

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

**THERMODYNAMIC PROPERTIES OF SOLID SOLUTIONS OF
LEAD CHLORIDE AND LEAD BROMIDE**BY A. WACHTER¹

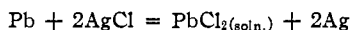
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The investigation described in this paper represents an extension of the experimental methods described in a previous paper² for the determination of the thermodynamic properties of solid salts and their solid solutions by a study of the e. m. f. of cells containing solid electrolytes. Such measurements give accurate data concerning activities over a large temperature range and are of great interest in connection with the general theories of solution and with the theories concerning the structure and properties of solid solutions. In the previous investigation a study was made of solid solutions of sodium chloride in silver chloride. In the present work solid solutions of lead bromide in lead chloride were studied. This system is especially suitable for the application of these experimental methods since the freezing point is a linear function of the composition,³ indicating the existence of a continuous series of solid solutions and the absence of either compound formation or a separation into two or more phases. The close proximity of the liquidus and solidus branches of the equilibrium diagram is of considerable assistance in the rapid attainment of a homogeneous solution when the molten mixture is cooled and annealed.

Experimental Part

The cell studied in this research can be represented by Pb/PbCl₂, PbBr₂/AgCl, Ag, where all the materials are solid and lead bromide is in solid solution with lead chloride. The cell reaction is



The preparation and purification of the substances employed in the cells as well as the experimental procedure are essentially the same as those described for the silver chloride-sodium chloride system,² with the following exceptions. Lead bromide was purified by bubbling dry hydrogen bromide, which was obtained by passing a mixture of hydrogen and bromine over a heated platinum catalyst, through the molten salt. The cell was prepared by pouring a molten solution of the lead salts into a Pyrex glass U-tube until the bend was completely filled. Before the melt solidified a silver wire was inserted into one arm of the tube about 1 cm. below the surface of the melt. It was then annealed at a temperature just below its melting point for about twenty-four hours. After slowly cooling to room

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² Wachter, *THIS JOURNAL*, **54**, 919 (1932).

³ Monkmeyer, *Neues Jahrb.*, **22**, 1 (1906).

temperature a 5-mm. layer of molten silver chloride was poured into the arm containing the silver wire and a layer of lead poured into the other arm. A tungsten wire made electrical contact to the lead electrode. The cells were then placed in a high temperature bath which could be varied from 200 to 300°. This bath was made up of a half liter wide-mouthed Pyrex Dewar flask filled with a low melting Wood's metal alloy. It was heated by means of an immersion resistance unit and stirred with a glass spiral.

TABLE I

E. M. F. IN VOLTS OF CELLS CONTAINING LEAD CHLORIDE OF VARIOUS MOLE FRACTIONS, N_1 , DILUTED WITH LEAD BROMIDE

$t, ^\circ\text{C.}$	E. m. f.	$t, ^\circ\text{C.}$	E. m. f.	$t, ^\circ\text{C.}$	E. m. f.
$N_1 = 1.000$		$N_1 = 0.781$		$N_1 = 0.539$	
201.5	0.4568	210.1	0.3829	220.8	0.3485
203.7	.4564	225.9	.3792	230.0	.3464
208.5	.4549	237.2	.3776	233.1	.3460
210.5	.4548	262.8	.3723	236.8	.3450
213.6	.4539	266.2	.3720	244.5	.3436
218.0	.4526	270.4	.3704	247.5	.3433
223.0	.4512	285.6	.3673	255.4	.3412
225.3	.4512	292.9	.3658	258.5	.3403
232.3	.4487	$N_1 = 0.752$		264.4	.3395
234.1	.4486	211.3	0.3794	268.7	.3391
238.9	.4474	213.3	.3788	271.8	.3378
243.2	.4468	264.9	.3688	279.1	.3367
245.9	.4462	275.3	.3669	281.7	.3357
250.4	.4454	286.0	.3648	288.5	.3344
253.7	.4446	287.5	.3644	290.7	.3337
261.6	.4424	290.6	.3636	$N_1 = 0.303$	
269.9	.4408	$N_1 = 0.680$		210.4	0.3286
272.6	.4400	220.4	0.3684	221.6	.3258
279.5	.4383	230.0	.3668	223.5	.3260
284.6	.4373	237.1	.3655	226.1	.3254
287.7	.4366	245.1	.3641	228.1	.3248
289.3	.4357	247.7	.3635	234.9	.3235
295.4	.4350	256.0	.3620	237.7	.3227
298.5	.4341	264.4	.3603	240.4	.3225
$N_1 = 0.892$		271.8	.3586	248.4	.3207
210.7	0.4057	281.7	.3576	259.1	.3184
218.9	.4047	287.0	.3560	$N_1 = 0.200$	
223.7	.4039	287.9	.3548	210.4	0.3206
230.9	.4021	290.7	.3550	223.7	.3178
237.4	.4011			228.1	.3168
247.8	.3987			235.2	.3151
256.9	.3971			237.6	.3145
264.8	.3955			240.4	.3144
268.9	.3948			248.7	.3128
				258.8	.3101

This construction insured a uniform temperature throughout the system. Within two days equilibrium was attained and potential measurements were made by means of a Leeds and Northrup Type K potentiometer in conjunction with a high sensitivity galvanometer. The composition of the cells was varied from mole fraction 0.200 to 1.000 of lead chloride.

The results of the e. m. f. measurements for eight different compositions are given in Table I and plotted in Fig. 1. The values for pure lead

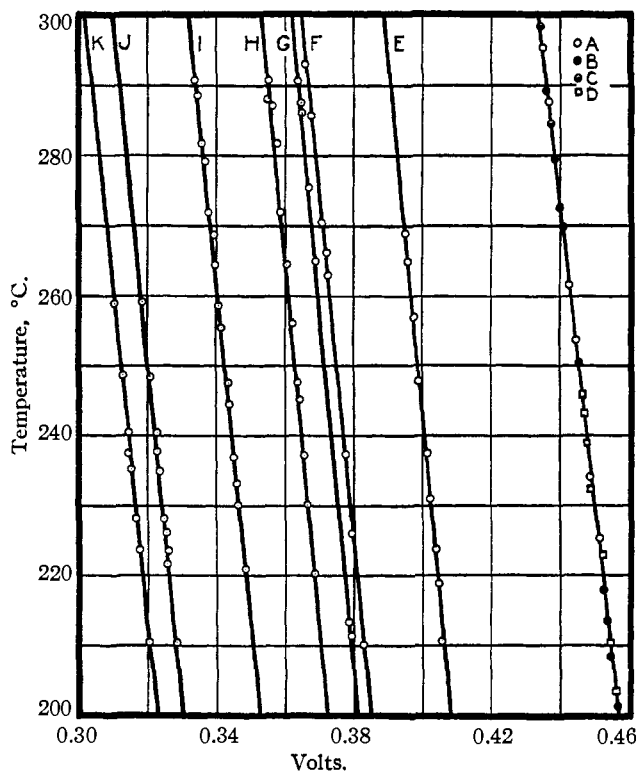


Fig. 1.—Temperature variation of e. m. f. of cells containing different lead chloride-lead bromide solid solutions. Mole fraction of lead chloride in A, B, C and D is 1.000, E is 0.892, F is 0.781, G is 0.752, H is 0.680, I is 0.539, J is 0.303 and K is 0.200.

chloride represent four different cells, indicated in the figure by points of different styles. The average deviation of the points from the straight lines of the plot is less than 0.3 mv. These curves were easily reproduced ascending and descending the temperature scale even after several weeks in the high temperature bath. From a large scale plot of Fig. 1 the e. m. f. at temperatures of 200, 250 and 300° were read off for each solution and plotted against the composition. This is given in Fig. 2.

Discussion of Results

The thermodynamic calculations employing the data obtained for this system were made as described in the previous paper on the silver chloride-sodium chloride system.² The results of the calculations are given in Table II and the activities, a_1 and a_2 , of both constituents of the solid solutions plotted against the mole fraction, N_1 , of lead chloride in Fig. 3. The broken diagonal lines in the figure represent Raoult's law. ΔF is the free energy of the cell reaction; $\Delta \bar{F}_1$, the partial molal free energy of lead chloride; ΔH , the change in heat content of the cell reaction; $\Delta \bar{H}_1$, the partial molal heat content of lead chloride; ΔS , the entropy change of the

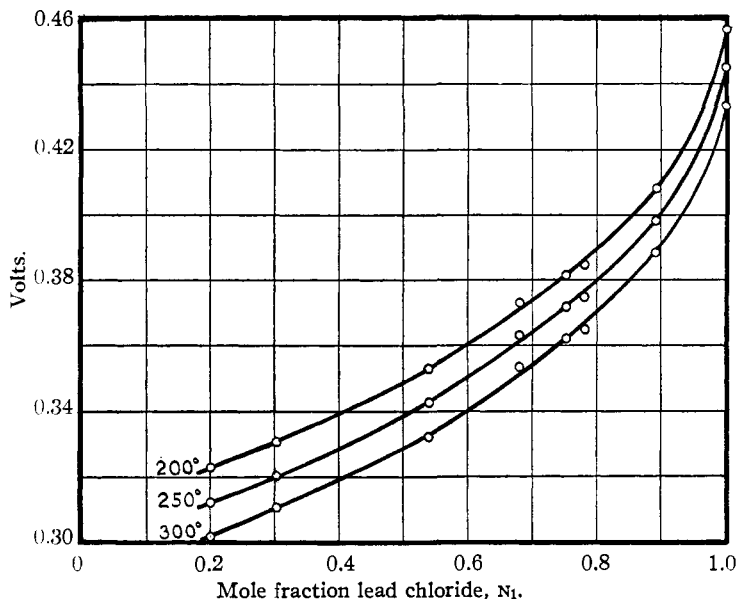


Fig. 2.—Change in e. m. f. of cells upon dilution of lead chloride with lead bromide at 200, 250 and 300°.

cell reaction; $\Delta \bar{S}_1$, the partial molal entropy; and a_1 and a_2 , the activity of lead chloride and lead bromide, respectively. The partial molal quantities and the activity of lead chloride in its solutions were calculated taking the pure salt as the standard state. Pure lead bromide was taken as the standard state for lead bromide in the solid solutions.

The activity curves of Fig. 3 are particularly interesting. It is observed that when lead bromide is added to lead chloride an enormous decrease in the activity of the latter occurs. Below mole fraction 0.9 of lead chloride its activity is less than 0.1. This large negative deviation from Raoult's law is most probably ascribable to a very strong tendency toward compound formation. On the other hand, the activity curve for lead bromide

TABLE II
THERMODYNAMIC PROPERTIES OF LEAD CHLORIDE DILUTED WITH LEAD BROMIDE^a

n_1	$-\frac{dE_dT}{(mv./deg.)}$	$-\Delta s$ (cal./deg.)	$\frac{\Delta \bar{s}_1}{(cal./deg.)}$	$-\Delta H$ (cal.)	$-\Delta \bar{H}_1$ (cal.)
1.000	0.234	10.80	0	26200	0
0.900	.199	9.19	1.61	23270	2930
.800	.184	8.49	2.31	21980	4220
.700	.194	8.95	1.85	21490	4710
.600	.197	9.09	1.71	20930	5270
.500	.202	9.32	1.48	20520	5680
.400	.202	9.32	1.48	20070	6130
.300	.200	9.23	1.57	19620	6580
.200	.215	10.2	0.60	19740	6460
200°					
n_1	E (volts)	$-\Delta F$ (cal.)	$-\Delta \bar{F}_1$ (cal.)	α_1	α_2
1.000	0.4570	21090	0	1.000	0
0.900	.4099	18920	2170	0.0991	0.000014
.800	.3892	17960	3130	.0359	.00561
.700	.3737	17250	3840	.0168	.0575
.600	.3604	16630	4460	.00873	.195
.500	.3490	16110	4980	.00500	.394
.400	.3393	15660	5430	.00310	.585
.300	.3304	15250	5840	.00200	.724
.200	.3228	14900	6190	.00138	.818
250°					
1.000	0.4452	20550	0	1.000	
0.900	.4011	18510	2040	0.141	
.800	.3800	17540	3010	.0554	
.700	.3636	16780	3770	.0268	
.600	.3503	16170	4380	.0148	
.500	.3388	15640	4910	.00891	
.400	.3293	15200	5350	.00584	
.300	.3203	14780	5770	.00392	
.200	.3120	14400	6150	.00271	
300°					
1.000	0.4336	20010	0	1.000	
0.900	.3900	18000	2010	0.171	
.800	.3708	17110	2900	.0785	
.700	.3543	16350	3660	.0403	
.600	.3407	15730	4280	.0232	
.500	.3288	15170	4840	.0143	
.400	.3191	14730	5280	.00968	
.300	.3104	14330	5680	.00681	
.200	.3013	13910	6100	.00470	

^a 1 volt-equivalent = 23,074 cal.

at first shows a small positive deviation when lead chloride is added which, beyond mole fraction 0.4 of lead chloride, rapidly becomes a larger and larger negative deviation. From the large downward pull on the curves in

the region of solid solutions most concentrated in lead chloride, one would suspect the existence of a rather strong compound or of a regular arrangement of the bromide ions in the lead chloride crystal lattice. Such a factor would reduce the activities of both components and would tend to annul the effect of any factor which produces abnormally large activities. This striking result is entirely unpredictable from the freezing point diagram, which gives no indication of any abnormality.

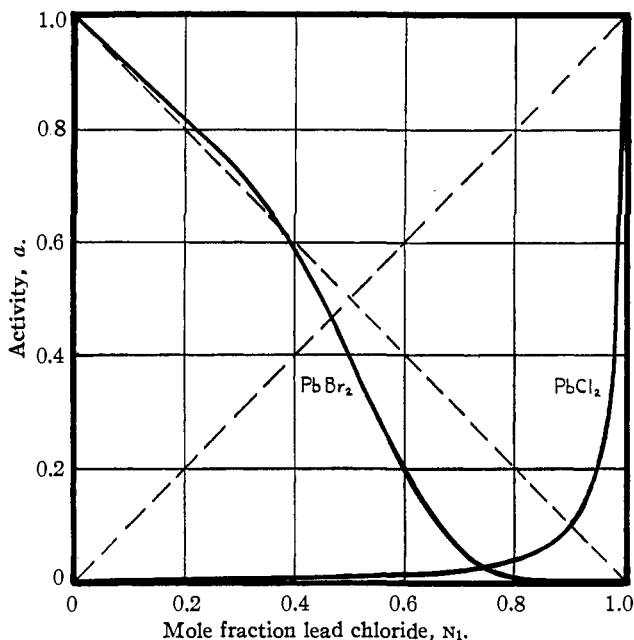


Fig. 3.—Activity curves for the system lead chloride-lead bromide at 200°.

Measurements of the partial vapor pressures of this system by Jellinek and Bolubowski,⁴ who found Raoult's law obeyed by the vapor pressures at temperatures from 660 to 740°, indicate that at these high temperatures the compound is completely dissociated and that the constituents form ideal liquid solutions. Salstrom and Hildebrand,⁵ making an electrochemical investigation of molten solutions of these fused salts at temperatures from 450 to 550° and at mole fractions 1 to 0.45 of lead bromide, found that the activities in this range are less than the simple mole fractions. Although, making allowance for the differences in temperature, the values they give at mole fractions 0.5 and 0.45 of lead bromide are in good agreement with those herein obtained, those given at higher concentrations of lead bromide are in marked disagreement.

⁴ Jellinek and Bolubowski, *Z. physik. Chem.*, Abt. A, **147**, 461 (1930).

⁵ Salstrom and Hildebrand, *THIS JOURNAL*, **52**, 4641 (1930).

For the existence of any one arrangement of foreign ions in a crystal lattice to be more probable than any other of the infinite variety of possible arrangements, that distribution must give the most stable solution. Tammann⁶ has strongly supported the assumption which originated with him that a regular or "normal" distribution is to be expected in solid solutions and that the most stable arrangements can be represented as multiples of one-eighth mole of one of the two constituents. Thermodynamically, the greatest total free energy change of solution must occur at some composition which can be expressed as a multiple of one-eighth mole in order

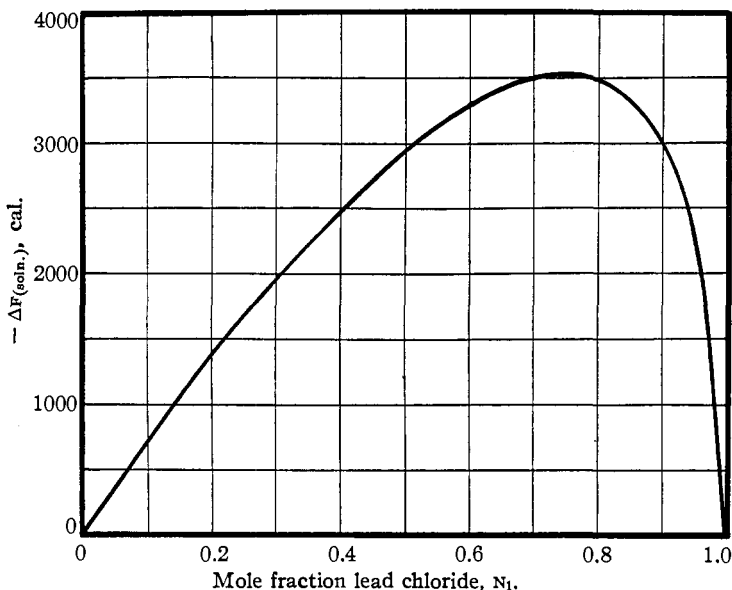


Fig. 4.—Variation with composition of the free energy change for the reaction $N_1 \text{PbCl}_2(s) + N_2 \text{PbBr}_2(s) = N_1 \text{PbCl}_2 \cdot N_2 \text{PbBr}_2(s, \text{soln.})$ at 200° .

to be in accord with the above views. The total free energy of solution as employed here signifies the free energy change involved in the formation of one mole of solution from the pure constituents at a given temperature. It can be calculated from the partial molal free energies by the relationship $\Delta F_{(soln.)} = N_1 \Delta \bar{F}_1 + N_2 \Delta \bar{F}_2$. When this is done for the lead chloride-lead bromide system and the results are plotted against the mole fraction of lead chloride, as in Fig. 4, one observes a rather sharp maximum at six-eighths mole of lead chloride. Tammann's conclusions are based upon the striking discontinuities observed in variations of the intensity of chemical action with the concentration. These resistance limits occur at compositions which can be expressed as multiples of one-eighth mole of one of the two constituents. In accordance with these ideas one would predict

⁶ Tammann, *Z. anorg. allgem. Chem.*, **107**, 1 (1919).

that the lead chloride-lead bromide solid solutions would exhibit a discontinuity in chemical action at mole fraction 0.75 of lead chloride.

Summary

1. The energy changes of solid lead chloride upon dilution with lead bromide have been determined at mole fractions of lead chloride varying from 1 to 0.200, between the temperatures of 200 and 300°.

2. The solid solution containing 0.75 mole of lead chloride is shown to be the most stable.

3. The thermodynamic properties of these solutions are considered compatible with the existence of a regular arrangement of bromide ions in the lead chloride lattice.

4. A discontinuity in chemical action of the solid solutions at mole fraction 0.75 of lead chloride is predicted.

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A NEW USE OF THE VACUUM TUBE IN ELECTROMETRIC TITRATIONS. I. POLARIZATION OF PLATINUM ELECTRODES IN OXIDATION AND REDUCTION REACTIONS¹

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Introduction

Since the advent of the radio it is generally known that electrons are drawn across the tube by means of a positive potential impressed on the plate. The plate current in the tube is controlled largely by means of a grid which is placed between the filament and the plate. If a positive potential is placed on the grid, electrons flow to the plate in greater number, and if a negative potential is placed on the grid fewer electrons will flow to the plate, lowering the plate current. Goode² utilized the fact that the grid will not pick up electrons when it is charged negatively with respect to the filament and connected the indicator electrode directly to the grid. This same principle has been employed by other investigators.³ In all of the investigations reported, in which a single electron tube was employed, it has been necessary to plot $\Delta E/\Delta v$ or to plot galvanometer deflections in place of ΔE to obtain the equivalence point. Daniels, Mathews and

¹ Paper presented before the Buffalo meeting of the American Chemical Society.

² Goode, *THIS JOURNAL*, **44**, 26 (1922).

³ Calhane and Cushing, *J. Ind. Eng. Chem.*, **15**, 1118 (1923); Treadwell, *Helv. Chim. Acta*, **8**, 89 (1925); Williams and Whitenack, *J. Phys. Chem.*, **31**, 519 (1927).