

## An Electromotive Force Study of Solutions of Bismuth in Bismuth(III) Chloride At 240°<sup>1</sup>

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Melts of BiCl<sub>3</sub> containing 0.2 to 20 mole % metal have been studied in sealed concentration cells without fixed reference at 240°. The marked nonideality required by the EMF data above about 1% Bi contrasts with the substantially ideal solutions of Bi<sup>+</sup> and Bi<sub>3</sub><sup>+</sup> (vice Bi<sub>4</sub><sup>4+</sup>) previously established at higher temperatures and lower metal concentrations. Combination of the EMF results with published cryoscopic data allows some limits to be placed on the activity coefficients of these species; in particular, positive deviation is required for the low-field Bi<sub>3</sub><sup>+</sup> over much of the range. Other thermodynamic measurements on the concentrated solutions at higher temperatures are also considered briefly.

### Introduction

The nature of solute species formed in dilute solutions of bismuth in its molten trichloride is relatively well established. EMF studies by Topol, Yosim and Osteryoung<sup>2</sup> clearly showed that Bi<sup>+</sup> is the sole product for up to 0.1 to 0.6 mole % metal at 238° to 350°, respectively, and that this polymerizes to a species such as Bi<sub>4</sub><sup>4+</sup> at higher concentrations, as identified by an 8-electron electrode reaction  $\text{Bi}_4^{4+} \rightleftharpoons 4\text{Bi}^{3+} + 8e$ . They derived equilibrium constants for the  $4\text{Bi}^{+} = \text{Bi}_4^{4+}$  reaction which described the data well, up to about 7% metal at 300 to 325°, for example. A convincing, non-thermodynamic support for this interpretation was provided by the spectral studies of Boston, Smith, and Howicks,<sup>3</sup> who showed that two and only two species were formed in solutions containing up to about 6% metal at 264° and 350° and 4% at 433°. A stoichiometric relationship which amounts to the ratio of the Nernst  $n$ 's for the two solutes was furthermore shown to be about 4, with 5 not excluded. It has also been noted that an ideal solution of Bi<sub>4</sub><sup>4+</sup> (or Bi<sub>4</sub>Cl<sub>4</sub>) in BiCl<sub>3</sub> gives a satisfactory description of the solvent pressures of solutions containing 5 to 25% metal at 300° where Bi<sup>+</sup> would be a minor constituent.<sup>4</sup>

The present EMF investigation was undertaken to extend the data to higher metal concentrations where evidence might be found for still higher species such as

Bi<sub>9</sub><sup>5+</sup><sup>5</sup> (or the more recently reported Bi<sub>5</sub><sup>3+</sup> and Bi<sub>8</sub><sup>2+</sup><sup>6-8</sup>). A lower temperature of 240° was also chosen so as to favor the formation of more complex solutes. However, it will be seen that the EMF data at 240° require a substantial nonideality of the solutions, and these results together with those of cryoscopic studies<sup>9</sup> allow a qualitative diagnosis of the character of these deviations.

### Experimental Section

The cell design and the techniques of its operation were substantially the same as described earlier;<sup>10</sup> *viz*, a one-piece Pyrex cell sealed under vacuum which contained outgassed carbon electrodes and an ultrafine fritted disk separating the anode and cathode compartments. Known amounts of metal and salt were added to each compartment, the latter being introduced under vacuum from weighed ampoules through the use of a magnetic breaker. The metal employed was  $\geq 99.99\%$  "reactor grade" for which spectrographic analysis showed Cu and Fe at the "trace" level, Pb, Ag, and Si as "faint trace", and B, Al, Sb, Sn, and Zn undetected. The BiCl<sub>3</sub> was prepared from the elements, vacuum sublimed, and melted down into the attached ampoules. Rechlorination was employed if the salt was not colorless, as this generally indicates carbon impurities and probably some reduction of bismuth(III). The entire apparatus save for the tubes insulating the leads was immersed in a molten nitrate thermostat. A constant potential was achieved in about 6 to 20 hours, depending on the amounts of metal being dissolved, and this was generally constant overnight. Several variations in cell design and operation were also tried. In several cases the frit was partially fused to reduce possible flow, which typically raised the cell resistance from about 200 to 1300Ω. Three cells with tantalum rather than carbon electrodes gave essentially the same results. The absence of irreversible junction potentials was evidently established with a cell containing both a single and a double frit in parallel tubes connecting the electrode compartments. Identical results were obtained

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) L. E. Topol, S. J. Yosim, and R. A. Osteryoung, *J. Phys. Chem.*, **65**, 1511 (1961).

(3) C. R. Boston, G. P. Smith, and L. C. Howick, *ibid.*, **67**, 1849 (1963).

(4) J. D. Corbett, *ibid.*, **62**, 1149 (1958).

(5) A. Hershaff and J. D. Corbett, *Inorg. Chem.*, **2**, 979 (1963).

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

(7) N. J. Bjerrum and G. P. Smith, *ibid.*, **6**, 1968 (1967).

(8) J. D. Corbett, *ibid.*, **7**, 193 (1968).

(9) S. W. Mayer, S. J. Yosim, and L. E. Topol, *J. Phys. Chem.*, **64**, 238 (1960).

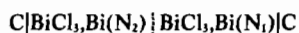
(10) J. D. Corbett and F. C. Albers, *J. Am. Chem. Soc.*, **82**, 533 (1960).

through each junction when these were alternatively utilized by tipping the entire cell; equilibrium at the electrodes appeared to be established very rapidly. The concentrations in three cells were also altered by electrolysis; however, this approach generally results in only a small change in the mean concentration of the cell unless a third compartment is utilized.

The anolyte and catholyte compositions were determined analytically after the measurements for 10 of the 17 separate cells studied; the results were in good agreement with the quantities added unless diffusion had been obvious during the run. Total bismuth and chlorine were determined by EDTA titration and AgCl precipitation, respectively, except that metal in the more dilute mixtures ( $\leq 0.03$  Bi/BiCl<sub>3</sub>) was weighed directly after volatilization of the salt in vacuum at 300°.

## Results and Discussion

The results obtained formally pertain to the concentration cell



and therefore may be expressed in terms of an apparent Nernst  $n$  as

$$EF/2.3RT = (1/n) \log [N_2(1-N_1)/(1-N_2)N_1] \quad (1)$$

for  $N_2 > N_1$ , where  $N$  hereafter denotes  $N_{\text{Bi}}$  in BiCl<sub>3</sub>. The data obtained at 240° are represented in Figure 1 as  $1/n$  vs.  $\log N/(1-N)$ . The endpoints of the line through each solid circle denote the anolyte and catholyte compositions (and not error estimates). The close agreement between runs with comparable values for  $N$  and  $n$  but with different values of  $N_2$  and  $N_1$  indicates the cells are properly additive.

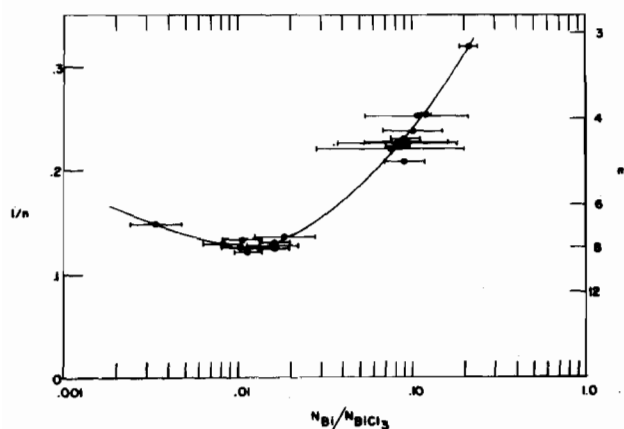


Figure 1. The reciprocal of the Nernst  $n$  vs.  $N_{\text{Bi}}/N_{\text{BiCl}_3}$  for concentration cells  $C|\text{BiCl}_3, \text{Bi}(N_2)||\text{BiCl}_3, \text{Bi}(N_1)|C$ . The endpoints of the horizontal lines mark the anolyte and catholyte composition for each cell studied.

The dependence shown in the Figure is not that from a simple association equilibrium expected from pre-

vious studies. A constant value of  $n$  would result from the formation of a single solute species in dilute solution, while a regular increase in the apparent  $n$  with metal concentration toward a value of 8 would be indicative of a polymerization reaction of the sort  $4\text{Bi}^+ = \text{Bi}_4^{4+}$ , as was seen in earlier studies in more dilute solutions and also at higher temperatures (see Introduction). The latter behavior appears to be present here only below about 1.5% metal. Because the prior evidence on species in this system seems so compelling, it will be assumed that the apparent decrease in  $n$  at higher concentrations is a result of substantial nonideality of the solutions. A similar decrease in  $n$  was observed by Topol *et al.*<sup>2</sup> for solutions containing more than about 7% metal at 300° and was likewise attributed to deviations from ideality. Activity effects would, of course, be expected to be more pronounced at lower temperatures.

Before considering this interpretation further, an interjection is necessary concerning the presumed formulae of the indicated species. These have generally been considered as simple  $\text{Bi}_n^{n+}$  entities, probably because BiCl was once thought to be the composition of what turned out to be a relatively complex  $\text{BiCl}_{1.67}$ .<sup>5</sup> However, both the EMF and spectral studies were carried out in sufficiently dilute solutions that the amount of participating solvent could not be reliably established so that these cations might be better represented as  $[\text{Bi}^+ \cdot x\text{Bi}^{3+}]$  and  $[\text{Bi}_3^+ \cdot y\text{Bi}^{3+}]$ . Although the simple ion  $\text{Bi}^+$  is now well established,<sup>6</sup> there is no further experimental evidence for  $\text{Bi}_4^{4+}$ , or in general  $[\text{Bi}_3^+ \cdot y\text{Bi}^{3+}]$ . However, one criterion of stability for such polynuclear species is that their symmetry should be such as to achieve not only the maximum bonding between the atoms but also a fairly uniform distribution of the total bond order and of the cationic charge.<sup>8</sup> The two arrangements which would best achieve this with four atoms are tetrahedral and square planar, but LCAO-MO calculations<sup>11</sup> show that these will be most stable (closed shell) with 12 and 6 electrons, respectively, rather than the 8 in  $\text{Bi}_4^{4+}$ . On the other hand,  $\text{Bi}_3^+$  ( $y=0$ ) has a very satisfactory bonding scheme for 8 electrons in a triangular ( $D_{3h}$ ) arrangement.<sup>11</sup> *A priori*,  $\text{Bi}_3^+ \cdot 2\text{Bi}^{3+}$  or  $\text{Bi}_5^{7+}$  ( $y=2$ ) would seem unreasonable on the basis of the high charge; in addition,  $\text{Bi}_5^{3+}$  is known.<sup>6,8</sup> At present there do not seem to be sufficiently accurate thermodynamic measurements available on sufficiently concentrated and ideal solutions to establish the correctness of this prediction.

The data shown in Figure 1 give a direct measure of the rate of change of the activity ratios of the species in any oxidation-reduction couple provided one electrode reaction is reversible and all species are in equilibrium in solution. Letting A, B, and C denote  $\text{Bi}^+$ ,  $\text{Bi}_3^+$ , and  $\text{Bi}^{3+}$ , respectively, this would mean

$$EF/2.3RT = 1/2 \log [(a_A/a_C)_2 / (a_B/a_C)_1] = 1/8 \log [(a_B/a_C)^2 / (a_B/a_C)^1] \quad (2)$$

(11) LCAO calculations analogous to those reported previously (Ref. 8 and J. D. Corbett and R. E. Rundle, *Inorg. Chem.*, 3, 1408 (1964)) give energy parameters  $x [E = \alpha + x(\beta_0 - \alpha)]$  of 0.437,  $a_1'$ ; 0.291,  $a_2''$ ; 0.239,  $e'$  and  $-0.258$ ,  $e''$  for the four lowest energy orbitals for 3 atoms with  $D_{3h}$  symmetry at 3.04 Å.<sup>8</sup> In contrast, 4 atoms in a square ( $D_{4d}$ ) give  $x = 0.288$ ,  $a_{1g}$ ; 0.266,  $b_{2g}$ ; 0.180,  $e_u$ ;  $-0.007$ ,  $e_g$ . The tetrahedral  $\text{Bi}_4$  is obviously analogous to  $\text{P}_4$  (R. A. Hart, M. B. Robin, and N. A. Kuebler, *J. Chem. Phys.*, 42, 3631 (1965)).

and so on, more than one activity quotient being determined by equilibrium constants. Implicit in equation (2) is that chloride ions transport substantially all of the current and that electronic conduction is not important. These assumptions are not unreasonable in view of the nature of the solvent  $\text{BiCl}_3$ , the relatively dilute solutions employed ( $N_B \sim 3N/8$  for the indicated large association<sup>2</sup>), and the conductivity results of Grantham<sup>12</sup> at 230°, where  $K$  decreases by about 40% out to 30% metal.

The data in the Figure may be utilized by noting from equations (1) and (2) that

$$\int_{N_0}^N (1/n) d \log(N/1-N) = 1/2 \log[(a_A/a_C)_N k_0^{-1}]$$

where  $k_0 = (a_A/a_C)_{N_0}$ . Denoting the integral as  $\log I_N$ ,

$$(a_A/a_C)_N = k_0 I_N^2 \quad (3)$$

Values of  $I_N^2$  for  $N_0 = 0.01$  obtained by graphical integration of Figure 1 are given in Table I. Additional constraints for a melt in which the only important equilibrium is



are the equilibrium constant

$$K = a_B a_C / a_A^4, \quad (5)$$

the gross composition in terms of mole fraction metal  $N$ , which means

$$N = (2N_A + 8N_B) / (3N_A + 9N_B + 3N_C) \quad (6)$$

and

$$N_A + N_B + N_C = 1 \quad (7)$$

**Table I.** Values of  $I_N^2$  from Figure 1.

$N/1-N$	$I_N^2$	$N/1-N$	$I_N^2$
.01	1.00	.07	1.816
.014	1.087	.10	2.130
.02	1.191	.14	2.532
.03	1.340	.2	3.122
.05	1.591	.3	(4.110)

These relationships can be suitably altered and amended to include additional species such as  $\text{Bi}_5^{3+}$ ,  $\text{Bi}_8^{2+}$  or  $\text{Bi}_9^{5+}$ . However, attempts to describe the EMF data in terms of ideal solutions containing even three such solutes were completely unsuccessful, as might be expected.

It is significant that the freezing point depression of  $\text{BiCl}_3$  by metal<sup>9</sup> is also irregular in the sense that the apparent  $\text{Bi}_2^{2+}$  (or  $\text{Bi}_2\text{Cl}_2$ ) solute is also inconsistent with substantially ideal solutions of  $\text{Bi}^+$  and  $\text{Bi}_3^+$  (or  $\text{Bi}_4^{4+}$ ) that give such an excellent description of the system at higher temperatures. Although the cryoscopic data alone might be rationalized in terms of fairly modest negative deviations of the solvent, this is clearly not appropriate for the EMF data where a ratio of solute

to solvent activity is determined. Since the melting point of  $\text{BiCl}_3$ <sup>9</sup> is only 6.4° lower than that employed here, it may be presumed that both measurements are troubled by the same general sort of non-ideality. At least a qualitative idea of the nature of this may be obtained with the plausible assumption that the temperature dependencies of the activity coefficients and of the equilibrium constant for the common equilibrium (4) are small. (The known  $\Delta C_p$  term<sup>9</sup> corresponds to a negligible effect on the activity of  $\text{BiCl}_3$ ). In this case description of the solvent activity in terms of ideal solutions of an apparent  $\text{Bi}_2^{2+}$  gives us the additional relationship<sup>13</sup>

$$a_C = 2(2-3N)/(4-3N) \quad (8)$$

Eliminating  $N_A$  from equations (6) and (7),  $a_A$  from (3) and (5),  $N_B$  from these results, and substituting  $a_C$  from (8) gives a relationship between  $\gamma_B$  and  $\gamma_C$ ,

$$4/\gamma_C + 3N - 4 = 48Kk_0^4 I_N^4 (1-N)(2-3N)^2 / (4-3N)^2 \gamma_B \quad (9)$$

Likewise eliminating  $N_B$  from (6) and (7) and  $N_A$  from this result and (3) yields, with (8),

$$(8-9N/2-3N) - 4/\gamma_C = 12(1-N)k_0 I_N^2 / (4-3N) \gamma_A \quad (10)$$

The lowest reference state  $N_0$  for which there are activity data for both equations (3) and (8) is about 0.01 since the cryoscopic data would presumably show deviations from (8) at higher dilution because of increased dissociation to  $\text{Bi}^+$ . For  $N_0 = .01$ , where  $\gamma_i = 1$  by definition, equation (9) gives

$$Kk_0^4 = 3N_0(4-6N_0)^2 / 48(1-N_0)(2-3N_0)^2 = 2.54 \times 10^{-3}$$

and likewise in (10),

$$k_0 = 3N_0(4-3N_0) / 12(2-3N_0)(1-N_0) = 5.04 \times 10^{-3}$$

which gives  $K = 4.0 \times 10^6$ , in good agreement with about  $7 \times 10^{6 \pm 1}$  given by Topol *et al.*<sup>2</sup> To some extent the close agreement results from a fortuitous choice of  $N_0$ .

The form of equations (9) and (10) allows some meaningful restrictions to be placed on the activity coefficient. In the former the limit  $\gamma_B = \infty$  corresponds to

$$\gamma_C(\text{max}) = 4/(4-3N)$$

and this in (10) means

$$\gamma_A(\text{min}) = 6.05 \times 10^{-2} (2-3) I_N^2 / 9N(4-3N)$$

Similarly  $\gamma_A = \infty$  in (10) gives

$$\gamma_C(\text{min}) = 4(2-3N)/(8-9N)$$

and then in (9),

$$\gamma_B(\text{min}) = 1.218 \times 10^{-1} I_N^4 (2-3N)^3 / 9N(4-3N)^2$$

(13) The Gibbs-Duhem equation does not furnish an additional constraint, as its application to this system reduces to a function of only  $N$  and the differentials of the equations (3) and (8) representing the experimental data. The relationship holds reasonably well considering the relative precision of the two sets of data and the small difference in temperature.

(12) L. F. Grantham, *ibid.*, 43, 1415 (1965).

The extremes possible for the activity of the solvent (C) are, for example, 0.980 and 1.029 at  $N = 0.05$ , 0.958 and 1.081 at 0.10, and 0.903 and 1.176 at 0.20. The minimum value is just the activity coefficient for  $\text{BiCl}_3$  necessary to explain the cryoscopic data on the basis of an ideal behavior of  $\text{Bi}_3^{3+}$  solute, though the concomitant condition  $\gamma_A = \infty$  makes this somewhat meaningless. The deviations required for  $\text{Bi}_3^{3+}$  (B) are the most informative, the minimum value of the activity coefficient being about 0.66 for 1 to 3% metal, and then rising to unity at 7.4%, 1.46 at 12%, and slightly over 2.0 at 16%. A substantial positive deviation is thus required for  $\text{Bi}_3^{3+}$ . The minimum values of the activity coefficients for  $\text{Bi}^+$  (A) are less informative, decreasing from 0.2 at 2% to 0.05 at 20%.

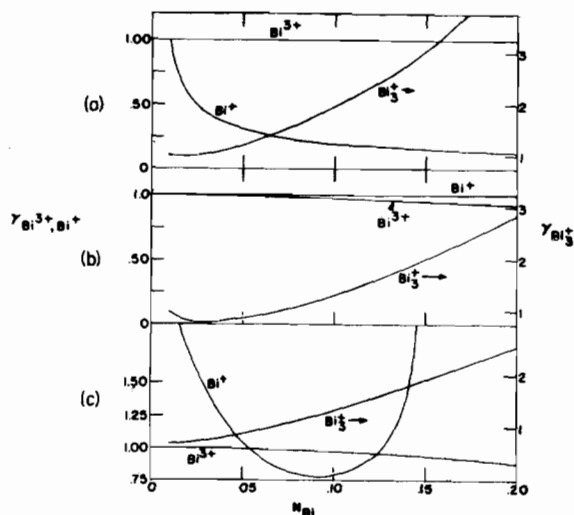


Figure 2. Three possible sets of activity coefficients for  $\text{Bi}^+$ ,  $\text{Bi}_3^{3+}$ , and  $\text{Bi}^{3+}$  according to equations (9) and (10). (a)  $\gamma_{\text{Bi}_3^{3+}} = 1$ . (b)  $\gamma_{\text{Bi}^+} = 1$ , (c)  $\gamma_{\text{Bi}_3^{3+}}$  estimated from cryoscopic data for KCl in  $\text{BiCl}_3$  (see text).

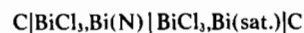
No further restrictions on the actual coefficients are required by the data. The application of equations (9) and (10) to three plausible, real situations is shown in Figure 2. At the top (a) are the values of  $\gamma_{\text{Bi}^+}$  and  $\gamma_{\text{Bi}_3^{3+}}$  necessary for an ideal solvent,  $\gamma_{\text{Bi}_3^{3+}} = 1$ . Positive deviation of  $\text{Bi}_3^{3+}$  (relative to the reference state) is required over the whole range while the trend for  $\text{Bi}^+$  is again less informative. The middle portion, Figure 2b, represents the result of a unity activity coefficient for  $\text{Bi}^+$ , which gives only slight negative deviations for  $\text{Bi}_3^{3+}$ , and  $\text{Bi}_3^{3+}$  behaves as before. Similar results are obtained if other constant (Henry's Law) coefficients are chosen for  $\text{Bi}^+$ . Finally the bottom third of the Figure is based on an attempt to estimate the activity of  $\text{BiCl}_3$  from an independent source. The cryoscopic data for NaCl and KCl in  $\text{BiCl}_3$ <sup>14</sup> suggest that the negative deviations found may come from the addition of the basic chloride ion to melts containing the high field  $\text{Bi}^{3+}$ , ultimately forming chlorobismuthate(III)

anions. The increase in pCl accompanying the formation of less acidic cations such as  $\text{Bi}^+$  and  $\text{Bi}_3^{3+}$  should act similarly, and indeed, such complex anions are found in  $\text{BiCl}_{1.167}$ .<sup>5</sup> The activity coefficient of  $\text{BiCl}_3$  in the metal solutions was therefore estimated from that for KCl in  $\text{BiCl}_3$  at the same concentration of added chloride, making the somewhat tenuous but necessary approximation that the  $\text{Bi}_3^{3+}$  resembles  $\text{K}^+$  in its secondary effect on the  $\text{Bi}^{3+}-\text{Cl}^-$  interactions. The result of this "ballpark" approximation on the activity coefficient of  $\text{Bi}_3^{3+}$ , Figure 2(c), is similar to that just previous, though  $\gamma_{\text{Bi}^+}$  now has an irregular dependence on concentration.

The small deviations for  $\text{BiCl}_3$  just estimated suggest that anionic complexes are not very important in this concentration range since, according to the Temkin model with ionic mole fractions,  $N_{\text{BiCl}_3} = N_{\text{Bi}^{3+}}(N_{\text{Cl}^-})^3$ . The absence of large deviations for the solvent also offers some support for a necessary assumption that has only been implied in the foregoing treatment, that the solutions may to a good approximation be considered in terms of mixed cations with a common chloride anion.

In general, it appears that a wide range of activity coefficients for  $\text{Bi}^+$  can be accommodated with the present information but that these have relatively minor effects on those of the predominant species  $\text{Bi}_3^{3+}$  and  $\text{Bi}^{3+}$ . The required positive deviations for  $\text{Bi}_3^{3+}$  seem particularly significant and entirely reasonable as well considering that it is the lowest field cation present. It should be noted that this conclusion is not altered by the use of  $N_0 = 0.002$  or  $\text{Bi}_4^{4+}$  rather than  $\text{Bi}_3^{3+}$  though the reason for the positive deviation would not be as obvious in the latter case. The question of the formation of yet higher polybismuth ions in these solutions should be much easier to answer with thermodynamic data obtained at substantially higher temperatures where activity problems should be less likely. In this connection it is interesting to note that the  $\text{BiCl}_3$  pressures of the solutions at 392°<sup>15</sup> show a very suggestive positive deviation from that expected with just equilibrium (4). The expected thermal dissociation of the higher species is very possibly responsible for the pronounced retrograde "solubility" of metal in  $\text{BiCl}_3$  between 323°, the melting point of  $\text{BiCl}_{1.167}$ , and about 550°.<sup>16</sup>

One set of EMF data has recently been reported which could provide such information at higher temperatures although some questions have been raised concerning their relationship to earlier work. Delimarskii and Roms<sup>17</sup> investigated concentration cells of the type



in which  $N$  was varied from zero (pure  $\text{BiCl}_3$ ) to 0.41 at 400°. They found the data were described by a linear equation of the form

$$-EF/2.3RT = a \log N + b$$

(15) D. Cubicciotti, F. J. Keneshea, and C. M. Kelley, *ibid.*, 62, 463 (1958); F. J. Keneshea, W. Wilson, and D. Cubicciotti, *ibid.*, 64, 827 (1960).

(16) S. J. Yosim, A. J. Darnell, W. G. Gehman, and S. W. Mayer, *ibid.*, 63, 230 (1959).

(17) Yu. K. Delimarskii and Yu. G. Roms, *Ukr. Khim. Zh.*, 30, 457 (1964).

(14) L. E. Topol, S. W. Mayer, and L. D. Ransom, *J. Phys. Chem.*, 64, 862 (1960).

(with  $a=0.237$  and  $b=0.0713$  according to our plot of all of their data). Since the average value of  $a$  found corresponded a Nernst  $n$  of 4.42 (4.22 with our slope), the solute was concluded to be  $\text{Bi}_2^{2+}$  over the entire range. Subsequently, there has been some discussion between these authors and Topol and Osteryoung<sup>18</sup> concerning the disagreement between this result and the EMF and spectral studies already mentioned. The latter questioned the small potentials obtained with "pure"  $\text{BiCl}_3$ , which instead extrapolate to the order of 0.4% Bi in the above equation, and the fact that the zero EMF extrapolation gives a higher metal content at saturation (49%) than indicated by the phase diagram (36%). It might also be observed that the latter composition is in better agreement with vapor pressure results ( $\sim 39\%$ )<sup>15</sup> and that the diamagnetism of the melts<sup>19</sup> will in general not allow a distinction to be made between any species which contain an even number of electrons,  $\text{Bi}_2^{2+}$  and  $\text{Bi}_4^{4+}$ , for example. More

important is the fact that the experimental results appear inconsistent with the conclusion regarding  $\text{Bi}_2^{2+}$ . The above linear equation in  $E$  vs.  $\log N$  would apply for the half reaction  $\text{Bi}_2^{2+} \rightleftharpoons 2\text{Bi}^{3+} + 4e$  only for dilute solutions in which  $a_{\text{Bi}^{3+}}$ , or  $N_{\text{Bi}^{3+}}$  for a practical interpretation, remains constant. This is certainly not the case for other than a  $\text{Bi}^0$  solute at the large metal concentrations employed, and in fact the plot of  $E$  vs. the more appropriate  $\log[N_{\text{Bi}^{3+}}^2/N_{\text{Bi}_2^{2+}}]$  is definitely curved, with values for the Nernst  $n$  of about 4.4, 5.0 and 8.2 at apparent mole fractions metal of 0.016, 0.07 and 0.25, respectively. The rate of change of  $n$  is too small to be described by such as the  $\text{Bi}^+-\text{Bi}_3^+$  equilibrium considered here, and no other interpretation is evident.

- (18) L. E. Topol and R. A. Osteryoung, *ibid.*, 31, 998 (1965); Yu. K. Delimarskii and Yu. G. Roms, *ibid.*, 31, 999 (1965).  
 (19) N. H. Nachtrieb, *J. Phys. Chem.*, 66, 1163 (1962); J. D. Corbett, S. v. Winbush, and F. C. Albers, *J. Am. Chem. Soc.*, 79, 3020 (1957).