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Effect of Halogens and Oxygen on the Emission of Thermal Positive Ions from the Tungsten Surface[*1]

Kumasaburo Kodera, Yoshifumi Kita,[*2] Isao Kusunoki, Hiroshi Kishi
and Atsuhiro Sakiyama

Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto

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The effect of chlorine, bromine, and oxygen on the emission of thermal positive ions from tungsten filaments has been studied. When a tungsten filament is heated in a vacuum, positive ion emission is always observed, and it cannot be removed completely by flashing the filament at high temperatures. This background ion emission increases greatly in halogen or oxygen. Main positive ions are K^+ and Na^+. The increase cannot be explained by the increase of the work function of tungsten by the formation of adsorbed layer of halogen or oxygen atoms. It is ascertained that the tungsten surface reacts with these gases and the reaction products evaporate as neutral particles. As the reaction proceeds, tungsten surface is removed successively and alkali metal atoms in the bulk are exposed to the surface and contribute to the positive ion emission.

For the measurement of the intensity of an alkali metal beam, surface ionization on a hot tungsten filament is usually utilized. This is an excellent method for the measurement of the alkali metal beam, because, in spite of the high ionization efficiency, it does not ionize residual gases in the vacuum system. However, even after the filament is flashed for a long time, background positive ion emission cannot be removed completely. The background positive ion emission increases markedly when halogen or halide molecules strike the filament. Sometimes this increase amounts to more than a hundred times the original background emission, and causes serious trouble in an experiment with halogen or halide crossed beam. Birely, Wilson, and Herschbach[1)] have alluded to this phenomenon, but so far no detailed study has been published.

Hendrick, Phipps, and Copley[2)] have studied the effect of halogens on the ionization of alkali metal atoms on a tungsten surface. They studied the ionization of potassium halide molecular beams on a tungsten filament and discussed the presence of potassium halide or halogen layer on the surface. Metlay and Kimball[3)] studied the effect of fluorine molecules on the surface ionization of alkali metals on a tungsten surface and concluded that a stable fluorine layer was formed which increased the work function of the tungsten. Zmbov[4)] found the increase of ionization efficiency of Mg and Al atomic beams on the tungsten surface when the filament was exposed to a stream of halogen molecules, and explained the fact by the increase of the work function of the tungsten. However, nothing is stated in his paper on the increase of the background ion emission. As a mass spectrometer was used for the detection of the ions, even if the background emission increased, it would not give any trouble so far as the background ions were different from Mg or Al.

In all these papers the increase of the ionization efficiency of the atoms hitting the surface was described, and the increase of the work function of the tungsten by the formation of an adsorbed layer of the halogen or alkali halide was assumed to be the cause of the increase. For the ionization of potassium, instead of Mg or Al in the case of Zmbov, the work function of even a clean tungsten surface is higher than the ionization potential of potassium. Therefore, according to the Saha-Langmuir equation, considerable part of potassium atoms which hit a tungsten surface should be ionized, and the large increase of the positive ion emission could not be expected.

The present study was undertaken to clarify the cause of the increase of the positive ion emission from the tungsten surface in halogen or oxygen atmosphere.

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[*2] Present address: Faculty of Engineering, Osaka University, Suita-shi, Osaka.

1) J. H. Birely, R. R. Herm, K. R. Wilson and D. R. Herschbach, *J. Chem. Phys.*, **47**, 993 (1967).

2) J. O. Hendricks, T. E. Phipps and M. J. Copley, *ibid.*, **5**, 868 (1937).

3) M. Metlay and G. E. Kimball, *ibid.*, **16**, 776 (1948).

4) K. F. Zmbov, *Adv. Mass Spectrometry*, **3**, 765 (1966).

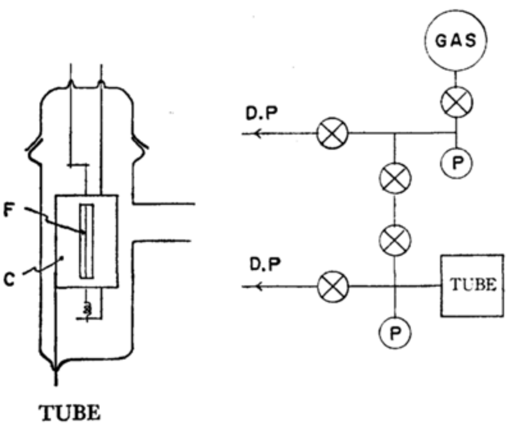


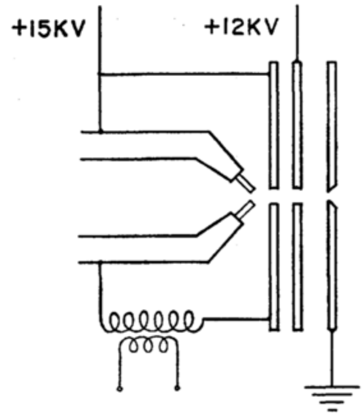
Fig. 1. Diode tube for the measurement of total positive emission and gas inlet system. F, filament; C, ion collector; P, Pirani gauge; D. P., diffusion pump.

Experimental

A diode tube shown in Fig. 1 was used to measure the increase of the total positive ion emission from a tungsten filament in halogen gas.

A Mattauch-Herzog type double focussing mass spectroscope was used for the analysis of impurities in tungsten filaments and for the identification of thermally emitted positive ions and neutral particles evaporated from the tungsten surface. Ilford Q-2 plates were used for the detection of the ions, and relative intensity of the ions was determined from the density of the lines on the plate by means of a microdensitometer.

For the analysis of the tungsten filament, bundles of about ten pieces of the filament each were fixed to the sample holder electrodes as shown in Fig. 2, and intermittent radio frequency voltage was applied between the electrodes for spark discharge ionization.



Spark Ionization source

Fig. 2. Spark ion source.

For the identification of thermal ions, the tungsten filament was fixed between the electrodes and heated by electric current. Halogen gases were introduced into the ion source through a glass tube from the outside. The end of the glass tube was drawn into a nozzle and placed just behind the filament as shown in Fig. 3 (a). Negative ions were also detected by reversing both the acceleration potential and the magnetic field.

To analyze neutral particles which evaporate from the filament, electron impact ionization by electrons emitted from the sample filament itself was utilized. 75 V was applied between the filament and the first slit to accelerate the electrons to ionize the neutral particles. The ions produced were accelerated and drawn into the analyzer by the negative potential applied on the second and the third slits as shown in Fig. 3 (b).

Two different samples of tungsten filament were used for the experiments, one of them was an ordinary doped filament of 0.13 mm diameter, and the other was a 0.18 mm diameter filament not doped with alkali. The latter was supplied from Matsushita Electronics Corporation.

The chemicals for the experiments were used without any treatment: Cl_2 and O_2, Takachiho Chemical Industry, pure: Br_2, Nakarai Chemicals, extra pure: K, Merck, extra pure.

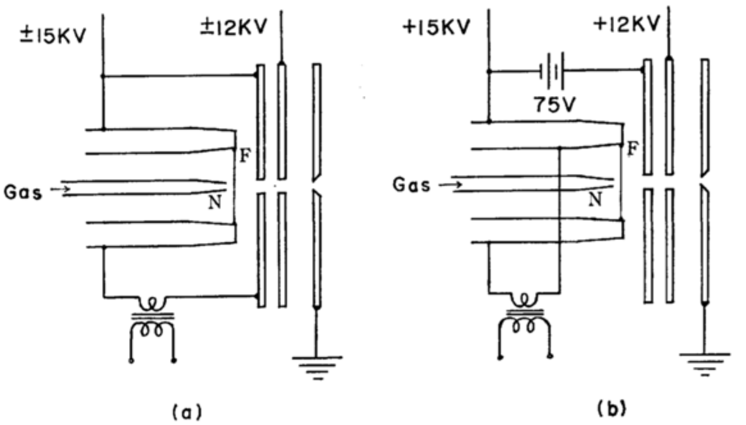


Fig. 3. (a) Surface ionization source with gas inlet nozzle, (b) electron bombardment source with gas inlet nozzle.

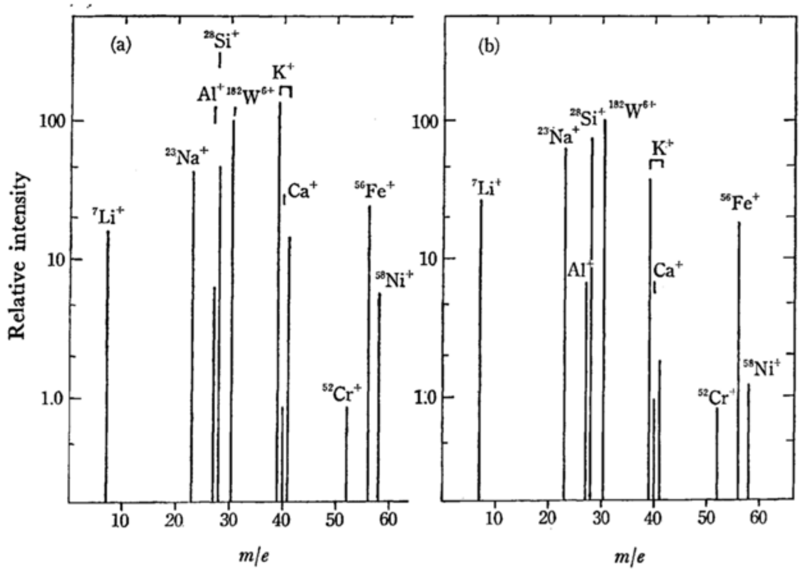


Fig. 4. Impurity spectra of tungsten filaments, (a) doped filamement, (b) undoped filament.

Results

Analysis of Impurities in the Tungsten Filaments. Mass spectra obtained by the spark discharge are shown in Fig. 4. (a) shows the result with the doped filament, and (b) shows that of the undoped filament. Both filaments contain K, Na, Li, Al, Si, Ca, Fe, Ni, and Cr as impurities. There is some difference in the quantitative distribution of these impurities between the two samples, but the difference is not remarkable. Therefore, it was found that unless a filament is manufactured particularly free of alkali metals, even an undoped filament contains some amount of alkali metal. As no precaution to remove surface contamination was taken before analysis, the impurities may include the surface contamination. Although a large difference of impurities was not observed between both filaments, after flashing, the background positive ion emission from the undoped filament was smaller than that of the doped one.

Total Positive Ion Emission. The total positive ion emission from the heated filament in vacuum and in halogen gas was measured by the diode tube shown in Fig. 1. The tungsten filament used here was the doped one. Before the measurement, the filament was flashed at about 2000°C for 30 min in a vacuum of 1×10^{-6} Torr. After the positive ion emission attained a constant value at a certain temperature, chlorine was introduced about 5×10^{-3} Torr by Pirani gauge, and then pumped out after a few minutes. The total positive ion emission during the procedure is shown in Fig. 5.

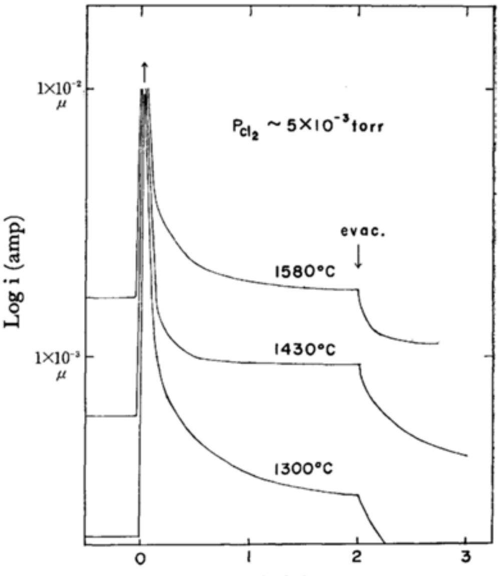


Fig. 5. Behavior of total positive ion emission in chlorine.

At the instant of introduction of chlorine, the positive ion emission increased for a moment and then decreased rapidly, but the final amount was greater than that before the introduction of the chlorine. When the chlorine was pumped out, the positive ion emission again decreased rapidly until it reached a value which was smaller than that before the introduction.

From these results, it was concluded that the positive ion emission in the chlorine is greater than that before the introduction and the increased background emission is greater at higher filament temperature.

Mass Spectroscopic Analysis of Thermally Emitted Ions. The thermally emitted ions from the tungsten filament were mass analyzed using the ion source shown in Fig. 3 (a). The doped filament was used for this purpose. Main ions observed were K^+ and Na^+. Quantity of the total ions measured by a monitor electrode of the mass spectroscope was larger by a hundred times in chlorine than in a vacuum.

Figures 6, 7, 8, and 9 show mass spectra of emitted positive ions. Figure 6 shows the spectra with and without chlorine under the same exposure time. In chlorine, intensity of K^+ increased greatly, and Cr^+, Ca^+, Fe^+, Cl^+ and Cl_2^+ were also observed. In Fig. 7, the effect of bromine for the same exposure is given. In bromine, emission of K^+ and Na^+ increased, and Al^+, Si^+, Cr^+, Mn^+, Fe^+, Co^+, Ni^+, Br^+, and Br^{2+} were observed.

Negative ions formed by surface ionization were also examined, but only Cl^- and Br^- were detected.

In Fig. 8, the emission from the doped filament in oxygen and in a vaccum is compared. In oxygen, emission of K^+ and Na^+ increased greatly as in chlorine and bromine. Difference in the

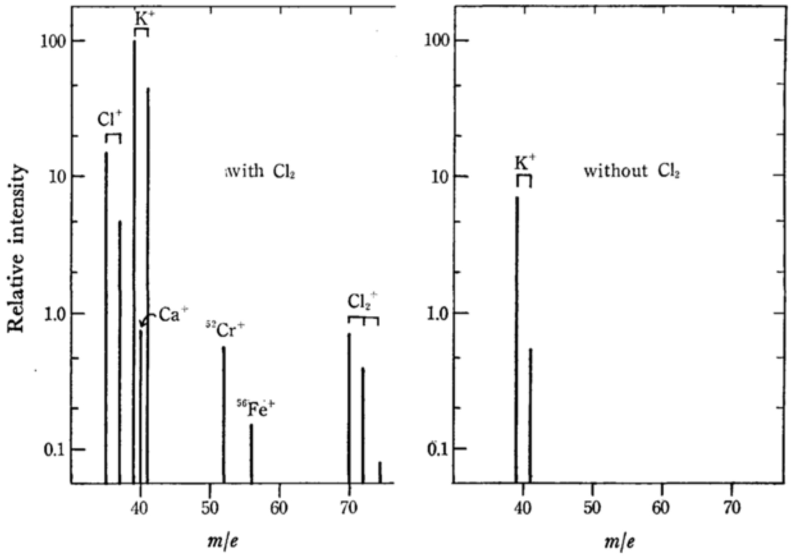


Fig. 6. Surface ionized ions from a doped filament, (a) in chlorine, (b) without chlorine.

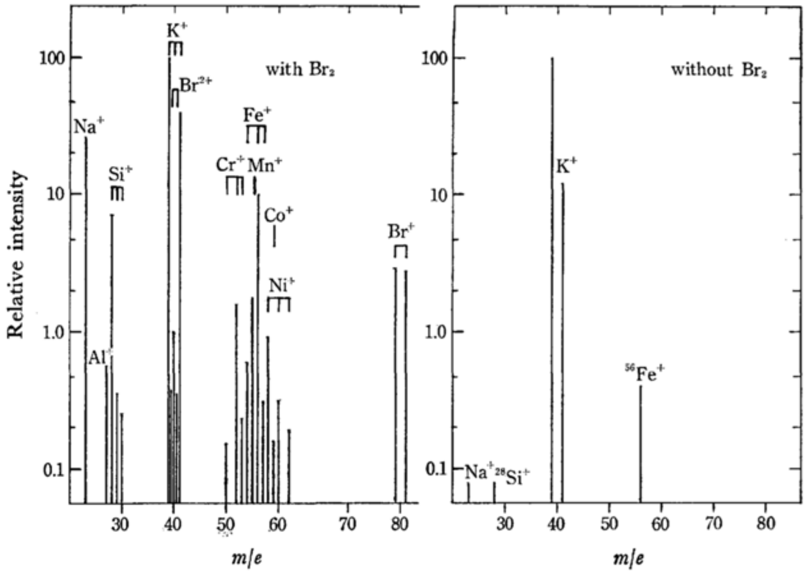


Fig. 7. Surface ionized ions from a doped filament, (a) in bromine, (b) without bromine.

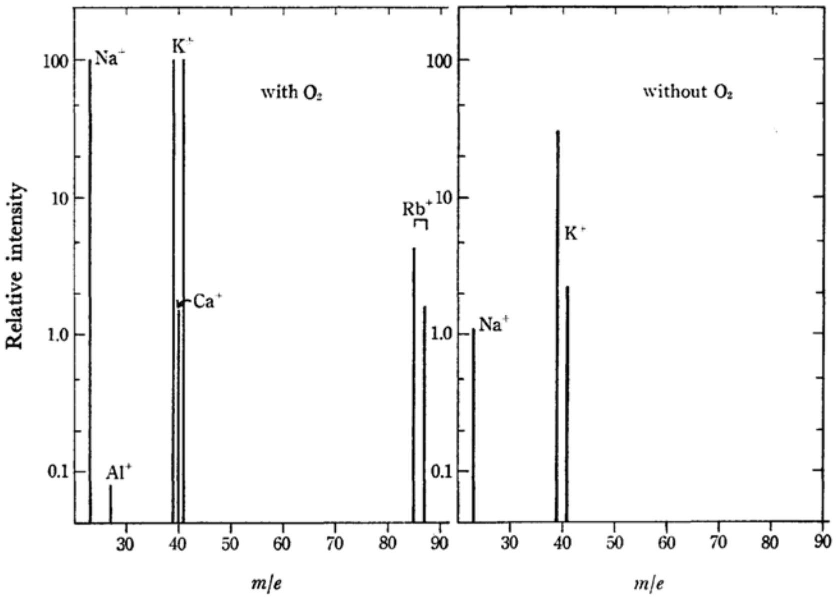


Fig. 8. Surface ionized ions from a doped filament, (a) in oxygen (b) without oxygen.

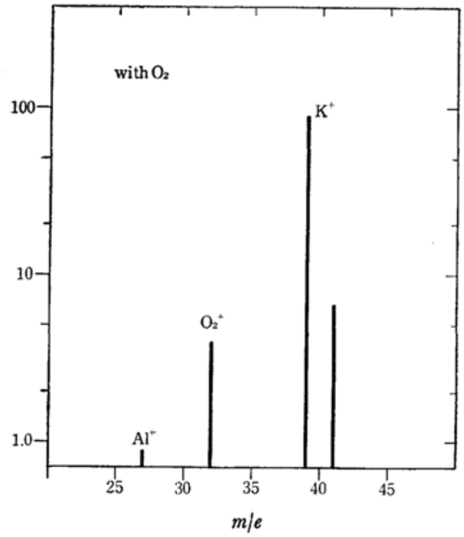


Fig. 9. Surface ionized ions from an undoped filament in oxygen.

emission in oxygen and in halogen is that no metal ions other than a small amount of Al$^+$ was observed in case of the former. With doped filament shown in Fig. 9, O$_2^+$ was detected. In both cases O$^+$ was out of the range of detection, and it is not certain that this ion was emitted or not. In some cases Rb$^+$ was found in oxygen but it was not possible to conclude under what condition Rb$^+$ emission could be detected, because the number of runs in oxygen was not enough. In runs with chlorine and bromine, Rb$^+$ was out of the range of detection.

In the above experiments, no ion of the reaction product of tungsten and halogen or oxygen were found. Thereforr, it is expected that tungsten halides or oxides formed evaporate as neutral particles.

Identification of Neutral Particles by Mass Spectroscopy. Mass spectrum of neutral particles formed in chlorine is shown in Fig. 10. Ions of tungsten atoms, tungsten oxides, tungsten chlorides, and tungsten oxychlorides were observed. The detected species are W$^+$, WO$^+$, WOH$^+$, WO$_2^+$, WCl$^+$, WO$_2$Cl$^+$, WCl$_2^+$, WOCl$_2^+$, WO$_2$Cl$_2^+$, WCl$_3^+$, WOCl$_3^+$, (WO$_2$Cl$_3^+$), WCl$_4^+$, and WCl$_5^+$. Thus, it is confirmed that the chlorine reacted with the tungsten filament and products formed evaporated as neutral particles.

In Fig. 11, neutral particles formed in oxygen are shown. WO$^+$ and WO$_2^+$ were found in addition to W$^+$, but not WO$_3^+$.

Discussion

By the experiment of the thermal emission, Cl$^+$, Br$^+$, Cl$_2^+$, Br^{2+}, and O$_2^+$ were found. As these atoms or molecules have higher ionization potentials than the electron affinity of tungsten or oxidized tungsten, it is impossible to assume that these ions were formed by the surface ionization from the standpoint of the Saha-Langmuir equation. A more probable explanation is that these ions were formed by the ion impact of chlorine, bromine or oxygen molecules around the filament, because increased positive ions (mainly alkali metal ions) could be accelerated sufficiently by the ion acceleration potential of 15 keV to ionize these molecules.

In the neutral particles evaporated from the

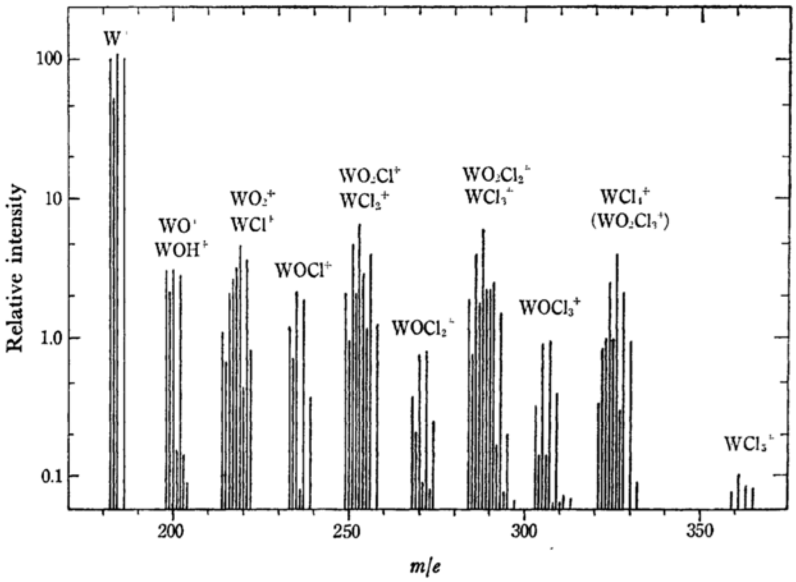


Fig. 10. Mass spectrum of neutral particles from a doped filament in chlorine.

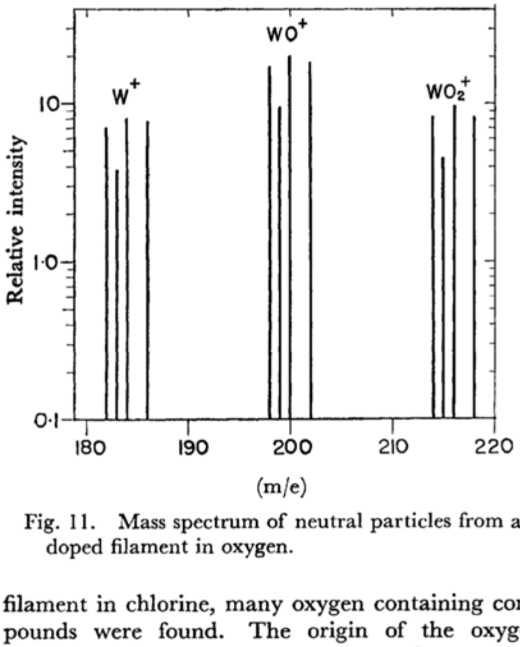


Fig. 11. Mass spectrum of neutral particles from a doped filament in oxygen.

filament in chlorine, many oxygen containing compounds were found. The origin of the oxygen should be traced. Probable sources of oxygen are the residual oxygen or water vapor in the ion source chamber, impurity in the chlorine, and the oxygen contained in the tungsten filament.

During the runs, vacuum in the ion source chamber was about 3×10^{-6} Torr and the amount of oxygen in the compounds was comparable with that of chlorine, so it is difficult to attribute the source of the oxygen entirely to the residual gas. However, there might be some contribution of the water vapor, because some hydroxy compound was seen in the mass spectrum. Impurity in the chlorine is not probable either, bacause pure sample was used and gas inlet system was evacuated carefull before the introduction of chlorine.

During the process of manufacture of tungsten filament, there are many chances that oxides are mixed. For this experiment, doped filament was used. In the process of doping, K, Na, Si, and Al are added to the tungsten powder in the form of salts. These salts are converted into oxides during the manufacturing procedure. Since the filament contains oxygen and impurities in approximately equivalent amount, it may be considered the most probable source of the oxygen.

In oxygen, W^+, WO^+, and WO_2^+ were observed as mentioned above. Berkowitz-Mattuck *et al.*[5] studied the reaction of oxygen with heated tungsten surface. They heated a piece of tungsten plate from the back by thermal radiation and electron bombardment from a W-Re filament placed behind it. A stream of oxygen from a nozzle was applied against the heated surface and neutral particles evaporated from the surface was introduced into the ion source of a mass spectrometer before any collision had occurred in the gas phase and were ionized by electron impact and mass analyzed. Oxides produced at the temperature region of 1500—2600° K were studied. Main oxides found were WO_2 and WO_3. At high temperatures WO_2 was more abundant than WO_3, but no WO was found. They proved that WO_2 was not a fragmentation product of WO_3. In a run under oxygen pressure of 7.2×10^{-4} Torr, the amount of WO_3 was

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5) J. B. Berkowitz-Mattuck, A. Büchler, J. L. Engelke and S. N. Goldstein, *J. Chem. Phys.*, **39**, 2722 (1963).

maximum at 1875° K and that of WO_2 was maximum at 2200° K. At 2600° K, almost no WO_3 was seen.

As the sample filament was used as an electron emitter in the present experiment, the filament temperature was considerably high. The filament temperature could not be measured, but it might be considerably higher than 2600° K considering from the heating current. At this temperature, existence of lower oxides WO may be probable. Existence of WO^+ has been observed by Bennighoven⁶⁾ and Rybalko, Kalot, and Fogel',⁷⁾ although their experiments were somewhat different from the present ones. In these studies, oxidized tungsten surface was bombarded by Ar^+. W^+, WO^+, WO_2^+, and WO_3^+ were found by Benninghoven, and in addition ot these oxides, many other oxides were found by Rybalko *et al.*

It should be noticed that the ions observed under the electron bombardment might come from the first slit surface where the tungsten compounds might deposit while the filament was heated in the gases. But the existence of the deposit also indicates that some neutral tungsten compounds were evaporated from the filament.

It is difficult to attribute the unusual increase of positive ion emission from the heated tungsten surface in chlorine, bromine, and oxygen to the increase of the work function of tungsten by adsorbed halogen or oxygen, because, as mentioned above, the ionization efficiency of potassium on clean tungsten surface should be high and no great increase of the positive ion emission can be expected. However, for the emission of metal ions other than alkali metals, the increase of the work function may be responsible. Therefore, an entirely different mechanism should be considered.

When halogen is introduced around the tungsten filament, it reacts with the tungsten surface and tungsten halides and oxyhalides will evaporate as the reaction products. By the evaporation of these products, alkali metal atoms contained in the bulk of the tungsten are exposed to the surface and emitted as positive ions. In Fig. 5, it is seen that, when chlorine is introduced, the positive ion emission increased for the moment and decreased rapidly again. This means there is a concentrated layer of alkali metal atoms at the filament surface, and removal of the surface by the reaction causes the sudden increase of the positive ion emission. When the filament is heated at high temperatures, alkali metal atoms inside the bulk diffuse towards the surface and evaporate. The difference between the diffusion rate and the evaporation rate will build a concentrated layer of alkali metal atoms just under the surface. After the concentrated layer of alkali metal atoms are removed by the reaction, rate of the emission of the positive ions is controlled by the corrosion rate of the tungsten by chlorine. But without chlorine, the emission rate is controlled by the diffusion rate of alkali metal atoms in the bulk of the tungsten.

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6) A. Benninghoven, *Z. Physik*, **220**, 159 (1969).

7) U. F. Rybalko, V. Ja. Kolot and Ja. M. Fogel' will be presented to the International Conf. on Mass Spectrometry, Kyoto (1969).