below that of chloride ion, indicating that no cation is present. Anions should have lower K_d values, the higher their field strengths. The K_d curve of silver is therefore consistent with that which might be expected of species such as $AgCl_3^{2-}$ and $AgCl_4^{3-}$.

Notwithstanding the different experimental techniques involved in high-temperature work, liquid-liquid extraction and ion exchange offer the same benefits to molten salt systems as do aqueous systems. The highly individualistic K_d curves for each solute in borate-salt distributions suggest that other solute species may be characterized in this manner. The large differences in K_d values of various solutes indicate possible application as a separation method.

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High-Temperature Calorimetry in Liquid Oxide Systems. II. The Enthalpies of Solution of Oxides of Type MO in Vanadium(V) Oxide

BY T. YOKOKAWA AND O. J. KLEPPA

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The enthalpies of solution of ten different solid oxides in liquid V_2O_5 at 685 ± 5° have been measured. All solutes studied except BeO and CuO showed negative enthalpies of solution, the magnitude increasing sharply in the sequence BeO < MgO < CaO < SrO < BaO. The results are discussed in terms of the acid–base character of the solution process.

Introduction

In a previous communication we reported the results of a calorimetric investigation of the system $PbO–V_2O_5$ at 680°.[1] In the present work this study is extended to a survey of the heats of solution of a series of divalent solid oxides in liquid V_2O_5 at the same temperature.

Experimental

Materials.—Vanadium pentoxide was the same Baker's Analyzed reagent used in our earlier work. The sources of the other oxides were as follows: BeO, Beryllium Corporation of America, Grade V; MgO, CuO, ZnO, Mallinckrodt Analytical Reagents; NiO, CoO, CdO, Baker Analyzed Reagents. These salts were used as received after appropriate drying. CaO, SrO, and BaO were prepared from the corresponding carbonates (Mallinckrodt Analytical Reagents) by heating them in air or under vacuum (barium carbonate) at about 1100°.

Procedures.—The experimental procedures were similar to those used in our previous work. In the case of SrO and BaO the experiments were performed in a nitrogen atmosphere in order to prevent reaction with CO_2 in the air. This was achieved by running purified, dry nitrogen at a rate of about 50 ml./min. through the silica envelope of the calorimeter. All experiments were performed at 685 ± 5°.

Each calorimetric experiment involved the use of 30–50 mmoles of the solvent and 1–4 mmoles of solute oxide. Due to solubility limitations and in some cases low rates of solution the present study was restricted to the concentration range below about 10 mole % of solute.

Results and Discussion

The experimental results obtained in about 50 separate calorimetric experiments on 10 different solute oxides are presented in graphical form in Figure 1. In each case we plot ΔH^M, the enthalpy of formation of 1 mole of liquid mixture from liquid V_2O_5 and solid solute, against the mole fraction of solute. The figure contains also a curve which represents the average of our earlier values for PbO in V_2O_5.

We note from Figure 1 that, in the concentration range studied and within our experimental uncertainty, the values of ΔH^M vary linearly with mole fraction of solute. This implies that in this range the partial heat of solution of the solute oxide is essentially constant and, correspondingly, that the partial heat of the solvent is zero (or near zero). We present in Table I a summary of the limiting values of the partial molal enthalpies of solution ($\Delta\bar{H}_{MO}$) of the considered solutes, derived from the data in Figure 1.

It will be noted that all the oxides studied except BeO and CuO show negative enthalpies of solution. The magnitude of $\Delta\bar{H}_{MO}$ increases sharply in the sequence BeO < MgO < CaO < SrO < BaO, *i.e.*, with increasing ionic radius of the cation or increasing *basicity* of the solute oxide. This is consistent with the strongly *acidic* properties of the solvent oxide, V_2O_5.

It is convenient to dicuss the acid–base character of oxides and oxidic melts in terms of the Lux–Flood approach,[2–4] which is analogous to the Brønsted–Lowry scheme for protonic systems. In the Lux–Flood approach the measure of the basicity of the melt is the oxygen ion activity according to the equilibrium: acid + O^{-2} = base. The stronger the base, the higher the oxygen ion activity.

For the vanadium(V)–oxygen system we may in this

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[1] T. Yokokawa and O. J. Kleppa, *Inorg. Chem.*, **3**, 954 (1964).

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

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

[4] A. M. S. El Din and A. A. A. Gerges, *Electrochim. Acta*, **7**, 285 (1962); **9**, 123, 613 (1964).

TABLE I

LIMITING VALUES OF PARTIAL MOLAL ENTHALPIES OF SOLUTION ($\Delta\bar{H}_{MO}$) IN LIQUID V_2O_5 AT 685 ± 5°[a]

Oxide	BeO	MgO	CaO	SrO	BaO	
$\Delta\bar{H}_{MO}$	1.0 ± 0.3	-9.4 ± 0.6	-32.7 ± 0.7	-47.9 ± 0.9	-61.7 ± 0.6	
Oxide	NiO	CoO	CuO	ZnO	CdO	PbO
$\Delta\bar{H}_{MO}$	-10.6 ± 0.7	-6.4 ± 0.4	4.3 ± 0.7	-3.0 ± 0.4	-15.9 ± 0.6	-18.4 ± 0.3

[a] Data in kcal./mole. Deviations quoted are standard deviations from the mean of about five experiments for each solute.

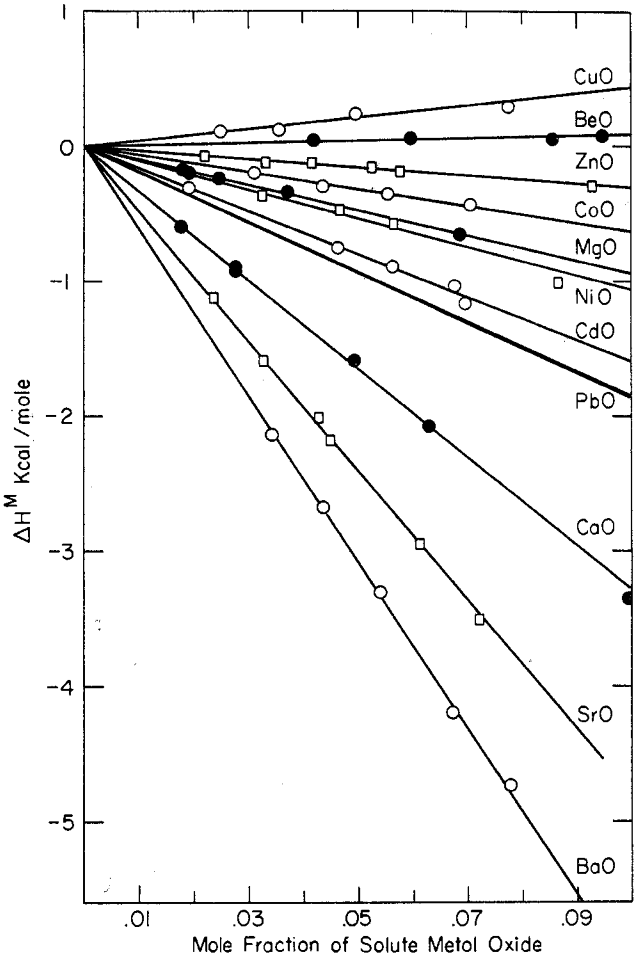

Figure 1.—The molar change in enthalpy, ΔH^M, associated with the solution of solid oxides in liquid V_2O_5 at 685 ± 5°.

scheme write a series of possible consecutive acid–base steps, involving species such as V^{+5}, VO^{+3}, VO_2^+, V_2O_5, VO_3^-, $V_2O_7^{-4}$, VO_4^{-3}. Similarly we may for each oxide, MO, consider the species M^{+2}, MO, MO_2^{-2}, etc.

In liquid V_2O_5 the addition of the basic solute MO clearly involves formation of vanadate species such as VO_3^-, $V_2O_7^{-4}$, VO_4^{-3}, or polymeric forms of these. To a first approximation the enthalpy change associated with the solution process

$$MO(s) + V_2O_5(l) = M^{+2} + \text{vanadate (in } V_2O_5)$$

will be a measure of the tendency of this acid–base reaction to proceed from left to right, *i.e.*, of the relative strength of V_2O_5 and M^{+2} as acids or of MO and vanadate as bases. The stronger the base MO (or the weaker the acid M^{+2}) the more negative the enthalpy of solution ($\Delta\bar{H}_{MO}$). The vanadate–V_2O_5 melt resulting from the solution experiment clearly will be a buffered acid–base system.

It is of particular interest to attempt to establish the composition and structure of the vanadate ions which form as a result of the dissolution of the divalent oxides in V_2O_5. In the case of the PbO–V_2O_5 system investigated in our earlier work the liquid range at 680° extends to about 60 mole % PbO. Throughout this range we observed an essentially linear dependence of ΔH^M on mole fraction, *i.e.*, constant partial heats of solution. This was interpreted to rule out the metavanadate ion (PbO:V_2O_5 = 1:1) as a principal anionic species in the melt. However, the data did not allow a choice to be made between the species $V_2O_7^{-4}$ and VO_4^{-3}.

From the early work on oxidic polyacids by Flood and co-workers,[5] we know that the relative basicity of a given acid–base pair may depend strongly on the nature of the cations present. Therefore, while V_2O_5–vanadate melts which contain oxides of basicity comparable to that of PbO are expected to behave in a similar manner, it may not be justified to draw firm conclusions for solutes of very different basicity. Unfortunately the calorimetric data reported in the present work do not cover a sufficient range in composition to throw further light on this problem.

In the course of the present work a few experiments were performed also on the enthalpy changes associated with the dissolution in V_2O_5 of oxides formed by ions of higher charge than two (Fe_2O_3, Al_2O_3, SiO_2). For these solutes we found that the rates of solution were inadequate to yield quantitative data. However, in all cases positive enthalpies of solution of the order of 5 to 10 kcal./mole were indicated. Thus the behavior of these more acidic oxides in V_2O_5 is entirely consistent with the trend established by the data for the oxides of the divalent ions.

When the oxide in question is strongly acidic, *e.g.*, has an acidity approaching that of the solvent V_2O_5, the acid–base character of the dissolution process in large measure will be suppressed. Thus the enthalpy of solution no longer serves as an approximate quantitative measure of the relative acid–base strength of the solutes. For these acid solutes one should of course instead use an oxidic solvent of basic character, such as liquid PbO (m.p. 890°).

Finally, it should be noted that certain mixed oxide melts (*e.g.*, nPbO–$m$$B_2O_3$) may combine a low melting point with intermediate acidity and *amphoteric* properties. We are at the present time exploring the possible use of such a mixed melt as a solvent medium for solution calorimetry of solid oxide systems. Of particular

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[5] H. Flood, T. Førland, and B. Roald, *Acta Chem. Scand.*, **1**, 790 (1947).

interest are studies of spinels, perovskites, and silicates, which often dissolve with difficulty in more conventional calorimetric solvents. A first report dealing with the enthalpy changes associated with the transformation of the metastable modifications of Al_2O_3 to α-Al_2O_3 (corundum) has been published.[6]

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[6] T. Yokokawa and O. J. Kleppa, *J. Phys. Chem.*, **68**, 3246 (1964).

Contribution from Argonne National Laboratory,
Argonne, Illinois

Reactions in Molten Salt Solutions. I. Uranate and Neptunate Formation in Molten Lithium Nitrate–Sodium Nitrate[1]

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The reaction of U(VI), Np(V), and Np(VI) with BrO_3^- in molten $LiNO_3$–$NaNO_3$ resulted in the formation of solid compounds which could be separated from the melt and which were characterized as new mixed alkali metal–actinide oxide phases. The infrared spectra of these compounds, and their cell constants evaluated from X-ray diffraction patterns, were compared with those of pure $Na_2U_2O_7$, $Na_2Np_2O_7$, and $CaUO_4$. A close structural relationship with the latter compounds was shown to exist. Interpretations of some of the infrared absorption bands of the compounds studied were offered, and U–O_I and Np–O_I bond distances were calculated.

In an attempt to prepare and isolate higher oxides of the actinides, we have for some time been studying certin reactions of these elements in anhydrous molten nitrate salt media. The present communication summarizes our results with uranium and neptunium in the $LiNO_3$–$NaNO_3$ eutectic.

Spectrophotometric studies have shown that lower oxidation states of uranium are rapidly oxidized to the hexavalent state, while those of neptunium are oxidized to the pentavalent state in molten nitrate salts.[2] Under certain conditions the hexavalent state of neptunium can also be observed in the melt, but the pentavalent state is the stable species.

In the course of our work it was found that the addition of solid anhydrous $NaBrO_3$ to solutions of U(VI), Np(V), or Np(VI) in $LiNO_3$–$NaNO_3$ initiated a reaction that resulted in the formation of a solid actinide-containing compound which could be separated from the bulk of the solvent by filtration. Duke and Lawrence[3] have studied the kinetics of the reaction of BrO_3^- with a number of metal ions in molten alkali nitrate media. In the case of Zn^{2+}, their results were consistent with the reaction

$$2Zn^{2+} + 4BrO_3^- = 2ZnO + 2Br_2 + 5O_2$$

By analogy, the reaction of BrO_3^- with the actinide species in solution might have been expected to yield the corresponding trioxide. However, the product actually separated proved to be complex and could be identified as a mixed alkali metal–actinide oxide.

There are numerous references to the characterization of compounds of the form $A_2O \cdot xUO_3$, the alkali metal uranates, where A is an alkali metal element and x may be a fractional or a whole number,[4] but much less work has been published with respect to the corresponding compounds of the transuranium elements, the actinates.[5]

The present technique of preparation is new. It involves reaction at much lower temperatures than normally required and thus is of particular interest in synthesizing alkali metal actinates which may have a limited region of thermal stability. Information relative to the structure of the compounds isolated was obtained from X-ray diffraction patterns and infrared spectra.

Experimental

The preparation and handling of the $LiNO_3$–$NaNO_3$ eutectic (m.p. 206°, 44.8 mole % $NaNO_3$) was carried out in a manner described previously for the $LiNO_3$–KNO_3 eutectic.[6] Reagent grade chemicals were employed. Spectroscopically pure UO_3 and NpO_2 were used to prepare the corresponding actinyl nitrates, which were then dried at ~200°, prior to combination with the eutectic in quartz or borosilicate glass tubes. Insoluble material was dissolved with the aid of NH_4NO_3.[6] The reaction vessel was frequently a spectrophotometer cell, which made it possible to check for the absence of H_2O absorption bands near 2.0 μ, after treatment of the melt with a stream of dry N_2 gas, before initiating the reaction.

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission. Presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

[2] D. M. Gruen, R. L. McBeth, J. Kooi, and W. T. Carnall, *Ann. N. Y. Acad. Sci.*, **79**, 941 (1960).

[3] F. R. Duke and W. W. Lawrence, *J. Am. Chem. Soc.*, **83**, 1269 (1961).

[4] V. I. Spitsyn, Ed., "Investigations in the Field of Uranium Chemistry," Moscow University Press, 1961. Argonne National Laboratory Translation 33 (1964).

[5] C. Keller, Kernforschungszentrum Karlsruhe Report KFK-225, Feb. 1964.

[6] W. T. Carnall, *Anal. Chem.*, **34**, 786 (1962