THE PREPARATION OF SOME OF THE LIQUID HALOGEN COMPOUNDS OF VANADIUM AND THE MEASUREMENT OF THEIR DIELECTRIC CONSTANTS

by

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# Table of Contents

I. **Introduction**
   1. Nernst-Thompson rule
   2. Relations between D. C. and Conductivity of solutions.
   3. Purpose of Investigation

II. **Description of Drude-Schmidt Apparatus**
    1. Parts of Apparatus and Connections
    2. Description of the Different Parts.

III. **Operation of the Drude-Schmidt Apparatus**

IV. **Standardization of Measuring Cells**

V. **Preparation of Vanadium Oxychlorid (VOCl₄)**
   1. Extraction of Vanadium Pentoxid from Carnotite Ore
   2. Extraction of Vanadium Pentoxid from Iron Vanadate
   3. General Methods for preparation of Vanadium Oxychlorid
   4. Preparation by the Method of Ephraim
   5. Preparation by Roscoe's Method

VI. **Preparation of Oxybromid (VOBr₃)**
   1. Unsuccessful Experiments
   2. Successful Experiments
   3. Determination of the Melting Point

VII. **Preparation of Vanadium Tetrachlorid (VCl₄)**
   1. General Methods
   2. Preparation of Metallic Vanadium
   3. Preparation by Mertes Method
VIII. Data Obtained in the Measurement of Dielectric Constants

1. For Vanadium Oxychlorid
2. For Vanadium Oxybromid
3. For Vanadium Tetrachlorid
4. Calibration of Cells
5. Curve Sheets

IX. Summary and Discussion of Results.

X. Acknowledgments.
List of Illustrations

Assembled Apparatus, Plate 1. 4 A.
Diagram of Connections, Plate 2. 4 B.
Diagram of Cells, Plate 4. 4 B.
Drude Apparatus, Plate 3. 4 C.
Apparatus for Purification of Vanadium Oxy-
chlorid, Plate 5. 16 A.
Apparatus for Preparation of Vanadium
Oxybromid, Plate 6. 19 A.
Cross Section of Reaction Tube, Plate 6. 19 A.
Apparatus for Distillation of Vanadium
Oxybromid, Plate 7. 21 A.
Curves for Vanadium Oxychlorid Cells 31 B, 31 C, 31 D, 31 E
Curves for Vanadium Tetrachlorid Cells 31 J, 31 K, 31 L
Introduction

The announcement of the ionic theory in 1887 by Arrhenius directed attention to the behavior of aqueous solutions. From this standpoint several important generalizations were developed such as (1) degree of dissociation, (2) migration velocity of ions, (3) conductivity of solutions, (4) the Ostwald Dilution Law, etc. When other solvents than water were investigated, however, for example, liquid sulphur dioxide (Walden and Centnerzwer, ) it was found that many difficulties not anticipated by the theory of electrolytic dissociation were encountered. Some of the generalizations developed for aqueous solutions were found not to hold in the case of liquid sulphur dioxide as a solvent, as an example, conductivity does not increase with dilution.

These discrepancies led to a closer study of the electrical phenomena of electrolytes and a sharper differentiation of the electrical constants and of the constituents of solutions: the mechanism of the transference of electricity through electrolytes, the ionic charges involved, etc. and the dielectric constant of the solvent. Numerous investigations were undertaken on the electrical conductivity of solutions; and the relation of the dielectric capacity of the solvent to the electrical conductivity of solutions.
To explain the electrical conductivity of solutions it is generally assumed that the dissolved substance is more or less dissociated into oppositely charged ions. Oppositely charged ions when free to move will, of course, continually recombine and this tendency to recombination will be directly proportional to the product of the charges and inversely as the square of the distance. But the electric force between two oppositely charged particles also varies as the dielectric capacity of the medium and the greater the dielectric capacity the less is the attractive force. Hence a solvent such as water whose dielectric constant is high would materially reduce this tendency of ions to recombine. Considerations of this kind and attempts at the correlation of other electrical properties led J. J. Thompson and Nernst and others in 1894 independently to the generalization that a close parallelism exists between the dielectric constant of the solvent and its dissociating power. This generalization is generally known as the Nernst-Thompson rule. Walden has worked out the numerical relationship between the dielectric constants and the dilutions in various solvents. The relation \( \frac{\sqrt[2]{D}}{D} = \frac{\sqrt[2]{D'}}{D'} = \frac{\sqrt[2]{D''}}{D''} = \text{constant} \)

where \( K, K', K'' \) represent the dielectric constants \( D, D', D'' \) of the individual solvents and \( D, D', D'' \) the corresponding
dilutions at which the value of the degree of dissociation is the same.

Walden has drawn, in subsequent investigations, the general conclusion that the dielectric constant of the solvent and hence the ionising power, as well as the ionic dissociation, rises upon solution of strong electrolytes (especially of binary salts of the alkali metals and the tetraethylammonium bases) in it; this rise increases proportionately to the increase of the salt concentration in very weak ionising media, while in good ionising media the presence of ions also produces a rise in the value of the dielectric constant.

As a result of these general conclusions the accelerating action of neutral salts on the saponification of esters and the catalytic action of acids on cane sugar inversion has been explained by Walden (Ibid). On this basis the deviation of strong electrolytes from Ostwald's Dilution Law has been satisfactorily explained and even the question why molecules dissociate into ions.

Only recently has the question of the effect of solute on the dielectric constant of the solvent been considered extensively. With the yet limited amount of data on the dielectric constant of solvents and solutions it is seen that this constant is of fundamental importance and promises to contribute materially to the explanation of the mechanism of ionic dissociation both of aqueous and of non-
aqueous solutions.

The present investigation consists of (1) a study of the different methods of preparing the halogen compounds of vanadium and (2) the measurement of the dielectric constant of the three compounds liquid at the ordinary temperatures, vanadium oxychlorid (\( \text{VOCI}_3 \)) vanadium oxybromid (\( \text{VOBr}_3 \)) vanadium tetrachloride (\( \text{VCl}_4 \)). Their solvent properties have received but limited study and it is proposed to extend these investigations to a study of the solvent properties of these liquid vanadium compounds and the electrical conductivity of the resulting solutions.

**Description of the Measuring Apparatus for Dielectric Constants**

For the measurement of the dielectric constants the Drude apparatus as modified by Schmidt was used. The newer form of Schmidt has the advantage over the older form of apparatus devised by Drude in that the capacity of the primary circuit may be changed at will and so is more convenient in measuring the constants of liquids that vary over a wide range. The different parts of the apparatus as set up for measurement are shown in plate (1) and diagrammatically in plate 2. The potentiometer circuit (a) is supplied by a 110 volt D.C. generator. By a trial the point(b) was found on the potentiometer so that 20 to 25 volts were supplied to the large induction coil C.
Plate 1.
Diagram of Cells

Diagram of Connections

Plate 2.

Plate 4.
The current from the secondary of the induction coil is led through the primary(e) of the Tesla transformer, which induces a powerful spark in the secondary w. The primary circuit includes a condenser f (a small Leyden jar) and the spark gap (d) between two rods of zinc. The current from the secondary w of the Tesla coil is led to the primary oscillator in which the standing electrical waves result as the spark passes between the proper terminals g immersed in kerosene. (Plate 3.)

The primary circuit consists of two copper wires (ll) held in place by the vulcanite clamps (ss) and by four wooden columns. On one end of the wires are the two copper knobs (g). On the other end fits the copper condenser plates (j), held in place by the wires (t) and the vulcanite rod (h). The rod (h) is provided with small metallic cylinders that fit snugly on to the ends of the wires (ll) and held fast by the small clamping screws (rt). The copper points (g) and the condenser plates (j) are immersed in a bath of kerosene contained in the vessels (nn) which may be adjusted to proper height by the screw (c). From the copper points (g) two copper wires (zz) extend vertically upward supported by the vulcanite frame (b) and ending in two small wire hooks ('h'). The current from the Tesla coil secondary is led through (zz). The distance (from one to one-half millimeters) between the points (g) may be adjusted.
by the screw (q). The width of the spark gap controls the intensity of the electric waves. By varying the capacity of the condenser (j) the capacity of the primary circuit can be varied over wide ranges.

The secondary or resonance circuit entirely separate from the primary circuit is supported by the rod (e) about twenty centimeters above the primary circuit. This circuit consists of two stout copper wires about two centimeters apart and about one meter long, completely insulated from each other and held in place by the clamps (m). A meter stick is placed under the wires as a scale. (L) is a bridge wire which is moved along the wires to bring them in resonance with the primary. The cell containing the liquid which is to be measured is placed at (h) where the electrode wires of the cell fit into two small mercury cups making contact with the wires (l'). A form of Geissler tube devised by Zehnder is placed just above and across the wires (l') which attains a maximum glow when the secondary is in resonance. In other words, the Zehnder vacuum tube serves as an indicator when resonance is established. The liquid to be measured is confined in cells of the form shown in plate (4). The volumes of the bulbs are from one cubic centimeter to two cubic centimeters and electrodes are about one millimeter apart.

Method of Operating the Drude-Schmidt Measuring Apparatus
When a measurement is to be made the cell with contained liquid is placed at (h) plate (3). The induction coil is then put in operation and the intensified spark from the secondary of the Tesla transformer causes sparking between the knobs (g) of the oscillator. This induces electrical waves in the primary resonance circuit. These waves move out into space and may be brought to resonance with the secondary circuit by moving the slide (l) along the wires. This point is carefully located as indicated by the maximum discharge in the Zehnder tube. At least ten settings were made in this way for each liquid measured and the average taken. These settings should be taken in a darkened room in order that the vacuum tube discharge will show plainly.

In order to find the values of the dielectric constant represented by the readings obtained the cells have to be calibrated with liquids of known dielectric constants. This operation is described under the next heading.

**Standardization of Measuring Cells**

The standard solutions were made by mixing acetone and benzene in the ratios as given by Drude. These ratios are tabulated in the following table.
<table>
<thead>
<tr>
<th>Percent of Acetone</th>
<th>D.C. at 19 degrees</th>
<th>c.c. of acetone</th>
<th>c.c. of benzene</th>
<th>D.C. per degree rise</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>2.26</td>
<td>0.000</td>
<td>10.0000</td>
<td>-0.1%</td>
</tr>
<tr>
<td>5.3</td>
<td>2.96</td>
<td>0.587</td>
<td>9.413</td>
<td>-0.2&quot;</td>
</tr>
<tr>
<td>9.8</td>
<td>3.56</td>
<td>1.079</td>
<td>8.921</td>
<td>-0.3&quot;</td>
</tr>
<tr>
<td>20.0</td>
<td>5.09</td>
<td>2.177</td>
<td>7.823</td>
<td>-0.3&quot;</td>
</tr>
<tr>
<td>31.0</td>
<td>6.90</td>
<td>3.334</td>
<td>6.666</td>
<td>-0.4&quot;</td>
</tr>
<tr>
<td>40.0</td>
<td>8.43</td>
<td>4.260</td>
<td>5.740</td>
<td>-0.4&quot;</td>
</tr>
<tr>
<td>49.5</td>
<td>10.20</td>
<td>5.219</td>
<td>4.781</td>
<td>-0.5&quot;</td>
</tr>
<tr>
<td>69.4</td>
<td>14.30</td>
<td>7.163</td>
<td>2.837</td>
<td>-0.5&quot;</td>
</tr>
<tr>
<td>84.7</td>
<td>17.30</td>
<td>8.608</td>
<td>1.392</td>
<td>-0.5&quot;</td>
</tr>
<tr>
<td>100.0</td>
<td>20.50</td>
<td>10.000</td>
<td>0.000</td>
<td>-0.6&quot;</td>
</tr>
</tbody>
</table>
Solutions of varying percentages of acetone as given in the table are used so that readings on the scale are obtained both above and below the reading obtained with the liquid whose dielectric constant is to be measured in the cell. Then a curve is obtained for each particular cell by plotting the mean of ten settings on the scale as ordinate and the corresponding dielectric constant at that temperature as abscissa. Then the point on the curve corresponding to the liquid under measurement gives the dielectric constant at that temperature.

The benzene used was the purest crystalline product which was dried over sodium and re-distilled. The acetone was dried with fused calcium chloride and re-distilled. The percentages were calculated and weighings made to the nearest milligram. These standard solutions have to be renewed after standing for some time due to the unequal rates of evaporation of the acetone and the benzene when samples are removed for calibration of the cells.

Preparation of Vanadium Oxychloride (\(\text{VOCl}_3\)).

For the first experiments on the preparation of vanadium oxychloride the vanadic acid required was obtained directly from carnotite ore. After the insoluble matter had been removed, the solution of vanadium, uranium and iron sulphates was evaporated to
dryness to remove excess sulphuric acid. Some aluminum and calcium were also present. This residue was taken into solution with water and boiled with excess sodium carbonate to precipitate the iron and aluminum as hydroxides the uranium and vanadium compounds remaining in solution in excess of this reagent. The filtrate was acidified with sulphuric acid and boiled thoroughly to expel carbon dioxide. Then it was made slightly alkaline with sodium hydroxide which precipitated the sodium uranate, the sodium vanadate remaining in solution. The filtrate was then made slightly acid with acetic acid and a solution of copper sulphate added to precipitate out the copper vanadate. The thoroughly washed precipitate was decomposed with hydrochloric acid and hydrogen sulphide passed in for an hour to precipitate out the copper as sulphide. Vanadic acid is not precipitated by hydrogen sulphide but is reduced to the vanadium trioxid condition, with liberation of free sulphur. The filtrate was evaporated to dryness. Vanadic acid obtained in this manner was rather impure since calcium is carried along through the process in quite appreciable quantity. This sample of vanadic acid was, however, used for the first experiments in preparation of vanadium oxychlorid. To obtain practically pure vanadic acid this sample should have been taken into solution with excess sodium carbonate and the vanadium precipitated out by adding ammonium chlorid to the solution. The ammonium
vanadate thus obtained on ignition at low red heat gives practically pure vanadic acid.

After this preliminary experiment our vanadic acid was obtained wholly from iron vanadate containing about thirty percent vanadic acid kindly furnished by the National Radium Institute through the courtesy of Mr. R. B. Moore in charge of the radium investigations, Bureau of Mines, Denver, Colorado. The vanadium oxid was extracted from this material in the following manner: The powdered iron vanadate was decomposed by hydrochloric acid and nitric acid. The nitric acid was added in order to oxidise the iron to the ferric condition and also vanadium trioxid to vanadium pentoxid. The excess acid was evaporated off, the residue taken into solution with water and boiled for 15 to 30 minutes with excess sodium carbonate. The iron calcium and traces of aluminum were thus precipitated as hydroxides and the sodium vanadate remained in solution. The filtrate was made slightly acid with acetic acid and then ammonia added until just neutral. Practically all the vanadic acid was precipitated out since the solubility of vanadic acid in water is one part per thousand of water (Comey). 7

The vanadic acid obtained in this manner is practically pure since most impurities remain in solution in the rather large volume of water employed. It is necessary to make the solution exactly neutral since
ammonium vanadate is very soluble and since vanadic acid is somewhat soluble in acetic acid. The iron hydroxide is rather bulky and hard to filter. Large jars were used as precipitating tanks and the supernatant solution of sodium vanadate was siphoned off and then filtered through a Buchner funnel. Vanadic acid obtained in this manner consists of both the yellow and red modifications.

Methods for the Preparation of Vanadium Oxychloride.

1. A stream of dry chlorine is passed over a heated mixture of vanadium trioxide and sugar charcoal. The distillate is colored red due to the formation of some vanadium tetrachloride. It is purified by fractional distillation over sodium in a carbon dioxide atmosphere (Berzelius and Roscoe)².

2. Chlorine gas is passed over vanadium trioxide heated in a reaction tube. The distillate is caught in a carbon dioxide atmosphere. It is rectified once over sodium (Roscoe)⁹.

\[ 3 V_2 O_3 + 6 Cl_2 = 4 VO Cl_3 + V_2 O_5 \]

3. A mixture of finely powdered vanadic acid and one part of charcoal is heated while dry hydrogen is passed over it, the hydrogen is displaced with carbon dioxide, then at red heat a dry current of chlorine is passed over it. The blood red distillate is purified by fractional distillation (Safarik)¹⁰, or better, the heated
mixture after the passing over of hydrogen is allowed to cool and then transferred to a retort, when chlorine is passed over at red heat. The distillate is purified in carbon dioxide and over sodium (Roscoe).

4. By passing the vapors of sulphur monochlorid over heated vanadic acid a mixture of sulphur monochlorid and vanadium oxochlorid is obtained in the receiver. The reaction begins at a low temperature and is ended by heating to redness. (Bourion).

5. By the action of dry hydrochloric acid on vanadium pentoxid between $60^\circ$ and $80^\circ$.

$$V_2O_5 + 6 HCl \rightleftharpoons 2 VOCl_3 + 3 H_2O.$$  
The water liberated in the reaction would immediately decompose the vanadium oxychlorid into vanadium oxydichlorid and chlorine.

$$2 VOCl_3 + 3 H_2O \rightleftharpoons V_2O_5 + 6 HCl$$

$$V_2O_5 + 6 HCl = 2 VOCl_2 + 3 H_2O + Cl_2$$

And to prevent this phosphorus pentoxid is mixed with the vanadium pentoxid. Pure vanadium oxychlorid distills over. (Ephraim)

6. A solution of vanadium oxychlorid is obtained by the action of concentrated hydrochloric acid on vanadium pentoxid (Ephraim). Also by the action of a solution of hydrochloric acid in acetic acid, ether or alcohol on vanadium pentoxid or ammonium vanadate (Koppel and Kaufmann).
7. Vanadium oxychlorid may be prepared from vanadium pentoxid, sulphur and chlorine. A mixture of 12 grams of vanadium pentoxid, 6 grams pure sulphur is acted upon by a stream of dry chlorine. The reaction begins at a low temperature and is completed by heating to about 600°. In the condenser is a mixture of vanadium oxychlorid, vanadium tetrachlorid, sulphur monochlorid, and sulphur dichlorid. The theory of the reaction is shown by the following equations.

\[
\begin{align*}
S_2 + Cl_2 &= S_2 Cl_2 \\
2V_2 O_5 + S &= 2V_2 O_4 + SO_2 \\
V_2 O_4 + Cl_2 &= 2VO Cl \\
2VO Cl + SCl_2 + Cl_2 &= 2VOCl_3 + SO_2 \\
2VOCl_3 + SCl_2 &= 2VCl_4 + SO_2
\end{align*}
\]

Pure vanadium oxychlorid may also be prepared from vanadium trichlorid and oxygen. The oxygen is passed over the vanadium trichlorid heated gently. Pure vanadium oxychlorid distills over boiling at 127° at 760 mm. pressure. (Ruff and Lickfett)\(^4\)

Preparation of Vanadium Oxychlorid by the Method of Ephraim

Ephraim's method of preparing vanadium oxychlorid (No. 5) was chosen. This method seemed to have the following advantages over the other methods: (1) phosphorus pentoxid mixed with the vanadium pentoxid takes
up all moisture which is a great advantage since vanadium oxychlorid is readily decomposed even by moist air, (2) the temperature required is only $60^\circ$ to $80^\circ$, which requires only gentle heating of the reaction tube with the Bunsen burner and dispenses with the furnace, (3) most important of all the product is pure vanadium oxychlorid unmixed with vanadium tetrachlorid.

The hydrogen chlorid gas was generated from concentrated hydrochloric acid by allowing concentrated sulphuric acid to mix with it from a drop funnel. The generated hydrochloric acid gas was dried with concentrated sulphuric acid, fused calcium chlorid, and phosphorus pentoxid before it was allowed to enter the reaction tube. For the tube a large adaptor was used in which was placed an intimate mixture of previously dried vanadium pentoxid and phosphorus pentoxid equal parts. A small flask sealed to the end of the adaptor served for a condensor. It was protected from outside moisture by two calcium chloride tubes.

This method was given numerous trials. It was found that practically pure vanadium oxychlorid was obtained but the yield was exceedingly small, due to the fact that the reaction mixture caked up badly on account of the absorption of moisture given off in the reaction and only a surface reaction resulted.
The cake became so hard that it was impossible to break it up properly without introducing moist air which is highly objectionable.

Ephraim’s method was finally abandoned and Roscoe’s method was given a trial. The same apparatus as described above was used. A mixture of equal parts of vanadium pentoxid and sugar charcoal was placed in the tube. A dry stream of hydrogen was passed over this mixture heated to redness and continued until no more moisture was given off. Then a dry current of carbon dioxid was substituted for the hydrogen and the tube and contents dried thoroughly by heating to redness for one hour. The condensor flask was then sealed on and a stream of dry chlorine was passed over the dry mixture of vanadium trioxid and charcoal. The chlorine was generated from hydrochloric acid and potassium permanganate and dried in the same manner as was the hydrogen. The reaction took place very readily and a practically quantitative yield was obtained. The condensed product was wine colored due to the presence of some vanadium tetrachlorid formed at the same time as the vanadium oxychlorid.

The distilate was transferred to flask (4) in which were placed several pieces of clean sodium, and fractionated by means of the three way cocks. The whole apparatus was filled with carbon dioxid before commencing the distilation. The boiling point of vanadium oxychlorid was found to be 124° to 125° at 740 mm. pressure.
As each cell was filled it was sealed off. The one way cock was closed while another cell was sealed on. The moisture due to the flame was driven out by heating. By means of a second three way cock only the middle portions were collected in the cells. Four cells were filled in this way. Two of the samples of vanadium oxychloride thus obtained were slightly colored red due to a trace of vanadium tetrachlorid, while two were colored citron yellow with no vanadium tetrachlorid present. All of the samples were perfectly transparent.

The method outlined above is the same method as was used by Prandtl and Bleyer for the preparation of pure vanadium oxychlorid from which the atomic weight of vanadium was determined.

The reaction takes place in two steps as indicated by the equations:

(1) \[ 3 \text{V}_2\text{O}_5 + 6 \text{Cl}_2 = \text{V}_2\text{O}_3 + 4 \text{VOCl}_3 \]
(2) \[ \text{V}_2\text{O}_3 + 3 \text{C} + 3 \text{Cl}_2 = 2 \text{VOCl}_3 + \text{CO} \]

Preparation of vanadium Oxybromid (VOBr₃).

There is only one recorded method for the preparation of vanadium oxybromid (Roscoe). This method is the same as our method chosen for the preparation of vanadium oxychlorid (See above). A mixture of vanadium pentoxide and sugar charcoal is reduced with dry hydrogen and them bromine vapor passed over the mixture heated to redness. The apparatus used in the first trial was the same as for the preparation of vanadium oxychlorid. It was found that
the rubber stoppers and joints were attacked so much by bromine and vanadium oxybromid that this apparatus was impracticable. The vanadium oxybromid was decomposed as quickly as it was formed, probably due to moisture from the decomposed rubber.

Next an apparatus was constructed in which there were no rubber joints, all glass joints being sealed together. We attempted to use a hard glass reaction tube but we were not able to join this to the remainder of the apparatus by glass seals due to the different coefficients of expansion of the hard and soft glass, which always caused the joints to crack. An attempt was made to make the joints by means of a collar of cobalt lead glass, but this was unsuccessful.

Finally a soft glass tube was used for the reaction tube. This was readily sealed to the remainder of the apparatus. A sheet of asbestos paper was wrapped around the two, then one layer of ni-chrome resistance wire. By means of a transformer the 110 volt D. C. lighting circuit was used to heat the tube. A current of bromine was procured by distilling bromine over from a flask. A drop funnel was sealed into the neck of the flask so that the supply of bromine could be regulated. It was found that a slight vacuum had to be applied in order to make the vanadium oxybromid collect into the distilling flask out of the reaction tube. This amount of suction, however, was always enough to cause the red hot reaction tube to collapse and so stop the progress.
of the reaction. It was also found that the heating could
be more advantageously controlled by means of a combustion
furnace and the electrical method of heating was abandoned.

Next a porcelain tube was procured and used instead
of the soft glass reaction tube. Joints were made of finely
cut asbestos as shown in figure (6). The bromine vapor was
generated as above. It was found after three attempts that
now the tube stopped up after the reaction had taken place
for a short time, and no more bromine could be passed through
the tube. On examination it was found that some vanadium oxy-
bromid had been formed which immediately decomposed into
solid vanadium oxydibromide and free bromine, probably as a
result of traces of moisture remaining in the tube. It was
recognized that a method had to be devised to get the vanadium
oxybromid out of the tube as soon as it was formed and it was
seen that the reaction should be carried out at considerably
below red heat, at least for as long a reaction tube as we
used. Hoscoe states that at 180° vanadium oxybromid suddenly
decomposes into solid vanadium oxydibromide and free bromine
and also decomposes gradually at ordinary temperatures.

The different parts of the apparatus are shown in
the figure and need no further description. The bromine
vapor was generated from liquid bromine contained in a
Dreschel bottle by passing carefully dried carbon dioxide
rapidly through it from a Kipp generator, which gave a
steady and sufficiently great supply of bromine. The carbon
dioxid, moreover, swept the vanadium oxybromid out of the tube as fast as it was formed, thus preventing decomposi-
tion taking place due to too long and intense heating. The reaction, moreover, was carried out at considerably below red heat, contrary to Hoscoe's statement that the reaction mixture should be maintained at red heat. Two samples of about fifteen or twenty cubic cc. were obtained in this way; it was found to be impossible to fractionate these samples, however. By means of a water aspirator a partial vacuum of 100 mm. to 25 mm. was supplied when the vanadium oxy-
bromid should have distilled over at 130° to 136°. However, on heating the samples obtained in an oil bath to 150° no liquid distilled over, only a solid cake of vanadium oxydi-
bromid remained in the flask. These unsuccessful attempts at the preparation of vanadium oxybromid greatly retarded the progress of the investigation.

At this point it was discovered that the presence of moisture in the reaction tube was responsible for the failures of previous experiments. This disturbing factor was remedied by heating the reaction tube to redness for 6 hours in a current of dry hydrogen and then dry carbon dioxid. After the tube had cooled somewhat a steady stream of carbon dioxid laden with bromine was passed over the mixture in the reaction tube as before, and it was now found that vanadium oxybromid could be obtained in quantity. The first samples
whose dielectric constant were determined were distilled
directly into the cells, and consequently may have contained
some impurities. Subsequently fresh samples were prepared
which were duly purified by distillation under diminished
pressure in a special form of apparatus shown in accompanying
figure (7). These were the samples used for the final measure-
ment of the dielectric constants. The boiling point at 90 mm.
pressure was 130° and at 78 mm. 118°. Roscoe gives 130° to
136° at 100 mm. pressure. This constant and the specific
gravity are the only physical constants of this compound re-
corded in the literature. The distillate was a beautiful
ruby red, mobile, transparent liquid of very much the ap-
pearance of bromine with the exception of its transparency.
The freezing point is -58° to -60° which was determined by
noting the temperature at which the compound previously sol-
idified in liquid air melted, when the temperature gradually
rose in alcohol in a Dewar tube previously cooled with liquid
air. The temperature readings were made with a standardized
Pentane thermometer. An attempt to solidify the liquid en-
closed in a sealed tube by immersing it in a mixture of
carbon dioxid snow and ether for fully 5 minutes failed to
solidify it. As the temperature of the Thilorier mixture
is -79° it seems that the liquid can be greatly super-cooled.

Methods for the Preparation of Vanadium Tetrachlorid (VCl₄)

1. Vanadium nitride is heated to redness in a cur-
rent of dry, air free chlorine, when a product of vanadium
tetrachlorid mixed with vanadium oxychlorid distills over.
The product is heated to boiling in a current of carbon dioxid
for some hours when the distillate remains pure in the flask.
(Gmelin-Kraut) 16

2. The vapors of vanadium oxychlorid mixed with
chlorine are led slowly over a long tube of sugar charcoal
heated red. The product is impure. Add one percent oxygen
and proceed through the same operation three or four times when vanadium
trichlorid remains in the retort which is slowly changed
to vanadium tetrachlorid by the action of chlorine (Roscoe).

3. By heating vanadium silicide \( VSi_2 \) or \( V_2Si \)
in a stream of chlorine.

\[
V_2Si + 2Cl_2 = 2VCl_4 + SiCl_4
\]

Six hundred amperes and 50 volts were used for four or five
minutes. The preparation of the silicide richest in vanadium
is indicated by the following equations:

\[
2V_2O_3 + 5Si = 2V_2Si + 3SiO_2
\]

\[
2V_2O_5 + 7Si = 2V_2Si + 5SiO_2
\]

Carbon was also used in the mixture but this formed some vanadium
carbide.

\[
2V_2O_3 + 2Si + 3C = 2V_2Si + 3CO_2
\]

(Moissan) (Holt) 17

4. Finely pulverized "Rohvanadis", a mixture of metallic
vanadium and vanadium monoxid obtained by the interaction of
aluminium with
vanadium pentoxid at high temperature is heated
in a porcelain dish in a combustion tube while dry chlorine is passed over it. The reaction begins at a low temperature and is completed by its own heat of reaction if this is utilized. Finally, the reaction ends at a moderate temperature. During the operation a thick, dark brown liquid distills which is caught in an ice-cooled receiver. If it is too freely or intensively heated violet vanadium trichloride crystals remain in the tube which do not again react with chlorine. The distillate consists of a mixture of vanadium tetrachloride and vanadium oxychloride which can be separated by fractional distillation. Vanadium tetrachloride boils at 154° with partial decomposition (Koppel, Goldmann, and Kaufmann).  

5. Action of chlorine and sulphur monochloride on vanadium pentoxide in a combustion tube at high temperature. Vanadium oxychloride is formed first, the vapor of which with excess sulphur monochloride is conducted through a tube 70 cm. long heated dark red. The condensed product is a mixture of vanadium tetrachloride and sulphur monochloride, which is easily purified by fractional distillation in a stream of chlorine vapor. (Matignon and Bourion).  

6. Vanadium carbide produced by fusing vanadium trioxide and carbon in the electric furnace and chlorine passed over when a mixture of vanadium tetrachloride and vanadium oxychloride is obtained. (Moissan).  

7. When chlorine is passed over vanadium trichloride heated to 600° it is converted quantitatively into pure vanadium
24.

tetrachlorid.  
\[ 2 \text{VCl}_3 + \text{Cl}_2 \rightarrow 2 \text{VCl}_4 \]

The vanadium trichlorid required may be prepared from vanadium oxychlorid by interaction with sulphur. The reaction is represented in the following equation:

\[ 2 \text{VOCl}_3 + S \rightarrow 2 \text{VCl}_3 + S\text{O}_2 \]

(Ruff and Lickfett).

8. Chlorine gas is passed over ferro-vanadium heated in a long reaction tube. Vanadium tetrachlorid distills over and is freed from any ferric chlorid carried over by fractionation or by dissolving the vanadium tetrachlorid in perfectly dry carbon tetrachlorid in which ferric chlorid is insoluble (Mertes).  

\[ \text{FeV} + 7 \text{Cl} \rightarrow \text{FeCl}_3 + \text{VCl}_4 \]

The method of Koppel, Goldmann, and Kaufmann (No. 4) appeared to be the most suitable for the preparation of vanadium tetrachlorid. The only difficulty with this method is to obtain the metal. As found by the authors of the above mentioned paper the reaction of chlorine on vanadium metal proceeds very easily and at a moderate temperature, thus obtained vanadium tetrachlorid with a minimum of decomposition due to two intense heating. Vanadium tetrachlorid boils at 154° with partial decomposition. This method then resolves itself into the problem of obtaining vanadium metal. The purer the metal the purer will be the vanadium tetrachlorid formed. Koppel, Goldmann, and Kaufmann prepared the metal by means of the Gallschmidt thermite process. However, this method gives only
80% vanadium metal while a large amount of vanadium monoxid is present. According to Hittorf's analysis the regulus obtained by the Goldschmidt method consists of entirely di-vanadium oxid (V₂O), and no vanadium metal is present. Other attempts were made to obtain metallic vanadium by reduction with aluminum (Moissan, Hélouët, Koppel, and Kaufmann). The percentage of vanadium obtained in each case was rather low, however. Vogel and Tammann obtained a fairly high grade product in the alumino-thermit way. Moissan prepared metallic vanadium by reduction of vanadium pentoxid by means of carbon in the electric furnace which was almost free from oxygen, but contained more or less vanadium carbide. Muthmann used as a reducing agent an alloy of cerium and ytttrium metal which gave pure vanadium metal. Weiss and Aichel claim that this method gives entirely pure vanadium metal but Wilhelm Prandtl found by his analysis of the sample furnished by Muthmann only 91% to 93% vanadium metal. Vanadium metal may be obtained electrolytically (Cowper-Coles) by the electrolysis of a sodium vanadate solution. The best results were obtained by using a current density of 18 to 20 amperes per square foot, E. M. F. 1.88 volts at terminals of cells. The temperature of the solution is kept at 180°F. If a cold solution or a higher or lower current density is used vanadium pentoxid is deposited at the same time as the metal. The anode was of carbon, the cathode of platinum. C. Setterberg
could not get vanadium metal by electrolysing a water solution. He used ammonium metavanadate and got vanadium pentoxid at the anode while ammonia was given off.

Vanadium metal may also be obtained by Roscoe's method of reduction of vanadium dichlorid with hydrogen, also by passing the electric current through thin rods of vanadium trioxid mixed with paraffin in a vacuum. (Werner v. Bolton), and by heating the trioxid and carbide in a zirconia crucible to 1950°C. (Ruff and Martin). These three last methods, however, give only small amounts of the metal, although very pure specimens.

The methods chosen were those of Vogel and Tammann and Frandtl and Bleyer. The method of Vogel and Tammann is said to give 99.07% vanadium metal. As described in their paper fire-clay crucibles were lined carefully with a paste of magnesia and water and then dried thoroughly by heating in an oven for several hours. Vanadium pentoxid and aluminum were mixed in the proportion as indicated by the equation:

$$3 V_2O_5 + 10 Al = 6 V + 5 Al_2O_3$$

This intimate mixture was packed tightly in the crucible and a thick asbestos sheet wired on the top of the crucible. A small hole was left in the sheet to allow any expanding gases to escape and through which a piece of magnesium ribbon was run in order to fire the mixture. A small amount of a mixture of aluminum, potassium perchlorate, and barium peroxid was placed
around the base of the ribbon. When this was fired a vigorous reaction took place. The regulus, however, contained only a small amount of metallic vanadium, just a few small grains. The experiment was repeated several times with the same negative result.

The method of Prandtl and Bleyer was next tried. The reducing agent used by this method is a mixture of metallic calcium and aluminum. The vanadium pentoxid was mixed with the calcium and aluminum in the following proportions as indicated by the following equations:

\[ 6 V_2O_5 + 15 Ca + 10 Al = 12 V + 5(Al_2O_3 \cdot 3 CaO) \]

100 grams \( V_2O_5 \), 55 grams \( Ca \), 24.7 grams \( Al \).

These proportions give 94.45% metallic vanadium in the regulus.

\[ V_2O_5 + 2 Ca + 2 Al = 2 V + Al_2O_3 \cdot 2 CaO \]

109.4 grams \( V_2O_5 \), 48.1 grams \( Ca \), 32.5 grams \( Al \).

These proportions give 93.25% metallic vanadium.

The proportions represented by the equations given above were used. It is necessary to add the proportionate part of aluminum to the calcium, although calcium alone used as in the Goldschmidt alumino-thermit process is a powerful reducing agent. The disadvantage that calcium oxid is formed which does not fuse at the temperature of the reaction and causes the formed vanadium metal to be finely divided in the regulus. Prandtl and Bleyer tried using calcium fluroid and cryolite but neither worked well. Goldschmidt mixed in some
aluminum and silicon so that calcium aluminate and calcium silicate would be formed which fuse at the temperature of the reaction. No silica can be present for it forms a compound with the produced vanadium metal. Prandtl and Bleyer found that by using three atoms of calcium + 2 atoms of aluminum (69+ 31 parts by weight) that a well melted mass was formed at about 1400° of the formula $3 \text{CaO} \cdot 2 \text{Al}_2\text{O}_3$ and $2 \text{CaO} \cdot \text{Al}_2\text{O}_3$.

According to the recommendation of Prandtl and Bleyer a crucible was made in the following manner. A tin can about 8.5 cm. in diameter and 23 cm. high was filled with fluorspar finely powdered. A section of a Volhard combustion tube was placed in the middle and a fluorspar packed tightly around this. A few cm. of fluorspar were also packed in the bottom of the glass tube. The thermit mixture was then introduced, packed tightly and the glass tube withdrawn slowly by rotating it. A piece of magnesium ribbon was then imbedded in the top of the mixture and a few cm. of a mixture of 10 parts aluminum, 40 parts barium peroxide, and 7 parts potassium perchlorate placed around its base. The regulus obtained from firing this mixture contains a lump of vanadium metal silver-white and crystalline. The metal may be exposed to the air indefinitely without change in appearance of any kind. The metal may be freed of any attached melt by boiling with hydrochloric acid since neither hot nor cold hydrochloric acid attacks the vanadium metal. No fluorspar enters the regulus. Ac-
According to Prandtl and Bleyer this metal is 91% to 94% pure, some carbon, silicon, aluminum, iron, being present from the calcium and aluminum, only a small percentage of vanadium monoxid present. Several samples of silver-white metal were obtained in this manner. However, the yield was extremely small, from 35 to 40 grams vanadium pentoxide only one to 2 grams of metal were obtained. Moreover, a good sample was obtained only in about half of the trials. The attempt to obtain sufficient metal for the preparation of vanadium tetrachlorid by this method was finally abandoned as our supply of vanadium pentoxid was rather limited.

In the meantime, a more promising method for the preparation of vanadium tetrachlorid was found. (Mertes). According to this method dry chlorine is passed over ferro-vanadium heated in a combustion tube in a furnace. The vanadium tetrachlorid obtained is separated from any ferric chlorid passing over by fractional distillation.

\[ \text{FeV} + 7 \text{Cl} = \text{FeCl}_3 + \text{VCl}_4 \]

Mertes separated the two products by dissolving the vanadium tetrachlorid in perfectly dried carbon tetrachlorid in which ferric chlorid is insoluble.

We had no supply of ferro-vanadium but attempted to make it from iron vanadate. According to Bleecker ferro-vanadium may be obtained from iron vanadate by reducing it with carbon in an electric furnace at 1500°. This method was tried in an arc furnace. From 5 to 35 amperes were used. Both
lamp black and graphite were used for the reduction. Only a small amount of ferro-vanadium could be formed, however, due probably to the fact that the furnace was too freely open to outside air which did not permit of a proper reducing atmosphere being obtained.

A supply of ferro-vanadium was obtained from the Primos Chemical Co. This alloy contained 56.6 percent metallic vanadium. The material was crushed and about 75 grams placed in the porcelain combustion tube with asbestos glass joints as described in connection with the preparation of vanadium oxybromid. A current of chlorine dried with calcium chlorid, sulphiric acid and phosphorous pentoxid was then passed through the tube which was heated just below redness in a combustion furnace. Vanadium tetrachlorid together with some ferric chlorid distilled over readily and constantly. About 25 to 30 cc. were obtained. This material was then fractionated using the apparatus shown in plate (5). Suction was applied in order that no decomposition should take place on boiling. The liquid was fractionated twice and then distilled into the cells as needed. Only the middle portions of constant boiling point were kept. The samples obtained were dark red, thickish, and opaque. The boiling point was found to be 150° to 153°.

The measurements were not made until 24 hours after the preparation of the liquid, when slight decomposition had
Data Obtained in Measurement of Dielectric Constants

Since the compounds here studied gradually decompose even in sealed vessels the measurements were made soon after their preparation. At least three specimens of each compound were measured in cells of different electric capacity and measurements were made on each sample at two or three temperatures. In this way data were obtained for the calculation of the temperature coefficient. In the case of vanadium tetrachlorid measurements were made at only one temperature. Temperatures lower than \(-50^\circ\) were obtained by a mixture of solid carbon dioxid and ether contained in a Dewar tube. For each measurement ten settings of the bridge wire were made, 5 by Dr. Schlundt and 5 by myself. The average of the ten settings was then taken and this point located on the calibration curve for the particular cell used. The value of the abscissa then represents the value of the dielectric constant of the specimen.

The two sets of readings given herewith are regarded as representative of numerous other series. Altogether for the calibrations and measurement of the dielectric constants of the vanadium compounds about 18 sets of 10 each were made in connection with the measurements of vanadium oxychlorid, 20 for vanadium oxybromid and 10 for vanadium tetrachlorid.
Table No. 2.

Readings Obtained with Liquid Vanadium Oxychlorid in the Cells
Temperature equals 21.0°

<table>
<thead>
<tr>
<th>No. of Settings</th>
<th>Scale Reading</th>
<th>Aver. Scale Reading</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cell Number I</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>48.5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>48.6</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>48.7</td>
<td>Loomis</td>
</tr>
<tr>
<td>4</td>
<td>48.3</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>48.7</td>
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<tr>
<td>6</td>
<td>48.0</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>48.4</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>48.2</td>
<td>Dr. Schlundt</td>
</tr>
<tr>
<td>9</td>
<td>48.3</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>48.5</td>
<td>48.42</td>
</tr>
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Readings Obtained with Liquid Vanadium Oxybromid in the Cells
Temperature equals 27.0°

Cell Number 2

<table>
<thead>
<tr>
<th>No. of Settings</th>
<th>Scale Reading</th>
<th>Average Scale Reading</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>46.5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>45.9</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>46.4</td>
<td>Dr. Schlundt</td>
</tr>
<tr>
<td>4</td>
<td>46.0</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>46.5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>45.8</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>46.2</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>46.3</td>
<td>Loomis</td>
</tr>
<tr>
<td>9</td>
<td>46.4</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>46.2</td>
<td>46.22</td>
</tr>
</tbody>
</table>
CELL NO. 1

Vanadium Oxychlorid

Curves & Dielectric Values.
CELL No. 2

Vanadium Oxichlorid

CURVES & DIELECTRIC VALUES.
CELL NO. 1.

Vanadium Oxybromid (V0Br₃).

Curves & Dielectric Values.
CELL NO. 3.
Vanadium Oxybromide (VOBr₃)
CURVES & DIELECTRIC VALUES.

Dielectric Constants.
CELL NO. 4.
Vanadium Oxybromid (VBr₆)
CURVES & DIELECTRIC VALUES.
CELL NO. 1.

Vanadium Tetrachloride (VCl$_4$)

CURVES & DIELECTRIC VALUES

Dielectric Constants
CELL NO. 3
Vanadium Tetrachlorid (VCl₄)
CURVES & DIELECTRIC VALUES

Dielectric Constants
CELL NO. 4.

Vanadium Tetrachloride (VCl₄)

CURVES & DIELECTRIC VALUES
### Table No. 3

**Vanadium Oxychlorid**

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>21.0°</td>
<td>Slight trace of Vanadium tetrachlorid present</td>
<td>3.47</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>22.0°</td>
<td>Pure</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-70.0° Pure</td>
<td>3.32</td>
<td>-.08 %</td>
</tr>
<tr>
<td>3</td>
<td>21.0°</td>
<td>Pure</td>
<td>3.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-70.0° Pure</td>
<td>3.32</td>
<td>-.01 %</td>
</tr>
<tr>
<td>4</td>
<td>21.0°</td>
<td>Purest</td>
<td>3.44</td>
<td></td>
</tr>
</tbody>
</table>

**Vanadium Oxybromid**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1'</td>
<td>20.0°</td>
<td>Freshly Re-distilled</td>
<td>3.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-70.0°</td>
<td>4.38</td>
<td>-.2 %</td>
</tr>
<tr>
<td>2</td>
<td>27.0°</td>
<td>Impure</td>
<td>3.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-2.0°</td>
<td>3.66</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27.0°</td>
<td>Measured 24 hrs. after preparation</td>
<td>4.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27.0°</td>
<td>hrs. after preparation</td>
<td>4.43</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>27.0°</td>
<td>4.00</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>32.8°</td>
<td>Freshly Redist.</td>
<td>3.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-2.0°</td>
<td>3.93</td>
<td>-.3 %</td>
</tr>
<tr>
<td>4</td>
<td>28.7°</td>
<td>&quot; &quot; &quot;</td>
<td>3.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27.0°</td>
<td>24 hrs. after Prep.</td>
<td>3.82</td>
<td>-.11 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-3.0°</td>
<td>3.95</td>
<td></td>
</tr>
</tbody>
</table>
No special difficulties were experienced in making settings, the maximum illumination was sharply defined for each sample measured. These solvents have a very high electrical resistance; their natural conductivity is of the same order of magnitude as chloroform and benzene. The calibration curves for the different cells are represented on separate sheets and points determined for each substance measured in the particular cell is represented by the particular symbol $(\circ)$ on the curve. All the values obtained are summarized in tables one for each substance.

In calibrating the cells the temperature varied from time to time. In plotting the curves the calibration data were always corrected by use of the temperature coefficients given in table 1. The temperature coefficients given in the last column of the tables represents the percentage change in dielectric constant per degree referred to the value at room temperature.

Summary
Summary and Discussion of Results

Values for the dielectric constants obtained are summarized in the following table:

Table Number 4

<table>
<thead>
<tr>
<th>Substance</th>
<th>Dielectric Const.</th>
<th>Tempt.</th>
<th>Tempt. Coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium Oxychlorid</td>
<td>5.29</td>
<td>21.0°</td>
<td>-0.05%</td>
</tr>
<tr>
<td>Vanadium Oxybromide</td>
<td>3.46</td>
<td>27.0°</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.93</td>
<td>-2.0°</td>
<td>-0.25%</td>
</tr>
<tr>
<td></td>
<td>4.38</td>
<td>-70.0°</td>
<td></td>
</tr>
<tr>
<td>Vanadium Tetrachlorid</td>
<td>3.69</td>
<td>25.7°</td>
<td></td>
</tr>
</tbody>
</table>

In the samples of vanadium oxybromide that were not redistilled a somewhat higher value for the dielectric constant was obtained than from the freshly prepared samples. Hence the values for the crude samples were not included in obtaining the average value in the above table. The individual values obtained in different cells show somewhat wide variation, for example: vanadium oxychlorid cell number 2, D.C. = 3.07, cell number 4, D.C. = 3.44. These variations are, in part, due to inherent experimental errors. Some of the variations, however, are apparently greater than can be attributed to experimental errors. We are unable to assign any reason to differences greater than 5%. We are inclined to believe that the variations are, in part, due to slight decomposition of the substances during the course of the measurements after they had been sealed up in the cells. Since one
of the products of the decomposition for each liquid is a solid a slight amount of solid deposited on the electrode would materially increase the dielectric capacity of the cell. It should be stated, however, in this connection that no decomposition was observed in the case of vanadium oxychloride, at least during the progress of the measurements. However, we wish to point out that the values obtained by different observers for the same substances by the use of the same apparatus as used in these investigations sometimes differ fully as much as the individual values here obtained.

The dielectric constants of these substances are relatively low, and hence, according to the Nernst-Thomson rule the dissociating power of these liquids when used as solvents should be very small. The dielectric constant of benzene is 2.3 and that of ether 4.1. The electrolytic dissociation of benzene and ether is exceedingly low but perceptible conductivity indicates traces of dissociation. Experiments on the solvent and dissociating power of vanadium oxychloride, vanadium oxybromide and vanadium tetrachloride have not been made.

The temperature coefficient of vanadium oxychloride is very small, (~0.5 %), while that of vanadium oxybromide is ~0.25 %. The temperature coefficient of vanadium tetrachloride was not measured.

The results show an increase in the dielectric constant with an increase in the atomic weight of the halogen in the oxy-halogen compounds. This result is in accord with the observations in the case of the tri-halogen bodies of phosphorus, namely, phosphorus trichloride, phosphorus tribromide and phosphorus tri-iodide, (Landolt, Bornstein, Meyerhofer.).
The dielectric constant of Vanadium oxychlorid is much lower than the corresponding compound of phosphorus, phosphorus oxychloride. The dielectric constant of vanadium tetrachloride is of the same order of magnitude as the tetrachlorides of sulphur and tin. These values are given in the following table. The values of thionyl chloride and of sulphuryl chloride are included.

Table Number 5

<table>
<thead>
<tr>
<th>Substance</th>
<th>Dielectric Constant</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphuryl Chlorid</td>
<td>9.15</td>
<td>22°</td>
</tr>
<tr>
<td>Thionyl Chlorid</td>
<td>9.05</td>
<td>22°</td>
</tr>
<tr>
<td>Phosphorus Oxychlorid</td>
<td>15.9</td>
<td>22°</td>
</tr>
<tr>
<td>Sulphur Tetrachlorid</td>
<td>2.40</td>
<td>16°</td>
</tr>
<tr>
<td>Tin Tetrachlorid</td>
<td>3.2</td>
<td>22°</td>
</tr>
</tbody>
</table>

Acknowledgements

The iron vanadate used in these experiments was supplied by the National Radium Institute through the courtesy of Mr. R. B. Moore, Physical Chemist in charge of the rare metals investigation of the United States Bureau of Mines, Denver, Colorado.
The investigation was suggested by Dr. Schlundt and was conducted under his supervision. I wish to take this opportunity of expressing my thanks for his invaluable help in the laboratory.

Approved:
Herman Schlundt
May 36, 1985
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BOOKS MAY BE RECALLED BEFORE THEIR DUE DATES

Form 104