



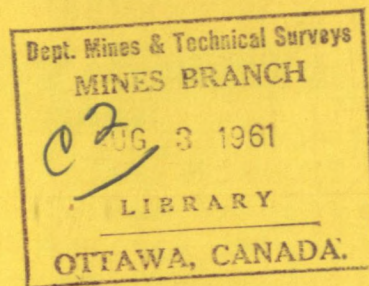
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ELECTRODE POTENTIALS OF THE URANIUM CHLORIDES IN FUSED ALKALI CHLORIDE SOLUTIONS

S. N. FLENGAS

EXTRACTION METALLURGY DIVISION

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ELECTRODE POTENTIALS OF THE URANIUM CHLORIDES IN FUSED ALKALI CHLORIDE SOLUTIONS¹

S. N. FLENGAS²

ABSTRACT

Using a silver - silver chloride reference electrode, the electrode potentials of the system U, UCl₃(KCl, NaCl) and the redox potentials of the system Pt, UCl₃, UCl₄(KCl, NaCl) were measured at various concentrations of the uranium chlorides and at temperatures between 650 and 850° C.

From the results, the electrode potential of the system U, UCl₄(KCl, NaCl) was calculated. In addition, the activity coefficients and partial molal properties of dilute solutions of UCl₃ and UCl₄ in the equimolar mixture of potassium and sodium chlorides were calculated.

INTRODUCTION

In previous publications (1-7) from the Mines Branch, measurements of the "apparent standard electrode potentials" of several metal - metal chloride systems in dilute solutions in fused alkali chlorides were reported. These measurements were made to provide fundamental information on the activities in fused alkali chloride solutions, to determine the equilibrium constants of chemical reactions in fused salts, and to provide some of the necessary data for studies of the electrolytic reduction of metals from alkali chloride melts.

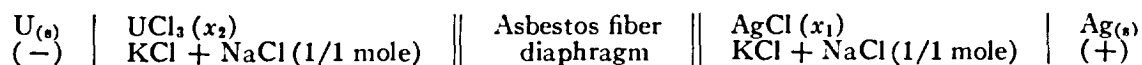
In determining the electrode potentials, an equimolar mixture of potassium and sodium chlorides was used as the solvent for the metal chlorides, and a silver - silver chloride electrode developed earlier in this work (1) was used as a zero potential reference electrode.

In the experimental work reported here, the technique has been applied to the determination of the potentials of the uranium chlorides dissolved in an equimolar mixture of potassium and sodium chlorides. There are only two stable uranium chlorides at temperatures above 500° C, namely uranium trichloride and uranium tetrachloride. The electrode potentials of the two uranium ions and the redox potentials of the tri- and tetra-valent uranium ions were determined.

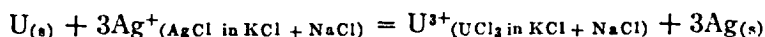
EXPERIMENTAL

The cells used for the measurement of the electrode potentials of uranium trichloride, and for the measurement of the redox potentials of the tri- and tetra-valent uranium chlorides, were similar in design to those described in the previous publications (6, 7).

The cell for measuring the electrode potential of uranium trichloride can be represented as follows:



The cell reaction is:



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Contribution from the Extraction Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada. Published with the permission of the Director, Mines Branch.

²Present address: Department of Metallurgical Engineering, University of Toronto, Toronto, Ontario.

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

$$[1] \quad E_{\text{cell}} = (E^{\circ}_{\text{UCl}_3} - E^{\circ}_{\text{AgCl}}) - (2.303RT/3\mathcal{F}) \log(x_2/x_1^3) - (2.303RT/3\mathcal{F}) \log(\gamma_2/\gamma_1^3)$$

where $E^{\circ}_{\text{UCl}_3}$ and E°_{AgCl} are the formation potentials of uranium trichloride and silver chloride in their standard states. The standard state will be defined as the state of the pure metal chloride at the temperature of the experiments.

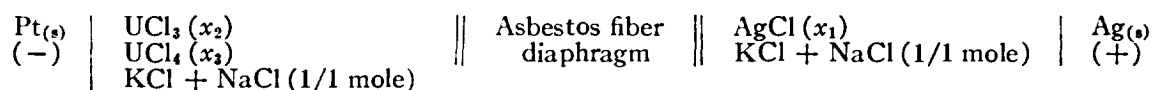
The γ and x terms are respectively the mean activity coefficients and the conventional mole fractions of the metal chlorides in the solutions in the two half-cells. The activity coefficient of silver chloride in these solutions was determined and found to be unity in a previous investigation (6), using a chlorine electrode.

Following the same method as used previously (6, 7), it is possible, from equation [1], to calculate the "apparent standard cell potential" of the system, by plotting the experimental potential E_{cell} against $\log(x_2/x_1^3)$ and extrapolating the linear relationship to zero log term. The "apparent standard cell potential" obtained in this way is a constant of the system investigated, and is related to the formation potentials of the metal chlorides and the activity coefficient of uranium trichloride by the equation:

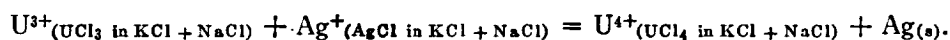
$$[2] \quad E^{\circ}_{\text{app}} = (E^{\circ}_{\text{UCl}_3} - E^{\circ}_{\text{AgCl}}) - (2.303RT/3\mathcal{F}) \log \gamma_2.$$

Since the formation potentials of the metal chlorides in their pure state are listed in the literature (8), equation [2] can be used for the determination of the activity coefficient of UCl_3 in the chloride melt.

The cell for measuring the "redox potentials" of the tri- and tetra-valent uranium ions can be represented as follows:



The cell reaction is:



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

$$[3] \quad E_{\text{cell}} = (E^{\circ}_{\text{UCl}_3/\text{UCl}_4} - E^{\circ}_{\text{AgCl}}) - (2.303RT/\mathcal{F}) \log(x_3/x_1 \cdot x_2) - (2.303RT/\mathcal{F}) \log(\gamma_3/\gamma_1 \cdot \gamma_2)$$

where the $E^{\circ}_{\text{UCl}_3/\text{UCl}_4}$ is the standard redox potential of the system UCl_3 , UCl_4 in the standard state. The x and γ terms are, respectively, the mole fractions and the activity coefficients of the metal chlorides.

The "apparent standard redox" potential of the system is determined by plotting the experimental cell potentials against $\log(x_3/x_1 \cdot x_2)$ and then extrapolating the linear relationship to zero log term.

It should be noted that the above-mentioned cells were operated in an inert atmosphere of purified argon gas.

PREPARATION OF MATERIALS

The equimolar mixture of potassium and sodium chlorides was prepared from analytical grade reagents, and was dehydrated by heating under vacuum at 500° C for 12 hours.

Anhydrous uranium trichloride was prepared in a tubular furnace at 500° C, by the reaction between reactor grade uranium metal and oxygen-free anhydrous hydrogen

chloride (9). Very pure and dry gaseous hydrogen chloride was prepared in a suitable apparatus by the reaction between concentrated hydrochloric acid and concentrated sulphuric acid (10). The product of the reaction, between uranium metal and hydrogen chloride, was finely divided uranium trichloride which adhered to the surface of the metal. This finely powdered product, which was separated from the coarse unreacted uranium by sieving in a dry box, was of a purity of 98.5%.

Anhydrous uranium tetrachloride was prepared by the reaction between hydrated uranium trioxide ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$) and hexachloropropene (11). The product obtained from this reaction was purified by sublimation *in vacuo*, and was of a purity of 99.0%.

The uranium chlorides were pelletized in an argon-filled dry box and were transferred to the cell using the piston-type feeding apparatus described previously (7).

The uranium electrode for these experiments was a rod of reactor grade uranium which had been swaged down to $\frac{1}{2}$ -in. diameter, and was about 3 in. long. It was connected to a platinum wire. Prior to its use, the electrode was polished to a silver-like finish in a dilute solution of nitric acid. The polished electrode was then washed with distilled water and dried with acetone.

The silver electrode was a rod of pure silver (99.9%) connected to a silver wire. The inert platinum electrode used for the redox potential measurements was a hollow platinum cylinder of $\frac{1}{2}$ -in. diameter and 3-in. long. It was connected to a platinum wire.

The thermoelectric potentials due to the bimetallic systems of these electrodes were measured separately, and the appropriate corrections were applied to the measurements of the electrode potentials.

RESULTS

1. *Electrode Potentials of the U/U³⁺ System*

In the preliminary experiments, the stability of a system consisting of uranium metal immersed in a solution of uranium trichloride in molten potassium and sodium chlorides was investigated by following the change of the cell potential with time.

The solutions of uranium trichloride were prepared *in situ* during the run, by adding weighed pellets of the anhydrous salt to the melt in the indicator electrode compartment. After each addition, the equilibrium potential was attained in about 30 minutes. Potential readings were then taken at regular time intervals over a period of about 20 hours. It was found that the shift of potential was of the order of only 1 mv. Furthermore, after the end of the run there was no indication of a chemical attack on the uranium electrode.

It was concluded that uranium metal is insoluble in dilute solutions of uranium trichloride under the conditions of the experiment. However, it was observed that electrodes which accidentally had been placed in contact with the side walls of the silica tubing in the cell were heavily corroded. The potentials obtained under these conditions were erratic and non-reproducible. In all probability, the observed solubility of uranium metal in the melt was due to the formation of a soluble uranium oxide or oxychloride through the exchange reaction between uranium metal and silica. For this reason, during the experiments, the uranium electrode was suspended by the platinum wire in the center of the cell.

The electromotive force of the U/U³⁺ cell was measured first as a function of temperature, at various mole fractions of uranium trichloride.

The variation of the cell potential with temperature, at mole fractions varying between 10^{-4} and 10^{-2} , is shown in Fig. 1. The results in this graph represent three independent runs. It is apparent that the curves are linear over the temperature range between 650

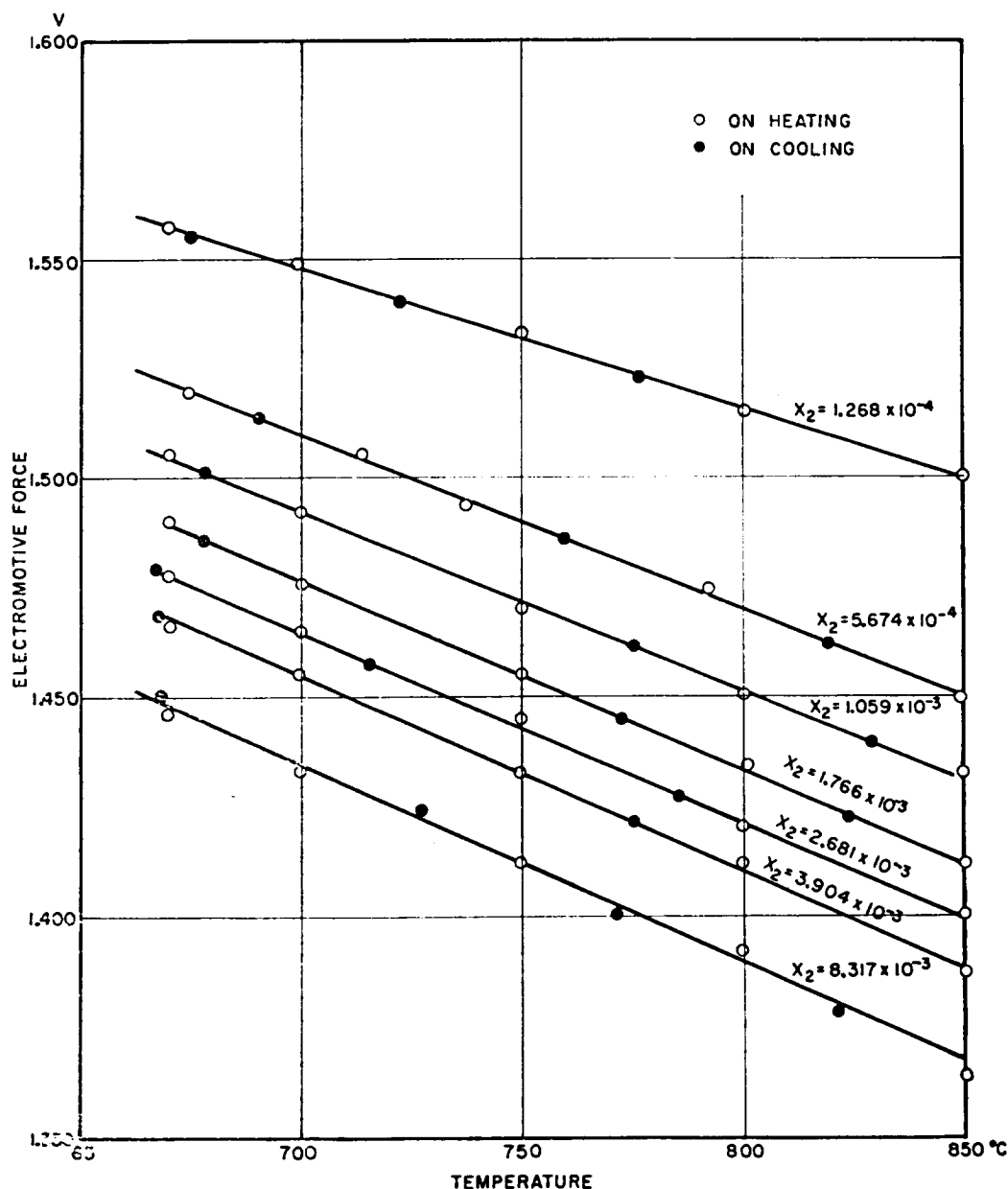
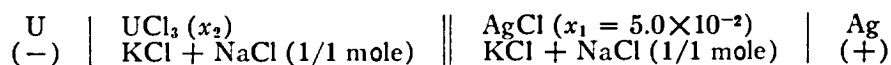


FIG. 1. Electromotive force of the cell:



as a function of temperature.

and 850° C, and the cell potentials have a negative temperature coefficient. Potential readings made while temperature was being increased were in good agreement with those made while the temperature was decreasing.

The relationship between the cell potential and the logarithm of the mole fractions, at temperatures between 670 and 850° C, is shown in Fig. 2. In this graph the straight lines through the experimental points are the best straight lines that can be drawn with a slope equal to the slope of the Nernst equation for a three-electron electrode reaction at these temperatures. It is seen that the results are in agreement with the Nernst equation. The linearity of the curves indicates that the activity coefficient of uranium trichloride in these dilute solutions is independent of concentration. The "apparent standard cell potential" of uranium trichloride was obtained by extrapolation of the curves to zero $\log (x_2/x_1^3)$ term. These results are given in Table I.

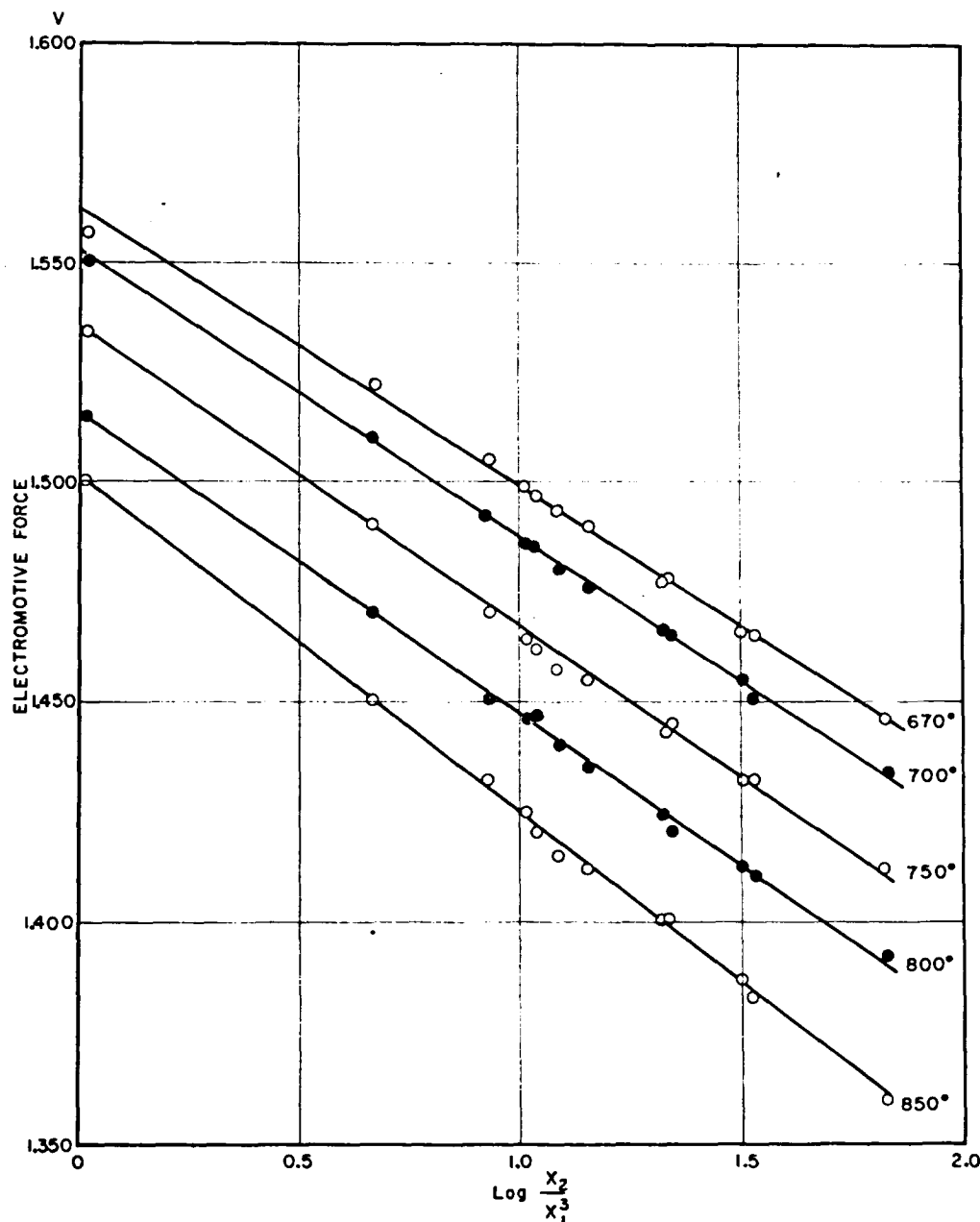


FIG. 2. Electromotive force of the cell:



as a function of $\log (x_2/x_1^3)$, at various temperatures.

2. "Redox" Potentials of the U^{3+}/U^{4+} System

The electromotive force of the U^{3+}/U^{4+} redox cell was measured, as a function of temperature, at various mole fractions of uranium tri- and tetra-chlorides. The stability of the potential measurements over a period of time exceeding 12 hours indicated that solutions of uranium tri- and tetra-chlorides in the equimolar mixture of potassium and sodium chlorides are very stable.

The results of the redox potential measurements at temperatures between 650 and 850° C, for mole fractions of uranium tri- and tetra-chlorides varying between 10^{-3} and 10^{-2} , are shown in Fig. 3.

It is seen that the curves are linear over the temperature range investigated, and that the potentials of the redox cells have a negative temperature coefficient.

TABLE I
Apparent standard potentials in 1/1 mole KCl + NaCl

Indicator electrode	E_0' (volts)*				
	670° C	700° C	750° C	800° C	850° C
U, U ³⁺	-1.563	-1.554	-1.535	-1.519	-1.502
U, U ⁴⁺	-1.295	-1.285	-1.269	-1.252	-1.239
U ³⁺ , U ⁴⁺	-0.494	-0.483	-0.473	-0.459	-0.450
Ag, Ag ⁺	0	0	0	0	0
Cl ⁻ , Cl†	+0.852	+0.845	+0.832	+0.820	+0.807

*It will be noted that the sign of the experimentally obtained apparent standard potentials shown in this table has been altered to conform with the recommendations of the IUPAC Stockholm convention, as reported by Light and deBethune (12).

†The potential of the chlorine electrode against the silver - silver (6) chloride electrode was determined in a previous investigation, and the results are shown here for comparison.

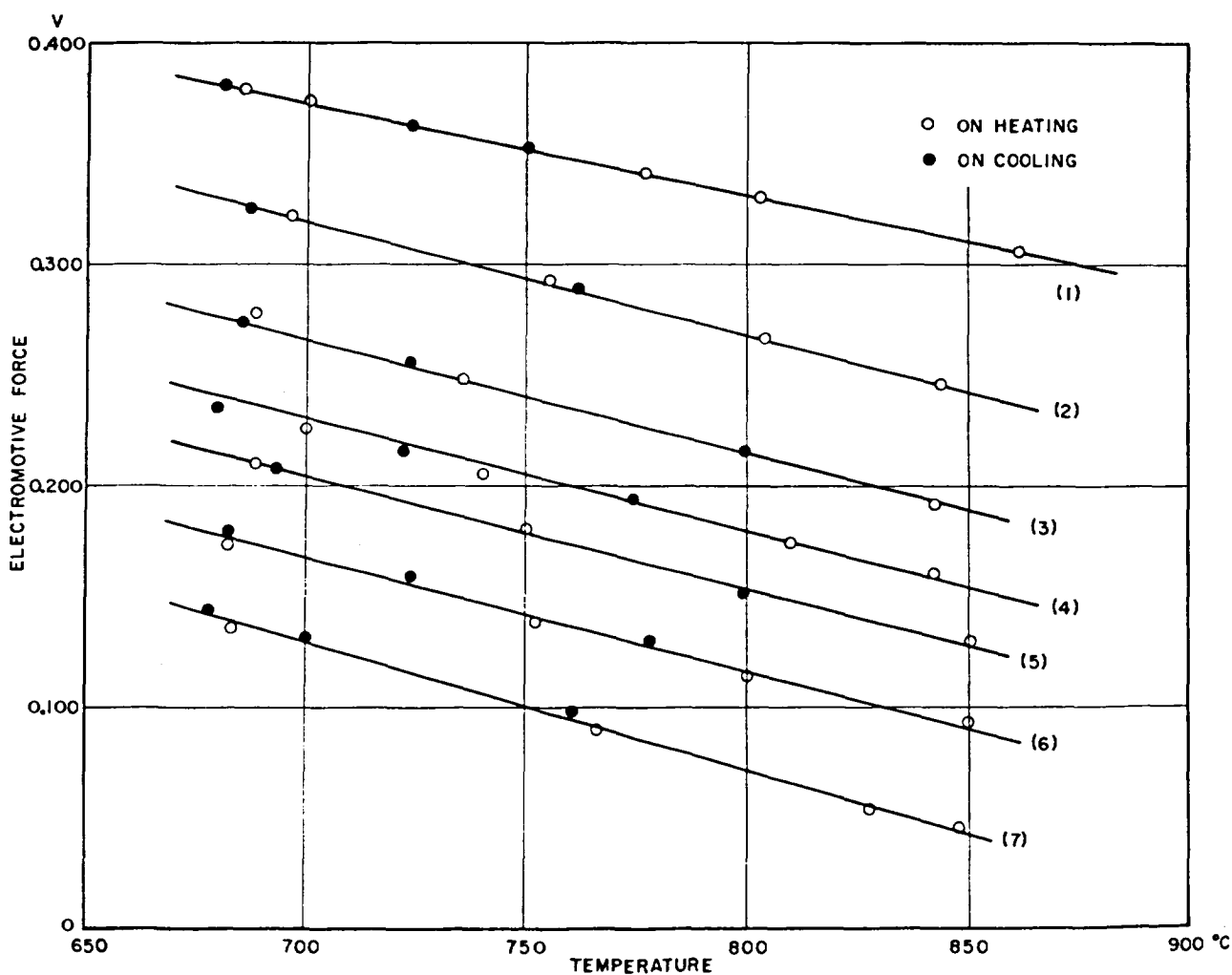
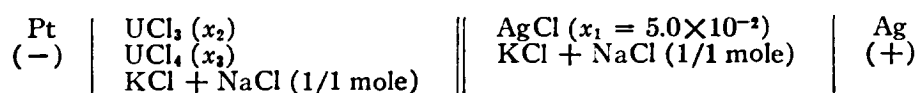


FIG. 3. Electromotive force of the cell:



as a function of temperature at mole fractions:

- | | | |
|--|--|--|
| (1) $x_2 = 8.303 \times 10^{-3}$
$x_3 = 1.703 \times 10^{-3}$ | (2) $x_2 = 8.287 \times 10^{-3}$
$x_3 = 3.527 \times 10^{-3}$ | (3) $x_2 = 8.232 \times 10^{-3}$
$x_3 = 6.254 \times 10^{-3}$ |
| (4) $x_2 = 2.445 \times 10^{-3}$
$x_3 = 2.671 \times 10^{-3}$ | (5) $x_2 = 5.697 \times 10^{-3}$
$x_3 = 9.601 \times 10^{-3}$ | (6) $x_2 = 2.447 \times 10^{-3}$
$x_3 = 5.723 \times 10^{-3}$ |
| (7) $x_2 = 2.438 \times 10^{-3}$
$x_3 = 9.629 \times 10^{-3}$ | | |

The relationship between the cell potential and the logarithm of the mole fractions, at temperatures between 670 and 850° C, is shown in Fig. 4. In this graph the straight

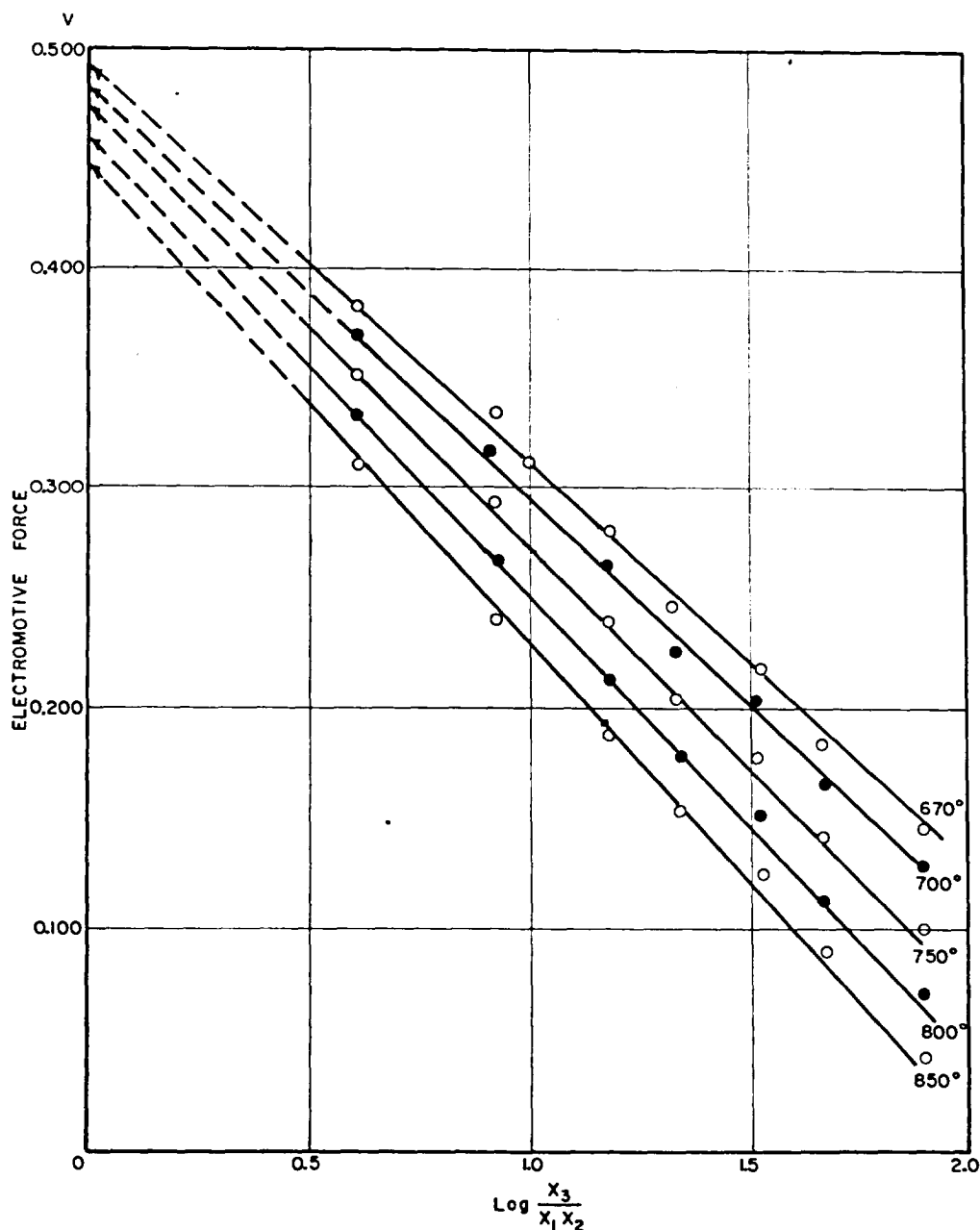
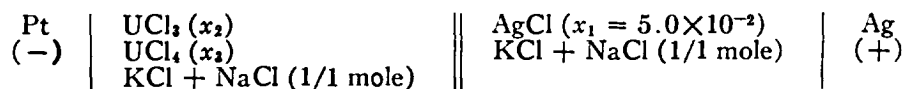


FIG. 4. Electromotive force of the cell:



as a function of $\log (x_3/x_1x_2)$, at various temperatures.

lines through the experimental points are the best straight lines that can be drawn with a slope equal to the slope of the Nernst equation for a one-electron electrode reaction at these temperatures. It is seen that the results agree well with the Nernst equation. The linearity of these curves indicates that the activity coefficient of uranium tetrachloride in these dilute solutions is independent of concentration.

The "apparent standard redox potential" of the system was obtained by extrapolation of the curve to zero $\log (x_3/x_2x_1)$. These results are given in Table I.

DISCUSSION

From the experimental values for the apparent standard potentials of the system $U/UCl_3(KCl + NaCl)$ and the apparent standard redox potential of the system $UCl_3/UCl_4(KCl + NaCl)$, the apparent standard potential of the system $U/UCl_4(KCl + NaCl)$ was calculated by application of the equation:

$$[4] \quad E^\circ_{UCl_4} = (3E^\circ_{UCl_3} + E^\circ_{UCl_3/UCl_4})/4.$$

The results of these calculations are shown in Table I.

The potentials of the chlorine electrode which were measured against the silver - silver chloride reference electrode in a previous investigation (6) are also included in this table. To refer the potentials of the uranium system to a chlorine reference electrode, it is only necessary to subtract the potential of the chlorine electrode, as given at the bottom of the table, from the corresponding uranium potential.

The graph of the "apparent standard potentials" of the uranium chlorides, as a function of temperature, is given in Fig. 5. In this graph, calculated standard potentials of the pure salts (8) are also included for comparison.

Apparent standard cell potentials of uranium tri- and tetra-chlorides, in a melt of potassium and lithium chlorides at 450° C, have been reported recently by Gruen and Osteryoung (13), and by Hill, Ferand, and Osteryoung (14). Inman, Hills, Young, and Bockris (15, 16) also investigated the potentials of uranium trichloride in the potassium chloride - lithium chloride eutectic.

When the results in Fig. 5 were extrapolated to 450° C, the "apparent standard cell potentials" of the uranium tri- and tetra-chlorides were found to be respectively 1.632 and 1.365 volts. These compare well with 1.611 volts for uranium trichloride, and 1.363 volts for uranium tetrachloride given by Gruen *et al.* (13), and Hill *et al.* (14). Also the "apparent standard cell potential" at 450° C, of uranium trichloride which can be calculated from the results of Inman *et al.* (15, 16), is of the same order of magnitude, i.e. about 1.66 volts.

For a variety of metal - metal chloride systems, the agreement between the apparent standard potential measured at 450° C in the eutectic of potassium and lithium chlorides (17), and those measured in the equimolar mixture of potassium and sodium chlorides, has been pointed out in a previous investigation (6). Furthermore, the same agreement was observed by Hill *et al.* (14) in their study of the uranium potentials in chloride melts containing comparatively light metal cations such as potassium, lithium, and magnesium. It appears that the partial molal free energy of mixing of the uranium chlorides is almost independent of the size of the cations present in the solvent, provided that these cations are much smaller than the uranium ions.

From the apparent standard potentials shown in Table I, it is possible to calculate the thermodynamic functions and the equilibrium constants of various reactions of metallurgical interest. The results of these calculations are given in Table II.

The magnitude of the equilibrium constant for reaction [4], shown in Table II, indicates that in the presence of uranium metal, uranium tetrachloride would be reduced quantitatively to the trichloride.

The equilibrium constants of reactions [1] to [3] indicate that uranium metal will displace silver ions from solution, and that at equilibrium, the predominant species will be uranium tetrachloride.

Using the results in Fig. 5, the partial molal properties and the activity coefficients

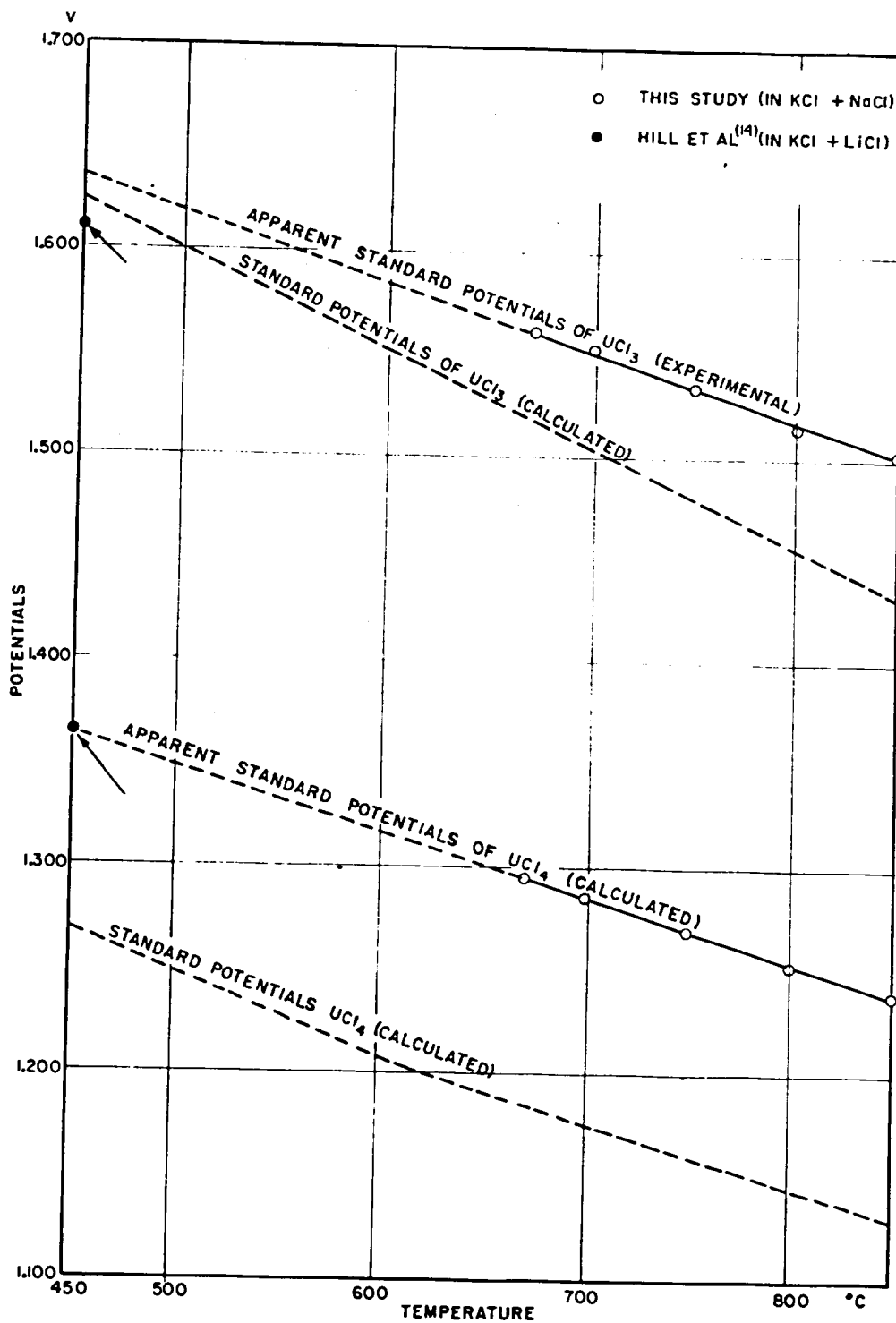


FIG. 5. Apparent standard potentials of UCl_3 and UCl_4 and the corresponding standard state potentials at various temperatures.

of the uranium chloride solutions were calculated from the differences between the "standard potentials" of the pure uranium tri- and tetra-chlorides and the "apparent standard potentials" in the fused salt solution. The results of these calculations are given in Table III.

The partial molal free energy of solution ($\Delta\bar{F}$), given in Table III, represents the difference between the free energy of the salt in its hypothetical standard state as a solute, i.e., "a solution containing a unit mole fraction of the salt but having in all other

TABLE II
Thermodynamic calculations for reactions involving the uranium ions

Reaction in 1/1 mole KCl + NaCl		Temperature				
		670° C	750° C	800° C	850° C	
(1)	$U_{(s)} + 3Ag^+_{(AgCl \text{ in } KCl + NaCl)} = U^{3+}_{(UCl_3 \text{ in } KCl + NaCl)} + 3Ag_{(s)}$	ΔH (kcal/mole)	-130.2	-130.2	-130.2	-130.2
		ΔF (kcal/mole)	-108.1	-106.2	-105.1	-103.9
		ΔS (e.u.)	-23.4	-23.4	-23.4	-23.4
		K	1.1×10^{25}	4.8×10^{22}	2.5×10^{21}	1.6×10^{20}
(2)	$U_{(s)} + 4Ag^+_{(AgCl \text{ in } KCl + NaCl)} = U^{4+}_{(UCl_4 \text{ in } KCl + NaCl)} + 4Ag_{(s)}$	ΔH (kcal/mole)	-136.0	-136.0	-136.0	-136.0
		ΔF (kcal/mole)	-119.4	-117.0	-115.5	-114.3
		ΔS (e.u.)	-17.6	-18.5	-19.1	-19.3
		K	4.7×10^{27}	1.0×10^{25}	3.3×10^{23}	1.7×10^{22}
(3)	$U^{3+}_{(UCl_3 \text{ in } KCl + NaCl)} + Ag^+_{(AgCl \text{ in } KCl + NaCl)} = U^{4+}_{(UCl_4 \text{ in } KCl + NaCl)} + Ag_{(s)}$	ΔH (kcal/mole)	-16.7	-16.7	-16.7	-16.7
		ΔF (kcal/mole)	-11.4	-10.9	-10.9	-10.4
		ΔS (e.u.)	-5.6	-5.6	-5.6	-5.6
		K	4.3×10^2	3.3×10^2	1.4×10^2	1.0×10^2
(4)	$3U^{4+}_{(UCl_4 \text{ in } KCl + NaCl)} + U_{(s)} = 4U^{3+}_{(UCl_3 \text{ in } KCl + NaCl)}$	ΔH (kcal/mole)	-112.8	-112.8	-112.8	-112.8
		ΔF (kcal/mole)	-74.2	-73.8	-73.9	-72.7
		ΔS (e.u.)	-40.8	-38.1	-36.3	-35.7
		K	1.5×10^{17}	5.4×10^{15}	1.1×10^{15}	1.4×10^{14}

TABLE III
 Partial molal properties of dilute solutions of uranium chlorides in 1/1 mole KCl + NaCl

<i>t</i> (°C)	UCl ₃ in KCl + NaCl				UCl ₄ in KCl + NaCl			
	$\Delta\bar{F}$ (kcal/ mole)	$\Delta\bar{H}$ (kcal/ mole)	$\Delta\bar{S}$ (e.u.)	$\gamma \times 10^4$	$\Delta\bar{F}$ (kcal/ mole)	$\Delta\bar{H}$ (kcal/ mole)	$\Delta\bar{S}$ (e.u.)	$\gamma \times 10^3$
670	-2.97	+6.170	+9.7	2.05	-10.15	+10.60	+22.0	4.46
750	-3.80	+6.170	+9.7	1.54	-10.05	+10.60	+20.1	7.14
800	-4.50	+6.170	+9.7	1.21	-10.05	+10.60	+19.2	8.97
850	-4.70	+6.170	+9.7	1.22	-10.05	+10.60	+18.4	11.1

respects the thermodynamic properties of the state of infinite attenuation of the solute", as defined by Lewis and Randall (18), and the free energy of the salt in its actual standard state of the pure salt. It is of interest to note that the partial molal free energy of solution of uranium tetrachloride is much greater than that of uranium trichloride.

The activity coefficients and the partial molal entropies of mixing indicate that uranium trichloride and uranium tetrachloride form complexes in solution. A comparison of the activity coefficients indicates that the uranium tetrachloride complex is stronger than the uranium trichloride complex. The variation of the activity coefficients of uranium tetrachloride with temperature shows the expected behavior; i.e., they increase with temperature. On the contrary, the activity coefficients of uranium trichloride decrease with increasing temperature, which indicates that the complexity of uranium trichloride is greater at higher temperatures.

The presence of complexes of tetravalent uranium ions in chloride melts has also been observed by Gruen and McBeth from spectrophotometric studies (19).

The constancy of the activity coefficients over the mole fraction range 10^{-4} to 10^{-2} indicates that the solutions of uranium tri- and tetra-chlorides in fused salts obey Henry's law.

ACCURACY OF RESULTS

It is rather difficult to evaluate the absolute accuracy of the potentials shown in Table I. Individual potential measurements shown in Figs. 1 and 3 were stable and reproducible. The slight scattering of the experimental points, which can be seen in the figures, is probably due to other side effects which are always present in high-temperature systems. These effects are: concentration gradients due to thermal convection currents; difficulties in obtaining a completely oxygen-free uranium metal surface; and slight impurities in the electrolyte. However, judging from the results presented in Figs. 1 to 4, it is reasonable to assume that the potential values obtained in this investigation are accurate to within ± 2 mv. This variation would also affect the calculation of the free energy listed in Tables II and III. It has been estimated that the variation of the free energy change should be about ± 0.3 kcal/mole for the uranium trichloride system, and about ± 0.4 kcal/mole for the uranium tetrachloride system.

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