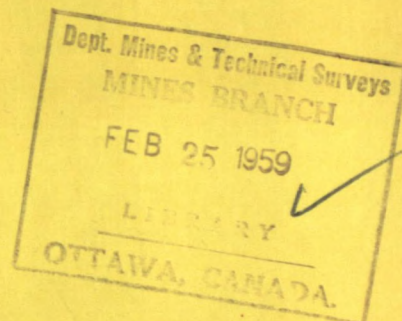




CANADA

VOLTAIC CELLS IN FUSED SALTS

PART V. THE SYSTEMS Sn/SnCl_2 (KCl-NaCl), Fe/FeCl
(KCl-NaCl), AND Mn/MnCl_2 (KCl-NaCl)



by

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S. N. FLENGAS AND T. R. INGRAHAM

ABSTRACT

Using a Ag/AgCl (KCl-NaCl) reference electrode, the standard electrode potentials of the systems Sn/SnCl₂ (KCl-NaCl), Fe/FeCl₂ (KCl-NaCl), and Mn/MnCl₂ (KCl-NaCl) were determined at 700° C and found to be 0.370 v, 0.520 v, and 1.205 v respectively. In each of the systems the Nernst equation was found to be applicable over the range of concentrations investigated.

The effect of temperature on the electromotive forces of the above cells was measured and the heats of the cell reactions were calculated from the data.

INTRODUCTION

In previous publications in this series (1, 2, 3, 4) standard potentials for several electrode systems in fused salts were reported. To determine the potentials, a silver - silver chloride electrode was used as a null point reference electrode, and an equimolar mixture of sodium and potassium chlorides was used as the solvent for the metallic salts.

In this investigation, the method was applied to the systems tin - stannous chloride, iron - ferrous chloride, and manganese - manganous chloride. These metal chlorides were found to give stable solutions in the alkali chloride - molten salt solvent.

PREPARATION OF MATERIALS

Because the anhydrous metallic salts required in this work were not commercially available, it was necessary to prepare them.

Anhydrous stannous (II) chloride was prepared from the corresponding hydrated salt of analytical grade by heating in a tubular electric furnace at 250° C under a continuous stream of dried gaseous HCl, produced by the action of concentrated H₂SO₄ on concentrated HCl.

Anhydrous ferrous (II) chloride was prepared from National Bureau of Standards certified iron filings by dissolution in concentrated HCl, and recovery of the hydrated ferrous salt by crystallization under an oxygen-free argon cover. The product was filtered under argon and washed with ether. Finally, the light-green hydrated ferrous chloride was dried by heating at 500° C in a stream of dry HCl. In the preparations of stannous chloride and of ferrous chloride, argon was used to flush the apparatus at the beginning and the end of the drying process. The dry divalent chlorides were stable in air and were pelletized without requiring any precautions against oxidation.

Anhydrous manganous (II) chloride was prepared from the corresponding hydrated salt of analytical grade, by heating at 600° C in the presence of a carbon tetrachloride vapor stream which was produced by flash distillation.

The anhydrous salts prepared by the foregoing methods were analyzed and found to be of a purity in excess of 99%. The impurity in each of the chlorides was the corresponding metal oxide.

Very pure (99.99%) tin was used as the liquid indicator electrode in the Sn-Ag voltaic cell. A 1/2-in. diameter rod of very pure electrolytic iron (99.99%) was used as the indicator

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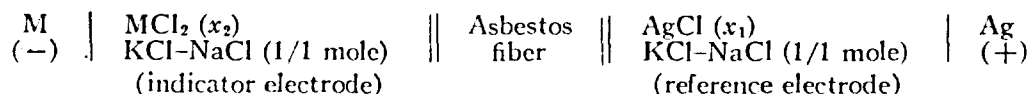
Contribution from the Mineral Dressing and Process Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa.

electrode in the Fe-Ag voltaic cell. The manganese metal indicator electrode for the Mn-Ag voltaic cell was prepared from pure electrolytic manganese metal (99.9%) which was remelted and cast into a cylindrical form. The casting was done in a water-cooled arc furnace, operated under reduced argon gas pressure. Platinum wire or tungsten wire was used as the indicator electrode connection to the potentiometer.

EXPERIMENTAL

The experimental technique and the apparatus used to study the tin, iron, and manganese systems were the same as in the previous experiments (3, 4) with solid and liquid metal indicator electrodes and cells under inert gas cover.

The experimental cells were of the type,



where M was respectively tin (pool of liquid metal), iron, and manganese metal, and MCl_2 was respectively SnCl_2 , FeCl_2 , and MnCl_2 at a mole fraction x_2 . The reaction in cells of this type is:



The relationship between the electromotive force and the metal ion concentration in the cell is given by the Nernst equation in the form:

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

where $E_{\text{M}/\text{M}^{2+}}^{\circ}$ and $E_{\text{Ag}/\text{Ag}^+}^{\circ}$ are respectively the standard electrode potential of the half-cells Sn/ SnCl_2 , Fe/ FeCl_2 or Mn/ MnCl_2 , and Ag/AgCl under the conditions of the experiments.

It will be observed that in equation [2] mole fractions are used instead of activities. The simplification is justified, as will be shown by the subsequent data, only when the activity coefficients or the complexity constants of the species involved in the cell reaction, or both, remain constant over the concentration range investigated. Thus, standard potentials calculated from equation [2] will include the effects due to both activities and complex formation.

From equation [2] it follows that when $\log(x_2/x_1^2)$ is equal to zero, the cell potential is the difference in the standard electrode potentials of the system.

RESULTS

The electromotive forces of the Sn-Ag, Fe-Ag, and Mn-Ag voltaic cells were measured first as a function of the metal ion concentration and then as a function of temperature.

The results of the experiments in which the concentration of the metal ion was varied at constant temperature are given in Table I. A 15 mv correction has been included for thermoelectric effects in the Sn-Ag cell and 9 mv in the Fe-Ag cell. No correction was required in the Mn-Ag cell.

When the electromotive forces of the cells were plotted against the term $\log(x_2/x_1^2)$, as calculated from the data given in Table I, the results were well represented by straight lines as shown in Figs. 1 and 2. The slopes of the experimental lines for Sn-Ag, Fe-Ag, and Mn-Ag systems agree well with the theoretical value for a two-electron electrode process as calculated from equation [2] (0.096, 0.095, and 0.097 as compared with

TABLE I

ELECTROMOTIVE FORCES OF VOLTAIC CELLS AT CONSTANT TEMPERATURE AS A FUNCTION OF THE METAL ION CONCENTRATION AT THE INDICATOR ELECTRODE

(a) Sn SnCl ₂ (x ₂) AgCl (x ₁) Ag (-) KCl-NaCl (1/1mole) KCl-NaCl (1/1 mole) (+)			
Mole fraction of AgCl (x ₁)	Mole fraction of SnCl ₂ (x ₂)	t, ° C	E _{cell} (volts)
6.235 × 10 ⁻²	6.322 × 10 ⁻⁴	680	0.453
6.235 × 10 ⁻²	1.433 × 10 ⁻³	680	0.418
6.235 × 10 ⁻²	2.251 × 10 ⁻³	680	0.397
6.235 × 10 ⁻²	4.606 × 10 ⁻³	680	0.366
6.235 × 10 ⁻²	7.585 × 10 ⁻³	680	0.342
6.235 × 10 ⁻²	1.264 × 10 ⁻²	680	0.323
(b) Fe FeCl ₂ (x ₂) AgCl (x ₁) Ag (-) KCl-NaCl (1/1 mole) KCl-NaCl (1/1 mole) (+)			
Mole fraction of AgCl (x ₁)	Mole fraction of FeCl ₂ (x ₂)	t, ° C	E _{cell} (volts)
6.235 × 10 ⁻²	8.853 × 10 ⁻⁴	695	0.582
6.235 × 10 ⁻²	2.122 × 10 ⁻³	695	0.546
6.235 × 10 ⁻²	3.771 × 10 ⁻³	695	0.523
6.235 × 10 ⁻²	7.541 × 10 ⁻³	695	0.491
6.235 × 10 ⁻²	1.385 × 10 ⁻²	695	0.467
(c) Mn MnCl ₂ (x ₂) AgCl (x ₁) Ag (-) KCl-NaCl (1/1 mole) KCl-NaCl (1/1 mole) (+)			
Mole fraction of AgCl (x ₁)	Mole fraction of MnCl ₂ (x ₂)	t, ° C	E _{cell} (volts)
6.235 × 10 ⁻²	5.867 × 10 ⁻⁴	680	1.284
6.235 × 10 ⁻²	1.391 × 10 ⁻³	680	1.249
6.235 × 10 ⁻²	2.566 × 10 ⁻³	680	1.226
6.235 × 10 ⁻²	4.779 × 10 ⁻³	680	1.200
6.235 × 10 ⁻²	1.087 × 10 ⁻²	680	1.116

the theoretical value of 0.096). In addition, the linearity of the curves in Fig. 1 shows that the activity coefficients or the complexity constants of the species involved in the cell reaction remain constant over the range of concentrations investigated.

The experimental standard electrode potentials for the tin, iron, and manganese systems, as obtained from interpolation at $\log(x_2/x_1^2) = 0$ on the curves in Fig. 1, are given in Table II. In addition, Table II also includes, for comparison, calculated (5) values for the standard potentials of the cell reactions in the absence of solvent.

It should be noted that all potential measurements shown above are equilibrium values. Equilibrium was attained in a few minutes after each change in the metal salt

TABLE II
SUMMARY OF RESULTS

Indicator electrode	Cell reaction in molten KCl-NaCl	t, ° C	Standard potential for:	Exptl.* (volts)	Calc.† (volts)
Sn, Sn ⁺⁺	Sn + 2AgCl = SnCl ₂ + 2Ag	700	$E_{\text{Sn/Sn}^{++}}^{\circ} - E_{\text{Ag/Ag}^{+}}^{\circ}$	0.370	0.405
Fe, Fe ⁺⁺	Fe + 2AgCl = FeCl ₂ + 2Ag	700	$E_{\text{Fe/Fe}^{++}}^{\circ} - E_{\text{Ag/Ag}^{+}}^{\circ}$	0.520	0.305
Mn, Mn ⁺⁺	Mn + 2AgCl = MnCl ₂ + 2Ag	700	$E_{\text{Mn/Mn}^{++}}^{\circ} - E_{\text{Ag/Ag}^{+}}^{\circ}$	1.205	1.010

*Experimental values corrected to refer to a temperature of 700° C.

†Potentials calculated from thermodynamic data on the pure salts in the absence of any solvent.

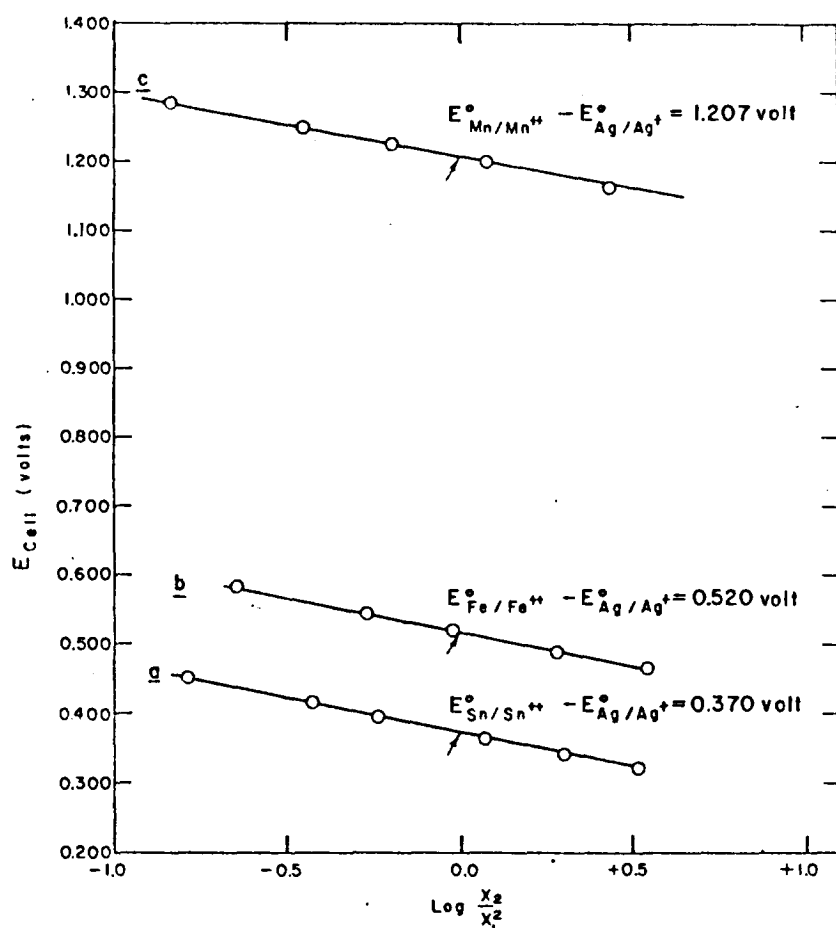
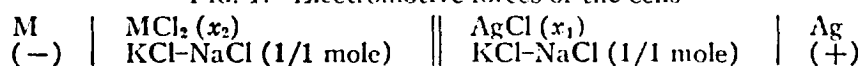


FIG. 1. Electromotive forces of the cells



as a function of $\log(x_2/x_1^2)$, at constant temperature. M is (a) tin, (b) iron, and (c) manganese. MCl_2 is respectively SnCl_2 , FeCl_2 , and MnCl_2 .

concentration. The potential was very steady and remained practically unchanged when the cells were left overnight.

The effect of temperature change on the electromotive forces of the tin, iron, and manganese cells was investigated next. The results of these experiments are given in Table III. The voltages have been corrected for thermoelectric effects. Also included in Table III are values for the standard potentials at different temperatures, calculated from the data, using equation [2].

From the standard potentials, using the procedure previously described (1, 2, 3, 4), it was possible to calculate for various temperatures the equilibrium constants (K) for the cell reactions given in Table II. The results of these calculations are given in Fig. 2, where $\log K$ was plotted against the reciprocal of absolute temperature. The curves are linear over the range of temperature investigated. The best straight lines were calculated by applying the least squares method.

The heat of reactions (ΔH_r) in cells of this type, as calculated according to the van't Hoff equation, is the difference between the heats of formation of the respective chlorides in the presence of the solvent.

The calculated values are:

$$\begin{aligned} \Delta H_{r(\text{Sn/Sn}^{++})} &= -23.4 \pm 1.0 \text{ kcal/mole,} \\ \Delta H_{r(\text{Fe/Fe}^{++})} &= -27.8 \pm 1.4 \text{ kcal/mole,} \\ \Delta H_{r(\text{Mn/Mn}^{++})} &= -61.8 \pm 1.5 \text{ kcal/mole.} \end{aligned}$$

TABLE III

EFFECT OF TEMPERATURE ON THE ELECTROMOTIVE FORCES OF THE CELLS

(a) Sn SnCl ₂ ($x_2 = 3.93 \times 10^{-3}$) AgCl ($x_1 = 6.235 \times 10^{-2}$) Ag (-) KCl-NaCl (1/1 mole) KCl-NaCl (1/1 mole) (+)			
$T, ^\circ\text{K}$	E_{cell} (volts)	$E^\circ_{\text{Sn/Sn}^{++}} - E^\circ_{\text{Ag/Ag}^+}$ (volts)	
On heating			
946	0.3771	0.3768	
996	0.3686	0.3686	
1053	0.3600	0.3597	
1109	0.3470	0.3467	
On cooling			
1057	0.3598	0.3596	
990	0.3710	0.3707	
949	0.3779	0.3776	
(b) Fe FeCl ₂ ($x_2 = 3.771 \times 10^{-3}$) AgCl ($x_1 = 6.235 \times 10^{-2}$) Ag (-) KCl-NaCl (1/1 mole) KCl-NaCl (1/1 mole) (+)			
$T, ^\circ\text{K}$	E_{cell} (volts)	$E^\circ_{\text{Fe/Fe}^{++}} - E^\circ_{\text{Ag/Ag}^+}$ (volts)	
On heating			
968	0.5231	0.5210	
1018	0.5199	0.5177	
1065	0.5154	0.5131	
1106	0.5073	0.5049	
1131	0.5047	0.5022	
1159	0.5010	0.4985	
On cooling			
1091	0.5147	0.5123	
1065	0.5162	0.5139	
1033	0.5213	0.5130	
981	0.5280	0.5258	
954	0.5299	0.5278	
(c) Mn MnCl ₂ ($x_2 = 4.779 \times 10^{-3}$) AgCl ($x_1 = 6.235 \times 10^{-2}$) Ag (-) KCl-NaCl (1/1 mole) KCl-NaCl (1/1 mole) (+)			
$T, ^\circ\text{K}$	E_{cell} (volts)	$E^\circ_{\text{Mn/Mn}^{++}} - E^\circ_{\text{Ag/Ag}^+}$ (volts)	
On heating			
943	1.204	1.211	
953	1.200	1.208	
1005	1.193	1.201	
1056	1.186	1.194	
1122	1.172	1.181	
1153	1.168	1.177	
On cooling			
1133	1.170	1.179	
1057	1.184	1.192	
1037	1.188	1.196	
1016	1.193	1.201	
995	1.196	1.204	
983	1.200	1.208	

Following the same procedure, and with the same reservations, as cited previously (1, 2, 3, 4), dissociation constants of complexes of SnCl₂, FeCl₂, or MnCl₂, respectively, in the molten salt solvent, have been calculated as follows:

$$\begin{aligned}
 K_{d(\text{SnCl}_2 \text{ complex})} &= 2.3, \\
 K_{d(\text{FeCl}_2 \text{ complex})} &= 5.9 \times 10^{-3}, \\
 K_{d(\text{MnCl}_2 \text{ complex})} &= 9.61 \times 10^{-3}.
 \end{aligned}$$

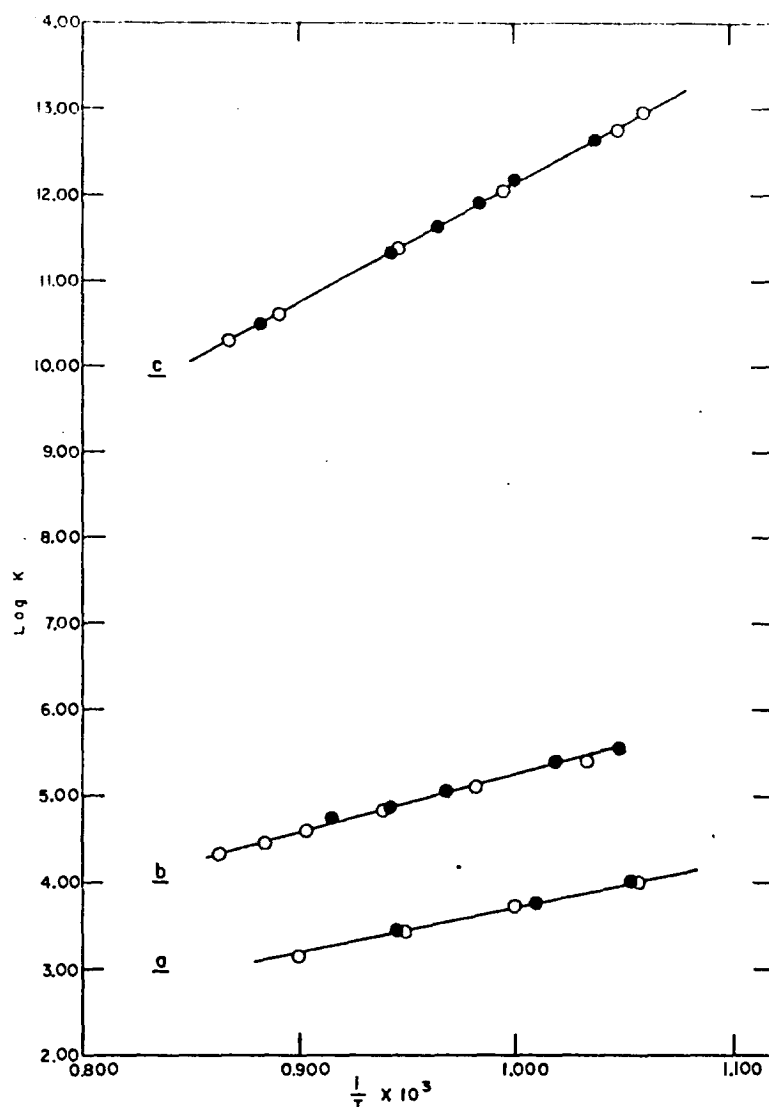


FIG. 2. The variation of $\log K$ with the reciprocal of absolute temperature for the systems:

(a)	Sn (-)	SnCl ₂ ($x_2 = 3.93 \times 10^{-3}$) KCl-NaCl (1/1 mole)		AgCl ($x_1 = 6.235 \times 10^{-2}$) KCl-NaCl (1/1 mole)		Ag (+)
$\Delta H = -23.4 \pm 1.0$ kcal.						
(b)	Fe (-)	FeCl ₂ ($x_2 = 3.771 \times 10^{-3}$) KCl-NaCl (1/1 mole)		AgCl ($x_1 = 6.235 \times 10^{-2}$) KCl-NaCl (1/1 mole)		Ag (+)
$\Delta H = -27.8 \pm 1.4$ kcal.						
(c)	Mn (-)	MnCl ₂ ($x_2 = 4.779 \times 10^{-3}$) KCl-NaCl (1/1 mole)		AgCl ($x_1 = 6.235 \times 10^{-2}$) KCl-NaCl (1/1 mole)		Ag (+)
$\Delta H = -61.8 \pm 1.5$ kcal.						

O with increasing temperature, ● with decreasing temperature.

It is of interest to note that both the iron and manganese complexes in the melt are substantially more stable than that formed by tin.

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