

The Solution of Alkaline Earth Metals in Their Molten Halides

II. The Magnetic Susceptibility of Melts in the Systems Barium-Barium Chloride and Barium-Barium Bromide

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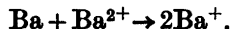
The magnetic susceptibilities of pure molten barium chloride and solutions with up to 7.22 mole % barium metal were measured in the temperature range from 970° to 1030°C. Similar measurements in the temperature range from 850° to 950°C were made in the barium-barium bromide system for compositions up to 7.35 mole % barium metal. Results for both systems showed that additions of barium metal introduced a paramagnetic component in the melt. The paramagnetic effect, however, was less than expected for a melt where the barium metal dissolves by the reaction $\text{Ba} + \text{Ba}^{2+} \rightarrow 2\text{Ba}^+$.

Molten barium chloride and bromide dissolve a considerable amount of barium metal.^{1,2} Each atom of barium metal dissolved in these halide melts, introduces an excess of two electrons compared with the Ba^{2+} species of the halide melt. Several hypotheses have been forwarded to describe how these excess electrons are incorporated in dilute solutions of the melt.

One possibility is that each excess electron pair in the melt becomes part of a cation species of the type $\text{Ba}_n^{(2n-2)+}$, where n is an integer one or larger. (n equal to one would amount to the uncharged barium atom.) The case for $n=2$, corresponding to Ba_2^{2+} ions is analogous to the well known Hg_2^{2+} ion. All electron traps of the $\text{Ba}_n^{(2n-2)+}$ type have an even number of electrons, and are thus likely to be diamagnetic.

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Alternatively the two excess electrons could occupy separated positions in the melt. A particularly simple single-electron model assumes the formation of monovalent Ba^+ ions according to the reaction scheme



Single electron models could generally be formulated as species of the type $Ba_n^{(2n-1)+}$. (An F-center-like trap, say $6Ba^{2+}$ -ions surrounding a vacant anion position, could also conceivably become stabilized by a single trapped electron. This would formally correspond to a Ba_6^{11+} -species.) The unpaired electrons would impart a paramagnetic component to the magnetic susceptibility.

The above model assumes localized electrons in the melt. Since at sufficiently high temperatures there is a continuous transition from an ionic melt to a metallic melt with increasing metal content, electrons delocalized in conduction bands certainly must become important at some composition. Perhaps "free" (*i.e.* loosely bonded) electrons exist even in dilute solutions, and more sophisticated models have to be sought.

Magnetic susceptibility measurements may provide an important clue to one aspect of these systems, namely the degree of pairing of electrons, and such measurements have therefore been undertaken.

EXPERIMENTAL

Materials. Anhydrous barium chloride was prepared from Merck $BaCl_2 \cdot 2H_2O$ "pro analysi" by dehydrating in an air bath at $200^\circ C$ for more than 20 hours and drying in vacuum at $400^\circ C$ for 15 to 20 hours. The manufacturer states the heavy metal impurity content of $BaCl_2 \cdot 2H_2O$ as approximately 0.0004 %, of which Fe constitutes 0.0001 %. Anhydrous barium bromide was prepared from barium carbonate (Merck *p.a.*) and hydrobromic acid (Merck *p.a.*). The hydrated barium bromide was crystallized from the slightly acid reaction mixture and recrystallized from distilled water. The product was dehydrated by heating in a dry nitrogen gas flow. The dehydrated product was analyzed by ion exchange titration and silver titration respectively. The barium and bromide content agreed with the stoichiometric value within the error of analysis, about 1 %. Spectroscopic analysis showed the Fe, Co and Ni content to be less than 0.001 %. The barium metal was provided as rods by Fluka AG. The product was labelled as "puriss (more than 99.5 %)" by the manufacturer. A spectroscopic analysis of the metal was performed, and showed the presence of about 0.001 % Fe, and less than that of Co and Ni. The major contaminations were 0.9 % Sr and 0.1 % Ca. Before use, the oxide film on the metal was carefully removed and the metal cut and weighed in a glove box with an argon atmosphere. During transfer, the metal was protected by a thin toluene coating.

Procedure. An apparatus based on the Gouy method, was constructed. A Mettler semimicro balance (H-16) with magnetic damping, was fitted into a housing which could be evacuated. The balance could be operated from the outside through air-tight transmissions. The sample was suspended from the balance into a silica tube, closed at the bottom. The upper end of the tube was connected with a detachable air-tight connection to the balance housing. The silica tubing was surrounded by a furnace capable of giving a sample temperature of $1050^\circ C$. The temperature was measured with a Pt-10 % Rh thermocouple at the centerline about 1 cm below the sample in the constant temperature zone of the furnace. (Over a length of 20 cm along the center of the furnace, the temperature did not differ by more than $\pm 2^\circ C$). The outer furnace diameter was sufficiently small to pass through the pole gap (40 mm) of a permanent magnet. A permanent magnet (field strength about 3000 gauss) could be accurately adjusted in vertical posi-

tion by a screw and easily swung away from the furnace assembly. The cylindrical molybdenum sample container was fitted with a conical lid. The container (length 108 mm, inner diameter 10 mm, wall thickness 1 mm) would take about 8 cm³ of melt. This volume extended across the non-homogeneous region (~85 mm) of the magnetic field. (The volume gave a sample weight from 23 to 30 grams). The samples were prepared and handled as described in an earlier paper.¹ They were exposed to the atmosphere for less than one minute during the transfer from the argon-filled drybox to the system. Then the system was evacuated and filled with argon gas (spectroscopic pure from Norsk Hydro) of one atmosphere in order to reduce any losses due to salt and metal evaporation at high temperatures. The sample was heated to a temperature well above the melting point of the salt. Heating for 2–3 hours appeared to be adequate for the dissolution and mixing process, since no further changes with time occurred in the magnetic properties of the sample after this period. The samples were weighed with and without the magnetic field a number of times at several different temperatures. Evaporation losses from the sample were negligible, as evidenced from the total weight loss (typically losses were 3 to 8 mg for sample weights 23 to 30 g in a 5 to 9 hour run at 850° to 1050°C). The free metal content of the samples after most runs was analyzed by volumetry of the evolved hydrogen gas on dissolving the sample in dilute hydrochloric acid. The results agreed closely with the weighed in amounts. The molybdenum metal of the sample container is paramagnetic, and a careful calibration for the container was made. The empty container would exhibit a weight change of about 14 mg (temperature dependent by a factor of 0.001 mg/degree) on removing the magnetic field. The container with the sample would show a corresponding weight change of about 10 mg, the diamagnetic sample effect thus being of the order of 4 mg. The apparatus was calibrated to obtain absolute scale with both cobalt chloride and nickel chloride solutions.

In order to obtain values for the susceptibility it is necessary to know the densities of the samples. Density measurements for the barium-barium chloride and bromide systems have been made, and will be reported in a separate paper.³

RESULTS

The molar magnetic susceptibilities derived from the measurements, are given in Table 1. The "mole weights" of the mixtures are calculated by multiplying the mole fractions with corresponding weights and adding. The standard deviation for each composition is obtained from a least

Table 1. Molar magnetic susceptibilities at 1000°C (column 2) as a function of composition (column 1). The standard deviations of these susceptibilities are 1.2 and 1.4 × 10⁻⁴ cgs/mole for the chloride and bromide systems, respectively. Column 3 gives the constant C in the observed temperature dependence $\chi_t = \chi_{1000} + C(t - 1000^\circ)$ of the susceptibility.

	mole % Ba	$\chi \times 10^4$ cgs/mole	C cgs/mole degree
Ba-BaCl ₂	0	-77.7	0.022
	1.82	-69.9	0.016
	3.90	-62.4	-0.002
	7.22	-57.1	0.016
Ba-BaBr ₂	0	-93.9	0.012
	1.26	-88.2	0.028
	3.39	-80.9	0.011
	5.57	-72.2	0.029
	7.53	-69.7	0.008

squares fit (to an equation linear in temperature) of the experimental results at several temperatures. About 10 separate observations were made for each composition. The standard deviations correspond to a weight change (on removing the field) of 0.07 mg. This value seems in reasonable accordance with the expected capability of the balance.

The results show a definite paramagnetic effect by adding the barium metal to the salt. The paramagnetic effect is at the highest barium concentration equivalent with a weight change of 1 mg, which is 14 times the standard deviation, and should therefore be well within the error limits of the present apparatus.

Some preliminary measurements made with a magnet of about half the strength, failed to exhibit any paramagnetic effect in the barium-barium chloride system. Since the weight change is proportional to the square of the field strength, it would have been necessary in this case to detect significantly weight changes as low as 0.25 mg to establish the presence of a paramagnetic component. Such weight changes appear to be too small, however.

The temperature dependence of the molar magnetic susceptibility is given in the last column of Table 1. The temperature coefficient is so small that we do not wish to attach any significance to it.

DISCUSSION

Theoretical values for the magnetic susceptibility can be calculated for various species which may exist in the solutions. From the Langevin equation⁴ and screening constants according to Slater,⁵ a "molar" diamagnetic susceptibility for some species of interest has been obtained. The paramagnetic component of the Ba^+ -ion has been estimated from the Van Vleck equation.⁴ The results are shown in Table 2. Assuming additivity of ionic susceptibilities, the molar susceptibility of barium chloride is calculated to be -84.9×10^{-6} as compared with -77.7×10^{-6} observed here. The discrepancy of these values is not particularly large in view of the approximations made in the theoretical calculations.

Table 2. Theoretical molar susceptibilities χ , estimated by the Langevin and Van Vleck equations, for various species which may be present in the barium-barium chloride and barium-barium bromide systems. T is the absolute temperature. The Ba_2^{2+} ion is assumed to have twice the susceptibility of the diamagnetic component of the Ba^+ ion.

Species	$\chi \times 10^6$ cgs/mole
Br^-	- 40.1
Cl^-	- 25.8
Ba^{2+}	- 33.3
Ba_2^{2+}	- 134.6
Ba^0	- 119.0
Ba^+	- 67.3 + 375 000/ T

From the estimated ionic susceptibilities given in Table 2, it is possible to calculate theoretical susceptibilities for a few different models for the mixture. Assuming that the solution contains a weighed in mole fraction N_{Ba} in $1 - N_{\text{Ba}}$ moles of barium chloride, the susceptibility for a model with the dissolved metal present as Ba_2^{2+} ions becomes:

$$\chi_1 = N_{\text{Ba}} \chi_{\text{Ba}^{2+}} + (1 - 2N_{\text{Ba}}) \chi_{\text{Ba}^{2+}} + 2(1 - N_{\text{Ba}}) \chi_{\text{Cl}^-}$$

Almost the same susceptibilities are calculated for mixtures with dissolved neutral barium atoms for barium metal additions below 10 mole per cent.

If the dissolution process takes place through the formation of the monovalent Ba^+ -ion, the theoretical susceptibility of the mixture in this case becomes:

$$\chi_2 = 2N_{\text{Ba}} \chi_{\text{Ba}^+} + (1 - 2N_{\text{Ba}}) \chi_{\text{Ba}^{2+}} + 2(1 - N_{\text{Ba}}) \chi_{\text{Cl}^-}$$

The above models involve localized electrons. On the other extreme one may consider all the excess electrons to be completely free. Supposing that the free electrons occupy degenerate states (obeying Fermi-Dirac statistics), the following expression may be derived for the mixture:

$$\chi_3 = \chi_{\text{Ba}^{2+}} + (1 - 2N_{\text{Ba}}) \chi_{\text{Cl}^-} + 1.567 \times 10^{-6} N_{\text{Ba}}^{1/3} V^{2/3}$$

Here V is the volume of the mixture containing N_{Ba} moles of (weighed in) barium metal and $1 - N_{\text{Ba}}$ moles of barium chloride. (For a derivation of the last term in the above equation, reference 6 may be consulted.) The extreme free electron model is presented here as a limiting case. More realistic calcula-

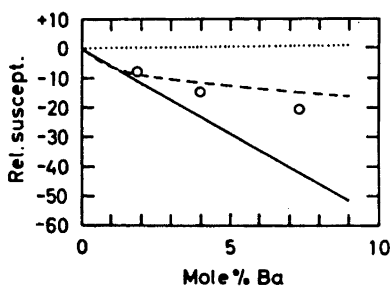


Fig. 1. System BaCl_2 -Ba. Theoretical and observed relative molar magnetic susceptibilities at 1000°C for the barium-barium chloride system. The ordinate gives change in molar susceptibility from that of pure barium chloride ($\chi_{\text{rel.}} = \chi_{\text{mix.}} - \chi_{\text{BaCl}_2}$), in units of -10^{-6} cgs/mole. The dotted curve is calculated for a model with the dissolved barium present as Ba_2^{2+} species. The dashed curve is calculated for free electrons in degenerate energy levels, and the solid curve is calculated for the presence of Ba^+ ions. The experimental results are shown as open circles.

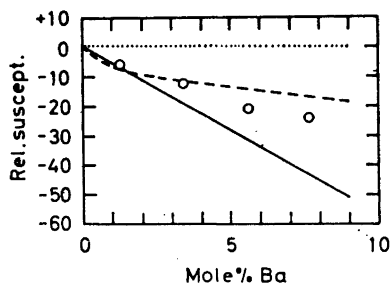


Fig. 2. System BaBr_2 -Ba. Theoretical and observed relative molar magnetic susceptibilities at 1000°C for the barium-barium bromide system. The ordinate gives change in molar susceptibility from that of pure barium bromide ($\chi_{\text{rel.}} = \chi_{\text{mix.}} - \chi_{\text{BaCl}_2}$), in units of -10^{-6} cgs/mole. The dotted curve is calculated for a model with the dissolved barium present as Ba_2^{2+} species. The dashed curve is calculated for free electrons in degenerate energy levels, and the solid curve is calculated for the presence of Ba^+ ions. The experimental results are shown as open circles.

tions would require knowledge, presently unavailable, about the distribution of energy states.

In Figs. 1 and 2 the theoretical values derived from the above equations are compared with the experimental results. (The values in the figures are plotted as relative susceptibilities, that is the change in the susceptibility of barium halide by adding barium metal: $\chi_{\text{relative}} = \chi_{\text{mixtures}} - \chi_{\text{BaX}_2}$). It is seen that the experimental results given as open circles in Figs. 1 and 2, agree with neither the formation of only diamagnetic species nor with the formation of Ba^+ ions. This justifies an increased interest in alternative models, such as models involving electrons delocalized at least to some extent (depending on concentration range and temperature). Models of this kind are attractive for other reasons. The electric conductivity of the mixtures, for instance, increases rapidly with the barium content^{7,8} as expected from models where not all the excess electrons are strongly localized. A more detailed discussion of the nature of these melts, however, will be given in a later paper, when more experimental data have been accumulated.

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