# Thermoelectric Power of the Molten Systems $PbCl_2-MeCl$ (Me = Li, Na, K, Rb, Cs)

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Initial thermoelectric power determinations where carried out by means of Pb electrodes and $Cl_2$ electrodes thermocells on the molten system $PbCl_2-MeCl$ (Me = Li, Na, K, Rb, Cs).

Combinations of the results coming from the two kinds of thermocells allowed to verify Reinhold's relation and to estimate the partial molar formation and excess entropies of $PbCl_2$.

## Introduction

In a previous work, where molten ionic binaries with common cation and differently charged anions were considered[1], unusual formal expressions for the ionic entropies were proposed: accordingly, the final expressions for the thermoelectric power were somewhat modified with respect to the cases where Temkin's model of molten salts had been assumed.

In the present work the opposite case, i.e., molten binaries with common anion and differently charged cations, viz. $PbCl_2-MeCl$ (Me = Li, Na, K, Rb, Cs), was investigated by checking the initial thermal e.m.f. of two kinds of thermocells, with liquid Pb and with $Cl_2$ electrodes, respectively.

Though the data coming from the cells of the first type might be conveniently worked out on the basis of the simple Temkin's model, Ref.[1] statements seemed more adequate to discuss combinations of the results of the two kinds of thermocells.

According to Ref.[1] the following expressions for the initial thermoelectric power were obtained:

$$F\,\varepsilon_j = \frac{1}{2}\left[S_{\mathrm{Pb(l)}} - ({}^0S_{\mathrm{Pb^{++}}})_j\right] + \frac{R}{2}\ln X_{\mathrm{Pb^{++}}} - \sum_i \frac{t_i}{z_i}\frac{Q_i^*}{T} \qquad \text{(I)}$$

for Pb electrodes thermocells and

$$F\,\varepsilon_j' = -\frac{1}{2}S_{\mathrm{Cl_2(g)}} + ({}^0S_{\mathrm{Cl^-}})_j - R\ln X_{\mathrm{Cl^-}} - \sum_i \frac{t_i}{z_i}\frac{Q_i^*}{T} \qquad \text{(II)}$$

for $Cl_2$ electrodes thermocells, where $j = 1, 2, 3$ refers to pure molten $PbCl_2$, pure molten MeCl and molten mixture, respectively; $j = 1$ was assumed as the reference state in the definition of partial molar excess entropies, while the transport quantities, $t_i$ and $Q_i^*$, were referred to the common ion $Cl^-$.

It can be easily verified that Eqs. (I) and (II) allow Reinhold's relation[2] to be satisfied for both pure $PbCl_2$ and any mixture; furthermore, from Eqs. (I) and (II) and from the definition of the excess entropies given in Ref.[1] one may directly obtain:

$$2F\left[(\varepsilon_3-\varepsilon_1)-(\varepsilon_3'-\varepsilon_1')\right] = R\ln\frac{27}{4}\,\frac{N_1(1+N_1)^2}{(2+N_1)^3} - (S^{\mathrm{e}}{}_{\mathrm{PbCl_2}})_3 \qquad \text{(III)}$$

where $N_1$ is the molar fraction of $PbCl_2$.

## Experimental

The employed chemicals were BDH Analar Pb; Carlo Erba RP $PbCl_2$, LiCl, NaCl, KCl; Merck p.a. RbCl and CsCl; S.I.A.D. puriss. $Cl_2$.

*Pb electrodes thermocells:* a silica cup containing liquid Pb was suspended in each arm of a U-shaped silica cell filled with the molten salt which rested over the heavier molten metal; a Platinel thermocouple and the free end of a W wire (which was prevented from the contact with the salt by a narrow silica tube) could reach the metal-salt interface and dip into the liquid Pb.

*$Cl_2$ electrodes thermocells:* the arms of the cell were tightly closed by suitably designed silica covers which allowed:

a) a Platinel thermocouple to reach the interior of the cell, being contained in a silica tube sealed to the cover itself;

b) one end of a spectroscopical graphite bar (VEB Elektrokohle type 2) to be pressure joined to the cover and contacted by a tungsten wire working as the terminal;

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c) a $Cl_2$ flow (from the $Cl_2$ container to the pump) to be provided in each arm of the cell.

The graphite bars were previously maintained in $Cl_2$ atmosphere at 250 °C for 48 hours; a $N_2$ stream was let to pass through the cell for about 30 minutes before starting the $Cl_2$ flow, which was maintained for about 90 minutes; finally the pump suction and the $Cl_2$ supply were interrupted and the internal $Cl_2$ pressure was allowed to reach the ambient one.

The arrangement for applying $\Delta T$ between the arms was previously described[3]. The whole apparatus was set in a high capacity furnace.

In both investigations e.m.f. signals were detected by means of a Leeds & Northrup K3 potentiometer.

## Results and Discussion

Direct experimental determinations, carried out on the cell

$$\mathrm{W}\,/\,\underset{T}{\mathrm{Pb}}\,/\,\text{ionic melt}\,/\,\underset{T+\Delta T}{\mathrm{Pb}}\,/\,\mathrm{W}$$

were slightly dependent on $T$; as for the pure molten $PbCl_2$ the results could be linearly fitted by the equation

$$\varepsilon\,(\mu\mathrm{V\,K^{-1}}) = 23.9\times10^{-3}\,t\,(^\circ\mathrm{C}) - 1.51\,.$$

Thermoelectric power data of actual Pb electrodes thermocells were obtained by subtracting the Peltier coefficient of the couple W/Pb (reported in [4]) from the directly detected values.

The values at $T = 1000$ K for all the investigated systems are shown in Figure 1.

Due to the low order of magnitude of these data no detailed discussion about them could be reasonably attempted.

Conversely, $Cl_2$ electrodes thermocells gave values lying around 500 $\mu$V $K^{-1}$, which could be worked out according the previously proposed procedure[1].

Data referring to pure $PbCl_2$ and pure alkali chlorides are close to the values reported by Fisher[5], whereas a 100 $\mu$V $K^{-1}$ discrepancy was found with respect to [4]. No relevant dependence on $T$ was found both for pure salts and for mixtures.

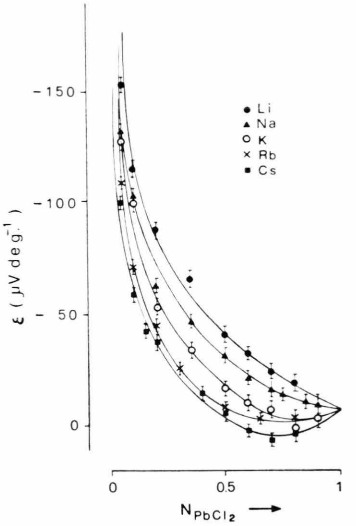

Fig. 1. Initial thermoelectric power at $T = 1000$ K of the molten systems $PbCl_2$-MeCl determined on Pb electrodes thermocells.

Data at $T = 1000$ K were reported in Table 1.

The trend of the function $P_j' = F\,\varepsilon_j' + R\ln X_{\mathrm{Cl}^-}$ for which a linear ideal behaviour was demonstrated in a previous work[1], $(P_j')_{\mathrm{id}} = N_1(P_1' - P_2') + P_2'$, is shown in Figure 2.

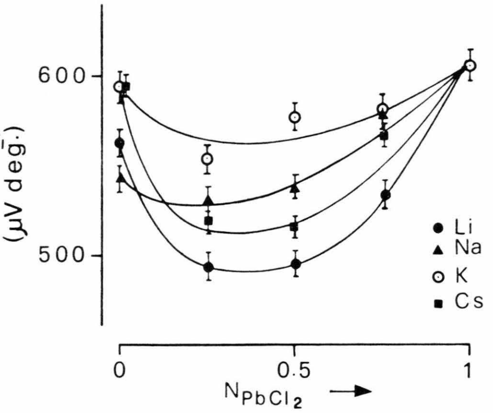

Fig. 2. The function $P_j' = F\,\varepsilon_j' + R\ln X_{\mathrm{Cl}}$ from $Cl_2$ electrodes thermocells: $T = 1000$ K.

| $N_{PbCl_2}$ | $PbCl_2$+LiCl | $PbCl_2$+NaCl | $PbCl_2$+KCl | $PbCl_2$+CsCl |
|---|---|---|---|---|
| 0.00 | −534 | −483 [a] | −504 [a] | −533 |
| 0.25 | −500 | −480 | −440 | −470 |
| 0.50 | −536 | −491 | −450 | −470 |
| 0.75 | −540 | −540 | −495 | −530 |
| 1.00 | −570 | −570 | −570 | −570 |

Tab. 1. Thermoelectric power values in $\mu$V degree$^{-1}$ at $T = 1000$ K for $Cl_2$ electrodes thermocells; "a": this value has been obtained by extrapolating the bevaviour at $T > T_{\mathrm{fusion}}$.

Deviations from ideality did not allow to recognize any critical composition range, i. e., the formation of complex ions.

Combinations of the data coming from the two kinds of thermocells according to Reinhold's relation and to Eq. (III) gave the results reported in Table 2 which allow to verify that:

a) as for $PbCl_2$, Reinhold's relation is quite satisfactory: from these determinations we obtained at $T = 1000$ K the value $-0.56$ mV $K^{-1}$ which is close to the literature data [$-0.60$ mV $K^{-1}$ (see [6]) coming from formation cells and $-0.58$ mV $K^{-1}$ coming from thermoelectric determinations [5]];

b) as for the general trend of $(S_{PbCl_2})_3$ and $(S^{e}_{PbCl_2})_3$ versus the composition (see Table 2) a satisfactory qualitative agreement with Markov's results [7] on formation cells was observed, differences being probably due to the different range of the investigated temperatures.

| $N_{PbCl_2}$ | $PbCl_2+LiCl$ | | $PbCl_2+NaCl$ | | $PbCl_2+KCl$ | | $PbCl_2+CsCl$ | |
|---|---|---|---|---|---|---|---|---|
| 1.00 | −26 | 0.0 | −26 | 0.0 | −26 | 0.0 | −26 | 0.0 |
| 0.75 | −24 | 1.4 | −24 | 1.1 | −20 | 2.7 | −25 | 0.2 |
| 0.50 | −24 | 1.7 | −21 | 3.8 | −20.5 | 4.6 | −21 | 3.2 |
| 0.25 | −20 | 3.4 | −19 | 3.7 | −18 | 5.0 | −20 | 2.9 |

Tab. 2. Every section of the table reports formation and excess entropies in the first and second column, respectively, for $PbCl_2$. Values are in e.u. and refer to $T = 1000$ K.

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