Vapor Pressure of the Cadmium Chloride–Lead Chloride System

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Vapor pressures of mixtures in the binary system $CdCl_2$–$PbCl_2$ were measured by the static-pressure method. Vapor pressure isotherms showed positive and negative deviations from additivity, with a pronounced discontinuity at the composition $9\,CdCl_2 \cdot 2\,PbCl_2$. This suggests that a mixed-salt complex of this composition is present in the molten mixtures. Vapor pressure equations for all mixtures of $CdCl_2$ and $PbCl_2$ investigated, and derived values of heat of vaporization and free energy of vaporization for high-purity $CdCl_2$ and $PbCl_2$, are presented.

THE PHYSICAL properties of salts and salt mixtures have long been of interest to researchers. Bloom (*2*) states that "Most investigations since the time of Faraday have been concerned with investigation of properties of mixtures, largely because they are used in practical applications instead of pure salts because of their lower melting point. Their properties lead in many cases to the speculation that complex ions are formed."

The research reported here is part of a U.S. Bureau of Mines investigation of vapor pressures and vapor compositions at the Rolla Metallurgy Research Center. The materials studied have been selected from the bromides, chlorides, and iodides of cadmium, lead, tin, and zinc, and their common anion mixtures.

Reports from other laboratories (*3, 4, 12, 13, 20*) have dealt with certain aspects of the $CdCl_2$-$PbCl_2$ system. Herrmann (*12*), Sandonnini (*20*), and Il'yasov and coworkers (*13*) have studied the phase diagram; Bloom and Heymann (*3*) the electrical conductivity and activation energy of ionic migration; and Boardman and coworkers (*4*) the density and molar volume for this system. Vapor pressures are available for mixtures containing either $CdCl_2$ or $PbCl_2$ as one of the components, but not of $CdCl_2$-$PbCl_2$ mixtures.

Fairly consistent vapor pressure results have been reported for the pure chlorides of Cd and Pb (*1, 6, 7, 14-19*). Kelley (*15*) evaluated many of the earlier data in 1935, and listed the results he considered the most reliable; our results agree with those of Barton and Bloom (*1*). Table I lists the thermodynamic functions for $CdCl_2$ and $PbCl_2$ obtained in this investigation and as reported by Barton and Bloom (*1*) and Kelley (*15*).

Vapor pressure measurements of solutions or mixtures provide one of the few direct methods of determining the heats and free energies of vaporization, although to evaluate the results fully, data on the vapor and melt compositions are needed. However, such corollary data were not available for $CdCl_2$-$PbCl_2$ mixtures; the data in the present study were evaluated with Raoult's law.

A numerical analogy (*9*) to the "sigma plot" method described by Kelley (*15*) was used to obtain the heat and free energy of vaporization by the second law of thermodynamics for the pure salts. This method was also used to obtain the vapor pressure equation parameters for each mixture in the absence of data on the heat capacity, vapor density, and other pertinent data, such as vapor species and their relative proportions for the $CdCl_2$-$PbCl_2$ mixtures investigated. The heat capacities for the $CdCl_2$-$PbCl_2$ mixtures were estimated by assuming that the heat capacities (Table I) of the pure components are additive.

EXPERIMENTAL PROCEDURE

The experimental procedures for the preparation of the pure salts from reagent grade materials by triple distillation, mixing of the pure salts, and the measurement of vapor pressures by an automatic static pressure method have been described in detail (*8, 9*).

RESULTS

The results of all the experimental vapor pressure observations obtained on 10 compositions of the $CdCl_2$-$PbCl_2$ system are summarized in Table II. For each composition data are presented for the mean of four to six runs. The last two columns show the parameters derived in the data processing. These parameters, also plotted in Figure 1 as a function of composition, can be used to calculate the pressure observed at a selected temperature in the range given by substitution in Equation 1:

$$\log_{10} P_{(\text{cm. Hg})} = -\frac{A}{2.303RT} + \frac{\Delta C_p}{R}\log_{10} T - \frac{B}{2.303R} \qquad (1)$$

Table I. Thermodynamic Functions for $CdCl_2$ and $PbCl_2$

	Phase Change: Liquid → Gas			
Reference	ΔC_p, cal./mole-° K.	Boiling point, ° K.	ΔH, cal./mole	$\Delta G°$, cal./mole
			$CdCl_2$	
This investigation	-10^a	1230	$41{,}931 \pm 64 - 10T^b$	$41{,}931 \pm 64 + (23.03 \log_{10} T - 105.23 \pm 0.06)T^b$
Barton and Bloom (*1*)	-10	1233	$42{,}000 - 10T$	$42{,}000 + (23.0 \log_{10} T - 105.36)T^c$
Kelley (*15*)	-10	1240	$42{,}260 - 10T$	$42{,}260 + (23.0 \log_{10} T - 105.23)T$
			$PbCl_2$	
This investigation	-13.2^a	1222	$45{,}821 \pm 116 - 13.2T^b$	$45{,}821 \pm 116 + (30.39 \log_{10} T - 131.33 \pm 0.11)T^b$
Barton and Bloom (*1*)	-13.2	1224	$46{,}500 - 13.2T$	$46{,}500 + (30.4 \log_{10} T - 131.99)T^c$
Kelley (*15*)	-13.2	1227	$45{,}800 - 13.2T$	$45{,}800 + (30.4 \log_{10} T - 131.22)T$

[a] ΔC_p value from Kelley (*15*). [b] Limits for 95% confidence. [c] Barton and Bloom (*1*) presented vapor pressure equations for $CdCl_2$ and $PbCl_2$, from which respective free energies were calculated.

Table II. Vapor Pressure Data for $CdCl_2$-$PbCl_2$ System

Composition, Mole %	No. of Runs	No. of Samples	No. of Observations	Temp. Range, ° K.	Boiling Point, ° K.	$\frac{A}{2.303R}$	$\frac{-B}{2.303R}$
$CdCl_2$	6	3	416	922–1248	1230	9164 ± 14	24.88 ± 0.01
91.4 $CdCl_2$–8.6 $PbCl_2$	5	3	354	908–1245	1229	9038 ± 14	25.25 ± 0.01
83.3 $CdCl_2$–16.7 $PbCl_2$	4	3	252	919–1248	1231	9337 ± 20	25.84 ± 0.02
82.0 $CdCl_2$–18.0 $PbCl_2$	4	2	243	930–1232	1234	9423 ± 18	26.01 ± 0.02
82.0 $CdCl_2$–18.0 $PbCl_2$[a]	4	2	343	925–1248	1234	9453 ± 21	26.03 ± 0.02
80.0 $CdCl_2$–20.0 $PbCl_2$	6	3	336	917–1283	1233	9280 ± 16	25.96 ± 0.01
71.7 $CdCl_2$–28.3 $PbCl_2$	6	4	385	912–1240	1232	9074 ± 28	26.20 ± 0.03
60.3 $CdCl_2$–39.7 $PbCl_2$	5	3	328	910–1241	1232	9240 ± 17	26.95 ± 0.02
45.0 $CdCl_2$–55.0 $PbCl_2$	4	2	260	912–1243	1231	9583 ± 39	27.94 ± 0.04
21.1 $CdCl_2$–78.9 $PbCl_2$	4	2	264	924–1245	1224	10013 ± 16	29.48 ± 0.02
$PbCl_2$	6	4	373	914–1249	1222	10014 ± 25	30.58 ± 0.02

[a] Results obtained for two additional samples of this composition 9 months after initial measurements were completed.

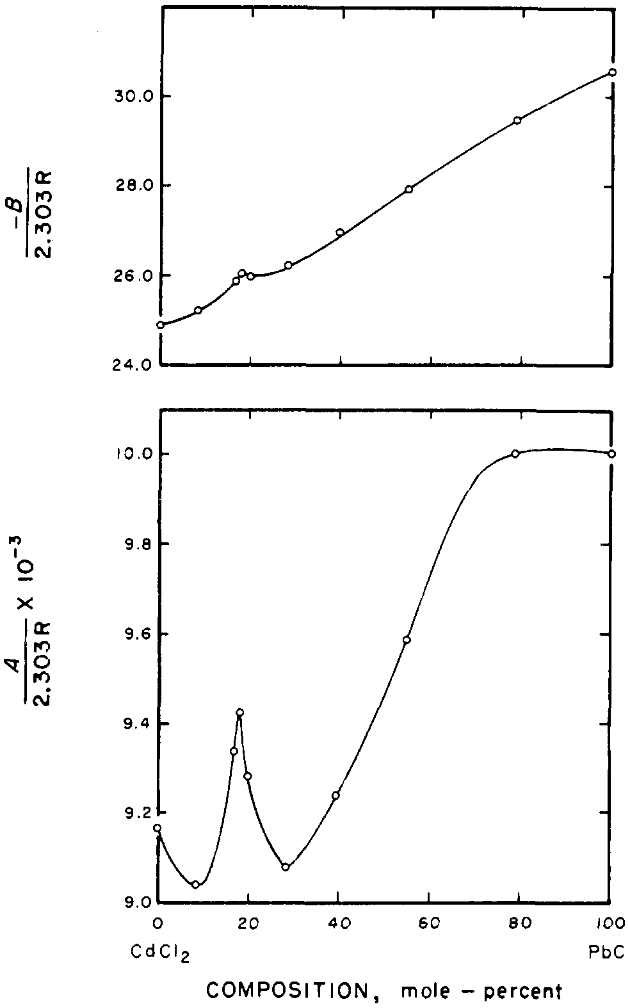

Figure 1. Parameters for vapor pressure equations

where

P = vapor pressure at temperature T, cm. Hg
R = gas constant, 1.9872 cal. per mole-° K.
T = temperature, ° K.
ΔC_p = change in heat capacity upon vaporization, cal. per mole-° K.

Cadmium Chloride. The published results and the results of this investigation are summarized in Table III. There is considerable lack of agreement as to the correct boiling temperature of $CdCl_2$, and our value is lower than those previously reported. Despite this discrepancy, good agreement is found for the value of ΔH_o except for the work of Maier (*18*).

Table III. Summary of Boiling Points and Heats of Vaporization at 0° K. for $CdCl_2$ and $PbCl_2$

Reference	Cadmium Chloride		Lead Chloride	
	Boiling point, ° K	ΔH_o, kcal./mole	Boiling point, ° K.	ΔH_o, kcal./mole
This investigation, 1968	1230	41.93	1222	45.82
Keneshea and Cubicciotti (*16*), 1964	1237[a]	42.77		
Brewer and coworkers (*6*), 1963	1235			
Barton and Bloom (*1*), 1956	1233	42.00	1224	46.50
Rossini and coworkers (*19*), 1952	1253	41.93[b]		45.80[b]
Kubaschewski and Evans (*17*), 1951	1252[a]	42.46[c]	1215[a]	45.76[c]
Kelley (*15*), 1935	1240	42.26	1227	45.80
Jellinek and Golubowski (*14*), 1930			1227	
Maier (*18*), 1925	1243	38.87[b]	1227	45.71[b]
Eastman and Duschak (*7*), 1919			1218	45.35[d]

[a] As determined from their vapor pressure equation. [b] Converted to ΔH_o by subtracting product of boiling temperature and ΔC_p from ΔH_v. [c] Presented vapor pressure equation, from which ΔH_o was determined by multiplying their coefficient, A, by R ln 10. [d] Obtained by using our method and their data.

The equation expressing the vapor pressure for $CdCl_2$ as a function of temperature, in the temperature range 922° to 1248° K., as determined in this investigation, is:

$$\log_{10} P_{(\text{cm. Hg})} = \frac{-9{,}164}{T} - 5.03 \log_{10} T + 24.88 \qquad (2)$$

Lead Chloride. The results of earlier work and those obtained in this investigation are in good agreement (Table III). Our value for ΔH_o obtained by the second-law evaluation is lower than Barton and Bloom's (*1*) value by 0.68 kcal., a difference of less than 2%.

The equation expressing the vapor pressure for $PbCl_2$ as a function of temperature, in the temperature range 914° to 1249° K., as determined in this investigation, is:

$$\log_{10} P_{(\text{cm. Hg})} = \frac{-10{,}014}{T} - 6.65 \log_{10} T + 30.58 \qquad (3)$$

$CdCl_2$-$PbCl_2$ System. The analysis of the vapor pressure data for molten $CdCl_2$-$PbCl_2$ mixtures obtained in this research leaves little doubt that this liquid system is fundamentally different from the $SnCl_2$-$ZnCl_2$ system and from other mixtures we have investigated.

The temperatures at which the various mixtures attain selected vapor pressure levels are plotted in Figure 2 as six curves showing the temperatures required for the mixtures to exert vapor pressures of 1, 5, 10, 20, 50, and 76 cm. of Hg pressure, respectively. Each curve has a prominent feature in the composition range from 10 to 30 mole % $PbCl_2$, which has the appearance of a cusp peaking near the composition 9 $CdCl_2 \cdot 2$ $PbCl_2$. The prominence is greatest in the lowest of these isobars.

In binary systems in which both components are volatile, the vapor is richer in the more volatile component than is the condensed phase, as a consequence of Raoult's law. To estimate the changed ideal vapor compositions corresponding to the changed melt compositions, vapor compositions were calculated by successive approximations (*16*). This analysis indicated that no correction to the data was necessary, since the largest estimated decrease in mole-fraction $PbCl_2$ for a 10-gram sample of mixture was about 0.002 in the experimental temperature and compositional ranges studied.

Vapor pressures at selected temperatures, ranging from 950° to 1250° K. in steps of 150°, are plotted in Figure 3 as a function of melt composition. Appreciable variation from the straight line representing Raoult's law results upon addition of $PbCl_2$ to $CdCl_2$. Departures of the observations from the straight-line values exceed 10% at some points. The deviations are proportionately higher at low temperatures, and a very pronounced discontinuity is observed near the molar ratio of $9\,CdCl_2 \cdot 2\,PbCl_2$. At higher temperatures the relative deviations are smaller, but they persist in revealing the discontinuity at the same composition.

The two derived parameters, $A/2.303R$ and $-B/2.303R$, plotted as functions of composition in Figure 1, also have sharp peaks in the curves at 82% $CdCl_2$–18% $PbCl_2$.

DISCUSSION

Vapor pressure data for mixed salt systems do not abound in the literature, and results of the type presented for the mixtures in the $CdCl_2$-$PbCl_2$ system have not previously

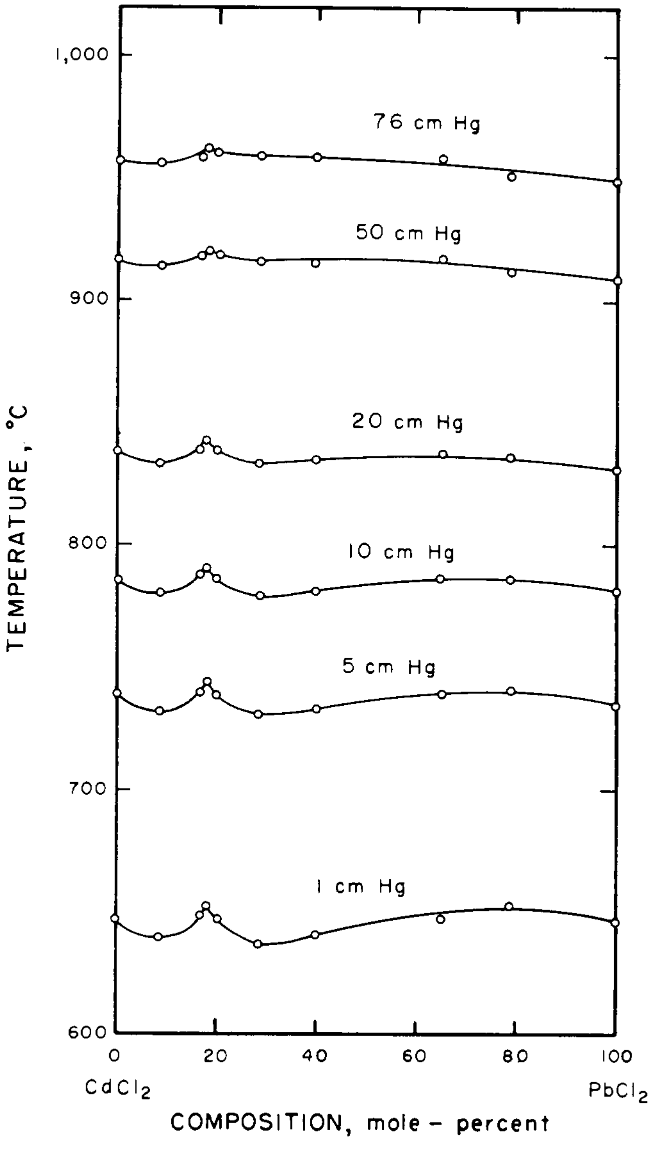

Figure 2. Plot of observed temperatures at selected vapor pressures

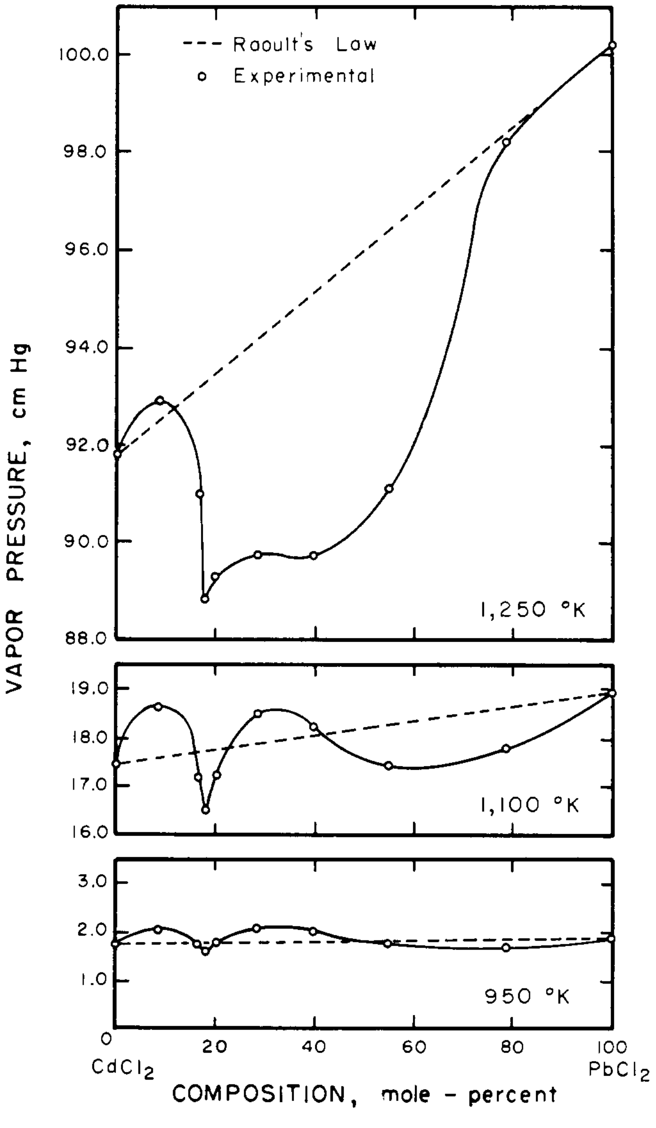

Figure 3. Vapor pressure as a function of composition at 950°, 1100°, and 1250° K.

appeared. In the $SnCl_2$-$ZnCl_2$ system (*9*) positive and negative deviations of the vapor pressure from additivity were observed at 800° K. At higher temperatures the positive deviations diminished until, at 1000° K., all observed or calculated pressures of mixtures were lower than predicted by Raoult's law. In none of the curves was there any evidence of discontinuities of the type observed for the $CdCl_2$-$PbCl_2$ system.

Heymann and associates investigated the $CdCl_2$-$PbCl_2$ molten salt system, and other ionic liquid systems, by measuring viscosity (*11*), molar volume (*4*), equivalent conductivity (*3, 11*), and surface tension (*5*). They reported that:

Observed positive deviations of the equivalent conductivity isotherm from additivity suggest an increase in the ionic character of the melt on mixing. Contraction in volume on mixing observed for the system is probably caused by an increase in the tightness of packing in the melt as a result of its increased ionic character. Small negative deviations in the viscosity isotherm are characteristic of a near-ideal system. Positive deviations from additivity in the surface tension isotherms could be due to formation of complex ions on mixing or to constitutional changes in one or both of the pure components on mixing.

Correlating observations on this system with other binary systems in which either $CdCl_2$ or $PbCl_2$ was a component, Boardman, Palmer, and Heymann (*5*) deduced that autocomplexes occur in pure molten cadmium chloride which dissociate upon addition of lead chloride, causing the mixtures to be more ionic. Cadmium chloride crystallizes in a layered structure consisting of octahedra of $CdCl_6$ held together by van der Waals forces, and they postulated that two-dimensional complexes exist in the liquid state. The fact that the surface tension of pure $CdCl_2$ is markedly lower than that of calcium chloride, although their cation radii are approximately equal, is consistent with the autocomplex theory.

Association of molecules in the vapor phase is another form of nonideal behavior that might also lead to deviations from Raoult's law for ideal mixtures. Such association has been reported; the stable complexes $KPbCl_3$ and $KRbCl_3$ were found (*10*) in the vapor phases during study of the systems KCl-$PbCl_2$ and KCl-$RbCl_2$.

Our vapor pressure isotherms show a positive deviation from additivity as $PbCl_2$ is added to pure $CdCl_2$ to the amount of 8%. As the mole per cent of the second phase is increased to 18; the vapor pressure isotherm dips to a value lower than that of $CdCl_2$. The curve at this point appears to have a discontinuity or reversal of slope, which may indicate the composition of a mixed-salt complex.

CONCLUSIONS

Precise vapor pressures have been determined for selected compositions in the $CdCl_2$-$PbCl_2$ system, and thermodynamic functions calculated for high-purity $CdCl_2$ and $PbCl_2$.

The results suggest the existence of a complex in molten mixtures of cadmium chloride and lead chloride of the approximate composition 9 $CdCl_2 \cdot 2\ PbCl_2$.

The relatively narrow range in composition over which these events are observed suggests that features of this type may occur in other mixed-salt systems and may be overlooked because of the insensitivity of the property measured—e.g., surface tension—or of the span in composition of samples taken from a system.

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