or the static method is suitable for such measurements. Some of the results obtained did not show close agreement with generally accepted values in the literature.

2. Interfacial tension values were obtained for certain halogen derivatives against mercury. These values are higher than those previously recorded.

3. Interfacial tension values were obtained for some liquids against mercury for which no data are given in the literature.

4. Data obtained for an homologous series of organic liquids against mercury indicated that, in the absence of solubility effects, the interfacial tension values of the members of an homologous series against a given liquid will decrease progressively if the surface tension values of the organic liquids increase progressively in the series.

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The Free Energy of Reactions Involving the Fused Chlorides and Bromides of Lead, Zinc and Silver

BY EDWARD J. SALSTROM

In the course of a series of studies on the thermodynamics of fused salt solutions, the free energy of formation of fused lead bromide,[1a] silver bromide,[1b] lead chloride[2] and zinc chloride,[2] calculated from the e. m. f. measurements on cells of the type, Pb(liq.), $PbBr_2$(liq.), Br_2(g), have already been given. With the aid of these data and measurements of the e. m. f. values of the cells Ag(s), AgCl(l), Cl_2(g) and Zn(l), $ZnBr_2$(l), Br_2(g) herein presented, the free energies of a series of chemical reactions have been calculated.

The apparatus and part of the experimental procedure were essentially the same as those previously described.[1a] Features peculiar to this research are briefly as follows. The silver chloride, containing a maximum impurity content of 0.014%, was obtained from commercial sources and used without further purification except for drying as described below. The zinc used as the negative electrode and the lead chloride serving as a source of chlorine were also from commercial sources of highest purity. The zinc bromide used in the cell and the lead bromide used as a source of electrolytic bromine were prepared as recently described.[3]

The chlorine gas used as an electrode in the cell (Ag(s), AgCl(l), Cl_2(g) was obtained by electrolyzing fused lead chloride which had been freed

(1) (a) Salstrom and Hildebrand, THIS JOURNAL, **52**, 4641 (1930); (b) *ibid.*, **52**, 4650 (1930).
(2) Wachter and Hildebrand, *ibid.*, **52**, 4655 (1930).
(3) Salstrom, *ibid.*, **55**, 1029 (1933).

TABLE I

Ag(s), AgCl(liq.), Cl_2(g)

Cell	A	A	B	A	B	B	A	B	A
Temp., °C.	470.7	471.4	479.1	482.3	495.7	498.1	509.8	512.1	536.3
E. m. f. obs., volt	0.9085	0.9083	0.9064	0.9054	0.9014	0.9009	0.8968	0.8964	0.8890
Cell	A	B	A	A	A	A	B	A	B
Temp., °C.	538.3	551.8	562.0	566.5	567.8	568.0	573.2	597.8	600.3
E. m. f. obs., volt	0.8883	0.8844	0.8822	0.8804	0.8802	0.8801	0.8786	0.8718	0.8712

Zn(liq.), $ZnBr_2$(liq.), Br_2(g)

Cell	A	B	B	A	A	A	B	B	A	B	C	C	C	C
Temp., °C.	401.7	406.2	417.4	427.2	429.4	430.4	437.2	445.8	448.3	456.9	473.5	491.1	502.1	504.4
E. m. f. obs., volt	1.3368	1.3340	1.3266	1.3199	1.3181	1.3176	1.3128	1.3070	1.3052	1.2994	1.2882	1.2765	1.2544	1.2675

TABLE II

All are liquids unless otherwise noted

Reactants	Zn $PbBr_2$	Zn $PbCl_2$	Zn 2AgBr	Zn 2AgCl	Pb 2AgBr	Pb 2AgCl	Cl_2(g) $ZnBr_2$	Cl_2(g) $PbBr_2$	Cl_2(g) 2AgBr	$PbCl_2$ $ZnBr_2$	$PbBr_2$ 2AgCl	$ZnBr_2$ 2AgCl
Products	$ZnBr_2$ Pb	$ZnCl_2$ Pb	$ZnBr_2$ 2Ag(s)	$ZnCl_2$ 2Ag(s)	$PbBr_2$ 2Ag(s)	$PbCl_2$ 2Ag(s)	$ZnCl_2$ Br_2(g)	$PbCl_2$ Br_2(g)	2AgCl Br_2(g)	$ZnCl_2$ $PbBr_2$	$PbCl_2$ 2AgBr	$ZnCl_2$ 2AgBr
E, volts 450°	0.2419		0.5033		0.2614				0.1138			
E, volts 500°	.2381	0.2995	.4837	0.6724	.2456	0.3729	0.3023	0.2409	.1136			
E, volts 550°	.2344	.2960	.4641	.6522	.2297	.3562	.3016	.2400	.1134			
E, volts 600°	.2307	.2925	.4443	.6321	.2137	.3396	.3010	.2391	.1132			
$-\Delta F$, cal. 450°	11,160		23,230		12,060				5250			
$-\Delta F$, cal. 500°	10,990	13,820	22,320	31,030	11,330	17,210	13,950	11,120	5240	2830	5880	8710
$-\Delta F$, cal. 550°	10,820	13,660	21,420	30,100	10,600	16,440	13,920	11,080	5230	2850	5830	8680
$-\Delta F$, cal. 600°	10,650	13,500	20,500	29,170	9,870	15,670	13,890	11,030	5220	2870	5780	8650
ΔS, cal./deg.	− 3.46	− 3.2	−18.09	−18.62	−14.63	−15.42	− 0.63	− 0.89	−0.10			
ΔH, kg. cal.	−13.67	−16.29	−36.30	−45.42	−22.64	−29.13	−14.44	−11.81	−5.32			

from moisture and hydrolysis products by bubbling dry hydrogen chloride gas up through the fused salt for about an hour. The cell was similarly freed from traces of moisture. The chlorine electrode was produced by bubbling the gas over a graphite rod dipping into the melt. The graphite rods used as electrodes in the cell and chlorine generator were first treated for about twenty-four hours with chlorine under several atmospheres pressure at 600°. They were then heated in the oxygen flame to a bright yellow heat until no more fumes were evolved, and allowed to cool in an atmosphere of chlorine. These rods were used over and over again, but with each new cell or generator the glowing and cooling process was repeated. The negative electrode was a pure silver wire inserted into the bottom of the cell through a glass tube.[1b]

As in previous studies these cells involved a thermoelectric effect due to the temperature gradient existing at each electrode. This effect has been measured and the experimental results including this correction are given in Table I.

When the e. m. f. values shown in Table I are plotted against temperature on a large scale the maximum deviation of the results from a straight line drawn through them is 0.5 mv. for silver chloride and 0.6 mv. for zinc bromide. These e. m. f. values may be expressed in volts by $E = 1.0461 - 0.000292t$ for the cell Ag, AgCl, Cl_2; and $E = 1.6112 - 0.000682t$ for the cell Zn, $ZnBr_2$, Br_2.

Using the e. m. f. values of such cells involving the fused chlorides and bromides of zinc, lead and silver, the free energy, ΔF, the heat, ΔH, and the entropy, ΔS, for a series of reactions have been calculated. These are shown in Table II.

For each reaction only one value is given for ΔH and one for ΔS, since in the range studied these do not change with temperature. In the three metathetical reactions shown at the end of the table the entropy changes were in each case less than one entropy unit, hence ΔS is not given and ΔH would thus be essentially the same as ΔF.

Summary

Measurements of the e. m. f. of the cells Zn(l), $ZnBr_2$(l), Br_2(g), and Ag(s), AgCl(l), Cl_2(g) have been made between the temperatures of 401 and 504°, and the temperatures 470 and 600°, respectively.

The free energy, entropy and heat of a series of reactions have been calculated.

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