

that the absorption by the mica window (3.0 mg. per cm.²) of the ionization chamber was 49.5 per cent, with a standard deviation of 4.2 per cent. This confirms the value mentioned earlier.

SUMMARY

The measurement of the activity of radiosulfur in barium sulfate precipitates can be carried out quantitatively when a definite weight of the solid is deposited uniformly on a polished brass disk and brought to a fixed position with respect to a thin counter window. A convenient arrangement is described for accomplishing this purpose, and the variability of the results is defined.

The half-life of radiosulfur is observed to be 87.1 ± 1.2 days, and the absorption by the mica window (3.0 mg. per cm.²) is 49.5 ± 4.2 per cent.

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DISTRIBUTION EQUILIBRIA BETWEEN MOLTEN METALS AND MOLTEN SALTS, WITH REFERENCE TO THE STABILITY OF INTERMETALLIC COMPOUNDS IN THE MOLTEN STATE

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Distribution equilibria of a metallic element between a molten metal phase and a molten salt phase have been used to investigate the nature of solutions of metals in molten salts (previously called "pyrosols"). The result of these investigations is clearly in favor of an atomic (and not a colloidal) solution (11, 12). In the case of solutions of cadmium in cadmium chloride, measurements of the magnetic susceptibility have shown that cadmium atoms may unite with cadmium ions to form Cd_2^{++} ("subchloride"; see reference 6).

By investigating the deviations of such distribution equilibria from ideality it is possible to obtain qualitative information about the activities in binary metallic mixtures and about the existence of intermetallic compounds in the molten state.

The variety of systems is rather restricted, because metals are generally soluble only in their own salts (except silicates), and because pure distribution

equilibria only exist when there is no chemical reaction between the metallic solvent and the molten salt, i.e., when the metallic solvent is much less basic than the metallic solute.

I. EXPERIMENTAL

The paper of Heymann and Weber (12) should be consulted with regard to details of the experimental procedure of establishing equilibrium, quenching, etc. The constituents of the respective systems were sealed in tubes of Supremax glass (Jena), and the distribution equilibrium was established in an electric furnace mounted on a rocking apparatus. The tubes were quenched by a blast of air in the case of systems containing sodium; other systems were quenched in carbon tetrachloride.

The analytical procedure in systems containing sodium was that described by Heymann and Weber.

In the system cadmium-antimony-cadmium chloride, antimony was determined by titration with potassium permanganate (14). The cadmium content of the metal phase was determined by difference. The content of cadmium metal in the salt phase was calculated from a chloride determination, making due allowance for the amount of metallic antimony in that phase. For the chloride determination 0.2 g. of the salt phase was weighed into a beaker and 10 ml. of water was added; then the solution was heated almost to boiling, and 20 ml. of standardized silver nitrate added, so that there was an excess of silver nitrate after precipitation of the chloride. Nitric acid was then added and the system heated gently to dissolve the metal, convert the antimony into Sb_2O_3 , and liberate any occluded cadmium chloride. When the precipitate had coagulated, the solution was cooled and filtered and the filtrate back-titrated with ammonium thiocyanate in the usual manner.

In the system cadmium-bismuth-cadmium chloride (or cadmium bromide), bismuth was determined by precipitation and weighing as bismuth oxychloride (14) and the cadmium in the metal phase determined by difference. The cadmium in the salt phase was calculated from the chloride content, making allowance for the small amount of metallic bismuth in the salt phase. The salt phase was boiled with 40 ml. of water to effect complete solution of cadmium chloride. After cooling to room temperature, 10 ml. of 15 *N* nitric acid was added. The solution, now 3 *N* with respect to nitric acid, was left for several hours until the metallic residue had completely dissolved. It was then diluted to 500 ml. with 3 *N* nitric acid and aliquots taken for the chloride determination. It was found that the concentration of nitric acid could not be safely brought much below 2 *N* without incurring the risk of formation of a precipitate. On the other hand, J. B. Bingley (3) in this department showed that a concentration of 3 *N* nitric acid is without effect on the chloride in the cold. The chloride determination itself followed substantially the Volhard method as modified by Caldwell and Moyer (5): After precipitation of the chloride by silver nitrate, the solution was boiled for 3 min. to expel lower oxides of nitrogen and nitrous acid formed in the process of solution of cadmium, and the precipitate was shaken after addition of nitrobenzene.

In all experiments the bottom and top parts of the salt phase were discarded in order to eliminate mechanically dispersed metal, and also cadmium which may have condensed from the vapor phase on the surface of the salt phase during quenching.

The metals and alkali-metal salts employed in this investigation were of A.R. quality (B.D.H., Kahlbaum, and Electrolytic Zinc Co., Tasmania). Cadmium chloride was prepared from purest electrolytic cadmium and subsequently fused whilst a stream of hydrogen chloride was passed through to remove the products of hydrolysis. Cadmium bromide (pure, May and Baker) was fused and then dissolved in water; a precipitate of organic matter was filtered off,

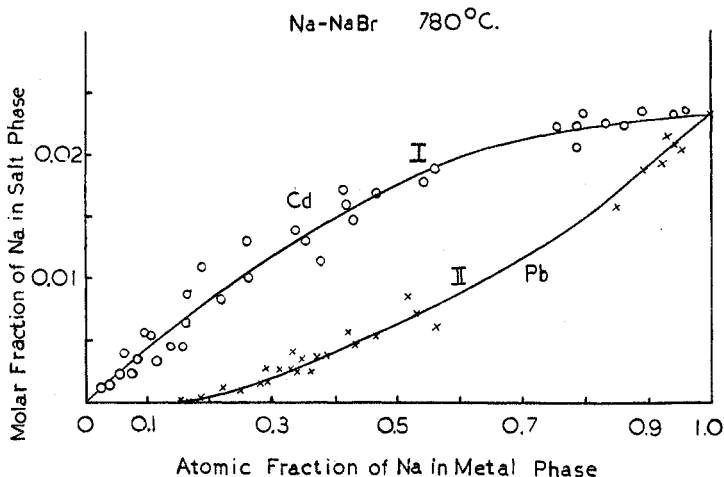


FIG. 1. Distribution equilibrium of sodium between molten sodium bromide and molten cadmium at 780°C. and of sodium between molten sodium bromide and molten lead at 780°C.

the solution was evaporated to dryness, and the solid was fused whilst a mixture of hydrogen bromide and bromine was passed through it.

II. DISTRIBUTION EQUILIBRIA INVOLVING SODIUM

Figure 1 (curve I) shows the distribution equilibrium of sodium between molten sodium bromide and molten cadmium at 780°C. (experiments by M. I. Homewood in this laboratory (15)). The molar fraction of sodium in the salt phase (N'_{Na}) is plotted against the atomic fraction of sodium in the metal phase (N_{Na}). In spite of considerable scattering of the experimental points, owing to experimental difficulties (see reference 12), it is obvious that the distribution curve shows positive deviations from Raoult's law. This is surprising, as the phase diagram cadmium-sodium reveals compound formation ($NaCd_2$, $NaCd_5$) in the solid state. If these compounds were stable in the liquid state, a negative deviation from Raoult's law would be expected. Hence it is probable that

the compounds are not stable in the liquid state at 780°C., which is about 400°C. above the melting point.

Conditions are different in the distribution equilibrium of sodium between molten sodium bromide and molten lead as a metal phase (figure 1, curve II). Strong negative deviations from Raoult's law are found (12). This is most probably due to the presence of stable intermetallic compounds in the liquid state; the phase diagram indicates Na_3Pb_8 , Na_2Pb , NaPb , and Na_2Pb_5 . Actually, at compositions of the metal phase below $N_{\text{Na}} = 0.15$, no sodium passes into the salt phase. If it be justifiable to apply classical reasoning, it may be concluded that, at these compositions, the dissociation of the respective compound is completely repressed by the excess of lead, thus rendering the activity of sodium zero. Similar conditions are found when molten sodium iodide is used instead of molten sodium bromide.

The concentration of sodium in molten sodium halides is small at the experimental temperature, and the distribution curves may therefore, at first sight, be regarded as activity curves. However, the shape of these curves differs somewhat from that generally experienced with partial vapor pressure curves (no asymptotic approach to the Raoult curve at high atomic fraction of the distribution component), and caution should be exercised in interpretation. The curves probably give a qualitative representation of the activity of sodium.

Negative deviations from Raoult's law are generally explained by dipole forces or by the formation of compounds between the two components. Metallic systems do not contain dipoles. However, whether or not negative deviations from Raoult's law are indicative of an intermetallic compound would seem to be largely a matter of definition of the "compound". We probably have to assume an attraction between the two species of atom which is stronger than ordinary van der Waals attraction, though our knowledge of the metallic bond does not admit of close characterization of such forces. A survey of the literature has shown that in most cases in which negative deviations from Raoult's law have been observed in metallic systems, there is independent evidence for the existence of intermetallic compounds in the liquid (maxima in the electric resistance curves, minima in the curves of its temperature coefficient; discontinuities of the magnetic susceptibility curves; intermediate phases with congruent melting points in the phase diagrams).

Heymann and Weber (12) have carried out a number of experiments with molten tin, bismuth, antimony, and gold as metal phases. These metals are not soluble in molten sodium bromide, yet, when alloyed with sodium, will pass into the salt phase together with the sodium. This is most probably due to the solubility of the respective intermetallic compounds of sodium with tin, bismuth, antimony, and gold in molten sodium bromide. The question arises: why do other intermetallic compounds of sodium (e.g., with lead, thallium) not exhibit solubility in molten sodium bromide? The explanation probably lies in the different nature of various types of intermetallic compounds (16). In the case of the compounds of sodium with gold, tin, and especially bismuth and antimony, we are dealing with normal valency compounds, possessing very high melting

points and high heats of formation, of ionic or semi-conducting character¹; little is known about their x-ray structure. These "salt-like" compounds may be expected to be soluble in ionic melts. On the other hand, most of the intermetallic compounds of sodium with lead, cadmium, and thallium, which are not soluble in molten sodium bromide, are not normal valency compounds and probably involve metallic bonds.

It is not surprising that the distinction between these two groups does not exactly coincide with the two groups ("polyionic" and "metallic") which were distinguished by Zintl and coworkers (32, 33, 34) with regard to solubility in liquid ammonia. There is, firstly, a great difference between the temperature of the action of liquid ammonia and that of an ionic melt. Moreover, ionic complexes, stabilized by ammonia, may be formed in cases in which the intermetallic compound is not ionic in character. At first sight, the solubility of an intermetallic compound in an ionic melt would appear to be a more suitable criterion for its "salt-like" nature than its solubility in liquid ammonia. On the other hand, it should be borne in mind that the solubility of intermetallic compounds in ionic melts is highly specific, as they are, with the exception of silicates, soluble only in a salt with which they have one radical in common.

III. THE SYSTEM CADMIUM-BISMUTH-CADMIUM CHLORIDE (CADMIUM BROMIDE)

Heymann and Friedlaender (11), who investigated the system cadmium-cadmium chloride previously, overlooked the fact that small amounts of bismuth passed into the salt phase together with the cadmium. Moreover, their distribution curve, especially for systems rich in cadmium, was found to be in error because of their unsatisfactory method of determining cadmium in the salt phase. The system was therefore reinvestigated. Figure 2 (curve I) shows the molar fraction of cadmium (N'_{Cd})² and curve II shows the molar fraction of bismuth (N'_{Bi}) in the salt phase in relation to the composition of the metal phase, expressed as atomic fraction of cadmium (N_{Cd}) and bismuth (N_{Bi}). It is evident that the solubility of pure bismuth in cadmium chloride is zero and that, in the equilibria between molten cadmium-bismuth alloys and cadmium chloride, the bismuth concentration in the salt phase rises to a maximum at $N_{Cd} = N_{Bi} = 0.5$.

The variation with temperature of N'_{Cd} and N'_{Bi} in equilibrium with a metal phase of $N_{Cd} = N_{Bi} = 0.5$ has also been investigated (table 1). It is interesting to note that N'_{Bi}/N'_{Cd} is virtually independent of the temperature.

¹ There are other indications in favor of this assumption. The normal valency compound Cu_3Sb has an electric resistivity 58.3 times as great as that of copper and 9 times as great as that of the metallic compound Cu_2Sb (28). Since Cu_3Sb , a compound of antimony with a subgroup element, has such a high resistance, the assumption that Na_3Sb is of an ionic or semiconductor type does not appear to be too hypothetical.

² It is seen from figure 2 that the solubility of pure cadmium in cadmium chloride at 690°C. is 15.6 mole per cent. Somewhat higher values were obtained by Aten (2) and by Hedger and Terrey (10). This may have been due to not rejecting the bottom part of the salt phase, thus including in the salt phase some suspended cadmium, or to failure to eliminate the sources of error which have been found (section I) to be inherent in the determination of chloride ions in these systems (*vide* 3).

There are two explanations for the solubility of bismuth, alloyed with cadmium, in molten cadmium chloride:

(A) The solubility of bismuth (expressed as N'_{Bi}) in the melt may possibly be due to the presence of a subchloride Cd_2Cl_2 (*vide* reference 6). In this case we would expect:

$$N'_{\text{Bi}} = K \times a_{\text{Bi}} \times a'_{\text{Cd}_2\text{Cl}_2} \quad (1)$$

where a_{Bi} is the activity of bismuth in the metal phase and $a'_{\text{Cd}_2\text{Cl}_2}$ the activity of Cd_2Cl_2 in the salt phase. It is fortunate that the activity of bismuth in

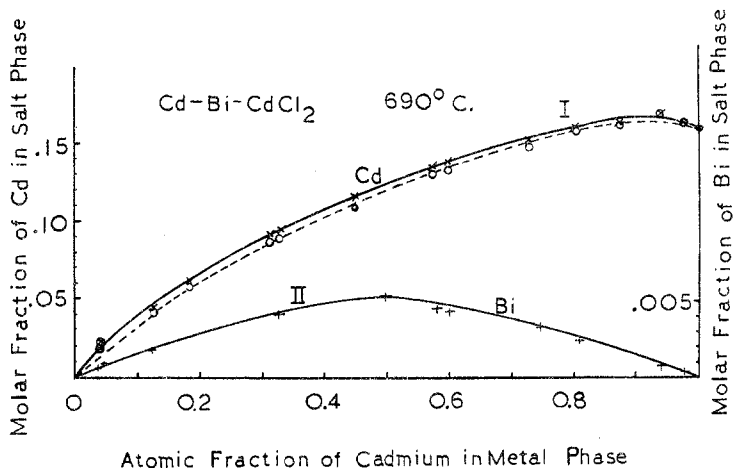


FIG. 2. The system cadmium-bismuth-cadmium chloride at 690°C.

TABLE 1

TEMPERATURE °C.	$100 N'_{\text{Cd}}$	$100 N'_{\text{Bi}}$	$100 \frac{N'_{\text{Bi}}}{N'_{\text{Cd}}}$
590	9.6	0.40	4.17
690	12.2	0.51	4.18
770	13.5	0.57	4.23

cadmium-bismuth alloys has been measured by Taylor (31) by the e.m.f. method between 431° and 533°C.; we have obtained a_{Bi} at 690°C. by extrapolating Taylor's values. $a'_{\text{Cd}_2\text{Cl}_2}$ is not known. If it is assumed to be equal to N'_{Cd} , we obtain

$$N'_{\text{Bi}} = K \times a_{\text{Bi}} \times N'_{\text{Cd}} \quad (2)$$

However, the last-mentioned assumption is open to criticism.

(B) It may be that small amounts of a compound CdBi exist in the metal

phase and that this compound is soluble in molten cadmium chloride (similar to CdSb; *vide* section IV). Since the solubility is small and since the phase diagram shows no indication of the compound in the solid state, the concentration of the compound in the liquid metal phase is probably very low. Moreover, the straight part of the distribution curve of bismuth (at low N_{Bi}) between metal and salt phase (figure 2) indicates that the hypothetical compound is in the same molecular state in both phases. Hence we obtain

$$a_{\text{CdBi}} = \text{const.} \times a'_{\text{CdBi}} \quad (3)$$

and

$$\frac{a_{\text{Cd}} \times a_{\text{Bi}}}{a_{\text{CdBi}}} = \text{const.} \quad (4)$$

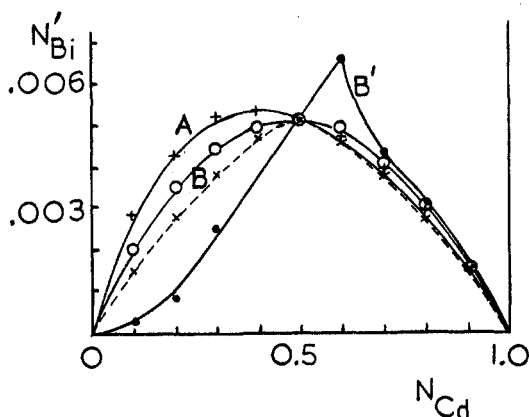


FIG. 3. N'_{Bi} plotted according to assumptions A, B, and B'

where the quantities a are the activities in the metal phase, and the quantities a' those in the salt phase. From equations 3 and 4 we obtain

$$\frac{a_{\text{Cd}} \times a_{\text{Bi}}}{a'_{\text{CdBi}}} = \text{const.}$$

or

$$N'_{\text{Bi}} = \text{const.} \times a'_{\text{CdBi}} = K' \times a_{\text{Bi}} \times a_{\text{Cd}} \quad (5)$$

Equations 2 and 5 differ only by the terms a_{Cd} and N'_{Cd} . For low concentrations N'_{Cd} should be proportional to a_{Cd} , and equations 2 and 5 identical. That this does not hold over a very large range is shown by the discrepancy between the distribution curve and the activity curve determined by Taylor (31). Figure 3 shows N'_{Bi} plotted according to assumption A (crosses in figure 3), assumption B (circles), and assumption B' (points). In the latter case (B'),

it is assumed that the compound is not CdBi, but Cd_3Bi_2 (by analogy to Zn_3Sb_2 , as suggested by Taylor), leading to a relation

$$N'_{\text{Bi}} = K'' \times a_{\text{Bi}}^2 \times a_{\text{Cd}}^3 \quad (6)$$

It is seen that assumptions A and B fit the experimental data (broken line) only moderately well, but B much better than A. It should, however, be borne in mind that in order to test hypothesis A, N'_{Bi} should be calculated from equation 1 rather than 2. If it is assumed that $a_{\text{Cd}_2\text{Cl}_2}$ is proportional to a_{Cd} , which is not unreasonable, equations 1 and 5 become identical, and assumptions A and B equally probable, as far as the formal analysis is concerned. On the other hand, assumption B' must be discarded on the evidence of figure 3.

The weakness of assumption A lies in the fact that there is no special reason to be seen why bismuth should be soluble in Cd_2Cl_2 . However, the fact that the ratio $N_{\text{Bi}}/N_{\text{Cd}}$ is independent of the temperature is compatible with assumption A. It implies that the amount of bismuth dissolved varies with the amount of Cd_2Cl_2 in the melt. On the other hand, there are serious objections against assumption B. A survey of the literature has shown that there is no convincing piece of evidence suggesting the existence of a compound between cadmium and bismuth either in the liquid or the solid state (phase diagram and thermal analysis (7, 17, 24, 29); thermoelectric power (4, 27); specific heat (8); temperature coefficient of electric resistance (8); x-ray analysis (30); density of liquid alloys (22)). The only experiments which might be regarded as being in favor of, or compatible with, compound formation are the slightly positive heat of mixing (13, 18) and the rather small activity coefficient (E.M.F.) of cadmium in molten cadmium-bismuth alloys which, contrary to expectations, decreases with increasing temperature (31); moreover, a slight break in the freezing-point curve, observed by Taylor (31), may be mentioned in this connection. Although the evidence in favor of the existence of a cadmium-bismuth compound is very slight, the possibility of a compound existing in the liquid which is not found in the solid state cannot be discarded, particularly in view of the fact that the lattice type of bismuth changes on fusion (19, 25, 26).

The distribution curve (at $690^\circ\text{C}.$) of cadmium between molten cadmium chloride (figure 2, curve I) and bismuth and that of cadmium between molten cadmium bromide³ (figure 4, curve I) and bismuth are very similar. Whatever the influence of the nature of the salt phase on the equilibrium may be, there appears to be very little difference in that respect between cadmium chloride and cadmium bromide. However, both distribution equilibria present a serious anomaly: The curves show maxima, which do not disappear even when N'_{Ca} is corrected for that amount of cadmium which may be present in the salt phase as CdBi, according to assumption B; these corrected values may be regarded as the "free cadmium" in the salt phase, shown by the broken lines in figures 2 and 4. The distribution curves (between two immiscible phases) correspond to

³ This system has also been investigated at $590^\circ\text{C}.$ The distribution curve is very similar to that shown in figure 4, but the positive deviation from Raoult's law is less marked than at $690^\circ\text{C}.$

partial vapor pressure of binary liquid systems. Maxima in partial vapor pressure curves have been found only in rare cases, e.g., the systems lead chloride-lead iodide and cadmium chloride-cadmium bromide (B. Greiner and K. Jelinek (9)). These authors assume that the maxima are due to the formation of molecular compounds in the vapor phase, although there seems to be no other evidence in favor of the existence of such compounds in the vapor. In our systems the concentration of cadmium in the salt phase is fairly high, so that the distribution curve is probably not an accurate representation of the activity of cadmium at all concentrations. However, it may be readily shown that no combination of two activity-concentration curves for cadmium in both phases can give rise to a maximum in the distribution curve, provided the slope of the activity curve da/dn is always positive. For the metal phase the positive slope

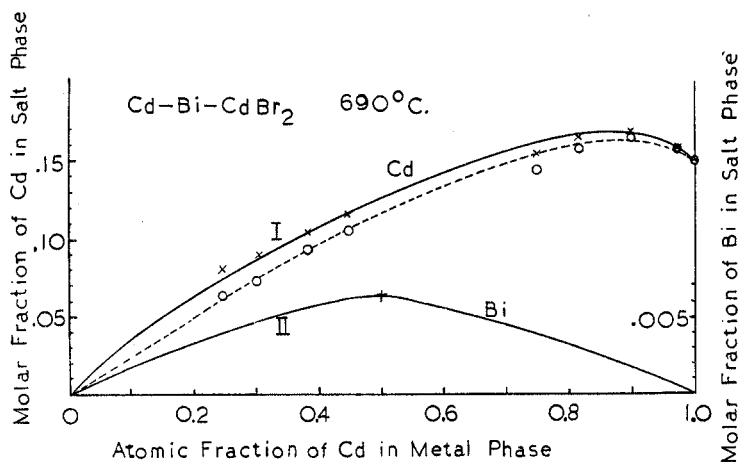


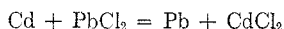
Fig. 4. The system cadmium-bismuth-cadmium bromide at 690°C.

at all atomic fractions has been verified by the E.M.F. measurements of Taylor (31). It appears, therefore, that the anomaly of the distribution curve is due to some property of the salt phase. However, the plausible assumption of a low activity coefficient of cadmium in the salt phase, as a consequence of solvation of cadmium ions or subchloride (Cd_2^{++}) formation, for which there is satisfactory evidence (6), is hardly sufficient to explain the anomaly of the distribution curve.

IV. THE SYSTEM CADMIUM-ANTIMONY-CADMIUM CHLORIDE

The distribution curve (at 690°C.) of cadmium between molten cadmium chloride and molten antimony (as a metal phase) is shown in figure 5. It is seen that, whilst antimony is insoluble in molten cadmium chloride, it shows high solubility when alloyed with cadmium (curve II). The solubility maximum

($N'_{sb} = 0.14$) occurs at $N_{cd} = 0.55$ in the metal phase. The obvious explanation of this high solubility is that an intermetallic compound (probably CdSb) is stable in the molten state and is soluble in the molten salt. The existence of this compound in the solid state is well established by the phase diagram. Its stability in the molten state is indicated by measurements of the electric conductivity and its temperature coefficient (21) and, though less conclusively, by the fact that the heterogeneous equilibrium



in the molten state is displaced to the left by addition of antimony (20). The solubility of antimony, when alloyed with cadmium, in molten cadmium chloride may be regarded as another piece of evidence for the existence of the compound

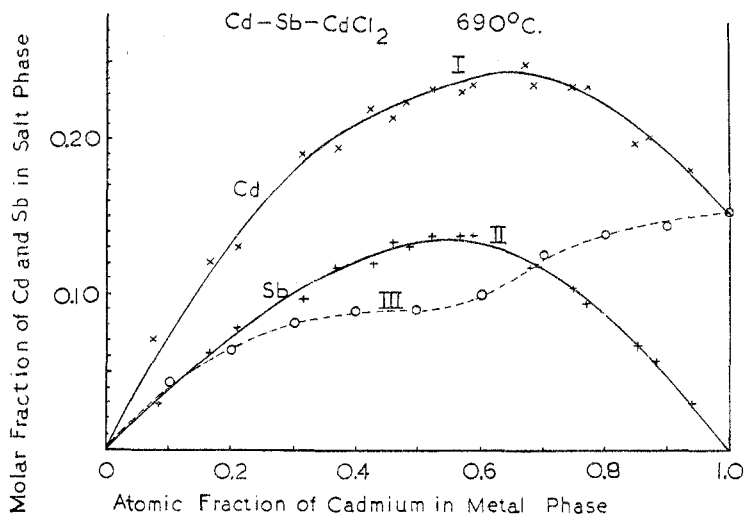


Fig. 5. The system cadmium-antimony-cadmium chloride at 690°C.

in the molten state. On the basis of the discussion in section II, we might be inclined to regard a normal valency compound (Cd_3Sb_2) as mainly responsible for the solubility of antimony in cadmium chloride; on the other hand, the phase diagram indicates only a metastable compound Cd_3Sb_2 , whereas CdSb is stable. The decisive evidence for the assumption of a compound CdSb, rather than Cd_3Sb_2 , in the molten state emerges, however, from the investigation of the electrical resistivity and its temperature coefficient (27) of molten cadmium-antimony alloys. The curves of these properties, plotted against composition, show sharp discontinuities (sharp maximum of the curve of electrical resistivity) at the composition CdSb, but not at that of Cd_3Sb_2 .

The experimental distribution curve of cadmium (curve I) is really due to two

distribution equilibria superimposed on one another, that of the free cadmium and that of the compound CdSb. It is possible to construct a distribution curve of free cadmium by subtracting from the total cadmium dissolved in the salt phase the amount present as CdSb. In this way curve III in figure 5 has been obtained, showing positive deviation from Raoult's law and a rather unfamiliar "dip" at medium atomic fractions. It is doubtful whether curve III has much significance with respect to the activity of cadmium in the molten metal mixture, as a high concentration of CdSb in the salt phase must alter the solvent properties of the latter considerably.

The specificity of solutions of intermetallic compounds in molten salts is also shown in this system. CdSb is soluble in molten cadmium chloride, but not in molten sodium halides. CdSb (orthorhombic (1); interpreted as distorted cubic (23)) appears to belong to a transition group between the salt-like and the metallic compounds. Its solubility in molten cadmium chloride is at first sight surprising in view of the results of section II. It remains to be shown, however, whether explanations valid for intermetallic compounds of the highly electropositive alkali metals may be extended to those of other metals. Moreover, as the discussion of the subsequent paper will show, molten cadmium chloride is a rather complicated system and not a purely ionic melt.

SUMMARY

1. The distribution curves of a number of metals between a molten metallic phase and a molten salt phase have been investigated. Deviations of these curves from Raoult's law have been discussed.

2. The distribution curve of sodium between molten cadmium and molten sodium bromide shows positive deviations from Raoult's law, presumably indicating that the compounds between sodium and cadmium are decomposed at the experimental temperature.

3. The distribution curve of sodium between molten lead and molten sodium bromide shows strong negative deviations from Raoult's law, indicating that intermetallic compounds between sodium and lead are stable in the liquid state at the experimental temperature. The solubility of intermetallic compounds of sodium with tin, antimony, and bismuth in molten sodium halides is discussed.

4. The distribution curve of cadmium between molten bismuth and molten cadmium chloride shows an anomalous maximum, suggesting that this curve does not represent the activity of cadmium in the metallic mixture. The possible reasons for this anomaly are discussed. Moreover, bismuth, in the presence of cadmium, is slightly soluble in the molten salt, the maximum solubility being at atomic fraction 0.5. The probable causes of this effect are carefully analyzed.

5. The distribution curve of cadmium between molten antimony and molten cadmium chloride is the result of superposition of two equilibria, that of the free cadmium and that of the compound CdSb between the metal phase and the salt phase. The compound is stable at the experimental temperature and soluble in molten cadmium chloride.

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