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1961

SovietRxiv

Fig. 1. Cell.

Figure 1: Fig. 1. Cell.

Abstract

Full Text

Chemistry

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Interaction of Bismuth Chloride with Alkali-Metal Chlorides

(Presented by Academician V. I. Spitsyn, July 14, 1961)

A number of works have been devoted to the behavior of bismuth in melts of halide salts. Some of them concern the determination of the possibility of purifying metals by electrolysis (^{1,2}). Others concern the determination of its electrode potentials ($^{3–5}$). The potentials of bismuth, measured by different investigators relative to different reference electrodes, are practically not comparable. Moreover, nowhere is the dependence of the equilibrium potential of the metal on the temperature and on the concentration of its ions in the melt given. Meanwhile, the study of such a dependence makes it possible to elucidate the nature of the interaction of bismuth ions with the other constituents of the electrolyte, in particular with the anions and cations of the solvent salt, and makes possible the proper organization of the electrolytic purification of bismuth.

The present work was devoted to determining the nature of the interaction of bismuth chloride with alkali-metal chlorides in the temperature interval 700–850°C. For this purpose, measurements were made of the equilibrium potentials of metallic bismuth in electrolytes with different contents of bismuth chloride. The experiments were carried out in a cell, the construction of which is shown schematically in Fig. 1. It consisted of a quartz test tube mounted in a massive steel block of a heating furnace and tightly closed with a rubber stopper.

Fig. 1. Cell. 1 –quartz test tube, 2 –chloride half-cell, 3 –graphite tube, 4 –electrolyte, 5 –asbestos diaphragm, 6 –molybdenum current lead, 7 –thermocouple, 8 –alundum cup, 9 –bismuth electrode.

An equimolar mixture of potassium and sodium chlorides of "chemically pure" grade, purified by preliminary electrolysis, was charged into the test tube, and an alundum crucible placed in it. After it had melted, metallic bismuth, previously purified from impurities by electrolysis, was introduced into the crucible. Bismuth chloride was introduced into the electrolyte by anodic dissolution of part of the metal charged into the crucible. The molybdenum cathode was

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

placed in the electrolyte located in the quartz test tube. Thus, in this case the alundum crucible served as a diaphragm separating the anolyte from the catholyte. The bismuth content in the melt was controlled by the amount of current passed—

···through the electrolyte electrically and was determined by chemical analysis of the contents of the crucible after completion of the experiment.

To avoid the action of air on the salt melt, the gas space of the cell, after evacuation of the air, was filled with purified helium. Measurements of the potentials of metallic bismuth relative to the chlorine reference electrode ([6,7]) were carried out using a high-resistance potentiometer PPTV-1. A galvanometer with a sensitivity of 10^{-9} a per division was used as the null instrument. The temperature of the melt was maintained constant within ±3° by an automatic transformer and

Fig. 2. Dependence of the emf of the cell on temperature. Concentration of Bi in the melt: 1—1.13 wt.%; 2—3.05 wt.%; 3—12.06 wt.%

Fig. 3. Dependence of the emf of the cell on the concentration N of bismuth chloride in the melt

was recorded by the high-resistance potentiometer PPTV-1 with a sensitive galvanometer.

Values of the emf were accepted as reliable if they remained constant for at least one hour within ±1 mV.

The emf values measured at different temperatures between the bismuth and chlorine electrodes in melts containing 1.13, 3.05, and 12.06 wt.% Bi are presented graphically in Fig. 2. As can be seen, the emf of the cell decreases linearly with temperature. The experimental points lie quite satisfactorily on straight lines corresponding to the following empirical equations:

$$\begin{aligned} E_1 &= 1.446 - 2.95 \cdot 10^{-4} T_\mathrm{B}, \\ E_2 &= 1.412 - 2.90 \cdot 10^{-4} T_\mathrm{B}, \\ E_3 &= 1.378 - 3.00 \cdot 10^{-4} T_\mathrm{B}. \end{aligned}$$

In our measurements, along with the electrochemical potential difference sought, there enters the thermoelectromotive force between the molybdenum and carbon current leads, opposite in sign to it, whose temperature dependence is expressed by the equation $\varepsilon_T = 0.008 - 0.17 \cdot 10^{-4} T_\mathrm{B}$ ([8]). Taking into account the thermo-emf between the graphite rod of the chlorine electrode and the molybdenum current lead to the bismuth, the equilibrium potentials of bismuth relative to the chlorine reference electrode in the molten equimolar mixture are found to be:

$$E_1 = -1.438 + 2.78 \cdot 10^{-4} T_{\mathrm{B}},$$
$$E_2 = -1.404 + 2.73 \cdot 10^{-4} T_{\mathrm{B}},$$
$$E_3 = -1.370 + 2.83 \cdot 10^{-4} T_{\mathrm{B}}.$$

In Fig. 3 the results of the measurements are presented in the form of isotherms showing how the e.m.f. of the cell changes with a change in the concentration of bismuth ions in the electrolyte. The experimental points fall on straight lines described by the empirical equations:

$$E_1 = 1.001 - 0.0650 \lg[\mathrm{Bi}^{3+}] \ (700^\circ),$$

$$E_2 = 0.983 - 0.0665 \lg[\mathrm{Bi}^{3+}] \ (750^\circ),$$

$$E_3 = 0.963 - 0.0695 \lg[\mathrm{Bi}^{3+}] \ (800^\circ).$$

In these equations the coefficients before the logarithms of the ionic mole concentration of bismuth in the electrolyte are close to the value of the prelogarithmic factor in the thermodynamic equation for the equilibrium electrode potential at the corresponding temperature:

$$E_{\mathrm{Bi/Bi}^{3+}} = E^0_{\mathrm{Bi/Bi}^{3+}} + \frac{2.3RT}{3F} \lg[\mathrm{Bi}^{3+}].$$

Consequently, the equilibrium potential of metallic bismuth relative to the chlorine reference electrode in a melt of alkali-metal chlorides is described by the thermodynamic Nernst equation. This means that the liquid bismuth electrode is reversible with respect to Bi^{3+} ions in chloride melts, which, in the investigated concentration region of bismuth trichloride, behave as ideal solutions. If it is assumed that the ideal behavior of the melts studied is retained over the entire range of $\mathrm{BiCl_3}$ concentrations up to pure molten bismuth trichloride, then the e.m.f. of the cell

$$\mathrm{Bi} \,|\, \mathrm{BiCl_3(melt)} \,|\, \mathrm{Cl_2}, \mathrm{C},$$

calculated from our experimental data, should be equal to:

$$E_{\mathrm{e}} = 1.338 - 3.376 \cdot 10^{-4} T_{\mathrm{B}}.$$

The temperature dependence of the e.m.f. of such a cell, calculated from literature data (^{9}), can be represented in the form of the following equation:

$$E_{\mathrm{t}} = 1.254 - 5.750 \cdot 10^{-4} T_{\mathrm{B}}.$$

The difference

$$E_{\mathrm{e}} - E_{\mathrm{t}} = 0.084 - 2.374 \cdot 10^{-4} T_{\mathrm{B}}$$

cannot be explained only by errors of measurement or by inaccuracy in determining the thermochemical quantities used for the calculation.

Obviously, this difference is due mainly to the fact that at high concentrations of bismuth trichloride the melts are no longer ideal solutions, i.e., the change in concentration is accompanied by rearrangements of bismuth ions. The nature of these rearrangements can be judged from the difference $E_{\mathrm{e}} - E_{\mathrm{t}}$ found above. It apparently corresponds to the change in isobaric potential upon passing from pure molten $BiCl_3$ to its dilute solutions in the molten equimolar mixture of sodium and potassium chlorides, which behave as ideal solutions:

$$\Delta Z_{\mathrm{mix}} = -3F(E_{\mathrm{e}} - E_{\mathrm{t}}) = (-5811 - 16.42T)\ \mathrm{cal/mole}.$$

As can be seen, when the salts are mixed a definite interaction occurs, accompanied by the liberation of heat ($\Delta H_{\mathrm{mix}} = 5.81$ kcal) and an increase in entropy ($\Delta S_{\mathrm{mix}} = 16.42$ cal/deg · mole). The fact that heat is evolved when the salts are mixed indicates strengthening of the bonds between Bi^{3+} ions and chloride anions with the formation of complex groupings of an anionic type.

Indeed, the transition from pure molten bismuth trichloride to its dilute solutions in the KCl—NaCl melt amounts, in essence, to replacement of part of the Bi^{3+} ions by alkali-metal ions. Since bismuth ions have a charge three times greater, this produces a change in the short-range order of the ions in the melt. The remaining Bi^{3+} ions

more strongly retain chlorine anions near themselves than do alkali-metal ions. In view of this, in dilute melts bismuth is evidently present mainly in the form of anionic complexes of the type $BiCl_n^{(n-3)-}$, where $n > 3$.

Complex formation of Bi^{3+} ions with chlorine anions in aqueous solutions was studied by Noyes, Holl, and Vitti [10]. On the basis of the data they obtained, Latimer [9] calculated the change in the isobaric potential for the following process:

$$BiCl_{3(\mathrm{cryst})} + Cl^- \rightleftarrows BiCl_4^-, \quad \Delta Z_{298} = -6.6\ \mathrm{kcal}.$$

The change in the isobaric potential of this process can also be calculated from the value of ΔZ_{mix} found by us by extrapolation to a temperature of 298° K, taking into account the latent heat (2.6 kcal/mol) and the entropy of fusion $\left(5.2\ \frac{\mathrm{kcal}}{\mathrm{deg \cdot mol}}\right)$ [11]:

$$\Delta Z_{\mathrm{BiCl4^-}} = -3.21 - 11.22 \cdot 298 \cdot 10^{-3} = -6.56\ \mathrm{kcal/mol}.$$

The very close agreement of the value of $\Delta Z_{\mathrm{BiCl4^-}}$ obtained by us with that cited in Latimer' s monograph makes it possible to conclude that, in alkali-metal chloride melts, bismuth is present in the form of anionic complex groups $\mathrm{BiCl_4^-}$.

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Received
10 VII 1961

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Note: Figure translations are in progress. See original paper for figures.