

H. C. Holland.

T H E S I S

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A.C. Holland

An investigation into the three component
system zinc oxide, hydrochloric acid, zinc chloride
and water.

Zinc hydroxide or oxide is soluble in an aqueous solution of zinc chloride, and when a concentrated solution is diluted with water, a basic salt, an oxychloride of zinc is precipitated. The formation of zinc oxychloride is also effected by adding water to solid zinc chloride, or by diluting a concentrated solution of zinc chloride.

An examination of the literature showed that up to the present time about sixteen different oxychlorides of zinc have been described by various workers. Writing the molecular ratio in the order $\text{ZnO} : \text{ZnCl}_2 : \text{H}_2\text{O}$, the following compounds have been reported:-

9:1:3, 8:1:10, 6:1:6, $5\frac{1}{2}:1:n$ 5:1:6, 5:1:8,
 9:2:12, 4:1:11, 4:1:6, 4:1:0, 3:1:x, 3:1:5,
 3:1:3, 5:2:26, 3:2:11, 1:3:1, $1:1:1\frac{1}{2}$, and 1:4:8.

According to A. Sordelli (Anal. Soc. Quim. Argentina 1914 2 97) water did not precipitate a basic chloride from concentrated solutions of zinc chloride, but the complex $2\text{ZnCl}_2 \cdot 11\text{H}_2\text{O}$ was precipitated from a saturated solution of zinc oxide in zinc chloride solution. Solubility determinations of zinc oxide in aqueous solutions of zinc chloride were found by A. Driot (Comp. Rend. 1910 150 1426) to indicate the existence of $\text{ZnCl}_2 \cdot 4\text{ZnO} \cdot 6\text{H}_2\text{O}$ and of $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 1\frac{1}{2}\text{H}_2\text{O}$ both of which were isolated. The composition of these two substances did not vary with temperature. The first was amorphous and lost $5\text{H}_2\text{O}$ at 200°C , and the latter, which occurred in microscopic crystals,

lost H_2O at 230°C . and decomposed at a higher temperature.

R. Schindler (Mag. Pharm. 1830 31 167 and 1836 36 43) reported the existence of $\text{ZnCl}_2 \cdot 9\text{ZnO} \cdot 3\text{H}_2\text{O}$ prepared by adding water to a syrupy solution of zinc chloride which had been evaporated till fumes of hydrochloric acid were evolved; and also by filtering a solution of zinc chloride treated with ammonia insufficient for complete precipitation. R. Kane (Annal. Chim. Phys. 1839 2 296) described the same substance obtained by adding potassium hydroxide to an aqueous solution of zinc chloride until it reacted alkaline.

By treating zinc diammino-chloride $\text{ZnCl}_2 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$ with hot water, G. André (Comp. Rend. 1882 94 903, 1524 and 1888 106 854) obtained an oxychloride to which he gave the formula $\text{ZnCl}_2 \cdot 8\text{ZnO} \cdot 10\text{H}_2\text{O}$. R. Kane reported $\text{ZnCl}_2 \cdot 6\text{ZnO} \cdot 6\text{H}_2\text{O}$ prepared by treating zinc monaminino-chloride, $\text{Zn}(\text{NH}_3) \text{Cl}_2$, with water; and also by adding aqueous ammonia to a solution of zinc chloride until the precipitate formed partly dissolved. The white powder was insoluble in water; when calcined, it lost water, and a residue was formed from which water extracted zinc chloride and a higher oxychloride remained. G. André described $\text{ZnCl}_2 \cdot 5\text{ZnO} \cdot 8\text{H}_2\text{O}$ obtained by adding water to a syrupy solution of zinc chloride. F. Perrot (Bull. Soc. Chim. 1895 13 975 and 1901 25 786) made the same substance by pouring one hundred grams of water at 10°C . on five grams of anhydrous zinc chloride and washing the mass free of undecomposed zinc chloride. By adding dilute aqueous ammonia with constant stirring, to a

boiling concentrated solution of zinc chloride until a precipitate appeared. Habermann obtained a white powder to which he assigned the formula $2\text{ZnCl}_2 \cdot 9\text{ZnO} \cdot 12\text{H}_2\text{O}$. If this substance was washed for a long time, G. André found that $\text{ZnCl}_2 \cdot 4\text{ZnO} \cdot 11\text{H}_2\text{O}$ was obtained. He also described the substance $2\text{ZnCl}_2 \cdot 3\text{ZnO} \cdot 11\text{H}_2\text{O}$ which when treated with alcohol, gave $\text{ZnCl}_2 \cdot 4\text{ZnO} \cdot 6\text{H}_2\text{O}$. This salt was also described by Driot. R. Schindler described $\text{ZnCl}_2 \cdot 3\text{ZnO} \cdot 2\text{H}_2\text{O}$ prepared by boiling a fairly concentrated solution of zinc chloride.

André boiled one hundred and fifty grams of fused zinc chloride, forty grams of zinc oxide, and four hundred grams water with ammonium chloride, and obtained a substance which he claimed was $2\text{ZnCl}_2 \cdot 5\text{ZnO} \cdot 26 \text{H}_2\text{O}$. He also reported $2\text{ZnCl}_2 \cdot 3\text{ZnO} \cdot 11\text{H}_2\text{O}$ obtained by boiling a solution of zinc chloride with zinc oxide and cooling the clear solution. F. Ephraim (Zeit. Anorg. Chem. 1908 59 67) described $3\text{ZnCl}_2 \cdot \text{ZnO} \cdot \text{H}_2\text{O}$. Dietrich and Johnston (J.A.C.S. June 1927 1419) have described the preparation of a crystalline product of the composition $\text{ZnCl}_2 \cdot 4\text{ZnO} \cdot 8\text{H}_2\text{O}$ which they prepared by the action of aqueous ammonia on zinc chloride solutions.

Mellor (Inorganic and Theoretical Chemistry Vol.1V) commenting on the numerous oxychlorides of zinc described says that, in the absence of a systematic study in the light of the phase rule, apart from chemical analyses, there is little to show which of these salts is a chemical individual

and which a mixture. There is little doubt that several of these oxychlorides are mixtures. Since the oxychlorides are decomposed by washing, as was shown by André who obtained $\text{ZnCl}_2 \cdot 4\text{ZnO} \cdot 11\text{H}_2\text{O}$ by prolonged washing of $2\text{ZnCl} \cdot 9\text{ZnO} \cdot 12\text{H}_2\text{O}$ and, if not washed, will be contaminated with mother liquor, the results obtained by analysis cannot be relied upon for determining the formulae of the oxychlorides.

The aim of this investigation was to find by the application of the principles of a phase rule diagram the formulae of the various oxychlorides of zinc which exist in stable equilibrium with solutions prepared from the three component system zinc oxide, hydrochloric acid, zinc chloride, water; and also to determine the solubility of zinc oxide in aqueous zinc chloride solutions..

METHOD.

By shaking at constant temperature till equilibrium was attained, sealed bottles containing mixtures of zinc chloride, zinc oxide and water, made up in definite proportions, and then analysing samples of the solution and wet solid, the composition of the solid phase was obtained. The system zinc oxide, hydrochloric and zinc chloride, water is a three component one, but since the triangular method of representation cannot be used owing to the separation of a fourth substance, the method of representation due to Janecke (Zeit. Physikal Chem. 1908 51 132 and 1911 71 1) was adopted. This method is for reactions of the type,

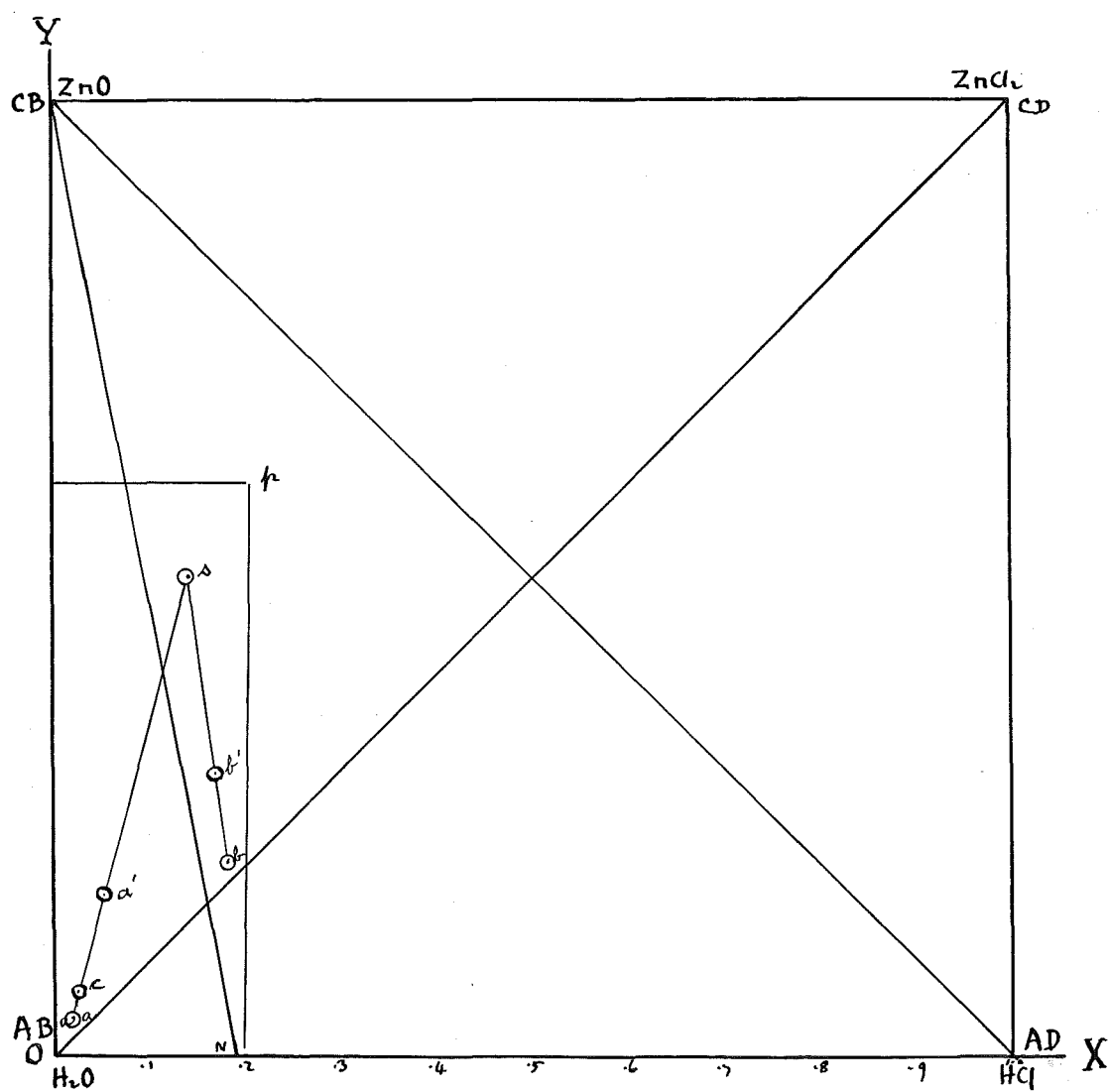


Fig. I



If in making up a complex, excess hydrochloric acid was added, all the zinc oxide dissolved giving the system zinc chloride, hydrochloric acid, water, but if zinc oxide was present in excess, all the acid reacted to form zinc chloride, so that the system became zinc chloride, zinc oxide, water. The term complex is used in the sense of a complex mixture of the components as by Rivett in "The Phase Rule".

Since in any particular phase the number of equivalents of the positive radicles must equal that of the negative, it follows that, if we take this number as unity, the composition may be expressed as

$$A(1-y) \quad B(1-x) \quad Cy \quad Dx.$$

In the system zinc oxide, hydrochloric acid, zinc chloride, water, A represents equivalents of hydrogen, B equivalents of Oxygen, C equivalents of zinc, and D equivalents of chlorine. By plotting x and y as coordinates, it is possible to represent the composition of all phases. Rectangular coordinates give the simplest case and the way in which the diagram is constructed may be followed from Figure 1. x values are plotted as abscissae on axis OX, and y values as ordinates on axis OY. The four corners of the diagram represent the pure substances. Any phase which contains two or more of these four substances and the composition of which is expressed in terms of any three of them, arbitrarily

selected as components, may be represented by a point either on the sides of, or within the square, as the case may be.

A phase containing,

- a. equivalents of AB (i.e. H_2O)
- b. equivalents of CD (i.e. $ZnCl_2$)
- c. equivalents of AD (i.e. HCl) and
- d. equivalents of BC (i.e. ZnO)

which may be written as

$$A_{a+c} B_{a+d} C_{b+d} D_{b+c},$$

is represented by a point p such that

$$y = \frac{b+d}{a+b+c+d} \quad \text{and} \quad x = \frac{b+c}{a+b+c+d}$$

since substitution of these values in the above composition

$A_{a+c} B_{a+d} C_{b+d} D_{b+c}$ reduces it to the general form

$$A_{1-y} B_{1-x} C_y D_x.$$

The composition of the point p may be expressed not only, as above, in terms of AB, CD, AD, and BC, but also as

$$(1-x-y) AB + y.BC + x.AD,$$

or again as

$$(1-y) AB + (y-x) BC + x CD,$$

since all these three statements give the same relative proportions between the radicles, namely those of the general formula

$$A_{1-y} B_{1-x} C_y D_x.$$

If, as in this case for point p, y be greater than x, the composition cannot be expressed in equivalent proportions

of $BC + CD + AD$, or of $AB + AD + CD$. These facts are immediately obvious from the square, since p besides falling in the square $AB-AD-CD-BC$, is also within each of the triangles $BC-AB-AD$, and $AB-BC-CD$, but it is outside of both $BC-AD-CD$ and $AB-AD-CD$. There is usually no more reason for choosing one set of components in particular, except convenience of preparation of the complexes or estimation of substances.

After separating the solid by filtration or other means, it is often a troublesome matter to free it completely from adhering solution, keeping the whole exactly at the temperature of the isotherm sought. A simple graphical procedure dependent upon the use of conjugation lines enables one to avoid the necessity for this. This method is illustrated in the diagram (Fig.1). a is a solution in equilibrium with a solid of unknown composition. By filtration, a portion of the moist solid, that is solid and adhering solution, is removed. Devices for maintaining constant temperature during filtration are necessary or not according to the temperature of the isotherm, and the rate at which the filtering is carried out. A known weight of moist solid or residue is then analysed. Since it is a mixture of the solution a , and the pure solid, its composition represented at a' in the figure must be somewhere on the straight line connecting those of solution a , and of pure solid. The more completely the adhering solution has been removed in the filtration, the nearer will it be to the latter. The composition of the pure solid is s somewhere on

a a' produced. By taking a mixture of different composition, giving solution b and residue b', the composition of the solid will be on b b' produced and this will pass through s, if the solid phases in contact with the two solutions are identical. This intersection of the two lines, the point s, gives at once the desired composition of the solid phase, and other solutions and residues will confirm or correct this point. Thus one arrives at a knowledge of the solid phase in equilibrium with known solutions without requiring to obtain it perfectly pure for analysis. The procedure is known as the residue or "rest" method of Schreinemakers (Zeit. Physikal.Chem. 1893 11 76) To get a good intersection of the various conjugation lines it is essential that a and a' should not be close together because here the extrapolation becomes a lengthy one and errors in composition of either solution or residue are magnified in that of the solid. For this reason, the method, sometimes adopted, of making up the complex very accurately, and then analysing only the solution was not used.

The only quantitative results for the solubility of zinc oxide in zinc chloride solutions available to the writer are those of Driot (Seidell: "Solubilities of Inorganic and Organic Substances p.750) These results are given below, Table 1, the weights of zinc chloride and zinc oxide being the amounts in a solution containing one hundred grams of water.

TABLE 1.

No.	ZnCl ₂	ZnO.	Solid phase.
1	8.22	.0137	ZnCl ₂ .4ZnO.6H ₂ O
2	23.24	.138	"
3	45.95	.497	"
4	51.5	.604	"
5	56.9	.723	"
6	62.85	.884	"
7	96.0	1.792	"
8	124.7	3.213	"
9	144.8	2.64	"
10	203.0	1.59	ZnCl ₂ .ZnO. 1½H ₂ O

By dividing the weight of each substance by its equivalent weight to obtain the values of a, b, c and d, and calculating x and y by the method given, the following values for Briot's solutions and solids were obtained (Table II).

TABLE II.

<u>No.</u>	<u>Solution</u>		<u>Solid phase</u>	
	<u>X</u>	<u>Y</u>	<u>X</u>	<u>Y</u>
1	.010	.010	.091	.455
2	.029	.030	"	"
3	.057	.058	"	"
4	.063	.064	"	"
5	.070	.071	"	"
6	.077	.078	"	"
7	.112	.115	"	"
8	.140	.147	"	"
9	.159	.164	"	"
10	.211	.214	.286	.572

These results are expressed in a diagram (Fig. II.) which shows that all the solutions represented by the curve ab are in equilibrium with a solid phase $\text{ZnCl}_2 \cdot 4\text{ZnO} \cdot 6\text{H}_2\text{O}$ while the solution represented by c has solid phase $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 1\frac{1}{2}\text{H}_2\text{O}$ in equilibrium with it, according to Briot's results.

Table III contains the other oxychlorides of zinc reported together with the coordinates of the point representing their composition on the diagram.

TABLE III

No.	Formula	x.	y.
1	$\text{ZnCl}_2 \cdot 9\text{ZnO} \cdot 3\text{H}_2\text{O}$	.077	.769
2	$\text{ZnCl}_2 \cdot 8\text{ZnO} \cdot 10\text{H}_2\text{O}$	.053	.473
3	$\text{ZnCl}_2 \cdot 6\text{ZnO} \cdot 6\text{H}_2\text{O}$	.077	.538
4	$\text{ZnCl}_2 \cdot 5\text{ZnO} \cdot 6\text{H}_2\text{O}$	.083	.500
5	$\text{ZnCl}_2 \cdot 5\text{ZnO} \cdot 8\text{H}_2\text{O}$	.071	.428
6	$2\text{ZnCl}_2 \cdot 9\text{ZnO} \cdot 12\text{H}_2\text{O}$	.087	.478
7	$\text{ZnCl}_2 \cdot 4\text{ZnO} \cdot 11\text{H}_2\text{O}$	.062	.312
8	$\text{ZnCl}_2 \cdot \text{ZnO}$	.500	.100
9	$\text{ZnCl}_2 \cdot 3\text{ZnO} \cdot 5\text{H}_2\text{O}$	.111	.444
10	$\text{ZnCl}_2 \cdot 3\text{ZnO} \cdot 3\text{H}_2\text{O}$	.143	.571
11	$2\text{ZnCl}_2 \cdot 5\text{ZnO} \cdot 26\text{H}_2\text{O}$	.060	.212
12	$2\text{ZnCl}_2 \cdot 3\text{ZnO} \cdot 11\text{H}_2\text{O}$	.125	.312
13	$3\text{ZnCl}_2 \cdot \text{ZnO} \cdot \text{H}_2\text{O}$	.600	.800
14.	$\text{ZnCl}_2 \cdot 4\text{ZnO} \cdot 8\text{H}_2\text{O}$	.077	.384

The points are plotted in Figure II being marked by crosses, whereas Driot's results are marked by circles.

For the first complexes prepared the substances used were hydrochloric acid, zinc oxide and water, the proportions of each being obtained from the triangle CB-AB-AD in Fig. II containing Driot's results. If the complex had a composition represented by a point c (Fig. 1), then, when equilibrium had

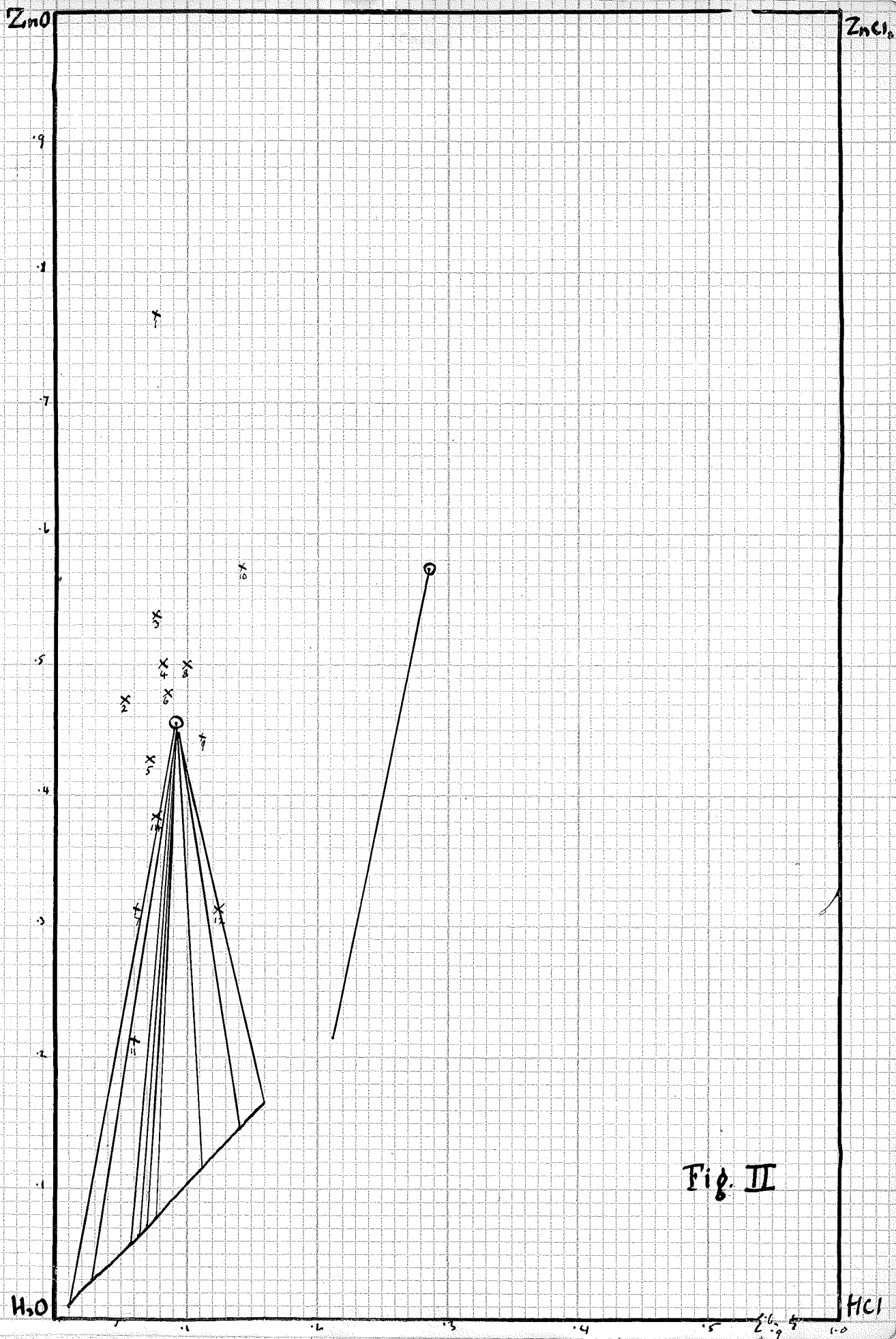


Fig. II

been attained, it would give a solution of composition represented by a and a solid represented by s. The respective amounts of solution and solid would be $\frac{cs}{as}$ and $\frac{ca}{as}$ of the total complex.

To obtain a large amount of solution and a small amount of solid it was necessary to take the point c close to the solution curve. The composition of the complex c was obtained by reading the coordinates of c, then as shown before, the composition is x equivalents hydrochloric acid, y equivalents zinc oxide and (1-x-y) equivalents water. These quantities were multiplied by their equivalent weights to get the proportions in grams of each substance, and then by a constant to give a suitable total weight of complex. It was possible to use concentrated hydrochloric acid for only a small portion (CB-AB-N Fig.1) of the zinc oxide, hydrochloric acid, water triangle because the concentrated acid contained only 32 per cent hydrochloric acid by weight or 19.1 per cent equivalents acid. When the composition of the complexes required was not in the area CB-AB-N, zinc chloride, zinc oxide and water were used, the respective amounts being obtained from the triangle AB-CB-CD in the manner already described.

Apparatus.

Bottles for shaking the mixture in were made from large diameter glass tubing by rounding off one end and drawing in the other, and then sealing on a piece of smaller tube of

sufficient length to form a neck which would allow the bottle to be sealed several times. The maximum length of the bottles was about nine inches, and their volumes were such that, when a mixture was placed in one, it was only half full. This was done to allow efficient shaking.

A large thermostat, made of copper and covered with several layers of thick felt was fitted with a mercury toluene regulator which automatically increased or decreased the amount of gas supplied to the burner, and so kept the bath at constant temperature. When the temperature of the thermostat was 25°C , the maximum variation was $\pm 1^{\circ}\text{C}$, while at 50°C , the variation was only half this amount. The thermometer used in the thermostat was standardized against a standard at the two temperatures used. When the water in the bath was at 50°C , a few cubic centimetres of transformer oil were placed on it to reduce evaporation as much as possible.

A shaker with eight rubber covered clamps for holding the bottles was fitted into the bath. This was driven by a chain from a shaft outside the water, the outside shaft being driven by an electric motor through two countershafts to reduce the speed. The bottles were held in such a position that their contents ran from one end of the bottle to the other each half revolution of the shaker. Besides holding the bottles, the shaker acted as an efficient stirrer and kept the water of the bath very evenly heated.

All the flasks and pipettes used were standardized with

distilled water as described by Cumming and Kay (Quantitative Chemical Analysis p. 36). The burettes used for the standard solutions were calibrated by weighing the amount of distilled water delivered every five cc mark. (Cumming and Kay p.43.). Each burette was standardized twice in this manner and graphs drawn for the corrections to be applied at all volumes.

CHEMICALS USED.

For making up the mixtures the following chemicals were used:-

Zinc oxide, Merck extra pure.

Zinc chloride, Merck pure fused white sticks, P.E. U.S.P.

IX.

Hydrochloric acid, Hopkins and Williams, pure redistilled.

Water, distilled.

The chemicals used for making the standard solutions were:-

Silver nitrate, Hopkins and Williams pure.

Potassium thiocyanate, Hopkins and Williams pure.

Potassium ferrocyanide, Merck extra pure.

Potassium ferricyanide, Kachler and Martini.

These solutions were standardized with A.R. grade of sodium chloride and zinc.

For estimation of chlorine tenth normal silver nitrate and twentieth normal potassium thiocyanate were used both solutions being standardized by means of A.R. sodium chloride in triplicate, concordant results being obtained. (Cumming and Kay p. 117).

The zinc was estimated by potassium ferrocyanide solution, but instead of the uranium nitrate indicator a new one consisting of one gram of diphenylbenzidine dissolved in 100 c.c. of concentrated sulphuric acid was used. W.H.Cone and L.C.Cady (J.A.C.S. Feb. 1927 356) have shown that this indicator gives more reproducible results than uranium nitrate besides allowing the titration to be completed in a much shorter time. The titrating solution was made by dissolving twenty two grams of potassium ferrocyanide and a third gram potassium ferricyanide to a litre of solution. This solution was standardized by taking a weighed amount of A.R. zinc dissolving it in 15 c.c. of 30 per cent sulphuric acid, diluting to 100 c.c. with distilled water, adding ten grams of ammonium chloride and a few drops of the indicator, and then titrating with the ferrocyanide solution. The sulphuric acid and ammonium chloride used in this titration were both free of zinc. After the addition of 2 to 3 c.c of the titrating solution with shaking, the blue colour, produced by the oxidation of the diphenylbenzidine, appeared. This colour darkened as the titration proceeded finally changing to purple within a few drops of the end point, if the addition of the titrating solution was sufficiently slow. At the end point the dark purple colour changed sharply to a pale green. The purple colour was stable even within a drop or two of the end point, and could be left for hours without

change.

This indicator gave best results when about 20 c.c. or more of the titrating solution was required for then, on addition of about half the titrating solution a deep blue colour was quickly formed, and the titration could be completed in a short time. To get a good sharp end-point, it was necessary to allow the blue colour to appear so that the purple, characteristic of the last stages of titration, appeared quickly.

All solutions were standardized in triplicate and restandardizations carried out every two weeks to see that the solutions had not altered in strength.

From the phase rule diagram based on the results of Driot for the solubility of zinc oxide in zinc chloride solution, the compositions of the mixtures were calculated so that, when equilibrium had been attained, there was only a small amount of solid phase. A bottle of suitable size was cleaned and dried, the required amount of distilled water run in from a burette and then most of the hydrochloric acid added. While the zinc oxide was being added through a long narrow funnel, the contents of the bottle were shaken to prevent the formation of lumps as much as possible. After all the zinc oxide had been added, the remainder of the hydrochloric acid was run in from the burette so as to dissolve any zinc oxide adhering to the

sides of the bottle. If any lumps were visible in the mixture they were broken up by means of a glass rod inserted through the neck. Before being sealed the bottle was placed in a beaker of boiling water for some time to expel any small amount of carbon dioxide present in the zinc oxide. Sometimes, when the lumps of zinc oxide could not be broken up with a rod, the complex was heated in boiling water to saturate the solution at the higher temperature and then shaken so that the fine precipitate of oxychloride was held in suspension while the complex was transferred to another bottle leaving the lumps in the first. After heating, the complex was allowed to cool down nearly to the temperature at which it was to be shaken, and then the end of the bottle sealed off in the blowpipe flame. In investigations of this nature it is not necessary to maintain pressure at a particular value. Equilibria between solids and liquids alter so very slightly with moderate or small changes of pressure, that the effect of failure to maintain the pressure at a chosen value is generally well within the limits of experimental error.

When the complexes were made from zinc chloride, zinc oxide and water it was found that, if several cubic centimetres of water were placed in the bottle and the zinc oxide added slowly with shaking, that a fine paste was formed. On addition of the zinc chloride dissolved in the remainder of the water no lumps were formed.

The bottles were left in the shaker for three days or longer and then placed vertically in a clamp at the side of the bath to allow the precipitate to settle to the bottom of the bottle. When the liquid had become clear, the bottle was opened by touching with a hot rod, a small mark made on the neck with a glass knife. Some of the liquid was drawn off in a dry standardized pipette - 5, 10 or 25 c.c. according to the strength of the solution - and transferred to a dry weighing bottle of known weight. The solutions usually settled clear and so filtering by means of a plug of asbestos in a piece of rubber tubing on the end of the pipette was necessary in only a few cases. After the required amount of solution had been removed the contents of the bottle were shaken and the solid filtered from most of the solution in a Hoesch funnel over a filter pump. Some of the wet solid was transferred to a dry weighing bottle and weighed. In filtering off the solid, it was not allowed to be sucked dry, as this would cause change in composition through loss of water vapour. This method was used for most of the solids at 25°C except those which were in equilibrium with a very concentrated solution of zinc chloride, as these zinc chloride solutions attacked the filter paper.

For the concentrated ones at 25°C. and all at 50°C. the solid was separated by the following method. A dry weighing bottle of known weight was placed in a dry bottle

and allowed to stand in the thermostat till it had reached the temperature of the water. The weighing bottle and the bottle containing the solid of the complex were then taken from the bath, and the solid plus adhering solution transferred to the weighing bottle which was replaced in the bath till the solid had separated out. The weighing bottle was then removed from the bath and the solution drawn off in a pipette leaving the solid in the weighing bottle.

By weighing the bottles containing samples of solution and wet solid the weights of these taken were obtained as a known volume of solution was always run into the weighing bottle from a standardized pipette and this amount was weighed, the density was easily calculated. To the solution in the weighing bottle a small amount of dilute sulphuric acid (zinc and chlorine free) was added, and then the contents of the weighing bottle washed into a standard flask, 200 c.c. or 500 c.c., according to the strength and volume of the solution. The solid was washed into a standard flask with distilled water, dissolved by addition of a few drops of dilute sulphuric acid and made up to volume.

By titration with potassium ferrocyanide solution as already described the amount of zinc was obtained. The chlorine was estimated by addition of a known volume of silver nitrate solution to a certain volume of the solution,

and back titration with potassium thiocyanate, after filtering off and washing the precipitate of silver chloride. From the total weight of zinc present in the solution or wet solid taken, the weight of zinc as chloride calculated from the weight of chlorine present was subtracted. This gave the weight of zinc as oxide and hence the amounts of zinc chloride, zinc oxide and water, in a known weight of solution or residue was obtained. From these weights the values of x and y were calculated and diagrams made.

TABLE IV 25°C.

The first line for each complex contains the results obtained from the solution and the second line the results obtained from the wet solid.

No.	Weight	Density	H ₂ O	ZnCl ₂	ZnO	x	y
1	25.0284	1.001	24.846	.183	-	.001	.001
	3.2122		1.892	.294	1.027	.018	.123
2	25.1126	1.004	24.900	.212	-	.001	.001
	8.7164		5.213	.913	2.591	.020	.117
3	25.9122	1.038	24.830	1.067	.015	.006	.006
4	10.5586	1.056	9.865	.692	.002	.009	.009
	4.7836		3.338	.449	.997	.016	.077
5	11.1819	1.118	9.657	1.510	.015	.020	.020
	5.2192		3.455	.722	1.042	.025	.086
6	27.9497	1.118	24.124	3.782	.044	.020	.020
	4.6466		2.947	.605	1.094	.024	.098
7	11.8469	1.185	9.353	2.454	.040	.033	.034
	5.1520		3.077	1.028	1.047	.039	.107
8	11.9368	1.194	9.374	2.528	.035	.034	.035
	4.7256		2.863	.953	.909	.039	.102
9	6.3520	1.270	4.546	1.778	.032	.049	.050
	6.1719		3.525	1.551	1.096	.052	.112

TABLE IV (Cont.) 25°C.

No.	Weight	Density	H ₂ O	ZnCl ₂	ZnO	x	y
10	13.202	1.320	8.753	4.347	.102	.061	.064
11	13.7383	1.374	8.506	5.115	.117	.073	.076
	10.4064		5.113	3.436	1.857	.075	.144
12	13.7902	1.379	8.457	5.220	.113	.075	.078
	2.7757		1.510	.942	.324	.073	.115
13	14.6125	1.461	8.096	6.357	.159	.094	.097
	1.9817		.952	.753	.276	.089	.144
14	15.5240	1.552	7.763	7.517	.244	.113	.119
	3.1682		1.396	1.371	.401	.108	.162
15	16.0903	1.609	7.404	8.451	.235	.130	.136
	8.3700		3.617	3.950	.803	.121	.162
16	16.3037	1.630	7.320	8.649	.335	.134	.142
	3.2895		1.360	1.576	.354	.126	.173
17	8.1720	1.634	3.670	4.360	.142	.134	.142
	6.9528		2.987	3.359	.607	.124	.162
18	8.1175	1.624	3.626	4.368	.123	.136	.143
	8.7970		3.662	4.353	.783	.130	.169
19	16.4644	1.646	7.286	8.858	.320	.137	.145
	2.9658		1.203	1.428	.335	.128	.178

TABLE IV (Cont.) 25°C.

No.	Weight	Density	^a H ₂ O	^b ZnCl ₂	^c ZnO	x	y
20	16.5865	1.659	7.192	9.020	.374	.141	.150
21	16.7940	1.679	7.121	9.302	.371	.148	.155
	9.0925		3.765	4.897	.431	.144	.165
22	8.4583	1.692	3.583	4.701	.174	.146	.155
	7.8710		2.973	3.933	.965	.140	.197
23	16.8520	1.685	6.995	9.437	.419	.149	.160
	11.2030		3.673	6.058	1.472	.167	.234
24	8.4946	1.699	3.499	4.775	.220	.151	.163
	11.2597		3.822	6.229	1.208	.167	.221
25	17.0724	1.707	6.929	9.770	.374	.155	.165
	7.0499		2.520	3.926	.804	.172	.231
26	17.2315	1.723	6.840	10.106	.286	.162	.169
	7.1779		2.343	4.092	.743	.177	.231
27	17.3051	1.731	6.766	10.257	.283	.165	.173
	13.9314		4.072	3.205	1.654	.183	.245
28	8.6854	-	3.418	5.110	.157	.163	.172
	10.9465		3.586	6.430	.931	.183	.227
29	8.9658	1.793	3.428	5.422	.116	.172	.177
	10.9373		3.566	6.585	.786	.189	.226

TABLE IV. (Cont.) 25°C.

No.	Weight	Density	H ₂ O	ZnCl ₂	ZnO	x	y
30	8.8407	1.768	3.336	5.408	.097	.176	.181
	5.0126		1.591	3.015	.407	.192	.235
31	17.7568	1.776	6.404	11.034	.318	.184	.193
	9.6895		2.540	5.850	1.299	.215	.294
32	8.9644	1.793	3.168	5.695	.101	.191	.196
	4.9349		1.566	3.093	.276	.201	.231
33	8.9680	1.794	3.135	5.777	.070	.195	.198
	10.7339		3.174	6.768	.792	.211	.252
34	18.3516	1.835	6.158	11.924	.270	.202	.209
	3.4447		1.039	2.204	.202	.211	.243
35	18.3082	1.831	6.071	11.982	.255	.205	.212
	3.2100		.783	1.999	.428	.231	.313
36	18.3176	1.832	6.062	11.971	.285	.205	.213
37	18.7307	1.873	5.793	12.649	.287	.222	.250
	9.8765		2.711	6.511	.654	.231	.270
38	3.7998	1.900	1.075	2.677	.047	.245	.252
	2.0457		.462	1.367	.216	.262	.331
39	19.7148	1.971	5.224	14.333	.158	.264	.269
	8.0666		1.966	5.708	.392	.266	.299

TABLE V. 50°C.

No.	Weight	Density	H ₂ O	ZnCl ₂	ZnO	x	y
1	10.4996	1.050	9.818	.672	.009	.009	.009
	10.3177		7.215	1.075	2.028	.018	.075
2.	11.2092	1.121	9.597	1.592	.020	.021	.021
3	14.5167	1.452	8.137	6.216	.164	.091	.095
	10.3077		5.344	4.162	.702	.091	.116
4	15.8174	1.582	7.592	8.008	.217	.121	.127
	11.0555		4.820	5.208	1.028	.119	.159
5	16.5330	1.653	7.186	9.010	.337	.141	.149
	11.8585		5.050	6.300	.509	.139	.157
6	8.1855	1.637	3.504	4.488	.194	.143	.153
	19.606		8.105	10.415	1.086	.141	.166
7	16.7312	1.673	7.154	9.207	.370	.144	.153
	11.4503		4.013	6.216	1.221	.161	.214
8	16.8910	1.689	6.945	9.690	.256	.154	.161
	11.9215		4.170	6.712	1.046	.167	.211
9	17.1100	1.711	6.865	9.955	.290	.159	.167
	13.8710		4.793	8.082	.996	.175	.211
10	8.5681	1.713	3.419	4.997	.152	.160	.168
	25.6003		8.740	14.943	1.917	.177	.215

TABLE V. (Cont.) 50°C.

No.	Weight	Density	H ₂ O	ZnCl ₂	ZnO	x	y
11	17.1615	1.716	6.753	10.182	.227	.165	.171
	9.4342		3.883	5.574	.977	.192	.248
12	18.1758	1.816	6.201	11.812	.163	.200	.205
	13.3175		4.010	8.469	.839	.211	.245
13	19.3533	1.935	5.427	13.739	.187	.249	.255
	12.938		3.012	8.680	1.246	.258	.321

Results and Discussion.

Since the time of shaking required for the contents of the bottles to reach equilibrium was dependent on the concentrations of the reacting substances, two complexes (Nos. 7 and 8 Table IV) were made up of exactly the same composition. Of these one was shaken for ~~seventy-two~~ twenty-four hours and the other for seventy-two hours before being set aside to settle out. Samples of the solutions and wet solids of these were analysed, and it was found that the composition of the solutions were identical, and, although the composition of the residues were not the same, since one had more adhering solution than the other, the solid phases both had the same composition because the conjugation lines from solution to wet solid were identical for both. This showed that for complexes of strength greater than 7 or 8 twenty-four hours shaking was sufficient, though three days, or even longer, was always given. By shaking several dilute complexes (Nos. 1, 5, 6.) for only three days, it was found that the conjugation lines did not intersect at a definite point.

To determine whether this was due to mixed crystal formation or to incomplete reaction, two complexes (Nos. 2 and 4) were shaken for twenty-one days. When the results of these were expressed in the diagram, it was found that their conjugation lines intersected those of 7 and 8 at a point E. The fact that longer shaking gave values indicating a definite solid phase represented in composition by E, showed that the

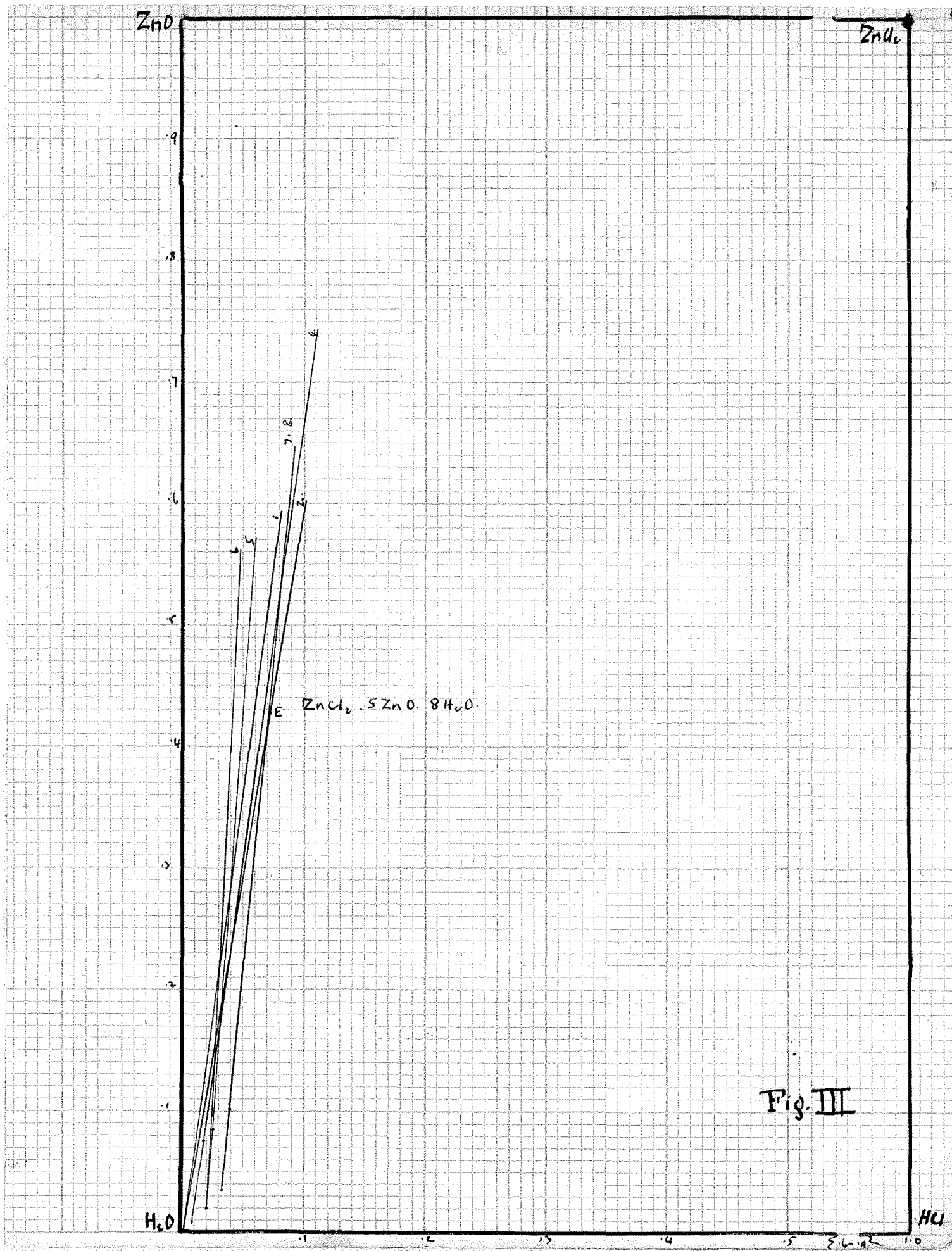


Fig. III

results obtained from complexes 1, 5 and 6 were due to incomplete reaction and not to mixed crystal formation. As the solution of complex 2, which had solid phase E, had values of x and y equal to .001 there was no area in which the solid phase was zinc oxide or zinc hydroxide. The conjugation lines for complexes 1 to 8 are given in Fig. III.

When the points in the solution curve oa (Fig. IV) were joined to the points representing the compositions of the wet solids and the lines produced, it was found that all the lines, except those accounted for in Fig. III, and one or two others, intersected at the point E. This point whose composition was obtained from the zinc chloride, zinc oxide, water, triangle of the diagram, had value of coordinates $x = .071$, $y = .428$ which corresponded to formula $ZnCl_2.5ZnO.8H_2O$. This was the same compound as André obtained by adding water to a syrupy solution of zinc chloride, and Perrot made by adding water to fused zinc chloride.

The conjugation lines of Fig. IV showed that the solid was not $ZnCl_2.4ZnO.6H_2O$ as reported by Driot or $ZnCl_2.4ZnO.8H_2O$ reported by Dietrich and Johnston these being the two whose compositions were nearest to $ZnCl_2.5ZnO.8H_2O$. These facts are made more obvious in the second method of representation used where numbers of molecules of zinc oxide to hundred molecules of water are plotted as ordinates, and number of molecules of zinc chloride to hundred molecules of water as abscissae.

For those complexes whose solutions were represented by the curve ab, the solid phase was represented by the point $x = .25$, $y = .50$ which corresponds to the formula $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 2\text{H}_2\text{O}$. The diagram showed that it was only over a small range of concentration that the solid phase in equilibrium was $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 2\text{H}_2\text{O}$. From the point b to c on the solution curve, the solid phase in equilibrium was represented by the point $x = .33$, $y = .66$ which gave formula of the solid phase $\text{ZnCl}_2 \cdot \text{ZnO} \cdot \text{H}_2\text{O}$.

Driot in his solubility determinations has described a solid phase $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 1\frac{1}{2}\text{H}_2\text{O}$ but no evidence was found for this oxychloride. As was shown later, the curve ab was increasing at the expense of one or both of the others as the temperature decreased, and it is quite probable that Driot's solution (No. 10 Table 1) when he obtained the solid phase $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 1\frac{1}{2}\text{H}_2\text{O}$ came on the transition point of the curve since he worked at a temperature lower than 25°C . If this was the case, Driot's solid was an equilibrium mixture of $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 2\text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot \text{ZnO} \cdot \text{H}_2\text{O}$. This explanation is strengthened by the fact that Driot reported only one solution with solid phase $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 1\frac{1}{2}\text{H}_2\text{O}$ in equilibrium. If he had reported two solutions in equilibrium with the solid phase $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 1\frac{1}{2}\text{H}_2\text{O}$, the above explanation would be untenable since both could not be transition points on the curve having the same two solid phases in equilibrium with each.

To obtain the position of the first break, a, in the

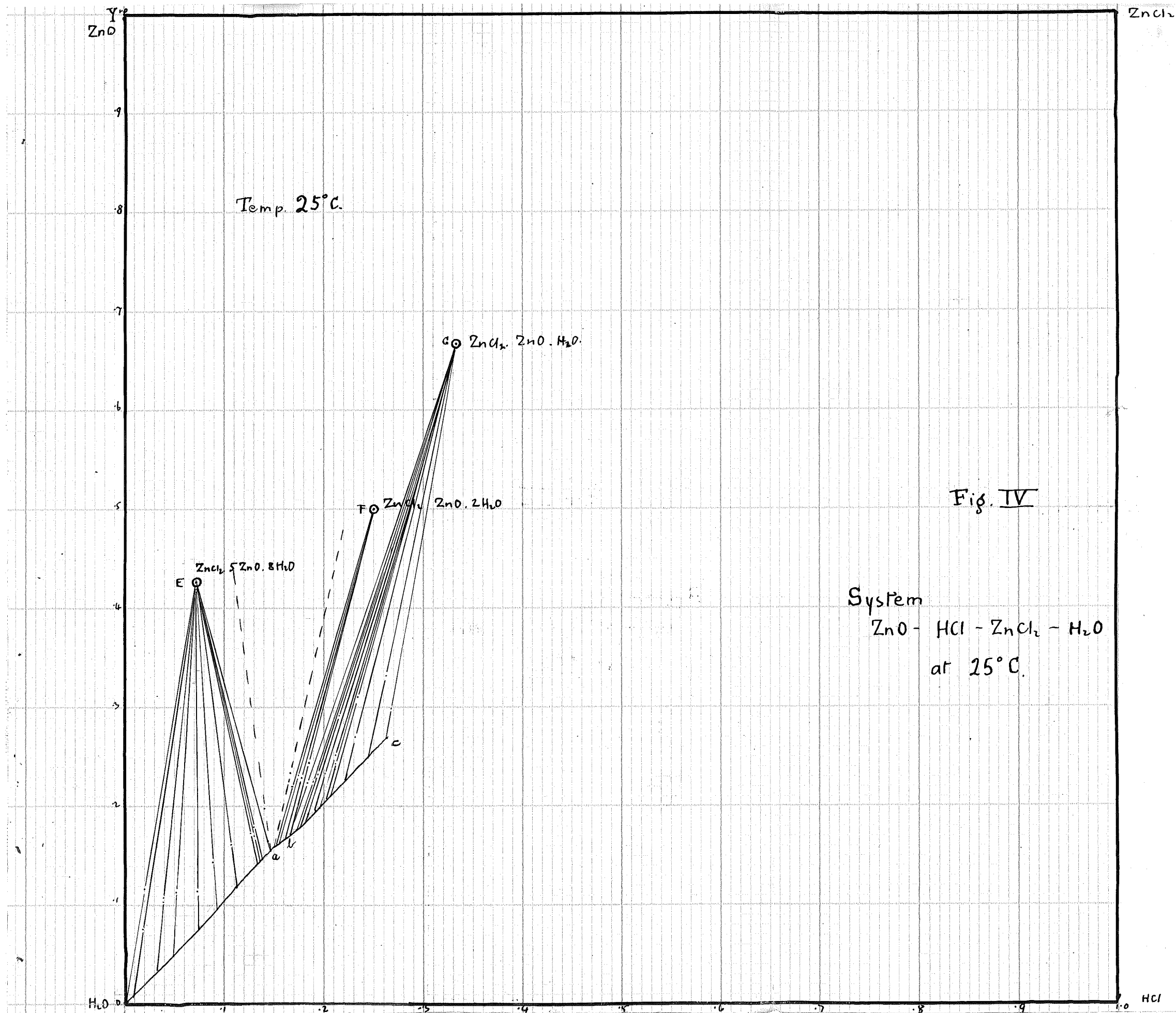


Fig. IV

System
 $\text{ZnO} - \text{HCl} - \text{ZnCl}_2 - \text{H}_2\text{O}$
at 25°C.

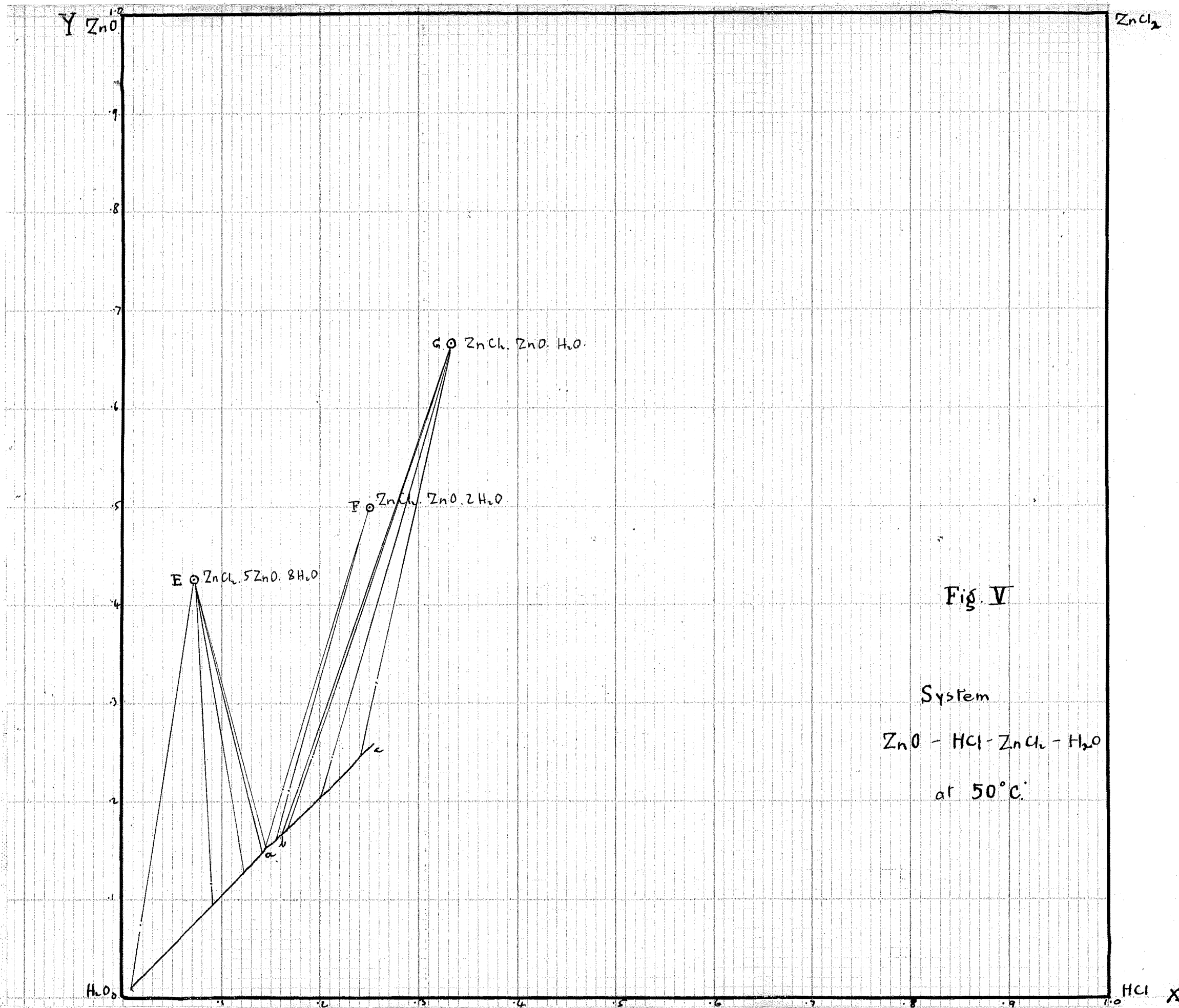


Fig. V

System
 $\text{ZnO} - \text{HCl} - \text{ZnCl}_2 - \text{H}_2\text{O}$
at 50°C .

solution curve two complexes were made up in the area Efa. These separated into a solution represented by the break in the curve and a mixture of the two solid phases $\text{ZnCl}_2 \cdot 5\text{ZnO} \cdot 8\text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 2\text{H}_2\text{O}$. The position of the second break, b, was found because one complex had solid phase $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 2\text{H}_2\text{O}$ in equilibrium with the solution represented by point b on solution curve, while another had solid phase $\text{ZnCl}_2 \cdot \text{ZnO} \cdot \text{H}_2\text{O}$ in equilibrium with solution b. The results obtained at 25°C . are given in Table IV.

At the higher temperature, 50°C ., the diagram (Fig.V) drawn from the results obtained, was of the same form, the only difference being that the area Gcb had expanded at the expense of the area Fba. The first break in the solution curves represented by a on both 25°C and 50° diagrams came at practically the same point. The second break b in the solution curve came at a lower concentration of zinc chloride at the higher temperature, showing that the solid phase $\text{ZnCl}_2 \cdot \text{ZnO} \cdot \text{H}_2\text{O}$ was more stable than $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 2\text{H}_2\text{O}$. Table V contains the results obtained at 50°C .

By plotting the results in the manner used by Roozeboom and Schreinemakers in the earlier work on three component systems, a different diagram was obtained. As ordinates the number of molecules of zinc oxide to one hundred molecules of water were plotted, while the abscissae were the number of molecules of zinc chloride to one hundred molecules of water.

TABLE VI. 25°C

Molecules pr. 100 Mols. Water.

Number	<u>Solution</u>		<u>Residue</u>	
	ZnCl ₂	ZnO	ZnCl ₂	ZnO.
1	.1	-	2.0	12.0
2	.1	-	2.3	10.9
3	-	-	-	-
4	.9	-	1.8	6.6
5	2.1	-	2.7	6.6
6	2.1	-	2.7	8.2
7	3.4	.1	4.4	7.5
8	3.5	.1	4.4	7.0
9	5.1	.1	5.8	6.8
10	-	-	-	-
11	7.9	.3	8.8	8.0
12	8.1	.3	8.3	4.6
13	10.4	.4	10.5	6.4
14	12.8	.7	12.9	6.3
15	15.1	.7	14.4	4.9
16	15.6	1.0	15.3	5.7
17	15.4	.8	14.8	4.5
18	15.9	.7	15.4	4.7
19	16.1	.9	15.6	6.1
20	-	-	-	-

TABLE VI (CONT.) 25°C

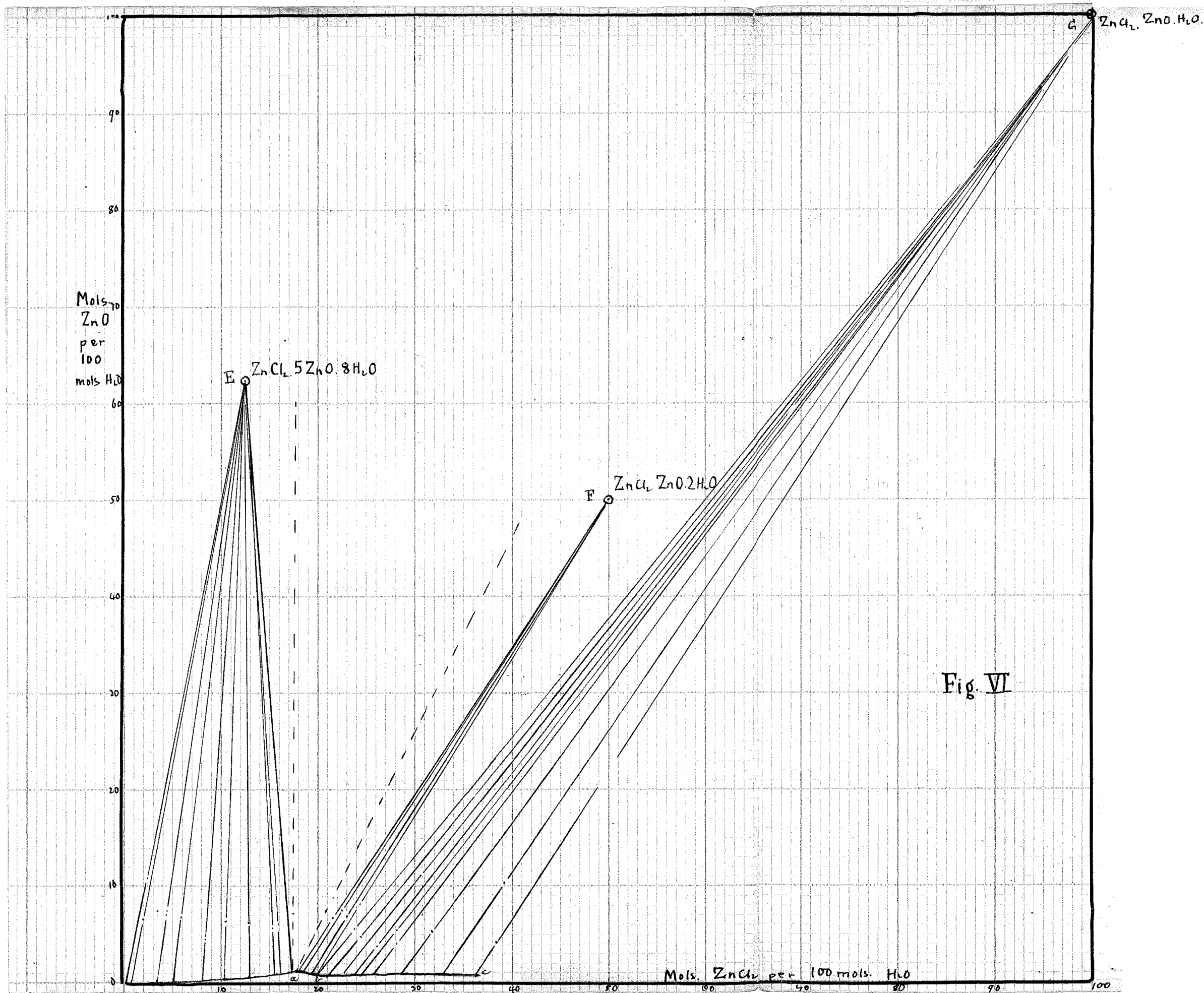
Molecules pr. 100 mols. H₂O

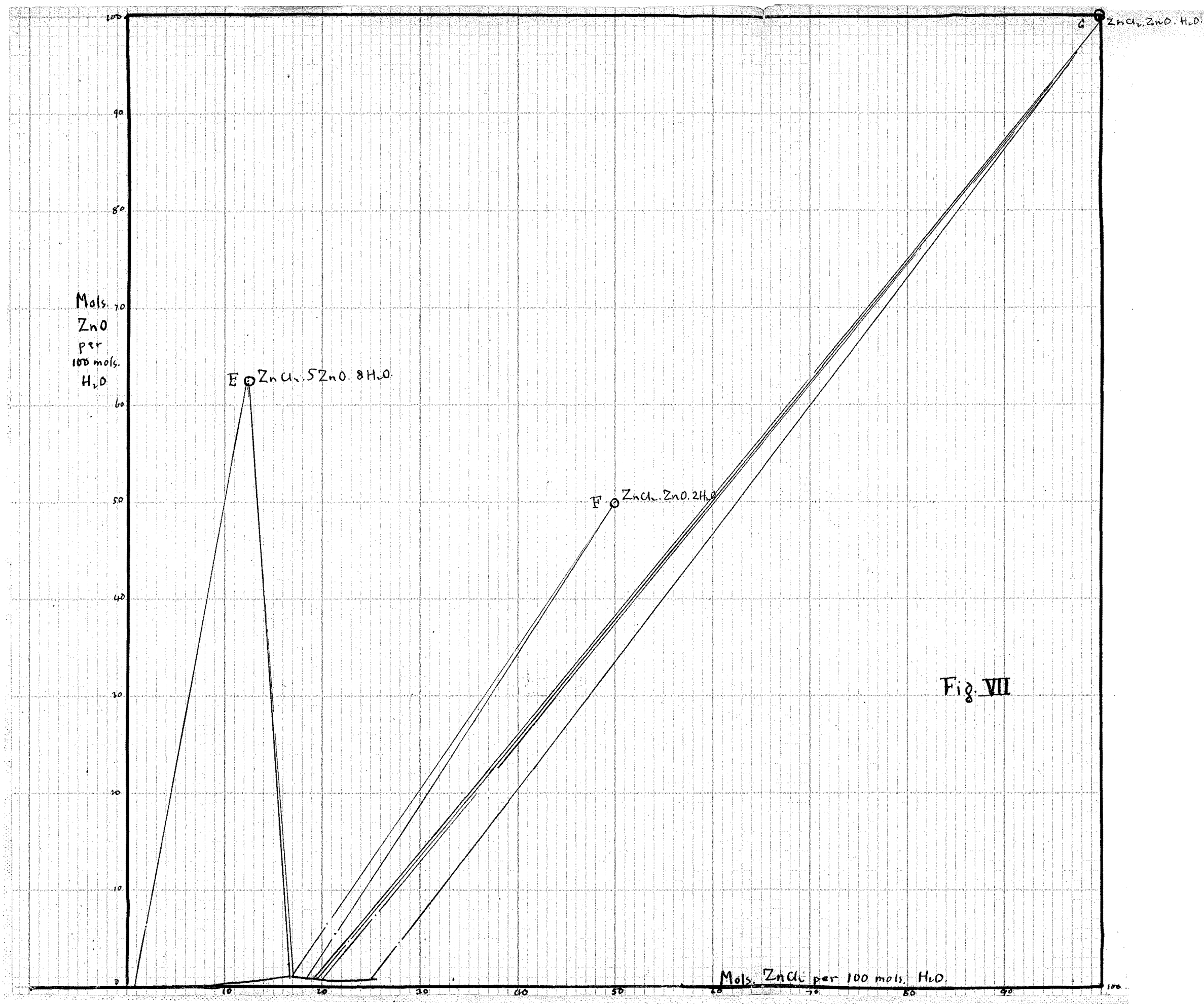
Number	<u>Solution</u>		<u>Residue</u>	
	ZnCl ₂	ZnO	ZnCl ₂	ZnO
21	17.3	1.1	17.2	2.5
22	17.3	1.1	17.5	7.2
23	17.8	1.3	21.7	8.8
24	18.0	1.4	21.5	6.9
25	18.6	1.2	22.4	7.6
26	19.5	.9	23.1	7.0
27	20.0	.9	24.3	8.2
28	19.7	1.0	23.7	5.7
29	20.9	.7	24.4	4.8
30	21.4	.7	25.0	5.6
31	22.7	1.1	30.4	11.3
32	23.7	.7	26.1	3.9
33	24.3	.5	28.1	5.5
34	25.6	.9	28.1	4.2
35	26.0	.9	33.6	12.1
36	-	-	-	-
37	28.8	1.1	31.7	5.3
38	33.0	.9	39.1	10.3
39	36.3	.7	38.4	4.4

TABLE VII 50°C.

Molecules pr. 100 mols.H₂O

Number	<u>Solution</u>		<u>Residue.</u>	
	ZnCl ₂	ZnO	ZnCl ₂	ZnO.
1	.9	-	1.9	6.2
2	-	-	-	-
3	10.1	.4	10.7	2.9
4	13.9	.6	14.3	4.7
5	16.6	1.0	16.4	2.2
6	16.9	1.2	16.9	2.9
7	17.0	1.1	20.4	6.7
8	18.4	.8	21.3	5.5
9	19.2	.9	22.2	4.5
10	19.5	1.0	22.6	4.8
11	19.9	.7	25.5	7.5
12	25.1	.6	27.8	4.6
13	33.4	.7	38.0	9.1





These results are recorded in Table VI. for 25°C . and Table VII for 50°C Figure VI contains the results for the 25° isotherm and VII for the 50°C . one as before E represents the solid phase $\text{ZnCl}_2 \cdot 5 \text{ZnO} \cdot 8\text{H}_2\text{O}$, F the phase $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 2\text{H}_2\text{O}$, and G the phase $\text{ZnCl}_2 \cdot \text{ZnO} \cdot \text{H}_2\text{O}$. This diagram shows more definitely than the other that the first solid phase is $\text{ZnCl}_2 \cdot 5\text{ZnO} \cdot 8\text{H}_2\text{O}$ and not $\text{ZnCl}_2 \cdot 4\text{ZnO} \cdot 6\text{H}_2\text{O}$ or $\text{ZnCl}_2 \cdot 4\text{ZnO} \cdot 8\text{H}_2\text{O}$.

The first two elements of group II of the periodic table, beryllium and magnesium are assigned to subgroup 2A with calcium, strontium, and barium, by some authors, and to 2B with zinc, cadmium and mercury by others. If beryllium and magnesium are placed in 2A, there is a steady increase in the basic nature of the oxide from the amphoteric beryllium oxide BeO to the strongly basic oxide of barium BaO . On the other hand, if the first two elements of the group are placed in 2B with zinc cadmium and mercury, there is no steady change in the nature of the oxides since BeO is amphoteric MgO basic, ZnO amphoteric and CaO and HgO basic. Also when the values of the atomic volumes of the elements are plotted against the atomic weights, the elements magnesium calcium strontium and barium occur at corresponding points on the curves. These facts favour the view that beryllium and magnesium should be placed in subgroup 2A.

The reasons given by some authors for placing the first

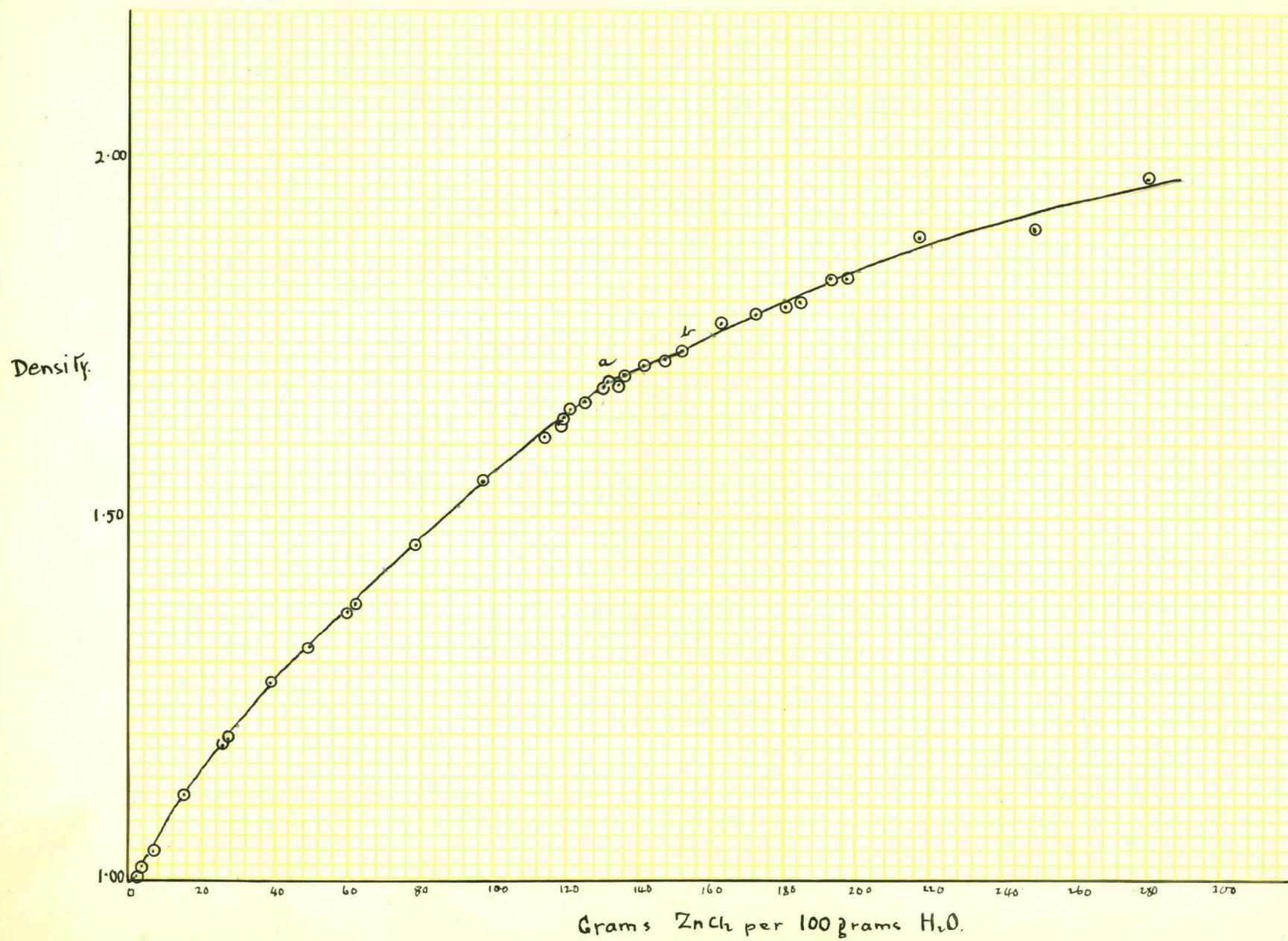


Fig. VIII

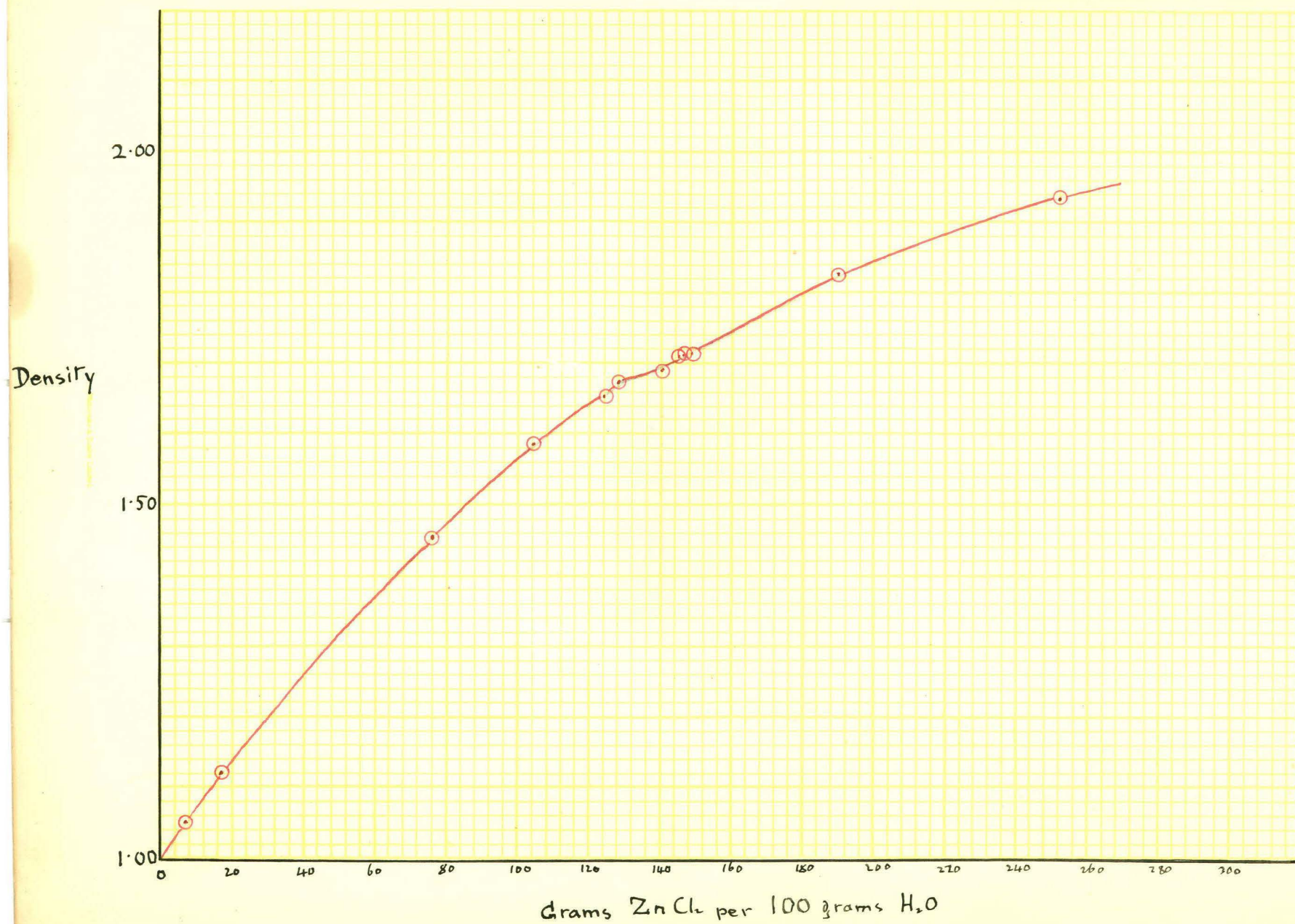


Fig. VIII

two elements in the B subgroup are similarity in properties such as formation of basic carbonates and organo-metallic compounds etc. Definite oxychlorides of magnesium and cadmium $\text{MgCl}_2 \cdot \text{MgO} \cdot \text{H}_2\text{O}$ and $\text{CdCl}_2 \cdot \text{CdO} \cdot \text{H}_2\text{O}$ have been established and the existence of a corresponding zinc oxychloride completes the series $\text{MgCl}_2 \cdot \text{MgO} \cdot \text{H}_2\text{O}$ $\text{ZnCl}_2 \cdot \text{ZnO} \cdot \text{H}_2\text{O}$ $\text{CdCl}_2 \cdot \text{CdO} \cdot \text{H}_2\text{O}$ and is evidence in favour of putting beryllium and magnesium in group 2B. On the other hand it must not be overlooked that a compound similar to the other oxychloride $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 2\text{H}_2\text{O}$ has been obtained in the case of calcium, $\text{CaCl}_2 \cdot \text{CaO} \cdot 2\text{H}_2\text{O}$.

The density graph obtained by plotting density as ordinates and weight of zinc chloride in one hundred grams of water as abscissae shows somewhat indefinite breaks at a and b in the 25°C curve. These breaks correspond to the breaks in the solution curves in the other diagrams. At 50°C the densities of the solutions were practically the same as at 25°C . The densities of the solutions are given in table VIII for 25°C . and IX for 50°C . and plotted in Fig. VIII, densities at 25°C being in black while those at 50°C are in red.

When the results of Driot for the solubility of zinc oxide in zinc chloride solutions were plotted as a graph with grams zinc oxide as ordinates and grams zinc chloride to one hundred grams water as abscissae a curve (Fig. 9) with a maximum at point 8, was obtained. One would expect any change in the composition of the solid phase to take place at this max-

imum, but Driot reported the same oxychloride $\text{ZnCl}_2 \cdot 4\text{ZnO} \cdot 6\text{H}_2\text{O}$ for this point 8 and also for the point 9. When the present results were expressed in the same manner a curve (Fig.10) was obtained which indicated greater solubility of zinc oxide than Driot's especially in a solution containing about 136 grams ZnCl_2 to 100 grams water. A solution was made up in the following proportions, water 100 grams, zinc chloride 136 grams, and zinc oxide 5.6 grams. This amount of zinc oxide was dissolved by heating to about 60°C for some time. On allowing the solution to cool no precipitation of oxychloride occurred down to 35°C but from that temperature to 25°C a very small amount of oxychloride was precipitated making the solution cloudy.

At 25°C , the curve rose to a maximum a, which corresponded to the first break in the solution curve and then decreased to a point b corresponding to second breaks in the curves of other diagrams. After the point b the solubility of zinc oxide probably depended more on the amount of water present in the solution than on the amount of zinc chloride present. The points to the right of b are not in a curve because the amount of zinc oxide was calculated from the difference between total zinc and zinc as chloride, calculated from amount of chlorine present. From this it is evident that any small error in either the zinc or the chlorine estimation causes a large error in the zinc oxide content, since the chloride is present in much greater quantity. The results obtained at 50°C are expressed in Fig.(11). This has the same form as the 25°C curve.

TABLE VIII 25°C.

Number	Density.	Grams per 100 gm. H ₂ O	
		ZnCl ₂	ZnO
1	1.001	.72	-
2	1.004	.84	-
3	1.038	4.30	.06
4	1.055	7.00	.02
5	1.118	15.53	.155
6	1.118	15.7	.180
7	1.185	26.2	.426
8	1.194	26.9	.370
9	1.270	38.9	.70
10	1.320	49.7	1.17
11	1.374	60.0	1.38
12	1.379	61.7	1.33
13	1.461	78.5	1.96
14	1.552	96.8	3.15
15	1.609	114.	3.18
16	1.630	118.	4.57
17	1.634	119.	3.90
18	1.624	120.	3.39
19	1.646	121.	4.40
20	1.659	125.	5.20

TABLE VIII. (Cont.) 25°C.

Number	Density	Grams per 100 grams H ₂ O	
		ZnCl ₂	ZnO.
21	1.679	130.	5.21
22	1.692	131.	4.80
23	1.685	135.	6.00
24	1.699	137.	6.20
25	1.707	141.	5.38
26	1.723	147.	4.20
27	1.731	151.	4.17
28	-	149.	4.60
29	1.793	158.	3.40
30	1.768	162.	2.90
31	1.776	172.	4.97
32	1.793	180.	3.18
33	1.794	184.	2.3
34	1.835	193.	4.3
35	1.831	197.	4.2
36	1.832	197.	4.7
37	1.873	217.	4.9
38	1.900	219.	4.40
39	1.971	280.	5.1

TABLE IX. 50°C.

Number	Density	Grams per 100 grams H ₂ O	
		ZnCl ₂	ZnO.
1	1.050	7.00	.09
2	1.121	16.6	.20
3	1.452	76.0	2.01
4	1.582	105.	2.90
5	1.653	125.	4.68
6	-	128.	5.5
7	1.673	128.	5.1
8	1.689	139.	3.9
9	1.711	145.	4.2
10	1.714	146.	4.4
11	1.716	151.	3.4
12	1.816	190.	2.7
13	1.935	253.	3.4

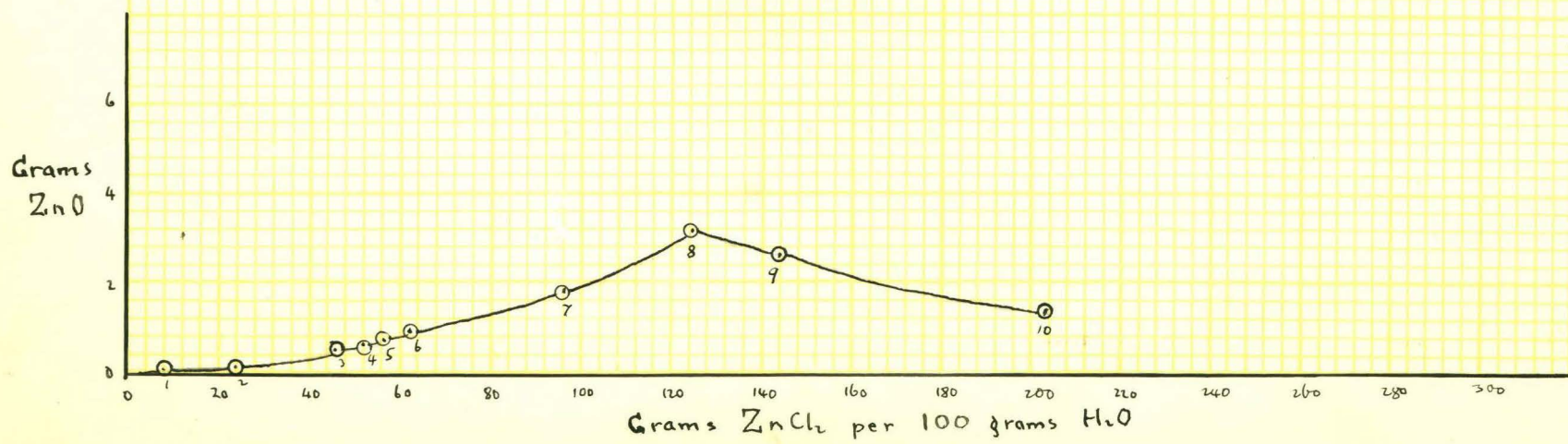
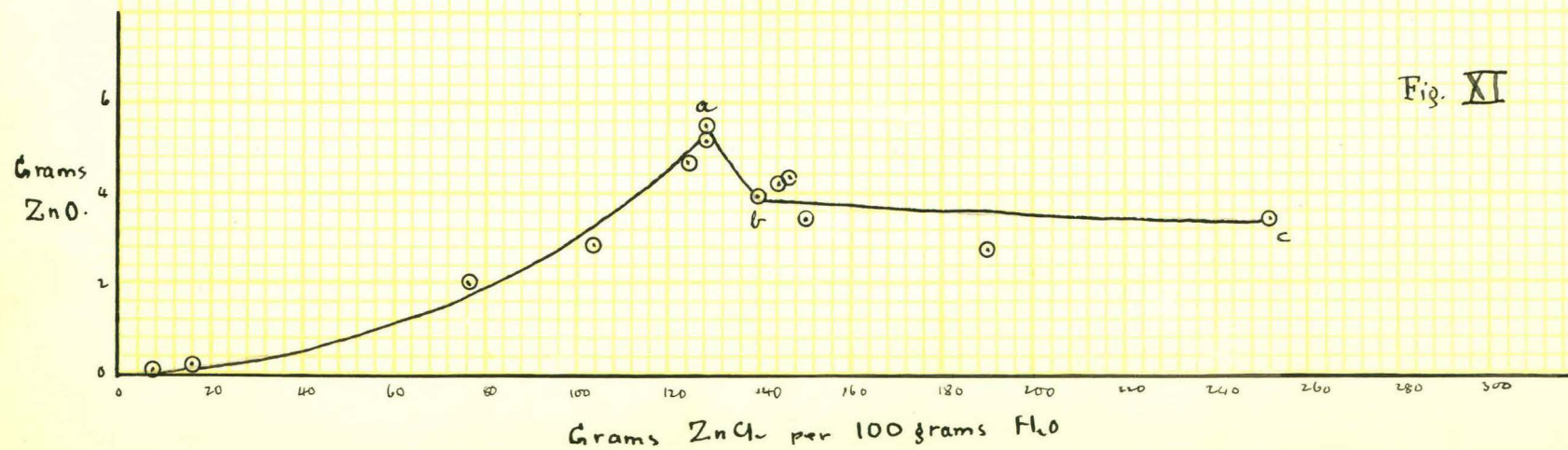
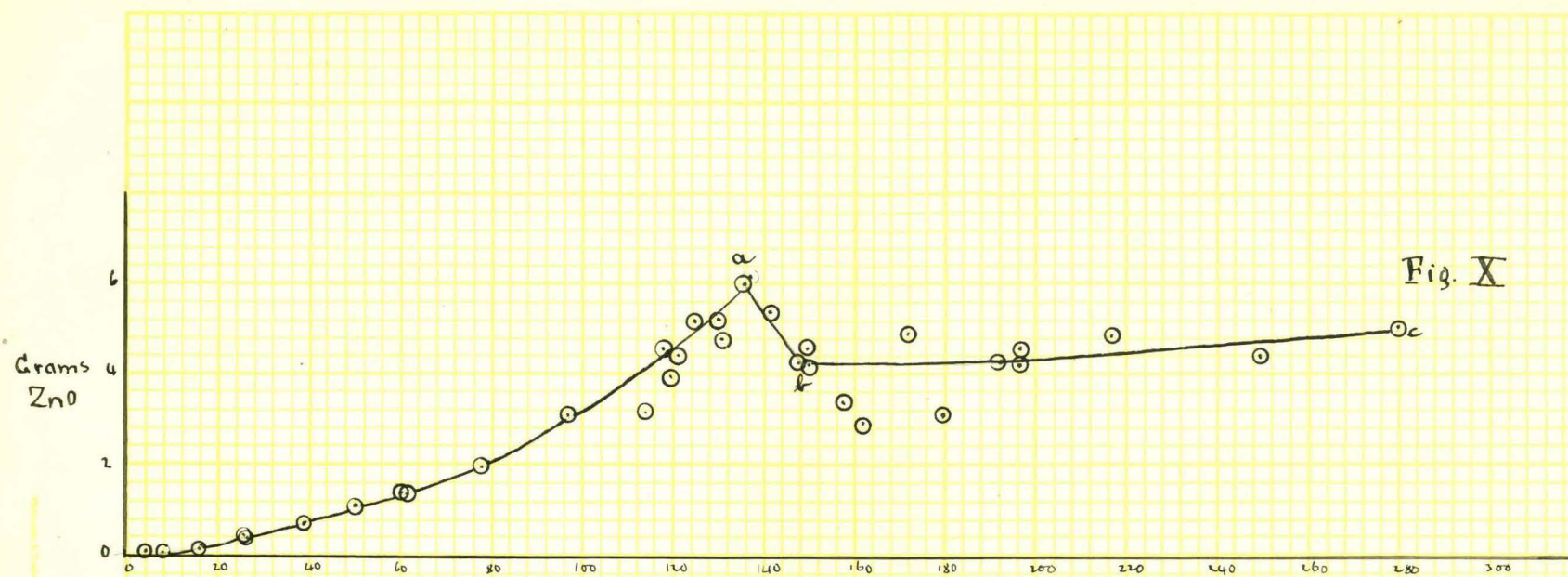


Fig. IX



Summary.

1. Equilibria existing in the three component system zinc oxide, hydrochloric acid, zinc chloride, water, have been studied at 25°C. and 50°C.
2. The composition of the solid phases existing in stable equilibrium with solutions of the above system have been obtained.
3. Evidence has been obtained for the existence of two new oxychlorides of zinc $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 2\text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot \text{ZnO} \cdot \text{H}_2\text{O}$.
4. The solid phase in equilibrium with all solutions up to a certain definite concentration was found to be $\text{ZnCl}_2 \cdot 5\text{ZnO} \cdot 8\text{H}_2\text{O}$.
5. For solutions more concentrated than those having $\text{ZnCl}_2 \cdot 5\text{ZnO} \cdot 8\text{H}_2\text{O}$ in equilibrium, the solid phase was $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 2\text{H}_2\text{O}$ up to a definite concentration and then $\text{ZnCl}_2 \cdot \text{ZnO} \cdot \text{H}_2\text{O}$. The oxychloride $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 2\text{H}_2\text{O}$ existed in equilibrium with solutions of only a small range of concentrations.
6. The same series of solid phases $\text{ZnCl}_2 \cdot 5\text{ZnO} \cdot 8\text{H}_2\text{O}$, $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 2\text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot \text{ZnO} \cdot \text{H}_2\text{O}$ was found at both 25°C. and 50°C. $\text{ZnCl}_2 \cdot \text{ZnO} \cdot \text{H}_2\text{O}$ was found to be more stable than $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 2\text{H}_2\text{O}$ at the higher temperature.

7. The solubility of zinc oxide in zinc chloride solutions has been determined.