soln}, kcal/mol
0.50	+3.81 ± 0.06 (11)	0.56	−3.69 ± 0.11 (3)
0.51	−0.64 ± 0.03 (3)	0.58	−3.46 ± 0.07 (3)
0.52	−1.62 ± 0.03 (3)	0.60	−3.52 ± 0.04 (3)
0.54	−3.04 ± 0.08 (3)	0.61	−3.53 ± 0.03 (3)

[a] Error limits are standard deviations from the mean; figures in parentheses indicate number of experiments performed.

Discussion

The Binary Metaphosphates.—It has been found that in the binary alkali nitrate, chloride, bromide, and iodide systems the enthalpies of mixing to a good first approximation can be represented by

$$\Delta H^M \simeq N_1N_2(U_0^{++} + \Omega\delta_{12}^2) \qquad (2)$$

In this expression U_0^{++} represents the estimated positive contribution to the enthalpy of mixing which arises from the London–van der Waals dispersion interaction between next nearest neighbor cations. $\delta_{12} = (d_1 -$

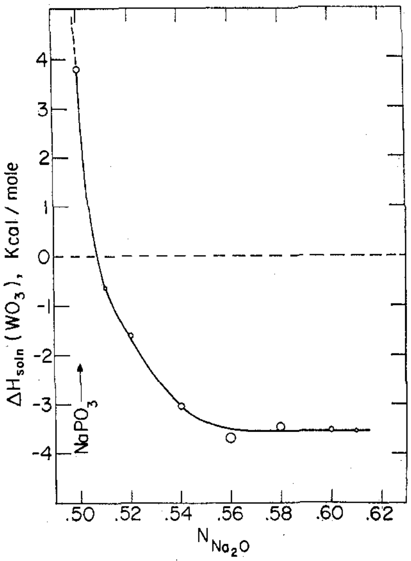

Figure 3.—Enthalpies of solution of WO_3 in liquid $NaPO_3$–$Na_4P_2O_7$ mixtures as a function of Na_2O content.

$d_2)/d_1d_2$ where d_1 and d_2 are characteristic interionic distances in the two salts. The coefficient Ω varies somewhat from one family of salts to another; for the chlorides, bromides, and iodides it changes from about -410 for the chlorides to -550 kcal Å^2/mol for the iodides.

It is of some interest to ascertain whether the new calorimetric data for the binary alkali metaphosphates can be represented by an empirical equation such as eq 2, and, if this should be the case, what does this imply with respect to our understanding of the problem of the enthalpy of mixing in simple fused-salt systems?

Our attempted application of eq 2 to the data for the binary metaphosphates immediately runs into a serious snag: How do we obtain meaningful values of interionic distance and of the size parameter δ_{12} for the liquid metaphosphates?

For the crystalline metaphosphates of sodium and rubidium X-ray structural data are reported by Corbridge.[7,8] From his work we know that these salts contain continuous phosphorus–oxygen chains which run in the direction of fibrous cleavage and consist of interconnected PO_4 groups. The alkali metal ions are located at various sites between the metaphosphate chains. The P–O distances in both metaphosphates are the same, 1.54 Å, and the O–O distances also are almost identical, 2.50 Å in $RbPO_3$ and 2.51 Å in $NaPO_3$, respectively.

When these salts melt their metaphosphate chains break up into fragments of different lengths, each fragment presumably still containing a significant number of PO_3 groups. Even so it is expected that the short-range arrangement of the alkali metal cations with respect to the anion chains will retain some similarity to that which applies in the solid state.

From the structural data of Corbridge it is calculated that the closest distance of approach of Rb^+ to the phosphorus atom is 3.59 Å, while the corresponding value for Na^+ to P in $NaPO_3$ is 3.21 Å. Since the ionic radii of Rb^+ and Na^+ are 1.49 Å and 0.96 Å, respectively,[9] this suggests an "effective ionic radius" of the metaphosphate ion from 2.10 to 2.25 Å.

Another estimate of the effective ionic radius of the metaphosphate ion may be obtained as follows. For the model ionic melt of Reiss, Mayer, and Katz[10] we have the relation $\theta_m = V/d_0^3$. Here V is the volume of the salt in the liquid state and d_0 is the sum of the radii of cation and anion, while θ_m is the reduced volume at the melting point. The values of θ_m for the alkali halides were calculated from d_0 and experimentally determined volumes. It was found that θ_m is essentially the same for all the halides of a given cation. If it is now assumed that the values of θ_m which hold for the alkali halides may be adopted also for the corresponding metaphosphates, we may evaluate d_0 and thus estimate the effective ionic radius of the metaphosphate ion. From the data on the alkali halides it is found that θ_m for the sodium salts is 1.77 and for the potassium salts 1.57. At the melting points the molar volumes of $NaPO_3$ and KPO_3 are 45.3 and 56.0 ml, respectively. This yields the values of $d_0 = r_{Na^+} + r_{PO_3^-} = 2.95$ Å and $d_0 = r_{K^+} + r_{PO_3^-} = 3.29$ Å. From these results we obtain $r_{PO_3^-} = 1.99$ and 1.95 Å, respectively; *i.e.*, the calculated values are some 5–10% smaller than those estimated above from the structural data. Since both methods of obtaining $r_{PO_3^-}$ are open to criticism, we have arbitrarily adopted 2.0 Å as the effective ionic radius of PO_3^-. This value is quite comparable to the commonly accepted values for the nitrate ion, for which Kleppa and Hersh[1] gave $r_{NO_3^-} = 2.18$ Å, while the "thermochemical radius" usually is given as 1.89 Å.[11] However, Meschel and Kleppa[12] suggested that 1.93 Å may be a more appropriate thermochemical radius for NO_3^- in fused nitrates.

For the liquid alkali halides it is commonly assumed that the structure of the liquid is roughly comparable to that of solid NaCl. Thus it is usually estimated that any ion in a pure liquid halide is surrounded by four or five nearest neighbors of the opposite sign at a distance of about $(r_+ + r_-)$ and by about ten next nearest neighbors of the same sign at a distance of roughly $\sqrt{2}(r_+ + r_-)$. In the context of the present discussion the latter figure is of particular importance since it forms the basis for the estimate of U_0^{++}, the London–van der Waals contribution to the enthalpy of mixing (see, *e.g.*, Hersh and Kleppa[2]). However, for the alkali metaphosphates one clearly must make other assumptions in order to estimate U_0^{++}.

From the structural data of Corbridge it is calculated that the average Na–Na distance in $NaPO_3$ (six ions) is 3.57 Å, while the corresponding value for Rb–Rb in $RbNO_3$ (six ions) is 4.25 Å. If we set $r_{PO_3^-} = 2.0$ Å, this gives a ratio of $d_{++}/(r_+ + r_-)$ of 1.21 ± 0.01. In estimating the values of U_0^{++} for the binary alkali metaphosphates we have assumed that this same ratio

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[7] D. E. C. Corbridge, *Acta Crystallogr.*, **9**, 308 (1956).

[8] D. E. C. Corbridge, *ibid.*, **8**, 520 (1955).

[9] M. E. Melnichak, unpublished work.

[10] H. Reiss, S. W. Mayer, and J. L. Katz, *J. Chem. Phys.*, **35**, 820 (1961).

[11] A. F. Kapustinskii, *Quart. Rev., Chem. Soc.*, **10**, 283 (1956).

[12] S. V. Meschel and O. J. Kleppa, *J. Chem. Phys.*, **68**, 3840 (1964).

holds for all the pure liquid alkali metaphosphates and that the number of next nearest neighbors in the melt similarly may be set equal to 6. In other respects we have proceeded according to the method of Hersh and Kleppa, with the only modification that in the London expression for the dispersion energy we have used the uncorrected values of I, the ionization energy of the ion, rather than $0.75I$ as adopted by these earlier authors. The higher value is justified by Melnichak and Kleppa.[4]

We present in Table IV a summary of the relevant enthalpy data for the seven binary alkali metaphosphate mixtures studied in the present work. The first column in this table gives the experimentally determined value of the interaction parameter for the equimolar mixture, $4\Delta H_{0.5}$. The second column gives the estimated value of the contribution to the enthalpy of mixing which arises from the London–van der Waals interaction between the cations, U_0^{++}, and the last column gives the "corrected enthalpy interaction parameter," $4\Delta H^{M}_{0.5} - U_0^{++}$. In Figure 4 we have plotted this last quantity against δ_{12}^2, with δ_{12} based on $d = r_+ + 2.0$ Å. We see that the experimental points fall very close to a straight line which passes through the origin and has a slope of -478 kcal Å^2/mol.

Table IV

Enthalpy Data for the Binary Alkali Metaphosphates (cal/mol)

System	$4\Delta H^{M}_{0.5}$(exptl)	U_0^{++}(calcd)	$4\Delta H^{M}_{0.5} - U_0^{++}$
(Li–Na)PO_3	-866	142	-1008
(Li–K)PO_3	-3236	563	-3799
(Li–Rb)PO_3	-4178	865	-5043
(Li–Cs)PO_3	-5007	1563	-6570
(Na–K)PO_3	-624	140	-764
(Na–Rb)PO_3	-1064	299	-1363
(Na–Cs)PO_3	-1390	763	-2153

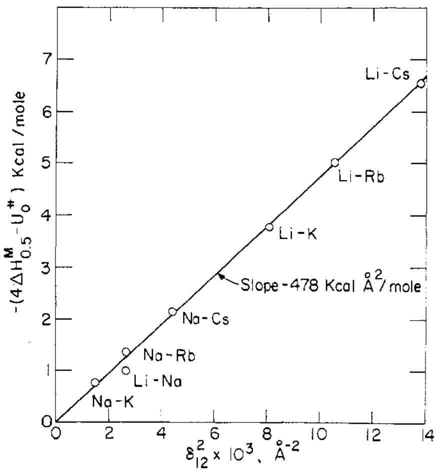

Figure 4.—Dependence of the corrected enthalpy interaction parameter, $4\Delta H^{M}_{0.5} - U_0^{++}$, on the size parameter δ_{12}.

In previous work on the binary liquid mixtures of salts of the alkali metals which have a common anion two different viewpoints have been adopted with respect to the microscopic origin of the enthalpy of mixing. According to the early suggestions of Førland,[13] the enthalpy of mixing should in the main arise from the reduction in next-nearest-neighbor Coulomb repulsion on mixing. Contrary to this, Lumsden has advanced the view that the main source of the mixing enthalpy is to be sought in polarization effects and principally in the polarization of the common anion by the two cations of different size.[14] Lumsden has shown that to a first approximation one might expect both of these models to give rise to expressions for the enthalpy of mixing of the form of eq 2. However, in the Lumsden model the coefficient Ω is also expected to be roughly proportional to α_-, the polarizability of the common anion.

It is to be expected that the polarizability of the metaphosphate ion will be very different in the direction of the metaphosphate chain and in directions perpendicular to the chain. Presumably these latter quantities would be the quantities which would have to be used in any attempt to apply the Lumsden model to the metaphosphate melts. However, it is perhaps not surprising that we have been unable to find any polarizability data in the literature for the metaphosphate ion. Therefore we have been unable to test the Lumsden point of view with any quantitative data.

Due to the uncertainties which are associated both with our estimates of U_0^{++} and of δ_{12}^2, we probably should not attach a great deal of significance to the actual numerical value of Ω given above, -478 kcal Å^2/mol. Even so, it is interesting to note that the metaphosphate results are very comparable to those which we previously found for the binary alkali bromides and iodides, for which we found values of Ω of -430 and -540 kcal Å^2/mol, respectively. We recall here that the ionic radii of Br^- and I^- are 1.95 and 2.17 Å, respectively. Hence, the new data for the metaphosphate mixtures appear to be quite consistent with the viewpoint that the origin of the enthalpy of mixing should in the main be the Coulomb interaction between the cations.

Sodium Metaphosphate–Pyrophosphate Mixtures.—According to the Lux–Flood[15,16] approach to the acid–base properties of oxide melts, the basicity of the melt is measured by the oxygen ion activity, which is governed by the equilibrium acid + O^{2-} = base.

In the Na_2O–P_2O_5 system we may write a series of possible consecutive acid–base steps which may occur when Na_2O is added to P_2O_5 (or P_2O_5 is added to Na_2O)

$$P_2O_5 + O^{2-} = 2PO_3^-$$
$$2PO_3^- + O^{2-} = P_2O_7^{4-}$$
$$P_2O_7^{4-} + O^{2-} = 2PO_4^{3-}, \text{ etc.}$$

As the basicity of the melt is increased, the polymeric P_2O_5 is replaced by the PO_3^- anion chains and then by pyrophosphate and orthophosphate anions.

In calorimetric studies of other oxide melts we have shown how one or both of the end members in the oxidic

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[13] T. Førland, "On the Properties of Some Mixtures of Fused Salts," N. T. H. Trykk, Trondheim, Norway, 1958.

[14] J. Lumsden, *Discuss. Faraday Soc.*, **32**, 138 (1961).

[15] H. Lux, *Z. Elektrochem.*, **45**, 303 (1939).

[16] H. Flood and T. Førland, *Acta Chem. Scand.*, **1**, 592 (1947).

acid–base system may be used to explore the dependence of the acid–base character on composition. However, in the considered sodium phosphate melts this approach is impractical due to the high volatility of P_2O_5 at 800–850° and the chemically aggressive character of Na_2O. Instead we have made use of the strong acid WO_3 as a basicity probe.

When small amounts of solid WO_3 are added to the phosphate melt, acid–base reactions may occur according to a scheme of the type

$$\text{phosphate-I (in melt)} + WO_3(s) = \text{phosphate-II (in melt)} + WO_4{}^{2-}\text{ (in melt)}$$

If WO_3 is a stronger acid than phosphate-II, this reaction will proceed to the right and might be expected to be associated with a certain evolution of heat. On the other hand, if phosphate-II is a stronger acid than WO_3, the reaction would have a tendency to proceed in the opposite direction. In this way the sign and magnitude of the enthalpy of solution of WO_3 may be used to survey the acid–base properties of the melt.

Let us now return to Figure 3, which gives the enthalpy of solution of solid WO_3 in sodium metaphosphate–pyrophosphate melts with mole fractions of Na_2O ranging from 0.50 to 0.61. At $N_{Na_2O} = 0.50$ the enthalpy of solution is +3.8 kcal/mol. This reflects the fact that P_2O_5, the corresponding acid to $PO_3{}^-$, is a very strong acid. As the mole fraction of Na_2O increases above 0.50, there is a sharp drop in the enthalpy of solution to −0.6 kcal at $N_{Na_2O} = 0.51$ and to −1.6 kcal at $N_{Na_2O} = 0.52$. Clearly the melt now contains significant amounts of a higher phosphate (presumably $P_2O_7{}^{4-}$), which will react with the added WO_3 to yield the weaker acid $PO_3{}^-$ and $WO_4{}^{2-}$. From about $N_{Na_2O} = 0.56$ to $N_{Na_2O} = 0.61$ the enthalpy of solution of WO_3 is essentially independent of composition, which reflects that the melt now contains two phosphate anions in comparable amounts, *i.e.*, it has buffer properties. At 843° the liquid range of the phosphate melts extends only to about $N_{Na_2O} = 0.63$. Therefore we were unable to explore at this temperature the interesting composition range near $N_{Na_2O} = 0.67$ associated with very high concentrations of pyrophosphate.

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Matrix Isolation Study of Borazine and Boroxine. A Vibrational Analysis

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A vibrational analysis of borazine based on the infrared spectra of matrix-isolated isotopic species $H_3B_3N_3H_3$, $H_3{}^{10}B_3N_3H_3$, and $D_3B_3N_3H_3$ and the gaseous Raman spectrum of $H_3B_3N_3H_3$ is presented. One of the E′ modes, ν_{16}, is reassigned to 1068 cm^{-1}. Two of the inactive A_2' modes, ν_6 and ν_7, are assigned to 1195 and 782 cm^{-1}, respectively. The literature assignment of the other modes is confirmed, although the position of the A_1' and E″ modes is slightly modified. Strong bands observed in the matrix spectrum of borazine in the regions 1440 and 2500 cm^{-1} but not resolved in the gas-phase spectra are satisfactorily interpreted as combination bands for a planar D_{3h} molecule without invoking matrix effects or postulating a species of lower symmetry. By using the information available for borazine it is possible, through a combination-band analysis, to assign all the fundamentals of boroxine.

Introduction

The gas-phase infrared and liquid Raman spectra of borazine, $H_3B_3N_3H_3$, were first investigated by Crawford and Edsall.[1] The molecule was assumed to be isoelectronic with benzene, with point group D_{3h}. The symmetric planar structure was proposed by Bauer on the basis of early electron diffraction studies.[2] The infrared spectra were reinvestigated by Price and coworkers,[3] as well as by Silberman.[4] These studies essentially confirmed the Crawford–Edsall assignments. Kartha, *et al.*, on the basis of observed band shapes and isotope effects reassigned absorption bands at 918, 713,

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[1] B. L. Crawford and J. T. Edsall, *J. Chem. Phys.*, **7**, 223 (1939).

[2] S. H. Bauer, *J. Amer. Chem. Soc.*, **60**, 524 (1938).

[3] N. C. Price, R. D. B. Fraser, T. S. Robinson, and H. C. Longuet-Higgins, *Discuss. Faraday Soc.*, **9**, 131 (1950).

[4] E. Silberman, *Spectrochim. Acta, Part A*, **23**, 2021 (1967).