CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS, OTTAWA

MINES BRANCH
RESEARCH REPORT

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PRICE 25 CENTS

VOLTAIC CELLS IN FUSED SALTS

PART II. THE SYSTEMS: (a) SILVER-SILVER CHLORIDE, LEAD-LEAD CHLORIDE; (b) SILVER-SILVER CHLORIDE, ZINC-ZINC CHLORIDE; AND (c) SILVER-SILVER CHLORIDE, NICKEL-NICKELOUS CHLORIDE

by

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REPRINTED FROM CANADIAN JOURNAL OF CHEMISTRY, VOL. 35, 1957, pp. 1254-1259

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S. N. FLENGAS[2] AND T. R. INGRAHAM[3]

ABSTRACT

Using a reversible silver – silver chloride reference electrode, described in the first paper of this series, standard electrode potentials have been established for the systems lead – lead chloride, zinc – zinc chloride, and nickel – nickelous chloride, in melts containing equimolar quantities of KCl and NaCl. Deviations from ideality were observed, and these were attributed to the formation of complexes. Dissociation constants for the complexes were calculated. The effect of temperature on the electromotive forces of the voltaic cells was also measured, and the heats of the cell reactions were calculated from the data.

INTRODUCTION

Part I of this series (1) described the development and use of a reversible silver – silver chloride electrode for measuring the electromotive forces of a cobalt–silver voltaic cell in chloride melts at high temperatures.

In this second paper of the series, experiments will be described in which the reversible silver – silver chloride electrode was combined with half-cells containing respectively lead – lead chloride, zinc – zinc chloride, and nickel – nickelous chloride electrodes. An equimolar mixture of molten potassium and sodium chlorides was used as the common solvent.

These results are an additional contribution to the program in these laboratories of establishing an electromotive series of metals in molten salts for different temperatures.

EXPERIMENTAL

The apparatus and technique used to study the lead, zinc, and nickel systems were essentially the same as those developed for studying the cobalt system, with the exception that the indicator electrodes for lead and zinc were redesigned to permit the use of the molten metals as electrodes. The simple electrode design is shown in Fig. 1, from which it will be evident that electrical connection with the pool of molten metal within the indicator electrode was made by a tungsten wire dipped into the metal. All of the metals used in these experiments were of high purity, e.g. 99.99%, and argon was used as an inert gas cover on the cells. As previously described (1), the argon flow was discontinued during the actual electromotive force measurements to permit steady values to be obtained.

The cell reaction for voltaic cells of the following type, in ideal solution, is:

$$M + 2Ag^{+} = M^{++} + 2Ag \qquad [1$$

$$\begin{array}{c|c||c||c|c} M & MCl_2\,(x_2) & & AgCl\,(x_1) & Ag \\ (-) & \text{KCl–NaCl (1/1 mole)} & \text{Asbestos fiber} & \text{KCl–NaCl (1/1 mole)} & (+) \\ & \text{(indicator electrode)} & & \text{(reference electrode)} & \end{array}$$

where M is, respectively, lead, zinc, or nickel.

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[1] *Manuscript received June 17, 1957.*
Contribution from the Department of Mines and Technical Surveys, Ottawa. Published with the permission of the Director, Mines Branch, Ottawa.

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The electromotive force of the experimental voltaic cell should obey the Nernst equation expressed as:

$$E_{\text{cell}} = (E^{\circ}_{\text{M}} - E^{\circ}_{\text{Ag}}) - (2.303RT/2\mathcal{F})\log(x_2/x_1^2), \qquad [2]$$

where E°_{M} and E°_{Ag} are respectively the standard electrode potentials of the half-cells $\text{MCl} \mid \text{M}_2$ and $\text{Ag} \mid \text{AgCl}$ under the conditions of the experiments, and x_1 and x_2 are respectively the mole fractions of AgCl and MCl_2 in the alkali chloride melt solvent.

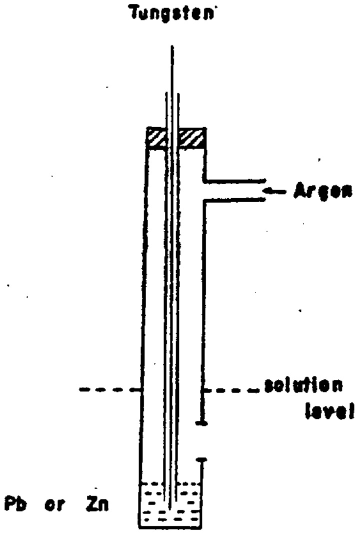


FIG. 1. All silica indicator electrode.

The electromotive forces of these cells were measured as a function of both the concentration of the indicator metal ion and the temperature of the cell.

RESULTS

The results of the experiments in which the concentration of the metal ion was varied at constant temperature are shown in Table I.

From equation [2] it follows that the relationship between E_{cell} and $\log (x_2/x_1^2)$ should be linear, and that when x_1 and x_2 are chosen so that the log term of this equation becomes zero, then

$$E_{\text{cell}} = E^{\circ}_{\text{M}} - E^{\circ}_{\text{Ag}}.$$

When the electromotive forces of the cells were plotted against $\log (x_2/x_1^2)$ as calculated from the experimental data given in Table I, the results were represented by straight lines, in agreement with the theory, as shown in Fig. 2. The slopes of the experimental straight lines agree well with the theoretical values calculated from equation [2], for a two-electron electrode process. The results of these calculations are given in Table II. Also included in the table are values for the standard potentials of the cells derived graphically from the curves in Fig. 2, and theoretical standard potentials calculated from data given by Hamer, Malmberg, and Rubin (2).

In the above table it is of theoretical interest to compare the experimentally obtained standard potentials of the voltaic cells with the theoretical values calculated from purely thermodynamic data. The differences have been attributed to the formation of complexes between the metal chlorides and the alkali chloride melt solvent. The dissociation constants, K_d, of these complexes have been calculated from the differences between the

TABLE I

ELECTROMOTIVE FORCES OF VOLTAIC CELLS AS A FUNCTION OF THE METAL ION CONCENTRATION IN THE INDICATOR ELECTRODE

(*a*) Pb (−) | $PbCl_2$ in 1/1 mole KCl–NaCl || AgCl in 1/1 mole KCl–NaCl | Ag (+)

Mole fraction of AgCl (x_1)	Mole fraction of $PbCl_2$ (x_2)	*t*, ° C.	E_{cell} (volts)
7.219×10^{-2}	3.254×10^{-4}	682	0.4638
"	9.808×10^{-4}	"	0.4318
"	1.827×10^{-3}	"	0.4107
"	3.818×10^{-3}	"	0.3822
"	8.116×10^{-3}	"	0.3533
"	6.276×10^{-2}	"	0.2775

(*b*) Zn (−) | $ZnCl_2$ in 1/1 mole KCl–NaCl || AgCl in 1/1 mole KCl–NaCl | Ag (+)

Mole fraction AgCl (x_1)	Mole fraction of $ZnCl_2$ (x_2)	*t*, ° C.	E_{cell} (volts)
7.201×10^{-2}	2.219×10^{-3}	684	0.876
"	6.438×10^{-3}	"	0.834
"	1.376×10^{-2}	"	0.801
"	2.496×10^{-2}	"	0.772
"	5.529×10^{-2}	"	0.738
"	7.710×10^{-2}	"	0.734

(*c*) Ni (−) | $NiCl_2$ in 1/1 mole KCl–NaCl || AgCl in 1/1 mole KCl–NaCl | Ag (+)

Mole fraction of AgCl (x_1)	Mole fraction of $NiCl_2$ (x_2)	*t*, ° C.	E_{cell} (volts)
6.235×10^{-2}	5.938×10^{-4}	705	0.2293
"	2.622×10^{-3}	"	0.1570
"	9.069×10^{-3}	"	0.1003
"	1.392×10^{-2}	"	0.0785
"	2.454×10^{-2}	"	0.0501
"	4.612×10^{-2}	"	0.0193
"	6.236×10^{-2}	"	0.0070

TABLE II

COMPARISON OF EXPERIMENTAL AND CALCULATED RESULTS FOR THE Pb, Zn, AND Ni ELECTRODE SYSTEMS

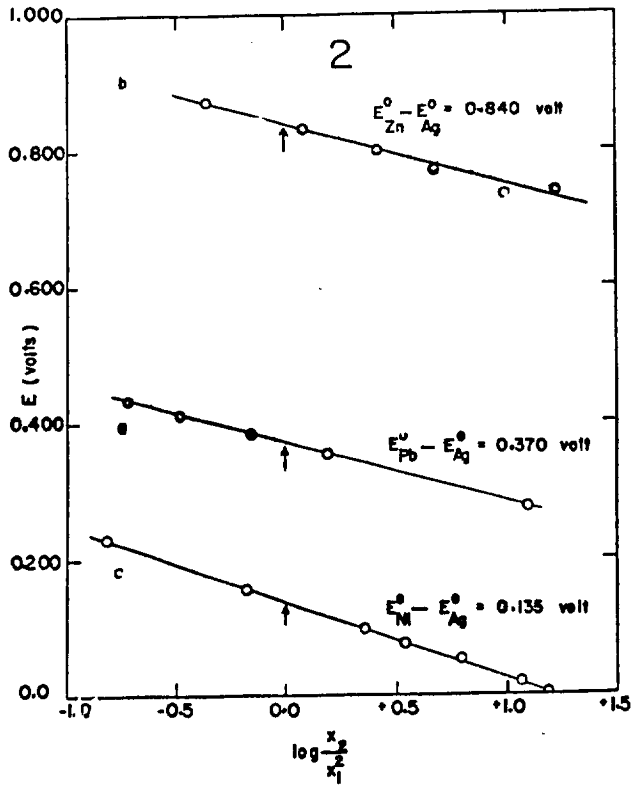
Cell reaction	*t*, ° C.	$E^\circ_M - E^\circ_{Ag}$ (volts)		Slope	
		Exptl.	Calc.	Exptl.	Calc.
$Pb + 2Ag^+ = Pb^{++} + 2Ag$	682	0.370	0.320	0.093	0.094
$Zn + 2Ag^+ = Zn^{++} + 2Ag$	684	0.840	0.665	0.093	0.095
$Ni + 2Ag^+ = Ni^{++} + 2Ag$	705	0.135	0.087	0.097	0.097

experimental and theoretical standard potentials, using the method previously described (1). The calculated values are:

$$K_d \text{ (Pb complex)} = 2.9\times10^{-1},$$

$$K_d \text{ (Zn complex)} = 1.5\times10^{-2},$$

$$K_d \text{ (Ni complex)} = 3.0\times10^{-1}.$$



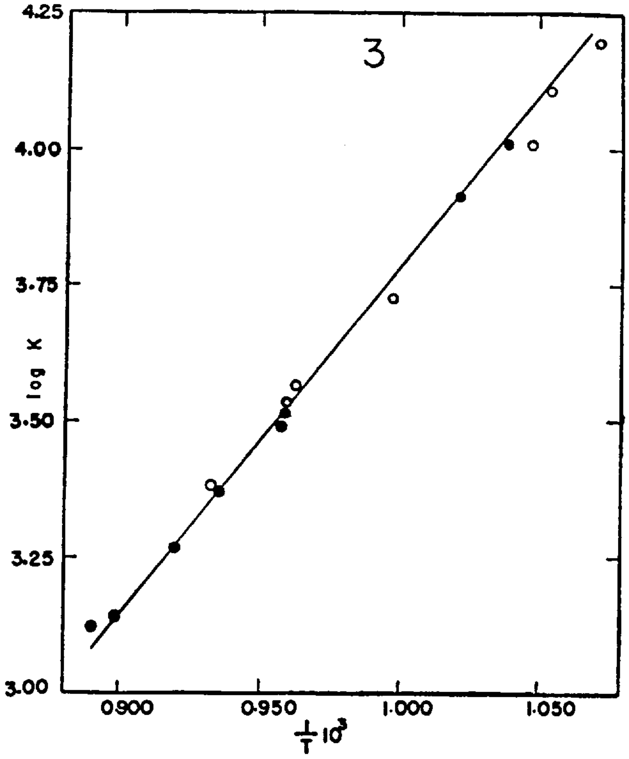


FIG. 2. Electromotive forces of the cells:

$$\begin{array}{l|l||l|l} \mathrm{M} & \mathrm{MCl_2}\ (x_2) & \mathrm{AgCl}\ (x_1) & \mathrm{Ag} \\ & \mathrm{KCl\text{-}NaCl}\ (1/1\ \mathrm{mole}) & \mathrm{KCl\text{-}NaCl}\ (1/1\ \mathrm{mole}) & \end{array}$$

as a function of log (x_2/x_1^2) at a constant temperature. M is respectively (*a*) lead, (*b*) zinc, and (*c*) nickel.

FIG. 3. The variation of log *K* with the reciprocal of absolute temperature for the system:

$$\begin{array}{l|l||l|l} \mathrm{Pb} & \mathrm{PbCl_2}\ (x_2 = 6.276\times10^{-2}) & \mathrm{AgCl}\ (x_1 = 7.219\times10^{-2}) & \mathrm{Ag} \\ & \mathrm{KCl\text{-}NaCl}\ (1/1\ \mathrm{mole}) & \mathrm{KCl\text{-}NaCl}\ (1/1\ \mathrm{mole}) & \end{array}$$

○ with increasing temperature, ● with decreasing temperature.

The magnitude of the constants indicates that the complexes formed by lead chloride and nickel chloride are very weak, and that the complex formed by zinc chloride is fairly stable.

The effect of temperature change on the electromotive force of the voltaic cells was also investigated. The results of these experiments, for a temperature range between 650° and 850° C., are given in Table III. Also included in Table III are values for the standard potentials calculated from the data using equation [2].

From the standard potentials given in Table III, using the well-known equations:

$$\Delta F^o = -nE^o\mathcal{F}, \qquad [3]$$

$$\Delta F^o = -2.303RT \log K, \qquad [4]$$

it was possible to calculate, for various temperatures, the effective equilibrium constants for the cell reactions given in Table II. These equilibrium constants are understood to include any effects due to the presence of the solvent.

The results of these calculations are shown in Figs. 3, 4, and 5, where log *K* was plotted against the reciprocal of the absolute temperature. The curves are linear over the temperature range investigated. For each curve, the best straight line through the experimental points was calculated by applying the least squares method. The average deviations of the experimental log *K* values were of the order of ±0.020.

The heat of reaction (ΔH_r), in cells of this type, is the difference between the heats of formation of the respective chlorides in the melt (ΔH_f), i.e.

$$\Delta H_r = \Delta H_{f(\mathrm{MCl_2\ in\ KCl-NaCl})} - 2\Delta H_{f(\mathrm{AgCl\ in\ KCl-NaCl})}.$$

TABLE III

EFFECT OF TEMPERATURE ON THE ELECTROMOTIVE FORCE OF THE CELLS

M | MCl_2 in KCl-NaCl || AgCl in KCl-NaCl | Ag

where M is, respectively, lead, zinc, or nickel

Pb–Ag voltaic cell*			Zn–Ag voltaic cell†			Ni–Ag voltaic cell‡		
T, ° K.	E_{cell} (volts)	$E°_{Pb}-E°_{Ag}$ (volts)	T, ° K.	E_{cell} (volts)	$E°_{Zn}-E°_{Ag}$ (volts)	T, ° K.	E_{cell} (volts)	$E°_{Ni}-E°_{Ag}$ (volts)
On heating								
933	0.2888	0.3890	940	0.7427	0.8490			
949	0.2858	0.3876	961	0.7394	0.8481	1013	−0.0200	0.1039
955	0.2775	0.3799	967	0.7378	0.8472	1021	−0.0237	0.1010
1003	0.2625	0.3700	989	0.7282	0.8462	1043	−0.0295	0.0979
1040	0.2560	0.3673	1001	0.7248	0.8378	1111	−0.0497	0.0859
1043	0.2543	0.3659	1015	0.7173	0.8319			
1073	0.2448	0.3597	1018	0.7155	0.8305			
			1033	0.7095	0.8261			
			1047	0.7036	0.8217			
			1058	0.6982	0.8176			
			1068	0.6918	0.8125			
			1088	0.6871	0.8098			
			1098	0.6838	0.8076			
			1103	0.6803	0.8046			
On cooling								
1123	0.2221	0.3470	1109	0.6791	0.8041	1103	−0.0448	0.0900
1113	0.2271	0.3459	1098	0.6848	0.8086	1083	−0.0402	0.0923
1088	0.2351	0.3516	1083	0.6920	0.8140	1063	−0.0340	0.0960
1069	0.2427	0.3570	1073	0.6962	0.8172	1037	−0.0292	0.0976
1045	0.2487	0.3616	1048	0.7071	0.8254			
1043	0.2517	0.3633	1028	0.7152	0.8312	988	−0.0105	0.1104
979	0.2747	0.3796	1009	0.7220	0.8360	938	−0.0082	0.1229
963	0.2805	0.3837	993	0.7294	0.8416			
			968	0.7419	0.8513			
			963	0.7446	0.8529			

The mole fractions of AgCl *and* $PbCl_2$ *were respectively* 7.219×10^{-2} (x_1) *and* 6.276×10^{-2} (x_2).

†*The mole fractions of* AgCl *and* $ZnCl_2$ *were respectively* 7.201×10^{-2} (x_1) *and* 7.150×10^{-2} (x_2).

‡*The mole fractions of* AgCl *and* $NiCl_2$ *were respectively* 6.234×10^{-2} (x_1) *and* 6.656×10^{-2} (x_2).

These heats of reaction were calculated from the slopes of the straight lines in Figs. 3, 4, and 5, in accordance with the van't Hoff equation:

$$d \ln K/dT = \Delta H_r/RT^2.$$

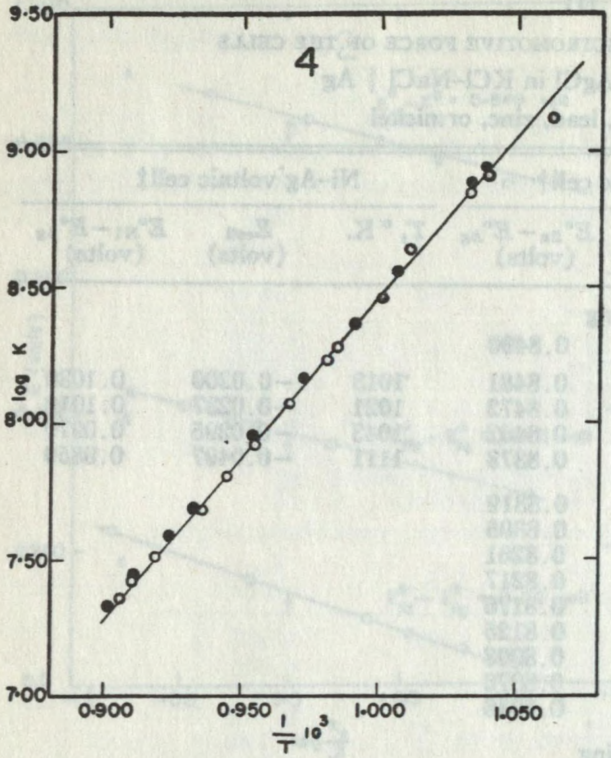
The results thus obtained are:

$$\Delta H_r \text{ (Pb–Ag)} = -29.0\pm1.0 \text{ kcal.},$$

$$\Delta H_r \text{ (Zn–Ag)} = -54.4\pm1.3 \text{ kcal.},$$

$$\Delta H_r \text{ (Ni–Ag)} = -14.0\pm1.0 \text{ kcal.}$$

It will be noted that these values include any effects due to the presence of solvent.



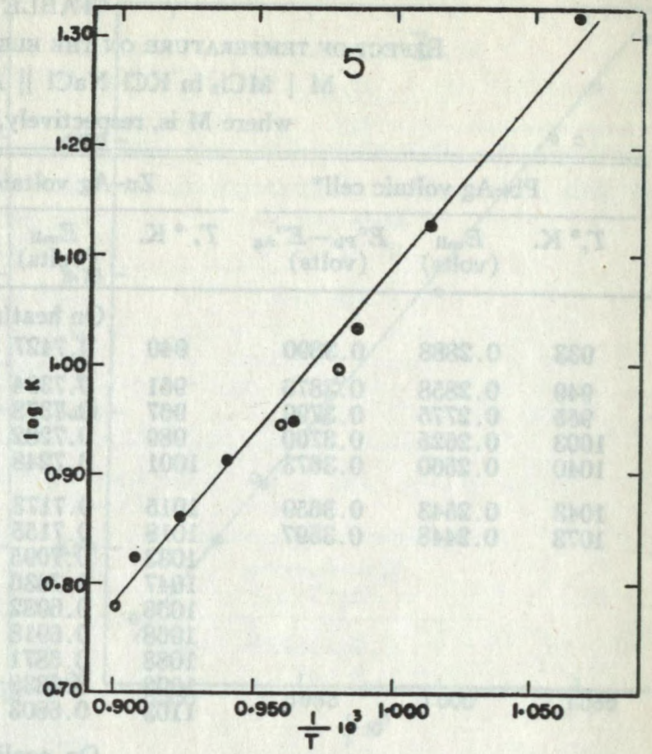


FIG. 4. The variation of log K with the reciprocal of absolute temperature for the system:

$\mathrm{Zn} \mid \mathrm{ZnCl_2}\ (x_2 = 7.150\times10^{-2}) \mid\mid \mathrm{AgCl}\ (x_1 = 7.201\times10^{-2}) \mid \mathrm{Ag}$

$\mid$ KCl–NaCl (1/1 mole) $\mid\mid$ KCl–NaCl (1/1 mole)

○ with increasing temperature, ● with decreasing temperature.

FIG. 5. The variation of log K with the reciprocal of absolute temperature for the system:

$\mathrm{Ni} \mid \mathrm{NiCl_2}\ (x_2 = 6.656\times10^{-2}) \mid\mid \mathrm{AgCl}\ (x_1 = 6.234\times10^{-2}) \mid \mathrm{Ag}$

$\mid$ KCl–NaCl (1/1 mole) $\mid\mid$ KCl–NaCl (1/1 mole) $\mid$

○ with increasing temperature, ● with decreasing temperature.

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2. HAMER, W., MALMBERG, M., and RUBIN, B. J. Electrochem. Soc. 103, 1, 8 (1956).