CCCXL.—*The System Cobalt Chloride–Zinc Chloride.*

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IN aqueous solutions zinc chloride has a reddening effect on cobalt chloride because it favours the kationic condition of cobalt (Bassett and Croucher, J., 1930, 1796). It is thus somewhat remarkable that in the anhydrous system, $CoCl_2$–$ZnCl_2$, all the melts and solids are blue. The fusion diagram of the system has now been examined in order to explain the different behaviour of zinc chloride in the two cases.

Since the present work was finished the system $CoCl_2$–$ZnCl_2$ has been examined by Ferrari and Inganni (*Atti R. Accad. Lincei*, 1930, **12**, 668), but this only came to our knowledge when our paper was in proof. The fusion and eutectic temperatures found by the Italian authors are all from 13° to 20° below those found by us. This may be due partly to lack of stirring and partly to failure to dehydrate each individual melt. Owing to an insufficient number of observations at the zinc chloride end of the system they draw their fusion curve as a continuous one with the eutectic point at 100% $ZnCl_2$ instead of at 93% as found by us. This we think partly accounts for their difficulty in interpreting their results.

EXPERIMENTAL.

The materials used were stick or lump zinc chloride, untreated before mixing, and cobalt chloride of the ordinary quality * unless otherwise stated. Anhydrous cobalt chloride was prepared from the hexahydrate by gentle heating in a porcelain dish. A mixture of the two chlorides, totalling about 50 g., was made up by weight to give approximately the desired composition. The mixtures were melted either in hard glass test-tubes (6 × 1 inch) immersed in a lead bath, or in silica tubes heated directly by three Bunsen burners according to the temperature at which fusion occurred. A steady stream of dry hydrogen chloride for removing oxide from the melt was bubbled through the mixture for about 3 hours, by which time purification appeared to be complete.

Oxidation of the melt at high temperatures was so rapid that it was difficult to avoid the formation of some oxide as soon as the passage of the hydrogen chloride ceased. The analysis was able to detect this (see p. 2482).

Determination of the Freezing Point of the Melt.—(a) *Thermometer experiments.* Sand contained in fireclay crucibles was heated to redness in a muffle furnace and poured round a piece of brass tubing (7″ × 1¼″) placed in a large fireclay crucible so as to fill the latter. Sufficient sand to fill the brass tube to a depth of 1½ to 2″ was poured in from a small crucible of the requisite size kept specially for the purpose. The tube containing the melt was disconnected from the stream of hydrogen chloride and placed inside the brass tube, which was then withdrawn, leaving the greater part of the tube surrounded by hot sand.

The temperature of the melt was determined with a mercury

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* Found on analysis to contain less than 0·1% of insoluble matter and 0·2% $NiCl_2,6H_2O$.

thermometer reading to 360° (or 445°), readings being taken every half minute, and the freezing point determined from the break in the cooling curve. The thermometer was calibrated in steam and aniline vapour after each experiment. The boiling points were corrected to the barometric pressure, those of water being obtained from tables and those of aniline deduced from the following formula.

The variation in the boiling point of aniline with pressure for a range of 145—185° is given by

$$\log_{10} p_m = (-0{\cdot}05223\ A/T) + B$$

where p_m = the barometric pressure, $A = 45{,}951$, $B = 8{\cdot}1278$, and T = the boiling point in degrees absolute (International Critical Tables, Vol. III, p. 221).

The temperature of the exposed stem of the thermometer below the level of the sand obviously differed considerably from that above it; hence the readings required for applying stem-exposure correction were obtained with two subsidiary thermometers.

The mouth of the tube was closed by a copper cap with three holes through which passed two thermometers and a platinum stirrer. The latter was constantly used, until solidification occurred, to prevent supercooling.

(b) *Thermocouple experiments.* An electric crucible furnace was heated to the requisite temperature (600—850°), the current switched off, and the tube inserted through a hole specially cut in the asbestos covering so that it rested in a small fireclay crucible placed on the bottom of the furnace. The rim of the silica tube rested on the asbestos cover when the base was supported by the crucible. Slipping of the tube was thus prevented. A platinum–platinum-5% rhodium thermocouple, which had been calibrated against a platinum resistance thermometer, was used to measure the temperature of the melt. The temperatures were read on a galvanometer scale graduated in 10° and could be estimated to 1—2° with the aid of a pocket lens. 2—4% of zinc chloride were volatilised during the heating and this had to be allowed for in making up the mixture.

A copper cap with two holes to allow the passage of the thermocouple and stirrer (if desired) covered the mouth of the tube.

Analysis of the Melt.—(I) *Experiments in which the melt was stirred.* The thermometer and the stirrer were melted out, the tube was allowed to cool and broken, and a convenient amount of solid was weighed, dissolved in water, and made up to 250 c.c. Accurate weighing of the solid was not attempted because of its deliquescence and the fact that the weight taken was not necessary for the determination of the composition of the melt.

(II) *Experiments in which the melt was unstirred.* Any volatilised zinc chloride having been rinsed from the upper part of the tube, the mixture was dissolved by immersing the tube and its contents in water in a large porcelain basin heated on a water-bath. Complications due to lack of homogeneity in the melt were thus avoided. A few drops of concentrated nitric acid were added to dissolve any flocculent zinc hydroxide. The solutions were made up to a suitable volume and a known portion was taken for analysis, which was performed as follows :—

1. The total chloride was determined by weighing as silver chloride after precipitation with silver nitrate.
2. The cobalt and zinc together were weighed as pyrophosphate after precipitation with diammonium phosphate. The slight amount of cobalt remaining in solution was precipitated by hydrogen sulphide and weighed as Co_3O_4 after strong ignition.
3. The cobalt alone was estimated by precipitation with α-nitroso-β-naphthol and weighed as Co_3O_4 after ignition over a powerful Bunsen burner.

The weight of zinc chloride calculated from the pyrophosphate determination was greater than that deduced from the weight of silver chloride, because the former included the zinc present as oxide as well as that present as chloride. The percentage of cobalt chloride calculated from the pyrophosphate result therefore decreased as the weight of zinc oxide in the melt increased and the difference between the percentages of cobalt chloride calculated from these two estimations indicates the basicity of the melt.

The Freezing Point of Zinc Chloride.—(a) *Previous determinations.* The melting point of zinc chloride has been given as 262° (Braun, *Pogg. Annalen*, 1875, **154**, 190), 240—258° (Foussereau, *Ann. Chim. Phys.*, 1885, **5**, 241), 250—260° (Lorenz, *Z. anorg. Chem.*, 1906, **3**, 17), 290—297° (Schultze, *ibid.*, 1899, **20**, 338), 365° (Grünauer, *ibid.*, 1904, **39**, 389), and 281—287° (Hachmeister, *ibid.*, 1919—1920, **109**, 145).

Imperfect purification of the zinc chloride was almost certainly responsible for melting points in the vicinity of 260°, no mention being made of any dehydration of the chloride used, but the last three experimenters in the above list worked with carefully purified material.

Schultze purified the zinc chloride by digesting the previously melted salt with concentrated hydrochloric acid, evaporating the resulting liquid until all the water and most of the acid were driven off, then removing the remainder by electrolysis. He did not follow a regular cooling curve, but observed the thermocouple to remain steady for a considerable time at 290° and 297° in two experiments. There is no mention of any stirring.

Hachmeister purified the zinc chloride by mixing it with ammonium chloride and then removing the latter by sublimation, thus obtaining " dry " zinc chloride, although no analysis was made to confirm this. The melting point was determined from the halt in the cooling curve, a thermocouple being used to measure the temperature. Again there is no mention of any stirring.

Grünauer made mixtures of zinc chloride and ammonium chloride in proportions such as 11 molecules to 1 molecule respectively, and added hydrochloric acid to dissolve the solids. The resulting solution was heated in an air-bath to 120° during 1 hour. This temperature was maintained for 3 hours, then gradually raised to 150°, kept there for 2 hours, after which it was kept at 260° for 5 hours. The residue was stirred and heated over a naked flame until above its melting point; it was then electrolysed until all evolution of hydrogen at the cathode ceased. Traces of ammonium chloride (0·14—0·31%) remained. The zinc chloride so prepared was melted in a tube and stirred with a thermocouple until solidification was seen to commence at the bottom of the tube, the temperature then remaining constant until the whole had solidified. The freezing point was thus found to be 360—365°.

He also dissolved zinc chloride in concentrated hydrochloric acid and gradually evaporated the solution in a current of hydrogen chloride at 300—350°, then fused the resulting solid and passed hydrogen chloride through it for $1\frac{1}{2}$ hours. The melting point of zinc chloride so purified, determined as above, was 365°. There is thus a difference of 80° in the three determinations of the melting point of carefully purified zinc chloride.

(b) *Our determinations.*

TABLE I.

Experiment.	Composition as shown by analysis of the solidified melt.	Freezing point (corrected value).	Remarks.
A	99·83% $ZnCl_2$ 0·17% $Zn(OH)_2$	313·1°	There were two different melts and two different analyses.
B	99·83% $ZnCl_2$ 0·17% $Zn(OH)_2$	313·1	Mercury thermometer used, with continuous stirring.
C	Prepared exactly as in Expts. A & B but not analysed.	311 ± 3	Thermocouple used with stirring. ± 3° was the possible error of the instruments.
D	Untreated commercial zinc chloride containing 96·34% $ZnCl_2$ and 3·66% $Zn(OH)_2$.	297·7	Mercury thermometer used *with* stirring.

TABLE I (*contd.*).

Experiment.	Composition as shown by analysis of the solidified melt.	Freezing point (corrected value).	Remarks.
E	(As in Expt. C)	298·2	Supercooled to 283° and rose to 298·2° on freezing. Mercury thermometer used *without* stirring.
F	,,	Crystals appeared at 355° ± 3°. Complete solidification occurred at 310° ± 3°, but caused little halt in the rate of cooling.	The melt was contained in an air-cooled hard glass tube. It was stirred with the thermocouple until completely solidified.
G	,,	Crystals appeared at 350° ± 3°, complete solidification at 310° ± 3°.	,,
H	,,	Crystals appeared at 370° ± 3°, complete solidification at 310—312° ± 3°.	Ditto, except that stirring was stopped as soon as crystals appeared at the bottom of the melt.
I	,,	Inoculated at 360° and 340°. No solidification induced. The melt froze at 310° ± 3°.	As in F, but inoculated with octahedral $ZnCl_2$ crystals.
J	,,	Inoculated at 365°, 350° and 335°. No solidification induced. The melt froze at 310° ± 3°.	As in F, but inoculated with bipyramidal $ZnCl_2$ crystals.
K	,,	The crystal remained in the body of the liquid, which froze at 310° ± 3°.	As in F, but inoculated with a crystal of $CoCl_2$.
L	,,	Supercooled to 292° and froze at 297·2°.	Inoculated with zinc chloride (which had frozen at 313°) just as the melt had begun to solidify. Mercury thermometer used without stirring.

Discussion of the Results obtained.—The freezing point of zinc chloride was found to be 313°. The values previously obtained below this figure were probably due to incomplete purification, or lack of stirring, or both. Experiments D and E show that appreciable errors are produced both by the zinc oxide or hydroxide present in commercial zinc chloride and by failure to stir the melt during solidification.

The value obtained by Grünauer is 52° higher than that obtained in the present investigation. It is reasonable to suppose that the bulk of the liquid would be at a much higher temperature than that on the outside which he saw solidifying and consequently the temperature he obtained for his freezing point is too high. Experiments F, G, and H simulate his determinations and, although slight solidification occurred at the bottom of the tube at about the temperatures found by him, the bulk of the melt did not solidify until the temperature fell to 310° ± 3°. His high result probably originated in this way, but it must be assumed that he erred in saying that the temperature remained constant at 365°. The method is clearly inaccurate, because rapid cooling causes a marked diminution in the length of the halt.

Anhydrous zinc chloride appears to exist in several distinct crystalline forms and three of these can be obtained by wet methods (Bassett and Croucher, *loc. cit.*, p. 1807). Mr. R. C. Spiller of the Mineral Department, University Museum, Oxford, has examined the crystals and reports as follows :—

" There are at least three distinct crystalline modifications which can be readily distinguished from each other.

(*a*) Cubic octahedra—quite isotropic.
(*b*) Acute tetragonal bipyramids with a perfect basal cleavage and negative birefringence.
(*c*) Crystals which are optically biaxial with positive birefringence. Such crystals may be either diamond-shaped rhombs, pseudo-hexagonal plates (twinned), star-shaped twins, or of indefinite shape.

" None of them is isomorphous with the rhombohedral anhydrous cobalt chloride as described by Pauling (*Proc. Nat. Acad. Sci.*, 1929, **15**, 709).

" On watching the crystallisation of molten zinc chloride under the microscope a monotropic polymorphic change is observed. If the cooling is slow, the change from the unstable to the stable form is very rapid. Quicker cooling arrests the rate of change and it is possible to get amorphous zinc chloride and the unstable and stable forms side by side. The stable form is too opaque to allow the determination of its optical properties. The unstable form appears to be biaxial, probably with negative birefringence, therefore presenting a fourth crystalline modification."

The differences in the stabilities of the three forms *a*, *b*, and *c* must be very slight, for they can exist for weeks at the ordinary temperature side by side in the same mother-liquor. We have only been able to obtain one freezing point for zinc chloride. Even by inoculation with forms (*a*) and (*b*) (see Expts. I, J) above, we were not able to induce crystallisation of molten zinc chloride at any temperature other than that at which it normally occurs (313°). It had seemed possible that the separation of different forms might partly account for the varied values for the freezing point of zinc chloride recorded in the literature.

Not having any of the pseudo-hexagonal plates of zinc chloride available, we tried inoculation with plates of cobalt chloride (Expt. K), but again without result.

It is conceivable that the difference between the freezing points obtained for pure stirred and unstirred zinc chloride is due to the fact that the latter may be an isomeric form possessing a lower freezing point. Experiment L, in which the supercooled melt was inoculated with pure stirred zinc chloride which had frozen at 313°, was accordingly performed, but the freezing point then obtained did not differ appreciably from the previous determinations without inoculation (Experiment E), so we conclude that there is no experimental evidence to justify the assumption that the different values recorded for the freezing point of zinc chloride are due to the existence of polymeric forms freezing at different temperatures.

The Freezing Point of Cobalt Chloride.—The freezing point of iron- and nickel-free cobalt chloride is given as 724° by Ferrari (*loc. cit.*). *Our determinations.*

Material and method used.	Freezing point found.	Co_3O_4 obtained from melt, as percentage of total cobalt chloride.
Ordinary cobalt chloride. The melt was unstirred	734° ± 7°	0·57
Iron- and nickel-free cobalt chloride. The melt was stirred	735 ± 7	0·45

In this case lack of stirring does not seem to cause supercooling. The cobalt chloride was dissolved in water after the experiment and the small amount of oxide formed (as black crystals) during the experiment was filtered off and weighed after ignition. Its amount is too small to affect the results appreciably. The freezing point of pure cobalt chloride may be taken as 735° ± 7°, the possible error of the instruments being 7° at this temperature.

Freezing Points of Mixtures of Cobalt Chloride and Zinc Chloride (Table II).—No stirring unless stated.

An earlier series of measurements (Table III) had been made by means of mercurial thermometers. The cooling curves were not started at a sufficiently high temperature to show the upper break and only show that due to the eutectic solidification. The thermometer readings were corrected as previously described and probably give more trustworthy values for the eutectic temperature than those of Table II.

TABLE II.

	Percentage $CoCl_2$. Calc. from silver chloride.	Calc. from pyrophosphate.	Mean.	Cooling curve shows upper halt at (See Fig. 1.)	lower halt at	No. on Fig. 1.
	7·15	7·19	7·17	300°	300°	XVII
	10·35	10·40	10·37	367	,,	XVIII
	18·10	18·17	18·14	480	,,	XIX
	27·00	26·91	26·95	550	,,	XX
	30·93	30·61	30·77	580	,,	XXI
	38·51	38·45	38·48	605	,,	XXII
	54·22	53·74	53·99	627	,,	XXIII
	69·01	66·42	67·72	650	not followed	XXIV
	73·75	73·08	73·41	682	300°	XXV
	96·59	95·26	95·93	720	,,	XXVI
	97·37	96	96·68	725	,,	XXX
	98·70	97·65	98·18	730	,,	XXXI
M.	Cooling curve of $CoCl_2$ followed down to 280°			735	—	XXXII

The following melts were stirred as long as possible.

				Slope of cooling. Curve changed at		
N.	25·0	Not analysed.	Stirred until solidified.	316	316	XXVII
O.	59·98	59·55	59·75	655	300	XXVIII
P.	83·17	82·40	82·79	700	,,	XXIX

Melts were made up to give about 94% and 30% $CoCl_2$. Portions from the top and the centre of the solid, which had not been stirred during solidification, were analysed.

Q.	93·94	93·26	93·50 (top)
	95·32	94·30	94·81 (centre)
	30·32	30·22	30·27 (top)
	29·64	29·49	29·56 (centre)

TABLE III.

	Percentage $CoCl_2$. Calc. from silver chloride.	Calc. from pyrophosphate.	Mean.	Eutectic point (corr.).
The following were stirred :—				
Zinc chloride (for comparison)				313·1°
2% $CoCl_2$ (not analysed)				312·2
	7·77	7·67	7·72	311·0
	16·56	16·29	16·42	311·4
	19·59	19·30	19·45	312·8
	27·44	26·61	27·03	312·0
	37·86	37·11	37·48	310·7
R.	42·03	40·84	41·44	310·8
The following were unstirred :—				
S. 40% (not analysed)				296·4
	52·35	52·04	52·20	294·7
	65·13	64·71	64·94	293·5
	76·37	76·02	76·20	292·7

Discussion of Results.

The values for the eutectic temperatures shown in Table III for the stirred experiments vary over a range of 2·4°, which is within the limit of experimental error, for several reasons :—

(*a*) The thermometer was only standardised at two temperatures, the higher being more than 100° below the freezing point, so an error might well be introduced which was not eliminated by the correction employed.

(*b*) The halt in the cooling curve due to the eutectic solidification was generally very sharp, but occasionally it was not.

(*c*) The most serious source of error probably arose from the basicity of the melts, some containing more than 1% of zinc hydroxide or oxide. Experiment D showed that the presence of zinc hydroxide in zinc chloride caused a considerable lowering of the freezing point and it is reasonable to suppose that the same effect would be produced on a zinc chloride–cobalt chloride melt, thus making possible an error of several degrees.

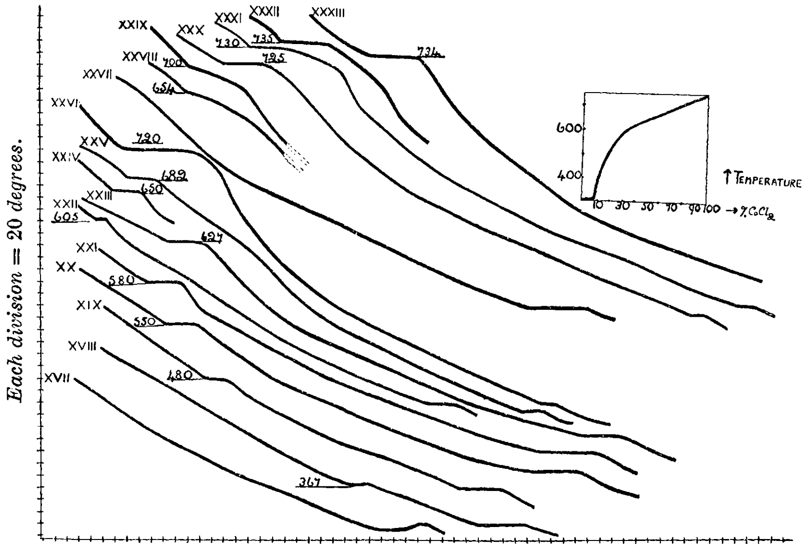
Melts containing more than 45% of cobalt chloride were too viscous to be stirred at temperatures below 450°, consequently the observations given in Table III were made with mercurial thermometers on such melts unstirred. The values for the eutectic point so obtained are 18—21° lower than those obtained for the stirred melts containing less cobalt chloride. Two experiments, R and S, made with mixtures containing about 40% of cobalt chloride, one stirred, the other unstirred, showed that the supercooling due to lack of stirring lowered the apparent value of the eutectic point from 310·8° to 296·4°.

It may be concluded, therefore, that the eutectic point of the system lies at 313—311° and at practically the same temperature as the melting point of pure zinc chloride.

As Table II and Fig. 1 show, the cooling curves of all melts containing more than about 7% of cobalt chloride show two well-defined halts if the observations are started at a sufficiently high temperature. The lower halt is clearly due to eutectic solidification and below it the mixtures are completely solid. When allowance is made for the errors due to supercooling and to the thermocouple equipment the temperature of the lower halt agrees very well with that of the halt found with mercury thermometers. If the temperatures of the upper halt are plotted against percentage composition of the melt (Fig. 1), they lie on a smooth curve which is a straight line from 100% $CoCl_2$ to about 40%; it then bends down sharply towards the composition axis, which it reaches at the point corresponding to 7% $CoCl_2$, where there is only one halt on the cooling curve, showing that this is the eutectic mixture.

The well-defined upper halt is shown to be due to supercooling of the melt, because it disappears when the melt is stirred (Expts. O and P) and is replaced by a marked alteration in the slope of the cooling curve. The supercooling which occurs when the melt is unstirred allows sufficient solid to separate rapidly enough to keep the temperature constant for a short time. When the melt is stirred, however, separation of solid is such a gradual process from the point at which it commences that it can do no more than cause a retardation in the rate of cooling. This retardation is large for melts containing from 100 to 40% $CoCl_2$, since a small temperature change corresponds to a large change in composition of the melt, but in the region 10—30% $CoCl_2$ exactly the opposite holds and with such melts the upper halt becomes quite obliterated by stirring (Expt. N). All the upper halt temperatures obtained without stirring will be slightly too low. The position of the sharp breaks in the cooling curves obtained without stirring is much easier to judge than that of the change of slope in cooling curves obtained with stirring.

Fig. 1.



It is evident from the temperature–composition diagram that two solid phases are concerned. The curve running from 100% to 7% $CoCl_2$ corresponds to the separation of pure cobalt chloride and not of a solid solution of zinc chloride in cobalt chloride. If the latter occurred, the eutectic halts in the cooling curves would not be found with melts very rich in cobalt chloride, whereas even a melt containing only 2% of zinc chloride gave a good eutectic halt.

The absence of any detectable freezing point depression at the zinc chloride end of the diagram makes it practically certain that the solid phase separating from melts containing 0—7% of cobalt chloride is a solid solution of cobalt chloride in zinc chloride. In this connexion it is of interest that in the two systems $CoCl_2$–$MnCl_2$ and $CoCl_2$–$CdCl_2$, both of which give continuous series of solid solutions (Ferrari and Inganni, *Atti R. Accad. Lincei*, 1928, **8**, 238), mixtures containing from 0—20% of cobalt chloride freeze at practically the same temperature. Only after this limit is passed do the freezing-point curves rise steadily to the freezing point of cobalt chloride. The appearance of the solidified melts, so far as we have been able to examine it, was consistent with the above interpretation of the freezing point curves. The cooling curves relating to the experiments in Table II are given in Fig. 1. The scale of all is the same and is indicated at the sides, but in order to separate the curves they are started at different points on the diagram. In each case the temperature at which the upper halt occurred is indicated. Assuming that cooling conditions were always the same, as was approximately the case, the length of the eutectic halt should get progressively smaller as the percentage of cobalt chloride in the melt increases. Inspection of the curves shows, however, that while in a general sense this does happen, the length of the halt is disproportionally long for the melts containing very little zinc chloride. It would seem that either the eutectic halt is too long in the case of melts containing least zinc chloride or else not long enough in the case of those containing most.

It was thought that there might possibly be some polymorphic change in the solid cobalt chloride occurring immediately after the eutectic solidification the heat effect of which served to increase the apparent length of the eutectic halt. To test this possibility a cooling curve of pure cobalt chloride was followed down to 280° (Expt. M, Table II), but no indications of heat evolution could be detected at any temperature other than the usual freezing point.

Another possibility was that segregation occurred during solidification of the unstirred melts. If this took place in such a way as to cause an accumulation of the eutectic mixture round the thermocouple, the effect would be to make the eutectic halt appear longer than it would have done if the mixture just round the thermocouple had the average composition of the whole melt. No such segregation could be detected in melts containing a high percentage of cobalt chloride (Expt. Q, Table II).

With the less viscous melts containing only moderate amounts of cobalt chloride there was the possibility of a type of segregation producing just the opposite effect and shortening the eutectic halt owing to cobalt chloride separating at the higher temperatures settling down in the melt and so removing some of the eutectic from the immediate vicinity of the thermocouple. (Crystals of cobalt chloride do actually sink in molten zinc chloride.) A melt containing 30% $CoCl_2$ did not show segregation of this type, however (Expt. Q, Table II).

The occurrence of slight segregation shows the need for dissolving the whole of the solidified melt prior to analysis in the case of experiments where there had been no stirring.

Although the irregularities in the length of the eutectic halt may be due partly to segregation, it is probable that they are mainly due to small differences in the rate of cooling, as shown by the thermocouple, owing to slight differences in the position of the latter in the melts in different experiments. This is bound to have varied somewhat, though the endeavour was made to have it always in the same position.

The inability of cobalt and zinc chlorides to form a continuous series of mixed crystals is due to the fact that the crystalline forms of the two compounds are different. The fact that cobalt chloride can dissolve to the extent of 7% in solid zinc chloride suggests that a second crystalline form of cobalt chloride probably exists, though it may well be too unstable to be isolated in the pure condition.

We are now in a position to explain the fact that all mixtures of anhydrous cobalt and zinc chlorides are blue. The colour is that of anhydrous cobalt chloride either liquid or solid according to the temperature. The reddening effect of zinc chloride in aqueous solutions is connected with the formation of definite ionic compounds. Under anhydrous conditions no such combination occurs, probably because of the complex, essentially covalent, character of cobalt chloride and of zinc chloride in both the solid and the molten condition (Bassett and Croucher, *loc. cit.*, p. 1812). The molten compounds are, of course, conducting, but there is no evidence to show the precise character of the ionisation involved and even if any red ions are formed their colour is entirely masked by the blue colour of the non-ionic cobalt chloride present in, proportionally, far greater amount.

The inability of cobalt and zinc chlorides to combine in the anhydrous condition in spite of the fact that they form several hydrated compounds is a striking instance of what is very likely of frequent occurrence. It shows how unwise it is to assume, as is sometimes done, that a hydrated double or complex salt remains a double or complex salt after dehydration.

Summary.

The freezing points of cobalt and zinc chlorides have been determined to be 735 ± 7° and 313° respectively. The freezing points of mixtures of the two chlorides have also been measured. The freezing-point curve consists of two branches, one corresponding to the separation of cobalt chloride and the other to a series of solid solutions of cobalt chloride in zinc chloride, containing up to a maximum of 7% of cobalt chloride.

The influence of stirring of the melts on the character of the cooling curves has been examined.

An explanation is given of the fact that all melts and solids in the anhydrous system $CoCl_2$–$ZnCl_2$ are blue.

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