

TABLE I
CONDUCTANCE PARAMETERS FOR Bu_4NBr IN METHANOL AT 25°

| Λ_0 | \bar{d} | K_A | σ_A |
|--------------|-------------|-----------|------------|
| 95.31 ± 0.02 | 2.85 ± 0.02 | | 0.02 |
| 95.32 ± 0.02 | 2.84 ± 0.03 | | 0.03 |
| 95.38 ± 0.02 | 3.2 ± 0.1 | 2.8 ± 0.6 | 0.01 |
| 95.42 ± 0.01 | 3.4 ± 0.1 | 4.3 ± 0.4 | 0.007 |

When the data for the nitrobenzene-methanol mixtures² were analyzed by the computer program for associated electrolytes negative \bar{d} or K_A resulted, or the standard deviations of the parameters were larger than the parameters. These data covered too narrow a concentration range for any kind of meaningful interpretation. On the other hand, the data of Witschonke and Kraus⁹ for this salt in pure nitrobenzene had the necessary precision and concentration range. Their data gave $K_A = 56 \pm 3$ and $\bar{d} = 4.9 \pm 0.7$ and $\sigma_A = 0.03$. Thus the \bar{d} is reasonable, the fit is good, and the K_A is large enough so that the assumption of association of this salt in nitrobenzene is justified. When treated as an unassociated electrolyte in nitrobenzene an \bar{d} of 0.12 results which is unreasonably low indicating considerable association.

Considering the above analysis the only experimental result needing explanation is why Bu_4NBr is associated in nitrobenzene and not in methanol or nitromethane¹⁰ although these solvents have about the same dielectric constant. Stabilization of the free ions by solvation will explain the lack of association in methanol, but solvation of the free ions by nitromethane and not by nitrobenzene is unlikely. Hyne's¹ suggestion of an interaction between the nitrobenzene molecule and the Bu_4NBr ion pair is one possible explanation. The dimensions involved could be correct for nitrobenzene but not for nitromethane.

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(9) C. R. Witschonke and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 2472 (1947).

(10) R. L. Kay, S. C. Blum, and H. I. Schiff, *J. Phys. Chem.*, **67**, 1223 (1963).

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The Enthalpy of Transformation, $\delta\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$

Sir:

It is well known that in the oxygen bomb calorimetry of aluminum compounds, a part of the reaction product sometimes occurs in the form of $\delta\text{-Al}_2\text{O}_3$. This is a metastable phase of tetragonal but so far not fully determined structure,¹ whose enthalpy of transformation to the stable form $\alpha\text{-Al}_2\text{O}_3$ (corundum) has not yet been established. As a result, there may be some uncertainty associated with the adopted value of the heat of combustion of aluminum to form Al_2O_3 .²

We have recently become interested in the possible use of high-temperature solution calorimetry for the study of the thermochemistry of certain inorganic solids. Of particular interest to us are solids such as Al_2O_3 , which cannot be dissolved in the common room-temperature

(1) H. P. Rooksby, *J. Appl. Chem.*, **8**, 44 (1958).

(2) R. C. King and G. T. Armstrong, private communication.

solvents. We have found that this oxide dissolves readily in a lead-cadmium borate melt (composition approximately $9\text{PbO} \cdot 3\text{CdO} \cdot 4\text{B}_2\text{O}_3$). Using this solvent we have determined the heats of solution of $\alpha\text{-Al}_2\text{O}_3$ and of $\delta\text{-Al}_2\text{O}_3$ at 705°. For $\alpha\text{-Al}_2\text{O}_3$ we have carried out several determinations with $\alpha\text{-Al}_2\text{O}_3$ of different origin. The mean value of the enthalpy of solution is $+7.6 \pm 0.2$ kcal./mole.

We used two different specimens of $\delta\text{-Al}_2\text{O}_3$ (I and II), both obtained as reaction products in a bomb-calorimetric study of Al_4C_3 .² Duplicate samples of these specimens were dissolved in the same solvent at the considered temperature. The enthalpies of solution were as follows: I, 4.9, 5.0; II, 4.5, 5.1; mean, $+4.9 \pm 0.3$ kcal./mole.

Finally we converted a small sample of $\delta\text{-Al}_2\text{O}_3$ to $\alpha\text{-}$ by heating it for 0.5 hr. at 1450°. The enthalpy of solution of this product was 7.4 kcal./mole, *i.e.*, within the range of the results obtained for the several other samples of $\alpha\text{-Al}_2\text{O}_3$.

Thus we have for the process: $\text{Al}_2\text{O}_3(\delta) = \text{Al}_2\text{O}_3(\alpha)$; $\Delta H^\circ_{978} = -2.7 \pm 0.4$ kcal./mole.

Experimental details of this work will be incorporated in a more extensive study of the various forms of Al_2O_3 and will be published elsewhere.

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Stereochemistry of the 1,2-Diaminocyclohexane- $\text{N,N}'$ - tetraacetatoaquoferrate(III) Ion,¹ $\text{Fe}(\text{OH}_2)\text{Z}^-$

Sir:

Inasmuch as 1,2-diaminocyclohexane- $\text{N,N}'$ -tetraacetic acid (hereafter DCTA or H_4Z) generally forms more stable complexes² with metal ions than does the closely related ethylenediaminetetraacetic acid (EDTA or H_4Y), one must suppose that the cyclohexane ring of DCTA somehow promotes chelation. It is clear, on the other hand, that the constraints imposed by multiple ring formation must be no less important for chelation by DCTA than by EDTA, and constraints of just this kind are assigned primary responsibility for the unconventional stereochemistry of the sexadentate seven-coordinate aquo complexes, $\text{Fe}(\text{OH}_2)\text{Y}^-$ and $\text{Mn}(\text{OH}_2)\text{Y}^{2-}$, formed by EDTA with $\text{Fe}(\text{III})$ ^{3,4} and Mn -

(1) Support of this study by the National Science Foundation, the National Institutes of Health, and the Advanced Research Projects Agency is gratefully acknowledged. We thank also the Cornell Computing Center Mr. Richard C. Lesser, Director.

(2) *Cf.*, S. Chaberek and A. E. Martell, "Organic Sequestering Agents," John Wiley and Sons, Inc., New York, N. Y., 1959, pp. 572-576, for tabulated stability constants of DCTA and EDTA chelates and Chapter 4 for discussion of chelate stabilities.

(3) M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *Inorg. Chem.*, **3**, 34 (1964).

(4) *Cf.* J. L. Hoard, G. S. Smith, and M. D. Lind in "Advances in the Chemistry of the Coordination Compounds," The Macmillan Company, New York, N. Y., 1961, pp. 296-302, for a *priori* analysis predicting the existence of seven-coordinate $\text{Fe}(\text{OH}_2)\text{Y}^-$.