Calculations of the Partial Pressure of OH Molecules in Argon-Plasma Emission Sources for Spectrochemical Analysis

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Calculations have been made for the partial pressure of OH molecules in argon plasmas into which a small amount of water vapor was introduced through a desolvation device. The Newton-Raphson method was applied to the calculation for a system consisting of O, H, OH, O_2, H_2, H_2O, and argon. In the temperature range above 4000 K, where the system consisted mainly of O, H, OH, and argon, an approximate analytical calculation provided results in a good agreement with those obtained by the Newton-Raphson method. The partial pressures in the plasma jet light source and the high frequency plasma torch were determined by the methods proposed. Calculated ratios of the OH band emission intensities at two different temperatures are also given and are discussed.

1. Introduction

The OH band emission occurs when water vapor is introduced into emission spectroscopic light sources such as a plasma jet and a high frequency plasma torch. Generally a depression in the band emission is desirable for analytical purposes because the band spectra often interfere with line spectra of analytes. The OH band spectra is, however, useful for measurements of the rotational temperature, usually identified with the gas temperature of plasma sources.

Our previous work on the plasma jet concerned with measurements of the band intensity and temperature distributions and calculations of partial pressures of the OH molecules and ratios of the OH spectrum intensities at two different temperatures. Also one of the authors calculated partial pressures of the OH molecules in the high frequency plasma torch using the method proposed in the former paper. The calculating method was based on the following assumptions.
1) H$_2$O molecules dissociate in the argon plasma whose temperature exceeds 3000 K, and the partial pressures of O$_2$, H$_2$, and H$_2$O can be neglected compared with those of O, H, and OH.

2) Total of the partial pressures of O, H, and OH in the plasma is considered to be constant. However, the lower the temperature, the less the H$_2$O molecules dissociate; in fact, at 3000 K, the partial pressure of H$_2$O as well as the pressures of O$_2$ and H$_2$ is not so low as to be neglected. Strictly speaking, the assumption 2) should also be corrected because the actual condition is more accurately given by the one that the concentration ratio of oxygen atoms to argon atoms and the ratio of hydrogen atoms to argon atoms are constant. The present paper describes the calculating method of dissociation equilibria and the results which are more accurate than those reported previously.

2. Calculations and Results

2.1 O-H-OH-O$_2$-H$_2$-H$_2$O-Ar system

For the argon plasma into which water vapor is introduced, the following equilibria (a) to (d) are generally accepted as being of importance.

\[
\begin{align*}
O & \rightleftharpoons (1/2)O_2 \\
H & \rightleftharpoons (1/2)H_2 \\
OH & \rightleftharpoons (1/2)(O_2 + H_2) \\
H_2O & \rightleftharpoons (1/2)O_2 + H_2
\end{align*}
\]

According to the conventional isotherm equation, we have

\[
(P_O/P^o)\sqrt{P_{O_2}/P^o} = \exp(-\Delta F_1/RT)
\] (1)

where $\Delta F_1$ is the free energy change (kcal/mole) in the reaction (1/2)O$_2$ $\rightarrow$ O under such the condition that the standard state is 1 atm, $T$ the temperature in degrees Kelvin, $R$ the gas constant (=1.98719 cal/deg mole), $P_O$ and $P_{O_2}$ the partial pressures of O and O$_2$ expressed in atm, and $P^o$ the pressure of the standard state in atm.

Substituting $P^o$=1 atm into equation (1), we obtain

\[
P_O/\sqrt{P_{O_2}} = \exp(-\Delta F_1/RT)
\] (2)

Similar equations hold for the equilibria (b) to (d).

\[
P_H/\sqrt{P_{H_2}} = \exp(-\Delta F_2/RT) \\
P_{OH}/\sqrt{P_{O_2}}\sqrt{P_{H_2}} = \exp(-\Delta F_3/RT) \\
P_{H_2O}/P_{O_2} = \exp(-\Delta F_4/RT)
\] (3) (4) (5)

where $P_H$, $P_{H_2}$, $P_{OH}$, and $P_{H_2O}$ are the partial pressure of H, H$_2$, OH, and H$_2$O in atm, respectively, and $\Delta F_1$, $\Delta F_2$, and $\Delta F_3$ the free energy changes in the reactions (b), (c), and (d) in kcal/mole, respectively. When $S$ is the ratio of the partial pressure of the water vapor in the argon stream to that of argon, we have with reference to oxygen atoms

\[
(P_O + P_{OH} + 2P_{O_2} + P_{H_2O})/P_A = S
\] (6)

and with reference to hydrogen atoms

\[
(P_H + P_{H_2} + 2P_{H_2O})/P_A = 2S
\] (7)

where $P_A$ is the partial pressure of argon in atm.

The sum of the partial pressures of all the species is 1 atm, namely

\[
P_O + P_H + P_{OH} + P_{O_2} + P_{H_2} + P_{H_2O} + P_A = 1
\] (8)

$P_A$ is approximately 1 atm because $P_O$, $P_H$, $P_{OH}$, $P_{O_2}$, $P_{H_2}$, and $P_{H_2O}$ are much less than $P_A$.

Taking logarithms of equations (2) and (3) and transposing, we obtain

\[
-\Delta F_1/RT - \ln P_O + (1/2)\ln P_{O_2} = 0
\] (9)

\[
-\Delta F_2/RT - \ln P_H + (1/2)\ln P_{H_2} = 0
\] (10)

To solve equations (2) to (8), the values of $P_O$, $P_{O_2}$, $P_H$, and $P_{H_2}$ were determined by means of the Newton-Raphson method so that the relations (9) and (10) might be satisfied. The calculating procedure is to start with proper initial pressures ($P_O$)$_0$ and ($P_H$)$_0$, and to compute the other unknown pressures $P_{OH}$, $P_{O_2}$, $P_{H_2}$, and $P_{H_2O}$ by use of equations (4) to (7). Inserting the results obtained into the following equations (11) and (12), we obtain corrected values ($P_O$)$_{n+1}$ and ($P_H$)$_{n+1}$, viz.

\[
(P_O)_{n+1} = (P_O)_n - g((P_O)_n)/g'((P_O)_n)
\] (11)

\[
(P_H)_{n+1} = (P_H)_n - f((P_H)_n)/f'((P_H)_n)
\] (12)
where \( g(P_0) \) and \( f(P_H) \) are the functions expressed as

\[
g(P_0) = -\frac{\Delta F_i}{RT} - \ln P_0 + (1/2) \ln P_{O_2} \quad (13)
\]

\[
f(P_H) = -\frac{\Delta F_i}{RT} - \ln P_H + (1/2) \ln P_{H_2} \quad (14)
\]

and the differential functions are put into the following forms.

\[
g'(P_0) \approx -1/P_0 - 1/P_{O_2} \quad (15)
\]

\[
f'(P_H) \approx -1/P_H - 1/P_{H_2} \quad (16)
\]

The corrected values are inserted into equations (2) and (3), and unless the equations hold, the values of the pressures must be corrected again in the same manner. Thus the correction is iterated until \( f(P_0) \) and \( g(P_0) \) are reduced to zero. (Then equations (9) and (10) hold for the corrected values of \( P_H, P_{H_2}, P_0, \) and \( P_{O_2} \).)

For example, let us consider the case where only argon is employed as a plasma-forming gas for the plasma jet source. The partial pressures of the species existing in the plasma can be calculated by the procedure described above. Values of free energy changes according to the JANAF Tables were used for the calculations. They are shown in Table I. When water vapor was removed through the desolvation device using dry ice, the ratio of the partial pressure of water vapor to that of argon was measured to be \( 1.78 \times 10^{-3} \); namely \( S_{PA} \) in equations (6) and (7) nearly equals \( 1.78 \times 10^{-3} \) atm. The results calculated at 3000 K, 4000 K, and 5000 K are shown in Table II.

### Table I. Gibbs free energy changes (kcal/mole).

<table>
<thead>
<tr>
<th>( T(K) )</th>
<th>( \Delta F_i )</th>
<th>( \Delta F_{F_i} )</th>
<th>( \Delta F_{F_2} )</th>
<th>( \Delta F_{F_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000</td>
<td>13.031</td>
<td>-3.107</td>
<td>-19.279</td>
<td></td>
</tr>
<tr>
<td>4000</td>
<td>11.030</td>
<td>-3.671</td>
<td>-18.447</td>
<td></td>
</tr>
<tr>
<td>5000</td>
<td>-0.893</td>
<td>-3.961</td>
<td>-6.882</td>
<td></td>
</tr>
<tr>
<td>6000</td>
<td>-18.438</td>
<td>-4.353</td>
<td>9.844</td>
<td></td>
</tr>
</tbody>
</table>

### Table II. Calculated partial pressures in the argon plasma jet (atm).

<table>
<thead>
<tr>
<th>( T(K) )</th>
<th>( P_{O_2} )</th>
<th>( P_0 )</th>
<th>( P_H )</th>
<th>( P_{H_2} )</th>
<th>( P_{H_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000</td>
<td>2.17 \times 10^{-3}</td>
<td>1.22 \times 10^{-5}</td>
<td>2.65 \times 10^{-3}</td>
<td>1.25 \times 10^{-4}</td>
<td>2.83 \times 10^{-4}</td>
</tr>
<tr>
<td>4000</td>
<td>4.41 \times 10^{-6}</td>
<td>1.75 \times 10^{-5}</td>
<td>3.52 \times 10^{-5}</td>
<td>1.43 \times 10^{-5}</td>
<td>4.93 \times 10^{-6}</td>
</tr>
<tr>
<td>5000</td>
<td>2.81 \times 10^{-7}</td>
<td>1.75 \times 10^{-3}</td>
<td>3.52 \times 10^{-3}</td>
<td>6.55 \times 10^{-3}</td>
<td>3.03 \times 10^{-7}</td>
</tr>
</tbody>
</table>

### 2.2 O-H-OH-Ar system

The results given in Table II indicate clearly that, in the temperature range above 4000 K, \( P_{O_2}, P_{H_2}, \) and \( P_{H_2} \) are three or more orders of magnitude lower than \( P_0 \) and \( P_H \). Therefore it is thought that an approximate analytical calculation, without considering \( P_{O_2}, P_{H_2}, \) and \( P_{H_2} \), will be available instead of the rather complicated trial-and-error method. Substituting \( P_{O_2} = P_{H_2} = P_{H_2} = 0 \) atm and \( P_1 = 1 \) atm into equations (6) and (7), we obtain

\[
P_0 + P_{O_2} = S \quad (17)\]

\[
P_H + P_{O_2} = 2S \quad (18)
\]

The equilibrium constant for the reaction \( OH \rightleftharpoons O + H \) are expressed as

\[
P_0P_H/P_{O_2} = K_p \quad (19)
\]

where \( K_p \) is given in atm. From equations (17) and (18), we derive \( P_0 = S - P_{O_2} \) and \( P_H = 2S - P_{O_2} \). Substituting these equations into equation (19) and rearranging, we have

\[
P_{O_2}^2 - (3S + K_p)P_{O_2} + 2S^2 = 0 \quad (20)
\]

\( P_{O_2} \) can be obtained by solving the quadratic equation.

† See appendix.

‡‡ As the right hand side of equation (17) means \( S_{PA} \), its dimension is atm, although \( S \) is a dimensionless constant.
\[ P_{oh} = \frac{3S + K_p - \sqrt{(3S + K_p)^2 - 8S^3}}{2} = \frac{4S^3}{(3S + K_p)^2 - 8S^3} \]  
\[ (21) \]

If \( S \ll K_p \), the following expressions are fairly good approximations, viz.
\[ P_{oh} \approx \frac{2S^3}{(3S + K_p)} \]  
\[ (22) \]
or
\[ P_{oh} \approx \frac{2S^3}{K_p} \]  
\[ (23) \]

The free energy change in the reaction \( \text{OH} \rightarrow \text{O} + \text{H}, \) \( \Delta F \) (kcal/mole), is given by
\[ \Delta F = -RT \ln K_p \]  
\[ (24) \]

and
\[ \Delta F_1 + \Delta F_2 - \Delta F_3 = \Delta F \]  
\[ (25) \]

\( \Delta F \) and \( K_p \) are calculated from the values \( \Delta F_1 \), \( \Delta F_2 \), and \( \Delta F_3 \) given in Table I. \( P_{oh} \) was computed by substituting \( S = 1.78 \times 10^{-3} \) into equation (22). The results are shown in Table III. The values of \( P_{oh} \) coincide well with those given in Table II. Accordingly it is concluded that the above analytical calculation gives a close approximation to the required values.

### Table III. Free energy changes and equilibrium constants for the reaction \( \text{OH} \rightarrow \text{O} + \text{H} \), and calculated partial pressures of hydroxyl in the argon plasma jet.

<table>
<thead>
<tr>
<th>( T(K) )</th>
<th>( \Delta F ) (kcal/mole)</th>
<th>( K_p ) (atm)</th>
<th>( P_{oh} ) (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4000</td>
<td>-2.817</td>
<td>1.425</td>
<td>4.4 \times 10^{-6}</td>
</tr>
<tr>
<td>5000</td>
<td>-30.844</td>
<td>22.29</td>
<td>2.4 \times 10^{-7}</td>
</tr>
</tbody>
</table>

The value of \( P_{oh} \) in the high frequency plasma torch, which had been reported previously, was computed again by using the formula (22). The amount of water vapor in the argon stream was 2.2 mg/l when dry ice was used for desolvation.

\[ S = 2.2 \times 10^{-3}/18 \times 22.4 = 2.74 \times 10^{-3} \text{ atm} \]

At 4000 K, we obtain \( P_{oh} = 1.05 \times 10^{-5} \text{ atm} \). On the other hand, \( S = 7.59 \times 10^{-3} \) when ice was used to remove the water vapor. In the latter case \( P_{oh} \) becomes \( 7.96 \times 10^{-5} \text{ atm} \) at 4000 K. Obviously the relationship \( P_{oh} / P_A < 0.01 \) holds true for both the cases, so that the discharge should be unstable in both the cases according to the discussion in the previous report. This is not consistent with the experimental observations. Hence further studies will be needed on the previous presumption that the instability of the discharge observed when using dry ice is ascribed to the less amount of the OH molecules in the plasma.

### 2.3 Ratios of the OH spectrum intensities at different temperatures

In the previous paper\(^1\), the ratios of the OH band spectrum intensities at two different temperatures have been calculated from the values of \( P_{oh} \). Strictly speaking, the use of the concentration \( N_{oh} \) expressed in cm\(^{-3}\) provides more accurate results. Also the partition function of the OH molecule, which is dependent on the temperature, should be taken into account.

The spectrum intensity at temperature \( T \) is given by
\[ I_T = C N_{oh(T)} \exp (-E/kT)/Z_{oh(T)} \]  
\[ (26) \]

where \( N_{oh(T)} \) is the concentration of the OH molecules at \( T \), \( Z_{oh(T)} \) the partition function at \( T \), \( E \) the energy level of the excited state and \( C \) the constant. The calculations were made with respect to the R\(_{28}\) line (306.83 nm, \( E = 4.2 \text{ eV} \)) of the (0,0) band in the \( ^2 \Sigma - ^2 \Pi \) system. The values of \( N_{oh} \) corresponding to those of \( P_{oh} \) given in Table II are

\[ N_{oh(4000)} = 5.31 \times 10^{14} \text{ cm}^{-3} \]
\[ N_{oh(4000)} = 8.09 \times 10^{12} \text{ cm}^{-3} \]
\[ N_{oh(5000)} = 4.17 \times 10^{11} \text{ cm}^{-3} \]

The partition function for one electronic state of a diatomic molecule can be approximated by\(^4\)
\[ Z = kT \gamma \exp (-\varepsilon/kT)/hcB \]
\[ (1 - \exp (-\hbar \omega/kT)) \]

where \( k \) is the Boltzmann’s constant, \( h \) the Planck’s constant, \( c \) the velocity of light, \( \varepsilon \) the electronic energy, \( B \) the rotational constant, \( \omega \)
the vibrational constant, and \( \eta \) the statistical weight of the electronic state. Generally it suffices to consider the lowest electronic level only. For the OH molecule, the constants are

\[
B = 18871 \text{ cm}^{-1}, \quad \omega = 3735.21 \text{ cm}^{-1}, \quad \eta = 2
\]

Substituting the numerical values for the constants into equation (27), we have

\[
Z_{\text{OH}}(3000) = 265, \\
Z_{\text{OH}}(1000) = 399, \\
Z_{\text{OH}}(5000) = 559
\]

The ratios of the intensities at two temperatures can be calculated from equation (26), into which the values of \( N_{\text{OH}} \) and \( Z_{\text{OH}} \) are inserted. Thus we obtain

\[
I_{5000}/I_{4000} = 1.70, \\
I_{3000}/I_{4000} = 4.04, \\
I_{1000}/I_{4000} = 2.38
\]

According to the results, in the temperature range of interest, the higher the temperature, the weaker is the intensity. As has been shown in Fig. 9 in the previous paper, the excitation temperature of the plasma jet source is approximately 5000 K at the central portion, lowering to about 4000 K at the outer region of the plasma. So, the intensity at the outer region should be stronger than that at the central portion. However, the radial distribution shown in Fig. 8 in the paper disagrees with the above conclusion. In the figure, the observed intensity at a 2.5-mm portion from the center is stronger than \( I_i \) (the observed intensity at a 3.5-mm portion from the center). This may be due to the followings:

1) The calculations were carried out on the system consisting of oxygen, hydrogen, and argon, whereas in the experiment nitrogen was added to the argon stream.

2) The plasma is not in the state of the complete thermal equilibrium.

3) In general the Abel inversion yields a remarkable error in the relative intensities at the outer regions.

The reason 3) out of these seems to be the greatest one for the disagreement.

### 3. Conclusions

In the application of the Newton-Raphson method to the calculation of the dissociation equilibria in the argon plasmas, the partial pressures of the species such as O, H, OH etc. were obtained with a high accuracy of more than three digits by 10 to 15 iterations, provided that the initial values were appropriately selected. Conventional emission sources used for spectrochemical analysis have higher temperatures than 4000 K. If the plasma temperature is higher than 4000 K and the water vapor is removed with the desolvation device, the partial pressures of \( O_2, H_2, \) and \( H_2O \) are so low as to be negligible in comparison with those of O and H. Hence the analytical calculation considering the equilibrium \( \text{OH} \rightarrow \text{O} + \text{H} \) only suffices for obtaining the partial pressure of the OH molecule with a satisfactory accuracy. The approximate calculation is also useful for the determination of the initial values required for the Newton-Raphson method.

### Appendix

Differentiating equation (14) with respect to \( P_H \), we have

\[
f'(P_H) = -1/P_H + (dP_{H_2}/dP_H)(1/2P_H) \quad (A1)
\]

When \( n \) is the number of moles and the subscript expresses the molecule, we have

\[
n_0 + n_H + n_{\text{OH}} + n_{O_2} + n_{H_2} + n_{H_2O} + n_A = n_T \quad (A2)
\]

and

\[
n_T R^* T = V \quad (A3)
\]

where \( n_T \) is the total numbers of moles of all the species, \( R^* \) the gas constant expressed in atm cm\(^3\) deg/mole and \( V \) the volume in cm\(^3\). If \( n_H \) increases by \( \Delta n_H \) in the reaction \( \text{H}_2 \rightarrow \text{H} \), we find

\[
\Delta n_H = -(1/2)\Delta n_{\text{H}_2} \quad (A4)
\]

So we have

\[
\Delta n_T = \Delta n_H - \Delta n_{\text{H}_2} \\
= \Delta n_H - 2\Delta n_H \\
= -\Delta n_H \quad (A5)
\]
When \( n_T \) changes by \( \Delta n_T \), the volume \( V \) changes by \( \Delta V \), so that we obtain
\[
\frac{\Delta V}{V} = \frac{\Delta n_T}{n_T} = -\frac{\Delta n_H}{n_T} \quad (A6)
\]
From \( P_H = n_H R^* T / V \), we derive
\[
\Delta P_H = \frac{R^* T}{V} \Delta n_H = (P_H / V) \Delta V = (1/n_T) \Delta n_H + P_H (\Delta n_H / n_T)
= (1 + P_H) \Delta n_H / n_T \quad (A7)
\]
Similarly, from \( P_{H_2} = n_{H_2} R^* T / V \) we have
\[
\Delta P_{H_2} = \frac{R^* T}{V} \Delta n_{H_2} = (P_{H_2} / V) \Delta V = (-2 + P_{H_2}) \Delta n_H / n_T \quad (A8)
\]
Thus, from equations (A7) and (A8), the ratio of \( \Delta P_{H_2} \) to \( \Delta P_H \) is expressed as
\[
\Delta P_{H_2} / \Delta P_H = (-2 + P_{H_2}) / (1 + P_H)
\]
The approximate form is
\[
dP_{H_2} / dP_H \approx -2 \quad (A9)
\]
Substituting equation (A9) into equation (A1), we obtain
\[
f'(P_H) \approx -1/P_H - 1/P_{H_2}
\]
In the similar manner we derive the following expression from equation (13)
\[
g'(P_H) \approx -1/P_H - 1/P_{H_2}
\]

**Correction**

The equations given in the previous paper\(^1\) are corrected as described below.
Page 244, Equation (5)
\[
\frac{P_0 P_{H_2}}{P_{H}} = \exp \left\{ -\frac{(\Delta F_1 + \Delta F_2 + \Delta F_3) / RT}{1} \right\} = K
\]
\[
\rightarrow P_0 P_{H_2} / P_H = \exp \left\{ -\frac{(\Delta F_1 + \Delta F_2 - \Delta F_3) / RT}{1} \right\} = K
\]

Equation (10)
\[
P_{OH} = \left( \frac{1}{4} \right) \{(5 + 9 K) - \sqrt{(5 + 9 K)^3 + 16 P}\}
\]
\[
\rightarrow P_{OH} = \frac{1}{4} \times (5 + 9 K - \sqrt{(5 + 9 K)^3 - 16 P})
\]

Also the authors present the numbers of \( P_0 \), \( P_H \), \( P_{H_2} \), \( I_{3000}/I_{4000} \), \( I_{3000}/I_{5000} \), and \( I_{4000}/I_{5000} \) given in this paper as the corrected values of the numbers reported previously.

**References**

2) Y. Fujishiro: ibid 25, 229 (1976).