3. Density determinations of 0.5 mole fraction lithium bromide in silver bromide were made between 517 and 555° and may be expressed by the equation $d^t = 4.504 - 0.000877\ t$.
4. The results have been discussed on the basis of simple assumptions as to ionization, but without taking into account any changes in interionic forces upon dilution.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THERMODYNAMIC PROPERTIES OF SOLUTIONS OF MOLTEN LEAD CHLORIDE AND ZINC CHLORIDE

BY A. WACHTER AND J. H. HILDEBRAND

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The following investigation represents a contribution to the program begun by Hildebrand and Ruhle[1] of gathering data upon free energy of dilution of molten salt solutions. The system selected, solutions of lead and zinc chlorides, seemed to be simpler than many others, for the freezing point-composition diagram, obtained by Herrmann,[2] shows no evidence of solid compounds. As in the research of Hildebrand and Ruhle, we started with measurements of the e. m. f. of the cell Pb (liq.) | $PbCl_2$ (liq.) | Cl_2 (gas), but instead of producing the chlorine electrode by polarization, as in the earlier work, and as was done by Lorenz[3] and co-workers for a number of molten chlorides, we succeeded in getting a reversible chlorine electrode, reproducible over a range of pressure and temperature. The lead chloride was then diluted with zinc chloride and the free energy of the dilution determined from the change of e. m. f. of the cell, a procedure which avoids the uncertainty of a liquid junction.

A similar study of certain bromide systems by Salstrom and Hildebrand[4] was carried out approximately at the same time as this one, and the procedure was developed more or less in common. We will therefore avoid needless repetition by referring the reader to the description already given and state here only the features peculiar to this research.

The chlorine, the lead and zinc and their chlorides were from commercial sources of high purity, analyses of which were furnished, and were considered by us to be free from impurities that could affect the e. m. f. Substitution of chlorine generated by electrolysis of pure fused lead chloride made no appreciable difference in the results. The most serious im-

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[1] Hildebrand and Ruhle, THIS JOURNAL, **49**, 722 (1927).

[2] Herrmann, *Z. anorg. Chem.*, **71**, 281 (1911).

[3] Lorenz, "Die Elektrolyse geschmolzener Salze," Dritte Teil, Elektromotorische Kräfte, Knappe, Halle a. S., **1906**; *Z. physik. Chem.*, **62**, 119 (1908); **63**, 109 (1908); *Z. angew. Chem.*, **39**, 88 (1926).

[4] Salstrom and Hildebrand, THIS JOURNAL, **52**, 4650 (1930).

purity to be avoided was water; hence not only was the chlorine carefully dried in a tower containing glass beads wet with sulfuric acid, but the lead and zinc chlorides were fused in dry hydrogen chloride gas before weighing and introduction into the cell, and the cell itself, after being made up, was treated with dry hydrogen chloride bubbled up through the molten salt for about an hour.

Reproducible values for the cells were reached after chlorine had been bubbled through them for from twelve to twenty-four hours. After that they responded very quickly to temperature changes with no evidence of hysteresis. The effect of changing the pressure of the chlorine was studied using five different pressures from 76 to 105 cm. The changes in e. m. f. so produced agreed within 0.3 millivolt with those calculated by aid of the usual formula. Electrolysis of the cells at 0.25 ampere for two hours caused no change in e. m. f., although a current of 3 amperes decreased the e. m. f. by several millivolts.

Since the theoretical treatment of our results will ultimately require a knowledge of the interionic distances, we considered it desirable to measure the densities of the two pure chlorides as well as their 50 molal per cent. solution. This was done by weighing a tungsten-weighted pyrex bulb in air, in water and in fused salt, correcting for the expansion of the bulb. The bulb was sharply tapped after each reading to remove any adherent bubbles of gas. The densities observed are given in Table I.

TABLE I

DENSITIES OF LIQUID LEAD AND ZINC CHLORIDES

100% $PbCl_2$		49.8% $PbCl_2$, 50.2% $ZnCl_2$		100% $ZnCl_2$	
t, °C.	Density	t, °C.	Density	t, °C.	Density
545.3	4.872	552.5	3.703	550.7	2.401
537.2	4.886	545.4	3.709	549.3	2.401
535.5	4.886	535.2	3.717	524.5	2.413
526.7	4.902	510.2	3.733	509.3	2.420
514.4	4.924			503.2	2.422
502.1	4.944			493.7	2.427
				485.7	2.431

The observed values yield the following equations: for the density of lead chloride: $d^t = 4.947 - 0.00164\ (t - 500)$; for the density of zinc chloride, $d^t = 2.424 - 0.00046\ (t - 500)$. Lorenz, Frei and Jabs,[5] using a platinum cube, obtained a density of 4.907 for pure lead chloride at 500°, differing from ours by 0.04 g. per cc. The molal volumes of lead and zinc chlorides at 500° are, respectively, 56.22 cc. and 55.82 cc., nearly identical. A 50 mole per cent. solution at this temperature has a molal volume of 55.31 cc., which is 0.7 cc. less than additive.

The results of the e. m. f. measurements are given in Table II and plotted in Fig. 1. The values for pure lead chloride represent three dif-

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[5] Lorenz, Frei and Jabs, *Z. physik. Chem.*, **61**, 468 (1908).

Table II

E. M. F. in Volts of Cells Containing Lead Chloride of Various Mole Fractions, N_1, Diluted with Zinc Chloride

t, °C.	E. m. f.	t, °C.	E. m. f.	t, °C.	E. m. f.	t, °C.	E. m. f.	t, °C.	E. m. f.
N_1 =	1.000	N_1 =	0.855	N_1 =	0.595	N_1 =	0.490	N_1 =	0.301
499.1	1.2731	515.6	1.2703	493.4	1.3021	495.0	1.3125	494.7	1.3341
510.5	1.2653	520.7	1.2670	512.6	1.2921	504.8	1.3068	503.4	1.3296
517.5	1.2631	527.6	1.2629	534.4	1.2792	528.2	1.2933	512.3	1.3253
521.7	1.2603	531.3	1.2609	538.0	1.2770	537.9	1.2882	517.0	1.3224
525.3	1.2563	536.7	1.2574	545.3	1.2728	562.3	1.2738	525.0	1.3185
529.2	1.2554	540.6	1.2549	547.5	1.2713	567.4	1.2708	529.0	1.3162
536.8	1.2507	554.6	1.2461	557.9	1.2650	595.5	1.2540	541.3	1.3098
539.4	1.2488	587.0	1.2248	561.3	1.2636	602.2	1.2503	545.7	1.3079
541.8	1.2469			563.0	1.2617			579.1	1.2910
544.8	1.2445	N_1 =	0.688	568.2	1.2584				
549.5	1.2417	495.8	1.2934						
554.8	1.2394	512.7	1.2828						
556.5	1.2374	525.2	1.2753						
560.3	1.2350	542.5	1.2650						
566.0	1.2310	551.0	1.2602						
572.0	1.2281	560.0	1.2546						
578.5	1.2249	566.2	1.2510						
582.1	1.2221	570.0	1.2492						

ferent cells, indicated in the figure by points of different styles. No systematic differences between these cells could be detected. The points for each composition, although recorded in the table in order of increasing temperature, were not obtained in this order, but some were approached from above and some from below. The average deviation of our points from the straight line of the plot is less than 0.5 mv.

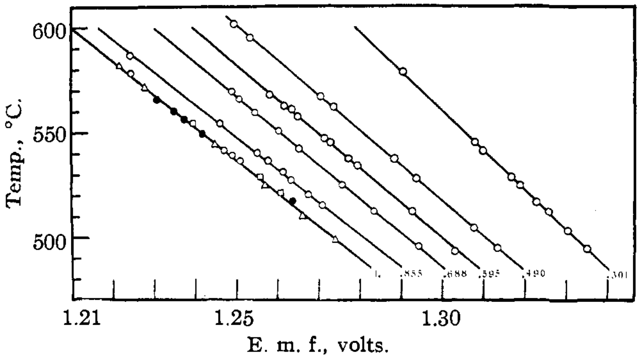

Fig. 1.—Temperature variation of e. m. f. of cells containing different mole fractions of lead chloride–zinc chloride solutions. Different symbols represent different cells at mole fraction 1.

In order to be sure that there was no danger of the lead electrode replacing zinc, we measured the e. m. f. of the cell Zn (liq.) | $ZnCl_2$ (liq.) | Cl_2.

The results are given in Table III. They show the e. m. f. to be sufficiently large to indicate that such displacement would not be a disturbing factor.

TABLE III

E. M. F. IN VOLTS OF THE CELL Zn (LIQ.) | $ZnCl_2$ (LIQ.) | Cl_2

t, °C.	501.0	504.1	518.7	527.8	531.4	541.0	550.2	565.2	575.5
E.m.f.	1.5721	1.5695	1.5593	1.5529	1.5498	1.5440	1.5369	1.5277	1.5199

Our results for the pure chlorides can be compared with those obtained by previous workers. Lorenz and Czepinski,[6] using a polarized electrode and taking no special precautions to exclude oxygen or moisture, obtained very fluctuating values, about 30 mv. less than ours for lead chloride and 60 mv. less for zinc chloride. Lorenz and Weber,[7] excluding air obtained values for lead chloride about 15 mv. less than ours, and Hildebrand and Ruhle,[1] taking proper precautions but using a polarized electrode, found values close to ours at 500° but falling off considerably at higher temperatures, 13 mv. at 600°. Recently Lorenz and Velde,[8] employing a procedure essentially the same as ours except that their preliminary treatment involved electrolysis of the cells for eight days at 0.25 ampere, obtained figures for lead chloride agreeing with ours to within 4 mv. For zinc chloride their values are 10 mv. less at 500° but in good agreement at 600°.

Since our main interest lies in the relation of free energy to composition at constant temperature, we obtained from Fig. 1, plotted on a large scale, the intersections at the round temperatures 500 and 600°, getting the values of e. m. f., $\mathbf{E}$, given in Table IV, together with the values of $d\mathbf{E}/dT$ at the different compositions. The temperature coefficients fall off almost linearly with N_1 except for the most dilute cell, in which case it is considerably smaller. Since such a difference can hardly be real, it seems to us that the figures for this composition, $N_1 = 0.301$, are probably less accurate than the others.

Table IV also contains the values of the entropy, ΔS_1, and free energy of formation, ΔF_1, of lead chloride, its partial molal free energy or free energy of dilution, $\bar{F}_1$, its activity, a_1 and its activity coefficient, a_1/N_1. All of these have been calculated from the observed data by the usual formulas. We have also calculated the molal heat of formation, getting $\Delta H_1 = -81{,}100$ cal. for the pure liquid; this varies scarcely at all with changing temperature or upon dilution with zinc chloride.

The values for zinc chloride in Table III yield in a similar manner $\mathbf{E} = 1.5725 - 0.000695(t - 500)$ for the e. m. f. between 500 and 600°, also, at 500°, $\Delta F_2 = -72{,}550$ cal. and $\Delta H_2 = -97{,}300$ cal.

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[6] Lorenz and Czepinski, *Z. anorg. Chem.*, **19**, 208 (1899).

[7] Lorenz and Weber, *ibid.*, **21**, 305 (1899).

[8] Lorenz and Velde, *ibid.*, **183**, 90 (1929).

TABLE IV

THERMODYNAMIC PROPERTIES OF LEAD CHLORIDE DILUTED WITH ZINC CHLORIDE

N_1	1.000	0.885	0.688	0.595	0.490	0.301
dE/dT, mv./deg.	−0.625	−0.615	−0.595	−0.585	−0.575	−0.515
ΔS_1, cal./deg.	−28.9	−28.4	−27.5	−27.0	−26.6	−23.8
			500°			
E, volts	1.2730	1.2800	1.2905	1.2990	1.3095	1.3315
$-\Delta F_1$, cal.	58,750	59,050	59,550	59,950	60,450	61,450
$-\bar{F}_1$, cal.	0	300	800	1200	1700	2700
a_1	1.000	0.820	0.595	0.455	0.330	0.175
a_1/N_1	1.000	0.930	0.865	0.770	0.675	0.575
			600°			
E, volts	1.2105	1.2185	1.2310	1.2405	1.2520	1.2800
$-\Delta F_1$, cal.	55,850	56,200	56,800	57,250	57,750	59,050
$-\bar{F}_1$, cal.	0	350	950	1400	1900	3200
a_1	1.000	0.835	0.580	0.445	0.335	0.155
a_1/N_1	1.000	0.945	0.840	0.750	0.685	0.515

The general nature of the results is most clearly indicated by the values of a_1/N_1, which are less than unity in the solutions, corresponding to negative deviations from Raoult's law, as found by Salstrom and Hildebrand[4] for the solutions of lead chloride with lead bromide. We find in this case, however, that the simple assumption of complete ionization of both salts, with no change in interionic forces, does not account for the direction of the deviation. Since the dilution with zinc chloride would, if both salts were completely ionized, make no change in the proportion of chloride ion, the only effect would be due to the substitution of lead ion by zinc ion, reducing the activity of the former and hence of the lead chloride, in proportion to N_1, the same as for the case of no ionization.

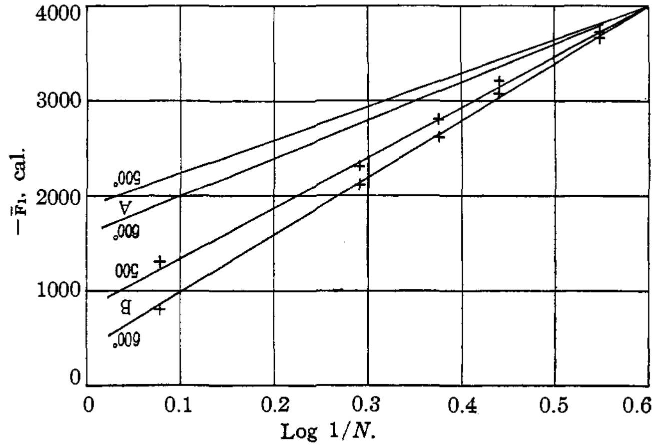

Fig. 2.—Variation of free energy of dilution with composition.

That a mere change in the interionic forces of a completely ionized mixture of these salts could affect the activities of the ions would seem plausible only in view of the contraction on mixing amounting to a little over one per cent., as shown by our density determinations. We will postpone till later any attempt to calculate the magnitude of this effect.

The deviation of the experimental results from the previous assumptions leading to $a_1 = \mathrm{N}_1$ is illustrated graphically in Fig. 2, where $-\bar{\mathrm{F}}_1$ is plotted against log $(1/\mathrm{N}_1)$ for 500 and 600°. In view of the equation $\bar{\mathrm{F}}_1 = RT \ln a_1$, this method of plotting yields the straight lines, A, when $a_1 = \mathrm{N}_1$. As a matter of fact the empirical relation $\bar{\mathrm{F}}_1 = 1.5\ RT \ln \mathrm{N}_1$, given by the curves B, reproduces the experimental values very well.

An explanation of the deviations from $a_1 = \mathrm{N}_1$ might be sought in a difference of dissociation between the two salts. Support for this view is lent by the fact that the electrical conductivity of zinc chloride at 500° is only one-sixteenth that of lead chloride, 0.084 mhos as compared with 1.33 mhos. Zinc chloride shows further evidence of low polarity in its low melting and boiling points and in its considerable solubility in various organic solvents. However, the most obvious difficulty in the way of an explanation along this line lies in the fact that we would not expect zinc chloride to have so much effect in small concentrations, but rather that curves B would begin tangent to curves A when N_1 is unity.

We will postpone a more searching treatment of this system till we have at hand data now being obtained for other systems, when we expect to make a comprehensive study of the whole subject.

Summary

1. The free energy of the formation of liquid lead and zinc chlorides has been measured between 500 and 600° by measuring the e. m. f. of reversible cells with metal and chlorine electrodes and fused salt electrolytes.

2. The e. m. f. of the $\mathrm{Pb} \mid \mathrm{PbCl_2} \mid \mathrm{Cl_2}$ in this range is given in volts by $1.2730 - 0.000625\ (t - 500)$, that of the corresponding zinc cell by $1.5725 - 0.000695\ (t - 500)$.

3. Dilution of the lead chloride by zinc chloride yields values for e. m. f. from which have been calculated the free energy of dilution and the activity over a range of composition from 30 to 100 mole per cent. of lead chloride.

4. It is pointed out that neither the assumption of no ionization or of complete ionization of both salts accounts for the observed values. Assuming the lead chloride to be ionized and the zinc chloride unionized accounts for the results only partially.

5. The densities of the pure salts and their 50 mole per cent. mixture have been measured in order to furnish information regarding interionic distances as a guide to a future theoretical treatment. The density of

lead chloride is given by 4.947 − 0.00164 (t − 500), that of zinc chloride by 2.424 − 0.00046 (t − 500).

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

AN ATTEMPT TO MEASURE THE VELOCITY OF DISSOCIATION OF NITROGEN TETROXIDE BY THE METHOD OF SOUND WAVES

BY GEORGE B. KISTIAKOWSKY AND WILLIAM T. RICHARDS

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For some years it has been apparent that sound waves offer an opportunity to investigate the velocity of dissociation of rapidly dissociating gases. The argument was at first[1] purely qualitative, it being supposed that when the compressions and rarefactions in the sound waves succeeded each other with sufficient rapidity the dissociating gas would no longer be able to attain equilibrium. An increased velocity of sound with increasing frequency was therefore to be expected when a certain critical region of frequency had been reached. Einstein gave this conception greater precision in a well-known paper[2] relating the velocity constant of the reaction to the increase in velocity of sound with increasing frequency. Since the velocity constants of rapid reactions are of the utmost importance for the kinetic interpretation of reaction velocities, Einstein's theory was soon tested, first by Selle[3] and later by Grüneisen and Goens.[4] Nitrogen tetroxide, which dissociates considerably in a convenient temperature range, was the object of study of both of these investigations. The work of Grüneisen and Goens was of an extremely scholarly character, the velocity of sound being measured by the resonance tube method to frequencies of 15,600 cycles per second from 10 to 35° and from 760 to 265 mm. pressure. The velocity being independent of frequency to a few tenths of a per cent. over this range, these authors estimated that the velocity constant of the reaction must exceed 10,000, a conclusion with which this communication is in entire accord. More recently Olson and Teeter[5] in a brief note, report an increase of velocity at 50 kilocycles. Their results have not been confirmed by this investigation. Their published data are limited, and no critique of their conclusion can be attempted here. It seems possible that they have underestimated their systematic error, a point of unusual importance in the calculation of the velocity constant.

[1] Keutel, "Inaug. Disser.," Berlin, **1910**.

[2] A. Einstein, *Sitzb. Berl. Akad.*, 380 (1920).

[3] H. Selle, *Z. physik. Chem.*, **104**, 1 (1923).

[4] E. Grüneisen and E. Goens, *Ann. Physik.*, **72**, 193 (1923).

[5] A. R. Olson and C. E. Teeter, *Nature*, **125**, 150 (1930).