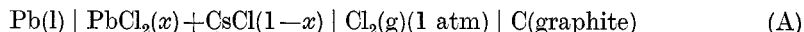


ACTIVITIES IN THE MOLTEN SALT SYSTEM $\text{PbCl}_2 + \text{CsCl}$ BY ELECTRO-MOTIVE FORCE MEASUREMENTS*

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Activities in molten salt systems have been studied by a variety of methods including measurement of vapour pressure,¹⁻³ by cryoscopy,^{4,5} and the e.m.f. of galvanic cells.⁶⁻⁸ Cryoscopy gives results for a system over a range of temperatures depending on the liquidus temperature and is limited to those systems and the range of compositions for which the pure components are precipitated on freezing. Vapour pressure measurements often give values which may be uncertain due to known (and unknown) formation of intermolecular compounds in the vapour phase.^{3,9} The e.m.f. method is free of the above limitations, the main problems being to discover suitable reversible cells⁸ and to eliminate diffusion potentials.

We have made up a number of molten salt cells of the type



These formation cells produce steady, reproducible values of e.m.f. which we have shown to follow the Nernst relations between e.m.f., temperature, and pressure of chlorine.

The measured e.m.f., E , of cell (A) is given by

$$E = E^\circ - \frac{RT}{2F} \ln a(\text{PbCl}_2) \quad (1)$$

where E° is the standard e.m.f., i.e. when the electrolyte is pure molten PbCl_2 at temperature $T^\circ\text{K}$. Activities of PbCl_2 in the various mixtures can be calculated readily from (1).

For the various mixtures the partial and integral thermodynamic quantities, Gibbs free energy, enthalpy and entropy of formation of PbCl_2 can be determined by making use of familiar thermodynamic relationships between these functions and the e.m.f.'s of cells (A) and their temperature coefficients.

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¹ Barton, J. L., and Bloom, H., *Trans. Faraday Soc.*, 1959, **55**, 1792.

² Bloom, H., and Welch, B. J., *Trans. Faraday Soc.*, 1961, **57**, 61; *Discuss. Faraday Soc.*, 1962, **32**, 115.

³ Bloom, H., and Hastie, J. W., *J. phys. Chem.*, 1968, **72**, 2361.

⁴ Sternberg, S., and Adorian, J., *Studia Cerc. Chim. Acad. RPR*, 1963, **11**, 315.

⁵ Jacoud, R., Reinsborough, V. C., and Wetmore, F. E. W., *Aust. J. Chem.*, 1966, **19**, 1597.

⁶ Salstrom, E. J., and Hildebrand, J. H., *J. phys. Chem.*, 1930, **52**, 4641.

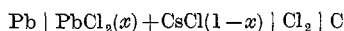
⁷ Bloom, H., and Welch, B. J., *Trans. Faraday Soc.*, 1963, **59**, 410.

⁸ Bloom, H., "The Chemistry of Molten Salts." (Benjamin: New York 1967.)

⁹ Bloom, H., and Hastie, J. W., *Aust. J. Chem.*, 1966, **19**, 1003.

Salts used were of analytical reagent purity and standard methods of analysis were used.³ The experimental details for measurement of e.m.f. have been described elsewhere.^{2,3}

TABLE 1
RELATIONSHIP BETWEEN E.M.F. AND TEMPERATURE FROM THE LINES OF BEST
FIT FOR THE FORMATION CELLS:



Composition $x(\text{PbCl}_2)$	E.M.F. at $t^\circ\text{C}$ (V)	Deviation* (mV)	Temp Range. ($^\circ\text{C}$)
0.886	$1.5632 - (5.791 \times 10^{-4})t$	0.4	540-800
0.848	$1.5479 - (5.461 \times 10^{-4})t$	2.2	540-840
0.789	$1.5463 - (5.418 \times 10^{-4})t$	0.8	550-800
0.745	$1.5540 - (5.476 \times 10^{-4})t$	0.5	540-820
0.676	$1.5639 - (5.496 \times 10^{-4})t$	0.2	580-800
0.622	$1.5822 - (5.589 \times 10^{-4})t$	0.8	550-800
0.485	$1.5802 - (5.109 \times 10^{-4})t$	1.1	550-800
0.398	$1.6145 - (5.113 \times 10^{-4})t$	1.5	600-840
0.307	$1.6415 - (4.948 \times 10^{-4})t$	0.7	600-820

* The mean deviation of experimental points from the line in the temperature range of measurement.

TABLE 2
ACTIVITIES OF PbCl_2 AT DIFFERENT COMPOSITIONS IN THE SYSTEM
 $\text{PbCl}_2 + \text{CsCl}$

Composition $x(\text{PbCl}_2)$	$a(\text{PbCl}_2)$ 600°C	$a(\text{PbCl}_2)$ 700°C	$a(\text{PbCl}_2)$ 800°C	Probable Error*
0.886	0.8435	0.8730	0.8976	± 0.011
0.848	0.7485	0.7247	0.7060	± 0.038
0.789	0.7290	0.7009	0.6776	$< \pm 0.005$
0.745	0.6519	0.6418	0.6351	± 0.005
0.676	0.5174	0.5241	0.5308	± 0.005
0.622	0.3682	0.3956	0.4193	± 0.005
0.485	0.1806	0.1862	0.1909	± 0.005
0.398	0.0732	0.0779	0.0787	± 0.005
0.307	0.0275	0.0331	0.0384	± 0.005
1.000	1.0000	1.0000	1.0000	± 0.005

* At 700°C .

Results and Discussion

The e.m.f.'s of cells of type A are linear with respect to temperature and can be described most concisely in terms of equations as listed in Table 1.

Activities of PbCl_2 in the various mixtures are listed at three temperatures within the range of measurement, in Table 2.

The only other reported activity determinations for this system are those by Bloom and Hastie³ who used transpiration vapour pressure measurements with correction for errors due to volatilization of the vapour phase complex CsPbCl_3 , the existence of which has been proved by mass spectrometry.^{9,10} A comparison of activities of PbCl_2 at 650°C determined by e.m.f. with the vapour pressure study is shown in Figure 1. The activities of CsCl in the molten mixtures determined from those of PbCl_2 by graphical integration of the Gibbs-Duhem equation are also shown. The very considerable deviations from ideal behaviour are compatible with the formation of complex ions such as PbCl_3^- , PbCl_4^{2-} , and PbCl_6^{4-} in the mixtures.⁸

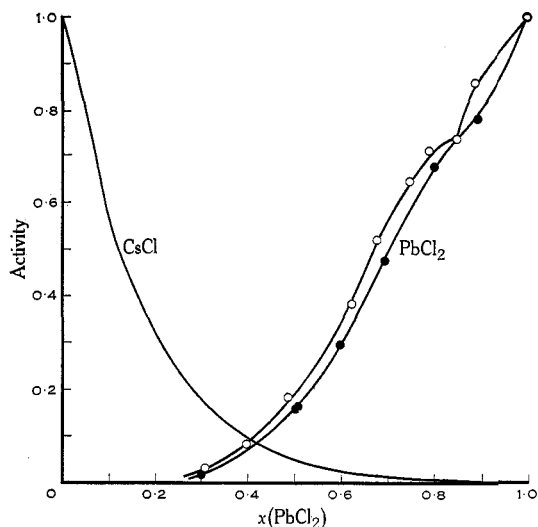


Fig. 1.—Activities of PbCl_2 and CsCl as a function of mole fraction of PbCl_2 in the system $\text{PbCl}_2 + \text{CsCl}$ at 650° :
 \circ $a(\text{PbCl}_2)$ by e.m.f.;
 \bullet $a(\text{PbCl}_2)$ by vapour pressure.⁸
 Other line, $a(\text{CsCl})$, by Gibbs-Duhem integration of activities of PbCl_2 .

The difference between activities of PbCl_2 determined by the two techniques is a little outside the combined maximum probable errors which are $\pm 4\%$ from vapour pressure and $\pm 1\%$ from e.m.f.; moreover, they always deviate in the same direction. A tentative explanation is that over-correction for the effect of volatilized CsPbCl_3 has been made in the vapour pressure study in which the uncorrected activity values would be higher than those by the e.m.f. method, over much of the composition range. The careful separation of anode and cathode compartments to prevent diffusion together of electrode materials, and the absence of junctions involving liquids of different composition, renders it unlikely that the values obtained by e.m.f. have any unaccounted errors.

Other thermodynamic properties of this system will be discussed in a subsequent publication.

¹⁰ Bloom, H., and Hastie, J. W., *J. chem. Phys.*, in press.