LXXXV.—*The Ternary System Zinc Oxide–Zinc Chloride–Water.*

By Harold Cecil Holland.

In the literature some 16 different oxychlorides of zinc are described (see, *e.g.*, "Gmelins Handbuch der anorganischen Chemie," 1924, "Zink," p. 175; Dietrich and Johnston, *J. Amer. Chem. Soc.*, 1927, **49**, 1419), but only a few need be cited in detail. From solubility determinations of zinc oxide in aqueous zinc chloride solutions,

Driot (*Compt. rend.*, 1910, **150**, 1426) inferred the existence of $ZnCl_2,4ZnO,6H_2O$ and $ZnCl_2,ZnO,1\frac{1}{2}H_2O$, both of which he isolated. By treating diamminozinc chloride, $ZnCl_2,2NH_3,H_2O$, with hot water, André (*ibid.*, 1882, **94**, 903, 1524; 1888, **106**, 854) obtained an oxychloride to which he gave the formula $ZnCl_2,8ZnO,10H_2O$; and by adding water to a syrupy solution of zinc chloride, he obtained a compound described as $ZnCl_2,5ZnO,8H_2O$, which was also prepared by Perrot (*Bull. Soc. chim.*, 1895, **13**, 975; 1901, **25**, 786) by adding water to the anhydrous salt.

There is little doubt that several of the supposed oxychlorides are mixtures and not chemical individuals, for analyses of solid phases are necessarily vitiated either by the retention of mother-liquor or by decomposition during washing. It was therefore decided to carry out a phase-rule investigation of the system in order to determine the formulæ of any oxychlorides which might exist in stable equilibrium with solutions.

Although the system is a three-component one, Jänecke's method of representation (*Z. physikal. Chem.*, 1908, **51**, 32; 1911, **71**, 1) was preferred to the triangular method. The compositions of the solid phases were found by Schreinemakers's "residue" method (*Z. physikal. Chem.*, 1893, **11**, 76).

Experimental.

The reagents used in the preparations and analyses were of a high standard of purity, and all volumetric apparatus was standardised before use. Chloride was estimated by the Volhard method with *N*/10-silver nitrate and *N*/20-potassium thiocyanate, and zinc by titration with potassium ferrocyanide, a concentrated sulphuric acid solution of diphenylbenzidine being used as indicator (Cane and Cady, *J. Amer. Chem. Soc.*, 1927, **49**, 356): fresh indicator solution had to be made every few weeks in order to get the best results. All solutions were standardised in triplicate and checked fortnightly.

The composition of the mixtures was arranged so as to give only a small amount of solid phase. At first they were prepared from zinc oxide and hydrochloric acid, but, as the most concentrated acid contains only 19·1 equivs. % of hydrogen chloride, the majority were prepared from zinc oxide and chloride and water. By adding some of the water and the zinc oxide in the form of a paste, followed by the hydrochloric acid or zinc chloride dissolved in the remainder of the water, a mixture was obtained free from lumps. If any lumps were present, the mixture, while still hot, was shaken so that the fine precipitate of oxychloride was held in suspension during transference to another bottle, which was then sealed and placed in a rotary shaker in a thermostat at 25° ± 0·1° or at 50° ± 0·05°. After the

required period of shaking, the bottle was placed in a clamp at the side of the thermostat to allow the precipitated oxychloride to settle. Some of the clear solution (5, 10, or 25 c.c. as convenient) was drawn off in a pipette and transferred to a weighing bottle; from the weights, the densities of the solutions were obtained. The solid was separated from most of the solution on a Hoesch funnel, and a weighed sample was taken (during filtration the solid was not allowed to become dry, as this would cause change in composition); for the concentrated mixtures at 25° and for all at 50°, the solid was obtained by transferring the remainder of the mixture to a weighing bottle at the temperature concerned, allowing the precipitate to settle, and then drawing off the supernatant liquid. The samples were washed into standard flasks, acidified with dilute sulphuric acid to dissolve oxychlorides, and analysed. From the weights of zinc and chlorine in a known weight of solution or residue the amounts of zinc chloride and oxide and hence of water were obtained.

Data at 25°.

	Solution.			Residue.		
No.	*D.*	*x.*	*y.*	*x.*	*y.*	
1	1·004	0·001	0·001	0·020	0·117	
2	1·056	0·009	0·009	0·016	0·077	
3	1·185	0·033	0·034	0·039	0·107	
4	1·194	0·034	0·035	0·039	0·102	
5	1·270	0·049	0·050	0·052	0·112	
6	1·379	0·075	0·078	0·073	0·115	*E*
7	1·461	0·094	0·097	0·089	0·144	
8	1·552	0·113	0·119	0·108	0·162	
9	1·630	0·134	0·142	0·126	0·173	
10	1·646	0·137	0·145	0·128	0·178	
11	1·692	0·146	0·155	0·140	0·197	*E*; *F*
12	1·699	0·151	0·163	0·167	0·221	
13	1·707	0·155	0·165	0·172	0·231	
14	1·723	0·162	0·169	0·177	0·231	*F*
15	1·731	0·165	0·173	0·183	0·245	
16	1·737	0·163	0·172	0·183	0·227	
17	—	0·172	0·177	0·189	0·226	
18	1·776	0·184	0·193	0·215	0·294	
19	1·793	0·191	0·196	0·201	0·231	
20	1·794	0·195	0·198	0·211	0·252	*G*
21	1·835	0·202	0·209	0·211	0·243	
22	1·873	0·222	0·230	0·231	0·270	
23	1·900	0·245	0·252	0·262	0·331	
24	1·971	0·264	0·269	0·266	0·299	

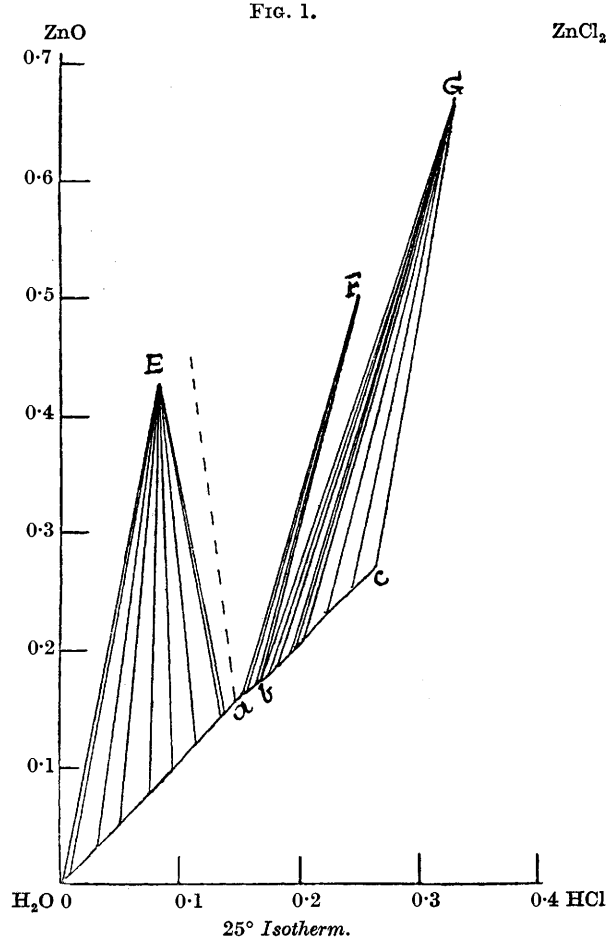
Data at 50°.

1	1·050	0·009	0·009	0·018	0·075	
2	1·452	0·091	0·095	0·091	0·116	*E*
3	—	0·143	0·153	0·141	0·166	
4	—	0·144	0·153	0·161	0·214	
5	1·689	0·154	0·161	0·167	0·211	*F*
6	1·711	0·159	0·167	0·175	0·211	
7	1·713	0·160	0·168	0·177	0·215	*G*
8	1·716	0·165	0·171	0·192	0·248	
9	1·816	0·200	0·205	0·211	0·245	

The equilibrium diagram is a square * of unit side, the corners representing the four substances in the equilibrium

$$\underset{a}{\tfrac{1}{2}H_2O} + \underset{b}{\tfrac{1}{2}ZnCl_2} \rightleftharpoons \underset{c}{HCl} + \underset{d}{\tfrac{1}{2}ZnO}$$

FIG. 1.



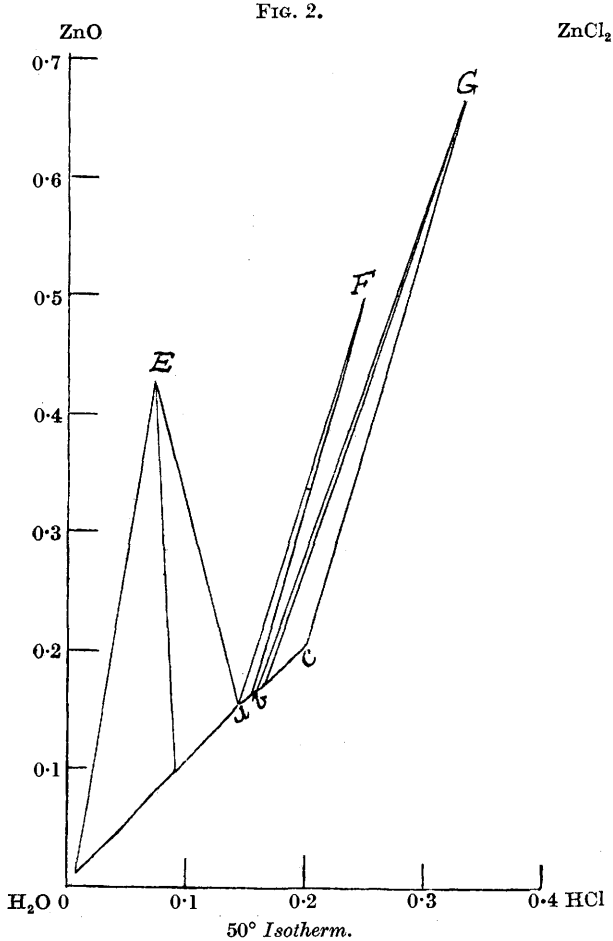
25° *Isotherm.*

the respective equivalents being as shown. Since these four substances correspond to only three independent variables, any phase may be fully defined by a point such that $x = (b+c)/(a+b+c+d)$ and $y = (b+d)/(a+b+c+d)$ and the composition will be given by the formula $(1-y)H_2O + (y-x)ZnO + xZnCl_2$, where x and y follow from the analyses.

* Only the relevant portion is shown in Figs. 1 and 2.

In the tables the compositions of the solutions and residues are given in terms of x and y, the solid phase being shown by the letter corresponding to the intersection of the tie lines in the diagrams; thus $E = ZnCl_2,5ZnO,8H_2O$; $F = ZnCl_2,ZnO,2H_2O$; $G = ZnCl_2,ZnO,H_2O$.

FIG. 2.



50° *Isotherm.*

Since the time of shaking required for the mixtures to reach equilibrium was dependent on the concentration, two complexes (Nos. 3 and 4) of similar composition were prepared. Although one of these was shaken at 25° for 24 hours and the other for 72 hours, the same solid phase was present in each case, showing that for mixtures of this or higher concentration one day's shaking was sufficient. When several very dilute mixtures were shaken for only

3 days, the conjugation lines did not intersect at a point; but when two such complexes (Nos. 1 and 2) were shaken for 21 days, these lines intersected those of other complexes at a definite point *E* (Fig. 1) corresponding to $ZnCl_2,5ZnO,8H_2O$, showing that 3 days' shaking was insufficient. This compound is the same as that obtained by André and by Perrot (*locc. cit.*). As the solution of complex 1 having this solid phase had $x = y = 0{\cdot}001$, it is clear that the range of existence of zinc oxide or hydroxide in contact with solutions containing zinc chloride must be very small.

No evidence was obtained for the existence of the solid, $ZnCl_2,ZnO,1\frac{1}{2}H_2O$, reported by Driot (*loc. cit.*). As the curve *ab* was increasing at the expense of the others with decrease in temperature, it is quite probable that his solution coincided with the transition point of the curve so that his solid was a mixture of $ZnCl_2,ZnO,2H_2O$ and $ZnCl_2,ZnO,H_2O$. This explanation is strengthened by the fact that he reported only one solution having the solid phase $ZnCl_2,ZnO,1\frac{1}{2}H_2O$ in equilibrium.

At 50°, the diagram (Fig. 2) was of the same form as at 25°, the only difference being that the area *Gcb* had encroached upon the area *Fba*, showing that $ZnCl_2,ZnO,H_2O$ can exist in stable equilibrium with solutions containing less zinc chloride than at 25°.

It is of interest that several other elements of Group II of the periodic system give oxychlorides corresponding with two of those now found for zinc: *e.g.*, $CaCl_2,CaO,2H_2O$, $MgCl_2,MgO,H_2O$, and $CdCl_2,CdO,H_2O$.

Summary.

1. Equilibria existing in the three-component system ZnO–$ZnCl_2$–H_2O at 25° and 50° have been studied, and the compositions of the stable solid phases determined.

2. Evidence has been obtained for the existence of two new oxychlorides of zinc, *viz.*, $ZnCl_2,ZnO,2H_2O$ and $ZnCl_2,ZnO,H_2O$; and only one of those formerly described, *viz.*, $ZnCl_2,5ZnO,8H_2O$, exists in stable equilibrium in the range of concentrations used.

3. The same series of solid phases was found at 25° as at 50°.

In conclusion, I wish to thank Dr. Denham and Mr. Packer for their interest in this work.

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