The Activity of Cd in the Molten System Cd-CdCl₂

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The vapour pressures of Cd in the molten system Cd/CdCl₂ have been determined at 600°C by a method involving the use of a thin probe of Ag forming an alloy with the Cd-vapour at 700°C. From the vapour pressure data activities and relative partial molar free energies of Cd and CdCl₂ have been calculated. The results obtained are in good agreement with emf measurements in this system supporting the view that at dilute solution Cd forms Cd_2^{2+} ions.

The solution of metals in molten salts is a problem of great importance from a technological as well as a theoretical point of view. In production of metals, *e.g.* by electrolysis of their molten salts, the interaction of the metal with the salt plays an important roll in the efficiency of the process. Although in recent years an increasing amount of work has been devoted to studies on metal -molten salt systems the nature of these solutions is not yet completely understood and further information is needed in order to be able to determine the molecular species present in such melts.

The Cd/CdCl₂ system has been the subject of many investigations. The phase diagram at lower temperatures is well known from cryoscopy and solubility measurements.[1-3] Self-diffusion and electrical conductance measurements have recently been carried out.[4] Thermodynamic properties have been derived from emf measurements by Mashovets and Poddymov[5] and by Crawford and Tomlinson.[6] Reviews of metal-molten salt systems have been published by Corbett,[7] Bredig,[8] and Lumsden.[9]

Accurate experimental work at high temperature is difficult and liable to errors and this is particular the case with emf measurements. It was therefore decided to make vapour pressure measurements as a check on earlier emf measurements. This work describes vapour pressure measurements carried out on Cd/CdCl₂ melts at 600°C. From the results, activities and Gibbs free energy data have been derived.

EXPERIMENTAL

Materials. Anhydrous CdCl₂ was prepared from AnalaR Reagent hydrated material. The water was removed by heating in vacuum. The salt was slowly heated to about 80°C over 2 h. During this stage the major part of the water was expelled. The tem-

perature was then slowly raised to 140°C and left so over night. The temperature was thereafter raised to 220°C and maintained for 8 h. The dehydrated salt was then melted and the pure salt distilled off. The cadmium metal was of spectrographic grade. The silver metal used as probes had a purity better than 99.95 %.

Apparatus and procedure. The vapour pressure of Cd over the $Cd/CdCl_2$ melts was determined by a relative method described earlier.[10] The melt to be investigated was contained in an evacuated vycor tube which was kept in a vertical position in a Kanthal wound furnace (see Fig. 1). The furnace had two temperature zones that were inde-
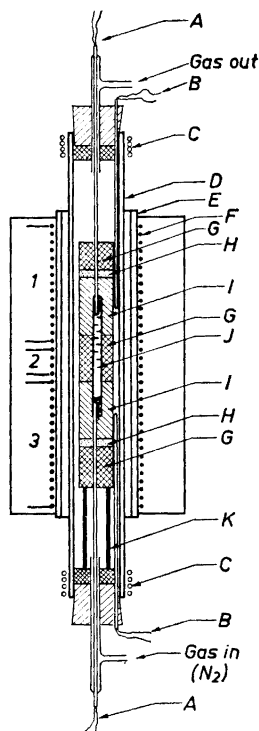

Fig. 1. Furnace with sample tube.

A. Thermocouple to potentiometer.
B. Thermocouple to regulator.
C. Cooling coil.
D. Vycor reaction tube.
E. Mullite furnace tube.
F. Heating element.
G. Refractory brick.
H. Graphite.
I. Copper block.
J. Sample tube.
K. Support.
1−3. Independently heated zones.

pendently heated and controlled. The lower part of the sample tube containing the melt was held constant at 600°C while the upper part containing an Ag-probe was kept at 700°C. Two copper blocks covering the bottom and the top parts of the sample tube were placed in the furnace to smooth the temperature distribution within each zone.

When preparing the sample tube the probe situated on a holder of vycor glass was first introduced and fixed in position by making small indentations in the tube with a thin graphite rod after the tube had been locally heated. The radiation shields were then placed in position and the weighed amount of Cd and CdCl₂ rapidly transferred to the tube which was then evacuated and closed in a hydro-oxygen flame. After equilibration the sample tube was withdrawn from the furnace and rapidly quenched in water in such a way that the lower part of the tube was first cooled to prevent condensation of Cd-vapour onto the probe. In the initial experiments the Ag-probe was made of a thick piece of metal. During equilibration the surface of the Ag-probe would rapidly come to equilibrium with the Cd-vapour. The composition of the Ag/Cd-alloy at 700°C in equilibrium with the $Cd/CdCl_2$ melt at 600°C could therefore be determined and hence also the Cd-pressure if the surface of the probe could be accurately analysed. This was

thought to be possible with the aid of electron probe microanalysis. However the accuracy of the microsond analysis was found to be too poor and it was therefore decided to try to make the probe so thin that the entire metal would come to equilibrium with the Cd-vapour within a reasonable time. A thickness of 50 μm of the probe was found to be suitable. With this arrangement the composition of the equilibrium alloy could then be determined simply by weighing the probe before and after an experiment. The weight of the probe was of the order of 35 mg. It was found that the melt and the probe came to equilibrium within less than 3 days. By starting with some probes having an initial composition higher than the expected equilibrium value it was found that the equilibrium values obtained in the experiments were independent of the side from which the equilibrium was approached. This was taken as an indication that equilibrium was reached within the allotted time.

RESULTS

If the Cd-pressure over Ag/Cd alloys at 700°C is accurately known the Cd-pressure over the corresponding Cd/CdCl₂ melt can easily be calculated from the equilibrium composition of the corresponding probe. Initial experiments with pure Cd-melts of variable temperature in equilibrium with an Ag-probe at 700°C showed that existing data on the Ag/Cd system were not accurate enough to be used for determination of Cd-pressures over Cd/CdCl₂ melts. The Ag/Cd system at 700°C had therefore to be redetermined.[11] The results from these experiments are presented as activities in Fig. 2, the standard
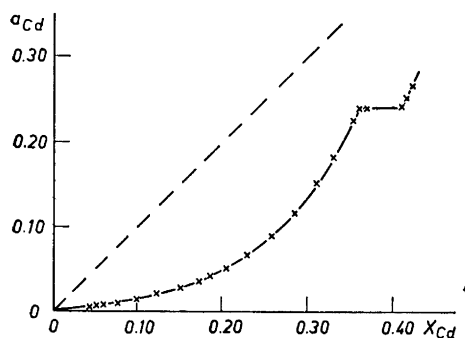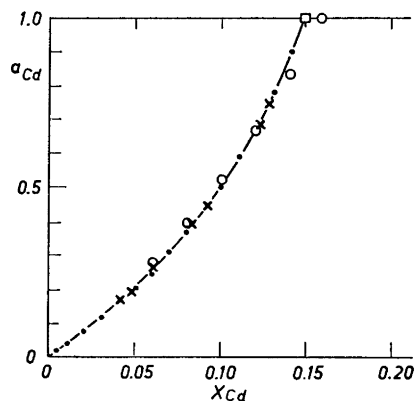

Fig. 2. Activities of Cd in Ag/Cd alloys at 700°C.

Fig. 3. Activities of Cd in molten Cd/CdCl₂ at 600°C. × This work. ● Crawford & Tomlinson.[6] ○ Mashovets & Poddymov.[5] ☐ Saturation solubility.[6]

state being pure liquid Cd at 700°C. The vapour pressure of pure Cd is taken from Hultgren et al.[12]

With this knowledge the vapour pressure of Cd over Cd/CdCl₂ melts with varying amount of Cd could be determined. The results are shown in Table 1. The composition of the melts was determined from the weight of the different components taking into account the amount of Cd going into the probe and

Table 1. Vapour pressures and activities of Cd over Cd/CdCl$_2$ at 600°C.

X_{Cd}	P_{Cd} torr	a_{Cd}
0.0412	13.9	0.170
0.0475	16.3	0.199
0.0606	21.1	0.267
0.0825	32.0	0.390
0.0928	36.75	0.448
0.1230	56.2	0.685
0.1285	61.5	0.750
0.1486	82.0	1.00

the amount staying in the vapour phase; the latter being very small. In Fig. 3 these results, converted to activities of Cd, are compared with results from earlier emf-measurements.

The activities of CdCl$_2$ were obtained by a graphical integration of the Gibbs-Duhem equation in the form:[13]

$$\ln \gamma_{CdCl_2} = \int_0^{X_{Cd}} \frac{\ln \gamma_{Cd}}{(1-X_{Cd})^2} \times dX_{Cd} - \frac{X_{Cd}}{1-X_{Cd}} \times \ln \gamma_{Cd}$$
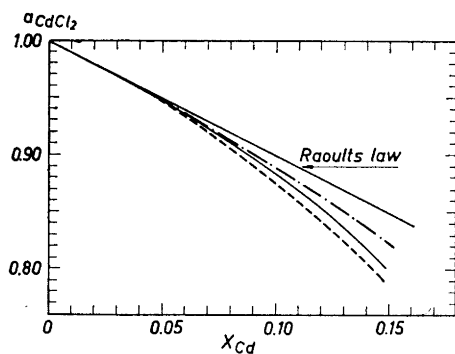
Fig. 4. Activities of CdCl$_2$ in molten Cd/CdCl$_2$ at 600°C.

——— This work.
— · — Ideal Temkin solution assuming Cd$_2^{2+}$ being formed.
— — — Ideal Temkin solution assuming Cd$_3^{4+}$ being formed.

The results are given in Fig. 4 where also the curves for ideal Temkin solutions [14] are shown assuming Cd$_2^{2+}$ and Cd$_3^{4+}$ ions being formed according to the solution models

$$Cd + Cd^{2+} \rightarrow Cd_2^{2+} \quad and \quad Cd + 2Cd^{2+} \rightarrow Cd_3^{4+}$$
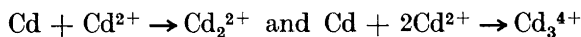
The excess partial molar free energies for Cd and CdCl$_2$ calculated from the activity data are given in Table 2. The values are referred to the ideal Raoult solution as well as to the ideal Temkin solution of Cd$_2^{2+}$ and Cd^{2+} ions.

Table 2. The excess partial molar free energies for Cd and CdCl$_2$ in cal/mole. G_i^E is referred to the ideal Raoult solution and (G_i^E) to the ideal Temkin solution of Cd$_2^{2+}$ and Cd^{2+} ions.

| X_{Cd}	G_{Cd}^E	$G_{CdCl_2}^E$	$(G_{CdCl_2}^E)$
0.05	2500	−6	−2
0.08	2670	−18	−3
0.10	2770	−27	−5
0.13	3060	−64	−24
0.1486^a	3300	−104	−51

^{a} Saturation solubility at 600°C.

DISCUSSION

From cryoscopy and magnetic susceptibility measurements [1] as well as from emf-studies [5,6] it has been conclusively established that Cd$^+$ ions are not formed when Cd dissolves in molten CdCl$_2$. The possibility of dissolution as neutral Cd atoms is also ruled out as the conductivity has been found to decrease continuously as cadmium is added to the melt.[4] It would also seem very unlikely to have neutral atoms in a highly ionized melt. Instead it has been shown that the formation of Cd$_2^{2+}$ ions according to the reaction Cd + Cd^{2+}→Cd$_2^{2+}$ is highly probable. This assumption has also been strengthened by Corbett,[15] who found with the aid of Raman spectroscopy that this ion exists in liquid as well as solid solutions of Cd$_2$(AlCl$_4$)$_2$ with Cd(AlCl$_4$)$_2$. In contradistinction to the case in the system Hg/HgCl$_2$ [16] a subchloride Cd$_2$Cl$_2$ does not exist in the Cd/CdCl$_2$ system. This is also evident from the value of $\Delta G°$ for the formation of this molten hypothetical subchloride which has been found [6] to be +3745 cal/mole at 600°C. From Table 2 and Fig. 4 it is evident that the activity of CdCl$_2$ shows a negative deviation from Raoults law. If we now assume that only Cd$_2^{2+}$ and Cd^{2+} ions are present in the melt the ideal activity according to Temkin [14] will be:

$$a_{CdCl_2} = \frac{X_{CdCl_2} - X_{Cd}}{X_{CdCl_2}}$$

As can be seen the system also shows a small but significant negative deviation from this Temkin activity at saturation but at low concentration of Cd the curves coincide. A possible explanation for this deviation is perhaps that some complex ions are formed. If Cd dissolves in the melt according to the reaction

$$Cd + nCd^{2+} \rightarrow Cd_{n+1}^{2n+}$$
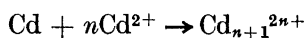
the ideal Temkin activity will decrease as n increases. With $n=2$ the ideal activity will be

$$a_{CdCl_2} = 1 - \frac{X_{Cd}}{2X_{CdCl_2} - 1}$$

In Fig. 4 this line has also been drawn for comparison. The Cd^{2+} ion like Hg^{2+} has an empty linear S-orbital which will, however, render the formation of, $e.g.$, Cd_3^{4+} ions difficult at higher concentration of Cd. It is therefore plausible that only a small amount of Cd_3^{4+} ions is formed together with Cd_2^{2+} ions at dilute solution.

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