[Contribution from the Chemistry Department of the University of California]

THE CHANGE IN ACTIVITY OF MOLTEN LEAD CHLORIDE UPON DILUTION WITH POTASSIUM CHLORIDE

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Introduction

In spite of the attention paid in recent years to the activities of substances in various types of solutions, practically no attention has been paid to solutions of molten salts, although these offer features of particular interest. The work described in this paper was undertaken with the intention of beginning the collection of data necessary for a general study of this problem.

In order to measure the effect of dilution upon the activity of a molten salt, a simple concentration cell might be used as in the investigations of Gordon[1] and of Goodwin and Wentworth,[2] wherein one silver electrode was surrounded by fused silver nitrate, and the other by silver nitrate diluted by potassium nitrate and sodium nitrate. Such a cell, however, involves the uncertainty of a liquid junction which it is desirable to avoid. One way to do this is to carry over into the realm of fused salts cells of the type used in aqueous solutions, such as $Hg \mid HgCl$ in $ZnCl_2$ aq. $\mid ZnHg_x$. The electromotive force of the second cell containing the zinc chloride at a different concentration, combined with the e.m.f. of the first, enables one to determine the change in the activity of the zinc chloride with dilution. With fused salts the analogous cell combinations require the use of the salt of a nobler metal which is but slightly soluble in the mixture of fused salts which would serve as electrolyte. Such combinations are difficult to find, however, because of the high degree of solubility of most salts in other molten salts. We therefore turned our attention to a third type of cell. Fused lead chloride provided with electrodes of lead and chlorine serves to measure the free energy of formation of lead chloride. The change in e.m.f. of this cell when the lead chloride is diluted with, say, potassium chloride, gives the free energy of dilution and hence the change in activity of the lead chloride.

The decomposition potentials of a number of fused salts[3] have been measured, but the effect of dilution by another salt has not been studied, so far as we know, in cases that will permit an attack upon the problem here presented.

Apparatus and Experimental Procedure

The cells used were of simple cylindrical form, 2 cm. in diameter and 12 cm. long, made of Pyrex. Tungsten wires were sealed through the bottom

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[1] Gordon, *Z. physik. Chem.*, **28**, 302 (1899).

[2] Goodwin and Wentworth, *Phys. Rev.*, **24**, 77 (1907).

[3] Lorenz, "Die Elektrolyse geschmolzener Salze, Dritter Teil, Elektromotorische Kräfte," Knapp, Halle a. S., **1906**.

to make connection with the cathode of molten lead. The tungsten leads were soldered on the outside, by means of German silver, to gold wires which provided connection with the outside apparatus. Copper was not suitable for this purpose because of its gradual oxidation at the temperature of the furnace. The anode was a graphite rod, 6 mm. in diameter, held by the tungsten lead.

The thermostat consisted of an electrical-resistance furnace very well insulated and of large heat capacity. Two iron fans circulated the air to prevent variations in temperature within the compartment. Uniformity in temperature was shown by testing with thermocouples. The temperature was controlled by rheostats and could be held within 3° for an hour.

Temperatures were measured by two thermocouples of chromel-alumel. These thermocouples were standardized by the melting points of tin, cadmium, lead, zinc and antimony, and were accurate to at least 0.2°. During the course of the investigation the thermocouples were repeatedly checked against each other and against the melting points of zinc and tin. All electromotive forces were measured on a potentiometer of high accuracy. The materials used were from commercial sources of high purity. The lead chloride was dried in a vacuum to prevent hydrolysis on fusion. The composition of the electrolyte was checked by analysis in each case, the lead and potassium gravimetrically as sulfates, the halogen volumetrically, by the Volhardt method.

The cells were charged with weighed amounts of lead chloride and potassium chloride and placed in a furnace, which was left open to maintain atmospheric pressure. The polarizing current of two to three amperes was passed for about half an hour in order to saturate the graphite electrode. Before each measurement, the cell was again polarized by a current of 10–20 milliamperes for 10–15 minutes. It was found that moderate variations in the current strength and the time had no effect on the potential of the cell. The agreement between the free energy of decomposition of fused lead chloride and the free energy of lead chloride at 25°, calculation of which is given later in the paper, constitutes good evidence that the e.m.f. of the polarized cell represents the true decomposition potential. The changes in concentration caused by the small currents necessary for repolarizing the cell had but a negligible effect upon the composition of the electrolyte.

Experimental Results

Experimental values for the various cells are given in Table I. Where different cells have been used to get the values for the same composition of electrolytes they are designated, respectively, by the letters A, B, C, etc. The data are plotted in Fig. 1, together with the values obtained by Czepinski[4] for pure lead chloride. It will be seen that the figures obtained by

[4] Czepinski, *Z. anorg. Chem.*, 19, 208 (1899).

this investigator are between two and three centivolts lower than our own, although the temperature coefficient is practically the same. The dotted line is the one selected by them to smooth out the results.

TABLE I

DECOMPOSITION POTENTIALS OF LEAD CHLORIDE DILUTED WITH POTASSIUM CHLORIDE

Mole fraction of KCl	Temp., °C.	Volts	Cell
0.000	501	1.2690	C
	507	1.2659	A
	514	1.2604	A
	545	1.2382	A
	550	1.2332	B
	598	1.1980	A
	607	1.1930	A
.050	534	1.2512	D
	553	1.2371	E
.100	525	1.2620	F
	553	1.2417	G
	560	1.2357	G
	564	1.2330	H
.200	540	1.2575	I
	560	1.2409	J
.300	542	1.2754	K
	560	1.2618	L
	585	1.2411	M
	602	1.2266	L
	605	1.2246	L
.400	560	1.2912	N
	610	1.2491	O

The relation between e.m.f. and composition at constant temperature was obtained by plotting Fig. 1 on a large scale and determining the intersections of the lines with the temperature ordinates at 550° and 600°, thereby obtaining the figures given in Table II and plotted in Fig. 2. It will be seen that the points fall on a smooth curve except those for $N = 0.2$, which fall a little below the curve. Since, however, these points were determined by fewer observations than those on both sides, we have considered that some larger experimental error was introduced here.

TABLE II

RELATION BETWEEN E.M.F., ACTIVITY AND COMPOSITION

	N_{KCl}	0.00	0.05	0.10	0.20	0.30	0.40
500°	E	1.234	1.239	1.244	(1.249)	1.270	1.300
	a	1.000	0.868	0.771	(0.655)	0.362	0.155
	γ	1.000	.914	.857	(.818)	.517	.258
600°	E	1.198	1.202	1.206	(1.210)	1.229	1.257
	a	1.000	0.900	0.809	(0.727)	0.448	0.208
	γ	1.000	.947	.898	(.908)	.640	.346

The activity of lead chloride in these solutions, also given in Table II, was calculated by means of the equation $\mathbf{E}_N - \mathbf{E}_0 = -(RT/2F)ln\ a$, where the activity, a, is referred to that of pure lead chloride as unity. Dividing the activity by the mole fraction of lead chloride gives the activity coefficient, γ, also included in Table II.

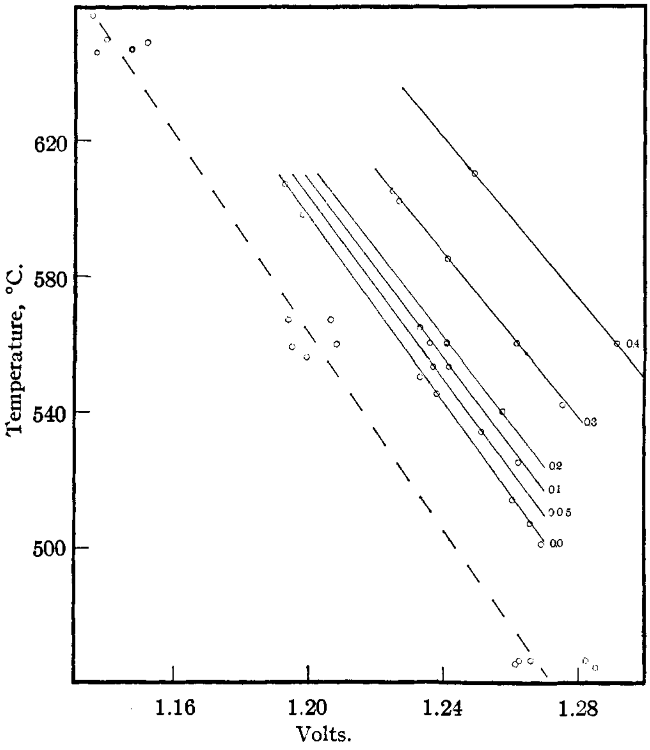

Fig. 1.

Interpretation of Results

The activity coefficients for 550°, given in Table II, are plotted in Fig. 3 against the mole fraction of potassium chloride. If we assume that neither component is ionized and that Raoult's law is obeyed, the addition of potassium chloride to lead chloride would give unit activity coefficient, represented by the horizontal, straight line A. It is evident, however, that the lowering of activity is approximately twice as great. This suggests at once the same explanation as is given in the case of aqueous solutions of potassium chloride, which is that the potassium chloride is ionized. If we assume that this is so and that the lead chloride is not ionized, and further that the activity of each substance present is given by Raoult's law, then if we take r moles of lead chloride to 1 mole of potassium chloride, the dissociation of the latter would make the total number of moles $r + 2$

so that the true mole fraction of lead chloride would be $r/(r + 2)$. The curve B in Fig. 3 represents the activity coefficient of lead chloride calculated upon this assumption. It is evident that even this does not sufficiently account for the observed points.

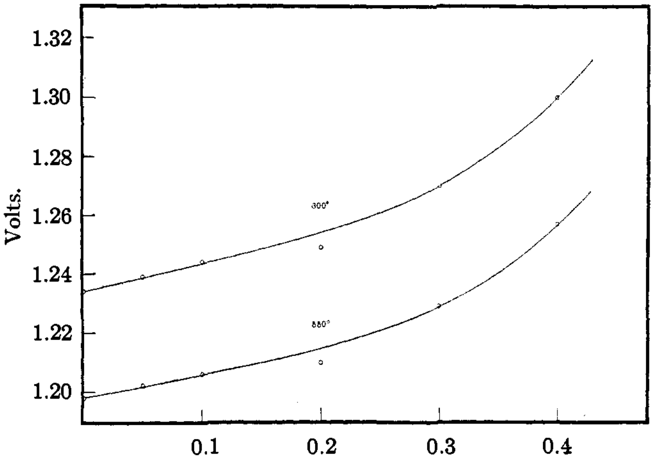

Fig. 2.

Investigation of the freezing points of this system, by Lorenz and Ruckstuhl,[5] has shown that the components unite to form three solid phases, $KCl.2PbCl_2$, $2KCl.PbCl_2$ and $4KCl.PbCl_2$. The composition of these compounds is indicated along the horizontal axis in Fig. 3. They showed, further, by transfer experiments that the lead seems to be present in the anion.

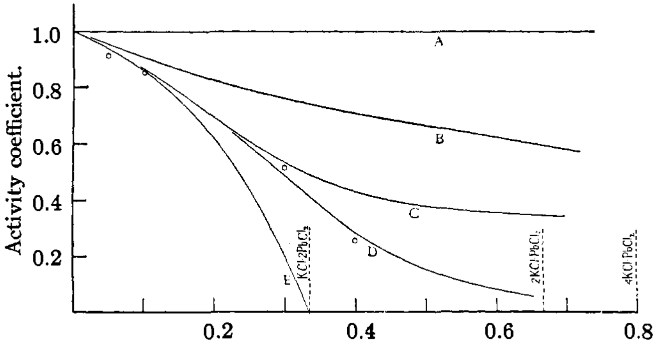

Fig. 3.

If we assume that all of the potassium chloride added to an excess of

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[5] Lorenz and Ruckstuhl, *Z. anorg. Chem.*, **52**, 41 (1907).

lead chloride forms K^+ and $Pb_2Cl_5^-$, then the mixture would contain $r-2$ moles of lead chloride and 1 mole each of K^+ and $Pb_2Cl_5^-$. The true mole fraction of lead chloride would then be $(r - 2)/r$. If Raoult's law is obeyed, the activity coefficient of lead chloride would then follow Curve E. It is observed that the upper portion of this curve, as we might expect, lies closer to the data than does Curve B, but that at high concentrations of potassium chloride the activity is not reduced as much as it would be if all of the chloride ion in the solution were united with lead chloride. We may accordingly assume that the complex ion is partly dissociated, so that r moles of lead chloride and 1 mole of potassium chloride form x moles of $Pb_2Cl_5^-$, leaving in the mixture $r - 2x$ moles of lead chloride, $1 - x$ moles of chloride and 1 mole of potassium ion. The total number of moles in the mixture then becomes $r - 2x + 2$. The true mole fraction of lead chloride and, we may assume, its activity also would then be

$$a = (r - 2x)/(r - 2x + 2) \tag{1}$$

that of the chloride ion would be $(1 - x)/(r - 2x + 2)$ and that of the ion $Pb_2Cl_5^-$ be $x/(r - 2x + 2)$. These activities should then be related through an equilibrium constant, K, by means of the equation

$$\left(\frac{r - 2x}{r - 2x + 2}\right)^2\left(\frac{1 - x}{r - 2x + 2}\right) = \frac{Kx}{r - 2x + 2} \tag{2}$$

which can be slightly simplified. Theoretically then, this equation can be solved for x, and the value obtained substituted in Equation 1 for the activity of the lead chloride and a value of K selected to reproduce the observed activities. It is somewhat simpler to assign a fixed value to K and a series of values to x, and to solve each equation thus obtained for r. The corresponding values of x and r are then substituted in Equation 1 to give a, from which γ is readily calculated. Curve C, in Fig. 3, was thus obtained by setting $K = 0.1$. The apparent mole fraction of lead chloride is, of course, $r/(r + 1)$, and that of potassium chloride is $1/(r + 1)$, which gives the abscissas. It is evident that this treatment reproduces the observed activity coefficients within the limit of error as far as mole fraction of 0.3, but that the last point lies considerably below Curve C. This is not surprising, however, in view of the existence of the other two solid compounds, which would tend to lower the activity coefficient of lead chloride still further as the mole fraction of potassium chloride becomes larger, thus accounting for the divergence between Curves C and D. It would be possible to assume a further equilibrium to form the ion $PbCl_4^{--}$ to account for Curve D, but this becomes algebraically somewhat complicated and seems hardly worth while in view of the probable inexactness of our assumption that the activity of each molecular species in the mixture is accurately given by its mole fraction. We can, therefore, hardly attach much significance to the numerical value of K. Nevertheless, the curves based on the other assumptions differ so much from the observed values that we believe there can be little doubt that the mixture is made up principally of the molecular species lead chloride, K^+ and $Pb_2Cl_5^-$ at low concentrations of potassium chloride together with the higher complexes at higher concentrations of potassium chloride. It is, of course, not at all certain that the only complexes existing in the liquid are those which separate as solids.

In view of the usual assumption of complete, or at least a high degree of ionization of all fused salts, it may seem paradoxical that we should have to assume that the lead chloride is largely un-ionized. Indeed, Goodwin and Kalmus[6] have given results upon the lowering of freezing point of mixtures of lead chloride and lead bromide which were interpreted as indicating a considerable degree of dissociation. At that time, Bray[7] pointed out that the evidence did not necessarily prove ionization into Pb^{++} and $2Cl^-$. He has recently called my attention to the fact that no ionization whatever need be assumed in mixtures of molten lead chloride and lead bromide, since the formation of a mixed un-ionized salt, PbClBr in the reaction $PbCl_2 + PbBr_2 = 2PbClBr$, would account for the observed lowering of freezing point in these systems. It seems to us, in this connection, that the undoubted existence of complex ions in the mixture renders all the more certain the presence of undissociated lead chloride. We may also emphasize the fact that to assume ionization of both potassium chloride and lead chloride would give activities far removed from those observed.

The activities at 600° are somewhat higher than at 550°, as might be expected from the greater dissociation of $Pb_2Cl_5^-$ that would undoubtedly occur at higher temperatures. We might repeat the calculation of K for this temperature but this seems hardly worth while.

In view of the uncertainty that always must attend a potential produced by polarization, we have compared the free energy calculated from our measurements with the very accurate value now known for the free energy of solid lead chloride at 25°. Two independent sets of data obtained by Gerke[8] give $\Delta F^\circ_{298} = -75{,}040$ cal. From various figures for the heat of formation given in Landolt-Börnstein, "Tabellen," we have selected $\Delta H = -85{,}600$. Using specific-heat data, we select as the difference in molal specific heat between lead chloride and its elements 4.3 in the temperature interval between 25° and 327°, the melting point of lead, and 5.8 between 327° and 498°, the melting point of lead chloride. Using these figures and the heat of fusion of lead, 1210°, we calculated by well-known

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[6] (a) Goodwin and Kalmus, *Phys. Rev.*, **28,** 19 (1909). See also (b) Bray, *Z. physik. Chem.*, **80,** 251, 378 (1919).

[7] Ref. 6 b, p. 253.

[8] Gerke, THIS JOURNAL, **44,** 1684 (1922).

methods, first, the change in $\Delta F°$ in going from 25° to 327°, and then the further change in going to 498°, which gave $\Delta F°$ at this latter temperature equal to —59,400 cal., corresponding to a decomposition potential of 1.285 v. The smooth line through our measured values for the pure lead chloride cuts this temperature at 1.272 v., corresponding to $\Delta F° = -58{,}700$ cal. The agreement lies well within the errors introduced by the uncertainties in the data used for making the calculation over the wide temperature range.

Summary

1. The decomposition potential of fused lead chloride, diluted with varying amounts of potassium chloride, has been measured at various temperatures from 500° to 600°.
2. The relation between composition and activity coefficient of molten lead chloride has been determined at mole fractions of potassium chloride between 0 and 0.4, for 550° and 600°.
3. The results have been interpreted upon the assumption that the complexes KPb_2Cl_5, K_2PbCl_4 and K_4PbCl_6, which separate as solids, and perhaps others as well, also exist as partly ionized in the solutions along with un-ionized lead chloride.
4. The decomposition potential of pure, molten lead chloride corresponds to a free-energy value of —58,700 cal. at 498°, which is shown to be in substantial agreement with the value at 25° obtained by Gerke.

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SOLUBILITY. X. SOLUBILITY RELATIONS OF STANNIC IODIDE

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The solubility relations of stannic iodide are particularly appropriate for the further testing of the theories of solubility elaborated by the senior author and his collaborators.[1] Stannic iodide is relatively non-polar, and has a melting point sufficiently low to allow solubilities large enough for convenient measurement, and it has a high internal pressure, so that it was expected to show solubilities falling off regularly from the ideal value with decreasing internal pressures of the solvents used. A substance of intermediate internal pressure may show approximately equal solubilities in liquids of both higher and lower internal pressures, hence the relation be-

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[1] (a) Hildebrand and co-workers, THIS JOURNAL, **38**, 1452 (1916); (b) **39**, 2297 (1917); (c) **41**, 1067 (1919); (d) **42**, 2180, (e) 2213 (1920); (f) **43**, 500, (g) 2172 (1921); (h) **45**, 682, (i) 2828, 2865 (1923); (j) *Phys. Rev.*, **21**, 46 (1923); (k) "Solubility," A. C. S. Monograph, Chemical Catalog Co., 1924.