not be explained satisfactorily by the no-bond structure contribution alone. They are probably due to some extent to the ionic contribution in excess of the amount required for the formation of the semiionic 3c–4e bonds. This seems plausible if we consider the contribution of the following structures to the over-all potential energy

$$\underset{\text{I}}{\text{Y–}\bar{\text{X}}\text{–Y}} \longleftrightarrow \underset{\text{II}}{\text{Y}^-\ \text{X–Y}} \longleftrightarrow \underset{\text{III}}{\text{Y–X}\quad \text{Y}^-}$$

The migration of the negative charge in II and III results in a shortening of the bond length of the remaining X–Y part causing a strong coupling effect. Therefore, an additional increase of the relative contribution of the ionic structures II and III should decrease the valence force constant, f_r, and, thereby, the bond order, n (since valence force constants represent only the covalent contribution to the over-all bond energy) and should increase the coupling constant, f_{rr}, over that of a pure semiionic 3c–4e bond.

(iv) The relative ionic bond contribution to the over-all potential energy should increase in the order anion > neutral molecule > cation, if otherwise comparable anions, neutral molecules, and cations are considered. This is due to a decrease in the amount of negative charge on the central atom resulting in a reduction of the electronegativity of this atom.

(v) The relatively low mass of the central atom in HCl_2^- and HF_2^- should further enhance the coupling effect in these anions.

(vi) The electronegativity difference between the X atom and the Y atom does not seem to be the dominating effect, since it does not agree with the observed orders: $HCl_2^- > HF_2^-$ and $BrCl_2^- > ICl_2^- > ClF_2^-$.

Acknowledgment.—We thank Dr. A. E. Pavlath for his helpful support and Dr. A. C. Jones of Shell Development Co., Emeryville, Calif., for the use of the Raman spectrophotometer.[30]

---

(30) After completing this paper we learned about the work of A. G. Maki and R. Forneris on the infrared and Raman spectra of some trihalide ions: ICl_2^-, IBr_2^-, I_3^-, I_2Br^-, and $BrICl^-$, to be published in *Spectrochim. Acta.* We are indebted to Dr. Maki for making a preprint of their paper available to us. Their findings on these anions are in good agreement with our results on ClF_2^-. Their observations on the infrared and Raman spectra of $RbICl_2$ are very similar to those made by us for $RbClF_2$ and $CsClF_2$. Their interpretation of the large interaction constants as being due to an unusually flat bottom of the potential well for the central atom of the trihalide ions parallel ours (which uses the bond order n) since both explanations assume that the interaction constant increases as the central atom to ligand bond strength decreases. Therefore, both Maki's interpretation and ours disagree with Coulson's prediction[28] for this type of molecules: "the greater the bond energy the larger f_{rr} would be, and only when the bond energy was very small would we expect negative f_{rr}."

CONTRIBUTION FROM THE METALS AND CERAMICS DIVISION,
OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENNESSEE 37830

Lower Oxidation States of Bismuth. Bi^+ and $[Bi_5]^{3+}$ in Molten Salt Solutions[1a]

BY NIELS J. BJERRUM, CHARLES R. BOSTON, AND G. PEDRO SMITH[1b]

Received December 10, 1966

Principal items reported here are the preparation, identification, and absorption spectra of Bi^+ and $[Bi_5]^{3+}$ contained in dilute solutions in the molten salt eutectics composed of 63 mole % $AlCl_3$–37 mole % NaCl and 72 mole % $ZnCl_2$–28 mole % KCl and equilibrium quotients for equilibria involving Bi^+ and $[Bi_5]^{3+}$. Topics of less significance, or else treated in less detail, are the following: procedures for preparing high-purity $AlCl_3$–NaCl and $ZnCl_2$–KCl mixtures suitable as spectrophotometric solvents, the density of the molten $ZnCl_2$–KCl eutectic as a function of temperature, and the absorption spectrum of Bi^{3+} in the $AlCl_3$–NaCl eutectic. The investigation consisted of spectrophotometric measurements on equilibrium reaction mixtures that involved bismuth metal (as a separate liquid phase), Bi^{3+}, Bi^+, and $[Bi_5]^{3+}$ in various combinations and concentrations. The data were insufficient to give any information on ligands coordinated to these entities.

Introduction

Bismuth metal reacts with dilute solutions of $BiCl_3$ in liquid eutectic mixtures of $AlCl_3$–NaCl or $ZnCl_2$–KCl to form colored melts. In a recent short communication[2] we asserted that the reaction products formed under most conditions are Bi^+ and $[Bi_5]^{3+}$ with a third (unidentified) product formed under special conditions. In the present paper we give the evidence upon which these claims are based. We have since prepared Bi^+ by hydrogen reduction of $BiCl_3$ in the $AlCl_3$–NaCl eutectic.

The designations Bi^+ and $[Bi_5]^{3+}$ are intended to specify the oxidation states and numbers of bismuth atoms per molecular unit of the reaction products. We do not intend these designations to imply anything regarding coordination between bismuths and surroundings atoms.

Previous studies of oxidation states of bismuth between zero and 3+ have produced only a few firm facts regarding molecular entities although partially supported speculations have been numerous. Much

---

(1) (a) Research sponsored by the U. S Atomic Energy Commission under contract with the Union Carbide Corp. Presented at the 22nd Annual Southwest Regional Meeting of the American Chemical Society, Albuquerque, N. M., Nov 30–Dec 2, 1966. (b) Department of Chemistry, University of Tennessee, Knoxville, Tenn.

(2) N. J. Bjerrum, C. R. Boston, G. P. Smith, and H. L. Davis, *Inorg. Nucl. Chem. Letters*, **1**, 141 (1965).

of this research has been concerned with homogeneous liquid mixtures of bismuth metal and pure bismuth trihalides. Entities postulated to occur in these mixtures include bismuth atoms, Bi_2 molecules, and $[Bi_n]^{n+}$ ions with *n* values from 1 to 4.[3-7] Most of the accumulated evidence points to the formation of Bi^+ when very small amounts of bismuth metal react with bismuth trihalide melts, but the evidence is by no means complete. On the basis of electrochemical experiments and phase-diagram studies Topol, Yosim, and Osteryoung[5] proposed that Bi^+ occurs at very low concentrations and polymerizes to $[Bi_4]^{4+}$ at higher concentrations. Spectrophotometric measurements by Boston, Howick, and Smith[6,7] supported this interpretation. However, the discovery by Hershaft and Corbett[8] of $[Bi_9]^{5+}$ in a crystalline material (previously believed to be BiCl) showed the possibility of fractional oxidation states and entities more intricate than $[Bi_n]^{n+}$ polymers.

Experimental Section

Materials.—Solvents used were the liquid eutectics $AlCl_3$–NaCl containing 63 mole % $AlCl_3$[9] and $ZnCl_2$–KCl containing 72 mole % $ZnCl_2$.[10] Commercial grades of $AlCl_3$ and $ZnCl_2$ were unsatisfactory because of impurities. Especially troublesome were organic impurities which gave a background light absorption and also reduced some solute $BiCl_3$. It was necessary, therefore, to synthesize $AlCl_3$ and $ZnCl_2$ from specially prepared HCl and high-purity metals. Aluminum and zinc were zone-refined products of 99.9999% purity from Cominco Products, Inc., and Gallard Schleisinger, Inc., respectively. Hydrogen chloride was prepared by allowing NaCl to react with H_2SO_4. The gas was then deoxidized by passage over copper at 350° (prepared by reducing CuO wire) and dehydrated by passage over $Mg(ClO_4)_2$. At 350° HCl did not react with copper.

Aluminum and zinc chlorides were prepared as follows. The metal was placed in a pure Al_2O_3 boat in a quartz tube. The tube was carefully dried, and a flow of HCl was started. In order to get satisfactory reaction rates, the aluminum was kept a little above its melting point, which is 660°, and the zinc was kept at about 750° so that the $ZnCl_2$ formed distilled away. (The boiling point of $ZnCl_2$ is 732°). The vaporized chlorides were passed through a sintered disk prior to condensation. Zinc chloride was distilled a second time through a sintered disk.

Anhydrous NaCl and KCl were prepared from reagent grade materials by a method similar to that used by Boston and Smith[11] for the purification of the LiCl–KCl eutectic.

For most experiments $BiCl_3$ was prepared from reagent grade bismuth metal and chlorine gas and purified by repeated distillation. In a few experiments in which we wished to make certain that some very weak bands were due to bismuth and not to impurities, $BiCl_3$ was prepared from zone-refined metal of 99.9999% purity from Cominco Products. The same results were obtained with both grades of $BiCl_3$.

The $AlCl_3$–NaCl and $ZnCl_2$–KCl eutectic mixtures were prepared by weighing the constituent salts into optical cells in a vacuum-type drybox filled with high-purity nitrogen.

Volumetric Determination.—The volumes of melts were computed from their weights and densities The density of the $AlCl_3$–NaCl eutectic was taken from the work of Boston.[12] The density of the $ZnCl_2$–KCl eutectic was measured over the range 348–454° and found to be $\rho = 2.604 - (7.03 \times 10^{-4}t)$, where *t* is the temperature in degrees centigrade and ρ is the density in grams per cubic centimeter.

The volume of a solution of $BiCl_3$ in a eutectic was computed by adding the volume of the pure $BiCl_3$ to the volume of the pure eutectic. Errors introduced by this approximate procedure were quite small because the volume of $BiCl_3$ never exceeded 1% of the volume of the eutectic and usually was much smaller than this.

Reaction products were present in solution only in exceedingly small amounts. Hence they were ignored in computing volumes.

Spectrophotometric Procedures.—Absorption spectra were measured with a Cary 14-H spectrophotometer equipped with a high-temperature furnace.[13]

The optical cells, which will be described in detail later, were essentially square silica cuvettes that contained a precision silica insert. The insert could be rotated by 90° to give two different short path lengths or could be removed from the light beam to give a 1-cm path length.

In outline the experimental procedure was the following. A cell was filled with a eutectic and the apparent absorbance of cell plus contents was measured at all three path lengths. Then $BiCl_3$ was added and the apparent absorbance measured again. The absorbance of dissolved $BiCl_3$ at all path lengths was calculated by subtracting the apparent absorbance of the eutectic from that of the solution.

In a few experiments, reaction products were formed by reduction of $BiCl_3$ with $^1/_3$ atm of hydrogen gas. In most experiments, however, the reduction was accomplished with bismuth metal. In these latter experiments the cell was opened, a weighed amount of bismuth metal was added, and the cell was resealed. Reaction between the metal and the $BiCl_3$ solution was generally slow so that the cell and contents were placed in a horizontal position in a special furnace and gently rocked for an extended period to improve mixing. When the reaction was complete, the apparent absorbance was measured. Subsequently, repeated additions of bismuth metal or $BiCl_3$ were made to the reaction mixture and the above procedure was followed after each addition to obtain the apparent absorbance. The absorbance of a reaction mixture was calculated by subtracting the apparent absorbance of the solvent from that of the mixture.

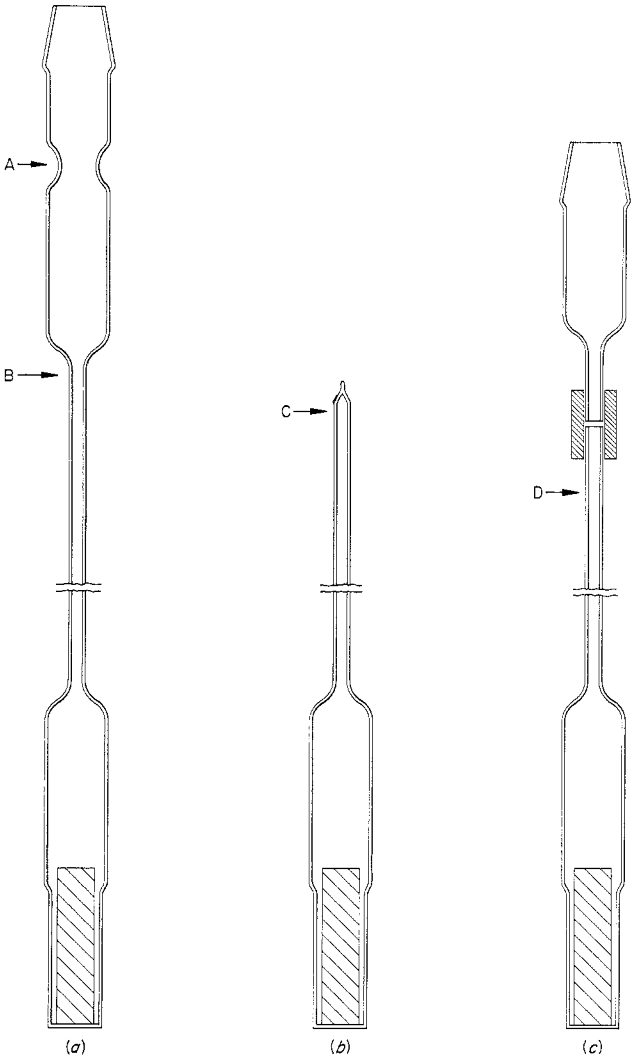
The above calculations and others more intricate were facilitated by recording all spectra as digital numbers punched into paper tape. These numbers were transferred to magnetic tape and read into a CDC 1604 computer with which the calculations were performed. Results were plotted on a Calcomp plotter.

Details regarding optical cells and the way in which they were manipulated are illustrated in Figure 1. A cell prior to loading is shown in Figure 1(a). It was made entirely of silica and consisted of two chambers connected by a 30-cm length of 0.6-cm tubing. The upper chamber was made of 1.7-cm tubing with a standard-taper joint on top and a constriction at position A in Figure 1(a). The lower chamber consisted of a 7-cm length of 1.7-cm diameter tubing attached to a cuvette of 1-cm² cross section. Inside the cuvette was a precision insert which provided two short path lengths by rotation through 90°. The insert was removed from the cuvette into the cylindrical part of the lower chamber by tilting the cell.

The cell was filled with weighed materials in a drybox and capped off at the standard-taper joint. It was then taken from the drybox, the cap was removed, and the cell was quickly joined to a vacuum system. After evacuation, the cell was backfilled with $^1/_3$ atm of high-purity nitrogen and sealed by fusing at the constriction [position A in Figure 1(a)]. Then the materials were melted into the lower chamber, and the upper chamber was removed by fusing at position B in Figure 1(a). The cell at this state is shown in Figure 1(b).

---

(3) M. A. Bredig, *J. Phys. Chem.*, **63**, 978 (1959).
(4) J. D. Corbett, *ibid.*, **62**, 1149 (1958).
(5) L. E. Topol, S. J. Yosim, and R. A. Osteryoung, *ibid.*, **65**, 1511 (1961).
(6) C. R. Boston and G. P. Smith, *ibid.*, **66**, 1178 (1962).
(7) C. R. Boston, G. P. Smith, and L. C. Howick, *ibid.*, **67**, 1849 (1963).
(8) A. Hershaft and J. D. Corbett, *Inorg. Chem.*, **2**, 979 (1963).
(9) W. Fischer and A. L. Simon, *Z. Anorg. Allgem. Chem.*, **306**, 1 (1960).
(10) Ya. A. Ugai and V. A. Shatillo, *Zh. Fiz. Khim.*, **23**, 744 (1949).
(11) C. R. Boston and G. P. Smith, *J. Phys. Chem.*, **62**, 409 (1958).
(12) C. R. Boston, *J. Chem. Eng. Data*, **11**, 262 (1966).
(13) C. R. Boston and G. P. Smith, *Rev. Sci. Instr.*, **36**, 206 (1965).



(a) (b) (c)

Figure 1.—Various stages in the filling of an optical absorption cell as explained in the text.

Small additions of bismuth metal or $BiCl_3$ were made in a drybox by cutting the cell open at position C in Figure 1(b) and adding a new upper chamber, as shown in Figure 1(c). This chamber was attached by means of a degassed section of rubber hose. Then the above procedure was repeated and the cell was sealed off at position D in Figure 1(c). During seal-off the rubber tubing was water cooled.

Absorption by Eutectics and $BiCl_3$ Solutions.—The solvent eutectics were completely transparent in the near-infrared and visible regions of the spectrum. Ultraviolet absorption of $AlCl_3$–NaCl at 130° in a 1-cm cell began near 250 mμ, but by using inserts it was possible to make measurements below 200 mμ. The $ZnCl_2$–KCl eutectic at 380° in a 1-cm cell began to absorb near 320 mμ.

Dilute solutions of $BiCl_3$ absorbed intensely in the ultraviolet region but were essentially transparent elsewhere. In the $AlCl_3$–NaCl eutectic at 130°, $BiCl_3$ had maxima at 297 and 210 mμ (33,700 and 47,600 cm^{-1}, respectively) with molar absorptivities of 5.4×10^3 and 22×10^3 l./mole cm, respectively.

Similar bands are known for Bi^{3+} in various other chloride systems.[14] The wavelength positions of these bands vary somewhat for different solvent media.

Spectrochemical Studies

Definitions and Assumptions Regarding Empirical Quantities.—For solution mixtures that were formed by reaction between bismuth metal and dilute solutions of $BiCl_3$ in one of the two eutectic mixtures, bismuth trichloride was always present in large excess. We shall refer to the amount of bismuth metal consumed by such reactions as the *excess bismuth* in the solution. The moles of excess bismuth per liter of reaction mixture will be denoted M_E.

The quantity

$$A(\text{prod.}) = A(\text{mix.}) - A(\text{BiCl}_3, \text{mix.}) \tag{1}$$

will be called the absorbance of the reaction products, where A(mix.) is the absorbance of the reaction mixture and $A(\text{BiCl}_3, \text{mix.})$ is the absorbance of a solution of $BiCl_3$ at its concentration in the reaction mixture.

For experiments in which reduction of $BiCl_3$ was accomplished with hydrogen, practically all of the $BiCl_3$ was consumed so that $A(\text{prod.}) = A(\text{mix.})$ at all wavelengths. This preparative method was used to obtain the ultraviolet spectrum of one of the reaction products.

For experiments in which reduction of $BiCl_3$ was accomplished with bismuth metal, a large excess of $BiCl_3$ was present and this prevented the determination of A(prod.) at wavelengths shorter than about 350–380 mμ depending on concentration. However, the absorbance of $BiCl_3$ was negligible in the near-infrared and visible regions so that $A(\text{prod.}) = A(\text{mix.})$ in these regions. At wavelengths approaching 350–380 mμ, $BiCl_3$ absorbed only moderately so that $A(\text{BiCl}_3, \text{mix.})$ in eq 1 was a term of relatively small magnitude. This term was estimated from the absorbance of the initial $BiCl_3$ solution, which we denote $A(\text{BiCl}_3, \text{intl})$, from the relation

$$A(\text{BiCl}_3, \text{mix.}) = [M(\text{BiCl}_3, \text{mix.})/M(\text{BiCl}_3, \text{intl})]A(\text{BiCl}_3, \text{intl}) \tag{2}$$

where $M(\text{BiCl}_3, \text{intl})$ and $M(\text{BiCl}_3, \text{mix.})$ are, respectively, the molar concentrations of $BiCl_3$ before reaction and in the equilibrium mixture. Since $BiCl_3$ was always present in large excess, the ratio of molar concentrations in eq 2 was near unity, and to a good first approximation $A(\text{BiCl}_3, \text{mix.}) = A(\text{BiCl}_3, \text{intl})$. Thus, even before the stoichiometry of the reaction was known, A(prod.) could be determined accurately in the visible and near-infrared regions and to a good approximation in the ultraviolet region. This provided sufficient information to unravel the reaction stoichiometry. After that was done, the ratio of molar concentrations in eq 2 could be calculated and the results applied to eq 1 in order to obtain accurate values of A(prod.) at all wavelengths down to 350 mμ.

As a matter of convenience we define the *formal molar absorptivity of reaction products*, ϵ(prod.), to be

$$\epsilon(\text{prod.}) = A(\text{prod.})/M_E l \tag{3}$$

where l is the pathlength in centimeters.

Most of the computations to be described are based on four assumptions, the first three of which are com-

---

[14] L. Newman and D. N. Hume, *J. Am. Chem. Soc.*, **79**, 4576 (1957); A. Glasner and R. Reisfeld, *J. Chem. Phys.*, **32**, 956 (1960); Ch. B. Lushchik, N. E. Lushchik, and I. V. Yaek, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **26**, 488 (1962); and G. P. Smith, D. W. James, and C. R. Boston, *J. Chem. Phys.*, **42**, 2249 (1965).

monly valid for solutions as dilute as those with which we dealt.

First is the law of additive absorbances. According to this assumption the absorbance of each entity in a mixture is independent of the presence of other constituents. Second is the Bouguer–Beer law according to which the absorbance of each entity is proportional to its concentration. We identified one situation in which deviations from these first two assumptions were found. There were some experiments in which M_E and $M(BiCl_3$, mix.) were both relatively large, and the spectra deviated from ideal behavior in a manner best interpreted as an interaction absorption effect such as is known to occur in other systems which contain a metal in two different valence states.[15]

The third assumption is Henry's law according to which activities are proportional to concentrations. Contributing toward the validity of this assumption were the high and approximately constant ionic strengths of the reaction media. Note that this situation does not obtain in pure (or nearly pure) $AlCl_3$, which is a molecular liquid. Furthermore, the concentrations of those reacting species that were varied over substantial ranges were held to small values.

The fourth assumption concerns the nature of the solvent eutectics. In liquid $AlCl_3$–NaCl mixtures aluminum bonds strongly to chlorides with a coordination number of 4. At 63 mole % $AlCl_3$, the composition of the eutectic, chlorides not coordinated to aluminum, which we label Cl^-, are few in number and highly buffered. It is this buffer action which makes the eutectic especially suitable for our purposes as contrasted with pure $AlCl_3$. The stabilizing reaction is probably

$$Cl^- + [Al_2Cl_7]^- = 2[AlCl_4]^- \qquad (4)$$

A similar situation exists in the $ZnCl_2$–KCl eutectic containing 72 mole % $ZnCl_2$ although the identity of the ions which contain chloride-bridged zincs is less certain. For these systems one can speak of Cl^- activity and pCl in the same sense that one speaks of H^+ activity and pH in aqueous systems. Our postulate is that the buffer capacity of the eutectic melts is large enough so that in our experiments the Cl^- activity can be treated as constant.

These postulates define a model of spectrochemical solution behavior in terms of which we shall formulate our results. We shall see that this model describes these results in a quantitatively satisfactory way.

Survey of the Spectra of Reaction Products.—In this section we describe the spectra of products formed by the reaction between bismuth metal and dilute solutions of $BiCl_3$ in the $AlCl_3$–NaCl and $ZnCl_2$–KCl eutectics. Results obtained when $BiCl_3$ solutions were reduced with hydrogen are described in a later section.

When the $AlCl_3$–NaCl eutectic was used as solvent, the spectra of reaction products, *i.e.*, *A*(prod.), approximated the Bouguer–Beer law quite accurately up to about 0.002 molar excess bismuth at 130° and up to above 0.009 molar at 250°. The spectrum at 130° in the Bouguer–Beer law range is given by curve A in Figure 2. Band maxima occurred at 585, 663, and 900 mμ (17,100, 15,100, and 11,100 cm^{-1}, respectively). A pronounced shoulder was found at about 690 mμ (14,500 cm^{-1}). The 585-mμ band was highly skew symmetric so that there were probably broad, unresolved bands on the high-energy side of the sharp maximum, but we found no clear evidence of shoulders.

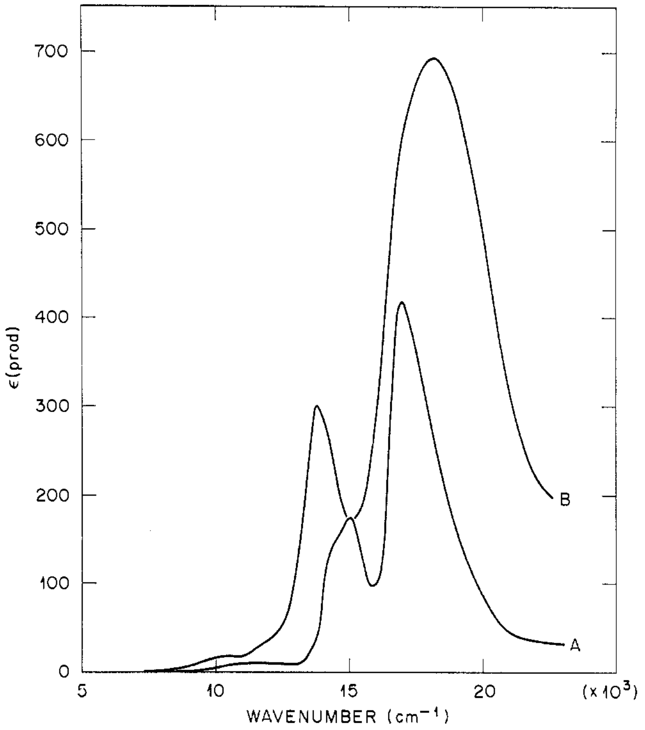


Figure 2.—Spectra of reaction products formed with small amounts of excess bismuth in the range in which the Bouguer–Beer law was obeyed. Conditions for the two spectra shown: A, $AlCl_3$–NaCl as solvent, $M(BiCl_3$, intl) = 0.117 *M*, M_E = 0.00144 *M*, 130°; B, $ZnCl_2$–KCl as solvent, $M(BiCl_3$, intl) = 0.118 *M*, M_E = 0.00121 *M*, 380°.

Changes in temperature over the range 130–310° produced only small changes in the spectrum. One of the larger changes was in the relative intensities of the overlapping 663- and 690-mμ bands that become almost equal at 310° so that they could not be distinguished as separate bands at this temperature.

Obeyance of the Bouguer–Beer law as a function of M_E ensures either that only a single reaction product was formed to any significant extent or else that if several products were formed, they remained in constant concentration ratios with changing M_E. The relative insensitivity of the spectrum to changes in temperature rules in favor of a single reaction product. It seems unlikely that the concentration ratios of products in equilibrium would not change significantly when the absolute temperature increased by 45%. We presume, therefore, that a single reaction product is formed in the Bouguer–Beer law range and we label this product I.

---

(15) J. E. Whitney and N. Davidson, *J. Am. Chem. Soc.*, **71**, 3809 (1949); H. McConnell and N. Davidson, *ibid.*, **72**, 3168, 5557 (1950); N. Davidson, *ibid.*, **73**, 2361 (1951).

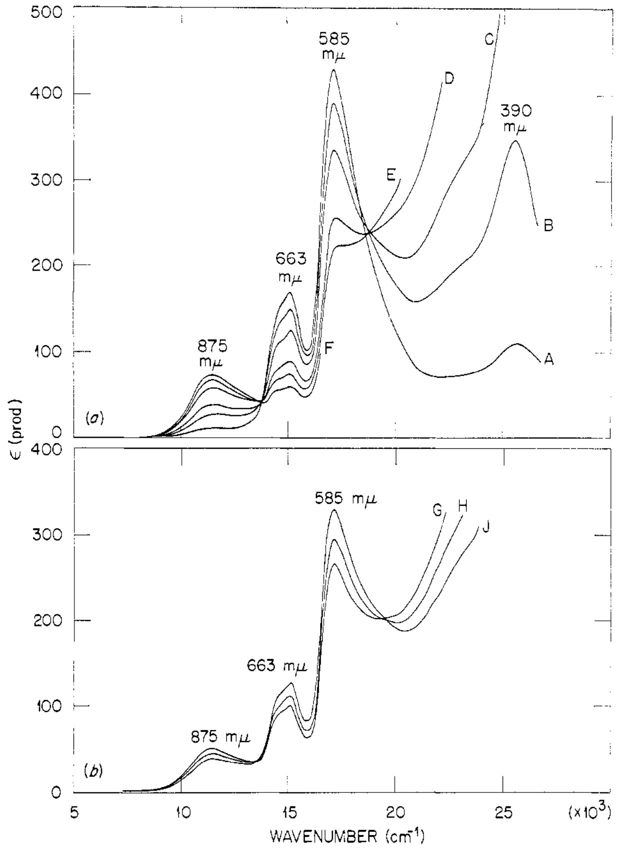


Figure 3.—Spectra of reaction products in the $AlCl_3$–NaCl eutectic at 130° for various solution compositions. (a) Series of spectra obtained by adding successive amounts of bismuth metal to a solution initially containing 0.117 *M* $BiCl_3$. Values of M_E: A, 0.00291; B, 0.00503; C, 0.00715, D, 0.0128; E, 0.0178; and F, 0.0259. (b) Series of spectra obtained by adding successive amounts of $BiCl_3$ to a solution containing 0.00578 *M* of excess bismuth. Initial molar concentration of $BiCl_3$: G, 0.0125; H, 0.0270; J, 0.0588.

As more and more bismuth metal reacted with a fixed initial concentration of $BiCl_3$, the Bouguer–Beer law based on M_E eventually broke down and the spectrum changed in pronounced ways as shown in Figure 3(a). The bands at 585 and 663 mμ diminished in formal molar absorptivity, ϵ(prod.), while an intense band grew in at 390 mμ, and the very weak band at 900 mμ was replaced by a somewhat stronger band at 875 mμ. Two isosbestic points were formed, and a plot of ϵ(prod.) at one wavelength against ϵ(prod.) at another wave length was linear.

Similar changes in the reaction product spectra were found when the $BiCl_3$ concentration was varied with a fixed concentration of excess bismuth. Typical examples of such spectra are shown in Figure 3(b). As before there were two isosbestic points, and a plot of ϵ(prod.) at one wavelength against ϵ(prod.) at another wavelength was linear.

All of these facts strongly support the view that there were two reaction products in equilibrium. One of these products we have already labeled I. The other, which we shall label II, had principal absorptions at 390 and 875 mμ.

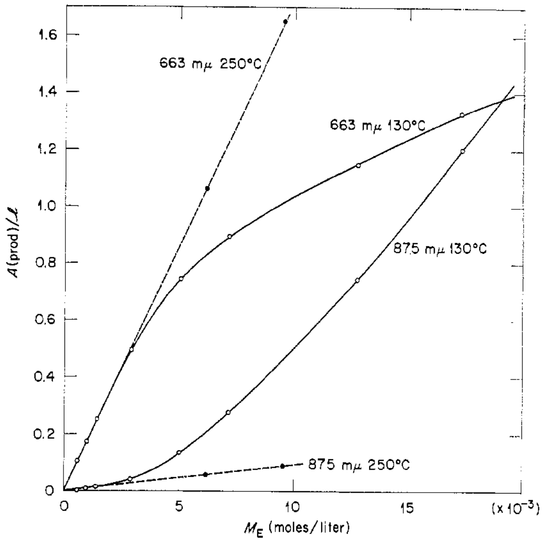


Figure 4.—Relations between the concentration of excess bismuth in the $AlCl_3$–NaCl eutectic and the absorbance of reaction products at representative wavelengths and temperatures. The initial concentration of $BiCl_3$ was 0.116 *M*.

In the Bouguer–Beer law range the solutions were blue while at relatively high values of M_E they were reddish brown.

The functional dependence of these spectra on the concentration of excess bismuth, M_E, is illustrated at representative wavelengths and temperatures in Figure 4. It is evident from this figure that the Bouguer–Beer law is approximated quite well at low concentrations of excess bismuth and that the Bouguer–Beer law slopes change little between 130 and 250°.

Reactions in which the $ZnCl_2$–KCl eutectic served as solvent differed in an important respect from those that utilized the $AlCl_3$–NaCl eutectic. In $AlCl_3$–NaCl, reaction continued as long as both bismuth metal and $BiCl_3$ were present and stopped when either one had been completely consumed. In $ZnCl_2$–KCl, on the other hand, if one began with a sufficient surplus of bismuth metal, reaction came to equilibrium while both unreacted metal and unreacted $BiCl_3$ were still present. Under this condition the bismuth metal was, of course, present as a second phase, and the extent of reaction (*i.e.*, the value of M_E) depended on the initial concentration of $BiCl_3$. As we shall see, this difference in behavior between the two solvents was a vital aid in unraveling the reaction stoichiometry.

The spectra of reaction products formed in the $ZnCl_2$–KCl eutectic were similar to those formed in the $AlCl_3$–NaCl eutectic, described above. At small M_E the spectra obeyed the Bouguer–Beer law. A spectrum in this concentration range at 380° is given by curve B in Figure 2. It bears many striking similarities to the spectrum of I in the $AlCl_3$–NaCl eutectic. Band maxima were found at 550, 722, and 950 mμ (about 18,200, 13,900, and 10,500 cm^{-1}, respectively). The relative intensities of these bands follow almost exactly the same pattern as found for the 585-, 663-, and 900-mμ bands, respectively, of I in the $AlCl_3$–NaCl eutectic, although the over-all intensity of the latter spectrum is only about 60% of that of the former. There appears to be a shoulder in curve B, Figure 2 ($ZnCl_2$–KCl), at about 850 mμ (about 11,800 cm^{-1}), and there seems to be a shoulder on the high-energy side of the 722-mμ peak.

At higher values of M_E the spectra of reaction products in $ZnCl_2$–KCl went through a progression of changes that were quite similar to those found when $AlCl_3$–NaCl served as solvent. The bands of I decreased in intensity, new bands appeared at places similar to those of II in the $AlCl_3$–NaCl eutectic, and isosbestic points were formed.

The numerous similarities between the spectra of reaction products in $AlCl_3$–NaCl and those in $ZnCl_2$–KCl lead us to conclude that the same two reaction products occurred in both systems. Application of this inference to a quantitative analysis of the data leads, as shown below, to a simple and consistent quantitative interpretation of the spectra for both systems.

There are, of course, differences between the spectra of reaction products in the two solvents that are not trivial. These differences are especially evident in the two spectra shown in Figure 2, which we now suppose to be two spectra of reaction product I. We shall be able to rationalize these differences after we have identified reaction product I and determined the electronic origins of its spectrum. It may be helpful, however, to indicate now the nature of the rationalization. From spectrochemical data we deduce reaction stoichiometry with respect to bismuth and conclude that I is Bi^+. However, reaction stoichiometry with respect to other elements remains unknown so that the analysis does not distinguish between different complexes of Bi^+. It will be shown in another paper that the observed transitions of Bi^+ are of the $6p^2 \leftrightarrow 6p^2$ type and are sensitive to differences in coordination. In $AlCl_3$–NaCl, Bi^+ is probably coordinated to chloroaluminate ions, while in $ZnCl_2$–KCl, it is probably coordinated to chlorozincate ions. It is reasonable to suppose that this difference in ligands accounts for the somewhat different spectra.

Reaction Stoichiometry at Small M_E.—This section deals with data from the Bouguer–Beer law range in $AlCl_3$–NaCl, where we suppose that only reaction product I is formed. A general equation for the formation of a single product from the reaction between bismuth metal and $BiCl_3$ can be written

$$[x - (y/3)]\text{Bi(metal)} + (y/3)\text{Bi}^{3+}\text{(soln)} = [\text{Bi}_x]^{y+}\text{(soln)} \quad (5)$$

where $[Bi_x]^{y+}$ is the product we have designated as I.

Experiments showed that in the Bouguer–Beer law range the intense ultraviolet bands of $BiCl_3$ decreased in absorbance as a linear function of increasing M_E. The percentage decrease was independent of wavelength. We conclude, therefore, that the absorbance of reaction products in this region of the spectrum is negligibly small compared with the change in absorbance of $BiCl_3$. Thus we can use this change in absorbance to measure the number of moles of $BiCl_3$ consumed by reaction with a known number of moles of bismuth metal. The experiments utilizing hydrogen reduction, described later, verify that I absorbs only very weakly at the positions of the intense $BiCl_3$ bands (see also Figure 7).

By using the information cited above, the oxidation state of I, *i.e.*, y/x, was computed in a straightforward way to be unity. Results at several temperatures are cited in Table I. The first column lists the number of moles of $BiCl_3$ initially present in the solution. The second column lists the number of moles of bismuth metal which reacted. The fourth and fifth columns give the percentage decrease in absorbance of the $BiCl_3$ spectrum in going from the initial solution with no reaction to the equilibrium solution after consumption of all of the bismuth metal. This percentage decrease in absorbance equals the percentage of bismuth initially present that reacted. The decrease is listed for two wavelengths in verification of the fact that it was wavelength independent. These wavelengths correspond to a band maximum (297 mμ) and the interband minimum (274 mμ) of Bi^{3+}. The final column lists values of the percentage decrease computed under the assumption that the oxidation state of I, that is, the value of y/x, is 1+. On the basis of this result I may be denoted $[Bi_n]^{n+}$. The value of n will be deduced later.

TABLE I

DETERMINATION OF OXIDATION
STATE OF REACTION PRODUCT I

Moles of reactants ($\times 10^{-5}$)		Temp,	Decrease in A of $BiCl_3$, %		
			Measd		Calcd assuming
$BiCl_3$	Bi	°C	297 mμ	274 mμ	$y/x = 1$
8.997	0.774	130	...	4.3	4.30
		190	4.3	4.3	
		250	4.3	4.4	
4.711	0.724	250	7.7	7.8	7.68
		310	7.5	7.6	
4.711	2.913	190	30.2	28.5	30.92
		250	29.6	29.1	
		310	30.3	29.3	

Effect of $BiCl_3$ Concentration on the $[Bi_n]^{n+}$ Spectrum.—The experiments described above were performed at very small $BiCl_3$ concentrations. At relatively large $BiCl_3$ concentrations (up to 0.1 *M*) the Bouguer–Beer law continued to be obeyed so long as M_E was small, but ε(prod.), *i.e.*, the Bouguer–Beer law slope, increased with increasing $BiCl_3$ concentration. For the most part, this effect was small and not very wavelength dependent. In the case of the 663-mμ band, for example, ε(prod.) increased linearly by 6.3% when the $BiCl_3$ concentration increased from very small values up to 0.1 *M*. The only qualitative change in the spectrum was the formation of an extremely weak shoulder at about 800 mμ at high $BiCl_3$ concentrations. This shoulder was not observed at low $BiCl_3$ concentrations.

A similar intensification of spectra has been observed in aqueous solutions containing an element in two different valence states.[15] We shall refer to this as a "valence interaction effect."

Analysis of Deviations from the Bouguer–Beer Law Based on M_E.—Breakdown in Bouguer–Beer law behavior was accompanied by the appearance of reaction product II. The measurements show that an increase in the concentration of Bi^{3+} results in a decrease in the concentration of II. Therefore, II and Bi^{3+} must be on the same side of the chemical reaction equation. Thus we may formulate this equation in a general way as

$$\alpha[\mathrm{Bi}_n]^{n+} = [\mathrm{Bi}_{\alpha n-\beta}]^{(\alpha n-3\beta)+} + \beta\mathrm{Bi}^{3+} \qquad (6)$$

where $[\mathrm{Bi}_{\alpha n-\beta}]^{(\alpha n-3\beta)+}$ is product II. Since both the number of atoms and the formal charge must be integers, the quantities $\alpha n - \beta$, $\alpha n - 3\beta$, and their difference, 2β, must be integers. Consequently, β is restricted to the values 0, $^1/_2$, 1, $^3/_2$, ...

The mass action relation for the reaction in eq 6 may be formulated with the help of Henry's law as

$$k_1 = [M(\mathrm{BiCl_3,\ mix.})]^{\beta} M_{\mathrm{II}}/M_{\mathrm{I}}^{\alpha} \qquad (7)$$

where M_{I} and M_{II} are the molar concentrations of I and II, respectively, $M(\mathrm{BiCl_3,\ mix.})$ is the concentration of $BiCl_3$ in the equilibrium mixture, and k_1 is a constant. In some sets of experiments M_{I} and M_{II} were varied over wide ranges while $BiCl_3$ was present in such large excess that $M(\mathrm{BiCl_3,\ mix.})$ remained almost constant. For these sets of experiments we may write the mass action expression as

$$k_1' = M_{\mathrm{II}}/M_{\mathrm{I}}^{\alpha} \qquad (8)$$

Using methods that will be described below, we employed eq 8 in conjunction with suitable experiments to estimate a value of α. Then, with this estimate of α, we employed eq 7 and experiments in which $M(\mathrm{BiCl_3,\ mix.})$ varied over a wide range to estimate β. Finally, as a check, we used a knowledge of α and β to determine the value of $M(\mathrm{BiCl_3,\ mix.})$ in the first set of experiments and verified that the small change in concentration of $BiCl_3$ had had no effect on the outcome of the calculation of α.

Determination of α.—We shall now show how α was deduced from experiments in which various amounts of bismuth metal reacted with a fixed initial concentration of $BiCl_3$. These experiments have already been discussed in a qualitative way and typical spectra are presented in Figure 3(a). In these experiments $BiCl_3$ was present in very large excess so that we regarded its concentration as constant.

Consider two wavelengths, λ_1 and λ_2, at which I and II absorb but Bi^{3+} does not. Under the postulate of additive absorbances, the total absorbances, $A(\lambda_1)$ and $A(\lambda_2)$, at these two wavelengths are given by

$$A(\lambda_1) = A_{\mathrm{I}}(\lambda_1) + A_{\mathrm{II}}(\lambda_1) \qquad (9)$$

$$A(\lambda_2) = A_{\mathrm{I}}(\lambda_2) + A_{\mathrm{II}}(\lambda_2) \qquad (10)$$

where $A_j(\lambda_i)$ is the absorbance of the jth product at the ith wavelength. Furthermore, let

$$A_{\mathrm{I}}(\lambda_2)/A_{\mathrm{I}}(\lambda_1) = g_{\mathrm{I}} \qquad (11)$$

$$A_{\mathrm{II}}(\lambda_1)/A_{\mathrm{II}}(\lambda_2) = g_{\mathrm{II}} \qquad (12)$$

where g_{I} and g_{II} are constants independent of concentration. Substitution of eq 11 and 12 into eq 9 and 10 yields

$$A_{\mathrm{I}}(\lambda_1) = \frac{A(\lambda_1) - g_{\mathrm{II}}A(\lambda_2)}{1 - g_{\mathrm{I}}g_{\mathrm{II}}} \qquad (13)$$

$$A_{\mathrm{II}}(\lambda_2) = \frac{A(\lambda_2) - g_{\mathrm{I}}A(\lambda_1)}{1 - g_{\mathrm{I}}g_{\mathrm{II}}} \qquad (14)$$

When these expressions for the absorbance are substituted into the Bouguer–Beer law, we obtain

$$M_{\mathrm{I}} = \frac{A(\lambda_1) - g_{\mathrm{II}}A(\lambda_2)}{(1 - g_{\mathrm{I}}g_{\mathrm{II}})l\epsilon_{\mathrm{I}}(\lambda_1)} \qquad (15)$$

$$M_{\mathrm{II}} = \frac{A(\lambda_2) - g_{\mathrm{I}}A(\lambda_1)}{(1 - g_{\mathrm{I}}g_{\mathrm{II}})l\epsilon_{\mathrm{II}}(\lambda_2)} \qquad (16)$$

where l is the path length and $\epsilon_j(\lambda_i)$ is the molar absorptivity of the jth reaction product at the ith wavelength. Finally, substituting eq 15 and 16 into eq 8 and taking logarithms yields

$$\log\,[A(\lambda_2) - g_{\mathrm{I}}A(\lambda_1)] - \alpha\log\,[A(\lambda_1) - g_{\mathrm{II}}A(\lambda_2)] = \log C_1 \qquad (17)$$

where C_1 is a constant, independent of concentration. The quantities $A(\lambda_1)$ and $A(\lambda_2)$ are functions of M_E and are directly obtainable from the measurements. The quantities g_{I}, g_{II}, and α are constants, independent of concentration. Of these g_{I} may be obtained directly from the spectrum of I, which was measured in the Bouguer–Beer law range. This leaves the constants α, g_{II}, and C_1 as unknowns in eq 17. For our purposes only the values of α and g_{II} are needed.

Our procedure for obtaining α and g_{II} was the following. We assumed a series of values for g_{II} and plotted $\log\,[A(\lambda_1) - g_{\mathrm{II}}A(\lambda_2)]$ against $\log\,[A(\lambda_2) - g_{\mathrm{I}}A(\lambda_1)]$ with M_E regarded as a parametric variable. The resultant curves are shown in Figure 5(a). If the various assumptions and deductions that led to eq 17 are correct, then the form of this equation is such that the following two conclusions are valid. First, the curves in Figure 5(a) for various assumed values of g_{II} will asymptotically approach a straight line of slope $1/\alpha$ at diminishing values of the coordinates. Second, the value of g_{II} that produces a straight line in Figure 5(a) is the physically correct value of g_{II}, and the slope of this line is $1/\alpha$. As will be seen from Figure 5(a) the experimental curves have the anticipated shape and we deduce that at 130° g_{II} has the value 0.20 and α the value 6.0 ± 0.5.

Determination of β.—In order to evaluate β in eq 6, we conducted experiments in which the concentration of $BiCl_3$ was varied while M_E was held constant. A typical series of spectra obtained in this way is shown in Figure 3(b). The mass action equation applicable to these experiments is given in eq 7.

We obtained an expression for $M(\mathrm{BiCl_3,\ mix.})$ in this equation from the following considerations. Under the

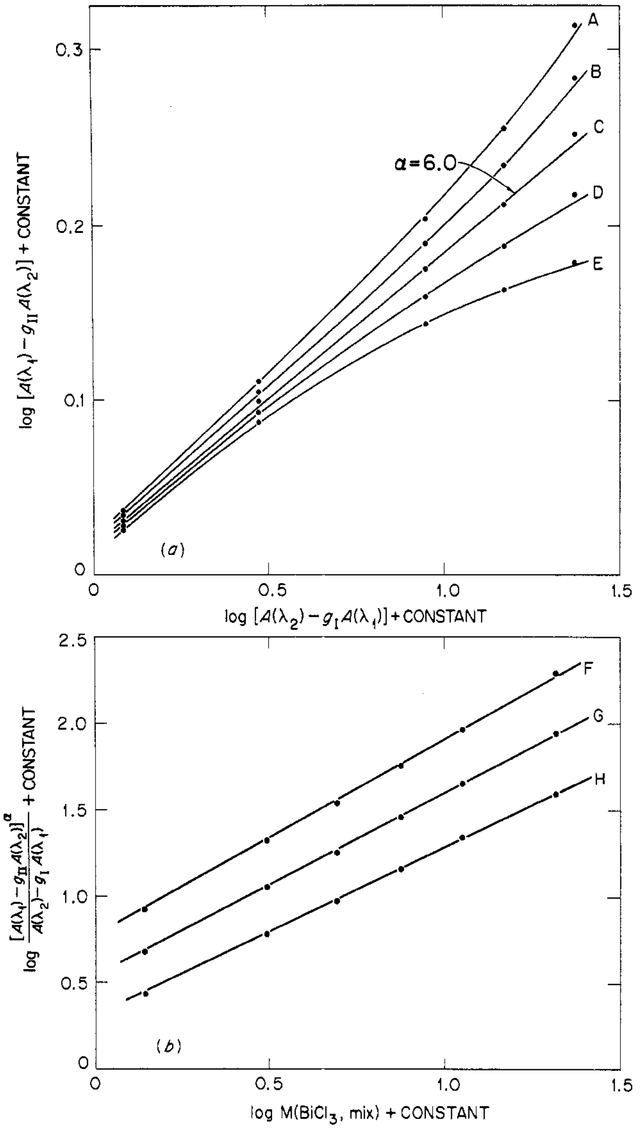


Figure 5.—Plots used to deduce the formulas of reaction products. The interpretation of the quantities plotted is given in the text. For these curves the temperature was 130°, g_I had the value 0.054, the initial concentration of BiCl$_3$ was 0.117 M, and M_E varied between 0.00503 and 0.0259 M. (a) Assumed values of g_{II}: A, 0.10; B, 0.15; C, 0.20; D, 0.25; E, 0.30. (b) The value of g_{II} was 0.20. Values of α: F, 6.5; G, 6.0; H, 5.5.

postulate that only I and II were reaction products, we write

$$M(\text{BiCl}_3,\ \text{mix.}) = M(\text{BiCl}_3,\ \text{intl}) - (\Delta M_I + \Delta M_{II}) \quad (18)$$

where ΔM_I is that part of the initial BiCl$_3$ which was reduced to form I, and ΔM_{II} is that part reduced to form II. Likewise we label that part of the bismuth metal that was oxidized to form I as M_{EI}, and that part oxidized to II as M_{EII}. Since I has the formula $[\text{Bi}_n]^{n+}$, we find that $\Delta M_I = (^1/_2)M_{EI}$. Although the formula of II was unknown, it had a lower oxidation state than I, as will be seen from eq 6, so that we may write $\Delta M_{II} = fM_{EII}$ where $0 < f < {}^1/_2$. Equation 18 takes the form

$$M(\text{BiCl}_3,\ \text{mix.}) = M(\text{BiCl}_3,\ \text{intl}) - [(M_{EI}/2) + fM_{EII}] \quad (19)$$

We computed $A_I(\lambda_1)$ from eq 13 and then determined M_{EI} from the proportionality between $A_I(\lambda_1)$ and M_{EI}, measured in the Bouguer–Beer law range. Because the concentration of BiCl$_3$ was relatively large in some of these measurements, we made the above evaluations from the data referred to in the section on valence interaction. The quantity M_{EII} came from the material balance $M_{EII} = M_E - M_{EI}$.

At this point we know all of the quantities on the right-hand side of eq 19 except f. Since f lies between 0 and $^1/_2$, the uncertainty in $M(\text{BiCl}_3,\ \text{mix.})$ was $\pm M_{EII}/4$. For most of our data this uncertainty amounted to only a few per cent of $M(\text{BiCl}_3,\ \text{mix.})$. Therefore, we used the value $^1/_4$ for f in eq 19 as a first estimate and proceeded to obtain a first estimate of β by the method described below. It will be noted that a poor estimate of f should lead to a fairly good estimate of β. Since f can be computed from a knowledge of β, our intended approach was to use our first estimate of β to obtain a corrected estimate of f, substitute this value into eq 19, and iterate. Actually, as we shall see, the value $^1/_4$ turns out to be the exact value for f so that iteration proved unnecessary.

The relation used to evaluate β was derived by substituting eq 15 and 16 into eq 7 followed by taking logarithms to give

$$\log \frac{[A(\lambda_1) - g_{II}A(\lambda_2)]^\alpha}{A(\lambda_2) - g_I A(\lambda_1)} - \beta \log M(\text{BiCl}_3,\ \text{mix.}) = \log C_2 \quad (20)$$

where C_2 is a constant independent of concentration and $M(\text{BiCl}_3,\ \text{mix.})$ is given by eq 19. We plotted the first term in eq 20 against log $M(\text{BiCl}_3,\ \text{mix.})$ with α values of 5.5, 6.0, and 6.5 as shown in Figure 5(b). The resultant sets of points lie close to straight lines as required by the model. These lines have slightly different slopes but all are in the neighborhood of unity. According to eq 20 the slope should equal β. Since β can have only integral or half-integral values, we chose 1 as the best value.

Determination of n.—In order to evaluate n in the formula $[\text{Bi}_n]^{n+}$, we made use of equilibria in which the ZnCl$_2$–KCl eutectic served as the solvent. As noted before, equilibrium in this solvent is reached in the presence of unreacted bismuth metal. Such an equilibrium may be expressed in terms of the two simultaneous relations

$$(2n/3)\text{Bi(l)} + (n/3)\text{Bi}^{3+}(\text{soln}) = [\text{Bi}_n]^{n+}(\text{soln}) \quad (21)$$

$$(2\alpha n/3)\text{Bi(l)} + [(\alpha n - 3)/3]\text{Bi}^{3+}(\text{soln}) = [\text{Bi}_{\alpha n-1}]^{(\alpha n-3)+}(\text{soln}) \quad (22)$$

In these equations the value $\beta = 1$ has been used but the value of α is left variable because data presented here provide a basis for reducing the uncertainty in this quantity.

Since the activity of Bi(l) is a constant, we may write the mass action quotients corresponding to eq 21 and 22, respectively, as

$$k_3 = M_I/[M(\text{BiCl}_3,\ \text{mix.})]^{n/3} \quad (23)$$

$$k_4 = M_{II}/[M(\text{BiCl}_3,\ \text{mix.})]^{(\alpha n-3)/3} \quad (24)$$

Substitution of eq 15 into 23 and eq 16 into 24 followed by taking logarithms yields, respectively

$$\log\,[A(\lambda_1) - g_{\rm II}A(\lambda_2)] - \frac{n}{3}\log M(\text{BiCl}_3,\ \text{mix.}) = \log C_3 \quad (25)$$

$$\log\,[A(\lambda_2) - g_{\rm I}A(\lambda_1)] - \frac{\alpha n - 3}{3}\log M(\text{BiCl}_3,\ \text{mix.}) = \log C_4 \quad (26)$$

These equations were evaluated by procedures analogous to those followed in evaluating eq 16 and 20. In this evaluation λ_1 was chosen to be 722 mμ, which corresponds to a band in the spectrum of product I, and λ_2 was chosen to be 950 mμ, which corresponds to a shoulder in the spectrum of product II. Results are presented in Figure 6. The best straight line in Figure 6(b) has a slope close to $^1/_3$ and corresponds to the value 1.8 for $g_{\rm II}$. We deduce therefore that n equals unity and we designate I as Bi^+.

The equilibrium between Bi^{3+}, I, and II may now be written

$$\alpha\text{Bi}^+ = [\text{Bi}_{\alpha-1}]^{(\alpha-3)+} + \text{Bi}^{3+} \quad (27)$$

Since the number of atoms and the formal charge must be integers, an α value of 6 is the only permissible value in the range 6.0 ± 0.5. This value is verified by the plot of eq 26 in Figure 6(a) where the slope of the line, which equals $(\alpha - 3)/3$, is found to be unity.

Equilibrium Quotients.—The chemical equilibria that we studied quantitatively were

$$6\text{Bi}^+(\text{soln}) \rightleftharpoons [\text{Bi}_5]^{3+}(\text{soln}) + \text{Bi}^{3+}(\text{soln}) \quad (28)$$

$$2\text{Bi(l)} + \text{Bi}^{3+}(\text{soln}) \rightleftharpoons 3\text{Bi}^+(\text{soln}) \quad (29)$$

$$4\text{Bi(l)} + \text{Bi}^{3+}(\text{soln}) \rightleftharpoons [\text{Bi}_5]^{3+}(\text{soln}) \quad (30)$$

The first of these three equilibria was studied in both the AlCl_3–NaCl and ZnCl_2–KCl eutectics, while the latter two were studied only in ZnCl_2–KCl. The mass action expressions for these reactions are, respectively

$$k_{\rm a} = M_{\rm II}M_3/M_{\rm I}^6 \quad (31)$$

$$k_{\rm b} = M_{\rm I}^3/M_3 \quad (32)$$

$$k_{\rm c} = M_{\rm II}/M_3 \quad (33)$$

where $M_{\rm I}$, $M_{\rm II}$, and M_3 are the molar concentrations of Bi^+, $[\text{Bi}_5]^{3+}$, and Bi^{3+}, respectively.

The following approximate values of the equilibrium quotients were extracted from the data. For ZnCl_2–KCl as solvent at 380° we found $k_{\rm a} = 1.7 \times 10^{10}$ l.^{4}/mole^4, $k_{\rm b} = 1.4 \times 10^{-6}$ mole^2/l.^{2}, and $k_{\rm c} = 3.1 \times 10^{-2}$, while for AlCl_3–NaCl as solvent we found $k_{\rm a} = 4.8 \times 10^8$ l.^{4}/mole^4 at 130° and 4×10^5 l.^{4}/mole^4 at 190°.

A comparison of the equilibrium quotient $k_{\rm a}$ in the two different eutectics leads to an interesting speculation. It is clear from the numbers cited above that if we make an extrapolation (which at best is extremely rough) of $k_{\rm a}$ for AlCl_3–NaCl as solvent up to 380°, it will have a value that is many orders of magnitude smaller than its value at this same temperature as measured for ZnCl_2–KCl as solvent. We believe that this large effect can best be accounted for in terms of a difference in solvation energy for Bi^+ (or, more precisely, hypothetical BiCl) in the two solvents. (Note that this difference in solvation energy enters the appropriate expressions multiplied by a factor of 6.) If this speculation is correct, we arrive at an estimate of the difference in heat of solvation which, although exceedingly rough, is still too large to account for in terms of purely Coulombic interactions between Bi^+ with chloroaluminate ions on the one hand and chlorozincate ions on the other. Hence, we suppose that the binding energy of a Bi^+ complex involves a substantial nonionic component so that there may be some reason to suppose that covalent forces play a large role in these complexes.

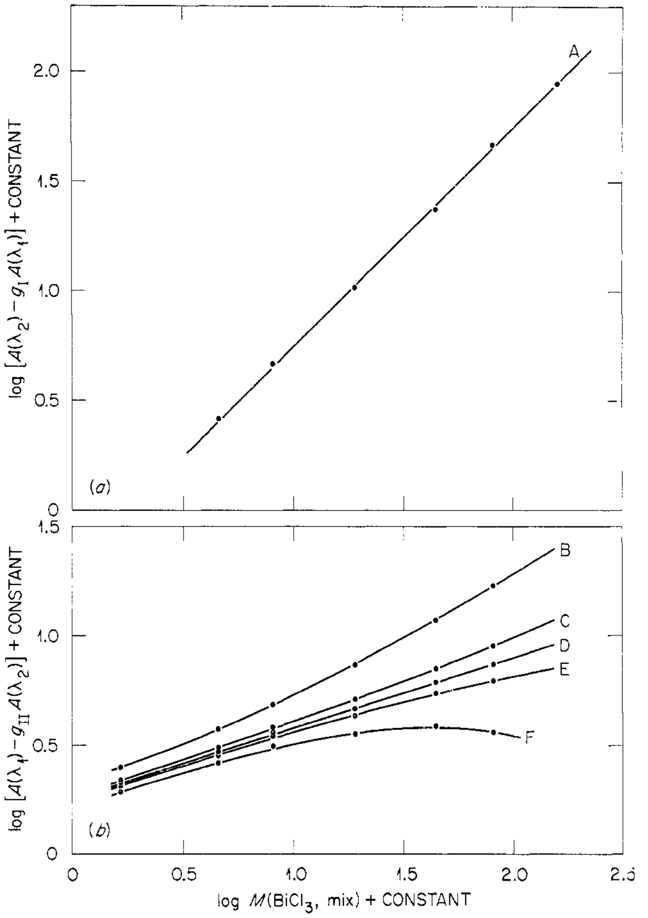


Figure 6.—Plots used to deduce the formulas of reaction products. The interpretation of the quantities plotted as given in the text. Data are for the reaction of bismuth metal with 0.00145 to 0.103 M solutions of BiCl_3 in the ZnCl_2–KCl eutectic at 380°. (a) The value of $g_{\rm I}$ was 0.060. (b) Values of $g_{\rm II}$: B, 0; C, 1.5; D, 1.8; E, 20; F, 2.5.

The estimates cited above involve numerous intuitive guesses regarding various free energy terms so that we do not pretend that our conclusion is anything more than a speculation.

A Third Reaction Product.—When a solution of BiCl_3 in the AlCl_3–NaCl eutectic reacts with an excess of bismuth metal, the BiCl_3 is essentially completely consumed and a third reaction product appears that can be distinguished from Bi^+ and $[\text{Bi}_5]^{3+}$ by its absorption spectrum. The identification of this third product, which has a lower oxidation state than $[\text{Bi}_5]^{3+}$, will be the subject of another paper.

Hydrogen Reduction of BiCl_3 and the Ultraviolet Spectrum of Bi^+.—The measurements described thus far give the near-infrared and visible parts of the

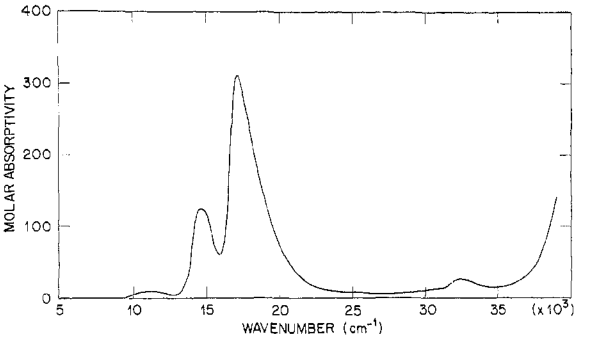


Figure 7.—Spectrum of Bi^+ prepared by reducing a 0.00015 *M* solution of $BiCl_3$ in the $AlCl_3$–NaCl eutectic with hydrogen gas at 310°. The weak band at about 25,000 cm^{-1} is believed to be due to a trace of $[Bi_5]^{3+}$.

Bi^+ spectrum. These are shown in Figure 2. The scale on this figure may be changed from ϵ(prod.) to the molar absorptivity of Bi^+ by multiplying by $^2/_3$. However, these data give only very limited information on the ultraviolet part of the spectrum because Bi^{3+}, which was always present, absorbs very strongly in that region. We only know that the ultraviolet spectrum of Bi^+ is very weak compared with that of Bi^{3+}.

There are substantial experimental difficulties that stand in the way of preparing Bi^+ essentially free of Bi^{3+} *via* the reactions we have described. However, we were able to prepare Bi^+ essentially free of Bi^{3+} by hydrogen reduction of dilute solutions of $BiCl_3$ in the $AlCl_3$–NaCl eutectic at 310°. Reduction was carried out under $^1/_3$ atm of H_2 in a sealed optical cell. Bismuth trichloride concentrations of $(1.19–6.73) \times 10^{-4}$ *M* were used. A typical spectrum is shown in Figure 7.

The Bouguer–Beer law was verified for the near-infrared and visible regions, which have exactly the same shape as the spectrum of Bi^+ prepared from the Bi–$BiCl_3$ reaction in $AlCl_3$–NaCl at 310°. Both methods of preparation yield the same molar absorptivity values for Bi^+ to within experimental uncertainty. For example, in the H_2–$BiCl_3$ reaction the assumption that $Bi^{3+} + 2e^- = Bi^+$ takes place yields the value 309 l./mole cm for the most intense band, whereas in the Bi–$BiCl_3$ reaction the assumption that $2Bi + Bi^{3+} = 3Bi^+$ takes place yields the value 305 l./mole cm for the same band.

The ultraviolet spectrum of the Bi^+ solutions prepared by hydrogen reduction showed very weak bands at about 25,500, 30,000, and 32,500 cm^{-1} (see Figure 7). The extremely weak band at 25,500 cm^{-1} did not appear in all spectra and we believe it to be due to traces of $[Bi_5]^{3+}$, which we know to have a very intense band at 25,600 cm^{-1}. The other two ultraviolet bands appear to be due to Bi^+ as the following considerations show.

First, the absorbance of these bands above the prevailing background was approximately proportional to the Bi^+ concentration. A precise check on the proportionality was not possible because of a small nonreproducibility of the eutectic absorbance in the ultraviolet region.

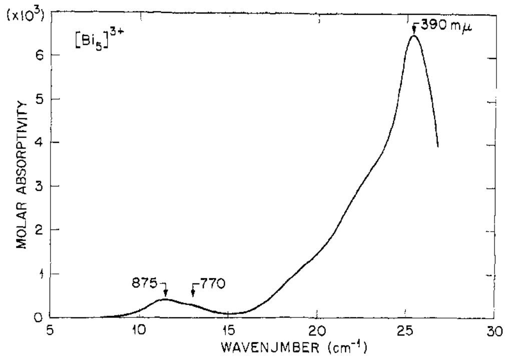


Figure 8.—Spectrum of $[Bi_5]^{3+}$ in the $AlCl_3$–NaCl eutectic at 130°.

Second, it is not likely that these bands are due to impurities in the $BiCl_3$, which was made from zone-refined bismuth of 99.9999% purity.

Third, several considerations suggest that these bands were not due to traces of unreduced Bi^{3+}. The Bi^{3+} band nearest the strongest ultraviolet band of Bi^+ was twice as broad as the latter and separated from it by 1200 cm^{-1}. Furthermore, a crude extrapolation of our equilibrium quotients to 310° leads to an estimate of 10^{-20} for the product of the concentration of $[Bi_5]^{3+}$ and Bi^{3+} so that the presence of an observable absorption from $[Bi_5]^{3+}$ (at 25,500 cm^{-1} in Figure 7) excludes any possibility of an observable absorption by Bi^{3+}. (Our estimate of the equilibrium quotient at 310° can be in error by several orders of magnitude and still not affect this conclusion, which comes primarily from the fact that in the appropriate expression the concentration of Bi^+ is raised to the sixth power.)

Oscillator Strengths for Bi^+.—Using all of the data for Bi^+ we have estimated oscillator strengths of the various bands and listed the results in Table II, where f is the oscillator strength and $\tilde{\nu}$ the wavenumber of the band maximum. Values for the stronger bands are probably accurate to within ±10% while those for the weaker bands are considerably less accurate. Numerical Gaussian analysis with a program written by G. S. Handler was used to separate overlapping bands. This analysis also gave better estimates of band positions than the visual estimates cited previously.

TABLE II

BAND PARAMETERS FOR Bi^+

$10^{-3}\tilde{\nu}$, cm^{-1}	$10^4 f$
11.1	0.7
14.4	4.5
15.2	5
17.1	37
30.0	0.3
32.5	1.5

Spectrum of $[Bi_5]^{3+}$.—With the aid of the data reported above it was possible to separate the spectrum of $[Bi_5]^{3+}$ from that of Bi^+ for mixtures of these two products. Equation 13 was used to determine the absorbance due to Bi^+ at one wavelength for a mixture of Bi^+ and $[Bi_5]^{3+}$. With this fixed point and the spectrum of Bi^+ on a molar absorptivity scale, we calculated the absorbance of Bi^+ in the mixture at all wavelengths and subtracted the result from the total absorbance to get the absorbance of $[Bi_5]^{3+}$. Having determined the concentration of $[Bi_5]^{3+}$ in the mixture, we converted absorbance to molar absorptivity. A spectrum calculated in this way is given in Figure 8.

Acknowledgment.—We record our thanks to Jorulf Brynestad, who repeatedly clarified our thinking during the course of this investigation.

CONTRIBUTION FROM THE METALS AND CERAMICS DIVISION,
OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENNESSEE 37830

Ligand Field Theory of $p^{2,4}$ Configurations and Its Application to the Spectrum of Bi^+ in Molten Salt Media[1a]

BY HAROLD L. DAVIS, NIELS J. BJERRUM, AND G. PEDRO SMITH[1b]

Received December 10, 1966

The theory of ligand field splittings of $p^{2,4}$ configurations and of the relative intensities of $p^2 \leftrightarrow p^2$ electric dipole transitions has been developed and is here reported. The previously published spectrum of Bi^+ in molten salt media is rationalized very well by this theoretical model with regard to both the positions of the experimental bands and their relative intensities.

Introduction

In a recent communication we reported the preparation of Bi^+ in molten salt media and asserted that its near-infrared and visible absorption spectrum could be accounted for in terms of $6p^2 \leftrightarrow 6p^2$ intraconfigurational transitions with the $6p^2$ states perturbed by ligand fields of less than cubic symmetry.[2] In the present paper we shall justify this assertion by developing the ligand field theory of $p^{2,4} \leftrightarrow p^{2,4}$ electric dipole transitions and showing that it rationalizes the experimental results very well. Quite recently the ultraviolet spectrum of Bi^+ in a molten salt medium has been reported,[3] and, as we shall show, these new results also are in excellent agreement with the theoretical model. It seems reasonable, therefore, to speak of bismuth(I) in the molten salt systems as having a partially filled p shell of electrons even though the exact nature of Bi^+–ligand bonding remains unknown.

So far as we know, the only previous attempt to deal with a partially filled p shell in terms that relate to our work was a very qualitative interpretation[4–7] of the spectrum and magnetic susceptibility of what was once believed to be I^+ with the configuration $5p^4$.

Theory

Our experimental information on Bi^+ is confined to its absorption spectra in the $AlCl_3$–$NaCl$ and $ZnCl_2$–KCl eutectics as solvents and its stoichiometric formula with respect to bismuth. The data[3] for the spectrum of Bi^+ in the $AlCl_3$–$NaCl$ eutectic are presented in Table I together with some theoretical quantities that will be explained later. In this table $\tilde{\nu}$ denotes the wavenumber position of a band, and f denotes its oscillator strength.

In the development that follows, it is not necessary to make any specific assumptions regarding the identification of the ligands or their mode of bonding to Bi^+. Nevertheless, in the case of Bi^+ the central bismuth atom is coordinated to something, and it seems likely that the ligands are chloroaluminate ions in the $AlCl_3$–$NaCl$ eutectic and chlorozincate ions in the $ZnCl_2$–KCl eutectic. The only other possible ligands are chloride ions unattached to aluminum or zinc, but these have a very low concentration because the chloroaluminate and chlorozincate ions present are unsaturated with respect to chloride. Although we have no experimental information on coordination geometry, theoretical progress proves possible by working from general geometrical considerations.

The free Bi^+ ion has the configuration $6p^2$ with $^3P_0$ as ground state.[8] Table II lists positions of intraconfigurational excited states as obtained from measurements[9] and as calculated from the Slater–Condon–Shortly model using $F_2 = 1175\ cm^{-1}$ and $\lambda = 5840$

---

[1] (a) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp. Presented at the 22nd Annual Southwest Regional Meeting of the American Chemical Society, Albuquerque, N. M., Nov 30–Dec 2, 1966. (b) Department of Chemistry, University of Tennessee, Knoxville, Tenn.

(2) N. J. Bjerrum, C. R. Boston, G. P. Smith, and H. L. Davis, *Inorg. Nucl. Chem. Letters*, **1**, 141 (1965).

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

(4) J. Arotsky, H. C. Mishra, and M. C. R. Symons, *J. Chem. Soc.*, 12 (1961); J. Arotsky and M. C. R. Symons, *Quart Rev.* (London), **16**, 282 (1962); *Inorg. Chem.*, **2**, 880 (1963).

(5) R. F. Pasternack and T. S. Piper, *ibid.*, **2**, 429 (1963).

(6) E. E. Aynsley, N. N. Greenwood, and D. H. W. Wharmby, *J. Chem. Soc.*, 5369 (1963).

(7) R. J. Gillespie and J. B. Milne, *Inorg. Chem.*, **5**, 1577 (1966).

(8) We follow convention and use the Russell–Saunders notation to designate free-ion states even though the strong spin–orbit coupling forces in bismuth prevent S and L from being good quantum numbers (except for the $^3P_1$ state).

(9) C. E. Moore, National Bureau of Standards Circular 467, Vol. III, U. S. Government Printing Office, Washington, D. C., 1958, p 221.