



CANADA

SOLUBILITIES OF $TiCl_4$ IN MIXTURES OF KCl-NaCl
and
THE ELECTRODE POTENTIALS OF THE TITANIUM
CHLORIDES IN 1/1 (MOLE) KCl-NaCl SOLUTIONS

by

S. N. FLENGAS

EXTRACTION METALLURGY DIVISION

DEPARTMENT OF MINES AND
TECHNICAL SURVEYS, OTTAWA

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SOLUBILITIES OF TITANIUM TETRACHLORIDE IN MIXTURES OF POTASSIUM CHLORIDE AND SODIUM CHLORIDE, AND THE ELECTRODE POTENTIALS OF THE TITANIUM CHLORIDES IN 1/1 (MOLE) KCl-NaCl SOLUTIONS

S. N. Flengas

Scientific Officer, Extractive Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada

INTRODUCTION

In previous publications¹⁻⁵ from the Mines Branch laboratories, the standard electrode potentials for several metal-metal chloride systems in dilute solutions in fused salts were reported. To make these measurements, an equimolar mixture of potassium and sodium chlorides was used as the solvent for the metal chloride, and a silver-silver chloride electrode, developed earlier in this work,¹ was used as the reference electrode in determining the electrode potentials.

The behavior of the silver-silver chloride electrode also was investigated,⁶ using a chlorine electrode, and the results indicated that the solutions of silver chloride in the molten-salt solvent were ideal.

In the present investigation, the technique has been applied to the determination of the potentials of the titanium chlorides in solution in an equimolar mixture of potassium chloride and sodium chloride.

During the course of the preliminary experiments, it became apparent that the determination of the potential of the tetravalent titanium depended on the preparation of stable solutions of titanium tetrachloride in the molten salt. For this reason the solubilities of titanium tetrachloride in this medium were studied first.

Both of these problems, namely, the solubilities of titanium tetrachloride and the electrode potentials of the titanium chlorides, are closely associated with the electrolytic preparation of titanium metal from fused salts. Many of the electrolytic processes use titanium tetrachloride as the source of titanium for the cell and an equimolar mixture of potassium chloride and sodium chloride as the fused salt solvent. However, despite industrial developments, the mechanism of the electrolytic process is still open to various interpretations because of the scarcity of information concerning the electrode potentials of the system and the extent of solubility of titanium tetrachloride in the fused salt.

SOLUBILITIES OF TITANIUM TETRACHLORIDE IN MIXTURES OF POTASSIUM CHLORIDE AND SODIUM CHLORIDE

Very little is known about the solubility of titanium tetrachloride in fused chlorides. In fact, it has been stated that titanium tetrachloride is insoluble in chlorides of the alkali and alkaline earth metals.⁷

Kreye *et al.*,⁸ in a recent investigation using a sampling and quenching technique, concluded that titanium tetrachloride is soluble to the extent of only 0.27 mole per cent in the equimolar mixture of potassium chloride and sodium chloride at 690° C. However, the authors stated that the methods used for this study were subject to serious errors, since dissolved titanium tetrachloride apparently was released from the melt during quenching.

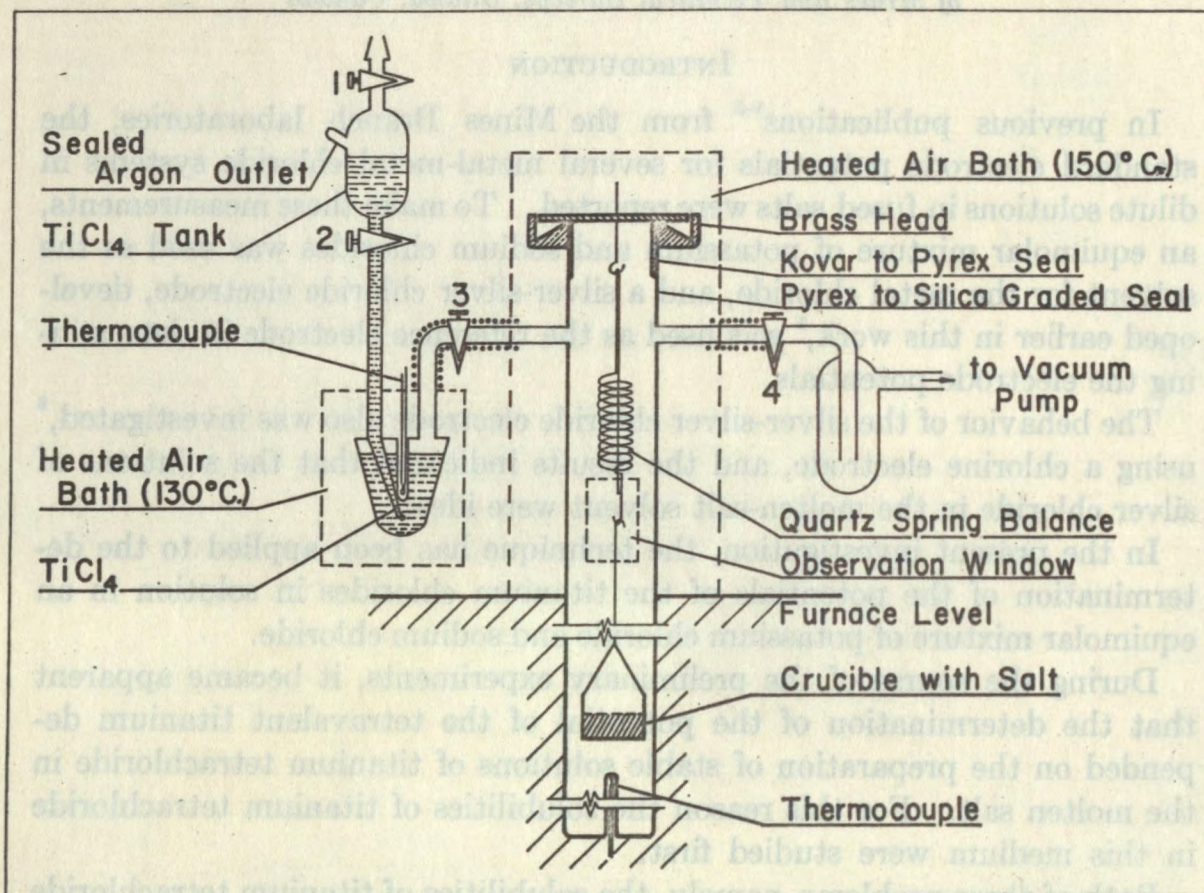


FIGURE 1. Apparatus for measurements of the solubilities of titanium tetrachloride in potassium chloride-sodium chloride mixtures.

Experimental

In the present investigation, the solubilities of titanium tetrachloride in the potassium and sodium chloride mixture were measured, using a quartz spring balance. The method involved direct observation of the increase of weight of the salt solution in contact with titanium tetrachloride vapor. It was free of the errors introduced by sampling and quenching techniques.

The apparatus used for these experiments is shown in FIGURE 1. It consists of three individually heated and temperature-controlled parts: the quartz spring balance suspended inside a silica tube, 2 in. diameter and 35 in. long; the quartz crucible containing the salt; and the titanium tetrachloride bath. Details of the apparatus are as follows:

The quartz spring had a maximum capacity of 10 gm., which corre-

sponded to an elongation of 20 cm. The elongation of the spring was measured, using a traveling microscope that could be read to 0.001 mm. The spring was suspended from a hook in the center of a brass plate at the top of the cell. The plate was lead-soldered to the metal top of the cell, which also was made from brass. A Kovar-to-Pyrex joining and a Pyrex-to-silica graded seal were used to connect the top of the cell to the silica tube. The high-vacuum valves in the apparatus were of an all-metal type and were operated through a metal bellows. These valves had stainless steel seated needles and were connected to the Pyrex tubing by metal-to-glass joints.

The lower part of the cell, which contained the crucible with the salts, was heated in a tubular furnace 20 in. long. The temperature was controlled by a Honeywell Pyrovane electronic controller. Using the double wiring circuit previously described,¹ a temperature control of $\pm 0.5^\circ\text{C}$. to a temperature of 850°C . was obtained.

The part of the cell projecting outside the furnace was enclosed in an asbestos box maintained at a temperature of 150°C . by a Sunvic thermostat. This temperature was above the dew point of titanium tetrachloride.

During the experiments, the temperature of the titanium tetrachloride in the bath was kept at $130 \pm 0.5^\circ\text{C}$., using a small electrically heated furnace that was regulated by a Fisher pyrometer and a thermocouple. The vapor pressure of titanium tetrachloride at this temperature is 660 mm. of mercury.⁹ Finally, all other exposed parts of the apparatus were heated with Nichrome wire and insulated with asbestos tape.

Commercially pure titanium tetrachloride was purified further by distillation in the presence of copper filings under a stream of argon gas. The first part of the distillate was rejected and the remainder was collected under argon in the storage tank shown in FIGURE 1. The product was colorless.

When the distillation was complete, the argon outlet at the side tube of the storage tank was sealed with a gas flame and all valves were closed. Titanium tetrachloride was then introduced under vacuum into the apparatus reservoir.

Prior to each run the cell was evacuated to a pressure of about $5\ \mu$, the temperature of the various parts was set as required, and the valve leading to the vacuum system was closed. Next, the valve leading to the titanium bath was opened and measurements of the elongation of the spring were begun.

Results

During the first run, it became apparent that the solubility of titanium tetrachloride in the 1/1 mole potassium chloride and sodium chloride melt at 690°C . was much higher than that reported previously.⁸ The weight

increase shown by the spring balance was continuous over a period of 30 hours, and solutions containing up to 14 per cent of titanium tetrachloride were obtained without any indication that the system had reached equilibrium. The extent of solubility was confirmed by chemical analysis of the contents of the crucible.

In all experiments, to ensure that the compound did not decompose, the salt solution was cooled in the cell under titanium tetrachloride pressure. When the temperature of the cell had reached 150° C., the top of the cell was opened by melting the solder and the crucible was withdrawn.

In the next group of experiments an equimolar mixture of powdered potassium chloride and sodium chloride was treated with TiCl_4 vapor at temperatures below the melting point (660° C.). It was found that the reaction rate was appreciably faster than with the molten mixture, and varied with the temperature of the salt. Using 1/1 mole potassium chloride-sodium chloride powder of a particle size of less than 325 mesh, the reaction was very fast. At 485° C. the equilibrium was attained in about 3 hours, and the saturation concentration of titanium tetrachloride in the mixture was 0.65 gm./gm. of potassium chloride-sodium chloride mixture.

Experiments at temperatures between 280° and 480° C. indicated that the reaction rate at the lower temperatures was slower, but the same saturation concentration ultimately was reached in each experiment.

Subsequent X-ray examination of the samples showed that the potassium chloride had almost completely disappeared from the mixture and was replaced by a compound having a diffraction pattern not previously reported in the literature.

To investigate the mechanism of the reaction, separate experiments were done using potassium chloride and sodium chloride powders of particle size less than 325 mesh.

With sodium chloride, at temperatures up to 750° C. there was no evidence of reaction over a period of 24 hours. At 800° C. a slow increase of weight was observed, but this was offset by evaporation of salt from the crucible. After 30 hours' exposure to the titanium tetrachloride vapor, a chemical analysis of the solidified mixture indicated a titanium tetrachloride content of only 4 per cent.

With potassium chloride at 350° C., a reaction was immediately evident. The weight of the crucible increased rapidly; at equilibrium the saturation concentration of titanium tetrachloride was 1.27 gm. per gram of potassium chloride. This amount corresponds exactly to a stoichiometric proportion $\text{KCl}/\text{TiCl}_4 = 2$. These results also explain the magnitude of the saturation concentration of titanium tetrachloride in the potassium chloride-sodium chloride mixture reported above. The observed value of 0.65 gm. of titanium tetrachloride per gram of 1/1 mole potassium chloride-sodium chloride mixture corresponds approximately to the formation of K_2TiCl_6 from the amount of potassium chloride present in the mixture. It was

concluded that the titanium tetrachloride reacted chemically with solid potassium chloride to give a complex of molecular formula K_2TiCl_6 , according to the reaction:



These conclusions were confirmed by subsequent chemical analysis of the product. The results of analysis are given in TABLE 1.

TABLE 1
CHEMICAL ANALYSES OF K_2TiCl_6

	Found in sample (per cent)	Calculated as K_2TiCl_6 (per cent)
Total titanium	14.2	14.16
Total chlorine	62.5	62.78
Total potassium	23.3	23.06

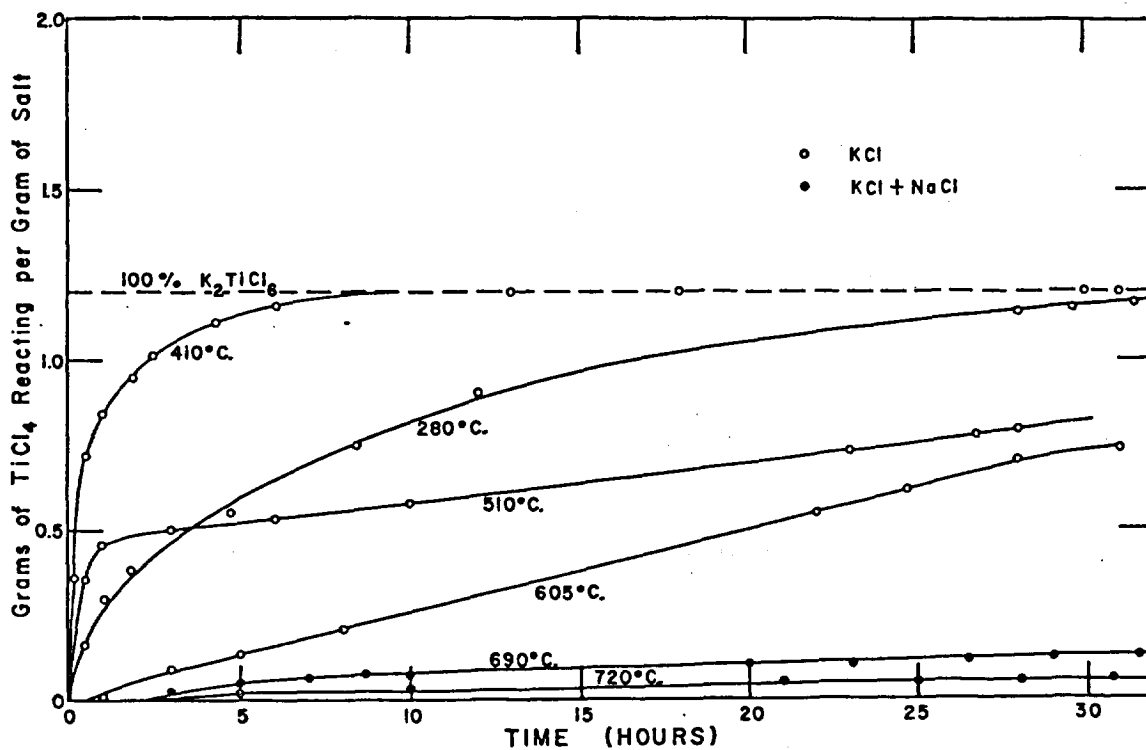


FIGURE 2. Reaction rates between gaseous $TiCl_4$, or 1/1 mole $KCl + NaCl$, at various temperatures.

The formation of K_2TiCl_6 by a wet method at room temperature already has been reported in the literature,¹⁰ where it is stated that attempts to prepare it at 300° C. in a sealed bomb were unsuccessful.

The effect of potassium chloride temperature on the rate of formation of K_2TiCl_6 also was investigated. The results are given in FIGURE 2. Included in this figure, also, are the results obtained with the fused equimolar mixture of potassium chloride and sodium chloride.

It is evident from the curves in FIGURE 2 that the reaction rate increases

rapidly with temperature and, at 410° C., the formation of 100 per cent K_2TiCl_6 takes place in about 6 hours. However, at higher temperatures the reaction behaves abnormally and the rate decreases. At 510° C. a sudden decrease of the rate occurs. Examination of the crucible after the run at 510° C. showed that fusion had taken place. It seems reasonable to assume that the slower reaction rate can be explained by the formation of a eutectic mixture between potassium chloride and the complex potassium chlorotitanate. The gradual formation of the molten phase of the eutectic would indeed reduce the reacting surface of the potassium chloride powder in the mixture. However, the possibility that the rate of the reverse process, that is, the thermal decomposition of potassium chlorotitanate, contributes to the decrease of the rate of formation should not be excluded. The data available at present are insufficient to explain the kinetic mechanism of the reaction.

The results of the experiments with fused equimolar mixtures of potassium chloride and sodium chloride at 690° and 720° C. indicate that in the molten phase the reaction rate is very slow. At 720° C., after 30 hours exposure to titanium tetrachloride vapor, the amount of titanium tetrachloride found in the mixture was only 5 per cent; at 690° C., the amount was 14 per cent. Neither result represents the attainment of equilibrium. It may be concluded that, by allowing sufficient time for reaction, the saturation concentration of titanium tetrachloride in the potassium chloride-sodium chloride melt would be reached eventually, and that potassium chlorotitanate would be formed in proportion to the amount of potassium chloride present in the mixture.

Potassium chlorotitanate has a bright yellow color and decomposes on heating under vacuum. It is stable in the presence of titanium tetrachloride vapor at 1 atm. pressure.

The X-ray diffraction pattern of pure potassium chlorotitanate indicated that the compound has a cubic cell of side 9.7 Å and is isomorphous with K_2PtCl_6 . The powder pattern has exactly the same series of lines¹¹ as has K_2PtCl_6 , but different intensities.

The density of K_2TiCl_6 was measured by the displacement method in carbon tetrachloride and was found to be 2.40 ± 0.15 gm./cm.³ at 27° C. This value may be compared with 2.45 gm./cm.³ calculated from the X-ray data on the basis of 4 formula units of K_2TiCl_6 per unit cell.

The melting point of K_2TiCl_6 also was determined in a sealed silica capillary and found to be $695 \pm 5^\circ$ C.

Potassium chlorotitanate is soluble in water. The resulting solutions were slightly opaque and strongly acidic. Hydrated TiO_2 was not precipitated even after these solutions were boiled.

Conclusions

The foregoing results indicate that titanium tetrachloride vapor reacts with potassium chloride to form a complex having the molecular formula

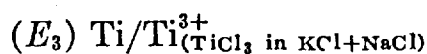
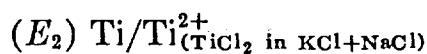
K_2TiCl_6 . The optimum temperature for the formation of this compound under a vapor pressure of titanium tetrachloride of 1 atm. is between 350° and 400° C.

At temperatures above 800° C. a reaction between titanium tetrachloride vapor and sodium chloride is evident, and the formation of the complex Na_2TiCl_6 may be postulated.

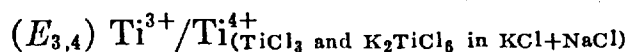
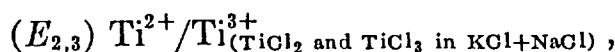
ELECTRODE POTENTIALS OF THE TITANIUM CHLORIDES IN SOLUTION IN 1/1 MOLE POTASSIUM CHLORIDE-SODIUM CHLORIDE MELTS

The potentials associated with titanium and its multivalent ions in the chloride system are as follows:

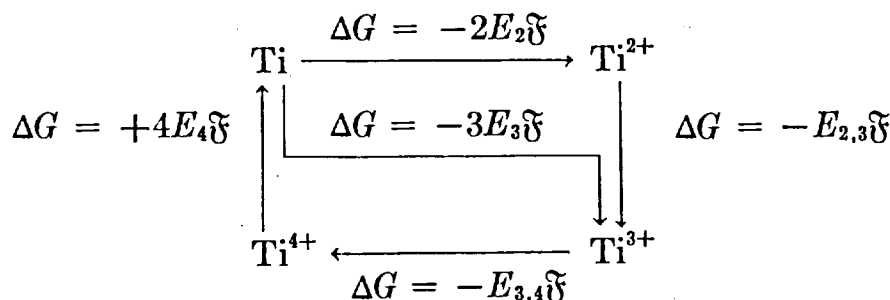
(1) The metal electrode potentials expressing the equilibria between the metallic electrode and its ionic species in solution, that is, the potentials



(2) The redox potentials due to the equilibria between two successive oxidation states of the ions, that is, the potentials



The relationship between these potentials is given by the following cyclic process



For a complete cycle, the equation relating the various potentials of the system is

$$\sum (\Delta G) = 0 \tag{2}$$

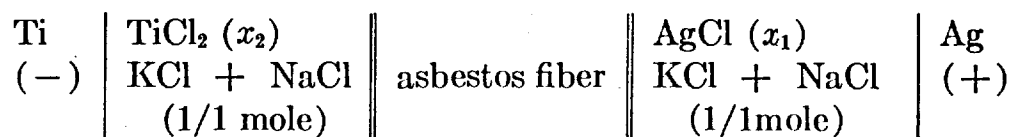
When any three of the four potentials are known, that is, one metal electrode potential and the two redox potentials, the unknown metal electrode potential can be calculated.

This method was applied to obtain the metal electrode potentials of the systems Ti/Ti^{3+} and Ti/Ti^{4+} , neither of which could be measured directly because of the reactivity of the metal with the corresponding metal chlorides in solution.

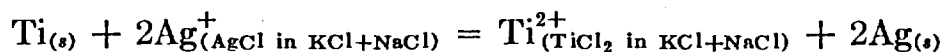
Experimental

In the course of the experimental work, two different types of cells were used for determining the electrode potentials: (1) for measuring metal electrode potentials, and (2) for measuring redox potentials.

(1) *A cell for measurements of metal electrode potentials of the system Ti/Ti_(TiCl₂ in KCl+NaCl)²⁺*. This was of the type



The chemical reaction in the cell is:



The relationship between the electromotive force and the concentrations of the reacting species in the cell is given by the Nernst equation in the form

$$E_2 = (E_{\text{TiCl}_2}^\circ - E_{\text{AgCl}}^\circ) - (2.303RT/2\mathfrak{F}) \log (x_2/x_1^2) - (2.303RT) 2\mathfrak{F} \log (\gamma_2/\gamma_1^2) \quad (3)$$

where $E_{\text{TiCl}_2}^\circ$ and E_{AgCl}° are the formation potentials of, respectively, titanium dichloride and silver chloride in their standard states. For the purpose of this paper, the standard state will be defined as the state of the pure metal chlorides at the temperature of the experiments. In so doing, all activity coefficients are referred to the state of the pure metal chlorides. The γ and x terms are, respectively, the mean activity coefficients and the mole fractions of the metal chlorides in the solutions in the two half-cells. Mole fractions are defined in the usual way, that is,

$$x_i = n_i / \sum n$$

where n_i is the number of moles of any one constituent.

From EQUATION 3, assuming that the activity coefficients for dilute solutions are constants, it is possible to calculate a cell potential that will be apparently independent of concentration. This is done simply by subtracting the $\log (x_2/x_1^2)$ term from the experimentally obtained potential, E_2 . The potential thus derived is constant over the range of concentrations for which the activity coefficients are constant and is given by the equation

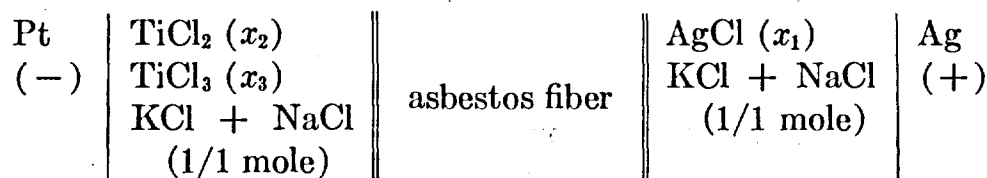
$$E_{\text{cell}}^\circ = E_2 + (2.303RT/2\mathfrak{F}) \log (x_2/x_1^2) = (E_{\text{TiCl}_2}^\circ - E_{\text{AgCl}}^\circ) - (2.303RT/2\mathfrak{F}) \log (\gamma^2/\gamma_1^2) \quad (4)$$

It follows from EQUATION 4 that, when $\log (x_2/x_1^2) = 0$, then $E_{\text{cell}}^\circ = E_2$. It will be observed that $\log (x_2/x_1^2)$ is zero for all mole fractions for which

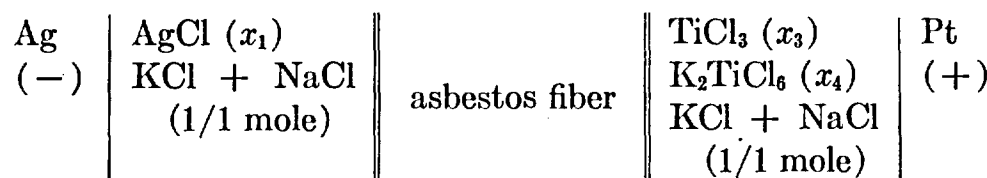
the relationship $x_2/x_1^2 = 1$, including the special case when both mole fractions x_1 and x_2 are unity. It is, therefore, permissible to call the potential E_{cell}° the apparent standard cell potential of the system.

Since the potentials of the standard state are known by calculation from thermal data¹² and the activity coefficients of silver chloride in solution in 1/1 mole potassium chloride and sodium chloride were found to be unity,⁶ EQUATION 4 can be used to calculate the activity coefficients of titanium dichloride solutions in fused salts.

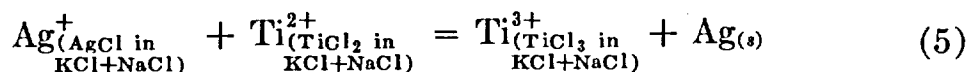
(2) *Cells for measurements of redox potentials of the systems $\text{TiCl}_2/\text{TiCl}_3(\text{KCl}+\text{NaCl})$ and $\text{TiCl}_3, \text{TiCl}_4(\text{KCl}+\text{NaCl})$.* These were of the type



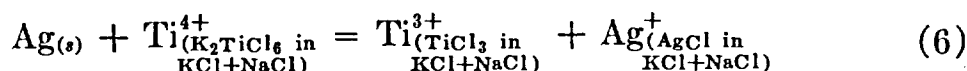
and



The cell reactions are, respectively,



and



The corresponding forms of the Nernst equation applied to each of the above redox systems are, respectively,

$$E_{2.3} = (E_{\text{TiCl}_2/\text{TiCl}_3}^\circ - E_{\text{AgCl}}^\circ) - (2.303RT/\mathfrak{F}) \log (x_3/x_1x_2) - (2.303RT/\mathfrak{F}) \log (\gamma_3/\gamma_1\gamma_2) \quad (7)$$

$$E_{3.4} = (E_{\text{AgCl}}^\circ - E_{\text{TiCl}_3/\text{K}_2\text{TiCl}_6}^\circ) - (2.303RT/\mathfrak{F}) \log (x_1x_3/x_4) - (2.303RT/\mathfrak{F}) \log (\gamma_1\gamma_3/\gamma_4) \quad (8)$$

where the $E_{\text{TiCl}_2/\text{TiCl}_3}^\circ$ and $E_{\text{TiCl}_3/\text{K}_2\text{TiCl}_6}^\circ$ are the redox potentials of the standard states. These potentials can be calculated readily from EQUATION 2 using the formation potential of the standard states.

Every x and γ is, respectively, the mole fraction and the mean activity coefficient of a metal chloride in solution.

Assuming constancy of the activity coefficients in dilute solutions, EQUATIONS 7 and 8 can be used to calculate an experimental apparent standard redox potential that will be apparently independent of concentrations, as in EQUATION 4.

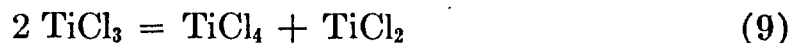
Preparation of Materials and Apparatus

The experimental technique and the apparatus used to study the potentials of the titanium chlorides were both similar to those described in the previous investigations.¹⁻⁶ The cell, however, was modified to contain the highly hygroscopic titanium dichloride and the pyrophoric titanium trichloride. The design of the silica cell is given in FIGURE 3.

To prevent contamination by air during operation, the cell was provided with a sulfuric acid bubbler and air trap, and the cell was flushed continuously with a slow stream of purified argon. Effective separation between the two half-cell solutions was achieved by an asbestos fiber sealed into the end of the silica tubing of the reference electrode. The fiber had the property of preventing diffusion and, at the same time of establishing electric contact between the two solutions. For dilute solutions the presence of a large excess of the same ionic solvent on both sides of the junction effectively eliminated junction potentials.

Titanium trichloride (99 per cent pure) was available from previous investigations.¹³

Titanium dichloride was prepared by the thermal disproportionation of titanium trichloride in a process involving two stages. In the first stage, the disproportionation reaction



was done under vacuum in an inverted U tube sealed on both sides. The arm containing the titanium trichloride was heated at 500° C. for 12 hours, during which the other arm was immersed in liquid air. At the end of this period the amount of titanium dichloride produced by disproportionation was calculated from the weight of titanium tetrachloride that had condensed in the tube. The proportion of $\text{TiCl}_2/\text{TiCl}_3$ in the mixture was close to 1/1. As a by-product of disproportionation, 0.5 per cent of finely divided titanium metal also was produced. The titanium dichloride and trichloride mixture prepared in this manner was used in the subsequent experiments to obtain the redox potentials of the system.

In the second stage of the preparation, titanium dichloride was sublimed under hydrogen at 650° C. over a period of 24 hours. The sublimed product had a Ti:Cl ratio of 2.02:1. This titanium dichloride was used in the experimental work on divalent titanium.

Pure potassium chlorititanate (99.5 per cent) was prepared from potassium chloride and titanium tetrachloride by a modification of the method established in the first part of this study. A Pyrex tube was bent at a right

angle and was sealed at one end; purified titanium tetrachloride was introduced into the closed vertical arm and was frozen with liquid air. A silica boat containing potassium chloride powder of particle size less than 325 mesh was placed in the horizontal arm, and the tube was evacuated and sealed. By heating titanium tetrachloride to 130° to 134° C. and the potassium chloride to 350° to 400° C. for about 12 hours, potassium chlorotitanate was formed quantitatively.

The titanium chlorides were pelletized in a dry box under an inert argon atmosphere, placed in the piston-type feeding apparatus shown in FIGURE

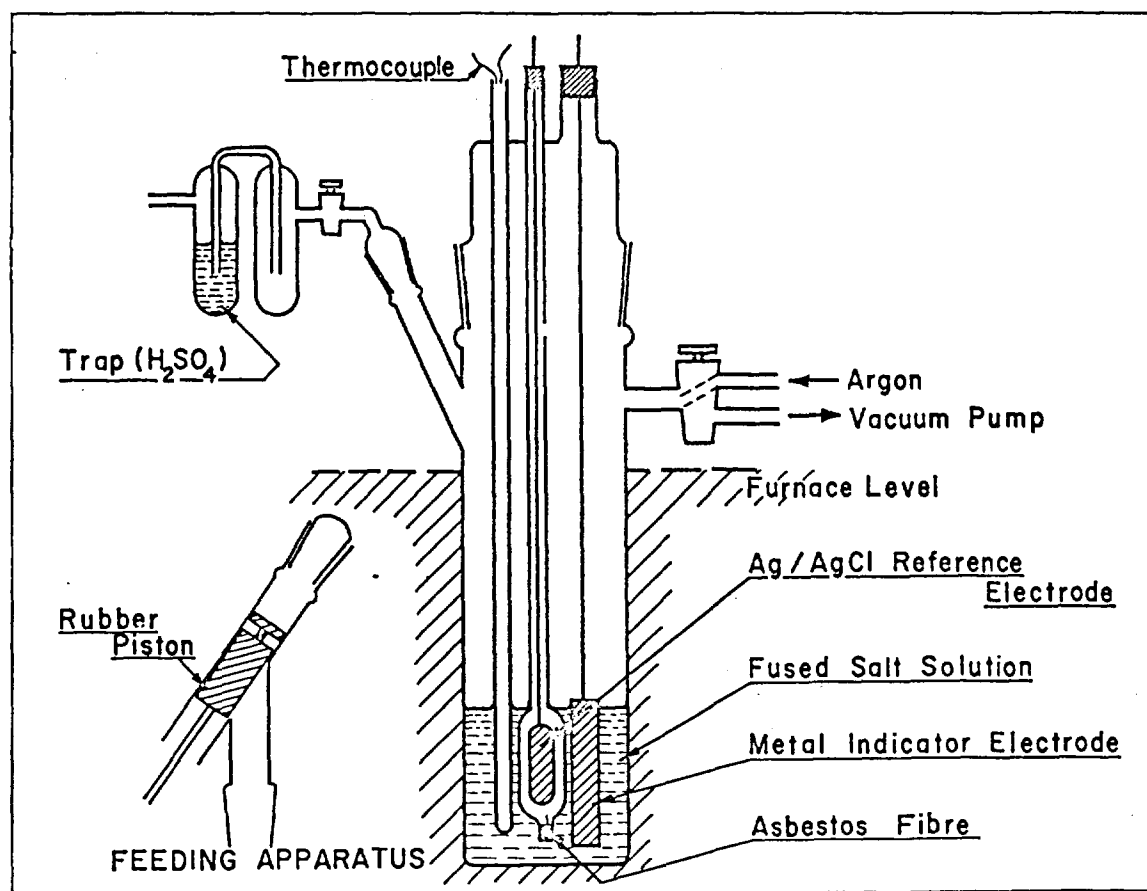


FIGURE 3. Cell for electrode potential measurements in fused cells.

3, and transferred into the cell. The dry box also was used for handling these salts during preparation.

The titanium electrode used in this study was a strip of pure iodide titanium connected to a titanium wire of the same purity. The silver electrode was a rod of pure silver (99.99 per cent) connected to a silver wire. The platinum electrode for the measurements of redox potentials was a platinum cylinder of $\frac{1}{2}$ -in. diameter and 3-in. length, connected to a platinum wire.

Thermoelectric potentials due to the bimetallic systems of the electrodes were measured separately, and the appropriate corrections were applied to the potential measurements.

Results

The electromotive forces of the titanium-titanium dichloride system were measured as functions of both temperature and concentration.

The variations of the cell potentials with temperature at various concentrations of titanium dichloride are given in FIGURE 4. It is seen that the curves are linear for the range of mole fractions investigated, namely from 2.6×10^{-3} to 1×10^{-2} .

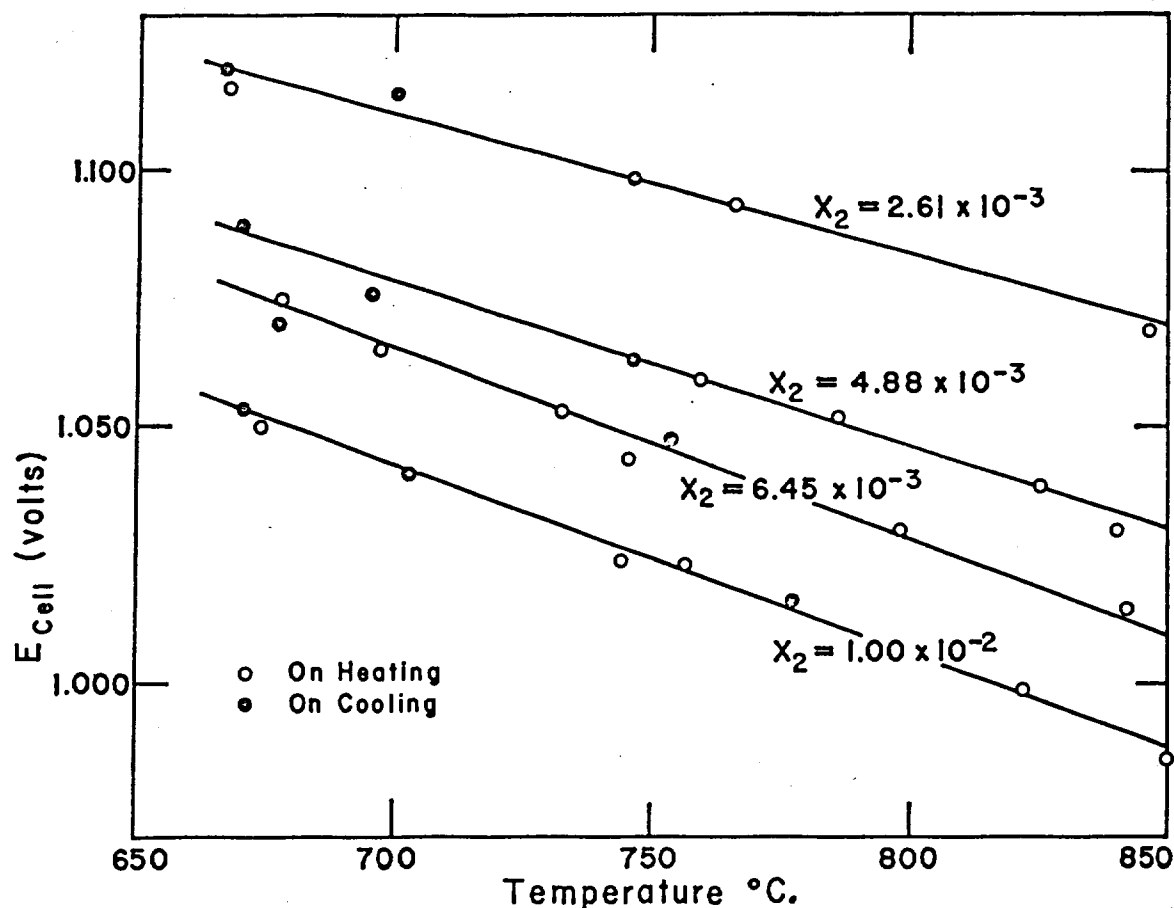


FIGURE 4. The effect of temperature on the potential of the cell at various mole fractions of titanium dichloride.



The potentials of these cells over a period of 48 hours were constant to within 0.5 mv. It was observed that titanium metal dissolved in the fused salt to the extent of about 0.5 per cent. However, the slow dissolution of titanium metal in the fused salt during the experiments did not interfere with the cell potential.

When the electromotive forces shown in FIGURE 4 were plotted against the logarithm of mole fraction, the results were well represented by straight lines. This is shown in FIGURE 5. The slopes of the straight lines are in agreement with the theoretical slopes for a two-electron electrode process, as calculated from the Nernst equation. The results of these calculations are given in the summary of results in TABLE 2.

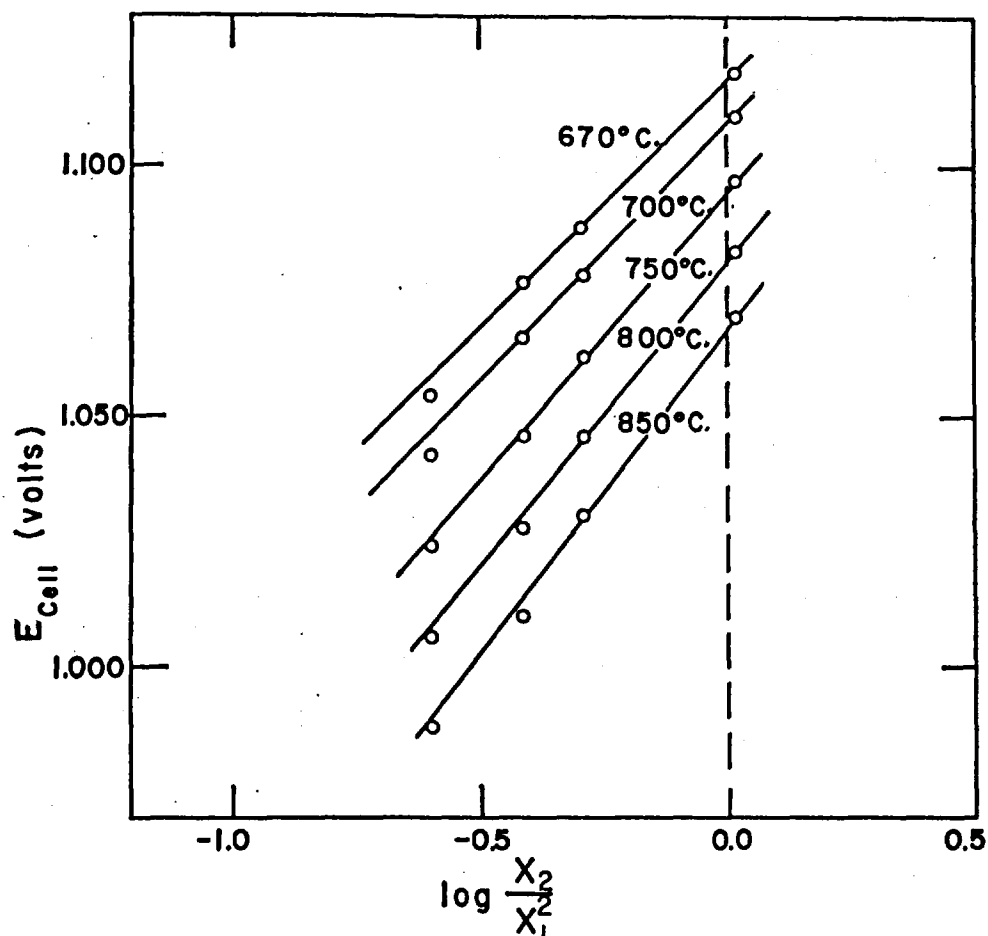


FIGURE 5. Electromotive forces of the cell as a function of $\log (x_2/x_1^2)$, at various temperatures..



TABLE 2
SUMMARY OF RESULTS

Indicator electrode	Cell reaction in molten KCl + NaCl	Cell potential at 670° C. (volts)		Slope of the Nernst equation at 670° C.	
		E_{cell}° experimental*	E_{cell}° calculated†	Experimental	Calculated
Ti, Ti ²⁺	Ti + 2Ag ⁺ = Ti ²⁺ + 2Ag	-1.115	-0.985	0.099	0.094
Ti, Ti ³⁺	Ti + 3Ag ⁺ = Ti ³⁺ + 3Ag	-1.046	-0.895	—	—
Ti ²⁺ , Ti ³⁺	Ti ²⁺ + Ag ⁺ = Ti ³⁺ + Ag	-0.910	-0.715	0.196	0.188
Ti, Ti ⁴⁺	Ti + 4Ag ⁺ = Ti ⁴⁺ + 4Ag	-0.697	—	—	—
Ag, Ag ⁺	—	0.0	0.0	—	—
Ti ³⁺ , Ti ⁴⁺	Ti ⁴⁺ + Ag = Ti ³⁺ + Ag ⁺	0.350	—	0.190	0.188
Cl ⁻ , Cl	Ag + ½Cl ₂ = AgCl	0.852‡	-0.854	—	—

* It will be noted that the sign of the experimentally obtained apparent standard potentials shown in this table has been changed to conform with the recommendations of the IUPAC Stockholm convention, as reported by Light and deBéthune.¹⁴

† Potentials calculated from existing thermodynamic data on the pure metal chlorides.¹²

‡ The potential of the chlorine electrode against the silver-silver chloride electrode has been determined in a previous investigation,⁶ and the value is given here for comparison.

The linearity of the curves in FIGURE 5 indicates that the activity coefficient of titanium dichloride in solution in the potassium chloride-sodium chloride molten solvent is constant for the range of concentrations studied. Thus the assumption for the derivation of EQUATION 4 is justified by the experimental results.

In FIGURE 5 the apparent standard cell potential for titanium dichloride at different temperatures can be obtained readily by interpolation at the zero $\log(x_2/x_1^2)$ term. The variation of the apparent standard cell potential with temperature, corrected for the thermoelectric effects, is given

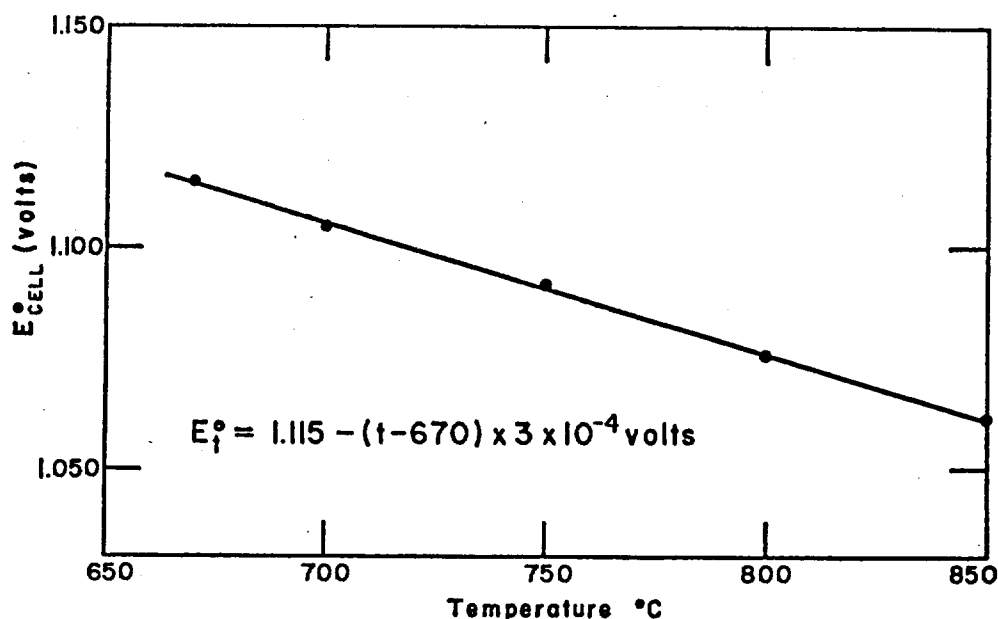


FIGURE 6. Variation of the standard cell potential of the titanium dichloride system with temperature.

in FIGURE 6. The curve is linear between 760° and 850° C.; the relationship can be represented by the equation

$$E_i^\circ = 1.115 - (t - 670) \times 3.0 \times 10^{-4} \quad (10)$$

where 1.115 is the apparent standard cell potential at 670° C.

The electromotive forces of the redox systems Ti^{2+} , $\text{Ti}_{(\text{TiCl}_2, \text{TiCl}_3, \text{NaCl})}^{3+}$, and Ti^{3+} , $\text{Ti}_{(\text{TiCl}_3, \text{K}_2\text{TiCl}_6 \text{ in } \text{KCl} + \text{NaCl})}^{4+}$ were measured as a function of the metal ion concentration at the indicator electrode. The results of these measurements at 670° C. are given in TABLES 3 and 4. The corresponding curves of the logarithmic plots are given in FIGURES 7 and 8.

The curve for the Ti^{2+} , Ti^{3+} redox system given in FIGURE 7 is linear over the range of concentrations investigated, which indicates that the activity coefficient of titanium trichloride in solution in the equimolar mixture of potassium chloride and sodium chloride is constant. The slope of the

straight line shown in FIGURE 7 is in agreement with the calculated slope for a one-electron electrode process (0.196 instead of the calculated 0.188).

TABLE 3
ELECTROMOTIVE FORCES OF THE REDOX CELL AS A FUNCTION OF THE METAL ION CONCENTRATION AT THE INDICATOR ELECTRODE AT 670° C.

Pt (-)	TiCl ₂ (x ₂) TiCl ₃ (x ₃) KCl + NaCl (1/1 mole)		AgCl (x ₁) KCl + NaCl (1/1 mole)		Ag (+)
Run	Mole fraction of AgCl (x ₁)	Mole fraction of TiCl ₂ (x ₂)	Mole fraction of TiCl ₃ (x ₃)		E _{cell} (v.)
1	4.9 × 10 ⁻²	1.44 × 10 ⁻⁴	1.54 × 10 ⁻³		0.439
	4.9 × 10 ⁻²	1.43 × 10 ⁻⁴	2.69 × 10 ⁻³		0.381
	4.9 × 10 ⁻²	1.43 × 10 ⁻⁴	4.36 × 10 ⁻³		0.354
	4.9 × 10 ⁻²	1.43 × 10 ⁻⁴	6.31 × 10 ⁻³		0.324
	4.9 × 10 ⁻²	1.43 × 10 ⁻⁴	8.53 × 10 ⁻³		0.284
2	4.9 × 10 ⁻²	2.47 × 10 ⁻³	8.47 × 10 ⁻³		0.560
	4.9 × 10 ⁻²	2.47 × 10 ⁻³	1.05 × 10 ⁻²		0.545
	4.9 × 10 ⁻²	2.47 × 10 ⁻³	1.40 × 10 ⁻²		0.486

TABLE 4
ELECTROMOTIVE FORCES OF THE REDOX CELL AS A FUNCTION OF THE METAL ION CONCENTRATION AT THE INDICATOR ELECTRODE AT 670° C.

Ag (-)	AgCl (x ₁) KCl + NaCl (1/1 mole)		TiCl ₃ (x ₃) K ₂ TiCl ₆ (x ₄) KCl + NaCl (1/1 mole)		Pt (+)
Run	Mole fraction of AgCl (x ₁)	Mole fraction of TiCl ₃ (x ₃)	Mole fraction of K ₂ TiCl ₆ (x ₄)		E _{cell} (v.)
1	5.0 × 10 ⁻²	2.27 × 10 ⁻³	7.00 × 10 ⁻⁴		0.498
	5.0 × 10 ⁻²	2.24 × 10 ⁻³	1.08 × 10 ⁻³		0.551
	5.0 × 10 ⁻²	2.22 × 10 ⁻³	1.43 × 10 ⁻³		0.561
	5.0 × 10 ⁻²	2.18 × 10 ⁻³	2.28 × 10 ⁻³		0.584
	5.0 × 10 ⁻²	5.83 × 10 ⁻³	2.27 × 10 ⁻³		0.520
	5.0 × 10 ⁻²	6.79 × 10 ⁻³	2.26 × 10 ⁻³		0.500
2	5.0 × 10 ⁻²	2.35 × 10 ⁻³	8.02 × 10 ⁻⁴		0.532
	5.0 × 10 ⁻²	2.33 × 10 ⁻³	1.78 × 10 ⁻³		0.579
	5.0 × 10 ⁻²	3.66 × 10 ⁻³	1.77 × 10 ⁻³		0.513
	5.0 × 10 ⁻²	4.57 × 10 ⁻³	1.75 × 10 ⁻³		0.488
3	6.23 × 10 ⁻²	5.33 × 10 ⁻³	3.03 × 10 ⁻³		0.541
	6.32 × 10 ⁻²	5.52 × 10 ⁻³	4.20 × 10 ⁻³		0.570
	6.23 × 10 ⁻²	5.50 × 10 ⁻³	5.09 × 10 ⁻³		0.580
	6.23 × 10 ⁻²	7.70 × 10 ⁻³	5.09 × 10 ⁻³		0.553

The potentials of these cells were reproducible and remained stable over long periods of time.

The experimental data for the Ti³⁺, Ti⁴⁺ system, as shown in FIGURE 8, are scattered as a result of the instability of the solutions. After the addition of the K₂TiCl₆ pellet to the melt, the concentration equilibrium was established in a few minutes. The potential of the cell remained constant

for about 20 min. and then began to drift slowly. The drift of potential was associated with the observation of TiCl_4 evaporation from the salt solution. In FIGURE 8, only the steady values of the experimental potentials are shown. The points shown are considered to represent the steady state within the cell. The best straight line that can be drawn through the experimental points has a slope of 0.190, which agrees well with the calculated slope of 0.188 for a one-electron electrode process.

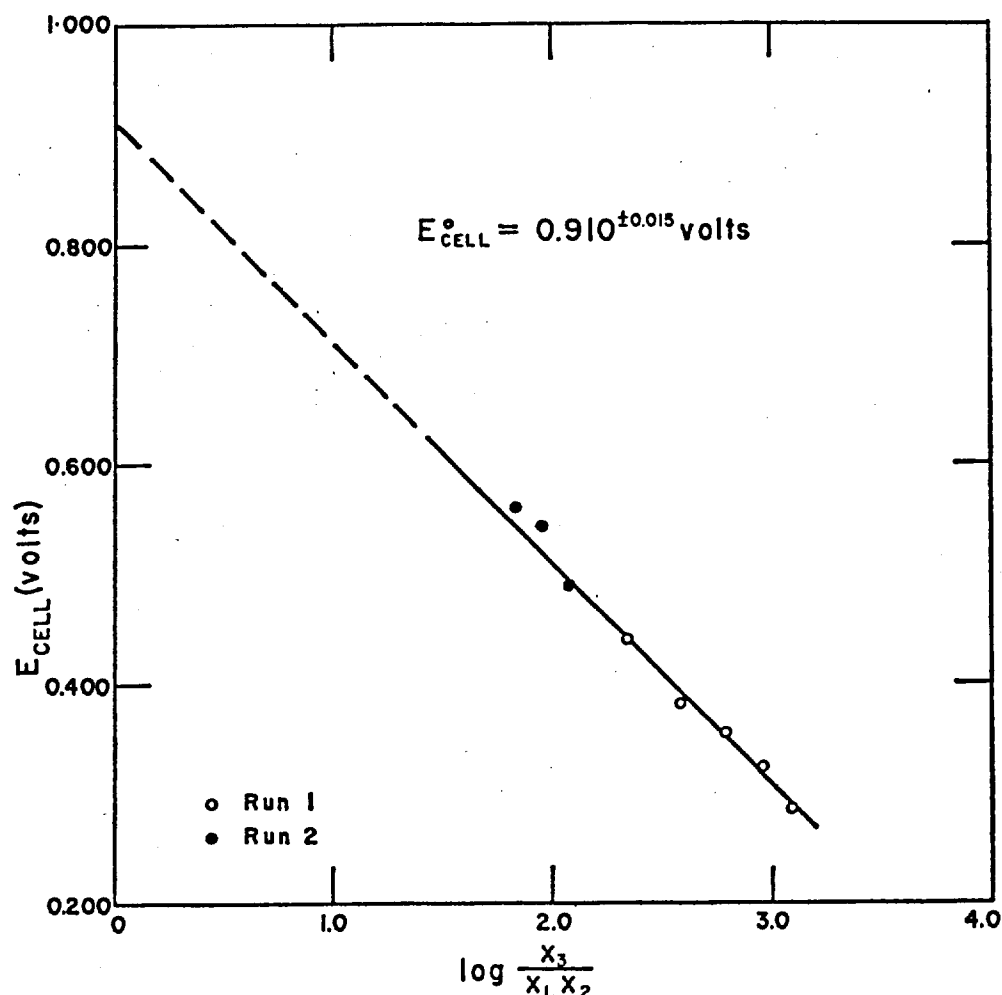
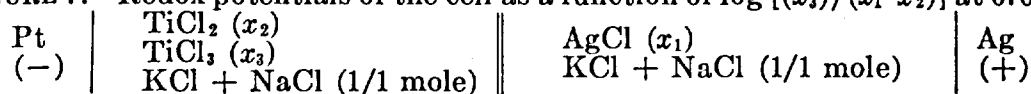


FIGURE 7. Redox potentials of the cell as a function of $\log [(x_3)/(x_1 \cdot x_2)]$ at 670°C .



The linearity of the curves indicates that the activity coefficient of the tetravalent titanium ion is constant over the range of mole fractions investigated, that is, from 7.0×10^{-4} to 5.0×10^{-3} .

Following the same procedure as used previously, apparent standard redox potentials of the systems were obtained by graphic extrapolation of the curves in FIGURES 7 and 8 to zero log terms. The potentials obtained by this method are given in TABLE 2. Standard cell potentials, calculated from the formation potentials of the metal chlorides given by Hamer *et al.*,¹² are also included in TABLE 2.

DISCUSSION

Having established the apparent standard cell potentials (E_{cell}°) of the system Ti , $\text{TiCl}_{2(\text{KCl}+\text{NaCl})}$ and the apparent standard redox potentials of the systems TiCl_2 , $\text{TiCl}_{3(\text{KCl}+\text{NaCl})}$ and TiCl_3 , $\text{K}_2\text{TiCl}_6(\text{KCl}+\text{NaCl})$, EQUATION 2 was applied to calculate the apparent standard cell potentials of the systems Ti , $\text{TiCl}_{3(\text{KCl}+\text{NaCl})}$, and Ti , $\text{K}_2\text{TiCl}_6(\text{KCl}+\text{NaCl})$, which are unobtainable by direct measurements. The results of these calculations are

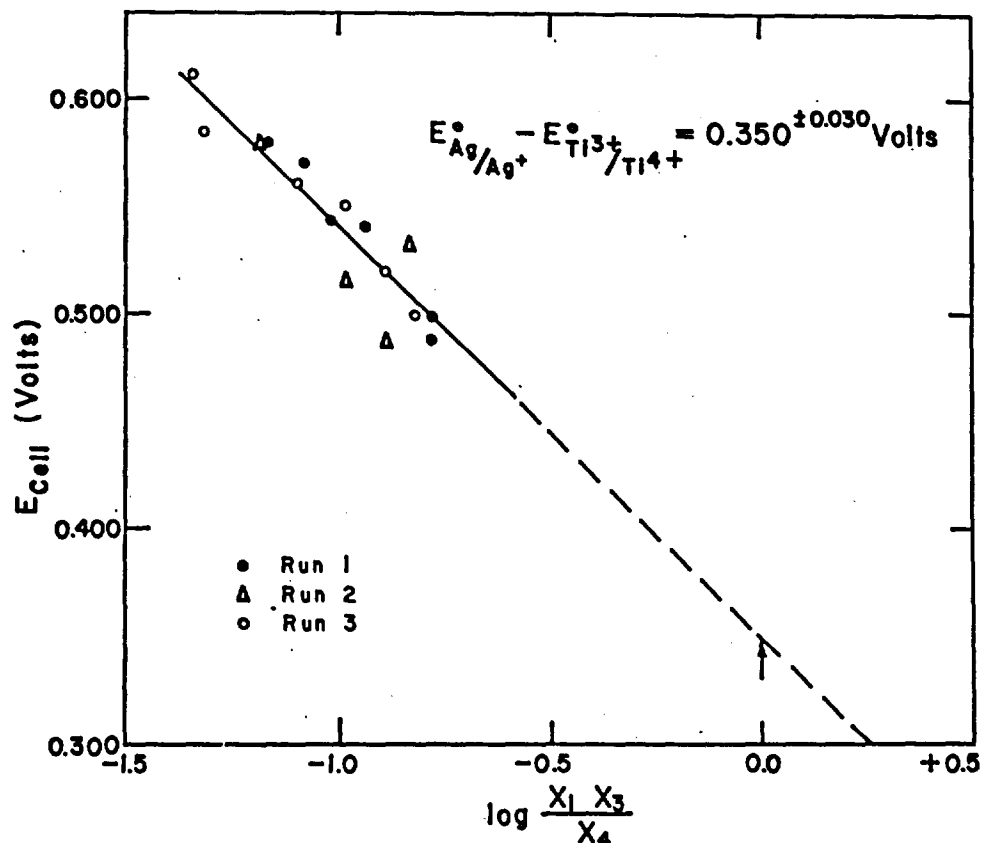
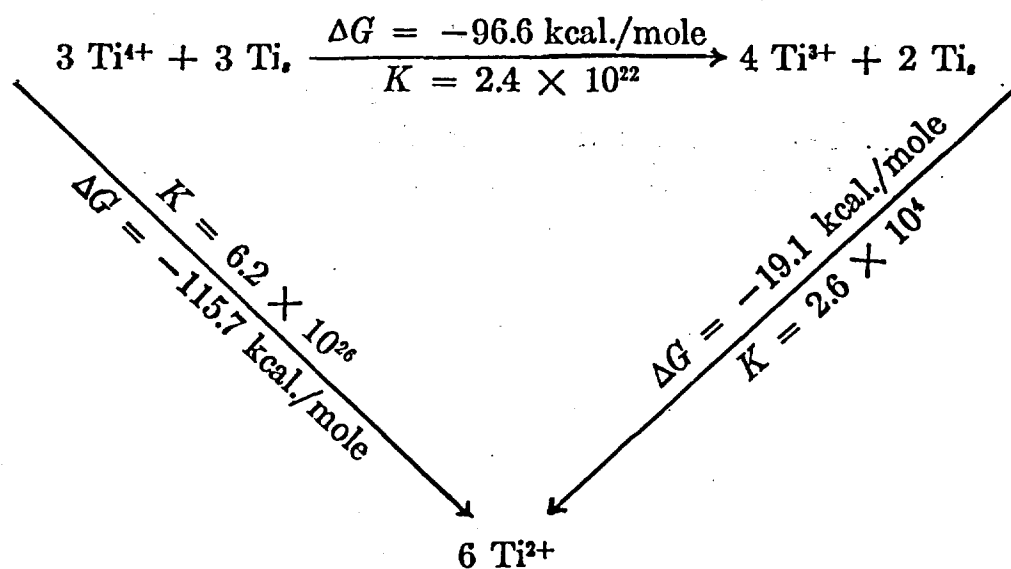


FIGURE 8. Redox potentials of the cell as a function of $\log [(x_1 \cdot x_2)/(x_4)]$ at 670°C .



given in the summary of results in TABLE 2. From the data in TABLE 2, it is possible to calculate the free energy and the equilibrium constants of the reactions between titanium metal and the various titanium ions in solution in the equimolar mixture of potassium and sodium chlorides. These equilibria are of interest because they are related to the chemical reactions that take place in a fused salt-electrolysis titanium cell. The results of these calculations are given in TABLE 5.

The relationship between the various reduction processes is best shown by the cycle appearing on the next page. It may be seen readily that in an electrolysis cell using titanium tetrachloride as the feeding material, the final cell reaction is likely to proceed through the divalent ion.



From these results, it is also possible to calculate that in a solution of titanium trichloride, in the presence of titanium metal, the composition of the solution at equilibrium should be a mixture of di- and trivalent titanium of a ratio about 9 to 1.

TABLE 5

Reaction in 1/1 mole KCl + NaCl at 670° C.	ΔG (kcal./mole)	$K_{\text{eqm.}}$
$\text{Ti}_2 + 2\text{Ti}^{3+} = 3\text{Ti}^{2+}$	-9.55	1.6×10^2
$\text{Ti}_2 + \text{Ti}^{4+} = 2\text{Ti}^{2+}$	-38.66	9.1×10^8
$\text{Ti}_2 + 3\text{Ti}^{4+} = 4\text{Ti}^{3+}$	-96.57	2.4×10^{22}
$\text{Ti}^{2+} + \text{Ti}^{4+} = 2\text{Ti}^{3+}$	-29.00	5.2×10^6

By taking the state of the pure metal chlorides at the temperature of the experiments as the standard state, the activity coefficients and the other thermodynamic properties of the solutions of titanium chlorides in the fused salt can be calculated.

Thus, from EQUATION 4, by substituting

$$E_{\text{MCl}_n}^{\circ} - E_{\text{AgCl}}^{\circ} = E_{\text{cell}}^{\circ'}$$

and noting that since the activity coefficients of silver chloride in solution in 1/1 mole KCl + NaCl were found in a previous investigation⁶ to be unity, the following relationship can be obtained:

$$\log \gamma_{(\text{MCl}_n)} = \frac{n\bar{S}}{2.303RT} (E_{\text{cell}}^{\circ'} - E_{\text{cell}}^{\circ}) \quad (13)$$

In this equation, $E_{\text{cell}}^{\circ'}$ is the calculated apparent standard cell potential with respect to the pure metal chlorides, and E_{cell}° the apparent standard cell potentials obtained experimentally in the present investigation.

Partial molal free energies of solution of titanium dichloride and trichloride and the partial entropy of mixing of titanium dichloride in the

melt can be calculated from the well-known relationships

$$\Delta\bar{G}_A = -RT \ln \gamma_A = n\bar{\gamma} (E_{\text{cell}}^{\circ'} - E_{\text{cell}}^{\circ}) \quad (14)$$

$$\left(\Delta \frac{\Delta\bar{G}_A}{\Delta T} \right)_p = -\Delta\bar{S}_A \quad (15)$$

where $\Delta\bar{G}_A$ is the partial molal free energy of mixing and $\Delta\bar{S}_A$ is the partial molal entropy of mixing. The quantity defined by EQUATION 14 represents the difference between the free-energy change of the salt in its hypothetical standard state as a solute (that is, a solution containing a unit mole fraction of the salt but having, in all other respects, the thermodynamic prop-

TABLE 6
THERMODYNAMIC PROPERTIES OF DILUTE SOLUTIONS OF TITANIUM CHLORIDES IN
1/1 MOLE KCl + NaCl

System	Range of mole fractions investigated $x \times 10^3$	Partial molal free energy of mixing ($\Delta\bar{G}_A$) (kcal./mole)			Partial molal entropy of mixing $\Delta\bar{S}_A$ (eu)			Activity coefficients $\gamma \times 10^3$		
		670° C.	750° C.	800° C.	670° C.	750° C.	800° C.	670° C.	750° C.	800° C.
TiCl ₂	2.60-10.0	-6.00	-6.36	-6.60	-5.0	-5.0	-5.0	4.1	4.3	4.5
TiCl ₃	1.5-14.0	-10.45	—	—	—	—	—	0.38	—	—

erties of the state of infinite attenuation of the solute, as defined by Lewis and Randall¹⁵) and the free energy of the salt in its actual standard state as the pure salt.

The results of these calculations are given in TABLE 6. Data for potassium chlorotitanate are not included in this table because the standard state potentials of this complex are not available in the literature.

The magnitude of the activity coefficients given in TABLE 6 indicates that titanium dichloride and trichloride, in solution in the equimolar molten mixture of potassium chloride and sodium chloride, are present as complexes. In fact, only 4×10^{-2} and 4×10^{-3} , respectively, of the amount present are free to contribute to the electrode potential. The activity coefficients of titanium dichloride show the expected behavior, that is, they increase with increasing temperature. The constancy of the activity coefficient at constant temperatures over the mole fraction range 10^{-3} to 10^{-2} indicates that in these solutions the complex species remain unchanged.

The partial molal entropies of mixing, as shown in TABLE 6, also suggest the formation of a complex for this system.

SUMMARY

The solubilities of titanium tetrachloride in mixtures of potassium chloride and sodium chloride at various temperatures were investigated, using a quartz spring balance.

It was found that titanium tetrachloride vapor reacted with potassium chloride to form the compound K_2TiCl_6 . Some of the physical properties of this compound, and the rates of its formation between 280° and 720° C., were investigated.

Using a silver-silver chloride reference electrode developed in a previous investigation, the apparent standard electrode potential of the system Ti, $TiCl_{2(KCl+NaCl)}$, and the apparent standard redox potentials of the systems $TiCl_2$, $TiCl_{3(KCl+NaCl)}$ and $TiCl_3$, $K_2TiCl_{6(KCl+NaCl)}$ were measured at 670° C., and found to be, respectively, 1.115, 0.910, and -0.350 volts.

From the data, the apparent standard electrode potentials of the systems Ti, $TiCl_{3(KCl+NaCl)}$, and Ti, $K_2TiCl_{6(KCl+NaCl)}$ were calculated and found to be 1.046 and 0.697 volts, respectively, at 670° C.

The activity coefficients and partial molal properties of titanium dichloride and titanium trichloride, in dilute solutions in the equimolar mixture of potassium chloride and sodium chloride, were calculated. It was found that for the range of mole fraction investigated, namely 10^{-4} to 10^{-2} , the solutions are nonideal and obey Henry's law.

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