

Table III. Heats of Solution of $\text{NR}_3\text{N}(\text{c})$ in Excess Acid

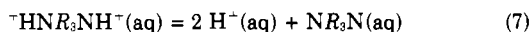
Moles HCl/950 Ml. ^a	<i>n</i> , Moles NR_3N^b	$-Q/n$, Kcal. Per Mole	$-\Delta H_6$ Kcal. Per Mole
1.04	3.902	16.61	16.64
1.05	3.568	16.50	16.54
2.12	3.792	16.73	16.76
2.96	3.144	16.94	16.96
3.00	4.330	17.02	17.02
4.23	4.255	17.14	17.14
4.31	3.413	17.24	17.25
4.31	5.027	17.18	17.18

$\Delta H_6^{\circ} = -16.4 \pm 0.3$ kcal. per mole

^a $\times 10^{-1}$. ^b $\times 10^{-3}$.



Although most of the $\text{NR}_3\text{N}(\text{c})$ dissolved according to Equation 6, some dissolved according to Equation 2, so it was necessary to correct the observed heats (Q/n values in Table III) for this secondary process by means of ΔH_2 and extent of reaction calculated from $\text{p}K = 11.55$ (2) for



The derived values of ΔH_6 are listed in Table III with the experimental data. The estimated uncertainty in ΔH_6° includes contributions from calculations and extrapolations, along with calorimetric uncertainties.

Combination of our ΔH_6° and ΔH_2° values leads to $\Delta H_7^{\circ} = 10.2 \pm 0.3$ kcal. per mole for the ionization represented by Equation 7. Further combination of $\Delta G_7^{\circ} = 15.77$ kcal.

per mole from $\text{p}K = 11.55$ with ΔH_7° gives $\Delta S_7^{\circ} = -18.8$ cal. deg.⁻¹ mole⁻¹.

There are no data in the literature that are directly comparable to the standard state thermodynamic data reported here. Paoletti, Stern, and Vacca (4) have made calorimetric measurements on triethylenediamine in 0.1M KCl as solvent and have reported results that lead to $\Delta H_6 = 7.30$ kcal. per mole (the authors' $\Delta H_6^{\circ} = 7.21$) and $\Delta H_7 = 10.31$ kcal. per mole (the authors' $\Delta H_7^{\circ} = 10.2$). The small differences between the present results and those of Paoletti, Stern, and Vacca (4) should probably be attributed mostly to differences in the solvent systems (water vs. 0.1M KCl) used in the two investigations.

ACKNOWLEDGMENT

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Electromotive Force Measurements of the Free Energy of Formation of Molten Lead Chloride

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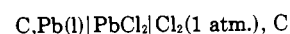
The e.m.f. of a formation cell of molten PbCl_2 has been measured at 500° to 620° C. The data obtained may be represented by e.m.f. (volt) = $1.2471 - 602 \times 10^{-6} (t - 550^\circ \text{C})$; agreement with some of the reported e.m.f. data is good. The estimation of the free energy of formation of molten PbCl_2 given in thermochemical tables has not included values for molten PbCl_2 obtained by direct e.m.f. methods. A new expression for the free energy of formation of molten PbCl_2 $\Delta G_f = 86,630 + 94.90 T - 8.860 T \ln T$, has been obtained by a best fit to the present data for the molten state and the previous data for the solid. These measurements lend support to the previous estimates and show that molten salt formation cells can be a reliable and valuable source of data on free energies of formation.

A LARGE NUMBER of e.m.f. measurements of the formation cell of molten PbCl_2 have been reported in the literature. References to most of the previous work may be found in a paper by Delimarskii and Roms (2). The agreement among the published data has not been too good, except for the two recent investigations by Lantratov and Alabyshev (7) and Markov, Delimarskii, and Panchenko (8). Attempts to assess the e.m.f. data, however, are beyond the scope of this paper.

The thermodynamic properties for molten PbCl_2 are estimated in the JANAF tables (4) by using the data

for the solid state, the values for the heat of fusion, the melting point, and a heat capacity value for the liquid. No measurements directly yielding the free energy of formation of the molten salt were included.

The data on pure molten PbCl_2 presented here are part of a more extensive study of ternary systems consisting of PbCl_2 and alkali metal chlorides. In order to evaluate the solution properties of the ternary systems, separate e.m.f. measurements have been made of the formation cell



at temperatures ranging from 500° to 620° C. The values have been reproduced in several runs, indicating that the data were reliable. It would, therefore, be of great interest to discuss the agreement between data estimated by JANAF and those obtained from the present measurements. Very few of the data on free energies of formation in the JANAF tables have been obtained from formation cells. The authors hope to demonstrate that cells of this type can be a reliable and valuable source of data.

EXPERIMENTAL

Measurements were made in the formation cell shown in Figure 1. The design is a modification of the cell of Laitinen and Pankey (6). A flat-bottomed tube, 1.5-inch O.D. × 12.5-inches long, served as the cell compartment. The melt was contained in a fused silica cup, 1.25-inch O.D. × 2-inches high, placed inside the cell compartment. To facilitate rapid exchange of samples, the cups were provided with hooks. The two electrodes and a thermocouple well were placed through a No. 10 rubber stopper. To obtain an accurate fit, the stopper was frozen in liquid nitrogen before the holes were drilled. The chlorine electrode was similar to the one utilized by Senderoff and Mellors (9). It was made of a 3/8-inch O.D. × 3/16-inch I.D.

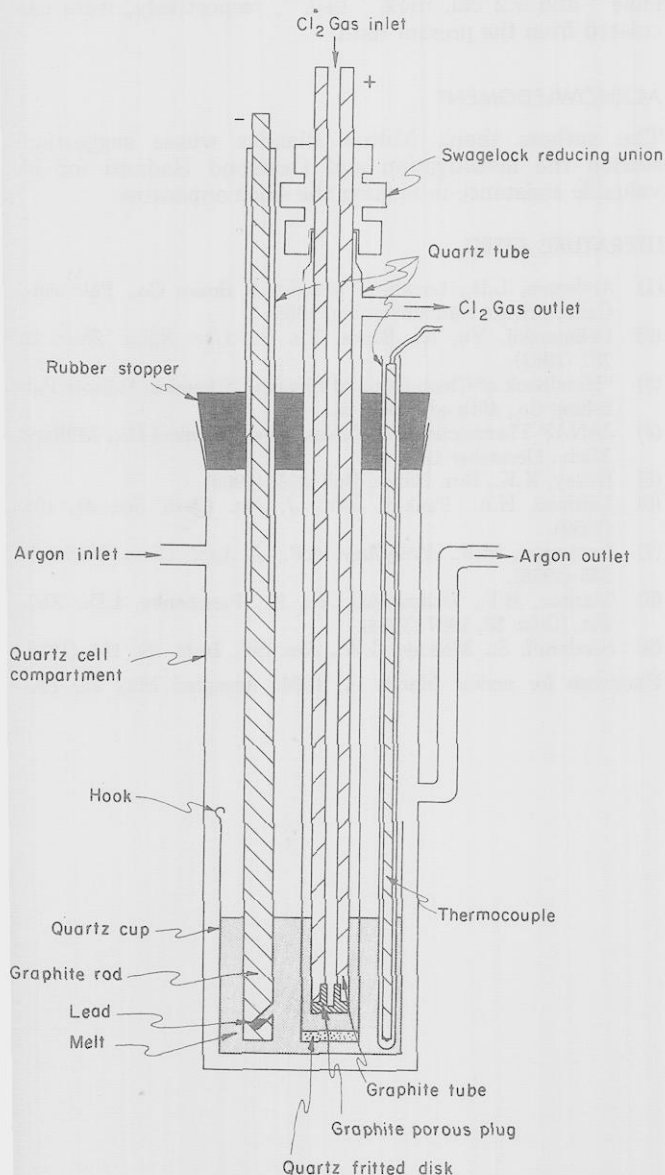


Figure 1. Schematic diagram of e.m.f. cell

× 22-inch graphite tube which was threaded on the inside at the lower end. A porous graphite plug of the same outer diameter was screwed and cemented to the graphite tube with National Carbon cement grade 12. The carbon tube was placed axially in a fused silica tube having a quartz fritted disk of medium porosity sealed into the lower end. A gas-tight connection between the graphite and the fused silica tube was obtained by means of a Swagelock M810-6-6 reducing union. In previous e.m.f. measurements, the anode and cathode generally have consisted of different materials. When the two electrodes are extended to room temperature, they act as a thermocouple and give rise to a thermal e.m.f. To avoid this correction, the cathode was a 3/8-inch thick graphite rod with a well containing the molten lead. In the presence of lead, the graphite will be inert to the melt. The cell compartment was located in a Marshall multi-tap furnace controlled to $\pm 1^\circ$ C. by a West Gardsman saturable core reactor controller. The temperature of the molten salt was measured by a calibrated Pt-Pt 10% Rh thermocouple; a Leeds & Northrup K3 Universal potentiometer was used for the e.m.f. reading.

The PbCl_2 was Baker analyzed reagent grade, or Matheson, Coleman, and Bell reagent grade; both gave the same e.m.f. values. Baker analyzed reagent grade metal was used. The Cl_2 gas from Matheson was 99.5% pure. To dry the Cl_2 gas and also to indicate the rate of flow, the gas was bubbled through concentrated sulfuric acid. The graphite electrode was pretreated by keeping it in 1-atm. Cl_2 gas at 900° C. for about 2 hours and then cooling it slowly to room temperature, maintaining the Cl_2 atmosphere. The PbCl_2 was heated at 200° C. in an argon atmosphere for 1 hour and then melted in the same atmosphere. In one experiment, the salt was melted in an HCl atmosphere, resulting in no change in the equilibrium e.m.f. values. Therefore, no further treatment of the salt was necessary. The Pb metal was also melted in an inert atmosphere. During the experiment, purified argon was passed over the molten salt. The applied Cl_2 pressure was equal to the with 0.5 ampere for about 1 minute. Additional electrolysis, about 0.2 ampere for 10 seconds, did not change the equilibrium e.m.f. during the course of the measurements. Measurements generally were taken at slowly increasing and decreasing temperature. The e.m.f. values obtained were very close to those obtained when the temperature was kept constant for over 1 hour, indicating that equilibrium was attained very rapidly. The measured e.m.f. values were corrected to 1-atm. pressure of Cl_2 . (These corrections were less than 0.8 mv.).

RESULTS

The corrected e.m.f. data from the formation cell of molten PbCl_2 are shown in Figure 2. A least-squares treatment of the data resulted in the linear expression e.m.f. (volts) = $1.2471 - 602 \times 10^{-6} (t - 550^\circ \text{C.})$. This expression is compared in Table I with two results from other e.m.f. measurements and with an e.m.f. expression calculated from the free energy function data tabulated by JANAF and represented as a linear function in the range 500° to 600° C. The absolute values at 550° C. from the different sources agree within 1 mv., (corresponding to 46 cal. in the free energy). The authors' value for the temperature dependence is in remarkably good agreement with the value reported by Markov *et al.* A value 603×10^{-6} volt deg.⁻¹ for the temperature dependence found by Anderson (1) in a thermocell investigation also supports the present data. On the other hand, the value for the temperature dependence given by Lantratov and Alabyshev (7) seems too low.

Because the JANAF tables, in their evaluation of the free energy data for molten PbCl_2 , did not consider any e.m.f. measurements of formation cells of molten PbCl_2 , an expression for the free energy of formation of molten

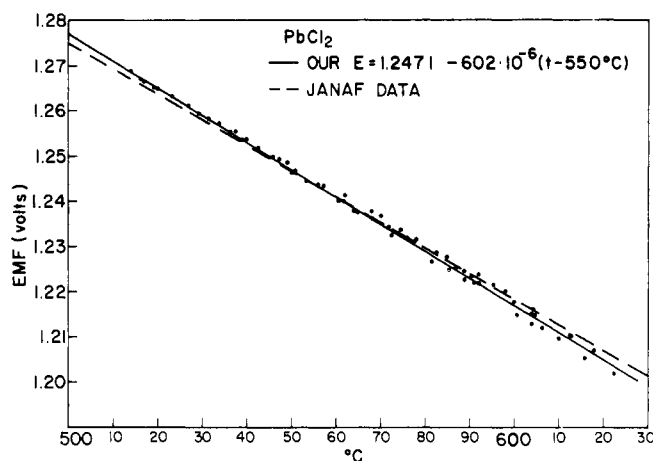


Figure 2. Experimental values for e.m.f. of formation cell of molten PbCl_2 as a function of temperature

— $E(\text{volt}) = 1.2471 - 602 \times 10^{-6} (t - 550^\circ \text{C.})$, obtained by least squares treatment of data. - - - Data calculated from JANAF's tables

Table I. E.M.F. Data for Formation Cell of Molten PbCl_2 .

E.M.F., Volt $^\circ$	Reference
1.2471 - 602 $^\circ$	This work
1.2480 - 600	(8)
1.2479 - 531	(7)
1.2466 - 565	(4)

$^\circ \times 10^{-6} (t - 550^\circ \text{C.})$.

PbCl_2 was evaluated by using the present data for molten PbCl_2 and the JANAF data for solid PbCl_2 . The free energy of formation of molten PbCl_2 , $\Delta G_f(l, T)$, may be expressed by

$$\Delta G_f(l, T) = \Delta G_f(s, T_m) + \Delta C_p T_m \ln T_m - [\Delta S_f(l, T_m) - \Delta C_p (\ln T_m + 1)](T - T_m) - \Delta C_p T \ln T$$

where l refers to the liquid, s to the solid, and T_m to the melting point. The heat capacity of formation, ΔC_p , is the mean value within the temperature range. The present data have been fitted to an expression

$$-nFE + \Delta C_p T \ln T = a + b (T - T_m)$$

where the constant $a = \Delta G_f(s, T_m) + \Delta C_p T_m \ln T_m = -13,745$ cal. is calculated from the JANAF tables, E is the measured e.m.f., $F = 23,062$ cal. volt $^{-1}$, and $n = 2$. The value $\Delta C_p = 8.860$ cal. mole $^{-1}$ deg. $^{-1}$ from JANAF's tables at 560°C. was adopted, as the present measurements cover only the temperature range 500 to 620°C. There is some discrepancy among the values for the melting point of PbCl_2 . Kelley

(5) adopted 498°C. , whereas 501°C. given by the "Handbook of Chemistry and Physics" (3) is used very often. In this case, a small uncertainty in the melting point has only small effect on the result. By setting the free energy of formation of the molten PbCl_2 equal to that of the solid at the melting point, the difference in the final result would be equal to $\Delta S_m \times \Delta T$, or about 40 cal. (ΔS_m is the entropy of fusion, ΔT is the error in the melting temperature.) To be consistent, the melting point 495°C. reported by JANAF was used here.

A least squares treatment of the data, represented as $-nFE + \Delta C_p T \ln T$, yielded $b = -[\Delta S_f(l, T_m) - \Delta C_p (\ln T_m + 1)] = 94.90$ cal. per deg. mole. Thus, one derives

$$\Delta G_f = -86,630 + 94.90 T - 8.860 T \ln T$$

for the free energy of formation of molten PbCl_2 in the temperature range 495 to 620°C. The results are in good agreement with the data given by the JANAF and, thus, confirm their estimates.

At the melting point, 495°C. , the entropy of formation from the new expression is $\Delta S_f = -27.17$ cal. mole $^{-1}$ deg. $^{-1}$ as compared to JANAF's value $\Delta S_f = -26.91$. Assuming the entropy of formation for the solid PbCl_2 is well known, a disagreement of 0.26 cal. mole $^{-1}$ deg. $^{-1}$ could be due to an error in the value for the heat of fusion adopted by JANAF. A heat of fusion and an entropy of 5.50 kcal. mole $^{-1}$ and 7.2 cal. mole $^{-1}$ deg. $^{-1}$, respectively, were calculated from the present data.

ACKNOWLEDGMENT

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