Studies of tungsten hexachloride

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STUDIES OF TUNGSTEN HEXACHLORIDE.

A dissertation presented to the faculty of Union College in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

by

Arthur A. Vernon
STUDIES OF TUNGSTEN HEXACHLORIDE

The purpose of this paper is to give a summary of the work done in studying the equilibrium conditions and rate of reaction of the compound tungsten hexachloride, together with some of its applications to the elimination of spots in coiled filaments. Tungsten hexachloride is a purple-colored crystalline compound formed by passing chlorine over red hot tungsten in a tube from which all the air has been washed. It is rather unstable at room temperature in the presence of moist air, forming an oxychloride of the formula WOCl₄ and then decomposing into tungsten oxide of the formula WO₂ and the vapor decomposes at still higher temperatures. It volatilizes appreciably at about 150°C in vacuum and at about 320°C in hydrogen.

PART I.

Equilibrium Constants.

The results on the equilibrium between the hexachloride vapor and chlorine may be expressed in the usual thermodynamic equation which can be derived briefly as follows from the equation for the change in free energy, namely:

$$\Delta F = RT \ln K$$
of WCl₆ was found. The values for three measurements are given in Table 2.

<table>
<thead>
<tr>
<th>α</th>
<th>Pressure-Air</th>
<th>Pressure WCl₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0660</td>
<td>5.3 μ</td>
<td>1.43 μ</td>
</tr>
<tr>
<td>.0772</td>
<td>6.4 μ</td>
<td>1.73 μ</td>
</tr>
<tr>
<td>.0888</td>
<td>7.9 μ</td>
<td>2.13 μ</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>1.76 μ</td>
</tr>
</tbody>
</table>

This value is at 25°C, and, considering the wide divergence in the method outlined in the beginning, which gave a pressure of about 3 μ, and the above method, the agreement is not so bad. This is particularly true in view of the fact that there were quite a few refinements on the first method which it was intended to make. One of the most important of these was a small furnace around the exhaust tube where it came out of the furnace. It is thought that, with some improvements on the first method, the agreement would have been even better. The value obtained by the fiber is accepted as the more reliable.

The experiments from which the equilibrium conditions were found were made as already described except that in this case frequent measurements of the damping coefficient of the fiber were made as well as of the resistance changes. Each test was continued until the values for those two quantities became constant.

At the lowest temperature, 1360°C, both methods agreed in giving the same chlorine pressure—a pressure which lay
where $K$ is the equilibrium constant and $\Delta F$ is the change in free energy on the useful work obtained. We also have the equation expressing the same thing in terms of the heat of reaction, namely:

$$\Delta F = \Delta H_0 - \Sigma \alpha T \ln T - \frac{\Sigma \beta}{2} T^2 - \frac{\Sigma \gamma}{6} T^3 + \Sigma \eta T$$

where $\Sigma \alpha$ and $\Sigma \beta$ and $\Sigma \gamma$ are sums of the respective terms in the specific heat equations of the substances into which the compound decomposes minus the respective terms of the specific heat equation of the compound decomposed. Equating these two we get the following:

$$\Delta H_0 - \Sigma \alpha T \ln T - \frac{\Sigma \beta}{2} T^2 - \frac{\Sigma \gamma}{6} T^3 + \Sigma \eta T + RT \ln K = 0$$

which expresses the relation between the equilibrium constant and the temperature when $\Delta H_0$ and the specific heat terms and the chemical constant are known.

In a preliminary attempt to find how the thermal decomposition of WCl$_3$ vapor could be expressed by means of a thermodynamic equation, some data were utilized from experiments which had, in fact, been made for another purpose, namely, to find to what extent two filaments of different diameters would approach each other in size when treated in WCl$_3$ vapor. In the
case of WCl₈, there is no record, it is true, of its specific heat nor of the heat of reaction. The experiments in question, however, can be used to yield equilibrium constants for three different temperatures. Using these and neglecting for the moment the $\Sigma \beta$ and $\Sigma \gamma$ terms, we have three simultaneous equations from which $\Delta H_0$, $\Sigma \alpha$, and $I$ can be found. With these values as first approximation, it should be easy to construct an equation involving the $\Sigma \beta$ and $\Sigma \gamma$ terms.

First, in order to calculate any equilibrium constant, we must know the vapor pressure of WCl₈ since our equilibrium constant will be

$$K = \frac{[P_{Cl_8}]}{P_{WCl_8}}^3$$

This was done by passing hydrogen at a known rate over WCl₈ in a tube which can be heated and held at constant temperature by an electric furnace. The outlet of this tube is connected to a coil immersed in liquid air. By weighing the coil before and after, the weight of WCl₈ carried over can be found, and together with the known volume of hydrogen which carried this WCl₈ over we can calculate the pressure of WCl₈ at the temperature of the furnace by finding the weight of WCl₈ per liter.
Apparatus For Determining The
Vapor Pressure Of \( \text{WC}_6 \)

*Electric Furnace*

*\( \text{H}_2 \)*

*\( \text{WC}_6 \)*

*Liquid Air*
of hydrogen. This weight, then, when under standard conditions gives the vapor pressure of the WCl₆ at that temperature. A diagram of the apparatus is shown in Figure 1. The curve of the vapor pressure against temperature, using values found in this manner is shown in Figure 2.

The experimental work referred to, from which equilibrium conditions could be calculated, was carried out by means of tungsten filaments mounted in glass bulbs which were evacuated and baked out and to which, after proper sintering of the filament, some WCl₆ powder was introduced. The filaments were then burned at different temperatures and the changes in resistance noted at frequent intervals. When the filaments are burned, the WCl₆ gas in contact with the filament decomposes and tungsten deposits on the filament, setting free chlorine gas. This will continue until a point of equilibrium is reached where chlorine combines with the tungsten as fast as the WCl₆ is decomposed and denoted by the attainment of a constant value of the resistance. Three different lamps were burned, starting at three different initial temperatures.

The next consideration is the fact that the temperature of equilibrium of the filament will be lower than the initial temperature due to the change in the
resistance of the filament and the cooling effect of
the gas liberated. This final temperature as given
in Table 1 can be found from curves which show the
variation with the temperature of the ratio of initial
and final temperature as cited by Forsythe and Worthing

We are now in a position to use our thermo-
dynamic equation if we know the equilibrium constants.
These can be calculated from the change of resistance
of the tungsten filament by finding the actual volume
increase and hence the amount of tungsten deposited.
Then, from this, the amount of chlorine equivalent to
it and its pressure can be found. Together with the
pressure of WCl₆ vapor we then have the data for cal-
culating the equilibrium constants.

As an example of the method of calculation,
the test at 1675⁰K can be cited. The filament had
an original diameter of 0.00382 cm and its resistance
at 25⁰C changed during treatment in WCl₆ from 9.36
ohms to a final constant value of 6.00 ohms. This
corresponds to the deposition on it of 0.000955 grams
of tungsten. The equivalent weight of chlorine is
0.001102 grams and in a bulb of 550 cc volume this
would have a pressure of 20⁰C of .431 mm.
The pressures of chlorine for all three cases were calculated in this way and are given in Table I, together with that of WCl₆, also at 20°C, as taken from the curve of Figure 1.

Table I.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>WCl₆</th>
<th>Cl₂</th>
<th>Kp</th>
</tr>
</thead>
<tbody>
<tr>
<td>1548°K</td>
<td>0.0000325</td>
<td>0.0001596</td>
<td>0.000001281</td>
</tr>
<tr>
<td>1678°K</td>
<td>0.0000325</td>
<td>0.001596</td>
<td>0.0000558</td>
</tr>
<tr>
<td>1730°K</td>
<td>0.0000325</td>
<td>0.000596</td>
<td>0.00000798</td>
</tr>
</tbody>
</table>

In this table $K_p = \left(\frac{P_{Cl}}{P_{WCl}}\right)^3$

If log $K_p$ is plotted against the reciprocal of the temperature a straight line should result. Accordingly, the values of log $K_p$ were plotted against and a curve drawn through an intermediate position laying emphasis on the determination at the lowest temperature as the most accurate. From this, three different values of $K_p$ could be found and these values give three separate equations and so three unknowns can be solved for. These are $\Delta H_0$, $\Sigma \alpha$, and $I$. These were solved as shown below.
\[ \Delta H_0 - \Sigma \alpha (1550) \ln 1550 + 1.98 \times 1550 \times 2.3 (-6.83) + I \times 1550 = 0 \]
\[ \Delta H_0 - \Sigma \alpha (1650) \ln 1650 + 1.98 \times 1650 \times 2.3 (-5.82) + I \times 1650 = 0 \]
\[ \Delta H_0 - \Sigma \alpha (1750) \ln 1750 + 1.98 \times 1750 \times 2.3 (-4.92) + I \times 1750 = 0 \]

\[ \begin{align*}
\Delta H_0 - 11380 \Sigma \alpha - 48200 + 1550 I &= 0 \quad \text{(0)} \\
\Delta H_0 - 12210 \Sigma \alpha - 43800 + 1650 I &= 0 \quad \text{(2)} \\
\Delta H_0 - 13080 \Sigma \alpha - 39200 + 1750 I &= 0 \quad \text{(3)}
\end{align*} \]

0 - 2: \[ 830 \Sigma \alpha - 4400 + 100 I = 0 \quad \text{(4)} \]
0 - 3: \[ 870 \Sigma \alpha - 4600 - 100 I = 0 \quad \text{(6)} \]
0 - 4: \[ 40 \Sigma \alpha = 200 = 0 \]

\[ \Sigma \alpha = 5 \]

From (4): \[ 5 \times 830 - 4400 - 100 I = 0 \]
\[ I = -2.5 \]

From (2): \[ \Delta H_0 = 65400 - 39200 - 4370 \]
\[ \Delta H_0 = 100,230 \]
Taking then the values as found, and assuming the value of \( \Sigma \beta \) to be .001, which seems to be about the average for substances of the type of WCl\(_6\), a thermodynamic equation can be constructed which will be as follows:

\[
\log_{10} K_p = \frac{\Delta H}{4.571T} + \Sigma \ln 1.75 \log T + \Sigma \ln C
\]

where \( \Sigma \ln \) is the change in the number of gaseous molecules formed upon decomposition and \( C \) is Nernst's conventional chemical constant. A review of values of \( C \) for most substances seems to show that for such a substance as WCl\(_6\), it would be about 3.1. The equation then is as follows, using the values of \( K_p \) and \( T \) at 1550\(^\circ\)K

\[
-6.83 = -\frac{\Delta H}{4.571 \times 1550} + 2 \times 1.75 \log 1550 + 2 \times 3.1
\]

whence \( \Delta H = 171,230 \) cal.

It will be well now to tie in the results of these two equations as near as possible. In the first place, \( \Delta H_0 \) in the rigid thermodynamic equation is the
heat of reaction at absolute zero. If the value of
in the Nernst equation is taken as the heat of reaction
at the temperature $T$, then there is a wide discrepancy
between it and the corresponding value calculated from

$$\Delta H = \Delta H_0 - \sum \alpha T + \sum \beta \frac{T^2}{2}$$

Using the values found for $\Delta H_0$, $\Sigma \alpha$, and $\Sigma \beta$, there
is obtained

$$\Delta H = 118,000$$

These two values of 118,000 and 171,000 represent, no
doubt, lower and upper limits for the heat of reaction.

These data having been obtained, it seemed that
it would be worth while to investigate the thermodynamics
of the compound with more care and accuracy. The most
important aspects which presented themselves in reviewing
the former calculations are the facts that the temperature
of the filament is continually changing as the resistance
changes and secondly, the uncertainty of the pressure
of chlorine under the equilibrium conditions. In order
to eliminate these sources of error, some new lamps were
made containing a 1.6 mil tungsten filament and a quartz
fiber which could be used as a pressure indicating device,
as a check on the values calculated from resistance changes. A diagram of this is shown in Fig. 3.

To eliminate the second objection, namely, that of the temperature of the filament, a pyrometer was used to keep the filament always at the same temperature at which it was set up.
To use the quartz fibers to measure the pressure of the chlorine gas at equilibrium, they first had to be calibrated with known pressures of air. The lamps used were, accordingly, calibrated at pressures of .05 microns, .01 microns, and .005 microns. As a further check on what kind of a curve the calibration would give, one lamp was also calibrated at .001. These points all fell in a straight line as shown in Figure 4, which is plotted on log-log scale. The ordinate of this scale is pressure, and the abscissa is the values for the damping coefficient. This damping coefficient is a factor which is dependent upon the pressure of the gas and the internal friction of the fiber. The coefficient is calculated from the formula,

$$\alpha = \frac{1}{t} \log \frac{I}{i}$$

where I is the initial and i the final value of the amplitude and t the time which it takes for the vibrations of the fiber to decrease from amplitude I to amplitude i. The way in which these amplitudes were measured is shown in Figure 3. The kind of gas which is to be measured is also of great importance since the curve of damping coefficient against pressure, while it will have the same general shape for all gases, will be displaced along the abscissa for different gases. This is described fully by A.S. Coolidge* in an article in which he finds that for low pressures, for a given value of $\alpha$, the pressure is inversely proportional to the molecular weight. At higher pressures, it has been found

*J.A.C.S. 45, 1637, 1923.
that the curve turns upward and finally the damping coefficient will become constant for increasing pressure. This deviation of the upper part of the curve is different, of course, for different gases and is proportional to the viscosities of the gases. In the lower range of pressures where a linear relation holds, the pressure of chlorine can be found from the curve for air by means of the ratio of the square roots of the molecular weights. In the particular case which we are considering, we have a mixture of gases. This has been studied by Haber and Kerschbaum* who find that

\[ \alpha = a + b \left[ \frac{P_A \sqrt{M_A}}{P_B \sqrt{M_B}} \right] \]

where \( a \) is the value of \( \alpha \) in an absolute vacuum and refers to the pressure and molecular weight of a gas \( A \) mixed with a gas \( B \). In one case, we know already that

\[ \alpha = a + P_{\text{AIR}} \sqrt{M_{\text{AIR}}} \]

and for the case where the damping coefficient is the same we have

\[ a + b \frac{P_{\text{AIR}} \sqrt{M_{\text{AIR}}}}{P_{\text{AIR}} \sqrt{M_{\text{AIR}}}} = a + b \left[ \frac{P_{\text{wcl}} \sqrt{M_{\text{wcl}}}}{P_{\text{cl}} \sqrt{M_{\text{cl}}}} \right] \]

or

\[ P_{\text{cl}} = \frac{P_{\text{AIR}} \sqrt{M_{\text{AIR}}}}{\sqrt{M_{\text{cl}}}} - \frac{P_{\text{wcl}} \sqrt{M_{\text{wcl}}}}{\sqrt{M_{\text{cl}}}} \]

In this manner, then, the pressures of chlorine can be calculated from the calibrated curve for air if we know the pressure of tungsten hexachloride.

Three lamps were exhausted with WCl\(_6\) in the bulb and from the curve of the quartz fibers for air, the pressure

* Z. Electrochemie 20, 296, 1944.
within the range for which the fiber had been calibrated. At higher temperatures, however, the pressure of chlorine ran above this range and apparently into the upper range where the linear relationship between damping and pressure no longer holds. For these higher temperatures, therefore, weight should be put on the pressures as calculated from resistance changes. At the highest temperature of 2000°K the equilibrium had not yet been reached when the experiment was closed by the burning out of the filament. The results of these experiments are shown in Figure 5 and the equilibrium constants calculated as before are given after further discussion in Table 4.

The values for these constants as derived from the resistance measurements, which give the more reliable results, as already discussed, are plotted in Figure 6 to show the relationship between log $K_p$ and $1/T$. It is evident that a straight line can be drawn to represent the relationship within the limits of error. This is a demonstration that the results can be expressed by some thermodynamic equation if all the facts are known. The important thing is to see how well this can be done.

In order to do this more accurately than in the preliminary tests, we must first know the heat of reaction for tungsten hexachloride. This can be found by a very easy method, namely, by allowing it to react with water and by then measuring the use in temperature.

The equations for this are as follows:
\[ WCl_6 + 3H_2O = WO_3 + 6HCl - Q \]
\[ W + 1\frac{1}{2}O_2 = WO_3 - 196,300 \text{ cal.} \]

Subtracting
\[ WCl_6 + 3H_2O = 6HCl + W + 1\frac{1}{2}O_2 - Q + 196,300 \]
Also
\[ 3H_2 + 3Cl_2 = 6HCl - 235,800 \]

Subtracting again
\[ WCl_6 + 3H_2O = W + 1\frac{1}{2}O_2 + 3H_2 + 3Cl_2 - Q + 432,100 \]
Also
\[ 3H_2 + 1\frac{1}{2}O_2 = 3H_2O - 207,000 \]
Adding
\[ WCl_6 = W + 3Cl_2 + Q + 225,100 \text{ cal.} \]

The value \( Q \) in this equation will be the actual heat evolution registered. Since the reaction takes place rapidly only above 80°C, the experiment was performed by pouring a known amount of hot water in a Dewar flask and, by means of a thermometer, finding the rate of cooling of the water. After this had assumed a constant rate, a known quantity of WCl₆ was poured in, and the temperature noted at frequent intervals until all the reaction had stopped and the liquid had again assumed the same constant rate of decrease of temperature with time as at the beginning. Curves for three such determinations are shown in Figures 7, 8, and 9. From these curves, the amount of heat evolved was found by calculating the maximum temperature which the water would have reached if it had not been cooled during the period of the reaction. Then from the total rise in temperature and the volume of water the heat evolved for the known quantity of WCl₆ can be found and, from this, the heat which would be evolved by one mol of tungsten hexachloride. This figure must now be corrected due to the fact that HCl is formed, and, when this goes into solution, heat is evolved. When this has been allowed for, we have the value
which corresponds to \( Q \) in the equation. Since this is heat given off and, according to our convention, is negative, it must be subtracted from 325,100 to obtain the heat of decomposition of \( \text{WCl}_6 \). Three determinations of this were made with results as given in Table 3.

<table>
<thead>
<tr>
<th>Curve</th>
<th>Heat of reaction - ( \text{WCl}_6 + \text{H}_2\text{O} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 7</td>
<td>-79,500 cal</td>
</tr>
<tr>
<td>Fig. 8</td>
<td>-61,500 cal</td>
</tr>
<tr>
<td>Fig. 9</td>
<td>-63,500 cal</td>
</tr>
</tbody>
</table>

Taking an average of these values, we have -68,200 cal and this gives for the heat of decomposition of \( \text{WCl}_6 \) the value of +156,600 cal. This lies within the range forecast by the study already given of the preliminary results. Now we are ready to use a thermodynamic equation. As a guide, the Nernst approximation formula was first applied. The value of the conventional chemical constant for chlorine is 5.1 and the value for \( \text{WCl}_6 \), while not known, seems to be about 5.1 from comparison with other values. As said before, we shall take \( K_p = \left( \frac{P_{\text{reactants}}}{P_{\text{resultant}}} \right)^3 \) and since the Nernst school has adopted the convention of \( K_p = \frac{P_{\text{reactants}}}{P_{\text{resultant}}} \) and also that heat evolved is positive, the value of \( Q \) to be substituted in the Nernst equation will be positive. We have the heat evolved since we are considering the \( \text{Cl}_2 \) and \( \text{W} \) as the reactants and \( \text{WCl}_6 \) as the resultant.

It should also be stated that in the Nernst equation is taken as reactants positive and resultants negative.
Solving then for $K_p$ for example at $1360^\circ K$
we have

$$\log K_p = -\frac{156800}{4.571 \times 1360} + 2 \times 1.75 \log 1360 + 6.2$$

$$K_p = 0.00000010$$

Similar measurements can be calculated from our
measurements for $1500^\circ K$ and $1600^\circ K$.

In the absence of data on the specific heat
of $\text{WC}_6$, a more rigid thermodynamic equation cannot
properly be applied. The observed equilibria, however,
are represented somewhat better by using the more
general Nernst equation, namely:

$$\log K_p = -\frac{\Delta H_o}{4.571T} + \sum \gamma \log T + \beta T + \Sigma \psi C$$

and the formula for the change with temperature of the
heat of reaction:

$$\Delta H = \Delta H_o + \sum \gamma T^2 + \beta T$$

neglecting the $\gamma T^2$ term. Inasmuch as $\Delta H$ is known
for $87^\circ C$, this value together with that for $K_p + C$
can be introduced into the equation for the condition
at $1500^\circ K$, and a value of $\beta$ then be obtained, amounting
to $-0.00159$. This gives $\Delta H_o = 154,380$ for the
formation of $\text{WC}_6$ from tungsten and chlorine.
In Table 4 all of the values are assembled.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>WCl₆ Fiber</th>
<th>Chlorine Fiber</th>
<th>Resistance Fiber</th>
<th>WCl₆ Resistance</th>
<th>Chlorine Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1860°K</td>
<td>0.00000232</td>
<td>0.0000375</td>
<td>0.0000368</td>
<td>0.000000231</td>
<td>0.00000023</td>
</tr>
<tr>
<td>1500°K</td>
<td>0.00000232</td>
<td>0.0000670</td>
<td>0.00167</td>
<td>0.0000013</td>
<td>0.000021</td>
</tr>
<tr>
<td>1600°K</td>
<td>0.00000232</td>
<td>0.0000680</td>
<td>0.000408</td>
<td>0.0000014</td>
<td>0.000026</td>
</tr>
<tr>
<td>2000°K</td>
<td>0.00000232</td>
<td>0.001628</td>
<td>0.0062</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


\[
\begin{array}{c|c|c}
\hline
\text{Temp.} & \text{WCl₆ Fiber} & \text{Chlorine Fiber} \\
\hline
1860°K & 0.00000010 & 0.00000008 \\
1500°K & 0.0000029 & 0.000018 \\
1600°K & 0.000098 & 0.000052 \\
\hline
\end{array}
\]

At the lowest temperature, the pressure of chlorine evolved is within the range at which the quartz fiber nanometer can be accurately used. At this temperature the agreement between the pressure measured by the fiber and that deduced from resistance measurements as the equivalent of the deposited tungsten is excellent and furnishes ample justification for accepting as reliable the pressures obtained in the latter way for the high temperatures.
At these higher temperatures, as already pointed out, the pressures run into the upper range where they are no longer linearly proportional to the damping coefficients given by the fiber. The comparative results in the table show how striking this divergence is. It is also noticeable that there is fair agreement between observed and calculated values for the equilibrium constants for the three lowest temperatures. In the experiment at 2000°K, as already mentioned, the equilibrium was not attained. The calculated values increase more rapidly with temperature than do the observed.

If the specific heat terms were known, an equation could no doubt be derived which would fit the results more closely by showing the same trend on change of temperature. The extent to which the results as found fit in with a linear relationship between $\kappa_P$ and $\gamma$ as already described, make it apparent that these results represent faithfully, within the limits of experimental error, the actual equilibrium conditions. More reliance is therefore to be put upon these than upon the values calculated from the Nernst equation. The latter have been discussed more for the purpose of showing how well the present results agree with what would be calculated.
CHLORINE PRESSURES AT EQUILIBRIUM

O - NERNST APPROXIMATION FORMULA

β - NERNST FORMULA + Β TERM

Δ - FIBER MEASUREMENTS

X - RESISTANCE CALCULATIONS

H-3604684
from the approximate equation. Of course, an equation which would fit the results satisfactorily could be obtained even now by altering the values of the constants in the amplified Nernst equation, or by inserting suitable values for the corresponding constants in the rigid thermodynamic equation. This is not done here as such an equation would have more mathematical than scientific interest. It must be remembered that we cannot use the rigid thermodynamic equation with any degree of confidence without knowing data for the specific heat of WCl₆.

These results are expressed graphically in Fig. 10, which shows the variation with temperature, of the chlorine pressures at equilibrium taken from Fig. 6. This is done for the sake of comparing the pressures as found with those calculated from the two equations.

It may be said confidently, then, that the agreement between the values is good considering that the Nernst equation is only an approximation and does not fit the facts rigidly. It also seems apparent that the values as found for the heat of reaction are within experimental error and within the range of approximation of the Nernst equation.
Part II - Rate of Reaction

The equilibrium of the compound $\text{WCl}_6$ has now been reviewed rather carefully and some results as to the heat of reaction arrived at, which seem to be fairly reliable. It will be well now to consider the practical aspects of such a reaction and system. The first way in which it was intended to use this compound was in the elimination of spots in coiled filaments. These so-called spots are, as mentioned previously, due to an actual difference in the diameter of the wire in a certain section of a coiled filament. This difference in diameter is due to unequal tensions when the wire is wound around a mandrel, causing the wire to be stretched a little in certain places. When the coil is then heated by an electric current, the elongated parts run at a high temperature and so evaporation occurs more readily there and the decomposition of $\text{WCl}_6$ becomes more complete as the temperature is increased, as demonstrated in Part I, it was thought that by burning the filament in a vapor of $\text{WCl}_6$, either in a vacuum or in hydrogen, the deposition would take place more completely at the hotter spot than at the rest of the filament. One of the first things that was found was that it was more desirable to flash the filament.
Fig. 11

Spotted Filament before Treatment.

Same Filament After Flashing in WCl vapor alone.
at a high temperature for short intervals rather than to burn it continually, in order to take advantage of the contrast in temperature. When a coiled filament was flashed in WCl₆ vapor alone, spots could be practically eliminated. This is shown in Fig. 11 where are shown pictures of a spotted filament before and after the treatment in WCl₆ vapor.

While the elimination of spots could be accomplished by flashing in WCl₆ vapor alone, the method was not readily applicable to high speed factory conditions. Here the conditions could not be static nor ideal but must be very flexible. With this aim in view, treating spotted filaments in WCl₆ vapor in a current of hydrogen was tried. This led to the discovery that in hydrogen the speed of the deposition is also involved, for when the filament was burned continuously the hotter portions of the wire were found to have less tungsten deposited on them than the cooler portions. As it is unusual to have a reaction whose speed decreases with increase in temperature, it seemed highly important to investigate the matter thoroughly.

In the first experiments, single filaments were burned in currents of hydrogen containing WCl₆.
vapor and the speed measured by following their change in resistance. The results checked what had been noticed visually during the similar treatment of spotted filaments, namely, that the rate of deposition decreased with increase in temperature.

In order to have assurance that we had not been misled by accidental variation in the speed of hydrogen or in the concentration of WC16 vapor, further tests were made under conditions where both could be maintained constant beyond any doubt.

Two wires of different diameters were burned in series in WC16 vapor in a current of hydrogen. The treatment was carried out over a wide range of temperatures, and in every case the cooler filament had the largest amount of tungsten deposited upon it. In the case where temperatures of 2000°K and 2400°K were used, it was found that in some instances the hotter filament showed actually a loss in weight. On the other hand when two filaments of different diameter and connected in series were flashed for periods of 1/1200 second at intervals of about 1.6 seconds under
the same conditions the hotter filament showed the greater increase in weight. This was also true over ranges of temperature from $1000^\circ$K to $2400^\circ$K.

The explanation of these peculiar differences lies in the condition under which decomposition of WCl$_6$ starts. In the case of the filaments which were flashed at intervals, the true reaction velocity is measured by the rate of deposition on the filament because only those molecules of WCl$_6$ will be decomposed which are at that instant in close proximity to the filament.

With filaments burned continuously however, the rate of deposition gives an erroneous and entirely misleading value for the rate of decomposition. The hot filament is surrounded by a film of gas, according to the Langmuir theory, in which the movement of gaseous molecules is one purely of diffusion. There will therefore be a temperature gradient, decreasing from that of the filament to the outer surface of the film, which is approximately that of the bulb. At some temperature point within this film WCl$_6$ molecules will decompose so appreciably as to lower decidedly the concentration of molecules which can reach the filament.
Of those which decompose within the film, only a fraction of the tungsten atoms produced can reach the filament, because in their diffusion they are liable to reach the outer surface of the film and then be carried away in convection currents of hydrogen. Heavy deposits of tungsten, in fact, collected on the stem and bulb above the filament.

The hotter the filament, the further away from it will the point be at which the temperature will be such as to allow of this decomposition and the less will be the chance of deposition on the filament. In fact, the condition may be reached under which the lighter and more readily diffusing chlorine atoms or HCl molecules may diffuse to the filament to a greater extent than the heavy tungsten atoms. This would lead to loss of tungsten by reaction with chlorine, an apparent anomaly which was observed at the highest temperature, 2400°K.

Another factor which influences this difference in speed is the fact that the density of the WCl$_6$ gas around the filament is decreased. Thus there would be more molecules to react near the cooler filament than would be the case around the hotter filament.
This difference in the speed of deposition is shown in the curves of Fig. 12 where the speed measured by the amount of tungsten deposited is plotted against the temperature. For every pair of filaments treated simultaneously each test yielded two values for the speed of deposition at temperatures about 400° apart. These temperatures were determined by a pyrometer. In some cases the differences in temperature were obtained by burning filaments of different diameters in series. In both cases filaments of the same diameter were burned on different circuits. In both cases, the resulting values for the speed showed the same relationship.

The temperatures of each pair of filaments were so chosen that they nearly or completely overlapped with the temperatures used in other tests. In this way relative values for the rates of deposition were measured over the range of 1050°K to 2500°K.

It must be borne in mind, as already expressed, that the rate of deposition is equivalent to the rate of the reaction only in the case of the filaments which were flashed intermittently. The other curve is given because of its importance in demonstrating that the proper experimental conditions for treating spotted filaments in WC16 vapor in hydrogen can be met only by flashing of the filaments and would be completely upset under continuous burning.
Fig. 13

Spotted Filament before Treatment

Spotted Filament after flashing in NaCl vapor in hydrogen.
The fact that the flashing in $\text{WCl}_6$ vapor in hydrogen gas improved the condition of spots was evidenced in the case of twelve lamps which were life tested. Six of these contained spotted filaments and six contained similar filaments flashed fifty times in $\text{WCl}_6$ gas. The life of the treated filaments was 30% longer than those untreated when burned at constant temperature and radiant efficiency. Pictures of a typical filament treated in $\text{WCl}_6$ vapor in hydrogen and one untreated are shown in Fig. 13.

From the pictures of treated filaments and from preliminary life test data, it appears without doubt that the life of spotted filaments can be improved by flashing in $\text{WCl}_6$ vapor in hydrogen and that absolute elimination of spots can be obtained by flashing the spotted filament in vacuum.
The heat of oxidation of WCl₆ in water is measured and from this the heat of decomposition of WCl₆ is determined. With these values, and using Nernst's equation, equilibrium constants are calculated for 1360°K, 1500°K and 1600°K, and are given above. The agreement between these and the values found by experiment is good, considering the approximations involved.

Measurements of the speed of reaction of WCl₆ vapor with a hot filament in hydrogen are given, an explanation being advanced as to why the reaction goes as expected when the filaments are flashed 1/1200 second, but takes place in the reverse way when the filaments are burned continuously.

The application to the elimination of spots in coiled filaments is shown and preliminary evidence given that the life of tungsten coiled filaments can be increased by flashing in WCl₆ vapor.