ray powder pattern revealed the presence of very small amounts of $[(C_2H_5)_3NH]_2B_{12}H_{12}$.

Decomposition of Tetraethylammonium Pentadecahydrodecaborate(1−).—A slurry of 1.0 g of $(C_2H_5)_4NB_{10}H_{15}$ in 20 ml of mesitylene was refluxed and stirred for 24 hr, then cooled to room temperature. The solid phase was collected on a filter, washed with pentane, and recrystallized three times from acetonitrile to yield 0.18 g of $[(C_2H_5)_4N]_2B_{12}H_{12}$.

The mesitylene filtrate was treated at reflux with 1.0 g of triethylamine for 6 hr in an attempt to convert any decaborane which might have been present in this solution to the insoluble $[(C_2H_5)_3NH]_2B_{10}H_{10}$. However, none was formed.

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CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY,
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The Optical Spectrum of Bismuth(I) in the Molten Aluminum Bromide–Sodium Bromide Eutectic[1a]

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Recently Bi^+ was prepared[2] by reduction of dilute solutions of $BiCl_3$ in the molten $AlCl_3$–NaCl eutectic at 310°. It was shown that the absorption spectrum of this ion is rationalized very well in terms of intraconfigurational $6p^2 \rightarrow 6p^2$ transitions split by a ligand field with a symmetry lower than cubic.[3] Because of the important role of the ligands in determining the details of the spectrum, it is interesting to observe the effects of changing from a chloride to a bromide environment. Accordingly, we prepared Bi^+ by reduction of dilute solutions of $BiBr_3$ in the molten eutectic consisting of 68 mole % $AlBr_3$ and 32 mole % NaBr and determined its absorption spectrum in the visible and near-infrared regions.

The experimental and theoretical procedures parallel the previous work[2,3] almost exactly and will not be repeated here. A small difference between these investigations was in the preparation of the hydrogen halides used for the synthesis of aluminum halides. In the present investigation HBr was prepared by direct reaction between H_2 and Br_2 in the presence of a platinum catalyst at 350°.

Figure 1 provides a comparison between the spectrum of Bi^+ in the $AlBr_3$–NaBr eutectic at 250° (curve A) and that of the same entity in the $AlCl_3$–NaCl eutectic at 310° (curve B). (The latter spectrum is taken from ref 2.) The ligands coordinated to Bi^+ have not been identified for either of these media but almost certainly they are either halide or haloaluminate ions. We favor the latter alternative because we expect the concentration of haloaluminate ions in the AlX_3–NaX eutectic melts (X = Cl or Br) to greatly exceed the concentration of halide ions that are not coordinated to aluminum. Thus, in Figure 1 we presume that curve A is a bromoaluminate complex of Bi^+ while curve B is a chloroaluminate complex. The striking similarity between these spectra is evident.

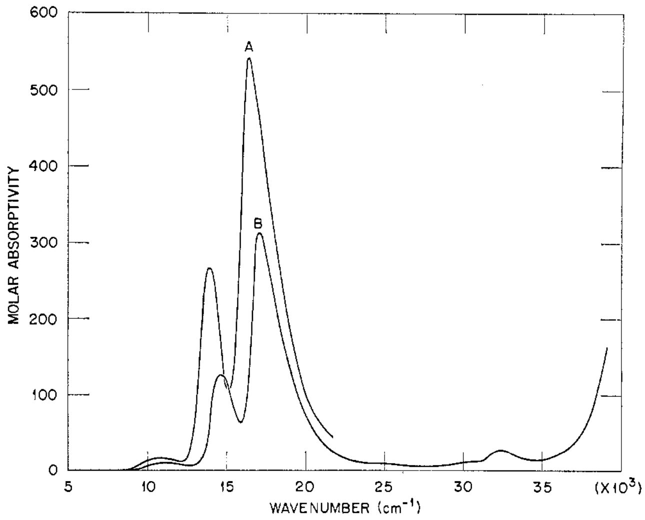

Figure 1.—Spectra of Bi^+ in haloaluminate media. (A) Solvent was molten $AlBr_3$–NaBr eutectic at 250°. (B) Solvent was molten $AlCl_3$–NaCl eutectic at 310° (from ref 2).

Curve A in Figure 1 shows three absorption bands with maxima at about 10,800, 13,900, and 16,400 cm^{-1}. The decidedly skewed shapes of the 10,800 and 16,400 cm^{-1} bands suggest that they consist of two or more unresolved component bands. The 13,900 cm^{-1} band is only slightly skew symmetric but the corresponding band in the chloride melt was unambiguously shown to be a doublet with a separation of about 900 cm^{-1}. We obtained a rough estimate of the splitting of the 10,800 and 13,900 cm^{-1} bands by performing a Gaussian profile analysis with a CDC-1604 computer (see ref 2). The results are listed in Table I.

TABLE I
EXPERIMENTAL AND CALCULATED TRANSITION ENERGIES FOR Bi^+ IN MOLTEN $AlBr_3$–NaBr

Exptl, cm^{-1}	Calcd,[a] cm^{-1}	Excited state[b]
10,300	10,300	$^3P_1$ (±1)
12,100	. . .	
13,700	13,800	$^3P_1$ (0)
14,200	14,200	$^3P_1$ (±2)
16,400	16,100	$^3P_2$ (0)
	16,400	$^3P_2$ (±1)

[a] Parameter values used were F_2 = 976 cm^{-1}, λ = 5020 cm^{-1}, $B_0{}^2$ = 8700 cm^{-1}, and $B_2{}^2$ = 0. [b] Notation gives the free-ion origin followed by the J_z value in parentheses.

The secular equation[2] for a p^2 electronic system was fitted to these data with the results shown in Table

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[1] (a) Research sponsored by U. S. Atomic Energy Commission under contract with the Union Carbide Corporation. (b) The Technical University of Denmark, Chemistry Department A, Lyngby, Denmark.

[2] N. J. Bjerrum, C. R. Boston, and G. P. Smith, *Inorg. Chem.*, **6**, 1162 (1967).

[3] H. L. Davis, N. J. Bjerrum, and G. P. Smith, *ibid.*, **6**, 1172 (1967).

I. The very weak band at 12,100 cm^{-1} is unaccounted for and is possibly related to a similar weak band found in the spectrum of Bi^+ in chloride melts under special conditions.[2] The ligand-field parameters used for this fit were $F_2 = 976$ cm^{-1}, $\lambda = 5020$ cm^{-1}, $B_0^2 = 8700$ cm^{-1}, and $B_2^2 = 0$. We cannot find an alternative set of parameters, decidedly different from these, that will fit the spectrum in a satisfactory way.

The electron-repulsion parameter, F_2, shows the expected downward shift over the series free ion, chloride ligands, and bromide ligands; namely, 1175, 1056, and 976 cm^{-1}, respectively.

Correspondence

Study of Some Cyano-Metal Complexes by Nuclear Magnetic Resonance. IV. The Activation Energy of Electron Transfer between Ferri- and Ferrocyanide Ions[1]

Sir:

We have previously reported[2] the study of the kinetics of electron transfer between the ferri- and ferrocyanide ions in aqueous solution by the N^{14} nuclear magnetic resonance (nmr) technique. The Arrhenius plot for the reaction rate (Figure 2 of ref 2) was found to be nonlinear and was tentatively interpreted as being due to a change in the reaction mechanism with the temperature. We felt that this is a rather puzzling effect and thus have remeasured the rate constants as a function of the temperature with higher precision and over a considerably larger range of concentrations.

The experimental procedure and the interpretation of the spectra were identical with those described previously.[2] We found that the main sources of error in our previous work were (a) line broadening due to slight overmodulation and (b) exchange broadening (denoted as $\Delta(1/T)$), which was in several cases within experimental error. In the present work we tried to avoid any overmodulation and rejected those measurements in which $\Delta(1/T) < 0.3$ gauss.

The Arrhenius plot for a variety of $K_3Fe(CN)_6$–$K_4Fe(CN)_6$ concentrations is given in Figure 1. The dependence of log K on $1/T$ is linear in the temperature range 25–65°. The result is $E = 4.2 \pm 0.6$ kcal/mole[3] and a preexponential factor equal to 1.2×10^8 sec^{-1}. The activation parameters are $\Delta H^{\ddagger} = 3.6$ kcal/mole and $\Delta S^{\ddagger} = -23.7$ eu/mole at 39°.

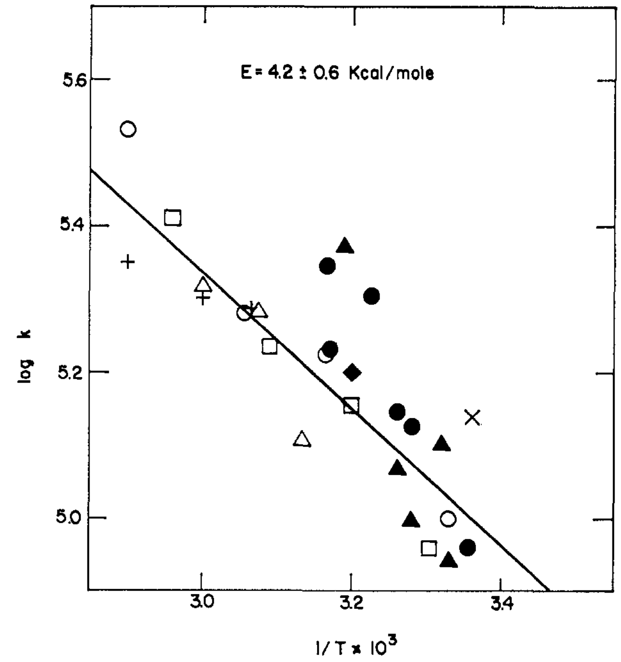

Figure 1.—An arrhenius plot of the rate of electron transfer between $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$. $K_3Fe(CN)_6$–$K_4Fe(CN)_6$: +, 0.15 *M*–0.15 *M*; △, 0.20 *M*–0.20 *M*; ○, 0.25 *M*–0.25 *M*; ●, 0.30 *M*–0.30 *M*; ×, 0.35 *M*–0.35 *M*; ◆, 0.30 *M*–0.20 *M*; ▲, 0.40 *M*–0.20 *M*; □, 0.20 *M*–0.40 *M*.

TABLE I

KINETIC RESULTS FOR $H_3Fe(CN)_6$–$H_4Fe(CN)_6$ MIXTURES

Concn,[a] *M*	*t*, °C	Line width, gauss	$\Delta(1/T)$, gauss	*k*, $mole^{-1}$ sec^{-1}
0.2	23.5	2.72	0.22	1.8×10^3
0.2	32.5	2.51	0.31	2.6×10^3
0.2	44	2.28	0.43	3.6×10^3
0.2	51.5	2.18	0.54	4.5×10^3
0.3	24	2.74	0.26[b]	1.4×10^3
0.3	38	2.40	0.36[b]	2.0×10^3
0.3	55	2.05	0.53[b]	3.0×10^3

[a] Concentration given for each component [b] The "natural" line width correction is taken from 0.4 *M* solutions because a concentration of 0.6 is not attainable.

It should be noted that the value of E given above is not necessarily the true activation energy of the reaction. Catiyn resonance measurements[1] have shown that their catalytic action is due to ion-pair formation which is a temperature-dependent process. The ΔH for complexation has been estimated[4] for $K^+Fe(CN)_6^{3-}$, the value being −8 kcal/mole, but it is unknown for $K^+Fe(CN)_6^{4-}$. Taking into account this factor might alter the value of E by as much as a factor of 2.

We have attempted to measure the effect of substituting the potassium with hydrogen or cesium cations on the activation energy. The results for the $H_3Fe(CN)_6$–$H_4Fe(CN)_6$ system are shown in Table I. The rates were evaluated using the slow-exchange approximation

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[1] Part III: to be published in the proceedings of the XIVth Colloque Ampere, Ljubljana, Yugoslavia, Sept 1966.

[2] M. Shporer, G. Ron, A. Loewenstein, and G. Navon, *Inorg. Chem.*, **4**, 361 (1965).

[3] Mean-square deviation calculated by least squares.

[4] D. W. Larsen and A. C. Wahl, *ibid.*, **4**, 1281 (1965).