



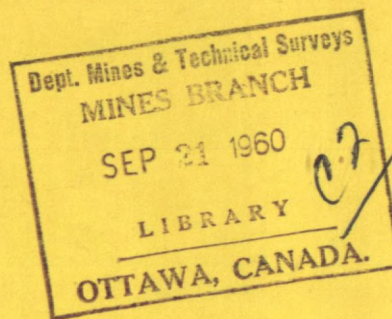
CANADA

DEPARTMENT OF MINES AND
TECHNICAL SURVEYS, OTTAWA

MINES BRANCH
RESEARCH REPORT

R 66

Price 25 cents.



EQUILIBRIUM DECOMPOSITION PRESSURES OF K_2TiCl_6

by

S. N. FLENGAS AND T. R. INGRAHAM

EXTRACTION METALLURGY DIVISION

FEBRUARY 1960

EQUILIBRIUM DECOMPOSITION PRESSURES OF K_2TiCl_6 ¹

S. N. FLENGAS AND T. R. INGRAHAM

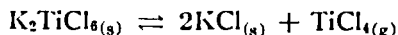
ABSTRACT

The equilibrium decomposition pressures of K_2TiCl_6 were measured at temperatures between 370° and 530° C, using a glass-bellows mercury manometer.

The pressure-temperature relationship was found to obey the equation

$$\log_{10} P(\text{cm of Hg}) = -\{(5.774 \times 10^3)/T\} + 9.120$$

and the heat of the reaction



was found to be

$$\Delta H = +26.4 \pm 1.3 \text{ kcal/mole.}$$

INTRODUCTION

Because of its relatively high degree of stability at room temperature, the compound K_2TiCl_6 offers interesting possibilities as a source of $TiCl_4$ for the electrolytic preparation of titanium in fused salt baths. Indeed, K_2TiCl_6 may be an intermediate in the chain of chemical reactions proceeding in electrolytic cells which are supplied with gaseous $TiCl_4$ and contain KCl as a constituent of the bath.

K_2TiCl_6 has been prepared by wet chemical methods involving the dissolution of the mineral ilmenite ($FeO \cdot TiO_2$) in aqueous sulphuric acid, and the salting out of K_2TiCl_6 by HCl in the presence of KCl (1) at 0° C. Unsuccessful attempts have been made to prepare the compound in an autoclave at about 300° C, by the direct reaction of KCl with $TiCl_4$ (2).

At higher temperatures, the direct reaction of KCl with $TiCl_4$ has been used successfully in these laboratories to prepare K_2TiCl_6 for use in studies of the potentials of the various titanium ions in molten salt solutions. In this preparation, which was reported in a previous paper (3), the experiments were done at temperatures from 230° to 500° C. It was observed that the rate of reaction was relatively slow at temperatures up to about 300° C, and attained a maximum rate at about 410° C. At temperatures substantially above 400° C, at which the rate of reaction might have been expected to increase, the rate of reaction decreased. It seemed probable that the compound K_2TiCl_6 was becoming increasingly unstable as the temperature was increased.

To confirm these implications, and to establish some of the thermodynamic properties of K_2TiCl_6 which might be of interest in evaluating it as a possible source of titanium tetrachloride for electrowinning cells, it was decided to study the equilibrium decomposition pressures of titanium tetrachloride over the compound.

Since our previous experience in preparing the compound had suggested that this solid-gas state reaction was relatively slow to establish equilibrium, a static method, rather than a dynamic method, of measuring the decomposition pressure was selected.

EXPERIMENTAL

The compound K_2TiCl_6 was prepared in a 1-in. diameter tube, bent in a right angle, and 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

¹Manuscript received February 10, 1960.

Contribution from the Extraction Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Ontario.

powder of a particle size less than 325 mesh was then placed in the horizontal arm and the tube was evacuated and sealed. By heating the titanium tetrachloride to a temperature between 130 and 134° C, and the potassium chloride to a temperature of about 400° C, for 12 hours, K_2TiCl_6 was formed quantitatively. When prepared by this method, the compound contained a small excess of adsorbed titanium tetrachloride. To prevent attack by moisture, the samples were transferred in a dry box to airtight glass containers.

The equilibrium decomposition pressures were measured in the apparatus shown diagrammatically in Fig. 1. The most important feature of the apparatus is the glass-

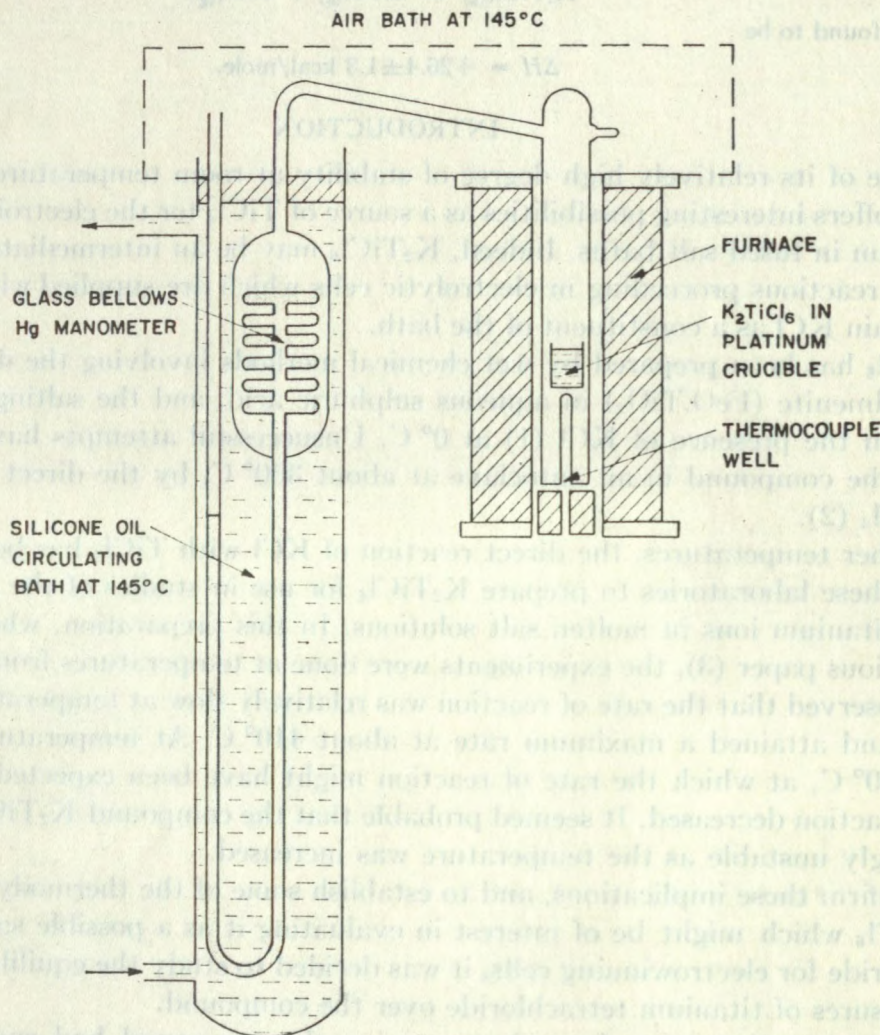


FIG. 1. Pressure measuring apparatus.

bellows mercury manometer, originally designed by Spence (4). It was modified for use in these experiments. This type of manometer is well suited to studies of equilibrium pressures in systems in which the decomposition product is a highly corrosive gas, which would be likely to attack conventional manometric liquids.

The manometer was calibrated at various pressures, and the relationship between the height of the mercury column of the manometer and the pressure was found to be linear over the pressure range between 1.2 and 76 cm. A deflection of 1.000 cm Hg was equivalent to a 1.540 cm of Hg pressure change. Pressure changes were observed with a cathetometer and were corrected for barometric fluctuations.

The reaction cell was constructed from Pyrex and Vycor. The Vycor section extended

out of the hot zone of the furnace, where it was joined, through a graded seal, to the Pyrex part of the apparatus. To avoid the condensation of titanium tetrachloride (b.p. 136.4°C), the bellows manometer was thermostatically controlled at a temperature of $145.0 \pm 0.1^\circ\text{C}$, using silicone oil (Dow Corning 550 fluid) as the heat transfer medium in a circulating bath. The connecting tube between the reaction cell and the manometer was also maintained at a temperature of $145.0 \pm 0.5^\circ\text{C}$ by means of a thermostatically controlled air bath.

The reaction cell was heated in a tubular furnace, the temperature of which was kept constant, within $\pm 1^\circ\text{C}$, by a thermocouple set in a well just below the sample and connected with a Kelwyn-Hughes phototransistor proportional temperature controller, type MIK IV.

To begin an experiment, about 10 grams of K_2TiCl_6 was transferred to a platinum crucible and the crucible was placed just above the thermocouple well. The open end of the reaction tube was then sealed and the apparatus was evacuated through a side arm for about 20 hours to remove excess titanium tetrachloride adsorbed on the K_2TiCl_6 powder. After evacuation was complete, the apparatus was sealed under vacuum and the furnace was heated to a predetermined temperature. Readings of the pressure were made at 2-hour intervals and equilibrium was considered to have been established when the pressure remained unchanged for a period of 12 hours. In the initial runs, it was observed that, at low temperatures, the same equilibrium pressure was not obtained readily when the temperature was approached from above and below. It was found that in spite of the 20-hour evacuation period, a small excess of $TiCl_4$ remained adsorbed on the sample. The $TiCl_4$ was removable by evacuation at higher temperatures, but it was found more convenient to mix excess KCl with the K_2TiCl_6 before beginning the run. When this was done, the same equilibrium pressures could be established readily on either an increasing or a decreasing temperature cycle.

RESULTS

The results obtained in three typical runs are shown in Table I.

TABLE I
Equilibrium decomposition pressures of K_2TiCl_6

Temperature ($^\circ\text{C}$)	P (cm of Hg)		
	Run 1, using K_2TiCl_6	Run 2, using K_2TiCl_6	Run 3, using $K_2TiCl_6 + KCl$
On heating			
373	—	—	1.89
432	—	—	8.44
456	—	21.52	—
469	22.33	—	—
485	—	—	29.33
489	—	36.77	—
494	—	39.16	—
506	—	48.47	48.75
515	—	—	55.65
518	—	65.32	—
525	52.84	—	—
529	66.44	—	72.67
On cooling			
512	—	53.40	—
509	—	51.86	—
432	—	—	8.58
374	—	—	1.83

From Table I it may be seen that the decomposition of K_2TiCl_6 begins at a temperature of about $350^\circ C$, and that the decomposition pressure of $TiCl_4$ at about $530^\circ C$ is 1 atm. The equilibrium constant for the decomposition of K_2TiCl_6 ,



is given by the equation

$$K_p = P_{TiCl_4}$$

The results shown in Table I were used to calculate $\log K_p$ and $1/T$, and when these were plotted, the straight-line relationship shown in Fig. 2 was obtained by applying the least-squares method. It is evident from Fig. 2 that the linear relationship holds

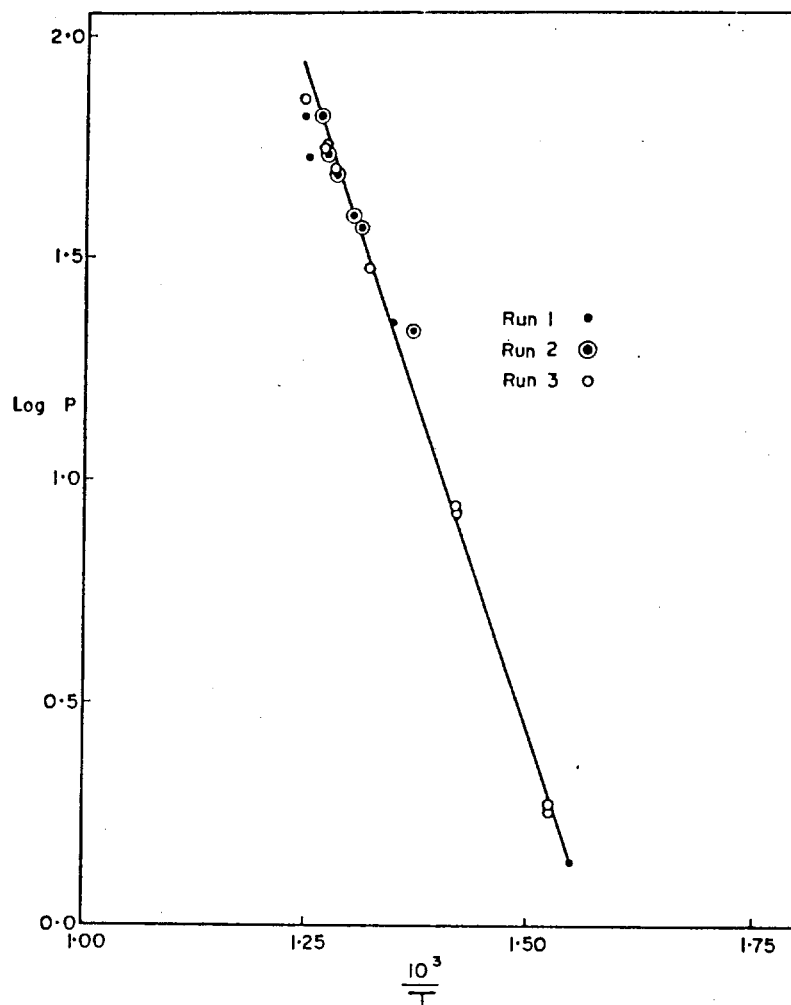


FIG. 2. The variation of $\log P$ with the reciprocal of the absolute temperature.

reasonably well for pressures between 2 and 76 cm. From Fig. 2, the variation of pressure with temperature corresponds with the equation

$$\log_{10} P(\text{cm of Hg}) = -\{(5.774 \times 10^3)/T\} + 9.120.$$

The average error, a , of a single observation, as calculated by the least-squares method, is

$$\log a = \pm 0.045.$$

The heat of reaction was calculated from the slope of the straight line in Fig. 2 in accordance with the van't Hoff equation

$$\Delta H = +26.4 \pm 1.3 \text{ kcal/mole.}$$

This is in good agreement with +27 kcal/mole obtained by Ehrlich and Framm (2) from their experiments using the isoteniscope method.

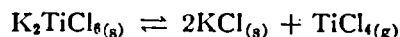
Free energy and entropy changes for the decomposition were calculated at selected temperatures. The results are shown in Table II.

TABLE II
Thermodynamic functions for the reaction
 $K_2TiCl_6(s) \rightleftharpoons 2KCl(s) + TiCl_4(g)$

Temp. (°C)	K_p (atm)	ΔH (kcal/mole)	ΔF (kcal/mole)	ΔS (e.u.)
350	9.36×10^{-3}	+26.40	+5.77	33.6
400	4.56×10^{-2}	+26.40	+3.88	33.4
450	1.79×10^{-1}	+26.40	+2.52	33.0
500	5.88×10^{-1}	+26.40	+0.81	33.1

CONCLUSIONS

Since the reaction



is endothermic, the formation of the compound is promoted at lower temperatures. However, from kinetic considerations (3) it appears that the rate of reaction at temperatures below 300° C is slow; this would explain the inability of Ehrlich and Framm (2) to prepare K_2TiCl_6 in an autoclave at 300° C.

Furthermore, the thermal stability of K_2TiCl_6 in the temperature range of 300–400° C indicates that the compound might be used as a constituent of a low-melting-point fused salt bath, e.g. $KCl + LiCl$, for the production of titanium metal by electrolysis. Indeed, it appears that the accepted practice of using fused salt baths at high temperatures, e.g. $KCl + NaCl$ at 700° C, would hinder the introduction of gaseous titanium tetrachloride into the melt, under circumstances where the introduction depended upon the formation of K_2TiCl_6 .

ACKNOWLEDGMENT

The authors wish to thank Mr. George Ensell, National Research Council of Canada glass blower, for constructing the glass-bellows mercury manometer.

REFERENCES

1. F. V. SCHLOSSBERGER. *Ind. Eng. Chem.* **51** (5), 669 (1959).
2. B. EHRLICH and E. FRAMM. *Z. Naturforsch.* **9b**, 326 (1954).
3. S. N. FLENGAS. Solubilities of titanium tetrachloride in mixtures of potassium and sodium chlorides, and the electrode potentials of the titanium chlorides in 1/1 mole $KCl + NaCl$ solutions. Paper presented at the New York Academy of Science, April, 1959.
4. R. SPENCE. *Trans. Faraday Soc.* **36**, 417 (1940).