217. *Volatility of Zinc in Zinc Halide Vapour.*

By D. H. KERRIDGE.

Metallic zinc has been shown to be more volatile in the presence of zinc halide vapour than in a vacuum, between 285° and 350°. Evidence suggests new molecular species $(ZnX)_2$ which disproportionate when cooled to room temperature.

INTEREST in the existence of metal halides in unusually low valency states has recently increased, as part of the revival of interest in the chemistry of high-temperature ionic liquids. Most investigations have been concerned with the nature of solutions of the parent metal in its molten halides, and with the solids which crystallise from such solutions, but comparatively little work has been done on the formation of a compound between metal and halide in the gaseous state.[1]

The latter type of investigation has now been carried out with the zinc–zinc halide systems and has yielded evidence of formally univalent halides. The existence of univalent zinc in the vapour phase has also been recently suggested as an explanation of the high volatility of zinc oxide in zinc vapour,[2] and of zinc oxide in a vacuum.[3]

EXPERIMENTAL

Materials.—Zinc chloride (sticks) (British Drug Houses) was purified by heating to 400° in a Pyrex tube with dry hydrogen chloride gas passing through for 1 hr., followed by dry nitrogen for 1 hr. (Found: Zn, 47·9; Cl, 52·1. Calc. for $ZnCl_2$: Zn, 48·0; Cl, 52·0%). Zinc bromide (B.D.H.) was heated to 300° under vacuum (2×10^{-2} mm.) for 1 hr. and then sublimed (Found: Zn, 29·4; Br, 70·1. Calc. for $ZnBr_2$: Zn, 29·0; Br, 71·0%). Zinc iodide (B.D.H.) was treated similarly (Found: Zn, 20·9; I, 79·1. Calc. for ZnI_2: Zn, 20·5; I, 79·5%).

Zinc sheet, made from AnalaR granulated zinc by melting, casting, and rolling down to 0·3 mm. thickness, was cut to appropriate surface area and given a mirror finish before use by agitation in 0·2N-nitric acid, followed by washing and thorough degreasing in acetone and ether.

Apparatus.—A Pyrex tube (1·8 cm. diameter), sloping slightly downwards to the closed end, was heated by a resistance furnace regulated by an Ether Transitrol controller, temperatures being measured by chromel–alumel thermocouples. The section of the tube outside the furnace was cooled by compressed air. The open end was connected *via* an acetone–solid carbon dioxide cold trap to a Pirani gauge and rotary vacuum pump.

Method.—Purified zinc halide was placed at the closed end of the tube and the weighed zinc sheet, suitably folded, was placed in a degreased porcelain boat which rested against a stop about 5 cm. from the halide. All handling was done in dry air, in the minimum of time, using a dry-box when this was advantageous, the tubes being evacuated as soon afterwards as possible.

The furnace was heated rapidly, and its temperature maintained (±2°) by the Transitrol controller, the pressure being adjusted to 2×10^{-2} mm. These conditions were maintained for a sufficient time (1—7 hr.) to accumulate 1—2 g. of sublimate in the cold portion of the tube. The condensed sublimate was washed out with dilute nitric acid and analysed, the zinc sheet

---

[1] Corbett and von Winbush, *J. Amer. Chem. Soc.*, 1955, **77**, 3964; Corbett, von Winbush, and Albers, *ibid.*, 1957, **79**, 3020.

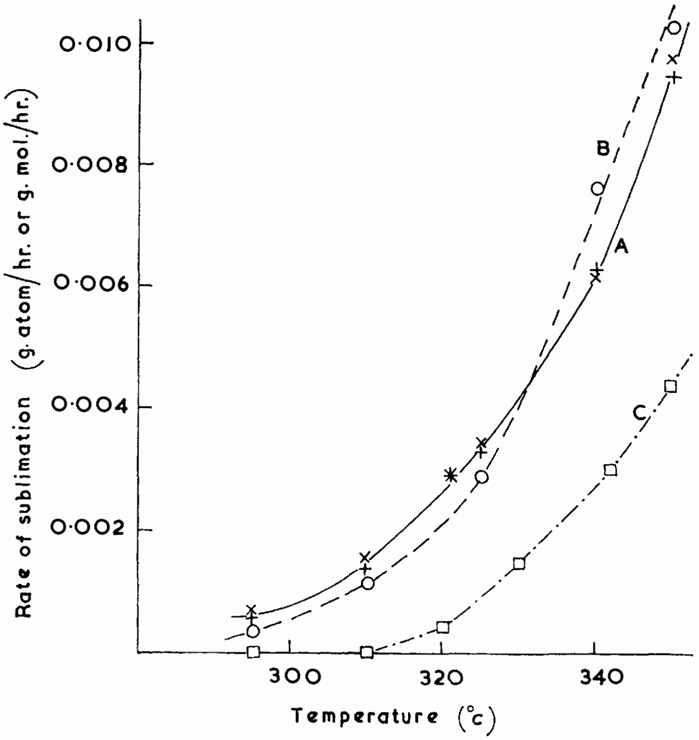
[2] Moore and Williams, *J. Phys. Chem.*, 1959, **63**, 1516.

[3] Secco, *Canad. J. Chem.*, 1960, **38**, 596.

which remained in the boat being reweighed. Zinc analysis figures reported are the experimentally determined values reduced by the weight of zinc (if any) which would have sublimed under identical conditions in the absence of zinc halide.

RESULTS AND DISCUSSION

Zinc–Zinc Chloride System.—Purified zinc chloride was sublimed over zinc metal at a series of temperatures from 295° to 350°. In each case the analysis of the sublimate was very close to that for ZnCl (Calc.: Zn, 64·8; Cl, 35·2%); analyses, expressed as the rates of sublimation at the various temperatures are given in the Figure.



Rates of sublimation at various temperatures. A, zinc (+) and chloride (×) (g.-atom/hr.); B, zinc chloride (mole./hr.) in the absence of zinc; C, zinc (g.-atom/hr.) in the absence of zinc chloride.

Curve A was obtained by using 12 cm.^{2} of zinc surface in each case. Reaction between zinc chloride and zinc appeared to be complete under these conditions, as an increase in the surface area of zinc did not alter the proportions of zinc and chloride (Table 1) but merely led to a decrease in the rate of sublimation, presumably because additional folded sheet decreased the space available for passage of zinc chloride vapour.

TABLE 1.

Surface area of zinc (cm.^{2})	12	24	29	40
Temperature (°c)	326	325	321	325
Sublimate composition (% Zn)	64·03	63·6	64·8	62·3
Rate of sublimation (g./hr.)	0·334	0·265	0·231	0·234

The evidence that equal numbers of zinc and chlorine atoms sublime from zinc–zinc chloride indicates that a new chemical species is stable in the vapour phase over this range of temperature. However, it is unlikely that this species is the diatomic molecule ZnCl.

Such molecules are known [4] but are stable only at much higher temperatures (800—1000°).[5] Similarly, recent theoretical calculations have shown solid ZnX halides to be unstable, with respect to solid Zn and ZnX_2, at room temperature.[6]

The molecules are therefore likely to be $(ZnCl)_x$ where $x > 1$. Comparison with the mercurous halides and the postulated Cd_2^{2+} ion in reduced cadmium halides [7,8] suggests that $x = 2$, and this is supported by the superposition of curves A and B in the Figure. Under the experimental conditions the vapour pressure of a species is approximately proportional to the number of molecules subliming, measured as moles/hr. Thus curve A indicates the change of vapour pressure with temperature of the molecule ZnCl, and curve B that of $ZnCl_2$. However, as vapour-pressure curves rarely cross one another, particularly when the molecles are related, it is more likely that the molecules in question are $(ZnCl)_2$, in which case the number of gram-molecules sublimed per hour would be halved and the corresponding vapour pressure curve would lie between those of zinc dichloride and zinc. This is the relationship of the vapour-pressure curves of the analogous mercuric and mercurous chlorides.

It is possible that $x > 2$, but this is less likely in the vapour phase, although such more complicated species, *e.g.*, Bi_3^{3+} [9] and Cd_3Cl_4,[8] have been suggested in liquids, and even more complicated structures, *e.g.*, $Bi_{12}Cl_{14}$,[10] for lower halides in the solid state.

Zinc–Zinc Bromide and Zinc–Zinc Iodide Systems.—The zinc contents of the sublimate for these systems, at varying temperatures and for varying surface areas of zinc, are shown in Table 2, the zinc contents of pure ZnX being indicated.

Complete reduction of the zinc dihalide vapour did not occur within the temperature range available, though the amount of reduction increased with temperature and with larger surface area of zinc. However, an increase in surface area again diminished the rate of sublimation and enforced an upper limit on the area which could be used. An upper limit of temperature was imposed by the undesirably fast sublimation of zinc dihalide when its vapour pressure exceeded 50 mm.

TABLE 2.

Zn–$ZnBr_2$ system [$(ZnBr)_x$ requires 45·0% Zn]			Zn–ZnI_2 system [$(ZnI)_x$ requires 34·0% Zn]		
Temp. (°c)	Surface area of Zn (cm.^{2})	Sublimate composition (% Zn)	Temp. (°c)	Surface area of Zn (cm.^{2})	Sublimate composition (% Zn)
304	12	29·7	285	12	21·2
304	36	30·2	285	36	21·6
304	60	29·8	285	60	21·9
315	12	29·9	315	12	22·1
315	60	30·7	315	36	22·9
330	12	29·2	315	60	23·2
330	36	29·5			
330	60	31·0			

The increased volatility of zinc in the dihalide vapour (Table 2) is again probably due to the formation of $(ZnX)_x$ molecules, although the percentage of these in the vapour would be less than 20%. As with the chloride, ZnBr and ZnI would not exist at these temperatures. However, $(ZnBr)_2$ and $(ZnI)_2$ would be expected to be more stable, though less so than $(ZnCl)_2$ if the stabilities vary in the same manner as those of the mercurous halides, where

---

[4] Herzberg, "Molecular Spectra and Molecular Structure," Van Nostrand, New York, 2nd edn., Vol. 1, 1950.

[5] Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials—Thermodynamics," ed. Quill, NNES IV–19B, McGraw-Hill, New York, 1950.

[6] Barker, Linnett, and Taylor, *J.*, 1961, 3323.

[7] Corbett, Burkhard, and Druding, *J. Amer. Chem. Soc.*, 1961, **83**, 76.

[8] Topol and Landis, *J. Amer. Chem. Soc.*, 1960, **82**, 6291.

[9] Levy, Bredig, Danford, and Agron, *J. Phys. Chem.*, 1960, **64**, 1959.

[10] Herschaft and Corbett, *J. Chem. Phys.*, 1962, **36**, 551.

the standard free energies of disproportionation of solid mercurous chloride, bromide, and iodide decrease in the order 8·0, 6·6, and 2·5 kcal./mole.[5]

Properties of the Sublimate.—In each system the sublimate consisted of three slightly overlapping bands: band I, nearest the furnace, was a thick, metallic, grey mirror; band II was thick, white to buff; and, in the coolest part, band III was a thinner mirror changing from brown to black to silver as the thickness increased with time. Analysis of individual bands indicated that bands I and III contained a high proportion of zinc, but with some halide, while band II was almost entirely zinc dihalide. Sublimate of similar appearance to band II was obtained from zinc dihalide with no zinc present, and sublimate similar to band I, with a very thin mirror in the position of band III, when zinc was heated alone. This suggested that disproportionation of the $(ZnX)_x$ molecules had occurred on cooling.

However, in view of the halide content of bands I and III, the properties of these bands obtained from zinc–zinc chloride sublimations were investigated to discover if disproportionation was complete. The bands were removed separately and adhering zinc chloride removed by extraction in ether (or acetone) until the solvent contained no dissolved chloride. On analysis the extracted band III contained an average of 10% of chloride and band I 6%. But both extracted bands were very like zinc in appearance and had no greater reducing powers than zinc. It thus seems possible that this rather small amount of retained halide might be present as pockets of zinc chloride completely sealed by sublimed zinc.

No evidence was thus obtained for the existence of solid lower zinc halides at room temperature, though the sublimation evidence does suggest that $(ZnX)_2$ molecules exist in the vapour phase at temperatures between 285° and 350°.

THE UNIVERSITY, SOUTHAMPTON.
UNIVERSITY COLLEGE OF GHANA, LEGON.

[*Received, July 27th,* 1962.]