

fects in a fashion identical with the case described, there is little point in repeating these descriptions here. The only differences among these photochemical preparations lie in the conditions of chlorination of the mixed disilane to produce the pure disilane. In the preparation of hexachlorodisilane this chlorination requires a temperature of 105° while in the preparation of 1,2-dichloro-1,1,2,2-tetramethyldisilane the chlorination proceeds smoothly at room temperature.

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A Calorimetric Study of Molten Na₂MoO₄–MoO₃ Mixtures at 970°K

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Liquid oxide mixtures which contain metal cations and complex oxygen-containing anions (such as borate, phosphate, or silicate species) form an interesting and important class of ionic melts. In this general area we have recently reported the results of calorimetric studies of the liquid systems PbO–V₂O₅ at 685°¹ and PbO–B₂O₃ at 800°.²

In this note, we wish to report a related study of the liquid mixtures formed by Na₂MoO₄ and MoO₃ at 970°K. More specifically, we have measured the enthalpies of solution of MoO₃(s) and Na₂MoO₄(l) in molten Na₂MoO₄–MoO₃ mixtures at this temperature. The present study was motivated by our interest in finding new solvents for high-temperature calorimetry of mixed solid oxides such as spinels and silicates. However, these new results have certain interesting features which have implications outside the immediate domain of calorimetry.

Experimental Section

The materials used in the present work were Baker Analyzed reagent Na₂MoO₄·2H₂O and MoO₃. Prior to each experiment, a mixture of these compounds of the desired composition was melted down in the gold crucible used for calorimetry. The calorimeter, sample container, and general experimental procedures have been described elsewhere.³ In each calorimetric experiment, a small sample of known weight of either MoO₃ or Na₂MoO₄ (0.5–1.0 mmole) was dissolved in about 15 g of molten oxide mixture. Both solutes dissolved rapidly in the nonviscous melts. As in our earlier work, calibration was by the gold drop method, based on the heat content equation for gold given by Kelley.⁴

Results and Discussion

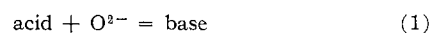
We present in Figures 1 and 2 graphs of the molar enthalpies of solution of MoO₃(s) and Na₂MoO₄(l) in molten Na₂MoO₄–MoO₃ mixtures as functions of melt composition. The composition variable adopted is the mole fraction of MoO₃ in the binary system Na₂O–MoO₃: $X_{\text{MoO}_3} = n_{\text{MoO}_3} / (n_{\text{MoO}_3} + n_{\text{Na}_2\text{O}})$. The composition range covered in the present study was from $X_{\text{MoO}_3} = 0.50$ (pure molten Na₂MoO₄) to $X_{\text{MoO}_3} = 0.9$, which is close to the liquidus at 700°.⁵ Because of the expected experimental difficulties associated with calorimetry in very basic melts (e.g., attack on platinum), no attempt was made to extend this study to the Na₂O-rich side of the system.

Each addition of solute changed the melt composition by 0.5 to 1.0 mole %. For those composition regions in which the partial enthalpy of solution changes rapidly with concentration (notably near $X_{\text{MoO}_3} = 0.5$), the precision of the calorimetric data does not permit a reliable extrapolation to zero moles of added solute. Therefore, all calorimetric data have been plotted against the average mole fraction of MoO₃

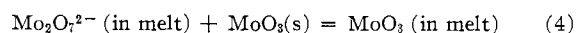
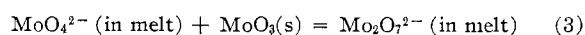
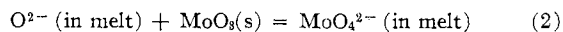
$$\bar{X}_{\text{MoO}_3} = \frac{X_{\text{MoO}_3}(\text{initial}) + X_{\text{MoO}_3}(\text{final})}{2}$$

Even so, our results will, to a good approximation, represent the partial molal enthalpies of MoO₃ and of Na₂MoO₄.

In discussing the experimental results we shall, as in our earlier work, adopt the Lux–Flood approach to the acid–base properties of oxide melts.^{6,7} In this approach, the basicity of the melt is measured by the oxygen ion activity, governed by the equilibrium



Among the considered oxides, Na₂O is a very strong base, while MoO₃ is a strong acid. We may write a series of possible consecutive acid–base steps that may occur when MoO₃ is added to an initially Na₂O-rich melt



Note that when the melt contains a mixture of several molybdate species such as those above or their polymers, it constitutes a buffered acid–base system.

The calorimetric results are in accord with an interpretation along these lines. Since Na₂O is a very strong base, it is reasonable to assume that the MoO₄²⁻ anion, which is present in high concentration at the Na₂–MoO₄ composition, has a relatively small dissociation constant. Presumably the composition $X_{\text{MoO}_3} = 0.50$ corresponds to the first equivalence point in the “titration” of Na₂O by MoO₃. The very pronounced composition dependence observed in the heat of solution of

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(3) A. Navrotsky and O. J. Kleppa, *ibid.*, **5**, 192 (1966).

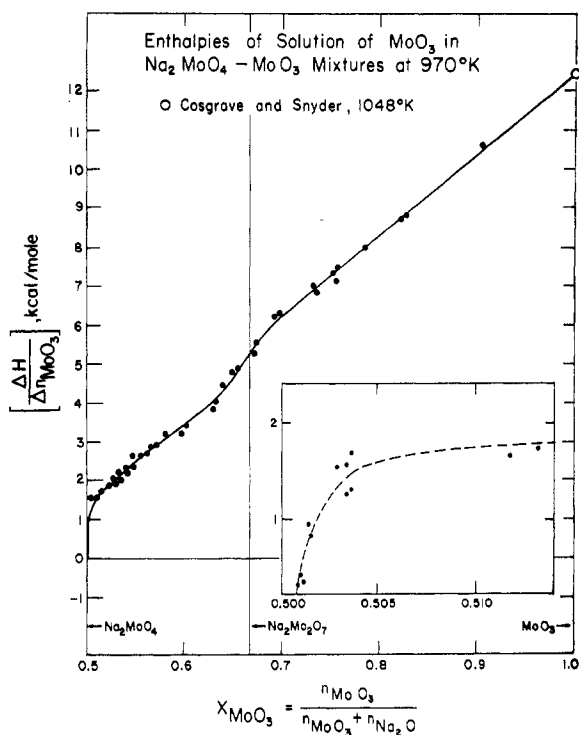


Figure 1.—Enthalpies of solution of $\text{MoO}_3(\text{s})$ in Na_2MoO_4 - MoO_3 mixtures at 970°K .

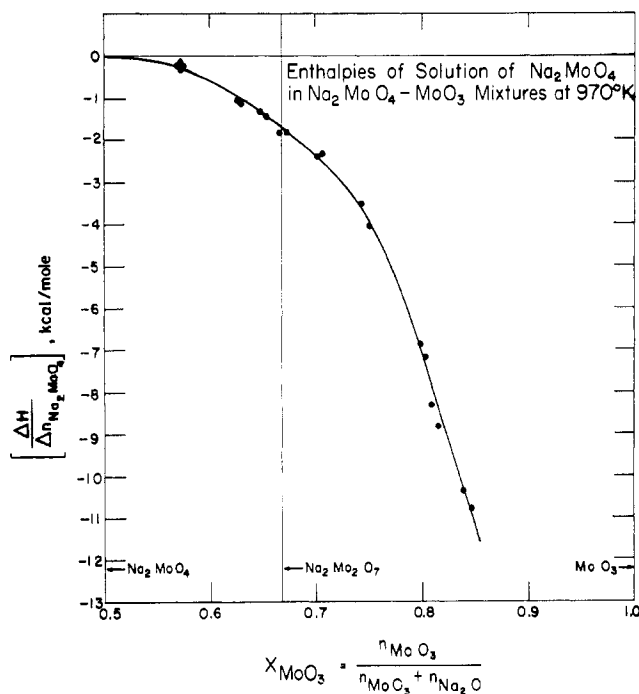


Figure 2.—Enthalpies of solution of $\text{Na}_2\text{MoO}_4(\text{l})$ in Na_2MoO_4 - MoO_3 mixtures at 970°K .

MoO_3 in the range $0.50 < X_{\text{MoO}_3} < \sim 0.52$ is consistent with this view. Since pure molten Na_2MoO_4 is not a buffered acid-base system, the acidity of the melt and the measured heat of solution of MoO_3 change rapidly with composition until enough MoO_3 is added to the melt to produce a significant concentration of the molybdate anion of the next higher Mo:O ratio.

A buffer region, in which the heat of solution of MoO_3 changes only slowly with composition, is observed in

the range $\sim 0.52 < X_{\text{MoO}_3} < \sim 0.63$. The slight break in the curve near $X_{\text{MoO}_3} = 0.65$ suggests that the second molybdate species present in the preceding buffer region probably is $\text{Mo}_2\text{O}_7^{2-}$ and that the second equivalence point would lie at $X_{\text{MoO}_3} = 0.67$ ($\text{Na}_2\text{O}:\text{MoO}_3 = 1:2$). However, since the break in the curve near this composition is much less pronounced than the one near the Na_2MoO_4 composition, we may infer that the anions of composition $\text{Mo}_2\text{O}_7^{2-}$ undergo significant dissociation in the molten state. A significant concentration of the next higher molybdate species after $\text{Mo}_2\text{O}_7^{2-}$, or, as is more likely, of free MoO_3 , is present in the melt even before the equivalence point is reached. These conclusions are consistent with the equilibrium phase diagram for the Na_2O - MoO_3 system,⁵ which shows a much flatter maximum for the solid compound $\text{Na}_2\text{Mo}_2\text{O}_7$ than for Na_2MoO_4 .

At high MoO_3 concentrations ($X_{\text{MoO}_3} > 0.7$), the variation of the enthalpy of solution of MoO_3 with X_{MoO_3} again appears to be linear. This seems to be another buffer region, probably involving a mixture of $\text{Mo}_2\text{O}_7^{2-}$ and free MoO_3 (or its polymer) as the principal species. The extrapolated value of the heat of solution of MoO_3 at $X_{\text{MoO}_3} = 1$ agrees well with the reported heat of fusion of MoO_3 at its melting point⁸ (12.5 kcal/mole at 1048°K).

The variation of the enthalpy of solution of Na_2MoO_4 with melt composition is more gradual. This is to be expected, since Na_2MoO_4 is not a component of the system Na_2O - MoO_3 , and its addition to the melt introduces both an acidic and a basic constituent. In the region $0.50 < X_{\text{MoO}_3} < 0.63$, the heat of solution of Na_2MoO_4 decreases by only a few tenths kcal/mole from its value of zero at $X_{\text{MoO}_3} = 0.50$. Beyond $X_{\text{MoO}_3} = \sim 0.63$, the heat of solution of Na_2MoO_4 becomes progressively more exothermic with increasing X_{MoO_3} . This may be attributed to a reaction of type (3), which is expected to occur to an increasing extent and possibly to become more exothermic with increasing MoO_3 concentration.

Since basicity increases in the sequence Li_2O , Na_2O , K_2O , we might expect the $\text{Mo}_2\text{O}_7^{2-}$ anion to undergo more dissociation in Li_2O - MoO_3 melts and less dissociation in K_2O - MoO_3 melts of comparable composition. Accordingly, the break in the curve of the heat of solution of MoO_3 near $X_{\text{MoO}_3} = 0.67$ should be more pronounced in the potassium system and less pronounced in the lithium system than in the sodium system studied here.

Lastly, we should like to note that, in part, as a result of the present study, we adopted a molybdate melt of composition $3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$ as a calorimetric solvent for spinels.⁹ This composition ($X_{\text{MoO}_3} = 0.57$) lies within the observed rather flat buffer region of the Na_2O - MoO_3 system. A buffered solvent offers two significant advantages compared to an unbuffered melt for calorimetry. On the one hand, we find that the

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melt is a good solvent both for acidic and basic solutes. On the other hand, the enthalpy of solution of a given solute does not change rapidly with composition. Therefore the enthalpy of solution remains a reproducible quantity despite small variations in melt composition or solute concentration.

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Properties of Lead Azide Prepared in Molten Salt Media

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Crystals are often prepared by precipitation or grown from aqueous solutions. Prepared in this way, often several hundred degrees centigrade below their melting points, they are not in thermodynamic equilibrium and are likely to be more imperfect than crystals grown at higher temperatures. They are traversed by grain boundaries which separate disoriented regions of the crystals having random networks of dislocations and containing isolated and clustered vacancies. The properties of these real crystals can be changed by annealing.¹ Below $0.25T_m$ (T_m = melting point) only defects in special positions near the surface are able to move. Around $0.25T_m$ surface ionic mobility begins to be significant. Above $0.5T_m$ bulk ionic conduction predominates and intergranular adhesion and grain growth become possible. In view of this, attempts were made to prepare inorganic azides at elevated temperatures where some of these defects might be formed in smaller numbers or in less severe form and thus lead to improved stability.

Lead azide is a widely used initiating explosive. Although it explodes before it melts, estimates predict a melting point as high as 500° .² Regardless of the accuracy of these estimates, lead azide is made far below its melting point when prepared by the usual procedures of precipitation in aqueous solution. Therefore, it seemed interesting to investigate the preparation of lead azide at elevated temperatures and compare its properties with those of normally prepared samples. Lead azide decomposes at considerably higher temperatures than many other azides. Nevertheless, it is

one of the most hazardous azides because of its sensitivity against shock and electrical discharge. Molten alkali nitrates and their eutectic mixtures have solvent properties similar to water.³ They were found to be suitable media for the preparation of lead, silver, and cupric azides. Also, transition metal azides like cobalt and nickel azides precipitated in molten alkali nitrates. However, cobalt azide is thermally not stable enough and nonaqueous solvents have to be found which would dissolve the alkali nitrates but not the transition metal azides. In preparative quantities only lead and silver azides were made.

Preparation of Lead Azide in Molten Alkali Nitrates as Media

The eutectic mixture of potassium nitrate and lithium nitrate melts at 129° , and that of potassium nitrate and sodium nitrate at 218° . All of these alkali nitrates and their mixtures dissolve alkali azides and many heavy metal nitrates but not heavy metal azides. Therefore, lead azide could be precipitated quantitatively by mixing two separate solutions of potassium azide and lead nitrate in molten alkali nitrates. The precipitation could equally well be performed by dropping finely powdered lead nitrate into a solution of potassium azide in molten alkali nitrates. Both procedures led to lead azide crystals having the same properties. This work was carried out either in beakers on a hot plate or in test tubes which fitted into wells of a temperature-controlled metal block. The melt could be poured into distilled water for separation of the lead azide crystals. However, the melt was usually permitted to solidify and then cool to room temperature. The alkali nitrates were leached out with distilled water and the lead azide crystals obtained by filtration with a sintered-glass filter. The residue was extensively washed with distilled water and finally with alcohol and acetone. The latter wash prevented the lead azide crystals from sticking together, and thus they became easier to handle. Dry lead azide is hazardous and one explosion occurred. Grounding of equipment and using a conductive floor and conductive shoes minimize the danger. Lead azide crystals submerged in molten alkali nitrates or water never exploded during more than 60 preparations.

The lead azide crystals prepared in alkali nitrate melts had a needlelike shape and were obtained in batches of fairly homogeneous crystal sizes. Some batches had an average crystal size of less than 5μ ; other batches, an average crystal size as large as 150μ . Only analyzed chemicals were used in the preparation and the only impurity which had to be controlled was water. Lead azide was obtained which had a purity of close to 100% when the chemicals used were carefully dried in the solid state and further dehydrated by bubbling dry nitrogen through the melts. Without the drying procedures 99.6% pure lead azide was obtained in KNO_3 - NaNO_3 melts and 98.0-99.0% pure lead azide

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