

240, 6.5 and 10 min. Mercury time being used for the two determinations.

The Fletcher-Powell minimization required, in this case, integration of a set of seven differential equations. For these, each integration over 50 points required 5.5 sec., but the same results as given by Rosenbrock's method were obtained with 22 and 31 integrations, consuming 2.1 and 2.7 min., respectively.

It may be seen from these examples that either minimization procedure, coupled with Runge-Kutta integration, yields a suitable method of determining rate constants when the rate equations cannot be integrated. In general, the Fletcher-Powell procedure will, because of its greater speed, be preferred for routine use after a mechanism has been established. The Rosenbrock method is usually preferable, however, for the preliminary investigation of a problem, as much less alteration in the computer program is required when a different set of rate equations is to be tried. Alternatively, preliminary investigation might be done on an analog computer, as the qualitative effect of variations in the rate constants could be easily determined. For determining the best values of the rate constants, however, digital computation is clearly superior, as the bookkeeping can be done by the machine. On an analog computer, the variation of the rate constants would have to be carried out by the operator, a procedure of very low efficiency, particularly if more than two constants are to be varied.

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The Association of Tetrabutylammonium Bromide in Methanol-Nitrobenzene Mixtures

Sir:

In a recent publication,¹ a molecular interpretation was presented to explain the abnormal association behavior of tetrabutylammonium bromide (Bu_4NBr) in methanol-nitrobenzene mixtures. It was claimed that association constants for this electrolyte in a large number of solvent systems gave a single straight line when the log was plotted against the reciprocal dielectric constant. The point for pure methanol was on this line, but as nitrobenzene was added, the association constant showed a minimum and finally increased to a point above the line for pure nitrobenzene. This behavior could not be explained by coulombic interactions since both solvents have approximately the same dielectric constant. The enhanced K_A for Bu_4NBr in the nitrobenzene-rich mixtures was explained by a specific interaction between a nitrobenzene molecule and a Bu_4NBr ion pair. In the methanol-rich mixtures a specific solvation of Br^- ion by methanol was postulated.

We believe that the minimum described above is an artifact due in part to the data and in part to the method used to calculate K_A . The association constants considered were those of Sadek and Fuoss² and were obtained from their conductance data by means of the Fuoss-Shedlovsky method. These data

cover far too narrow a concentration range ($1-8 \times 10^{-4} N$) for the accurate determination of association constants. Furthermore, in the Fuoss-Shedlovsky method, the Onsager limiting conductance equation is used to evaluate the conductance of the free ions. This procedure is known to be completely unreliable for K_A much less than 100. The association constants under consideration here ranged from about 26 for methanol to 45 for nitrobenzene solutions. The more recent conductance data for this salt in pure methanol³ were not considered nor was the much more recent analysis⁴ based on the Fuoss-Onsager conductance theory.⁵ In that analysis, Fuoss claimed definite association in both pure solvent components but no association for the intermediate mixtures. However, the not too reliable Λ_A method was used in that analysis. An ion size $\bar{a} = 6$ was found to fit the data in other solvent mixtures of lower dielectric constant where association was substantial. Fuoss used this same value of \bar{a} to eliminate one of the unknowns in the conductance equation. This assumption of a constant \bar{a} for every solvent mixture is extremely risky since it has been shown to be invalid for dioxane-water mixtures.⁶

We have analyzed the data^{2,3} by the Fuoss-Onsager conductance theory⁷ on an IBM 7070 computer using a Fortran program similar to that described by Kay.⁸ The early data² for Bu_4NBr in methanol solution gave an extremely low \bar{a} and poor precision when treated as an unassociated electrolyte and a negative value of \bar{a} when treated as an associated electrolyte. The 1954 data for methanol solutions, on the other hand, gave $\Lambda_0 = 96.20 \pm 0.03$ and $\bar{a} = 2.8 \pm 0.3$ with a standard deviation of 0.03 when Bu_4NBr was treated as unassociated and gave a negative K_A when treated as an associated electrolyte. These latter results indicate that Bu_4NBr is slightly, if at all, associated ($K_A < 10$) in methanol.

In order to verify this result, precise conductance measurements were carried out for Bu_4NBr in anhydrous methanol over the concentration range $3-47 \times 10^{-4} M$. The actual conductances will be reported with a more comprehensive study of the quaternary ammonium salts in H_2O , D_2O , and methanol at a later date. The results of a Fuoss-Onsager analysis⁷ of two runs are recorded here in Table I where the first two entries resulted from treating Bu_4NBr as an unassociated electrolyte while the last two entries resulted from treating Bu_4NBr as an associated electrolyte. These results indicate, as found above with the older data, that Bu_4NBr is in fact associated only to a very slight extent, if at all, in methanol. The association constant of about 3.5 could be the result of about a 10% error in the evaluation of the electrophoretic effect, or a small amount of $c^{1/2}$ dependence that has been neglected in the conductance theory. In any case K_A is considerably less than 26, the value used by Hyne, and there is no doubt that association of this salt in methanol solutions is considerably less than that predicted from the association behavior in solvent mixtures of much lower dielectric constant.

(3) H. Sadek and R. M. Fuoss, *ibid.*, **76**, 5897 (1954).

(4) H. Sadek and R. M. Fuoss, *ibid.*, **81**, 4507 (1959).

(5) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **61**, 668 (1957).

(6) J. E. Lind, Jr., and R. M. Fuoss, *ibid.*, **65**, 999, 1414 (1961).

(7) R. M. Fuoss and F. Accascina, "Electrolyte Conductance," Interscience Publishers, Inc., New York, N. Y., 1959.

(8) R. L. Kay, *J. Am. Chem. Soc.*, **82**, 2099 (1960).

(1) J. B. Hyne, *J. Am. Chem. Soc.*, **85**, 304 (1963).

(2) H. Sadek and R. M. Fuoss, *ibid.*, **72**, 301 (1950).

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.

Acknowledgment.—We are indebted to Drs. G. T. Armstrong and R. C. King of the National Bureau of Standards for providing us with the samples of $\delta\text{-Al}_2\text{O}_3$. This work has been supported in part by the National Science Foundation (GP-1993).

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

Sir:

Inasmuch as 1,2-diaminocyclohexane-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. 372-376, 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 $\text{Fe}(\text{OH}_2)\text{Y}^-$.