moles of solvent are expanded by 41 cc. and the (liquid) I_2 then dissolved in it, the contribution of the expansion to the entropy would be 6.7 cal. deg.$^{-1}$. This agrees remarkably well with the value 6.9 calculated earlier by Hildebrand and Scott.[2] The sum of the entropy of fusion, expansion and dilution to $x_2 = 1.80 \times 10^{-4}$ is thus $8.0 + 6.7 + 18.3 = 33.0$ e.u. The experimental value is 34.4 e.u. The difference, 1.4 e.u., must represent mainly the shortcoming of the simple F–H equation with respect to this system. We postpone a more detailed consideration of the matter pending completion of the study of the bromine–f-heptane system.

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TRANSPORT NUMBER MEASUREMENTS IN PURE FUSED SALTS

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In all previous attempts to determine transport numbers in molten salts, the gravitational flow of melt in the reverse direction to that produced by the flow of electricity, has introduced large errors which have never been completely overcome by the insertion of narrow tubes or sintered disks between the anode and cathode compartments. In the present work, gravitational flow has been eliminated completely by the use of an accurately horizontal transport cell. The transport numbers of the chloride ion in molten lead chloride and cadmium chloride have been determined by measuring the movement of electrolyte in a capillary tube during the passage of a known quantity of electricity. The values of the measured transport number are $PbCl_2$, $t_- = 0.393 \pm 0.01$ (527–529°), $t_- = 0.382 \pm 0.01$ (602–608°); $CdCl_2$, $t_- = 0.340 \pm 0.007$ (602–608°). These values indicate that previous assumptions that these salts are predominantly anion conductors were incorrect. No evidence has been found for the presence of autocomplexes in these salts.

Comparison of the electrical conductivities of molten salts has led to the assumption that conduction in the molten alkali halides is predominantly cationic but the conduction process in the alkaline earths together with those of lead and cadmium is mainly anionic.[1,2] To verify such assumptions determinations of transport numbers in pure fused salts are necessary.

For molten salts such measurements have not, in the past, yielded reliable results because, as Duke and Laity[3,4] have pointed out, the transfer of electrolyte by the passage of current in a Hittorf type apparatus builds up a hydrostatic pressure which tends to nullify the electrolytic movement of the melt. Previous workers have attempted to counteract this gravitational flow by inserting a deterrent to such flow between the anode and cathode compartments. These devices, such as sintered glass disks or narrow capillary tubes, will slow down but do not prevent the gravitational movement of the melt.

Lorenz and Fausti[5] attempted to determine the transport number of chloride ion in fused mixtures of lead chloride and potassium chloride. Two small porous cells immersed in the fused salt mixture formed the anode and cathode compartments, respectively. The measurements were carried out at about 800° and were inconclusive. Wirths[6] used cells separated into three compartments by sintered disks for the investigation of lead chloride and added lead chloride containing radioactive lead (Th B) to the center compartment so as to permit radiochemical analysis. Temperature fluctuations and gravitational flow in the reverse direction made the transport measurements inconclusive. Baimakov and Samusenko[7] also used a Hittorf type apparatus for investigation of lead chloride but without success. Karpachev and Pal'guev[8] used a similar method to investigate lead chloride but obtained results of poor reproducibility. Duke and Laity[3,4] modified the usual Hittorf method. Their Pyrex glass transport cell consisted of two compartments separated by a sintered glass disk and joined above the disk by a capillary. Two lead pools at the bottom of the compartments formed the electrodes and the apparatus was filled so as to leave an air bubble in the capillary. To carry out a run, the air bubble was displaced by adding a weighed amount of powdered lead chloride to one compartment and electrolysis was carried out until the bubble returned to its original position, the quantity of electricity being measured. In this method the error due to gravitational flow of electrolyte in the opposite direction to that of electrolysis was not eliminated. This will be discussed below. There also have been attempts to investigate other salts.[9,10]

The present research project was planned so as to eliminate errors due to gravitational flow of the melt in the direction opposite to that of the electrolysis.

Experimental

Materials.—These were all of analytical reagent purity. **Lead Chloride** was prepared by precipitation from analytical reagent lead nitrate solution by analytical reagent hydrochloric acid. The product was filtered and evaporated to dryness several times with hydrochloric acid to remove any traces of nitrate.

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Cadmium Chloride was prepared by direct chlorination of molten cadmium, purity 99.99%, which was supplied by Electrolytic Zinc Co. of Australia.

Apparatus.—The transport cell was constructed of transparent silica. Pyrex was first tried but was abandoned because of deformation above 560° (553° is given as the annealing temperature of Pyrex[11]). The cell consisted of two compartments (internal diameter 6 mm., length of each 1 cm.) separated by a sintered silica disk. Disks of various porosities from 2 (medium) to 4 (fine) were used in different runs without any systematic variation of results. Each compartment terminated in a capillary of length 10 cm. and bore 0.5 to 1.0 mm. These capillaries were calibrated and checked for uniformity by weighing with mercury inside. Tungsten wires of diameter 0.01 inch were introduced into the capillaries to carry the electrolysis current to the molten metal electrodes.

A transparent silica tube wound with nichrome V wire (8 turns per inch) formed the heating element. This element was mounted in an insulating case containing slits through which its contents could be viewed. By focusing a light source and cathetometer telescope on the boundary between molten salt and molten metal in the capillary, its movement during electrolysis could be measured. Temperature was measured by means of a chromel–alumel thermocouple in contact with the transport cell and a Leeds and Northrup type K2 potentiometer. Temperature was controlled by a variable voltage transformer and did not vary more than 0.5° during a run. The current source was carefully stabilized,[12] the current being measured by determination of potential drop across a standard resistance in the circuit, by means of the potentiometer.

The furnace was mounted so that it could be rotated in the vertical plane perpendicular to its axis. This allowed the transport cell to be filled in a vertical position, then rotated to a horizontal position to carry out the run.

Experimental Procedure.—To fill the transport cell, the empty cell with tungsten wires removed was attached at one end to a vacuum system and the cell was heated in the vertical furnace. Lead chloride melt was drawn into the bulk of the cell and then a small quantity of lead to form one of the electrodes. When the furnace was made horizontal the tungsten wires were introduced into the capillaries—one into the molten lead and the other into the lead chloride. The latter was made the cathode so that after a preliminary electrolysis this wire also became surrounded by molten lead. The current was then stopped and any movement of the boundary between lead and lead chloride noted. Levelling adjustments of the furnace were made until there was no gravitational movement of the boundary in 1 hour.

To carry out a determination of transport number, current was passed at 10 ma. and the rate of movement of the anolyte boundary measured over a time interval of 1–2 hours.

Results and Discussion

According to Duke and Laity[3,4] the transport number of the chloride ion is equal to the fraction of an equivalent of salt transferred from catholyte to anolyte during the passage of one faraday of electricity. The transport number of the anion is thus given by the equation

$$t_- = \frac{2 \times 96500Vd}{qM}$$

where

V = increase in vol. of molten salt in the anode compartment
q = no. of coulombs of electricity passed
d = density of salt
M = molecular weight of salt

Similar experiments were conducted to determine the anion transport number in cadmium chloride with molten cadmium electrodes.

	Temp. range, °C.	Transport no.
$PbCl_2$	527–529	$t_- = 0.393 \pm 0.01$
	602–608	$t_- = 0.382 \pm 0.01$
$CdCl_2$	602–608	$t_- = 0.340 \pm 0.007$

The determinations were not sufficiently accurate to decide whether there is a real variation of transport number with change of temperature.

It is clear however that the cations in molten $PbCl_2$ and $CdCl_2$ carry relatively more of the current than the anions. This is in agreement with the postulate by Bloom and Heymann[2] that the smaller ion will be expected to carry most of the current. These authors however further stated that $PbCl_2$ and $CdCl_2$ may be expected to be anion conductors because they are anion conductors in the solid state and the conductivity of molten lead and cadmium halides changes considerably with change of anion.

It can also be seen that autocomplex formation, involving the presence of lead and cadmium in the form of large complex anions, *e.g.*, $PbCl_6^{4-}$, is ruled out by the results obtained. If autocomplexes were present in appreciable concentration the transport number of the cation would be very low or even negative.

Considering the relative magnitude of the t_+ values of $PbCl_2$ and $CdCl_2$ (where $t_+ = 1 - t_-$) it can be seen that $\frac{t_+ \ PbCl_2}{t_+ \ CdCl_2} = 0.94$ which is approximately equal to $\Lambda_{PbCl_2}/\Lambda_{CdCl_2}$ at corresponding temperatures (10% in degrees absolute above the melting point[2])—Λ refers to equivalent conductivity. This would be anticipated as we are comparing salts with common anion, hence the ratio of their conductances should be equal to the ratio of the cation mobilities.

The results for anion transport number in lead chloride do not agree with those obtained by Karpachev and Pal'guev or Duke and Laity, who obtained the value of $t_- = 0.75$. The latter authors criticized the work of Karpachev and Pal'guev even though their results agreed with those of the Russian workers. Duke and Laity's method does not overcome the problem of gravitational flow through the sintered disk in the opposite direction to that of electrolysis. These authors reduced the hydrostatic head causing this flow to very small values but in doing so they measured a correspondingly small movement of electrolyte. The net error due to gravitational flow therefore remains the same. To overcome the problem of gravitational flow Duke and Laity recommend the use of "ultrafine" disks—coarse disks did not give them any meaningful results. In the present work there is no gravitational flow as the apparatus was carefully levelled before each run, the porous disk being present merely to enable the detection of the movement of electrolyte relative to the bulk of the melt.

Other criticisms which apply to the experiments of Duke and Laity are as follows: (1) Pyrex glass at 565°, *i.e.*, slightly above its annealing temperature (553°) is likely to be slightly plastic and the relatively bulky apparatus may be subject to deformation at this temperature. (2) The temperature was "not too carefully controlled" which may

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[11] C. J. Phillips, "Glass—The Miracle Maker," Pitman, New York, 1941.

[12] M. Spiro and H. N. Parton, *Trans. Faraday Soc.*, **48**, 263 (1952).

introduce errors due to thermal expansion both of the melt (if the apparatus is not perfectly symmetrical) and the air bubble. (3) The electrolysis currents used by Duke and Laity (up to 0.5 amp.) cause considerable local heating of the disk.

The present authors agree with Duke and Laity that the disk does not introduce errors due to electroösmosis. In the present investigation voltages varying from 0.2 to 6 volts were applied across the transport cell without any systematic variation of the measured transport number.

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MEASUREMENT OF OPTICAL ABSORBANCY OF $TiCl_4(g)$ IN THE ULTRAVIOLET REGION[1]

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The optical absorbancy of gaseous $TiCl_4$ was measured at 25° at wave lengths from 240 to 360 mμ. A maximum in absorbancy occurs at 280 mμ where the molar absorbancy index was found to be 7.29×10^3 liter/mole cm. The partial pressure of $TiCl_4(g)$ in the equilibrium $2TiCl_3(s) \rightleftarrows TiCl_4(g) + TiCl_2(s)$ was measured by optical absorbancy and found to be about 1 mm. at 475°. By successively removing $TiCl_4$ and measuring the optical absorbancy of the system, solid solution of $TiCl_2$ in $TiCl_3$ was shown to be non-existent in this equilibrium.

I. Introduction

Few data are available on the absorption spectrum of gaseous $TiCl_4$ in the ultraviolet range.[3] Such data were obtained to supplement kinetic and thermodynamic studies involving $TiCl_4$, particularly the equilibrium of disproportionation of $TiCl_3(s)$. In measurement of this equilibrium using the Knudsen effusion method,[4,5] initially high partial pressures of $TiCl_4(g)$ were obtained which leveled out at a lower value as the measurement progressed. This behavior suggested solid solution of $TiCl_2(s)$ in $TiCl_3(s)$ causing initially low activity of $TiCl_2(s)$ and therefore high $TiCl_4$ pressure. This behavior was studied in an isochoric system using absorbancy to measure equilibrium pressures of $TiCl_4$. The absorbancy of $TiCl_4(g)$ was first measured as a function of wave length for use with these other physiochemical measurements.

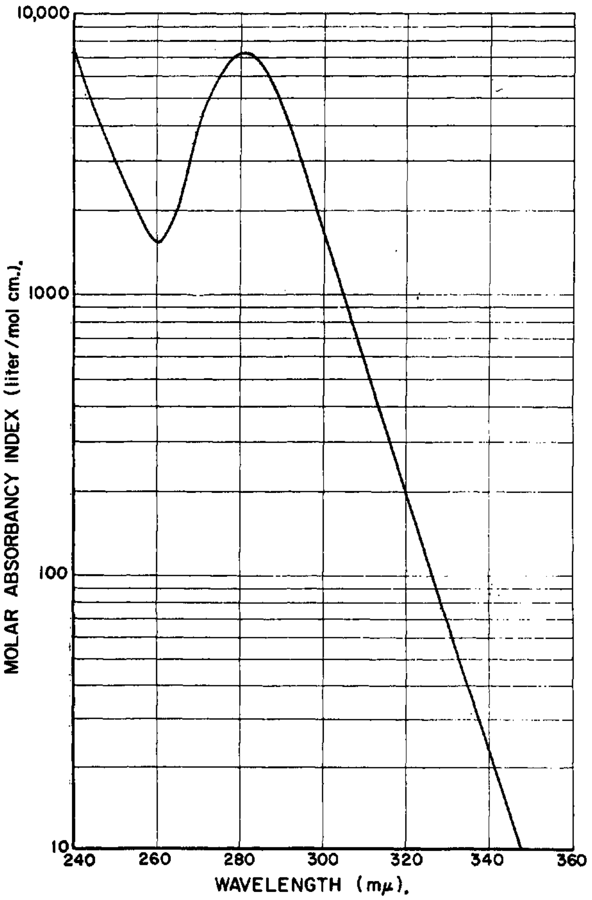

Fig. 1.—Optical absorbancy of $TiCl_4(g)$.

II. Experimental

The absorbance measurements were made with a Beckman Model DU spectrophotometer using quartz cells either 1 cm. or 5 cm. in depth. A vertical quartz stem, which was bent over and sealed to a bulb, was attached to the cell. The bulb was kept in a constant-temperature liquid bath outside the spectrophotometer. This bulb was partially filled with $TiCl_4(l)$ of 99.999% purity provided by the National Bureau of Standards. The $TiCl_4$ was frozen by immersing the bulb in liquid nitrogen, and the glass system was then evacuated and sealed. The cell temperature was maintained to within ±0.1° by controlling a special air bath surrounding the spectrophotometer cell holder. Most of the measurements were made with the cell at around 25°, although several measurements were made at 50° to check possible deviations from Beer's law. The concentration of $TiCl_4(g)$ was varied by varying the temperature of the liquid $TiCl_4$ in the temperature range 0 to 8°. The molar absorbancy index was calculated from the measured absorbance together with vapor pressure data for $TiCl_4$.[6]

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