

The Thermoelectric Power of the Molten Chlorides, Bromides and Iodides of Lead, Tin and Zinc with Reversible Molten Metal Electrodes

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A metal electrode for measurements of the thermoelectric power of molten salts above the melting point of the metal has been developed. The electrode has been tested with good results for a number of tin, lead and zinc salts.

The thermoelectric power of a great number of pure salts and salt mixtures has been measured by different authors¹⁻⁵,

where mainly electrodes of solid metal or gas have been used. Especially the silver and the copper salts have been thoroughly investigated. Many electrode materials are, however, difficult to handle and for several salts the melting point of the electrode material is lower than that of the salt. This has of course limited the number of studied salts.

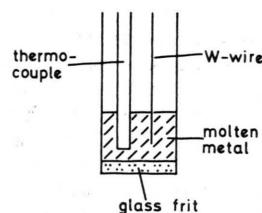


Fig. 1. The electrode used for the thermoelectric power measurements.

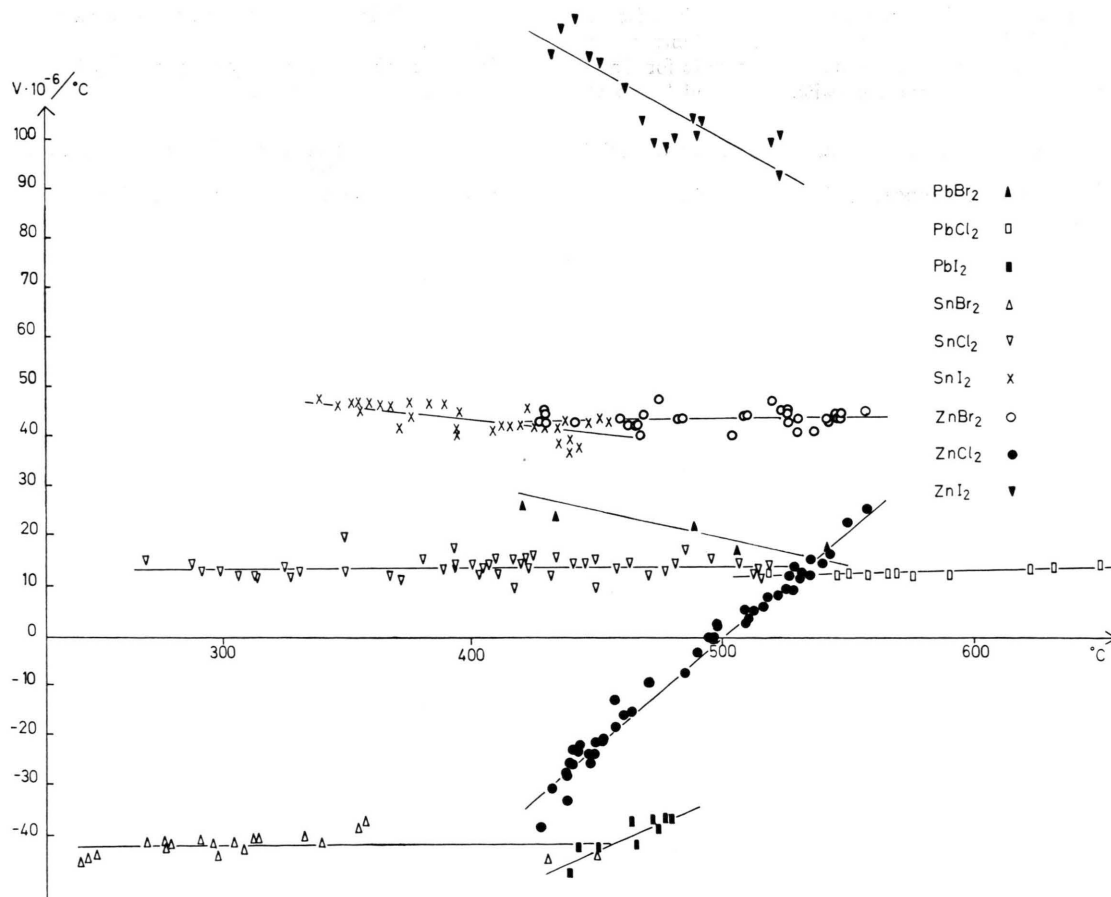


Fig. 2. The thermoelectric power of the investigated salts.

¹ J. RUCH and J. DUPUY, C. R. Acad. Sci. Paris **261**, 957 [1965].

² A. KVIST, Z. Naturforsch. **19 a**, 1159 [1964].

³ K. WALLIN and A. LUNDÉN, Z. Naturforsch. **22 a**, 591 [1967].

⁴ C. SINISTRI, Z. Naturforsch. **21 a**, 753 [1966].

⁵ S. SENDEROFF and R. I. BRETZ, J. Electrochem. Soc. **109**, 56 [1962].



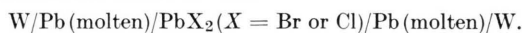
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If we consider for instance the chlorides, bromides and iodides of tin, lead and zinc, only the thermal emf of PbCl_2 and PbBr_2 have been studied; DETIG and ARCHER⁶ measured the emf of the cell



For these two salts we found that it was rather easy to measure the emf and we could use a small cup filled with the molten metal. For the other salts no reproducible results could be obtained with these electrodes or the cells used by DETIG and ARCHER⁶. A great number of electrode designs were therefore tried. The best results were obtained with the electrode showed in Fig. 1. The metal is here separated from the salt by a fritted disc. The salt can easily pass the frit, but for the metal the surface tension is too great. Tungsten wires were brought in constant with the metals and the electrodes were placed in the U-cells described before⁷.

The results for the investigated salts are given in Fig. 1. Table 1 gives the equations of the straight lines. The magnitude of the emf for these salts is smaller than for the silver salts^{1,7-9} and it is also seen that the temperature dependence varies from salt to salt. The results for PbCl_2 and PbBr_2 are in good agreement with DETIG and ARCHER⁶.

⁶ R. H. DETIG and D. H. ARCHER, J. Chem. Phys. **38**, 661 [1963].

⁷ A. KVIST and A. RANDSALU, Z. Naturforsch. **21a**, 278 [1966].

Salt	$a \cdot 10^3$ $\mu\text{V}/^\circ\text{C}^2$	b $\mu\text{V}/^\circ\text{C}$	s $\mu\text{V}/^\circ\text{C}$	Temperature interval ($^\circ\text{C}$)
PbCl_2	12.2	5.7	1.0	519—650
PbBr_2	— 67.9	53.7	1.7	421—506
PbI_2	219.5	— 141.6	1.7	438—478
SnCl_2	1.3	13.3	1.8	230—520
SnBr_2	8.3	— 44.4	2.1	244—440
SnI_2	— 53.7	65.0	2.2	339—455
ZnCl_2	431.3	— 216.1	2.4	428—550
ZnBr_2	7.2	39.9	1.6	428—548
ZnI_2	— 272.5	238.3	4.8	439—530

Table 1. The thermoelectric power of the investigated salts described by the relation $\varepsilon = at + b$, where t is the temperature in $^\circ\text{C}$. s is the standard deviation.

The thermal emf of a salt with reversible electrodes is generally written as the sum of several entropy terms⁷, but for the studied salts very little is known about the formation entropies and it is at present impossible to calculate the different terms.

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⁸ A. KVIST, A. RANDSALU and I. SVENSSON, Z. Naturforsch. **21a**, 184 [1966].

⁹ C. SINISTRI, Z. Naturforsch. **20a**, 1045 [1965].