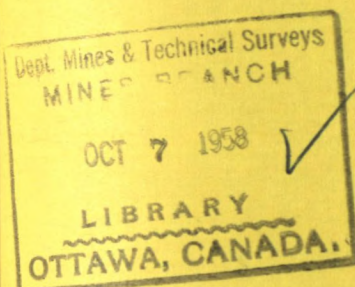




CANADA



DEPARTMENT OF MINES AND
TECHNICAL SURVEYS, OTTAWA

MINES BRANCH
RESEARCH REPORT

R 20

PRICE 25 CENTS

VOLTAIC CELLS IN FUSED SALTS

PART IV. ELECTRODE POTENTIALS OF THE SYSTEMS:
Tl/TlCl (KCl-NaCl), Cu/CuCl (KCl-NaCl), Cu/CuCl₂
(KCl-NaCl), Cr/CrCl₂ (KCl-NaCl), AND Cr/CrCl₃
(KCl-NaCl). REDOX POTENTIALS OF THE SYSTEMS:
Pt/CuCl, CuCl₂(KCl-NaCl), AND Pt/CrCl₂, CrCl₃ (KCl-NaCl)

by

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REPRINTED FROM CANADIAN JOURNAL OF
CHEMISTRY, VOL. 36, 1958, pp. 1103-1115

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S. N. FLENGAS² AND T. R. INGRAHAM

ABSTRACT

Using a Ag/AgCl (KCl-NaCl) reference electrode, the standard electrode potentials of the systems TI/TICl (KCl-NaCl), Cu/CuCl (KCl-NaCl), Cu/CuCl₂ (KCl-NaCl), Cr/CrCl₂ (KCl-NaCl), and Cr/CrCl₃ (KCl-NaCl) were measured and found to be: 0.650 volt at 680° C., and 0.250, -0.175, 0.755, and 0.423 at 700° C. respectively. The standard redox potentials of the systems Pt/CuCl₂, CuCl (KCl-NaCl), and Pt/CrCl₂, CrCl₂ (KCl-NaCl) were also measured at 700° C. and found to be 0.600 and 0.240 volt respectively. 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.

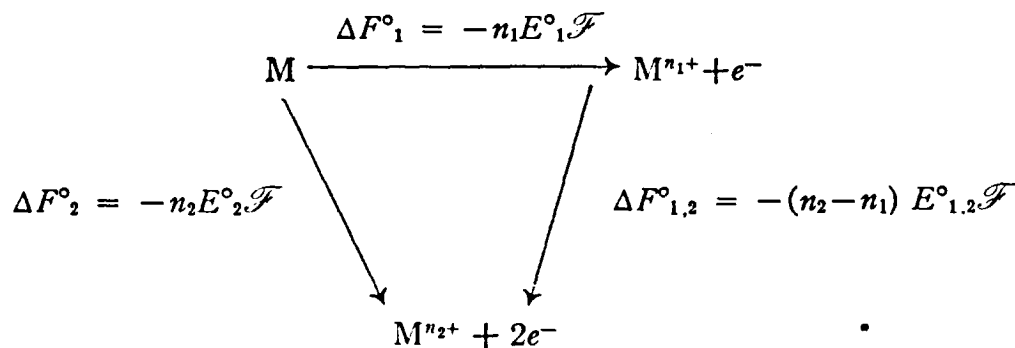
INTRODUCTION

In previous publications (1, 2, 3) in this series, standard potentials for several electrode systems in fused salts were reported. To make these measurements, an equimolar mixture of sodium and potassium chlorides was used as the solvent for the metal chloride in the system investigated, and a silver-silver chloride electrode, developed earlier in this work (1), was used as a reference in determining the electrode potential.

In the present investigation, the method has been applied to thallium, copper, and chromium. Both copper and chromium yield ions with two or more stable valency states at high temperatures. The potentials for each of the valence states and the associated redox potentials were determined.

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

When a metal, M, yields two positive ions, M^{n₁+} and M^{n₂+}, where n₂ > n₁, there are three standard potentials associated with the system. These are the potentials E[°]₁ and E[°]₂ of the electrodes M/M^{n₁+} and M/M^{n₂+} respectively, and the oxidation-reduction potential E[°]_{1,2} of the system M^{n₁+}/M^{n₂+}. The relationship between these three potentials can be seen from the following cyclic diagram:



The equation relating these potentials is:

$$[1] \quad n_2 E^{\circ}_2 - n_1 E^{\circ}_1 = (n_2 - n_1) E^{\circ}_{1,2}.$$

¹Manuscript received March 11, 1958.

Contribution from the Mines Branch Laboratories, Department of Mines and Technical Surveys, Ottawa.

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When any two of the three potentials are known (i.e. one electrode potential E°_1 , and the standard redox potential $E^\circ_{1,2}$) the unknown electrode potential E°_2 can be calculated.

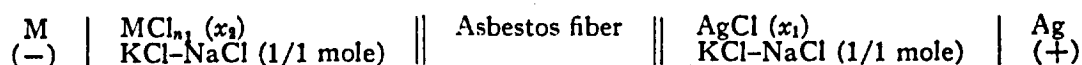
This method was applied to obtain the standard electrode potentials of the systems copper-cupric chloride and chromium-chromic chloride, neither of which could be measured directly because of the reactivity of the metals with their metal chlorides in solution.

EXPERIMENTAL

In the course of the experimental work, two different types of cells were used for determining potentials:

(a) Cells for Measurements of Metal Electrode Potentials

These were of the type



where M was respectively thallium, copper, or chromium metal, and MCl_{n_1} was respectively TlCl , CuCl , or CrCl_2 , at a mole fraction x_2 .

The reaction in voltaic cells of this type is:



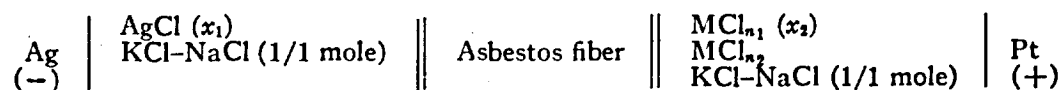
The relationship between the electromotive force and the metal ion concentration in the cell is given by the Nernst equation in the form:

$$[2] \quad E_{\text{cell}} = (E^\circ_{\text{M}/\text{M}^{n_1+}} - E^\circ_{\text{Ag}/\text{Ag}^+}) - (2.303RT/n_1 \mathcal{F}) \log(x_2/x_1^{n_1}),$$

where $E^\circ_{\text{M}/\text{M}^{n_1+}}$ and $E^\circ_{\text{Ag}/\text{Ag}^+}$ are respectively the standard electrode potentials of the half-cells Cu/CuCl , Cr/CrCl_2 , or Ag/AgCl , under the conditions of the experiment. It will be observed that in equation [2], mole fractions are used in preference to activities. The simplification is justified, as will be shown by the subsequent data, 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 electrode potentials calculated from equation [2] will include the effects due to both activities and complex formation.

(b) Cells for the Measurement of Redox Potentials

These were of the type:



where MCl_{n_1} was respectively CuCl or CrCl_2 at mole fraction x_2 , and MCl_{n_2} was respectively CuCl_2 or CrCl_3 at mole fraction x_3 .

The reaction in redox cells of this type is:



where $n_2 - n_1 = 1$.

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

$$[3] \quad E_{\text{cell}} = (E^\circ_{\text{Ag}/\text{Ag}^+} - E^\circ_{\text{M}^{n_1+}/\text{M}^{n_2+}}) - (2.303RT/\mathcal{F}) \log(x_1 x_2/x_3)$$

where $E^\circ_{M^{n_1+}/M^{n_2+}}$ is the standard redox potential of the half-cells Pt/CuCl, CuCl₂, or Pt/CrCl₂, CrCl₃, under the conditions of the experiment.

It will be noted that here, as in equation [3], mole fractions are used in preference to activities.

Preparation of Materials

Anhydrous cuprous chloride was prepared by recovery from an aqueous solution in which cupric chloride was reduced with sulphurous acid (4). The anhydrous cuprous chloride was washed with glacial acetic acid, anhydrous ether, and absolute alcohol.

Anhydrous chromic (III) chloride was prepared from the corresponding hydrated salt of analytical grade, by heating at 600° C. in the presence of carbon tetrachloride vapor (5). The compound thus obtained was in the form of violet-colored "greasy" scales, which were very stable in air. Anhydrous chromous (II) chloride was prepared by hydrogen reduction of the anhydrous chromic (III) chloride (6) in a tubular furnace heated at 550° C. To observe the end of the reduction, the HCl produced during the reaction was dissolved in water and titrated with normal sodium hydroxide solution. When purified dry hydrogen was used, the product was pure white.

All of the compounds thus prepared were pelletized and kept in closed containers in a desiccator over sulphuric acid until they were used. Analysis of the various samples of the different batches indicated that for all of the materials, a purity of over 99% had been attained.

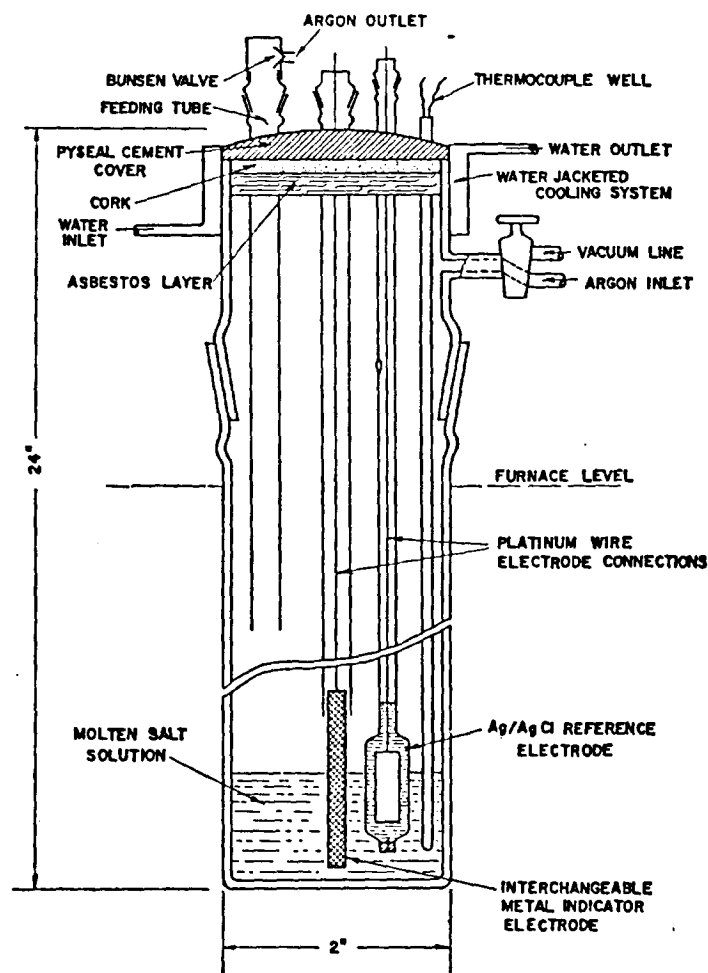


FIG. 1. All silica cell.

Apparatus and Procedure

The technique used to study the Tl-Ag, Cu-Ag, and Cr-Ag systems was essentially the same as that described in earlier papers of this series (1, 2, 3). Because the chlorides used in these experiments were reactive to both moisture and oxygen, the cell design was modified to permit evacuation to dehydrate the solvent salts before a run was begun. The modified apparatus is shown diagrammatically in Fig. 1. Slight improvements in the furnace design, over that used in previous work (1), have reduced temperature variations to $\pm 2^\circ$ C. at 900° C.

At the beginning of a run the cell was loaded with KCl-NaCl and heated for 12 hours under vacuum at 600° C. Purified argon was then introduced, the temperature increased to melt the salts, and the metal electrodes inserted into their respective positions. To protect the contents of the cell from air contamination, a small stream of argon was continuously introduced into the cell and released under a slight positive pressure through a Bunsen valve. Pellets of the metal chloride reagents were introduced, as required, through the feeding tube.

A pool of pure molten thallium metal (99.9%), copper wire of 99.99% purity or a block of 99.4% chromium metal were used as the indicator electrodes for the respective standard electrode potential measurements.

The indicator electrode for the measurement of redox potentials was a platinum tube 2 inches long and $\frac{1}{2}$ inch I.D. After each addition of reagent, equilibrium was attained in 2-3 hours. In the absence of any form of stirring this was attributed either to the slow process of dissolution of the pellet in the fused-salt solvent or to the subsequent slow diffusion of the salt through the solution.

After equilibrium had been established in a cell, the potential measurements were reproducible to within one millivolt over a 2-day period.

RESULTS

The electromotive forces of the Tl-Ag, Cu-Ag, and Cr-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 ions was varied at constant temperature are shown in Table I.

From equation [2], it follows that when x_1 and x_2 are chosen so that the log term of this equation becomes zero, then:

$$[4] \quad E_{\text{cell}} = E^\circ_{\text{M}/\text{M}^{n_1+}} - E^\circ_{\text{Ag}/\text{Ag}^+}.$$

When the electromotive forces of the cells were plotted against the log term $x_2/x_1^{n_1}$, as calculated from the data given in Table I, the results were well represented by straight lines, as shown in Fig. 2.

The slopes of the experimental lines for the Tl-Ag and Cu-Ag systems agree well with the theoretical value for a one-electron electrode process as calculated from equation [2] (0.191 and 0.196 respectively, as compared with the theoretical value 0.195 volt). That obtained with the Cr-Ag system corresponds to a two-electron electrode process (0.094, as compared with the theoretical 0.097 volt). In addition, the linearity of the curves in Fig. 2 shows that the activity coefficients or the complexity constants of TlCl, CuCl, and CrCl₂ in alkali chloride melt solution remain practically constant over the concentration range investigated.

The experimental standard electrode potentials for the copper, chromium, and thallium systems, as interpolated at $\log(x_2/x_1^{n_1}) = 0$ on the curves in Fig. 2, are given in Table II.

TABLE I
ELECTROMOTIVE FORCES OF VOLTAIC CELLS AS A FUNCTION OF THE METAL ION
CONCENTRATION AT THE INDICATOR ELECTRODE

(a) Tl (-)		TlCl (x_2) KCl-NaCl (1/1 mole)		AgCl (x_1) KCl-NaCl (1/1 mole)		Ag (+)
Mole Fraction of AgCl (x_1)	Mole fraction of TlCl (x_2)		$t, ^\circ\text{C.}$			E_{cell} (volts)
6.235×10^{-3}	3.610×10^{-3}		680			0.875
6.235×10^{-3}	6.907×10^{-3}		680			0.822
6.235×10^{-3}	1.425×10^{-3}		680			0.752
6.235×10^{-3}	2.503×10^{-3}		680			0.724
6.235×10^{-3}	3.645×10^{-3}		680			0.690
6.235×10^{-3}	4.140×10^{-3}		680			0.685
6.235×10^{-3}	5.540×10^{-3}		680			0.658
6.235×10^{-3}	6.026×10^{-3}		680			0.655
(b) Cu (-)		CuCl (x_2) KCl-NaCl (1/1 mole)		AgCl (x_1) KCl-NaCl (1/1 mole)		Ag (+)
Mole fraction of AgCl (x_1)	Mole fraction of CuCl (x_2)		$t, ^\circ\text{C.}$			E_{cell} (volts)
6.235×10^{-3}	1.080×10^{-3}		700			0.588
6.235×10^{-3}	3.961×10^{-3}		700			0.478
6.235×10^{-3}	1.296×10^{-3}		700			0.390
6.235×10^{-3}	2.372×10^{-3}		700			0.343
6.235×10^{-3}	3.912×10^{-3}		700			0.289
(c) Cr (-)		CrCl ₂ (x_2) KCl-NaCl (1/1 mole)		AgCl (x_1) KCl-NaCl (1/1 mole)		Ag (+)
Mole fraction of AgCl (x_1)	Mole fraction of CrCl ₂ (x_2)		$t, ^\circ\text{C.}$			E_{cell} (volts)
6.235×10^{-3}	2.822×10^{-4}		703			0.861
6.235×10^{-3}	5.640×10^{-4}		703			0.834
6.235×10^{-3}	1.323×10^{-3}		703			0.802
6.235×10^{-3}	2.359×10^{-3}		703			0.781
6.235×10^{-3}	3.467×10^{-3}		703			0.761
6.235×10^{-3}	6.027×10^{-3}		703			0.738
6.235×10^{-3}	9.352×10^{-3}		703			0.715

In addition, the table also includes calculated (7) values for the standard potentials of the cell reactions in the absence of solvent. The significance of the differences between the experimental and calculated potentials will be discussed later in the text.

TABLE II
SUMMARY OF RESULTS

Indicator electrode	Cell reaction in molten KCl-NaCl	$t, ^\circ\text{C.}$	Standard potential for	Exptl.* (volts)	Calc.† (volts)
Tl, Tl ⁺	Tl + AgCl = TlCl + Ag	680	$E_{\text{Tl/Tl}^+}^\circ - E_{\text{Ag/Ag}^+}^\circ$	0.650	0.665
Cu, Cu ⁺	Cu + AgCl = CuCl + Ag	700	$E_{\text{Cu/Cu}^+}^\circ - E_{\text{Ag/Ag}^+}^\circ$	0.250	0.140
Cu, Cu ⁺⁺	Cu + 2AgCl = CuCl ₂ + 2Ag	700	$E_{\text{Cu/Cu}^{++}}^\circ - E_{\text{Ag/Ag}^+}^\circ$	-0.175	(-0.410)‡
Cr, Cr ⁺⁺	Cr + 2AgCl = CrCl ₂ + 2Ag	703	$E_{\text{Cr/Cr}^{++}}^\circ - E_{\text{Ag/Ag}^+}^\circ$	0.755	0.565
Cr, Cr ⁺⁺⁺	Cr + 3AgCl = CrCl ₃ + 3Ag	703	$E_{\text{Cr/Cr}^{+++}}^\circ - E_{\text{Ag/Ag}^+}^\circ$	0.423	0.336
Cr ⁺⁺⁺ , Cr ⁺⁺	Ag + CrCl ₃ = AgCl + CrCl ₂	703	$E_{\text{Ag/Ag}^+}^\circ - E_{\text{Cr}^{++}/\text{Cr}^{+++}}^\circ$	0.240	0.122
Cu ⁺⁺ , Cu ⁺	Ag + CuCl ₂ = AgCl + CuCl	700	$E_{\text{Ag/Ag}^+}^\circ - E_{\text{Cu}^+/\text{Cu}^{++}}^\circ$	0.600	0.960

*Experimental values obtained during this investigation on voltaic cells containing alkali chloride molten salt solvent.

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

‡Obtained by extrapolation of low temperature data.

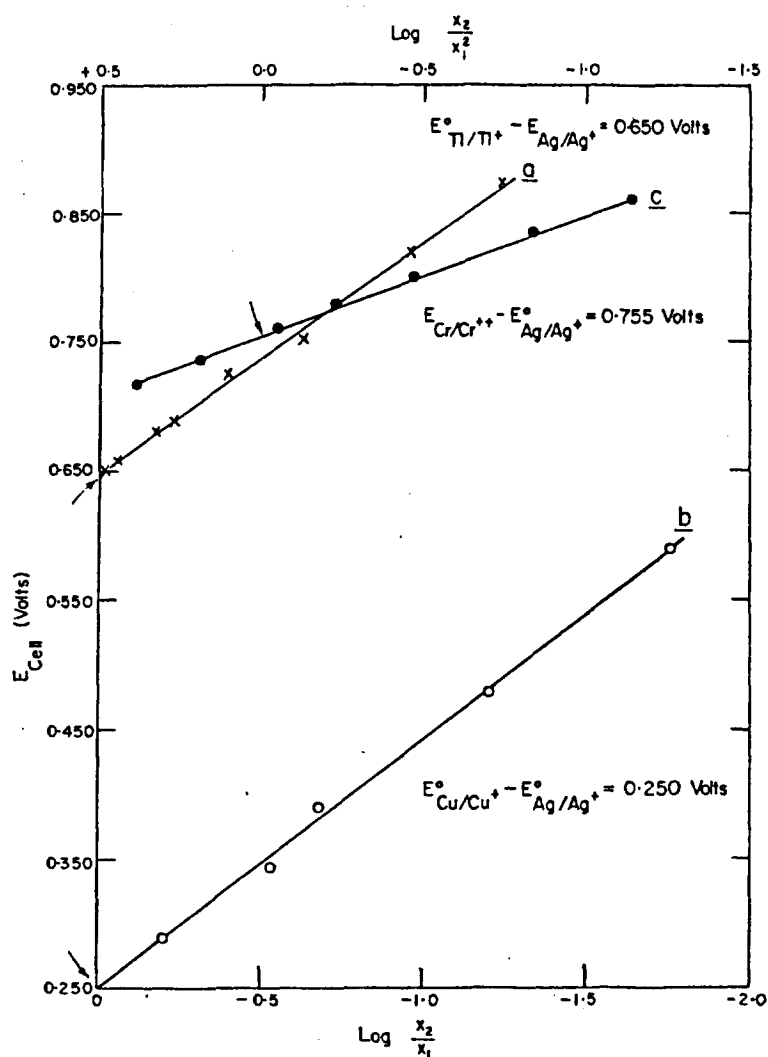
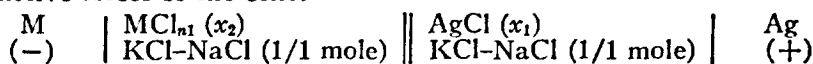


FIG. 2. Electromotive forces of the cells:



as a function of $\log(x_2/x_1^{n_1})$, at constant temperature.

M is (a) thallium, (b) copper, and (c) chromium (top scale). MCl_{n_1} is respectively TlCl , CuCl , and CrCl_2 .

The effect of temperature change on the electromotive forces of the voltaic cells previously cited was next investigated. Because of the volatility of TlCl (b.p. 720°C .), measurements above 700°C . were not possible with the Tl-Ag voltaic cell.

The results for the Cu-Ag and Cr-Ag voltaic cells are given in Table III. Also included in Table III are values for the standard potentials at different temperatures, calculated from the data using equation [2].

From Table III it is readily seen that temperature has practically no effect on the standard potential of the Cu-Ag voltaic cell.

From the standard potentials of the Cr-Ag voltaic cell given in Table III, using the well-known equations,

$$[5] \quad \Delta F^\circ = -n E^\circ \mathcal{F} = -2.303RT \log K$$

it was possible to calculate, for various temperatures, the equilibrium constants for the cell reactions given in Table II. The results of these calculations are shown in Fig. 3, where $\log K$ was plotted against the reciprocal of absolute temperature. The curve is linear over the temperature range investigated.

TABLE III

EFFECT OF TEMPERATURE ON THE ELECTROMOTIVE FORCES OF THE CELLS

(a)

Cu (-)	CuCl ($x_2 = 3.912 \times 10^{-2}$) KCl-NaCl (1/1 mole)		AgCl ($x_1 = 6.235 \times 10^{-2}$) KCl-NaCl (1/1 mole)		Ag (+)
		$T, ^\circ K$	E_{cell} (volts)	$E^\circ_{\text{Cu/Cu}^+} - E^\circ_{\text{Ag/Ag}^+}$ (volts)	
On heating					
		975	0.282	0.243	
		1033	0.287	0.246	
		1071	0.288	0.245	
		1103	0.289	0.245	
		1143	0.293		
On cooling					
		1137	0.290	0.244	
		1069	0.287	0.244	
		973	0.282	0.243	

(b)

Cr (-)	CrCl ₂ ($x_2 = 3.467 \times 10^{-2}$) KCl-NaCl (1/1 mole)		AgCl ($x_1 = 6.235 \times 10^{-2}$) KCl-NaCl (1/1 mole)		Ag (+)
		$T, ^\circ K.$	E_{cell} (volts)	$E^\circ_{\text{Cr/Cr}^{++}} - E^\circ_{\text{Ag/Ag}^+}$ (volts)	
On heating					
		978	0.761	0.756	
		1021	0.755	0.750	
		1051	0.750	0.745	
		1068	0.745	0.740	
		1090	0.746	0.740	
		1108	0.741	0.735	
		1121	0.739	0.734	
		1142	0.734	0.723	
On cooling					
		1023	0.755	0.750	
		1008	0.757	0.752	
		989	0.759	0.754	
		972	0.762	0.757	

The best straight line through the experimental points was calculated by applying the least-squares method.

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

$$[6] \quad \Delta H_r = \Delta H_f (\text{CrCl}_2 \text{ in KCl-NaCl}) - \Delta H_f (\text{AgCl in KCl-NaCl}).$$

The heat of reaction was calculated from the slope of the straight line in Fig. 3, in accordance with the van't Hoff equation,

$$[7] \quad d \ln K/dT = \Delta H_r/RT^2.$$

The value thus obtained is:

$$\Delta H_{r(\text{Cr, Cr}^{++})} = -42.46 \pm 0.5 \text{ kcal./mole.}$$

In the case of the Cu-Ag voltaic cell, where it was found that $dE/dT = 0$, the heat of reaction is equal to the free energy change and can be calculated directly from equation [5]. The result of the calculation is:

$$\Delta H_{r(\text{Cu, Cu}^+)} = -6.10 \text{ kcal./mole.}$$

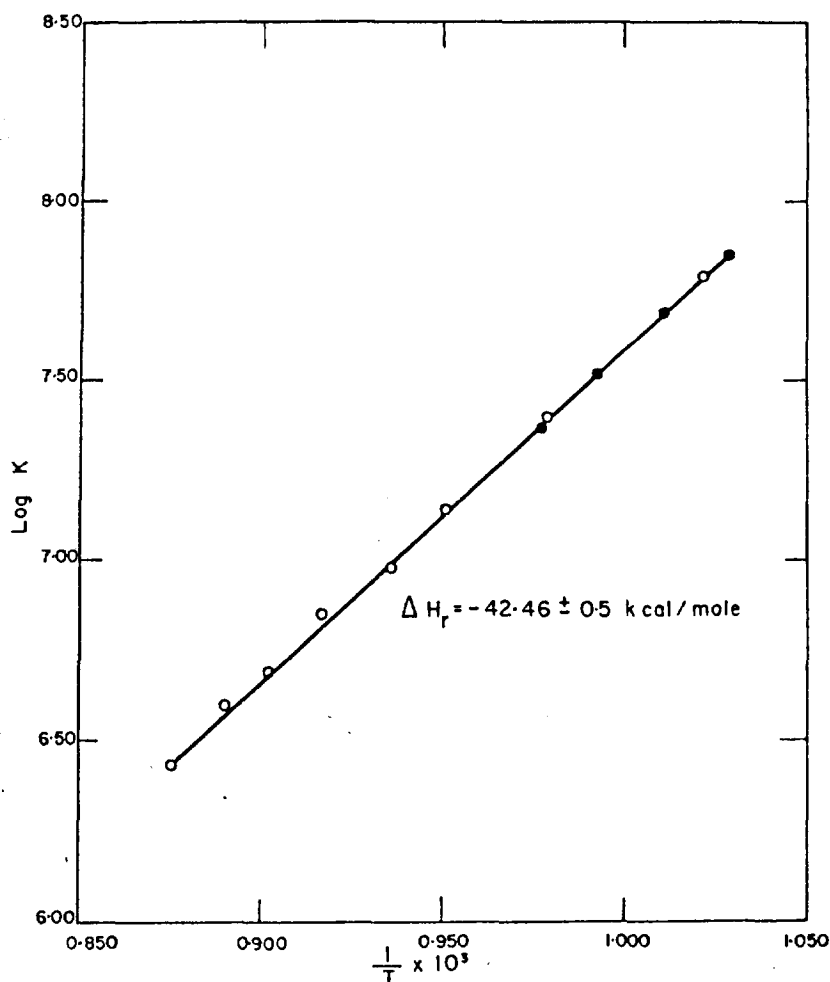
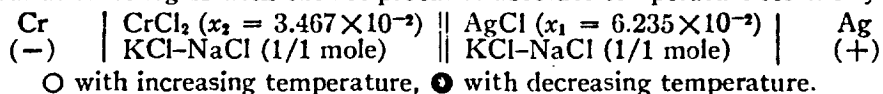


FIG. 3. The variation of $\log K$ with the reciprocal of absolute temperature for the system:



Measurement of Redox Potentials

The electromotive forces of the $\text{Cu}^+/\text{Cu}^{++}$ and $\text{Cr}^{++}/\text{Cr}^{+++}$ redox cells were measured first as a function of the salt concentrations, and then as a function of temperature. The results of the experiments in which the concentration of the metal chlorides was varied at constant temperatures are shown in Table IV, and the plot of $\log(x_1 \cdot x_2 / x_3)$ versus the electromotive forces is given in Fig. 4.

Following the same procedure as used previously, the standard redox potentials of the systems were obtained by graphical interpolation at zero log concentration. The results are grouped in the summary given in Table II.

It will be observed that the curves in Fig. 4 are effectively linear over the concentration range investigated, which again indicates that the activity coefficients or the complexity constants of the species involved in each of the reactions remain constant.

The slopes of the experimental lines for both redox systems agree well with the theoretical value for a one-electron reduction process (0.197 as compared with 0.195 volt) at this temperature.

The effect of temperature change on the electromotive forces of the two redox cells above was investigated next. The results are shown in Table V.

Also included in Table V are values for the standard redox potentials at different

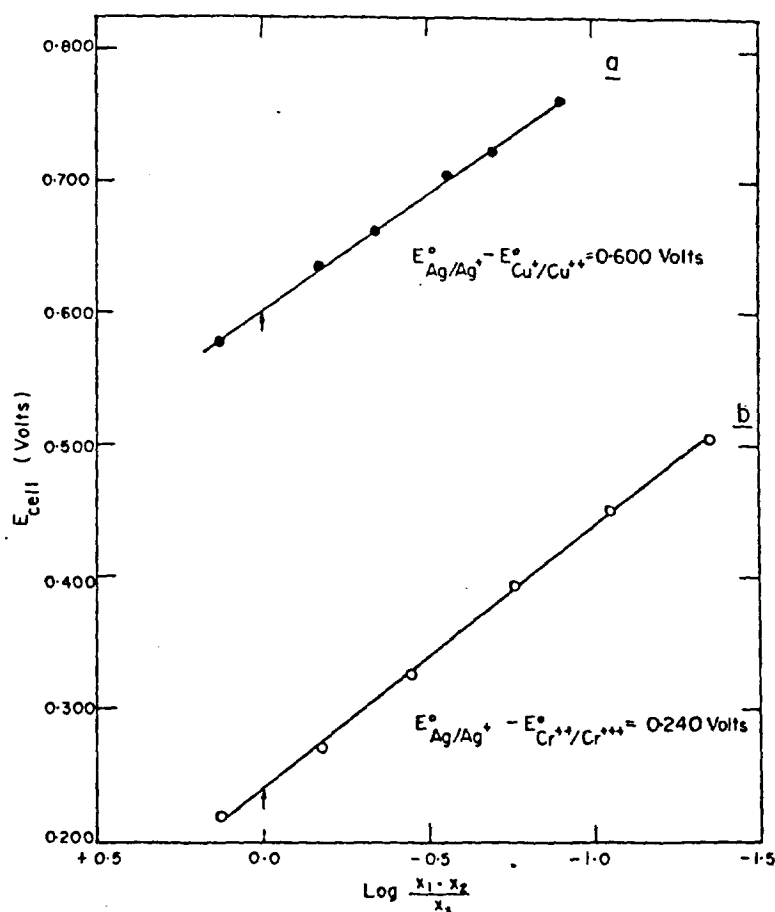
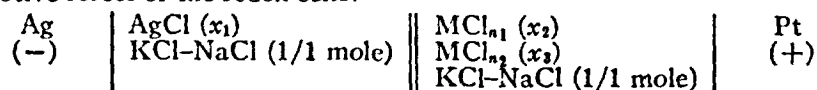


FIG. 4. Electromotive forces of the redox cells:



as a function of $\log(x_1 \cdot x_2 / x_3)$, at constant temperature.

M is (a) copper and (b) chromium, and MCl_{n_1} and MCl_{n_2} are respectively CuCl , CuCl_2 , and CrCl_2 , CrCl_3 .

temperatures, as calculated from the data using equation [3]. From these values, by applying equations [5], the effective equilibrium constants for the redox cell reactions were calculated. The results of these calculations are shown in Fig. 5, where $\log K$ was plotted against the reciprocal of the absolute temperature. The curve is linear over the temperature range investigated. For each curve the best straight line was calculated by applying the least squares method.

The heat of reaction in cells of this type is best expressed by the equation:

$$[8] \quad \Delta H_r = \Delta H_{I(\text{MCl}_{n_2})} + \Delta H_{I(\text{AgCl})} - \Delta H_{I(\text{MCl}_{n_1})},$$

where ΔH_I is the heat of formation of the metal chlorides in the molten alkali chloride salt solution. These heats of reactions were calculated from the slopes of the straight lines in Fig. 5, in accordance with the van't Hoff equation, and the results are:

$$\Delta H_r(\text{Cu}^{2+}, \text{Cu}^+) = -9.15 \pm 0.6 \text{ kcal./mole}$$

$$\Delta H_r(\text{Cr}^{3+}, \text{Cr}^{2+}) = +11.84 \pm 0.5 \text{ kcal./mole}$$

Having established the standard metal electrode potentials of the systems Cu/CuCl (KCl-NaCl) and Cr/CrCl_2 (KCl-NaCl), and the standard redox potentials of the systems $\text{CuCl}_2/\text{CuCl}$ (KCl-NaCl) and $\text{CrCl}_3/\text{CrCl}_2$ (KCl-NaCl), equation [1] was then applied to calculate the standard electrode potentials of the systems Cu/CuCl_2 (KCl-NaCl)

TABLE IV

ELECTROMOTIVE FORCES OF "REDOX" CELLS AS A FUNCTION OF THE METAL ION CONCENTRATIONS AT THE INDICATOR ELECTRODE

(a)		Ag (-)	AgCl (x_1) KCl-NaCl (1/1 mole)		CuCl (x_2) CuCl ₂ (x_3) KCl-NaCl (1/1 mole)	Pt (+)
Mole fraction of AgCl (x_1)	Mole fraction of CuCl (x_2)	Mole fraction of CuCl ₂ (x_3)	$t, ^\circ\text{C.}$	E_{cell} (volts)		
6.235 × 10 ⁻²	4.821 × 10 ⁻²	2.242 × 10 ⁻³	700	0.578		
6.235 × 10 ⁻²	4.810 × 10 ⁻²	4.400 × 10 ⁻³	700	0.634		
6.235 × 10 ⁻²	4.799 × 10 ⁻²	7.074 × 10 ⁻³	700	0.660		
6.235 × 10 ⁻²	4.781 × 10 ⁻²	1.080 × 10 ⁻²	700	0.706		
6.235 × 10 ⁻²	4.761 × 10 ⁻²	1.471 × 10 ⁻²	700	0.724		
6.235 × 10 ⁻²	4.721 × 10 ⁻²	2.302 × 10 ⁻²	700	0.761		

(b)		Ag (-)	AgCl (x_1) KCl-NaCl (1/1 mole)		CrCl ₂ (x_2) CrCl ₃ (x_3) KCl-NaCl (1/1 mole)	Pt (+)
Mole fraction of AgCl (x_1)	Mole fraction of CrCl ₂ (x_2)	Mole fraction of CrCl ₃ (x_3)	$t, ^\circ\text{C.}$	E_{cell} (volts)		
6.235 × 10 ⁻²	9.348 × 10 ⁻³	4.350 × 10 ⁻⁴	703	0.220		
6.235 × 10 ⁻²	9.344 × 10 ⁻³	8.900 × 10 ⁻⁴	703	0.270		
6.235 × 10 ⁻²	9.335 × 10 ⁻³	1.649 × 10 ⁻³	703	0.325		
6.235 × 10 ⁻²	9.319 × 10 ⁻³	3.355 × 10 ⁻³	703	0.393		
6.235 × 10 ⁻²	9.291 × 10 ⁻³	6.565 × 10 ⁻³	703	0.449		
6.235 × 10 ⁻²	9.232 × 10 ⁻³	1.269 × 10 ⁻²	703	0.506		

TABLE V

EFFECT OF TEMPERATURE ON THE ELECTROMOTIVE FORCES OF THE REDOX CELLS

(a)		Ag (-)	AgCl ($x_1 = 6.235 \times 10^{-2}$) KCl-NaCl (1/1 mole)		CuCl ($x_2 = 4.741 \times 10^{-2}$) CuCl ₂ ($x_3 = 1.745 \times 10^{-2}$) KCl-NaCl (1/1 mole)	Pt (+)
$T, ^\circ\text{K.}$	E_{cell} (volts)	$E^\circ_{\text{Ag}/\text{Ag}^+} - E^\circ_{\text{Cu}^+/\text{Cu}^{++}}$ (volts)				
On heating						
973	0.745	0.596				
1049	0.769	0.609				
1091	0.784	0.617				
1133	0.795	0.622				
On cooling						
1075	0.775	0.611				
1015	0.755	0.600				
991	0.746	0.595				
971	0.737	0.589				
947	0.729	0.584				

(b)		Ag (-)	AgCl ($x_1 = 6.235 \times 10^{-2}$) KCl-NaCl (1/1 mole)		CrCl ₂ ($x_2 = 9.232 \times 10^{-3}$) CrCl ₃ ($x_3 = 1.269 \times 10^{-2}$) KCl-NaCl (1/1 mole)	Pt (+)
$T, ^\circ\text{K.}$	E_{cell} (volts)	$E^\circ_{\text{Ag}/\text{Ag}^+} - E^\circ_{\text{Cr}^{++}/\text{Cr}^{+++}}$ (volts)				
On heating						
975	0.506	0.246				
1031	0.561	0.286				
1079	0.616	0.328				
1144	0.687	0.376				
On cooling						
1128	0.663	0.363				
1073	0.610	0.324				
1011	0.517	0.278				
990	0.524	0.261				
969	0.498	0.210				

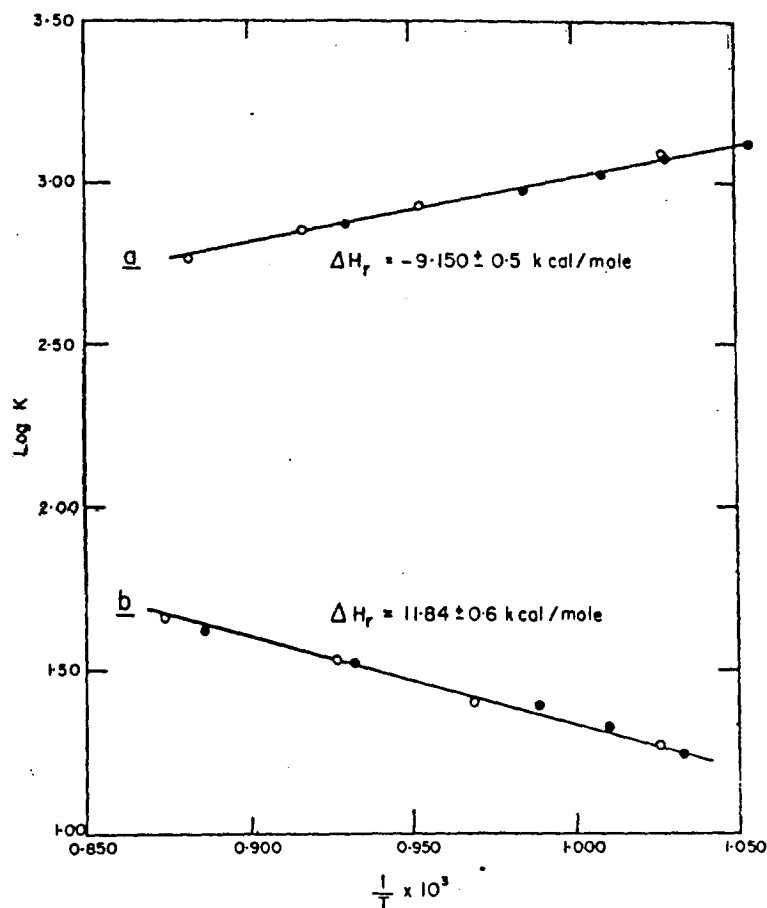


FIG. 5. The variation of log *K* with the reciprocal of the absolute temperature for the systems:

(a)	Ag	$\left[\begin{array}{l} \text{AgCl } (x_1 = 6.235 \times 10^{-2}) \\ \text{KCl-NaCl (1/1 mole)} \end{array} \right]$	$\left[\begin{array}{l} \text{CuCl } (x_2 = 1.741 \times 10^{-2}) \\ \text{CuCl}_2 (x_3 = 1.745 \times 10^{-2}) \\ \text{KCl-NaCl (1/1 mole)} \end{array} \right]$	Pt
(-)	(-)			(+)
(b)	I' Ag	$\left[\begin{array}{l} \text{AgCl } (x_1 = 6.235 \times 10^{-2}) \\ \text{KCl-NaCl (1/1 mole)} \end{array} \right]$	$\left[\begin{array}{l} \text{CrCl}_2 (x_2 = 9.235 \times 10^{-3}) \\ \text{CrCl}_3 (x_3 = 1.269 \times 10^{-2}) \\ \text{KCl-NaCl (1/1 mole)} \end{array} \right]$	Pt
(-)	(-)			(+)

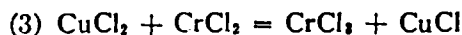
○ with increasing temperature, ● with decreasing temperature.

and Cr/CrCl₃ (KCl-NaCl), which are unobtainable by direct measurement. The results of these calculations were given previously in the summary of results in Table II. The heats of the cell reactions for these systems can be calculated by applying the equation, $\sum(\Delta H_r) = 0$, to a cyclic process similar to that used to derive equation [1]. The values thus obtained are:

$$\Delta H_{r(\text{Cu, Cu}^{++})} = +3.05 \text{ kcal./mole}$$

$$\Delta H_{r(\text{Cr, Cr}^{+++})} = -54.30 \text{ kcal./mole}$$

From the data in Table II it is also possible to calculate the free energies and the equilibrium constants of the following chemical reactions as they occur in the melt:



The results of these calculations are given in Table VI.

It can be readily deduced that reactions (1) and (2) will proceed effectively to completion, whilst with reaction (3) a chemical equilibrium between the reacting species will be attained.

TABLE VI
FREE ENERGIES AND EQUILIBRIUM CONSTANTS OF REACTIONS IN FUSED SALTS

Reaction at 700° C. in KCl-NaCl solvent	ΔF° , kcal./mole	$K_{eq.}$
$Cu + CuCl_2 = 2CuCl$	-19.80	2.85×10^4
$Cr + 2CrCl_3 = 3CrCl_2$	-45.94	2.08×10^{10}
$CuCl_2 + CrCl_2 = CrCl_3 + CuCl$	- 8.30	7.33×10^1

DISCUSSION

It is of theoretical interest to compare the experimental electrode potentials, and the experimental heats of the cell reactions, with values calculated from thermodynamic data on the pure metal chlorides (8) without solvent. The calculations for the standard potentials are given in Table II. If the free energy change associated with the difference in standard potentials is attributed entirely to the formation of complexes in melts, the dissociation constants for these complexes can be calculated using the method previously (1) described. It must be emphasized that, in calculating dissociation constants, no assumption has been made about the structure of these compounds. Accordingly, these values could equally well represent the ratio of the activity coefficients. However, following the same procedure used previously (1, 2, 3), these values were calculated as "complex dissociation constants" and the results are:

$$K_d(\text{CuCl complex}) = 2.7 \times 10^{-1} \text{ at } 700^\circ \text{ C.}$$

$$K_d(\text{CuCl}_2 \text{ complex}) = 2.9 \times 10^{-3} \text{ at } 700^\circ \text{ C.}$$

$$K_d(\text{CrCl}_2 \text{ complex}) = 1.07 \times 10^{-2} \text{ at } 700^\circ \text{ C.}$$

$$K_d(\text{CrCl}_3 \text{ complex}) = 4.14 \times 10^{-2} \text{ at } 700^\circ \text{ C.}$$

From Table II it will be observed that in the case of $TiCl$, the small difference between the experimental and the calculated potential indicates almost ideal behavior.

Heats of the cell reactions calculated from existing thermodynamic data (8) on the pure metal chlorides are given in Table VII. In this table are also included values obtained experimentally in the present investigation in the presence of the KCl-NaCl solvent.

In Table VII, it will be observed that the experimental average heats of reactions are of the same order as the calculated ones.

The magnitude of the complex dissociation constants above, and the small difference between the heats of reaction, indicate that the over-all energy change which occurs when the metal ions are transferred from the solid or liquid phase of the pure metal chloride to an alkali chloride molten salt solvent is quite small.

TABLE VII

Reaction*	Heats of reaction in kcal./mole					Experi- mental† between 973- 1173° K.
	Calculated* temp., ° K.					
	773	873	973	1073	1173	
$Cu_{(s)} + AgCl_{(l)} = CuCl_{(l)} + Ag_{(s)}$	-5.48	-4.71	-5.19	-4.86	-5.12	-6.10
$Cu_{(s)} + 2AgCl_{(l)} = CuCl_{2(l)} + 2Ag_{(s)}$	-1.44	-0.74	(-0.0)	(+1.0)	—	+3.05
$Cr_{(s)} + 2AgCl_{(l)} = CrCl_{2(s)} + 2Ag_{(s)}$	-40.13	-39.83	-39.87	-39.95	-40.58	-42.46
$Cr_{(s)} + 3AgCl_{(l)} = CrCl_{3(s)} + 3Ag_{(s)}$	-49.08	-48.92	-48.41	-48.44	-49.10	-54.30
$Ag_{(s)} + CuCl_{2(l)} = CuCl_{(l)} + AgCl_{(l)}$	-4.04	-3.91	—	—	—	-9.15
$Ag_{(s)} + CrCl_{3(s)} = CrCl_{2(s)} + AgCl_{(l)}$	+9.36	+9.10	+8.54	+8.49	+8.54	+11.84

*Heats of reaction calculated on the basis of the heats of formation of the pure salts without any solvent present.

†Average heats of reaction calculated from the experimental data in the presence of KCl-NaCl solvent.

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