

which will give a pressure decrease of about 11% if the species on the right are the chief products. This decrease is in accord with the order of magnitude observed experimentally.

Observations on the thermal stability of $(\text{BOCl})_3$ in this and other published work^{4,5} might appear to be inconsistent at first sight. In the present study decay of the trimer is found to be quite rapid at room temperature (Figures 1 and 2), while in the studies at elevated temperature the compound is formed and presumably has significant stability at 1400°K. However, the high-temperature observations indicate that the reaction



is endothermic and is favored thermodynamically as the temperature is increased. The existence of the trimer as a transient species at low temperature is then evi-

(4) J. Blauer and M. Farber, *J. Chem. Phys.*, **39**, 158 (1963).

(5) J. Blauer and M. Farber, *Trans. Faraday Soc.*, **60**, 301 (1964).

dence of a sufficiently slow rate of reversion to the equilibrium state to permit observation of some of its properties. Gaseous boroxine ($\text{B}_3\text{O}_3\text{H}_3$) appears to behave in a similar fashion.^{6,7}

The low-temperature decay of the trimer appears to involve a wall reaction yielding a solid product with an infrared spectrum (Figure 3) corresponding approximately to B_2O_3 but analysis shows that this deposit still contains chlorine. Molecular chlorine is also a significant decay product of the trimer. BCl_3 may also be produced but this is not easy to establish satisfactorily in the presence of excess BCl_3 from the preparative stage. In the light of these comments it is clear that the reverse of reaction 7 is not the only operative mode of thermal decomposition of $(\text{BOCl})_3$ at low temperatures.

(6) G. H. Lee, W. H. Bauer, and S. E. Wiberley, *J. Phys. Chem.*, **67**, 1742 (1963).

(7) R. F. Porter and S. K. Gupta, *ibid.*, **68**, 280 (1964).

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Liquid-Liquid Extraction in the Sodium Oxide-Boron Oxide-Sodium Chloride System¹

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Liquid-liquid extraction has been accomplished in molten salt media by the use of molten borates as the extracting phase. Radioactive tracers were used to measure the distribution of micro quantities of Cs, Rb, Ba, Sr, Nd, Eu, and Ag between the two conjugate liquid phases throughout the immiscibility region in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{NaCl}$ at 830°. Borate/salt distribution coefficients are extremely sensitive both to phase compositions and to the nature of the solute ion. Cations of the alkali metal, alkaline earth, and rare earth groups show good separation factors and an order of selectivity dependent upon field strength. Selectivity appears to be based largely upon cation-exchange properties of the borate phase. The distribution behavior of silver is compatible with that which might be expected of a highly charged chloro anion.

Introduction

Efforts to apply analytical tools such as liquid-liquid extraction and ion exchange to the study of chemistry in molten salts have been hampered by the scarcity of immiscible liquid pairs and ion-exchange materials which are both effective for the separation of solutes and stable at the high temperatures involved. Molten alkali borates are generally immiscible with molten electrolytes and they show excellent selectivity between various ionic species in the latter phase. Molten boron oxide is generally thought of as a non-ionic, covalently bonded, high polymer, in contrast to most molten salts which are ionic fluids. As would be expected, the two liquids are usually quite immiscible. As alkali oxide is added to a molten system of salt and boron oxide, the phases gradually become mutually soluble, but before complete miscibility

occurs there is normally an extensive immiscibility region. Within this region solute ions are distributed between the two conjugate phases in a ratio strongly dependent upon both the phase compositions and the nature of the solute ion. For the investigation of this behavior, the solvent system studied in this work was that of $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{NaCl}$ at 830°. Distribution of solute ions from the alkali metal, alkaline earth, and rare earth groups was measured to determine the effect of size and charge of cations which are expected to show a minimum of complex ion formation. Distribution of silver was measured to observe the behavior of an element suspected of complex anion formation.

Experimental

Preparation of Borate Glasses.—Reagent grade boron oxide (B_2O_3), anhydrous borax ($\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$), and mixtures of borax and sodium metaborate ($\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$) were melted and heated at 900° until bubbling stopped, which removed all but a small amount of residual water. The glasses were then cooled, coarsely crushed, and stored in desiccators. From these glasses of known

(1) This work was supported by the U. S. Atomic Energy Commission under Contract No. AT-(49-2)-1107.

composition, appropriate mixtures were selected for each run to give the desired $\text{Na}_2\text{O}:\text{B}_2\text{O}_3$ ratio in the region of immiscibility.

Radioactive Tracer Solutes.—Solutions of the following radio-nuclides were prepared in dilute hydrochloric acid: Cs^{137} , Rb^{86} , Na^{22} , Ba^{133} , Sr^{90} , Ag^{111} , Nd^{147} , and $\text{Eu}^{152-154}$. For each solution radiochemical purity was verified by γ -ray pulse-height distributions and for Rb^{86} and Nd^{147} solutions by decay measurements as well. Each tracer solution contained also a small amount of the corresponding inactive metal as the chloride salt. When added to the borate-salt mixture, the solute metal generally constituted 1-10 p.p.m. of the total solids. No difficulties from surface adsorption were apparent with this amount of solute, yet the amount was not enough to affect the phase diagram data of the three-component solvent system.

Equilibration.—Equilibrations were made either in tall, J. Lawrence Smith type, platinum crucibles of about 12-cc. capacity or in high density, low ash graphite crucibles with inside dimensions $\frac{5}{8}$ in. diameter \times $2\frac{3}{8}$ in. deep. A motor-driven, platinum wire stirrer was used. All equilibrations were made at 830° , in a small crucible furnace controlled to $\pm 5^\circ$.

Solutes were added to one phase or the other before equilibration. When the solute was to be associated initially with the borate phase, the solute aliquot was first dried on the crushed borate glass and melted in the crucible. Salt was then added slowly by funnel to the molten borate glass. It was particularly necessary to add the salt slowly to borate melts of low Na_2O content, which have greater tenacity for residual water. This residual water will react with molten chloride to release HCl gas, which may cause the borate to foam out of the crucible if care is not taken. When the solute was to be associated with the salt phase, the borate was first melted with part of the salt, to remove the moisture. Then the mixture was cooled, the rest of the salt and the solute were added, and the mixture was dried and remelted.

The phases were stirred for 30 min. to equilibrate them; then they were allowed to separate by standing. The usual settling time was also 30 min., but up to 2 hr. was sometimes necessary in cases where alkali content in the system was very low, in which cases the higher viscosity of the borate phase resulted in slow phase separation.

When the $\text{Na}_2\text{O}:\text{B}_2\text{O}_3$ ratio in the solvent system was less than that corresponding to borax (1:2), the fluid upper salt phase could be easily separated from the more viscous lower borate phase by pouring the melt out of the crucible onto a heavy aluminum trough. The resulting clear, glassy phase could then be easily distinguished from the opaque salt phase when samples of each phase were selected. Platinum crucibles were generally used in this composition region. In the region near the plait point, however, the phases became more similar in appearance, viscosity, and density. Graphite crucibles were used when this region was examined. This allowed the phases to be quickly frozen, by cooling the crucible with an air jet, and then removed by breaking the crucible. Pure samples of each phase were separated by chipping and grinding. The graphite crucibles were protected from burning in the open atmosphere by a salt glaze. The glaze was applied before equilibration by coating the crucible with a paste of finely ground NaCl and water and firing this onto the graphite.

Distribution of Solutes.—Several samples of each phase were taken for replicate counting and analysis in order to be able to select pure samples of each phase confidently. Each sample was weighed and then radioassayed by γ -ray counting in a well-type scintillation counter. From the specific activities of the two phases the distribution coefficient, K_d , was calculated

$$K_d = \frac{\text{moles of solute per unit weight of borate phase}}{\text{moles of solute per unit weight of salt phase}} \quad (1)$$

$$= \frac{\text{specific activity of borate phase}}{\text{specific activity of salt phase}}$$

Composition of Phases.—Each phase was analyzed for Na_2O , B_2O_3 , and NaCl , and the data were used to construct the immiscibility curve. Na_2O was determined by titration with

hydrochloric acid to the methyl red end point. B_2O_3 was determined on the same aliquot by converting the boric acid just formed to a strong acid with mannitol and back titrating this with NaOH to the phenolphthalein end point. NaCl was determined by chloride analyses on separate aliquots. The Volhard method was used primarily, but for many of the borate phase samples of low chloride content a mercurimetric titration² was used.

Attainment of Equilibrium Conditions.—When equilibrations are made in platinum crucibles open to the atmosphere there is a slight corrosion of the crucible, particularly when the alkali content of the system is low. Also, any moisture present will react with molten chloride to form alkali oxide. However, immiscibility diagram data resulting from platinum crucible and graphite crucible equilibrations in the present work, and from closed system equilibrations in graphite at 810° ,³ show no significant differences which may be attributed to differences in containers or atmosphere. The distribution of solutes was approached from both directions by associating the tracers with either salt or borate glass before equilibration. The 30-min. stirring period appeared to be adequate to obtain reproducible values of the distribution coefficients of the solutes studied, regardless of the phase with which the solute was initially associated. The rapid exchange of sodium between phases was demonstrated by experiments in which Na^{22} -labeled borax was equilibrated with unlabeled sodium chloride in one trial and unlabeled borax was equilibrated with Na^{22} -labeled sodium chloride in another trial. In both cases, with 10 min. mixing after fusion, complete exchange of Na^{23} with inactive sodium had occurred in each phase.

Results

Figure 1 shows the immiscibility curve of the solvent system constructed from phase analysis data. It will be noted by observation of the tie lines in the expanded view of the NaCl corner that very little borate phase dissolves in the salt phase until the Na_2O content of the system becomes rather high. The same compositions of conjugate phases, and hence the same distribution coefficient values, result when the total composition of the solvent system corresponds to any point along a particular tie line. The variable chosen to fix the compositions of the two phases, M_B , is the mole per cent Na_2O of $\text{Na}_2\text{O} + \text{B}_2\text{O}_3$ in the borate phase. The value of this quantity varies regularly as the tie lines go from the $\text{B}_2\text{O}_3-\text{NaCl}$ binary line to the plait point and may be illustrated on Figure 1 by projecting a line from the NaCl corner through the borate phase point on the curve onto the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ binary line.

Figure 2 shows the variation of the distribution coefficients of solute ions as a function of M_B . For comparison, the distribution coefficient curves of the macro ionic constituents Na^+ and Cl^- are shown, calculated from phase analysis data in terms of moles per unit weight (eq. 1). It is seen that the differences among the behaviors of different groups in the periodic table are large. Also, the variation of K_d with M_B is larger with the more highly charged cations.

The manner in which K_d values of individual elements vary with phase composition is sufficiently characteristic that individual element as well as group separations may be made. Alkaline earth and rare

(2) W. G. Domask and K. A. Kobe, *Anal. Chem.*, **24**, 989 (1952).

(3) B. L. Dunicz and R. C. Scheidt, "Solute Distribution in the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{NaCl}$ System. III. Immiscibility Diagrams of Molten Sodium Halide-Sodium Polyborates." USNRDL-TR-752, May 22, 1964.

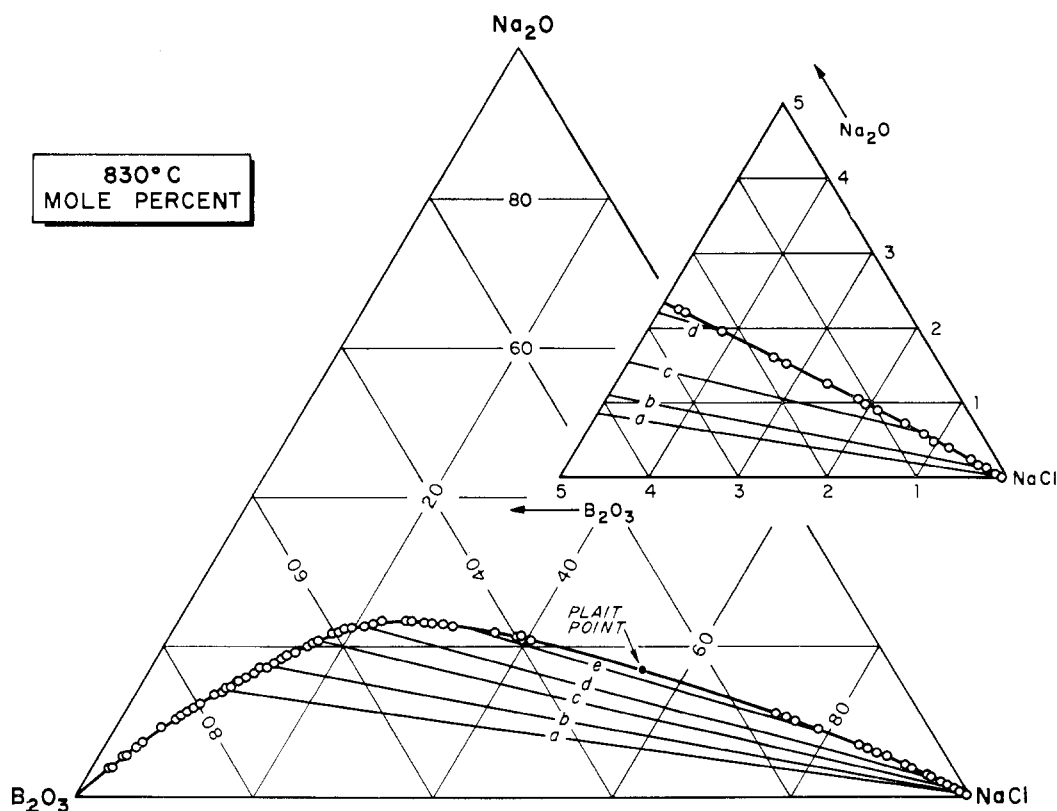
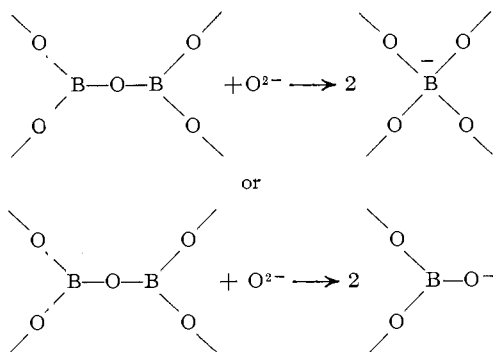


Figure 1.—Immiscibility curve in the Na_2O - B_2O_3 - NaCl system at 830° .

earth ions show good separation near their peak values. Here, the separation factor for Ba^{+2} and Sr^{+2} is about 2.7. The maximum separation factor for Nd^{+3} and Eu^{+3} is about 1.9, which is rather good for rare earths only 3 atomic numbers apart. The K_d curve for silver is much lower than that of any other solute studied.

Discussion

The structure of liquid B_2O_3 is still controversial. It is believed to be a polymer whose extent is, according to one extreme of opinion, an infinite three-dimensional network of trigonally coordinated boron atoms with oxygen,⁴ or, at the other extreme of opinion, B_4O_6 molecules tied together by dative bonds.⁵ In any case, it is generally agreed that when alkali oxide is added to boron oxide, the oxygen adds to the structure as follows



These negatively charged groups have a structural resemblance to the functional groups in organic resin

(4) W. H. Zachariasen, *J. Am. Chem. Soc.*, **54**, 3841 (1932).

(5) B. Ottar and W. L. Ruigh, *Phys. Chem. Glasses*, **3**, 95 (1962).

cation exchangers. Alkali metal ions do not enter the covalently-bonded boron-oxygen structure but locate themselves near the negatively charged groups by ionic bonding so as to screen their positive charges. In contrast to boron and oxygen atoms, they are quite labile and may be readily replaced by other cations whose charges require more screening than do alkali metal ions. The buildup of highly localized negative charges in the borate phase as alkali oxide is added is indicated by the sharply increasing preference of highly charged cations for this phase.

When a molten salt and its solutes are in equilibrium with molten borate, solutes are distributed between borate and salt phases on the basis of two mechanisms: First, there is the relative tendency of the solute to dissolve in the ionic liquid on the one hand or in the relatively nonpolar liquid on the other. Second, if the solutes are cations, they will compete with the alkali metal ions and with each other for positions near the negatively charged functional groups in the borate phase. In the latter instance the borate phase acts as a liquid cation exchanger. It has been demonstrated by a separate experiment⁶ that the mechanism of ion exchange is actually involved. The degree to which each mechanism contributes to the distribution coefficient is strongly dependent upon the alkali oxide content of the solvent system.

Reasons for the individual nature of the K_d curves are now evident. Maxima and minima in the rubidium and cesium curves may be explained as follows: At low values of M_B , cations in general prefer the ionic

(6) R. C. Scheidt and E. C. Freiling, *J. Phys. Chem.*, **69**, 1784 (1965).

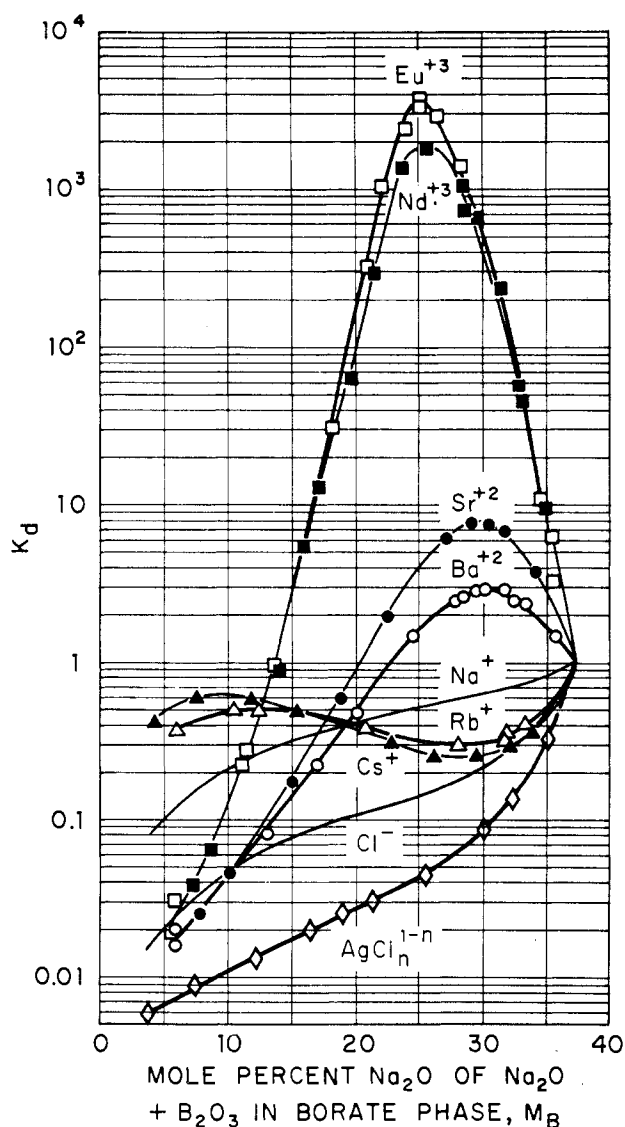


Figure 2.—Distribution of solutes between immiscible liquid phases in the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{NaCl}$ system at 830° .

salt phase, since their charges may be better screened. Smaller cations, having higher field strength, prefer it more than do larger ones, so that the order of K_d is $\text{Cs}^+ > \text{Rb}^+ > \text{Na}^+$. Since the concentration of negatively charged sites in the borate phase is low at this point, the selectivity of cations is due more to the difference in solvation efficiency than to cation exchange. Both of these factors affecting the selectivity are changed as the sodium oxide content in the borate phase increases. First, more sodium chloride dissolves in the borate phase, increasing its ionic strength and increasing the solubility in general of ionic solutes in this phase. Second, the increasing Na_2O produces additional negative exchange sites in the borate phase, and the selectivity of cations becomes more dependent on competition for exchange sites rather than difference in ionic strength of the phases. The smaller Na^+ ion, with higher field strength, wins out over Cs^+ and Rb^+ for the exchange sites, and when these sites are plentiful there is a reverse in the order of selectivity, this time with the higher field strength ions preferring

TABLE I
DISTRIBUTION COEFFICIENTS AND FIELD STRENGTHS OF IONS

Ion	Radius, Å.	Field strength,		K_d at $M_B = 25$
		Z/r^2		
Cs^+	1.67	0.36		0.275
Rb^+	1.48	0.46		0.32
Na^+	0.98	1.04		0.51
Ba^{2+}	1.31	1.17		1.7
Sr^{2+}	1.15	1.51		4.0
Nd^{3+}	0.99	3.06		1750
Eu^{3+}	0.97	3.19		3400

the borate phase. The variation in the influence of these two factors causes the cesium and rubidium curves to go through maxima and then to cross each other as the selectivity is reversed. As the plait point is approached, all the K_d values must approach unity, causing minima in the curves at high M_B values.

The higher charge of alkaline earth ions gives rise to differently shaped curves. At low M_B , these ions have more affinity for the ionic melt than do alkali ions. As M_B increases, their K_d values then increase much more rapidly until peak values are approached, due to greater influence of the negative functional groups on the higher charges. This influence also causes an order of increasing selectivity for the borate phase with decreasing ion size to occur at lower values of M_B . However, it may be seen by extrapolating the alkaline earth K_d curves to a low M_B value that these curves should cross as do alkali metal curves. This is true also of the K_d curves of rare earth ions, which have the same general shape as those of alkaline earths except that their higher charge magnifies all the effects. K_d values of both alkaline earth and rare earth ions begin to decrease shortly after $M_B = 25$, because the two phases become rapidly more miscible after this point.

Of the groups of elements giving +1, +2, and +3 ions, the alkali metal, alkaline earth, and rare earth groups should show the least tendency toward complex ion formation and should allow the best evaluation of the effects of ionic size and charge. If the selectivity of the borate network for cations depends only upon coulombic forces, then the distribution of the cations should have the same order as their field strengths. Table I shows the field strengths of these cations and their K_d values at $M_B = 25$, where exchange sites are plentiful. The order of selectivity is indeed that of the field strength.

Evidence has been offered that silver forms chloride complexes in molten salts,⁷ although in $\text{LiCl}-\text{KCl}$ melts it has been observed to migrate toward the anode during electrolysis.⁸ It seems quite possible, however, that a trace of silver in a chloride melt might be present as a complex chloro anion. If silver were present as Ag^+ in molten NaCl , its K_d curve would be expected to at least vaguely resemble that of Na^+ or Rb^+ , since the ionic radius of Ag^+ is between that of Na^+ and Rb^+ . Actually, the K_d curve falls well

(7) H. T. Tien and G. W. Harrington, *Inorg. Chem.*, **3**, 215 (1964); *ibid.*, **3**, 1333 (1964); J. Braunstein, H. Braunstein, and A. S. Minano, *ibid.*, **3**, 1334 (1964).

(8) G. Alberti, G. Grassini, and R. Trucco, *J. Electroanal. Chem.*, **3**, 283 (1962).

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

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The enthalpies of solution of ten different solid oxides in liquid V_2O_5 at $685 \pm 5^\circ$ have been measured. All solutes studied except BeO and CuO showed negative enthalpies of solution, the magnitude increasing sharply in the sequence $\text{BeO} < \text{MgO} < \text{CaO} < \text{SrO} < \text{BaO}$. 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 $\text{PbO}-\text{V}_2\text{O}_5$ 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 $685 \pm 5^\circ$.

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 ($\Delta \bar{H}_{\text{MO}}$) 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 $\Delta \bar{H}_{\text{MO}}$ increases sharply in the sequence $\text{BeO} < \text{MgO} < \text{CaO} < \text{SrO} < \text{BaO}$, *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 discuss 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: $\text{acid} + \text{O}^{2-} = \text{base}$. 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).