

STUDIES ON THE SYSTEM LEAD CHLORIDE-ZINC CHLORIDE

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LEAD CHLORIDE-ZINC CHLORIDE

By

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I. INTRODUCTION

The purpose of this investigation was to study the system lead chloride-zinc chloride from the point of view of the thermo-dynamics of solutions. A previous investigation of activity co-efficients in this system, made by Wachter and Hildebrand (1) in 1930, using the electromotive force method of determining the activities of the lead chloride in the solutions, showed activity coefficients less than unity, indicating negative deviations from Raoult's law. Since available data on the freezing points of such solutions (2) were not in agreement with these results, it was felt desirable to repeat the work on freezing points. The results reported in this paper in general confirm the earlier data of Herrmann (2) on the freezing points of solutions of zinc chloride in lead chloride.

The problem of determining the activities (and activity coefficients) of the components of solutions reduces essentially to the determination of the partial molal free energies of these solutions. This may be done in a number of ways, the most usual being from measurements of the freezing points of the solutions, measurements of their vapor pressures, or of the electromotive force of appropriate cells. The theory of the determination of activities from freezing point data is discussed and an equation for utilizing these data is developed in the following section. The experimental method is then discussed in some detail and the results obtained in this investigation are reported and used to calculate the activities and activity coefficients for

various solutions of zinc chloride in lead chloride. Finally, a possible explanation of the discrepancies between the results of freezing point and electromotive force measurements is presented.

II. The Determination of Activities from Freezing Point Data

The activity of a component of a solution is defined as a function of the free energy change resulting on transferring one mole of the substance from a reservoir of the pure substance to the solution. The state of the pure material in the reservoir is taken as a standard or reference state in which the activity of the substance is defined as unity. As is shown schematically in figure 1, the free energy of transfer of the solvent from the standard state to the solution may be divided into four parts. In the first of these, the solvent is transferred from the reference temperature T to some other temperature T_f at which the solution is in equilibrium with the pure solid solvent. This temperature is defined as the freezing point of the solution. Second, the pure liquid solvent is allowed to solidify. In the third step, the solid solvent is transferred into the solution at the temperature T_f . The fourth step is the bringing of the solution from the temperature T_f to the temperature T at which it is desired to know the activity of the solvent.

Since the solution is in equilibrium with pure solid solvent at the temperature T_f , the free energy change for the third step is zero. Thus, the desired free energy change, ΔF , is equal to the sum of the three terms ΔF_1 , ΔF_2 , and ΔF_3 . It is easily seen that ΔF_2 is simply the free energy of solidification of the solvent at the temperature T_f . This term may be readily evaluated from the heat of fusion of the

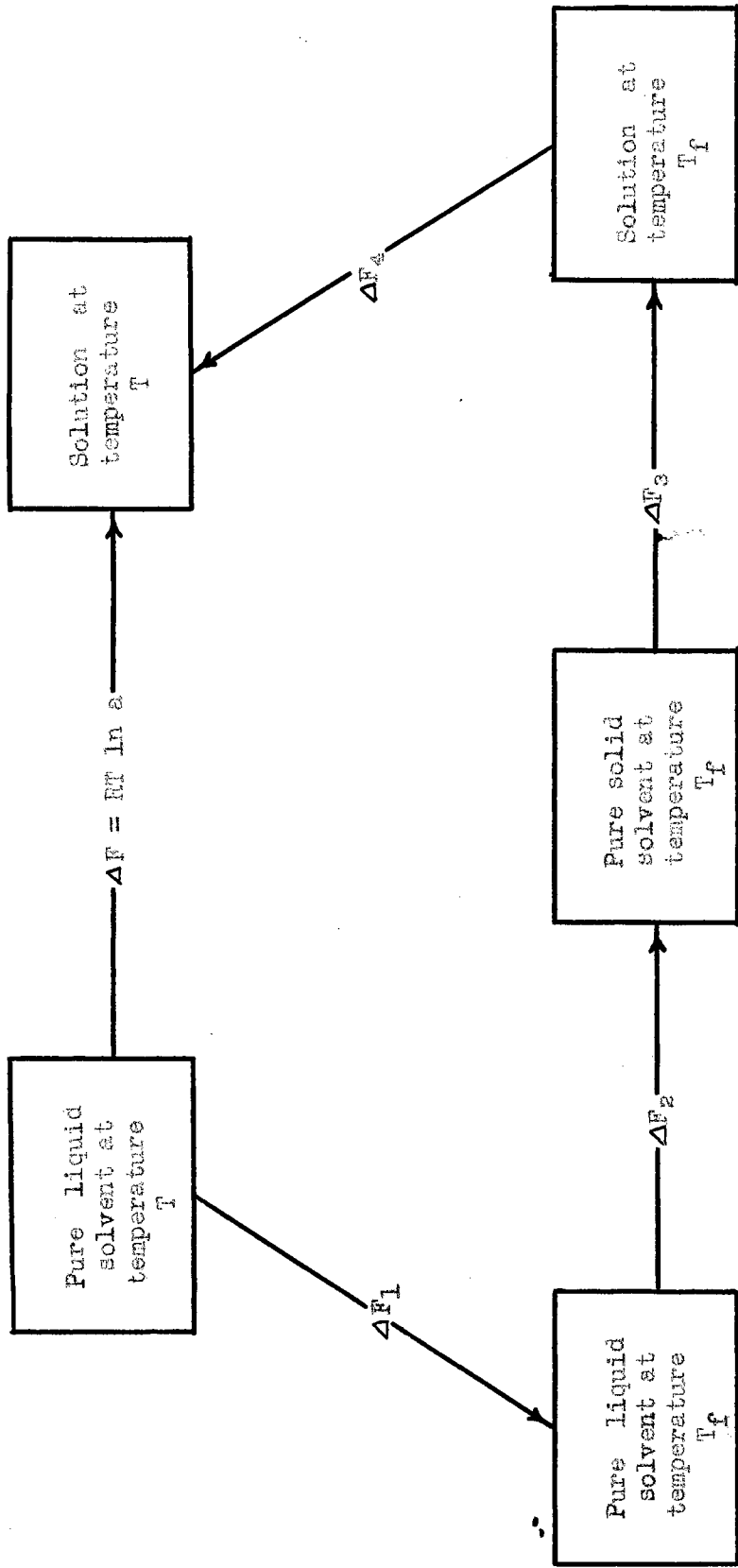


FIGURE 1

Schematic representation of free energy changes in formation of solution from pure liquid solvent

TABLE 1

THERMODYNAMIC PROPERTIES OF LEAD, CHLORINE, AND LEAD CHLORIDE

a. Melting Points and Heats of Fusion

	<u>Melting Point</u>	<u>Heat of Fusion</u>	<u>Ref.</u>
Lead	600.5°K.	1224 cal. mole ⁻¹	3
Lead Chloride	771	5650	3

b. Specific Heat Equations

$$C_p = a + b T \quad \text{cal. mole}^{-1} \text{ deg.}^{-1}$$

	<u>a</u>	<u>b x 10³</u>	<u>Error, %</u>	<u>Range, °K.</u>	<u>Ref.</u>
Lead(solid)	5.77	2.02	2	273-600.5	3
(liquid)	6.8	--	5	600.5-1,273	3
Chlorine(gas)	8.28	0.56	1.5	273-2,000	3
Lead Chlorine					
(solid)	15.88	8.35	2	273-771	3
(liquid)	27.2	--	10	771-851	3

c. Entropies

	<u>S_{298.2°K.}</u>		<u>Ref.</u>
Lead(solid)	15.49 ± 0.05	cal.mole ⁻¹ deg. ⁻¹	13
Chlorine(gas)	53.31 ± 0.01		13
Lead Chloride			
(solid)	32.6 ± 0.6		13

d. Heat of Formation

	<u>ΔH_{298.2°K.}</u>	<u>Ref.</u>
Lead Chloride(solid)	- 85,710 cal. mole ⁻¹	14

solvent and the heat capacities of the liquid and solid solvent.

While ΔF_1 and ΔF_4 may be theoretically calculated, the numerical values are not so readily computed due to a lack of suitable data. The sum of ΔF_1 and ΔF_4 may be related to the relative partial molal heat content of the solvent in the solution, which is the difference between the molal heat content of the solvent in the standard state and the partial molal heat content of the solvent in the solution.

In dilute solutions, this quantity is very small, making the sum of the first and fourth free energy changes approximately zero. In more concentrated solutions, however, this is not the case, and the sum of these terms must be evaluated. The relative partial molal heat content of the solvent in the solution as a function of temperature may be determined from electromotive force measurements. The necessary data for the system lead chloride-zinc chloride may be computed from the data of Wachter and Hildebrand (1) but is not believed to be sufficiently accurate for the purposes of this investigation. Nevertheless, an approximate calculation based on their data was made which revealed that the sum of ΔF_1 and ΔF_4 would increase the values of the activities reported in this paper by approximately 0.4%.

If the pure liquid solvent at the freezing point of the solution is taken as the standard state, the free energy of transfer of one mole of solvent from the standard state to the solution at the same temperature reduces to the free energy of solidification of the solvent at this temperature. This quantity may be related to the heat of fusion of the solvent by means of the Gibbs-Helmholtz equation.

$$\left(\frac{\partial(\Delta F/T)}{\partial T}\right)_p = -\Delta H/T^2 \quad (1)$$

where ΔH is the heat of solidification of the solvent. Since

$$\Delta F = RT \ln a$$

then

$$\left(\frac{\partial(\Delta F/T)}{\partial T}\right)_p = R \left(\frac{\partial \ln a}{\partial T}\right)_p \quad (2)$$

where R is the universal gas constant and a is the activity of the solvent in the solution. Substitution of equation (2) into equation (1) and replacement of the heat of solidification by the heat of fusion yield

$$\left(\frac{\partial \ln a}{\partial T}\right)_p = \Delta H_f / RT^2 \quad (3)$$

where ΔH_f is the heat of fusion of the solvent at the temperature T .

It is now only necessary to integrate equation (3) to arrive at an expression for the activity of the solvent in a solution at the freezing point of the solution, referred to the pure liquid solvent at the same temperature as the standard state. Since the heat of fusion of a substance is generally a function of temperature, it is first necessary to introduce an expression for the variation of the heat of fusion with temperature into equation (3). The familiar relation

$$\left(\frac{\partial \Delta H}{\partial T}\right)_p = \Delta C_p \quad (4)$$

may be integrated to give the desired function, provided ΔC_p is known as a function of temperature. It is necessary to resort to an empirical relationship at this point, no general one being available. K.K. Kelley (3a) in reporting the heat capacities of many inorganic substances uses equations of the types:

$$\text{Solid: } C_p = a + bT$$

$$\text{Liquid: } C_p = a'$$

where a , b , and a' are empirical constants. From these equations the expression for the difference between the heat capacities of the solid and liquid solvent is given by an equation of the form

$$\Delta C_p = \alpha + \beta T \quad (5)$$

Substitution of this relationship into equation (4) and subsequent integration between the proper limits gives

$$\Delta H_f = \Delta H_f^0 + \alpha(T - T_0) + \frac{1}{2}\beta(T^2 - T_0^2) \quad (6)$$

where ΔH_f^0 is the heat of fusion at the melting point T_0 . Substitution of equation (6) into equation (3), followed by integration between the proper limits, yields

$$R \ln a = \Delta H_f^0(1/T_0 - 1/T) - \alpha(1 + \ln T_0/T - T_0/T) - \beta(T_0 - \frac{1}{2}T - \frac{1}{2}T_0^2/T) \quad (7)$$

This equation may be readily used to evaluate the activity of the solvent in a solution from measurements of the freezing point of the solution.

The most convenient way in which to use equation (7) is in the form of a graph, from which activities corresponding to any temperature may be read. The graph resulting when the values of the constants for lead chloride are substituted into equation (7) is given in figure 2. The data of Kelley (3), used in evaluating this equation, are given in table 1 and the calculated points used in plotting figure 2 are given in table 2. It should be noted that for consistency the value 498.3°C. is used for the melting point of lead chloride, rather than the value given by Kelley. The deviations given for the activities in table 2 are estimated from Kelley's statements on the accuracy of his specific heat equations and his value of the heat of fusion.

FIGURE 2
Activity of $PbCl_2$ from
freezing point measurements

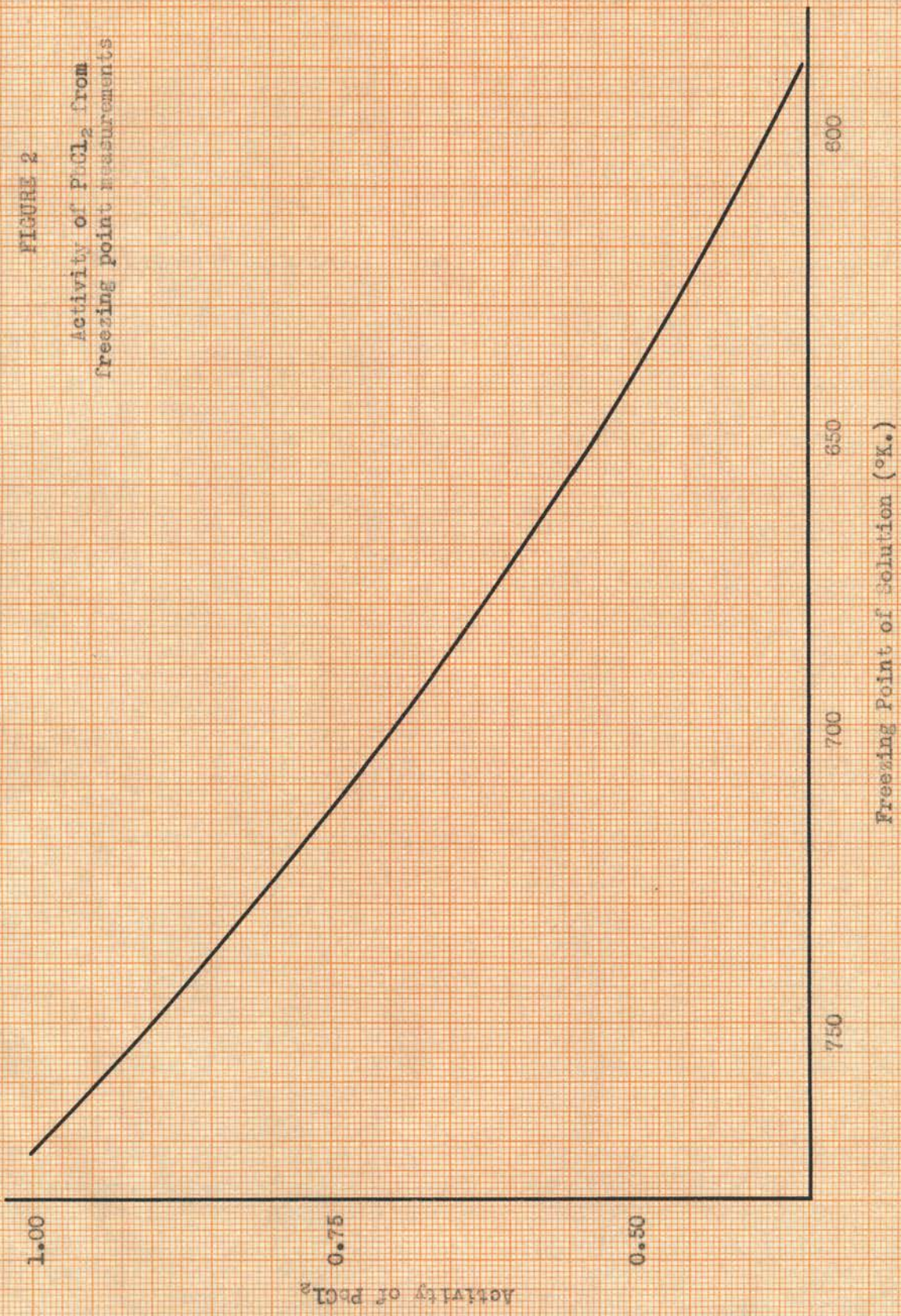


TABLE 2

ACTIVITY OF SOLID LEAD CHLORIDE

(Referred to liquid lead chloride as standard state)

<u>T°K.</u>	<u>Activity</u>	<u>Deviation</u>
771.5	1.000	---
770	0.993	---
750	0.901	0.005
730	0.814	0.008
710	0.733	0.010
690	0.658	0.012
670	0.588	0.014
650	0.522	0.016
630	0.469	0.016
610	0.409	0.016
590	0.358	0.016

Since it is not possible to determine the activity or activity coefficient of the solute directly from the measurements of the freezing points of the solutions, it is necessary to develop another approach to the determination of these quantities. The usual method is to use the Gibbs-Duhem equation, but this is not possible with the data found in this investigation since it is necessary to know the activities of the solvent as a function of concentration at a constant temperature. As was remarked earlier in this section, the freezing point method gives the activities of the solvent at varying temperatures, making it necessary to know the relative partial molal heat content of the solvent in the solution in order to convert these values to some common temperature. It is therefore necessary to use another approach to this problem.

In 1895 M. Margules proposed an empirical equation to express the variation of vapor pressure of any liquid mixture with composition. Glasstone (4) applies this equation, in a somewhat modified form, to the calculation of the activity coefficients of one component of a

binary solution, provided the activity coefficients of the other component are known. This equation may be expressed as

$$a_1 = N_1 \exp (1/2\beta_1 N_2^2 + 1/3\gamma_1 N_2^3 + \dots) \quad (8)$$

where a is the activity, N the mole fraction, β and γ empirical constants, and the subscripts refer to the components. Neglecting all terms in the exponential but the first, and taking natural logarithms, yields

$$\ln a_1 = \ln N_1 + \frac{1}{2}\beta_1 N_2^2 \quad (9)$$

Differentiating equation (9) with respect to $\ln N_1$,

$$\left(\frac{\partial \ln a_1}{\partial \ln N_1}\right)_{p,T} = 1 - \beta_1 N_1 N_2 \quad (10)$$

Equations analogous to (8), (9), and (10) may be written for the other component as well. Since, according to the Gibbs-Duhem equation

$$\left(\frac{\partial \ln a_1}{\partial \ln N_1}\right) = \left(\frac{\partial \ln a_2}{\partial \ln N_2}\right)$$

it follows that

$$\beta_1 = \beta_2 \quad (11)$$

Since

$$\gamma = a/N$$

where γ is the activity coefficient, it follows from equations (9) and (11) that

$$\ln \gamma_1 = \frac{1}{2}\beta_1 N_2^2 \quad (12)$$

From this expression it is possible to calculate the activity coefficients of the solute when those for the solvent are known. Since this approach is empirical, it is well to note that the use of it is restricted to systems in which the deviations from Raoult's law are not great. As will be shown, this condition is fulfilled in the system lead chloride-zinc chloride. It is probable that the results obtained by use of the Margules equation are sufficiently accurate for this work.

III. Experimental Techniques

It is now necessary to discuss the experimental techniques used in determining the freezing points of solutions. Essentially, the method employed in this investigation was to heat the materials in a furnace to a point well above the freezing temperature and then to allow the solution to cool slowly, making readings of the temperature at frequent intervals. From a plot of this data, it was possible to determine the temperature at which solvent first began to crystallize from the solution. At this point there is a momentary "halt" in the cooling curve, resulting from the release of the heat of fusion of the material crystallizing. In pure substances, this halt is quite long and easy to detect, but in mixtures it is often little more than a change in slope. The problem which must be solved is one of making this halt as long or as obvious as possible.

All writers on freezing point determinations advise that small samples be used. White (5) suggests the use of quantities of the order of one milliliter. If this technique is not used, it is necessary to stir the solution very efficiently. Both methods were used during the course of this investigation. With pure materials either method gives good results. In some of the early work of this research, large stirred samples were used. This was successful with pure metals, such as tin and zinc, and with pure lead chloride. However, all attempts to obtain unambiguous results using large stirred samples of the solutions were failures. The use of small samples, the smaller the better, seems to be imperative in order to get satisfactory results.

It was also found that the nearer a solution was in composition to one of the pure components, the easier it was to determine its

freezing point. Pure lead chloride and the solutions which were dilute in zinc chloride gave fairly good freezing points. Super-cooling was evident and good halts were observed. However, in solutions containing about fifty mole per cent zinc chloride, the only obvious break in the cooling curves was that corresponding to the end of crystallization. This is not the freezing point of the solution, but the eutectic temperature. Pure zinc chloride, like the other pure substances used gave very good cooling curves. A great many attempts were made to determine the freezing points of solutions in the range of composition intermediate between 75 mole per cent lead chloride and pure zinc chloride without particularly successful results. It seems probable that control of the furnace temperature to a greater degree and perhaps more sensitive methods of measuring temperature might have made it possible to determine unambiguous melting points for these solutions.

IV. Instrumentation

A. Furnace. Two different furnaces were used in the course of this investigation. The first one was used during the part of the work in which large samples were used. However, when it became apparent that it would be necessary to use very small samples of the solutions for the determination of the freezing points, a new furnace was designed and built for this work by the instrument shop of the Engineering Experiment Station of Oklahoma Agricultural and Mechanical College. Since this furnace was the one used for most of the research, it will be described in some detail.

The furnace consisted of a rather massive copper block, bored in such a way that a small test tube, supported in a copper collar, could be suspended in it. The block was heated by a helical nichrome heating

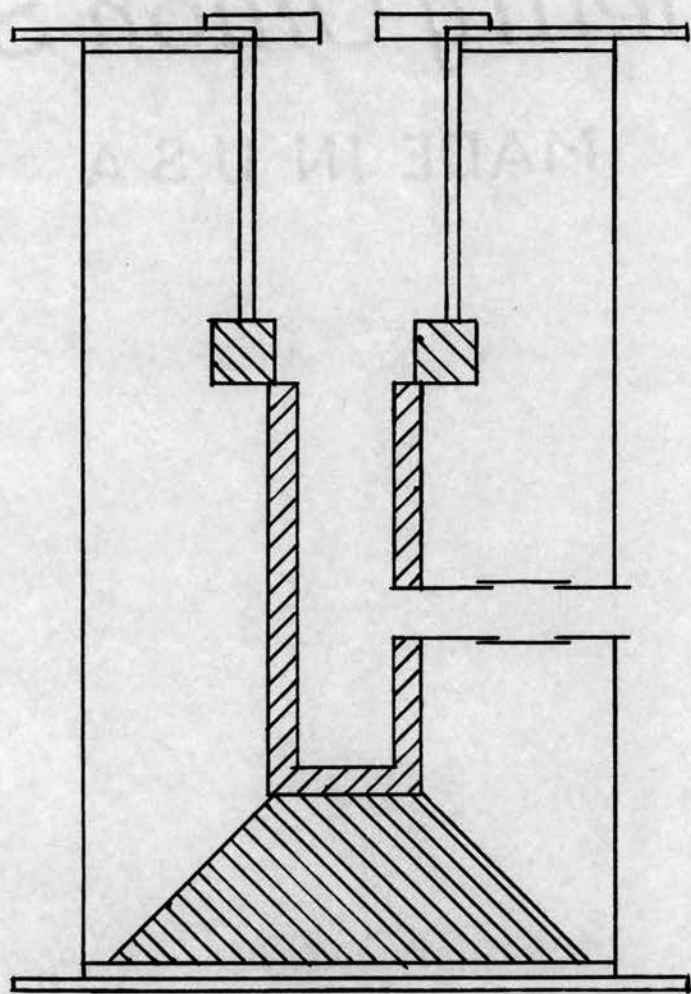


FIGURE 3

Cross-sectional sketch of furnace

One-half scale



Fire clay



Copper block

element. An additional hole was made in the side of the block for the purpose of observing the solutions while still liquid, but it was not possible to make use of this feature. The entire furnace was contained in a metal can, insulated with asbestos, and closed at the ends with "Transite" asbestos board. A cross-section of the furnace is shown in figure 3. The current used to heat the block was controlled by means of a "Variac" variable voltage transformer and measured by a sensitive alternating current ammeter. Ordinary 110 volt alternating current was used. Currents were of the order of one or two amperes. The copper block was fairly large in order to minimize local variations in the furnace temperature and to make possible the very slow cooling of the furnace.

B. Measurement of Temperature. The temperatures of the solutions were measured using a thermocouple which had its cold junction immersed in a dewar flask containing a mixture of ice and water. In the first work done, a single junction chromel-alumel thermocouple was employed, but in the interests of greater sensitivity, it was felt desirable to use a double-junction thermel of the same materials. This couple did not prove overly satisfactory, however, even when the hot junction was immersed directly in the melts, since there was some evidence that the solutions attacked the couple and there was definite evidence that the couple was quite slow in coming to thermal equilibrium with the solutions. For these reasons, a platinum-platinum, 13% rhodium thermocouple was substituted. This couple, calibrated at the melting points of zinc and of sodium chloride by Mr. Robert S. Munger in connection with work on a fellowship with the Ozark-Mahoning Company, was found to read 55 microvolts low at these temperatures. Consequently this amount was

added to each freezing point determination made with this couple.

The electrical potential existing between the junctions of the thermocouple was measured by means of a Leeds and Northrup Type K-1 potentiometer, coupled with a sensitive, wall-mounted galvanometer of the D'Arsonval type. This instrument could be read to one microvolt (0.000001 volt). In the preliminary work, a Queens potentiometer of the student type, sensitive to 10 microvolts was used, but this did not seem satisfactory, even for the relatively large potentials of the double junction chromel-alumel thermel. It would, of course, have been impossible to use this instrument with the small potentials of the noble metal couple. Some attempts were made to record the cooling curves directly, using a Brown Recording Potentiometer, but the small sensitivity of this instrument, at least in the temperature range covered in this investigation, made it useful only in preliminary work designed to determine the order of magnitude of the "halt" in the cooling curves. Furthermore, the Brown potentiometer did not satisfactorily reproduce the values of the potential of the couple. This fact was determined by direct comparison with the type K-1 instrument.

Some difficulty was encountered on account of fluctuations in the galvanometer reading due to vibrations in the building, a temporary frame structure. These were caused by a multitude of factors, the chief among them being the movement of people in the building and the sudden slamming of doors. It was also noted on occasion, especially when using the noble metal thermocouple, that strong winds oscillated the building sufficiently to cause the galvanometer to move rather erratically. In one case work had to be abandoned on this account.

C. Measurement of Time. Time was measured in the earlier parts

of this investigation using a stopwatch which could be read in motion to about 0.05 minutes. Closer reading was not deemed important.

Later acquisition of a good electric wall clock with a sweep second-hand made the reading of time somewhat easier, as the larger size and conspicuous markings of the wall clock more than compensated for its somewhat lower sensitivity. It was also read to about 0.05 minutes.

9. Stirring. As was mentioned above, the large samples which were used in the earlier work in this investigation were stirred. A stirrer was designed and built like that reported by Campbell and Prodan (6), but was not particularly successful due to its tendency to splash mercury all over the room. A somewhat similar stirrer was constructed which operated on the same principle, but avoiding the use of mercury. The melt was agitated by a rapidly moving column of air, oscillated by means of a piston driven by an electric motor. The piston was contained in a small brass cylinder. A sidearm was provided with a pinch clamp so that the amount of stirring could be regulated. This method of stirring seemed to be quite efficient, but did not improve results sufficiently for use in this particular work.

V. Preparation of Materials

A. Lead Chloride. The lead chloride used in this investigation was Merck chemically pure $PbCl_2$. According to the label, this material contained a maximum of 0.056% impurities. On drying in an oven at $170^\circ C$. for 4.75 hours this material lost 0.0068% of its weight. The material dried in this manner was used directly, with no further purification or other treatment. The purity of the material is shown by its melting point, determined in this work to be $498.3 \pm 0.3^\circ C.$, whereas the value given by Kelley (3) is $771^\circ K$. ($498^\circ C.$).

B. Zinc Chloride. The problem of preparing pure, anhydrous zinc chloride is far more difficult than the preparation of lead chloride, due to the extreme hygroscopicity of the material. Mellor (7) states that zinc chloride is more hygroscopic than phosphorus pentoxide. To examine this point, a sample of Merck chemically pure ZnCl_2 was dried for 18 hours at 240°C ., losing 4.64% of its weight. This dried material was then allowed to stand undisturbed in a crucible in the open laboratory for eight days, in which time it absorbed enough water to completely dissolve. The sample gained over 20% of its dry weight, clearly showing its great affinity for water. Five methods were tried before a satisfactory one for the preparation of zinc chloride was found. These were: 1) Simple drying of C.P. ZnCl_2 ; 2) Synthesis from zinc and hydrogen chloride in ether solution; 3) Distillation of U.S.P. zinc chloride under reduced pressure; 4) Drying of C.P. zinc chloride by passing dry hydrogen chloride gas through the molten salt; and 5) Distillation of a carefully dried sample of C.P. zinc chloride under high vacuum. These methods will not be discussed in detail.

1. Simple drying of C.P. ZnCl_2 . According to the label on a bottle of Merck chemically pure zinc chloride, the material contained not less than 95% ZnCl_2 and not more than 0.230% impurities. The remaining 4.77% was probably water. Fusion of a sample of this material in a crucible, followed by drying in an oven for 18 hours at 240°C ., resulted in loss of 4.64% of the weight of the sample. An attempt was made to dry another sample in an oven at 240°C ., without prior fusion, but after 118 hours the material showed definite discoloration, indicating partial decomposition. In this time the zinc chloride lost 4.88% of its original weight. Another attempt was made to dry a sample

at a temperature slightly above its melting point, using a muffle furnace, but this failed because the furnace got out of hand during the night and the temperature rose to about 500°. The material was found to be evaporated from the crucibles and condensed on the walls of the furnace. This deposit had a bright yellow-green color, indicating extensive decomposition to the oxide or oxychloride. Due to this ready reaction of zinc chloride with the water contained in the commercial materials, it was decided that this method of preparation was not feasible.

2. Synthesis of zinc chloride from zinc and HCl in ether solution. An attempt was made next to prepare pure zinc chloride by the method of Hamilton and Butler (8). In this experiment, 93.5 grams of finely divided zinc metal were placed in a 500 ml. roundbottomed flask, fitted with a standard taper joint, and about 300 ml. of anhydrous diethyl ether (dried over sodium) were distilled in. The flask was then connected to a tank of hydrogen chloride gas through a drying tower containing anhydrous magnesium perchlorate. The gas was bubbled through the mixture until all of the zinc chloride had reacted. The reaction proceeded as described by Hamilton and Butler, the zinc reacting readily with the ethereal solution of HCl, with the release of hydrogen. After some time the reaction mixture separated into two layers, the lower an extremely viscous solution, presumably of ether in zinc chloride, the upper a very mobile solution of zinc chloride in ether. After all of the zinc had dissolved, the excess ether and HCl were removed by distillation under reduced pressure. The product was brown in color and did not appear to be very satisfactory for this work. However, the method seems to have possibilities, particularly if

small samples are desired.

3. Distillation of U.S.P. zinc chloride under reduced pressure.

The next method which was tried for the preparation of anhydrous zinc chloride was the distillation of fused ZnCl₂, U.S.P. The zinc chloride sticks were placed in one end of a glass tube, bent at an angle of about 120°. The material was distilled under reduced pressure until most of it had passed over to the other end of the tube. The method was not overly successful, probably due to using samples which were far too large. Extensive bumping occurred, undoubtedly resulting in contamination of the distillate. A mixture of this material with lead chloride, containing 85 mole per cent lead chloride, had a freezing point of 465.8°C., about ten degrees too low.

4. Drying C.P. ZnCl₂ by passing dry HCl gas through the molten salt.

An attempt was made to apply the method used by Wachter and Hildebrand (1) in preparing the zinc chloride used in their research. Dry hydrogen chloride gas was bubbled slowly through fused zinc chloride in an all-glass apparatus. The flask, containing the commercial C.P. zinc chloride, was heated in a sand bath, and the HCl, dried by magnesium perchlorate, was passed through it very slowly until no more water passed over. The product was gray in color, but was believed to be satisfactory for this research. A sample of this material was analyzed for zinc by titration with standard potassium ferrocyanide solution, using as indicator two drops of a 1% solution of diphenylamine in concentrated sulfuric acid and four drops of a 1% solution of potassium ferrocyanide (9). The material was also analyzed for chloride, using the method of Fajans (9), titrating with standard silver nitrate, with metanil yellow as indicator. This indicator was used instead of

the more usual dichlorofluorescein because of the low pH of the solutions used. The sample was found to contain $46.35 \pm 0.02\%$ zinc and $50.47 \pm 0.17\%$ chloride. This indicates that the material prepared by dehydration with hydrogen chloride gas contained 96.82% zinc chloride.

5. Distillation of a carefully dried sample of C.P. zinc chloride under high vacuum. The material finally used in this investigation was prepared by distilling chemically pure zinc chloride under reduced pressure. The material, contained in an all-glass apparatus was carefully dried by gently heating, then fusing in a vacuum in order to dry the material as completely as possible without too extensive decomposition. The vapors were drawn over phosphorus pentoxide before leaving the apparatus. After this drying, the material was distilled into a sidearm under a high vacuum. The sidearm, still under vacuum, was drawn off, to prevent the anhydrous zinc chloride from contamination with moisture. The material resulting from this treatment was white, with a very pale green tinge. Its melting point was found to be $303.7 \pm 0.5^\circ\text{C}$., as compared to 556°K . (283°C .) given by Kelley (3). This value is higher than any value which has been found in the literature. Hachmeister (10) records melting points found by a number of observers over a period of almost fifty years ranging from 250° to 340° . Only two investigators report values above 283°C . and their results are far from satisfactory. It is interesting to note, however, that the second edition of Lange's "Handbook" gives the value 365° for the melting point of zinc chloride. In the absence of any data on the system $\text{ZnCl}_2\text{-ZnO}$, however, no definite interpretation can be placed on our high value.

This zinc chloride was analyzed for zinc by converting a weighed sample to zinc sulfate by fuming down with sulfuric acid. The anhydrous

zinc sulfate was weighed. Chloride was determined gravimetrically in the usual way as silver chloride. The sample was found to contain $47.64 \pm 0.10\%$ zinc and $51.70 \pm 0.01\%$ chloride, as compared to the theoretical values of 47.97% Zn and 52.03% Cl. The ratio of chlorine to zinc in this material is, therefore, 1.0852, compared to 1.0846 for the formula $ZnCl_2$. The material is believed to be at least 99.4% zinc chloride, with the principal impurity being water.

VI. Experimental Determination of Freezing Points

The lead and zinc chlorides described in the preceding section were used to make up the solutions whose melting points were determined in this research. The chlorides were weighed into small pyrex test tubes which were then supported in the furnace as described in section IV.A. The furnace was then heated sufficiently to melt the sample and held above the melting point long enough to allow the materials to mix completely. Then the melts were cooled slowly, data being taken in order to plot a time versus temperature curve, until a break in the cooling curve was passed, or, in less successful runs, until the material was found to be solidified. To illustrate the type of data gathered in this investigation, typical results are given for one of the better runs encountered. Data are also given for one of the poorer runs to illustrate the difficulty often encountered in interpreting the results obtained. The "good" run is given in table 3a and the "poor" run in table 3b; these data are plotted in figures 4a and 4b respectively. The run given in table 3a was made using the second furnace and the platinum-platinum, 13% rhodium thermocouple, while that in table 3b used the first furnace and the chromel-alumel thermel. The data finally gathered in this investigation are based on cooling curves of

TABLE 3

TYPICAL DATA ON THE COOLING OF A SOLUTION OF ZINC
CHLORIDE IN LEAD CHLORIDE

a. A "Good" Run

b. A "Poor" Run

	<u>PbCl₂</u>	<u>ZnCl₂</u>		<u>PbCl₂</u>	<u>ZnCl₂</u>
Weight(gms.)	2.2914	0.1842	Weight(gms.)	118.31	10.203
Moles	0.00823	0.00135	Moles	0.4254	0.0749
Mole fraction	0.859	0.141	Mole fraction	0.850	0.150

<u>Time</u>	<u>E.M.F.</u>	<u>Time</u>	<u>E.M.F.</u>
10:13 a.m.	4.429 mv.	5 min.	39.006 mv.
14	4.400	6	38.745
15	4.371	7	38.495
16	4.344	7.5	38.395
17	4.315	8	38.301
18	4.286	8.6	38.236
19	4.261	9	38.199
20	4.236	9.5	38.151
21.15	4.208	10	38.105
22	4.189	10.5	38.050
22.5	4.176	11.15	37.986
23	4.165	11.67	37.905
23.5	4.156	12	37.863
24	4.141	12.5	37.805
24.5	4.134	13	37.739
25.5	4.122	13.5	37.654
25.55	4.111		
26.1	4.102		
26.6	4.131		
27.1	4.117		
27.6	4.104		
28.1	4.091		

Freezing pointE.m.f. = 38.330 mv.
Temp. = 465.5°C.Freezing pointE.m.f. = 4.131 mv.
Temp. = 474.9°C.

the type in figure 4a. It is obvious that "breaks" such as that in the second run are far too difficult to detect to make one at all sure of their precise location. This difficulty was encountered throughout the research. Almost all of the results using the chromel-alumel couple were unusable on this account. It seems probable that this

FIGURE 4a

A "good" cooling curve
(See Table 3a for data)

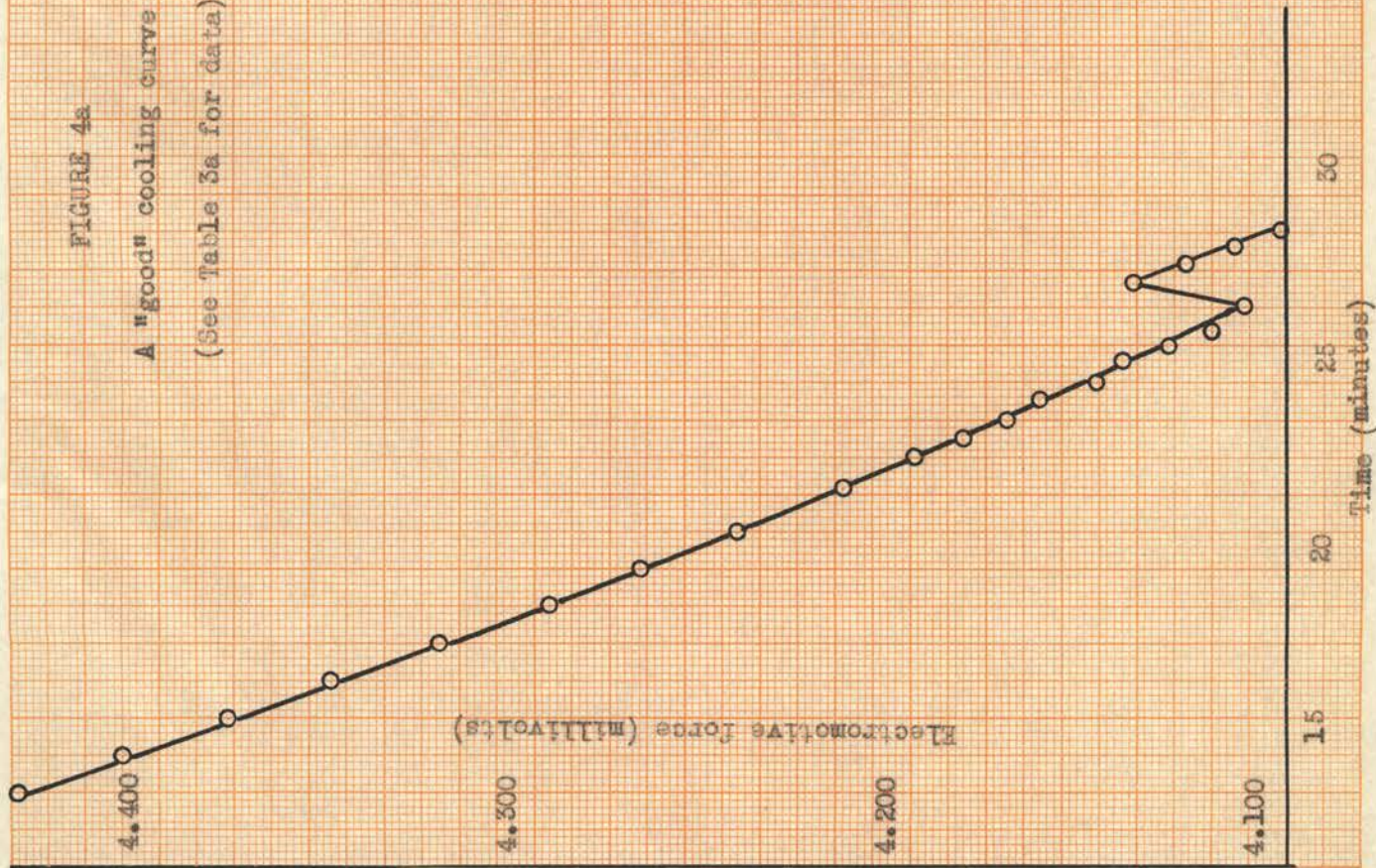
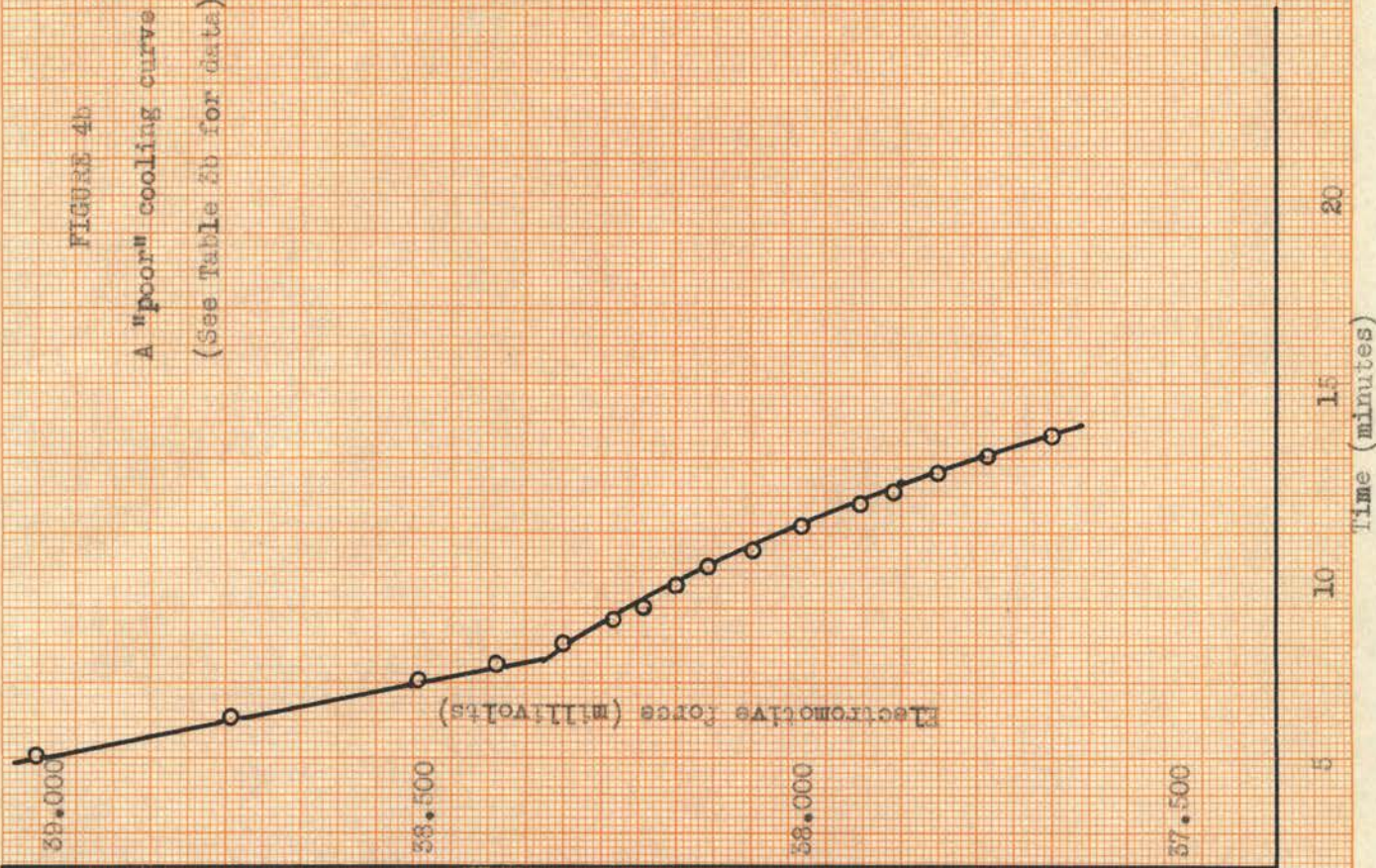


FIGURE 4b

A "poor" cooling curve
(See Table 3b for data)



rests in part on the observed slowness of this thermel in reaching thermel equilibrium with the melt.

Except for two points, all data reported in this investigation were gathered using the noble metal thermel. These two points (marked by an asterisk in table 4) were made usable by direct comparison of the chromel-alumel couple with the platinum-platinum, 13% rhodium couple. The discrepancy determined in this manner was applied to the readings of the base metal couple as a correction factor. The data, with their observed deviations computed from the values of several runs on each sample, are given in the first two columns of table 4. These data and those of Herrmann (2) are plotted in figure 5.

VII. Miscellaneous Observations

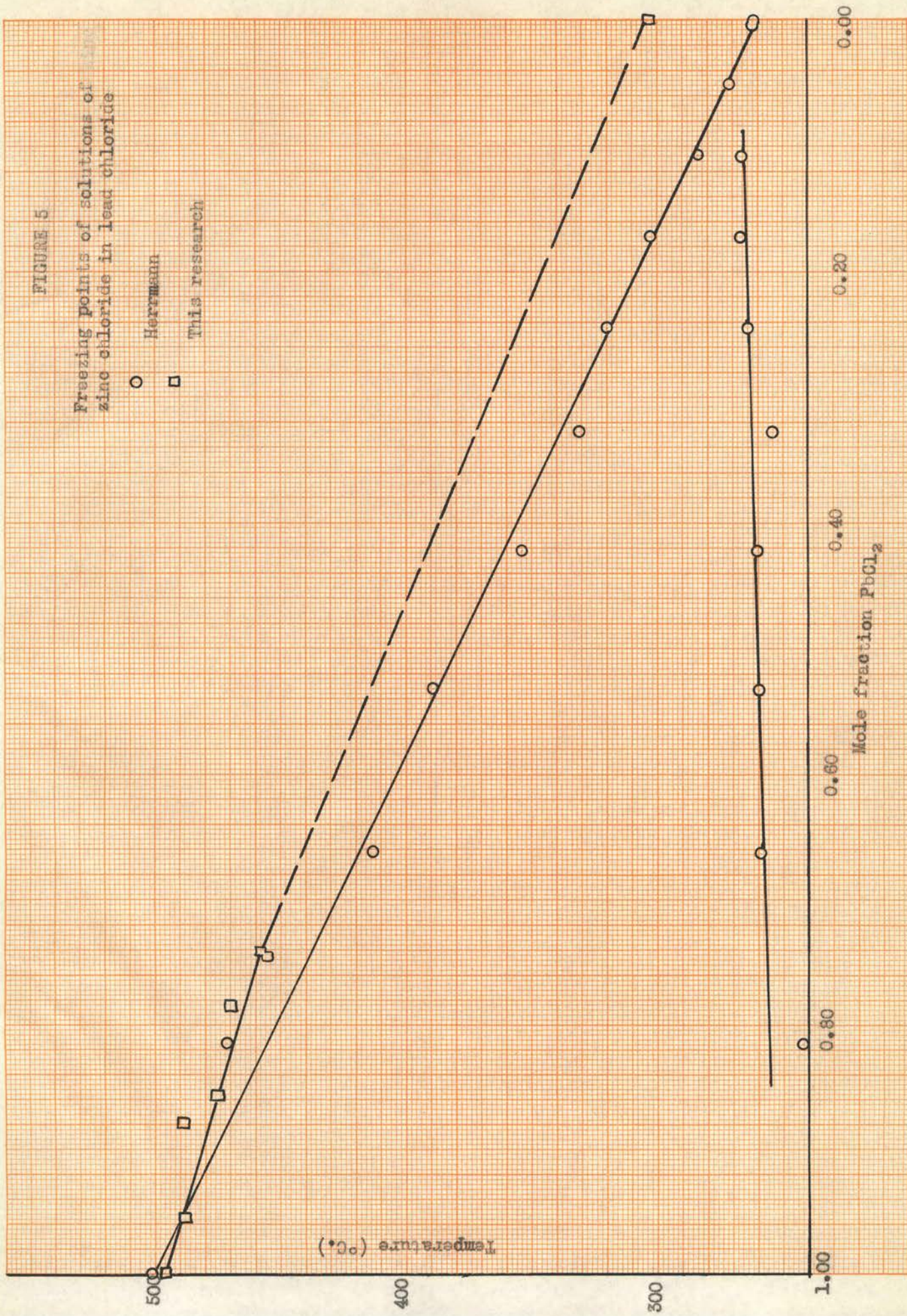
Several observations were made during the course of this investigation which might well be the bases of further research. These include observations on the colors of the melts, their reaction with moisture and air, the viscosity of zinc chloride, and the eutectic temperature of the system lead chloride-zinc chloride.

Several times during the course of this research, observations were made on the color of the melts and of the solutions after they had solidified. As was remarked in an earlier paragraph, zinc chloride reacts quite readily with moist air to form the oxychloride. It was noted that the pure zinc chloride, which was quite white before determination of the melting point, became gray in color after four fusions. In none of these did the temperature exceed about 350°C. The lead chloride also reacted readily with moist air, forming an oxychloride. It was noticed early in the course of this research that after a short time the lead chloride melts became colored a pale orange-yellow.

FIGURE 5

Freezing points of solutions of
zinc chloride in lead chloride

○ Herrmann
□ This research



This color intensified after the sample had been fused for a considerable time. However, the solid material remained fairly white until a great deal of opportunity was given for reaction. It seems probable that this coloration was due to small amounts of a lead oxychloride (probably PbO.PbCl_2). In one instance, a moist thermocouple was accidentally inserted into the molten material. A noticeable hissing resulted, followed by a strong odor of hydrogen chloride. This behavior is consistent with the observations of Eastman and Duschak (11), who noted that lead chloride reacts readily with moist air to give hydrogen chloride at low temperatures and chlorine above 550°C . Many of the small samples of lead chloride used in the latter part of the investigation were very dark brown in color after one or two fusions, but others were only a pale orange. The solutions varied in color from white to gray after fusion, although there was no really consistent behavior in this respect.

Another feature which was noticed several times was the high viscosity of the fused zinc chloride. The liquid resembled glycerol in this respect. It is quite possible that this high viscosity may have been in part responsible for some of the erratic results obtained. White (12) mentions this as a possible cause of oblique "flats" in cooling curves.

In two runs, it was not possible to determine the freezing points of the solutions under investigation. However, excellent breaks were observed in the cooling curves. Since these were found at essentially the same temperature for two solutions differing markedly in composition, these breaks were interpreted as being the eutectic temperature for this system, i.e., the temperature at which the two components separate

together. The value observed for the eutectic was $291.4 \pm 0.5^\circ\text{C}$. in a sample containing 47.2 mole per cent lead chloride. Slightly higher results were found in solutions containing more zinc chloride. This value is to be compared with Herrmann's value (2) of 261°C . The discrepancy between these results is about the same as that found for the melting point of zinc chloride. This determination is not of any particular importance for the calculations of this research, but will be useful in the discussion of them.

VIII. Discussion of Results

The freezing points reported in this investigation are believed to be accurate to within 0.5°C ., except in those cases where larger deviations are noted. It was not felt desirable to multiply the number of results in order to increase the precision of the data, since the accuracy of the thermocouple is not greater than these values. Errors in the time measurements are not believed to be important. Since it was possible to read the time to 0.05 minutes, an unimportant amount in the plotting of cooling curves.

TABLE 4

ACTIVITIES OF LEAD CHLORIDE DILUTED WITH ZINC CHLORIDE
FROM FREEZING POINT MEASUREMENTS (THIS RESEARCH)

Mole fract. <u>PbCl₂</u>	Freezing point ($^\circ\text{C}$.)	Activity <u>PbCl₂</u>	Activity <u>PbCl₂</u>	Coefficients <u>ZnCl₂</u>
1.000	498.3 ± 0.3	1.000	1.000	---
0.955	488.3 ± 0.1	0.953	0.998	0.405
0.880	$489.7 \pm 1.2^*$	0.959	1.090	104.
0.859	475.1 ± 0.2	0.893	1.040	4.29
0.787	$470.5 \pm 1.4^*$	0.874	1.111	4.21
0.745	455.5 ± 0.5	0.810	1.087	2.04
0.743	458.8	0.824	1.109	2.37
0.000	303.7 ± 0.5	---	---	1.000

*Chromel-alumel thermocouple

The value of the activity coefficients of lead chloride are calculated from the data obtained by means of equation (7). These values are listed in the fourth column of table 4. The values of the activity coefficients of zinc chloride are given in the last column of table 4. These were calculated from those for lead chloride, using equation (12).

The freezing points of the solutions which we have examined, while showing some slight variations, generally confirm the results obtained by Herrmann (2). His data are given in table 5.

TABLE 5
FREEZING POINTS OF SOLUTIONS OF ZINC CHLORIDE
IN LEAD CHLORIDE (HERRMANN)

<u>Mole fraction PbCl₂</u>	<u>Freezing Point</u>	<u>Eutectic Point</u>
1.000	501°C.	---
0.815	472	243°C.
0.662	414	260
0.533	390	260
0.424	355	262
0.329	332	256
0.246	321	265
0.174	304	268
0.109	285	268
0.052	273	?
0.005	262	?
0.000	261.5	---

In addition to confirming the values which he obtained for the freezing points of lead chloride rich solutions, the value of the eutectic has been established to exist at about the same temperature. It is therefore safe to assume that the data of Herrmann are substantially correct. The only assumption which must be made in applying equation (7) to these data is that lead chloride separate alone from the solutions when they are allowed to solidify until the eutectic composition is reached. That this assumption is a reasonable one for this system is evidenced by the existence of the eutectic break in certain cooling

curves obtained during the investigation. There was no evidence for the formation of solid solutions or of other phenomena which might complicate the phase diagram. For this reason, it is believed that the application of the theory developed in a preceding section to the data obtained in this research is valid. It may be seen by examination of table 4, that the values of the activity coefficients of lead chloride in the solutions are slightly larger than unity in all cases but one. This solution yields a value so close to unity that it may be so considered. In any case, the deviations from Raoult's law are seen to be quite small in magnitude and positive in sign. Therefore, the restriction on the application of the Margules equation is seen to be fulfilled. Application of this equation in the form of equation (12) results in the values for the activity coefficients of zinc chloride given in table 4. The extremely large value obtained for the sample containing 0.880 mole fraction lead chloride only emphasizes the opinion of the investigators that the value of the freezing point of this particular solution is highly inaccurate.

As has been noted previously, the results obtained for the activity

TABLE 6

ACTIVITY OF LEAD CHLORIDE DILUTED WITH ZINC CHLORIDE
AT 500°C. (WACHTER AND HILDEBRAND)

<u>Mole fract.</u> <u>PbCl₂</u>	<u>-ΔS₁</u> <u>cal./deg.</u>	<u>E</u> <u>volts</u>	<u>-ΔF₁</u> <u>cal.</u>	<u>-F₁</u> <u>cal.</u>	<u>Activity</u> <u>PbCl₂</u>	<u>Activity</u> <u>coefficient</u>
1.000	28.9	1.2730	58,750	0	1.000	1.000
0.885	28.4	1.2800	59,050	300	0.820	0.930
0.688	27.5	1.2905	59,550	800	0.595	0.865
0.595	27.0	1.2990	59,950	1200	0.455	0.770
0.490	26.6	1.3095	60,450	1700	0.330	0.675
0.301	23.8	1.3315	61,450	2700	0.175	0.575

coefficients of lead chloride by the freezing point method are in violent disagreement with the results obtained by Wachter and Hildebrand(1)

by the electromotive force method. Their data are given in table 6. It is possible to arrive at independent checks on some of their data by using the data of Kelley (3, 13) for the specific heats and entropies of lead, chlorine, and lead chloride. Using these data, it is possible to calculate the entropy of formation of liquid lead chloride from liquid lead and chlorine gas at 500°C. (773,2°K.). This value may be compared with that obtained by Wachter and Hildebrand from the temperature coefficient of the electromotive force of their cell containing pure lead chloride. The data used in this calculation are given in table 1, and the results in table 7.

TABLE 7

CALCULATED FREE ENERGY OF FORMATION OF LEAD CHLORIDE

	<u>Entropy at 773,2°K.</u>
Lead (liquid)	21.90 cal. mole ⁻¹ deg. ⁻¹
Chlorine (gas)	61.47
Lead chloride (liquid)	59.0
 Pb (1) + Cl ₂ (g) = PbCl ₂ (1) (773,2°K.)	
$\Delta S = - 24.4 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$	
$\Delta H = - 78,877 \text{ cal. mole}^{-1}$	
$\Delta F = - 60,010 \text{ cal. mole}^{-1}$	

The value obtained by this process is $\Delta S = - 24.4$ calories per mole per degree. This may be compared with Wachter and Hildebrand's value of -28.9 calories per mole per degree. The difference (18%) between these results is balanced, however, by a difference between the values of the heat of formation of lead chloride from its elements from the data of Bichowsky and Rossini (14) and that which may be calculated from Wachter and Hildebrand's data. That this is the case may be seen by computing from the value of the heat of formation of lead chloride (14) and the entropy of formation the free energy of formation. In this way, the value $\Delta F = -60,010$ calories per mole is

obtained, compared to -53,750 calories per mole from Wachter and Hildebrand. The difference between these values, while small (3.6%), is more than sufficient to account for the discrepancy between the results of Wachter and Hildebrand and those of this investigation. Use of the value of the free energy of formation of lead chloride calculated in table 7 instead of that found by Wachter and Hildebrand from their electromotive force measurements in the determination of the activities of the lead chloride in their solutions leads to values for the activity coefficients of lead chloride which are larger than unity. This indicates positive deviations from Raoult's law, the same behavior noted in this research.

It is not pretended that the apparent error which has been ascribed to the data of Wachter and Hildebrand is actually as great as it appears. An increase of only 112 calories (0.18%) in their value of $-\bar{F}_1$ would give an activity coefficient of 1.000 for their solution containing 0.885 mole fraction lead chloride. This corresponds to an error of only 2.4 millivolts in the electromotive force of one of the cells studied. The point of this discussion is to emphasize the fact that the thermodynamic constants derivable from the data of Wachter and Hildebrand are not consistent with those recorded in the literature (3, 13, 14) and used in this investigation. It is perhaps significant in this regard that Bichowsky and Rossini (14), in making their authoritative compilation of thermochemical data, some six years after Wachter and Hildebrand completed their study, did not even take notice of their value for the free energy of formation of lead chloride.

In conclusion, although the results of this investigation (and of the freezing point method in general) are apparently in violent disagreement with results obtained by the electromotive force method,

the discrepancy may be easily explained on the basis of the inconsistencies in the thermodynamic data used. Since precautions were taken in this study to use only the best recommended data (3, 13, 14), it is believed that the behavior described by the freezing point method is the correct one. Solutions of zinc chloride in lead chloride, then, show positive deviations from Raoult's law, but deviations which are quite small, at least in the concentration range studied in this investigation.

IX. Summary

The system lead chloride-zinc chloride has been investigated in the region extending from 0.743 mole fraction of lead chloride to pure lead chloride (mole fraction 1.000). In this region, the solutions show small positive deviations from Raoult's law, as is evidenced by the activity coefficients of the lead chloride, which were found to be slightly greater than unity.

A method for the preparation of pure anhydrous zinc chloride has been described, and the experimental determination of freezing points has been discussed. The theory of the determination of activities from freezing point measurements has been outlined and applied to the experimental results determined in this investigation.

An apparent discrepancy between these results and those from the electromotive force measurements of Wachter and Hildebrand (1) has been discussed and explained on the basis of an inconsistency in the thermodynamic functions used.

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VITA

Mark Tabor Robinson was born in Oak Park, Illinois, on June 23, 1926. He grew up in Oak Park and was educated in the public schools of that village, graduating from the Oak Park-River Forest Township High School in June, 1943. He entered the University of Illinois immediately upon graduation from high school. He received the degree of Bachelor of Science in Chemistry "with Highest Honors" from the University in February, 1946. During his undergraduate days he was active in the Theatre Guild on the campus. He became a member of Phi Eta Sigma, Phi Lambda Upsilon, Pi Mu Epsilon, Phi Kappa Phi, and Sigma Xi while an undergraduate. He holds the University of Illinois Scholarship Key and is a member of three local dramatic societies on the campus of the University of Illinois.

After a short stay at the University of Wisconsin, he went to Stillwater, Oklahoma, where he was employed as an instructor in the Department of Chemistry of the Oklahoma Agricultural and Mechanical College. He first began work in June, 1947. He has been employed as an instructor and a part-time instructor in the Department of Chemistry since that time.

On August 30, 1947, he married Margaret Elizabeth Dohr of Madison, Wisconsin.

In addition to the societies previously mentioned, he is a member of the American Chemical Society.

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