

empirically in the manner used by Kim *et al.* (2). A distribution coefficient (β) and reduced temperature (T^*) were defined as follows:

$$\beta = R_2/R_1 \quad (1)$$

and

$$T^* = (T - T_{\text{LCST}})/(T_{\text{type } K} - T_{\text{LCST}}) \quad (2)$$

The resulting distribution coefficients and reduced temperatures are tabulated in Table II. Both the experimental distribution coefficients and smoothed distribution coefficients are presented in Table II. The smoothed distribution coefficients were determined from a modified version of a least squares computer program. A regular minimizing type of least squares program produces a polynomial fit of the data with the minimal standard deviation from the experimental data regardless of the possibility or impossibility of maxima or minima in the experimental variables. The modified version of the least squares program, which was used here, was biased by the authors' feeling that the largest value of β should be at the type *K* temperatures. The resulting smooth data presented in Table II and shown in Figure 2 fit the data with a standard deviation of ± 0.054 . Figure 2 appears to indicate that the distribution coefficient is not a function of the overall heavy hydrocarbon composition in the cell. If the data presented here on the separational effect on *n*-hexadecane and *n*-eicosane are compared with those of Kim *et al.* (2) on *n*-nonadecane and *n*-eicosane, evidently the separational effect is appreciably greater in the *n*-hexadecane-*n*-eicosane system. Thus the separational effect increases with an increase in the carbon number difference between the two heavy hydrocarbons.

NOMENCLATURE

- L_1 = liquid phase less rich in ethane
 L_2 = liquid phase more rich in ethane

- LCST = lower critical solution temperature (the L_1 phase is critical with the L_2 phase in the presence of a vapor phase)
 R = molar ratio of *n*-hexadecane to *n*-eicosane
 R_1 = molar ratio of *n*-hexadecane to *n*-eicosane in the L_1 phase
 R_2 = molar ratio of *n*-hexadecane to *n*-eicosane in the L_2 phase
 T = temperature in °C.
 T^* = reduced temperature defined in Equation 2
 T_{LCST} = temperature of LCST critical phenomenon for the *n*-hexadecane-*n*-eicosane composition charged to the cell
 $T_{\text{type } K}$ = temperature of type *K* critical phenomenon for the *n*-hexadecane-*n*-eicosane composition charged to the cell
Type *K* = type *K* singular point (the L_2 phase is critical with the vapor in the presence of the L_1 phase)
 V = vapor phase
 X = mole fraction *n*-hexadecane on ethane-free basis
 β = distribution coefficient defined in Equation 1

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Thermodynamic Properties of Molten Mixtures of CdCl_2 and PbCl_2

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The enthalpies of mixtures in the system CdCl_2 - PbCl_2 were determined over the temperature range 400° to 950° K. relative to 300° K. Measurements were made by drop calorimetry on compositions corresponding to mole fractions of PbCl_2 of 0.8808, 0.7749, 0.6468, 0.4277, and 0.2008 in addition to the pure components. Heat capacities averaged 20.4 and 19.7 cal. per mole -° K. for solid PbCl_2 and CdCl_2 , respectively, and 26.6 cal. per mole -° K. for each in the liquid state. Enthalpies of fusion were 7.59 ± 0.2 kcal. per mole for CdCl_2 at 841° K. and 4.2 ± 0.1 kcal. per mole for PbCl_2 at 774° K. Entropies were calculated from the enthalpy data for the components and mixtures. The experimental data and derived quantities indicate the system is ideal within an estimated experimental accuracy of $\pm 1.5\%$.

THE PURPOSE of this work was to determine the enthalpies and entropies for mixtures in the binary system PbCl_2 - CdCl_2 over a substantial temperature range.

The enthalpies were determined experimentally by drop calorimetry. The entropies were derived from the enthalpy measurements of the mixtures; permissible in this system

since its phase diagram (9) shows no solid solutions or intermediate compounds.

Enthalpies of mixing may be obtained by taking the difference between the enthalpy of a mixture measured directly and the enthalpy of the pure components at the same temperature. This technique is not as well suited for precise determinations of the enthalpies of mixing as is the differential calorimeter method pioneered by Kleppa (7), but it does have the significant advantage of yielding information over the complete temperature range in addi-

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tion to permitting calculation of the entropies of mixing in simple eutectic systems.

Bloom and Tricklebank (1) have also determined enthalpies in the PbCl_2 - CdCl_2 system using a diphenyl ether drop calorimeter. They limited their investigation to three mixtures and temperatures above the liquidus; therefore, they were unable to determine entropies. In this work, data for five compositions and for temperatures between 400° and 950° K. are reported; entropies relative to 300° K. have been calculated. With entropies and enthalpies available, the ideality of the system was determined.

EXPERIMENTAL PROCEDURE

The PbCl_2 used was Baker analyzed reagent reported to be 99.96% PbCl_2 ; the CdCl_2 used (K & K Laboratories) was reported to be 99.99% CdCl_2 . No additional purification was deemed necessary.

Seven platinum capsules were made from chemically pure Pt tubing (Englehard Industries). The tubing was 0.25-inch I. D. with a 0.010-inch wall thickness. Each capsule was 1.5 inches long, crimped flat at one end, and welded shut before filling. The salts were melted in a platinum crucible and then poured into the capsule. In filling a capsule, the liquid CdCl_2 was first introduced followed by the molten PbCl_2 . A small glass stopper was inserted into the open end of the capsules immediately after filling with each salt to prevent reactions with the air. The amount of each salt was determined accurately by weighing the capsule before and after filling with each salt. Table I summarizes the weights of each capsule and salt. After the capsule was filled, the other end of it was crimped flat to just above the solidified salts to minimize air entrapment, and it was sealed by careful welding. The capsule was weighted before and after welding; in no case was a change in weight observed.

In each enthalpy determination, a capsule was heated in an electric tube furnace to a specified temperature. The furnace was allowed to reach thermal equilibrium at the desired temperature before dropping the capsule into it. Initially, this took about 10 hours. The temperature was measured at the top and bottom of the zone in which the sample was held. A Pt vs. Pt + 10% Rh thermocouple calibrated by the National Bureau of Standards was used for this measurement. The temperature variation within this zone was adjusted to within 1° C. by trial adjustments of Variacs regulating power to the three separately controlled furnace windings. The capsule was dropped in the furnace and the thermocouple placed in the furnace with the bead in contact with the capsule. The sample was soaked in the furnace for 2 hours before being dropped into the calorimeter.

The calorimeter used was an isothermal diphenyl ether calorimeter designed and calibrated by Kurtz (8). The temperature within the calorimeter was measured with a platinum resistance thermometer calibrated by the National Bureau of Standards and was 300.0° K. This is in excellent

agreement with the temperature for the triple-point of diphenyl ether reported by Furukawa *et al.* (3), which is $300.03 \pm 0.01^\circ$ K.

The central tube through which the capsule dropped from the furnace into the calorimeter was closed by a water cooled copper gate which was never open longer than 3 seconds.

The capsule in cooling from the furnace temperature to 300.0° K. melts some of the diphenyl ether previously frozen around the central well of the calorimeter. The consequent volume expansion upon melting (proportional to the amount of heat liberated by the capsule) was measured by the weight of mercury displaced from the constant volume system.

The calorimeter constant was determined by Kurtz (8) to be 19.32 ± 0.09 cal. per gram of mercury displaced. This value is somewhat higher than that reported by others—for example, Morries *et al.* (10) report a value of 19.03 cal. per gram of mercury displaced. The calorimeter constant used here represents the average of 10 runs over the complete temperature range and is believed to be the best value for this apparatus. The calibration runs were conducted using both an empty platinum capsule and a capsule filled with Baker analyzed powdered aluminum oxide. Greater consistency was obtained with the capsule filled with aluminum oxide. The enthalpies relative to 300° K. of platinum and aluminum oxide were calculated from the equations given by Kelley (6).

Each determination was corrected for heat leakage from the calorimeter. The constant temperature water bath surrounding the calorimeter was maintained at a temperature slightly above 300° K. This resulted in a steady heat leakage from the bath into the calorimeter which was determined by measuring the constant rate of Hg displacement before and after each capsule drop. The total mercury displaced was corrected for this heat leakage, which was never more than 0.5%. This procedure was preferable to the difficult task of maintaining the water bath at exactly 300° K. in an effort to eliminate temperature gradients.

The enthalpy of the salts within the capsule relative to 300.0° K. was calculated by subtracting the enthalpy of the platinum and the heat leakage from the total heat liberated.

Enthalpy determinations were repeated several times for each capsule over the temperature range 400° to 950° K., covering both solid and liquid phases of the salts and their mixtures, until a good plot of the molar enthalpy change vs. the absolute temperature was obtained. For the mixtures, the eutectic temperature and liquidus temperatures were taken from the CdCl_2 - PbCl_2 phase diagram (9).

The probable experimental error is $\pm 1.5\%$ for the enthalpy determination. This does not include any error which may be inherent in the equations given by Kelley (6) for the enthalpies of platinum and aluminum oxide. The maximum deviation in observed values and those calculated from Kelley's equation (6) in the calibration procedure was 0.6%. Accepting Kelley's equation as the standard of comparison, one might state the basic accuracy of

Table I. Weight of Platinum Capsules and Salts

Capsule Weight, Grams	CdCl_2 , Mol. Wt. 183.32		PbCl_2 , Mol. Wt. 278.12		Mole Fractions of	
	Grams	Moles	Grams	Moles	CdCl_2	PbCl_2
4.1773	0	0	3.3121	0.011909	0	1.0000
4.2406	0.2513	0.001371	2.8165	0.010127	0.1192	0.8808
4.2379	0.4919	0.002683	2.5686	0.009235	0.2251	0.7749
4.3222	0.8922	0.004867	2.4784	0.008911	0.3532	0.6468
4.1620	1.3952	0.007611	1.5819	0.005688	0.5723	0.4277
4.1443	1.1337	0.006184	0.4320	0.01553	0.7992	0.2008
4.1883	2.3587	0.01287	0	0	1.0000	0

Table II. Enthalpy of Molten CdCl_2 , PbCl_2 and Their Mixtures Relative to the Pure Salts at 300° K.

Mole Fraction CdCl_2	$H_T - H_{300}$ Cal./Mole T in ° K.	Temp. Range, ° K.	Max. Dev. from Experimental Data, %
0	$26.65T - 5856$	774-963	0.5
0.1192	$27.75T - 6674$	745-949	0.6
0.2251	$27.97T - 6770$	714-950	0.8
0.3532 ^a	$26.74T - 5514$	660-940	0.4
0.5723	$26.99T - 5332$	740-947	0.9
0.7992	$27.23T - 5156$	800-969	1.5
1.0	$26.55T - 4139$	841-958	0.7

^a Eutectic composition.

the apparatus and procedure as $\pm 0.6\%$. In work of this sort, however, one must grant the possibility of a cumulative error in the several readings taken during the determination (time, volume, temperature) and make due allowances for this in addition to the allowance for the accuracy of the instrumentation per se. A conservative estimate of this total effect appears to be 0.3%. If the maximum deviation observed during the calibration is assumed to be equally likely in every use of the calorimeter, doubling the value should give the maximum variation expected. The stated figure of 1.5% is the total of these possible errors. While this means more of a maximum possible error than a probable error, it can serve as a conservative estimate for the latter.

RESULTS AND DISCUSSION

The results are presented in Tables II and III. Table II gives the equations evaluated by the method of least squares from the enthalpy data for the molten mixtures and pure salts.

Table III gives smoothed values of enthalpy and entropy for each composition studied. The enthalpies of the solid mixtures were measured at two or more temperatures but are not shown because they were equal to the enthalpy of the corresponding composition of pure salts.

Table IV compares these results with those reported by Bloom and Tricklebank (1). These results are consistently higher and increase with increasing temperature. The maximum difference is approximately 5% for pure CdCl_2 at 923° K. This difference is higher than one expects owing to the maximum probable experimental error which would be 3%. Sources of error, which are not included in the estimate of experimental error, are the equations for the enthalpies of platinum and aluminum oxide used for calibration in this work. Sources of error in the work of Bloom and Tricklebank (1) may be that, apparently, they did not make an independent determination of the calorimetric constant but used the value reported by Jessup (5), and that they encapsulated their salts in silica capsules which were attacked slowly and progressively by the molten salts.

The enthalpy of fusion of CdCl_2 was 7.59 ± 0.23 kcal. per mole compared with 7.4 kcal. per mole reported by Bloom and Tricklebank (1) and 7.22 ± 0.17 reported by Topol and Ransom (11). The enthalpy of fusion of PbCl_2 was 5.20 ± 0.16 kcal. per mole as compared with 5.3 reported by Bloom and Tricklebank (1). Hagemark and Hengstenberg (4) calculated the enthalpy of fusion of PbCl_2 to be 5.50 kcal. per mole from electromotive force measurements of the free energy of formation of molten lead chloride. The calorimetrically determined quantities fall within the reported spread of probable experimental error.

Figure 1 presents the enthalpy data at selected temperatures plotted as a function of mole fraction CdCl_2 . Figure 2 shows the entropy on a similar plot. In these figures, the solid lines separate regions of phase stability. The dashed lines for temperatures of 850°, 900°, and 950° K.

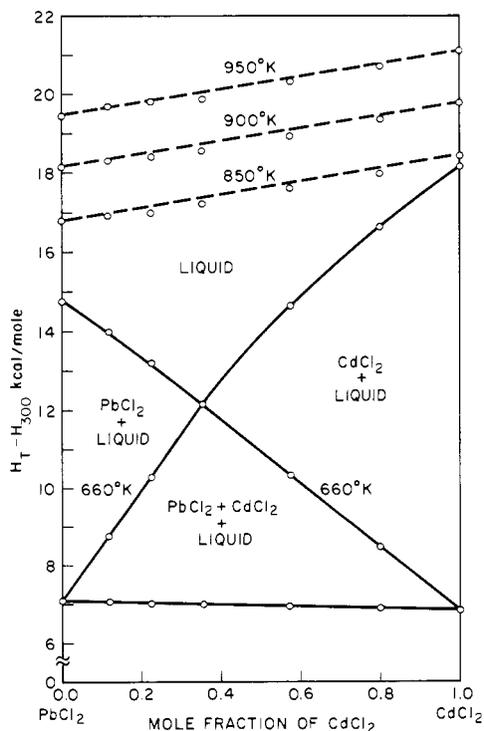


Figure 1. Enthalpy vs. composition diagram for the system CdCl_2 - PbCl_2

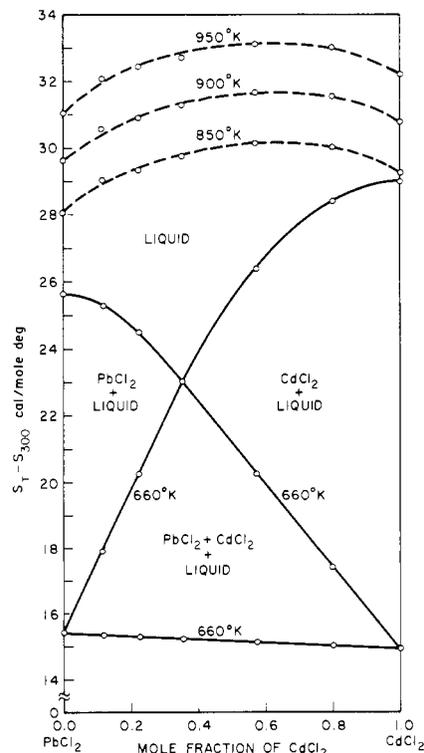


Figure 2. Entropy vs. composition diagram for the system CdCl_2 - PbCl_2

Table III. Enthalpy and Entropy of $PbCl_2$, $CdCl_2$ and Their Mixtures

Reference state: pure components at 300° K.

Temp., ° K.	Composition: Mole Fraction $CdCl_2$																					
	Pure $PbCl_2$			0.1192			0.2251			0.3532			0.5723			0.7992			Pure $CdCl_2$			
	$H_T - H_{300}$	$S_T - S_{300}$		$H_T - H_{300}$	$S_T - S_{300}$		$H_T - H_{300}$	$S_T - S_{300}$		$H_T - H_{300}$	$S_T - S_{300}$		$H_T - H_{300}$	$S_T - S_{300}$		$H_T - H_{300}$	$S_T - S_{300}$		$H_T - H_{300}$	$S_T - S_{300}$		
350	950	2.92																	940	2.90		
375	1420	4.23																	1400	4.16		
400	1900	5.46																	1880	5.40		
425	2390	6.64																	2340	6.52		
450	2870	7.75																	2810	7.59		
475	3350	8.78																	3290	8.63		
500	3850	9.81																	3750	9.58		
550	4840	11.70																	4700	11.38		
600	5850	13.45																	5650	13.04		
660 ^c	7080	15.41		7050	15.34	15.30	7030	15.24	7000	15.13	6940	15.02	6890	15.02	6840	14.92	6840	14.92	6840	14.92		
670			(8780)	(10300)	(17.96)	(20.26)	(10300)	23.01	12130	20.28	(10760)	17.43	8480	17.43					7650	16.12		
674													(9070)	(18.08)								
698																						
700	7950	16.69		(10220)	(20.09)																	
708																						
714																						
725							(13200)															
740																						
745																						
745																						
750	9040	18.19		14000	25.29																	
750	9570	18.89																				
774 ^a	14770	25.61																				
791																						
800																						
841 ^a																						
850	16790	28.08																				
900	18130	29.61		16910	29.01	29.35	17000	29.78	17210	29.78	18960	31.58	19350	31.58	18430	29.25	18430	29.25	18430	29.25		
950	19460	31.04		18300	30.59	30.94	18400	31.31	18550	31.31	20310	33.12	20710	33.12	19760	30.77	19760	30.77	19760	30.77		
				19690	32.10	32.45	19800	32.76	19890	32.76												

^aSolid. ^bLiquid. ^cParanthesis indicates both solid and liquid phases present.

Table IV. Comparison of Results with Those Obtained by Bloom and Tricklebank (1)

Mole Fraction CdCl ₂	$H_{823} - H_{300}$, Kcal./Mole		$H_{873} - H_{300}$, Kcal./Mole		$H_{923} - H_{300}$, Kcal./Mole	
	This work	Ref. (1)	This work	Ref. (1)	This work	Ref. (1)
	0	16.08	15.60	17.41	16.65	18.74
0.3	16.39	15.75	17.76	17.05	19.12	18.30
0.5	16.75	16.10	18.10	17.40	19.44	18.70
0.7	17.09	16.70	18.45	17.80	19.80	18.90
1.0	17.74	17.25	19.04	18.25	20.34	19.30

indicate the properties calculated assuming ideal solutions.

Figure 1 shows that the enthalpy of mixing in this system is less than 200 cal. per mole. The entropy data indicate that the entropy of mixing is ideal assuming random mixing of the lead and cadmium ions.

Boardman, Darman, and Heymann (2) found negative deviations from additivity in molar volumes for the CdCl₂-PbCl₂ system. An exothermic enthalpy of mixing is expected to be associated with this result. The enthalpy data of Figure 1 indicate small negative deviations from ideality, a trend also reported by Bloom and Tricklebank (1).

The enthalpy measurements may be used to compute molar heat capacities. Assuming that the effect of the change in pressure is negligible, C_p was computed from the slope of the curves of enthalpy vs. temperature. The results are summarized in Table V and compared with those of Bloom and Tricklebank (1), Kelley (6), and Topol and Ransom (11). The latter work was limited to a temperature range 60° to 100° K. above and below the melting point of CdCl₂. The range of possible error must be increased for the C_p values, since differences must be taken in the calorimetric values and temperatures in determining slopes.

The error in C_p was taken as 3%, double that of the enthalpy values. The values agree well with those suggested by Kelley (6) and with the value for liquid CdCl₂ reported by Topol and Ransom (11). The values reported by them for solid CdCl₂ seems high which may account for their

Table V. Comparison of Heat Capacity Determinations

	Temp. Range, ° K.	C_p , Cal./Mole - ° K.			
		This work	Ref. (1)	Ref. (6)	Ref. (11)
PbCl ₂ (solid)	300-773	20.4	19.8	20.2 ^a	...
PbCl ₂ (liquid)	774-963	26.6	22.6	27.2	...
CdCl ₂ (solid)	300-840	19.7	18.9	20.2 ^b	28.5 ^c
CdCl ₂ (liquid)	841-958	26.6	21.8	...	26.3 ^c

^a Average value from $C_p = 15.96 + 8 \times 10^{-5}T$. ^b Average value from $C_p = 14.54 + 9.6 \times 10^{-5}T$. ^c Temperature range 60° to 100° K. above and below the melting point.

somewhat lower enthalpy of fusion. The agreement between these values and those of Bloom and Tricklebank (1) for solid PbCl₂ and CdCl₂ is satisfactory.

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Surface Tensions of Water-Methyl Ethyl Ketone Mixtures

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Surface tensions of water and methyl ethyl ketone mixtures are reported for concentrations from 0 to 10 weight % of methyl ethyl ketone and for temperatures from 20° to 60° C. The surface tensions, measured by the maximum bubble pressure method, were determined for use in analyzing boiling heat transfer data.

VARIOUS investigators discovered that the addition of certain volatile organic components to water affects the nucleate boiling process, especially the critical heat flux at which nucleate boiling fails and film boiling begins (6, 7, 9). Van Wijk, Vos, and von Stralen (9) experimented with several substances and found that methyl ethyl ketone (M.E.K.) increased the critical flux from heated wires by as much as 230%. Tests by Pitts and Leppert (7) also

show an increase in the critical flux, but those of Owens (6) with larger diameter heaters did not show this effect. Leppert, Costello, and Hoglund (5) reported on nucleate boiling and observed the pronounced effect of additives on bubble size and frequency.

EXPERIMENTAL

Materials. The water was doubly distilled and the M.E.K. was Eastman Kodak reagent grade. Reagent grade M.E.K.

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