# Zinc–Zinc Chloride Solutions

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THE nature of the species existing in solutions of metals in their molten halides has been studied by several authors[1] through the study of the distribution of the metal between an alloy and the salt phase. Since, before the publication of a recent Paper by Van Norman *et al.*,[2] the only attempt to determine the dissolution mechanism of zinc in its chloride[3] gave no consistent result, we undertook the study of the equilibrium Zn–Au–$ZnCl_2$.

Zinc chloride was distilled in the presence of zinc metal, and then redistilled *in vacuo* directly into fused silica ampoules which contained either pure zinc or a zinc–gold alloy. The ampoules were maintained at the selected temperatures (975 or 1050°K) for 1—3 days and successively quenched in water. The salt phase was dissolved in a standardized aqueous iodine solution and the zinc content of the salt was determined from the decrease of iodine concentration.[4] The activity of zinc in zinc–gold alloys was determined by separate e.m.f. measurements.[5]

The average values $N_0$ of the solubility of pure zinc in the chloride were $1{\cdot}3 \times 10^{-2}$ and $2{\cdot}4 \times 10^{-2}$ mole/mole $ZnCl_2$ at the two temperatures. These values are about 20% lower than those found by Corbett *et al.*[6] [mole fraction $1{\cdot}64 \times 10^{-2}$ at 971°K and $3 \times 10^{-2}$ (extrapolated) at 1050°K]; in view of the different experimental methods the agreement can be considered satisfactory.

A plot of the ratio $N/N_0$ (where $N$ is the solubility of zinc in zinc chloride equilibrated with an alloy of activity $a$) against $a$ should give a parabola if the dissolution mechanism were

$$Zn + Zn^{2+} \rightleftharpoons 2\,Zn^{+} \qquad (1)$$

and a straight line of unit slope if the mechanism were

$$Zn + Zn^{2+} \rightleftharpoons Zn_2^{\,2+} \qquad (2)$$

(see Egan[1]). From Figure 1 it can be seen that the experimental values fall in the region intermediate between the two curves. Since this discrepancy cannot, in our opinion, be entirely justified by experimental errors in either the solubility or the

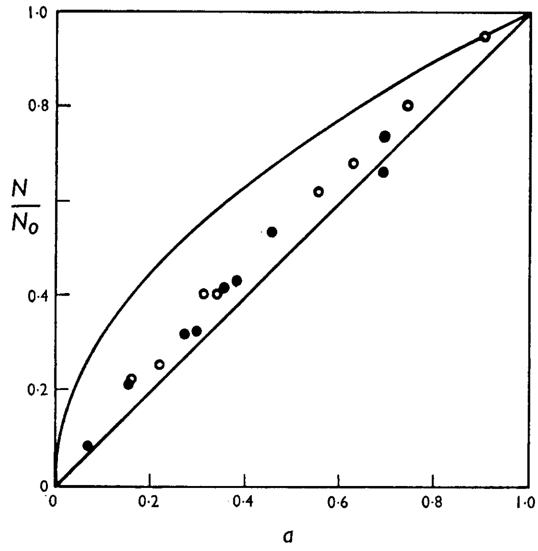

FIGURE 1. *Plot of* $N/N_0$ *against* a *at* 975°K (*open circles*) *and at* 1050°K (*full circles*).

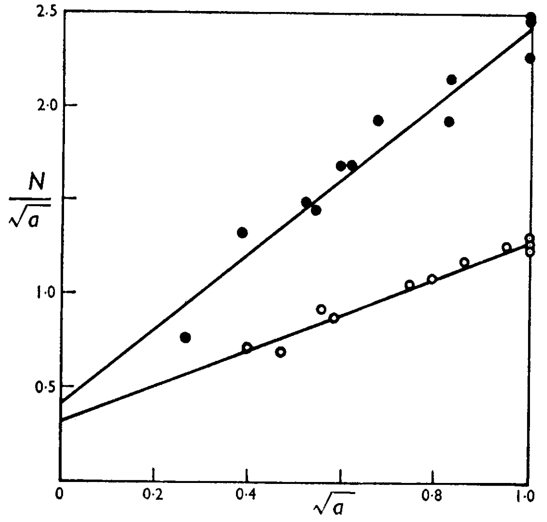

FIGURE 2. *Plot of* $N/\sqrt{a}$ *against* $\sqrt{a}$ *at* 975°K (*open circles*) *and at* 1050°K (*full circles*). *The straight lines were computed by the least-squares method.*

activity measurements, it has been supposed that both mechanisms are simultaneously operating. In this hypothesis it can be easily shown that the solubility is given by

$$N = \tfrac{1}{2}\sqrt{K_1 \cdot a} + K_2 \cdot a$$

where $K$ and $K_2$ are the equilibrium constants of reactions (1) and (2). If only mechanism (1) or mechanism (2) were operating, the plot of $N/\sqrt{a}$ against $\sqrt{a}$ should be either a horizontal line or a straight line through the origin, respectively; in the presence of both $Zn^+$ and $Zn_2^{2+}$ species, the plot should have positive intercept and slope. From Figure 2 this appears to be the case at both temperatures; the values of the equilibrium constants obtained from the plots are:

at 975°K: $K_1 = 4 \times 10^{-5}$; $K_2 = 1 \times 10^{-2}$;

at 1050°K: $K_1 = 7 \times 10^{-5}$; $K_2 = 2 \times 10^{-2}$.

This result conflicts with the qualitative paramagnetism measurements by Corbett *et al.*[6] and with the recent results by Van Norman *et al.*,[2] who studied the distribution of zinc between zinc–bismuth alloys and zinc chloride by chronopotentiometric measurements, and found proportionality between solubility and zinc activity in the alloy. It is also noteworthy that hitherto no metal has been definitely ascertained to dissolve in its bivalent halides with the formation of univalent monomeric cations.[7]

Our results are therefore quite surprising; at present, however, no explanation other than the presence of $Zn^+$ has been found.

(*Received, July* 12*th*, 1966; *Com.* 490.)

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