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CHEMICAL REACTIONS AT VERY LOW PRESSURES.
I. THE CLEAN-UP OF OXYGEN IN A TUNGSTEN LAMP.[1]

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About three years ago we had occasion to measure the amounts of gas given off by a tungsten wire when heated in a vacuum. We were surprised to find that amounts of gas as great as 1000 times the volume of the filament were apparently given off without any indication that the source of supply was nearing exhaustion. Careful investigation showed that the gas really came from the decomposition of the vapor of vaseline used on a stopcock, placed between the vacuum pump and the lamp containing the tungsten wire. The apparatus was therefore reconstructed, avoiding the use of stopcocks, but still the steady evolution of gas was observed when the filament was heated, although at a much smaller rate than previously. The source of this gas was found to be water vapor given off by the glass of the bulb, which, coming into contact with the heated wire, produced hydrogen and oxidized the tungsten. The hydrogen was indicated by the McLeod gage, whereas the water vapor had not been. Further study showed that, to avoid such evolution of gases, the bulb must be heated to a temperature of at least 360° for an hour or more, after the lamp has been exhausted with a mercury pump. During this heating of the bulb, it is necessary to absorb the water vapor with phosphorus pentoxide, or, much better, with liquid air. In order to be able to measure the quantities of gas accurately, we avoided the use of charcoal or any other porous material in connection with liquid air, but depended simply upon the low temperature to condense out water vapor and carbon dioxide. For this purpose the tube connecting the lamp bulb with the rest of the

apparatus was bent in the form of a U, which was kept immersed in liquid air during the whole of the experiment.

When these precautions were taken, it was found that relatively little gas was evolved when the filament was heated. The gas actually obtained from the filament was given off nearly instantaneously when the metal was heated for the first time to a temperature exceeding about 1500°. This gas usually amounts to from three to ten times the volume of the filament,[1] and consists mostly of carbon monoxide.

It may be of interest to give the results of the analysis of the gas given off from the bulb during the heating to 360°. Before heating the bulb, it was thoroughly dried out at room temperature over liquid air and the gases obtained in this way were pumped out and rejected. Upon then heating the bulb to 360° for an hour, the gases given off were approximately as follows:

> 300 cu. mm. water vapor
> 20 cu. mm. carbon dioxide
> 4 cu. mm. nitrogen

The bulb in this case was an ordinary, 40 watt tungsten lamp bulb, made of lead glass. For a description of the method of analysis used, see THIS JOURNAL, **34,** 1313 (1912).

In all of the work described in this paper, pressures were measured by a McLeod gage which was capable of measuring accurately to pressures as low as 0.01 micron of mercury (0.00001 mm. of mercury). From the known volume of the system and the pressure in it, we calculated the number of cubic millimeters of gas in the system, and the results in general are given in terms of quantity of gas, rather than in pressures.

We have very carefully tested out the reliability of the McLeod gage and find that for all gases that are not condensed in a vacuum system at the temperature of —78° (solid carbon dioxide and acetone), the McLeod gage gives extremely accurate results. But this gage does not correctly indicate the pressure of such easily condensible gases as water vapor, oil vapor, or mercury vapor, nor does it indicate correctly the pressure of any gas in the presence of even small amounts of water vapor.

During some of the experiments on the evolution of gas from a tungsten wire, we noticed that, if the filament was heated at a high temperature in gas which had previously been given off by the filament or obtained in any other way, the pressure would gradually decrease.

This clean-up of gas was known to exist in ordinary commercial tungsten lamps. There are several indications of this. In the first place, it was known that when a tungsten lamp is first lighted, after having been sealed off from the pump, there nearly always occurs a flash of blue glow in the

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[1] All volumes of gas given in this paper are supposed to be measured at atmospheric pressure and at room temperature.

lamp. This gradually becomes less intense, and finally, after flickering a few times, completely disappears. Other indications were obtained by attaching a radiometer to the lamp bulb. If, by swinging the lamp, the radiometer vanes were set in rotation, the time necessary for them to come to rest was at first only a few minutes. After the lamp had been burning several hours, the time necessary for the radiometer to stop increased to about an hour. Another and more accurate way of indicating this change in pressure is by means of quartz fiber, placed in the lamp bulb, close to the filaments, one end being attached to the glass close to the base of the lamp, and the other end swinging freely in the vacuum. In one typical experiment the pressure had been 0.018 micron, at the moment of sealing the lamp off from the pump. Upon shaking the lamp so that the fiber was set in vibration and then placing the lamp in a quiet place, it was found that it took 66 minutes for the amplitude of the vibrations to become one-half the original amount. After this lamp had been running at 1 w. p. c. for about 3 hours, the time necessary for the amplitude to decrease 50% had become 115 minutes. In other words, the amount of damping of the filament had decreased in the ratio of 1.75 : 1. This indicates that the pressure must have been at least as low as 0.010 microns, and presumably very much lower, because even in a perfect vacuum, the filament would probably not have vibrated much longer than 115 minutes to half amplitude.

Evidence of a clean-up of gas in presence of electric discharges is not uncommon. For example, it is well known that in the Moore tube, or in Geissler tubes in general, the vacuum steadily improves. The same observation has repeatedly been made in Röntgen ray tubes. It has been generally assumed that the gas in these cases is driven into the electrodes, or into the glass, or is absorbed by the metal which sputters from the cathode.

In order to gain a clear insight into the nature of the changes occurring in tungsten lamps during life, it was decided to investigate in some detail the causes of the clean-up in such lamps and to study the behavior of various gases in this regard.

Clean-up of Hydrogen.

When a tungsten filament is heated above 1300° K[1] in hydrogen, at low pressures, the hydrogen gradually disappears. It has been shown in a previous paper[2] that this action is caused by the hydrogen becoming dissociated into atoms in contact with the filament, the atoms then being driven on to the bulb, and there held by adsorption or some other cause.

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[1] In this paper the letter K (Kelvin) will be used to denote absolute temperatures, in accordance with the recommendations of the Association International du Froid. See *Chem. Ztg.*, **35**, 3 (1911).

[2] This JOURNAL, **34**, 1310 (1912).

The hydrogen on the bulb is in a particularly active form and is capable of reacting, at room temperature, with oxygen.

Since these experiments were made, further investigation of the clean-up of hydrogen has been carried on and interesting results have been obtained. These, however, will be given in a subsequent paper.

Clean-up of Oxygen.

It is well known that metallic tungsten oxidizes in the air at a red heat and becomes covered with a layer of the yellow oxide, WO_3. At a white heat, the oxide volatilizes easily, forming a yellowish white smoke.

The first experiments with a heated tungsten filament in oxygen at a very low pressure showed that the oxygen disappeared fairly rapidly, without producing any darkening of the bulb. The rate of disappearance was proportional to the pressure of oxygen, but if the temperature of the filament was above $1500°$ K the rate did not seem to increase very rapidly with rising temperature. Also, when different lengths of filament were heated in the same bulb, the rate was found not to vary in proportion to the surface of the filament. Further investigation showed that the measured rate was to some extent limited by the rate of diffusion of the gas from the pump bulb and McLeod gage over into the lamp bulb. At low pressures much longer times are necessary for the equalization of pressures than at ordinary pressures.

To avoid this resistance to the flow of the oxygen, several changes were made in the apparatus.

The apparatus used for the final experiment (Exp. 265) is diagrammatically represented in Fig. 1. The lamp bulb B was made large (1020 cc.), so as to have as large a proportion of the oxygen as possible in immediate contact with the filaments. Below the lamp is a tube, L, immersed in liquid air, which serves to exclude mercury vapor from the lamp. The lamp contained three sections of filaments with four leading-in wires, so that any one of the sections could be heated to any desired temperature.
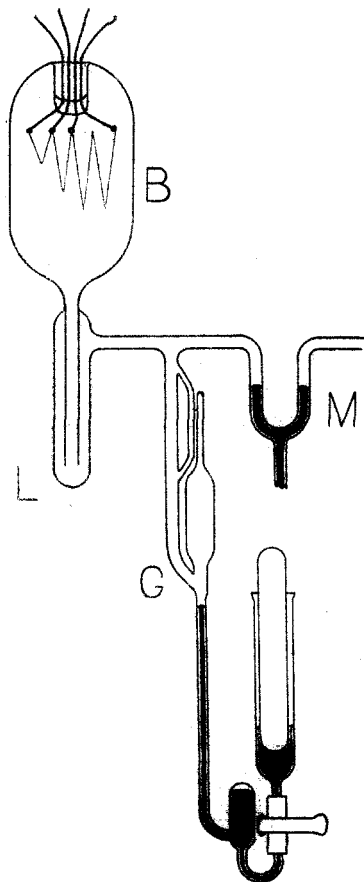

Fig. 1.

The diameter of the wire was 0.0394 mm.   The lengths of the sections were:

Section.	Length.	Area.
a	5.4 cm.	0.067 sq. cm.
b	14.6 "	0.181 " "
c	47.0 "	0.583 " "

The tubing between the bulb and the McLeod gage G was made as short as possible, about 25 cm., and of large diameter (about 0.8 mm. internal diameter), so that the resistance offered to the flow of gas would be as small as possible.   For the same reason the volume of the McLeod gage was made small (50 cc.).   The apparatus was exhausted by a Töpler pump through the mercury seal M, through which also fresh supplies of oxygen were admitted.

After thoroughly exhausting the system (bulb heated 1 hour at 360°) and freeing from water vapor and carbon dioxide, a definit amount of pure oxygen was admitted, and the seal M closed.   After taking a reading of the gage the current was suddenly turned on the filament, so as to heat it very rapidly to the desired temperature.   Readings of the gage were taken regularly every minute.   With the longest section of filament, especially at the higher temperatures, the oxygen disappeared so rapidly that it was nearly gone in one minute.   In these cases the current was turned off after a few seconds and a reading of the gage taken.   The time intervals were measured by a stopwatch.

When the filament was heated to a temperature between 900° and 1200° K in oxygen, it immediately became coated with an oxide film which was at first straw-colored and gradually changed to dark blue and then to a dull brown.   Simultaneously, the filament cooled off considerably and ceased to be even red hot, so that the current had to be increased considerably to maintain the original temperature.   If the temperature was now raised to 1300°, bright spots appeared which gradually extended along the whole filament.   When the filament had become uniform, it was found that the oxide film had entirely disappeared and that a given current would heat the filament to the same temperature as originally.

The reason for the cooling of the filament is undoubtedly that the oxide is a better radiator of heat than the bright metal.   The experiment indicates that the oxide volatilizes in a vacuum at a temperature of about 1300°.   The disappearance of the oxide is not due to dissociation of the oxide, for no evolution of gas occurs when the oxide film disappears.

At temperatures above 1250°, the surface of the filament always remains bright, even after long treatment in oxygen.

Fig. 2 gives a typical curve showing the way the pressure of oxygen decreases with the time.   In this case section a of the filament was heated to 1470°.   The ordinates represent the total amount (in cubic mm.) of

oxygen gas remaining in the system (bulb, gage, and tubing). The volume of the system being 1075 cc., one cubic mm. of gas corresponds to a pressure of 0.706 microns.
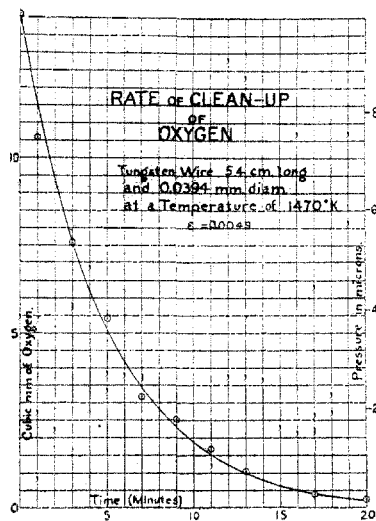

In practically every case the curves obtained were as smooth as this. Sometimes the gas would not completely disappear, but a slight residue, which proved to be nitrogen or carbon monoxide, would remain. In these cases this amount was subtracted from the other readings before drawing further conclusions from the results. Before admitting fresh oxygen, these residues of foreign gases were always pumped out.

In some of the early experiments it had been found that the rate of clean-up of the oxygen was nearly independent of the temperature of the filament. One of the hypotheses that seemed to account for this was that the observed rate was simply the rate at which the oxygen came into contact with the filament.

Fig. 2.

It became of interest, therefore, to calculate from the kinetic theory at what rate a gas at low pressures would come into contact with a solid body.

Calculation of Greatest Possible Rate of Clean-up.—Let us consider a square centimeter of a surface exposed to the pressure of a gas. According to the kinetic theory, the pressure is caused by the impact of the molecules. Let v be the average velocity with which the molecules strike the surface and let m be the mass of the molecules which strike a square centimeter of surface per second. Now, according to the laws of mechanics, the force exerted by a series of collisions is equal to the momentum given up to the surface per unit time. Since the molecules leave with the same velocity with which they strike the surface, the momentum given up per second will be m $\times$ 2 v. This is equal to the pressure, whence

$$(1) \qquad\qquad m = p/2v.$$

We can thus calculate the mass of gas which comes into contact with each sq. cm. of surface, if we know the pressure and the average velocity of the molecules.

According to the kinetic theory, the mean square velocity $\overline{v}^2$ of the molecules in a gas can be calculated from the equation

$$(2) \qquad\qquad p = \tfrac{1}{3}d\overline{v}^2$$

where d = density of the gas.

The ordinary gas law $pv = RT$ can be written

(3) $$p = \mathbf{d}RT/M$$

where M = molecular wt.

Combining this with equation (2), we get

(4) $$\bar{v} = \sqrt{3RT/M}.$$

If we assume that $\bar{v} = v$ then from (1) and (4) we may obtain the approximate formula

(5) $$\mathbf{m} = \sqrt{M/RT} \cdot \frac{p}{2\sqrt{3}}.$$

Knudson[1], by making use of Maxwell's distribution law, has avoided the above assumption and has obtained equations which should be rigorously correct. Careful experimental investigations have proved the accuracy of the equation. From Knudson's formulas, the following equation for the value of m is readily obtained,

$$\mathbf{m} = \sqrt{M/RT} \cdot p/\sqrt{2\pi},$$

which gives results 38% larger than the previous formula.

To apply this formula to the case in hand, we place $R = 83.2 \times 10^6$ and for oxygen $M = 32$. For room temperature (25°) T is 298°, whence

$$\mathbf{m} = 14.3 \times 10^{-6}\, p.$$

Here p is to be expressed in dynes per sq. cm. If we express p in microns of mercury, we have

$$\mathbf{m} = 19.1 \times 10^{-6}\, p \text{ grams per sec. per cm}^2.$$

One cu. mm. of oxygen at room temperature and atmospheric pressure weighs 1.30×10^{-6} grams. Hence the rate at which oxygen, at a pressure of p microns, comes in contact with one sq. cm. of surface is: $14.6 \times p$ cubic mm. per second per cm^2.

Now, in general, not all of the oxygen molecules which strike the filament will combine with it, but only a certain proportion will do so.

Let us represent by ε the ratio of the actual rate at which oxygen disappears to the rate which would prevail if the oxygen combined with the filament as fast as it comes into contact with it. Let q be the quantity of oxygen in the system at any time, t. Then we have

(8) $$dq/dt = \varepsilon \times 14.6\, pA$$

where q is expressed in cu. mm. at 298° K and atmospheric pressure

p = pressure in microns of mercury

A = area of filament in sq. cm.

t = time in seconds

ε = fraction of molecules of oxygen which strike the filament that combine with it.

The quantity of gas q in the system can be readily calculated from the

[1] Knudson, *Ann. Phys.*, **28**, 999 (1908).

pressure and temperature of the gas and the volume of the system. In the present experiments, the volumes of the different parts of the apparatus had been measured. If the lamp bulb is at room temperature, we have

$$q = pv/760$$

where

q = quantity of gas in the whole system in cubic mm. at 760 mm. pressure and $25°$

p = pressure in microns

v = volume of system in cc.

When any part of the apparatus, for example, the lamp bulb, is heated above room temperature, then in calculating v we add the volumes of the various parts at room temperature and then add the product of the lamp volume by the square root of the ratio of the absolute room temperature to the bulb temperature. That is, if the bulb is at $300°$ ($573°$ abs.), instead of taking its real volume, 1020 cc., we take $1020 \times \sqrt{298/573} = 734$ cc. Knudson[1] explains fully the reason for multiplying by the square root of the temperature ratio. We have thoroughly tested out this rule and find that at pressures below about 10 microns, it holds accurately. Let v_0 be the effective volume of the system, as calculated above; then we have

(9) $$q = pv_0/760$$

By combining (8) and (9) we obtain:

$$dq/dt = 11,100 \, \varepsilon \, q \, A /v_0$$

whence

(10) $$\varepsilon = 207 \times 10^{-6} \frac{v_0}{At} \log \frac{q_0}{q}.$$

Here q_0 is the amount of gas originally present and q is the amount after t seconds. v_0 and A are expressed in cm. units.

Results of Experiments.—Such a large number of experiments were made that it would be impracticable to give anything more than a summary of the results along with a few typical illustrations. A particular study was made of the effect of the following four factors on the rate of clean-up:

1. Pressure.
2. Length of filament.
3. Temperature of filament.
4. Temperature of bulb.

Previous experiments with smaller bulbs had shown that the oxygen, even at the lowest pressures, combined with the filament to form WO_3. This was found by determining the loss in weight of a filament during treatment in oxygen and comparing this loss with the amount of oxygen which disappeared. An additional check was had by measuring the in-

[1] *Ann. Phys.*, 31, 205 (1910).

crease in the electrical resistance of the filament when cold and also when heated. The specific resistance and the temperature coefficient of the resistance are not affected by heating in oxygen. From the changes in resistance, the change in diameter could be calculated and was found to agree well with that obtained by direct weighing after breaking open the lamp. In all the experiments, the ratio of loss of weight to the weight of oxygen cleaned up was very close to that calculated from the ratio $W : 3O$.

Only in rare instances was enough oxide deposited on the bulb to be visible; whereas, if the equivalent amount of tungsten had been on the bulb, it would have been nearly black. This is an indication that the oxide must be of very light color.

It is an interesting fact that when tungsten is heated to a very high temperature in nitrogen which contains traces of oxygen the blue oxide W_2O_5 is formed. In pure oxygen at either high or low pressures this oxide never seems to be formed, except when the temperature is so low that the oxide remains on the filament instead of distilling off. This fact would indicate that the yellow trioxide is produced extremely rapidly directly on the filament while the blue oxide is formed only by subsequent reduction of the trioxide.

All the experiments with oxygen gave results that were easily reproducible. The errors seemed to be only such as would occur from errors in the measurements of the temperature of the filament. In marked contrast with the experiments on the clean-up of hydrogen, we never found any indications of fatigue in the clean-up of oxygen.

1. Effect of Pressure.—In every case the value of ε was found to be practically independent of the pressure. For example, in the experiment from which the curve in Fig. 2 was obtained, the following values of ε were obtained:

Time. t.	Quantity of O_2. q.	ε.
0	14.09	
1	10.58	
3	7.59	0.0051
5	5.42	
7	3.20	
9	2.50	0.0045
11	1.66	
13	1.05	
17	0.40	0.0049
20	0.25	
23	0.18	

The curve given in Fig. 2 was calculated from equation (10) by taking $\varepsilon = 0.0049$, $A = 0.067$, $v_0 = 1075$. The equation thus becomes:

$$\varepsilon = \frac{0.0554}{t} \log \frac{q_0}{q}$$

where t is the time in minutes. It was from this equation also that the values of ε in the above table were calculated. It is seen from Fig. 2 that the calculated curve agrees well with the points determined by experiment.

This independence of ε from the pressure has been tested and found to hold for pressures as high as 50 and as low as 0.2 microns.

The fact that ε is independent of the pressure means simply that the rate of clean-up is strictly proportional to the pressure; in other words, the reaction acts like a monomolecular reaction.

2. *Effect of Length of Filament.*—Sections A, B, and C were, respectively, 5, 15, and 47 cm. long, yet as is shown clearly in Tables I, II, and III, the values of ε obtained were practically the same from each. This simply means that the rate of clean-up is strictly proportional to the surface of the filament.

TABLE I.—Values of ε from Exp. 265.

Temp. of filament.	Section A.	Section B.	Section C.
1270° K	0.0010	0.0011	0.0014
1470	0.0049	0.0049	0.0055
1470			0.0059
1570	0.0092	0.0091	0.0099
1770	0.021	0.024	0.027
1770	0.025	0.027	0.027
1770	0.026	0.024	. .
1770	0.028	. .	. .

TABLE II.—Effect of heating bulb.

Values of ε from Exp. 265.

Temp. of filament.	Section B. Temperature of bulb.		Section C. Temperature of bulb.	
	23°.	300°.	23°.	300°.
1270° K	0.0011	0.0012	0.0014	0.0013
1470	0.0049	0.0042	0.0057	0.0053
1570	0.0091	0.0078	. .	. .
1770	0.0250	0.0183	. .	. .

TABLE III.—Values of ε from Exp. 265.

Temp. of filament.	Section A.	Section B.	Section C.
900–1070° K	0.00036	0.00035	0.00033
1270	. .	0.0016	0.0015
1770	0.022	0.026	0.023
2020	0.043	0.049	0.046
2290	0.095	0.068	0.080
2340	. . .	. . .	0.084
2520	0.122	0.075	0.090
2770	0.15	0.095	0.115

3. *Effect of Temperature of Filament.*—In Tables I, II, and III are given the values of ε from Exp. 265, in which the apparatus was arranged as indicated in Fig. 1. The separate runs were made in about the order

given in the table. The temperatures were obtained from photometer measurements on a lamp made from another piece of the same wire. From the candle power per sq. cm. of surface the temperature was obtained and from this a curve giving the relation between current and temperature was plotted by use of a formula previously given.[1] After the lamp in Exp. 265 had been exhausted and the filaments aged by heating one-half hour at a very high temperature, the relation between voltage and current, and hence temperature, was obtained. From these data a curve was plotted giving $V\sqrt[3]{A}$ for each of the filaments as a function of the temperature. (Here V = volts; A = amperes.) This function remains constant even when the diameter of the filament changes between wide limits, and it was by its use that the temperature measurements were made after the filament had been attacked, to any serious extent, by the oxygen. Towards the end of the experiment the resistances (at 25°) of the three sections of the filament had increased up to the following percentages of the original resistance:

Section A increased to 142%
B   191%
C   121%

The areas A were therefore reduced as follows:

See A reduced to 84% of orig. surface
B reduced to 72% of orig. surface
C reduced to 90% of orig. surface

In Table III corrections were made in ε to correspond to these changes in surface. The filaments were reduced very uniformly in diameter, as was apparent from the uniform intensity of the light emitted from them.

The irregularities in the values of ε at higher temperatures and in the latter runs are probably due to errors in temperature measurements and to the difficulties in measuring the extremely high rates of clean-up which occurred at the highest temperatures.

TABLE IV.—Rate of clean-up of oxygen at various temperatures.

Temp. K.	ε observed.	ε cal. by (12).	ε cal. by (26).
1070° K	0.00033	0.00016	0.000171
1270	0.0011	0.00123	0.00124
1470	0.0053	0.00525	0.00528
1570	0.0094	0.0095	0.00953
1770	0.0255	0.0256	0.0256
2020	0.049	0.066	0.0664
2290	0.095	0.148	0.150
2520	0.12	0.26	0.264
2770	0.15	0.42	0.426
3000	...	0.60	0.64
3500	...	1.16	1.28

At 2770° K the rate of clean-up was so rapid with Section C that the

[1] *Trans. Amer. Electrochem. Soc.*, **20**, 233 (1911).

quantity of oxygen decreased from 14.90 cu. mm. to 2.64 cu. mm. in three seconds. With Section A, at the same temperature, the gas changed from 7.55 to 2.88 cu. mm. in 12 seconds.

The second column of Table IV gives the most probable values of ε taken from Tables I, II, and III. The data for temperatures from 1220 to 1770 are obtained by taking the means of the values in Table I, these being considered the most reliable, as the filaments had not been altered much by oxidation during these runs. For temperatures above 1770 the highest of the values in Table III were chosen, for the possible errors would seem to make the observed values too low.

The rate of increase of ε with the temperature agreed well with Arrhenius' formula

(11) $d \ln \varepsilon / dT = \mathbf{A} / T^2$

The following equation, obtained from the above by integration and choice of suitable constants, was found to be in excellent agreement with the experimental results obtained between 1220 and 1770°,

(12) $\log \varepsilon = 1.76 - 5940 / T.$

The values of ε calculated for various temperatures from this equation are given in the third column of Table IV. The deviation of the observed from the calculated results at high temperatures is to be expected, as the above equation leads at 3500° to values of ε above unity and this we know, from the kinetic theory, must be impossible.

4. *Effect of Temperature of the Bulb.*—The conditions which prevail during the reaction of the oxygen with the tungsten in the present experiments differ in several essential features from those which obtain in ordinary reactions between solids and gases at atmospheric pressure.

The pressures we deal with are so low that the normal free path of the molecules is between about 1 and 10 cm. This means that relatively few of the oxygen molecules which travel from the surface of the bulb to the filament strike other molecules on the way. With the relatively small surface of the filament as compared with that of the bulb, the chance that a molecule leaving the filament should get back to the filament without first striking the bulb several times is negligibly small. The average velocity of the oxygen molecules striking the filament is therefore not perceptibly influenced by the temperature to which the filament may be heated. In other words, the filament may be at one temperature and the oxygen with which it comes into actual contact may be at a totally different temperature. At ordinary pressures this would be quite impossible, for the gas, within a layer many hundreds of times thicker than the length of the free path, would be heated nearly to the temperature of the filament, so that the gas in actual contact with the metal would be practically at the same temperature as the metal itself.

That there is no great temperature drop at the surface between a metal and a gas at ordinary pressures has been amply proven.[1]

A direct experimental indication that the behavior of a gas at low pressures may be quite different from that at high pressures is easily obtained. For example, we find that with nitrogen at atmospheric pressures or even down as low as 100 microns, there is a sudden and marked increase in pressure upon lighting the filament. When, however, the pressure is 10 microns or less, there is no indication whatever on the McLeod gage of any such change in pressure upon lighting the filament, although the sensitiveness of the gage would be ample to detect such a change if it were relatively nearly as great as at higher pressures.

All of our previous knowledge of reactions between solids and gases is based upon results obtained when the two are at the same temperature. There were therefore no data which would indicate whether it was the temperature of the metal or that of the gas which would be the more important factor in the reaction.

In the earlier experiments (Exp. 211) the rate of clean-up had appeared nearly independent of the temperature of the filament. At that time the effect of heating the bulb to 360° and of cooling it to −183° by immersing it in liquid air was tried, and it was found that the temperature of the bulb was entirely without effect. The value of ε obtained in these experiments was 0.0072 at a temperature of 1770° K with a filament having a surface of 0.126 sq. cm. When we found that these results were too low because of the resistance to diffusion in the tubing, it became necessary to test out the effect of the bulb temperature again with the new apparatus (Exp. 265). The bulb, however, in this case was so large that it was impracticable to cool it with liquid air and we had to remain content with heating it to 300°. The results obtained in this way are given in Table II, columns 3 and 5.

It will be seen that raising the temperature of the oxygen around the filament from 25 to 300° makes no appreciable change in the value of ε.

This result is rather surprising. According to the ordinary conceptions of the mechanism of a chemical reaction, the effect of increasing temperature is somewhat as follows: In order that a collision between two molecules may result in a chemical combination, the impact of the two molecules against each other must exceed a certain amount. At low temperatures no molecules, or only few, have velocities sufficient to produce strong enough impact. As the temperature rises the relative proportion of molecules which meet this requirement increases extremely rapidly, although still only a small proportion of the total number of collisions result in chemical action.

If the above theory is correct, one would expect that both the tem-

[1] See Knudson, *Ann. Phys.*, **34,** 593 (1911).

perature of the oxygen and that of the tungsten would influence the rate of reaction. That the actual impact between such molecules would be very greatly affected by the temperature of the oxygen appears from the following considerations:

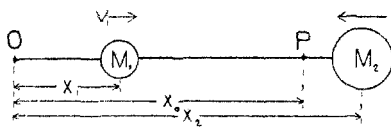Let us consider two molecules, one of molecular weight M_1 and the other of the weight M_2. Let v_1 and v_2 be the velocities of these molecules, and T_1 and T_2 the temperatures corresponding to these velocities. Let us imagine these two molecules in the positions indicated in Fig. 3 moving towards each other with the velocities v_1 and v_2. Let x_0 be the distance from O to P, the center of gravity of the system of the two molecules. Let v_0 be the velocity with which P moves from O.

Fig. 3.

By the definition of center of gravity, we have

$$\frac{x_0 - x_1}{x_2 - x_0} = \frac{M_2}{M_1}$$

or

$$\frac{x_0 - x_1}{x_2 - x_1} = \frac{M_2}{M_1 + M_2}$$

and for the corresponding velocities,

$$(13) \qquad \frac{v_0 - v_1}{-v_2 - v_1} = \frac{v_1 - v_0}{v_1 + v_2} = \frac{M_2}{M_1 + M_2}.$$

Now the impact with which they strike is proportional to the product of the mass of one of them by the velocity with which it approaches the common center of gravity. That is, the impact is measured by $(v_1 - v_0)M_1$, but from (13) this gives for the impact I,

$$(14) \qquad I = \frac{M_1 M_2}{M_1 + M_2}(v_1 + v_2).$$

Neglecting constant factors, which would ultimately cancel out, we can place, according to the kinetic theory,

$$(15) \qquad T_1 = M_1 v_1^2 \text{ and } T_2 = M_2 v_2^2,$$

whence, combining with (14),

$$(16) \qquad I = \left(\sqrt{\frac{T_1}{M_1}} + \sqrt{\frac{T_2}{M_2}}\right)\frac{M_1 M_2}{M_1 + M_2}.$$

What we now wish to find is the effect that will be produced by a change in the temperature of M_1 as compared with a change in temperature of M_2. We obtain by differentiation

$$(17) \qquad dI = \frac{\frac{1}{2}M_1 M_2}{M_1 + M_2}\left(\frac{dT_1}{\sqrt{M_1 T_1}} + \frac{dT_2}{\sqrt{M_2 T_2}}\right).$$

If we represent by dT_1 and dT_2 the temperature changes of M_1 and M_2, respectively, which will change the impact by equal amounts, we get

(18) $$\frac{dT_1}{dT_2} = \sqrt{\frac{M_1 T_1}{M_2 T_2}}.$$

Taking for oxygen, $M_1 = 32$, $T_1 = 298$, and for tungsten $M_2 = 184$, $T_2 = 1600$, we get

$$dT_1/dT_2 = 1/5.5.$$

That is, raising the temperature of the oxygen $1°$ would increase the impact between the molecules as much as raising the temperature of the tungsten $5.5°$. From Table IV we see that at $1600°$ the value of ε doubles in about $140°$ rise in temperature. Dividing this by 5.5, we see that raising the bulb temperature about $25°$ should double the value of ε if the rate of reaction is determined by the impact of the molecules. From equation (16) it can be readily calculated that with the filament at $1600°$ the impact between oxygen molecules and tungsten atoms would be increased in the ratio $6.00 : 7.20$ by raising the temperature of the oxygen from $25°$ to $300°$. If the oxygen be maintained at $25°$ we find that to produce the same increase (*i. e.*, from 6.00 to 7.20) in impact by raising the temperature of the filament, it would be necessary to raise it from $1600°$ to $3160°$. According to Table IV we see that this would increase ε from 0.010 to about 0.200. Actually, however, we find no appreciable change in ε upon heating the bulb and we must therefore conclude that it is *not* the impact of the oxygen molecules with the tungsten atoms which determines the rate of reaction.

According to the electron theory of metallic conduction of heat and electricity, metals contain free electrons which participate in the heat vibration, and have the same kinetic energy at a given temperature as the atoms of the metal. Oxygen, being an electronegative element, easily takes up electrons, so it seems probable that an oxygen molecule would be more apt to take up an electron in striking the filament than it would to combine directly with the tungsten.

Let us consider this case from the view-point of the foregoing theory. That is, let us consider the impact of an oxygen molecule and a negative electron. We will place, therefore, in equation (18)

$$M_1 = 32 \qquad\qquad T_1 = 298$$
$$M_2 = 0.0005 \qquad\qquad T_2 = 1600$$

Here, in place of $M_2 = 184$, we take $M_2 = 0.0005$, the "atomic weight" of an electron. Whence, from (18)

$$dT_1/dT_2 = 109.$$

This completely reverses the previous result, and we see that a change of $109°$ in the temperature of the oxygen would have no more effect on the amount of impact between the oxygen and the electrons than a change of

only one degree in the temperature of the filament. In other words, if the first step in the reaction consists of a collision between an electron and an oxygen molecule, we would expect to find just what the present experiments have shown, namely, that the value of ε is not affected appreciably by changing the temperature of the bulb.

This hypothesis is an entirely reasonable one. We do not need to assume that the oxygen molecule takes up more than one electron to begin with, or that the oxygen molecule is dissociated or undergoes any other change. The taking up of a single negative charge would bring into play electrostatic forces tending to hold the molecule on the surface long enough for secondary reactions to occur. These may be, for example, the taking up of more electrons, the dissociation of the molecule into charged atoms, and the combination of these with each other and with tungsten atoms to form WO_3. All these secondary reactions, however, would not influence the velocity of the reaction, since once an oxygen molecule was retained on the surface by taking up a single electron, there would then be ample time available for the subsequent changes.

On this hypothesis, the temperature coefficient of the reaction velocity may be due to two causes. First, the increased velocity of the electrons at higher temperatures, which gives a higher percentage of them capable of giving sufficient impact to produce the reaction. Second, an increase in the number of free electrons at high temperatures might cause an increase in the reaction velocity with increasing temperature of the filament.

The electron theory[1] seems to make it probable that the number of free electrons in a metal is very large and that the number of them changes very little with increasing temperature. Partly from this reason and partly because of the very high velocities of the electrons, it is probable that every oxygen molecule that strikes the filament is struck by many electrons, but is only capable of combining with those that happen to have an unusually high velocity.

There are other hypotheses, however, which may be advanced to explain the fact that ε is independent of the bulb temperature. We may assume, for example, that the surface of the metal is more or less completely covered with a film of oxide, through which the oxygen must diffuse before it can react with the metal. As the temperature of the metal increases, the oxide film would rapidly become thinner, and this fact would account for the increase in the rate of reaction as the temperature increases.

On this hypothesis, the oxygen would only react with the tungsten after it had diffused through the oxide film and hence reached the same temperature as the metal. The temperature of the bulb in this case would naturally be without effect. Undoubtedly this sort of film plays an im-

[1] See Richardson, *Trans. Am. Electrochem. Soc.*, 21, 69 (1912).

portant part in gas reactions between solids and gases at atmospheric pressure (see, for example, Bodenstein and Fink, *Z. physik. Chem.*, **60,** 46 (1907)) but it seems extremely improbable that such would be the case at very low pressures and at high temperatures. The strongest argument, however, against this theory is that the thickness of the film and hence the value of ε would vary with the pressure of the oxygen. This is, however, contrary to the results of the experiments. Another fact that indicates at least that any such film must be extremely thin is that the emissivity of the filament for both light and heat is entirely unaffected by the presence of oxygen (except below 1300°).

It must be pointed out that the reaction between oxygen and tungsten at low pressures obeys very simple laws and does not appear to be sensitiv to slight variations in the conditions. Reactions in heterogeneous systems at atmospheric pressure are usually enormously sensitive to catalytic disturbances and other irregularities which are probably characteristic of reactions that take place through an adsorbed film. Bodenstein's work on the reaction $2H_2 + O_2 = 2H_2O$ in contact with solid bodies is an example of this type of reaction. Another example is the contact process for SO_3.[1]

For all these reasons it would seem extremely improbable that there is any surface film which limits the rate of reaction. The theory that the oxygen reacts primarily with electrons in the metal is therefore made still more probable. It will be worth while to analyze the consequences of this theory more fully.

Electron Theory of Chemical Combination.

We have seen that the impact between oxygen molecules and tungsten atoms cannot be the determining factor in the reaction of oxygen with hot tungsten. The fact that the velocity of the reaction is not affected by the temperature of the oxygen indicates that the oxygen molecules react primarily with particles of very much smaller mass than themselves, therefore presumably with free negative electrons in the metal.

Since the mass of the electrons is very small, their velocity must be very large in order that they may have the same average kinetic energy as the atoms of tungsten.

From equation (16) we see that when two particles collide the amounts of impact contributed by each are proportional to $\sqrt{T/M}$. If we consider the impact between oxygen molecules with an average temperature of 298° and negative electrons with velocities corresponding to 1600°, we find that the share of the impact contributed by the oxygen is to that contributed by the tungsten as $\sqrt{298/32}$ is to $\sqrt{1600/0.00055}$. That is, the movement of the oxygen molecule is only $1/560$ as effective as that of

[1] See Bodenstein and Fink, *Z. physik. Chem.*, **60,** 1 (1907).

the electron. This difference is so great that we can neglect the velocity of the oxygen entirely in its effect on the reaction.

We have assumed that it is necessary for an electron and an oxygen molecule to collide with an impact exceeding a certain lower limit, in order that chemical combination may ultimately result. Since the velocity of the oxygen molecules is of so little importance, it is simply necessary, for chemical combination, that the electron shall strike the molecule with a velocity which exceeds a certain limit v_0.

Let us now calculate what proportion of the electrons in a metal reach the surface with a velocity exceeding a certain value v_0 and let us determin how this proportion increases as the temperature of the metal increases.

This calculation is identical with that made by Richardson[1] in determining the number of electrons that escape from incandescent metals.

Let $\mathbf{N}$ be the number of electrons in each cc. of the metal. Then, according to Maxwell's law, the number $d\mathbf{N}$ per cc. which have velocity components perpendicular to the surface of the filament lying between v and $v + dv$ is

$$(19) \qquad d\mathbf{N} = \frac{\mathbf{N}}{\sqrt{\pi}} e^{-(v/a)^2} d(v/a)$$

where

$$(20) \qquad a = \sqrt{2/3}\, \bar{v}$$

Here $\bar{v}$ is the square root of the mean square velocity of the electrons in the metal and can be calculated by equation (4).

$$(21) \qquad \bar{v} = \sqrt{\frac{3RT}{M}}.$$

The number of electrons dn with velocities between v and $v + dv$ which reach a unit surface of the metal per second can be obtained by multiplying the number per cc. having this velocity by the velocity component perpendicular to the serface. That is, from (19)

$$(22) \qquad dn = v d\mathbf{N} = \frac{\mathbf{N}}{a\sqrt{\pi}} v e^{-(v/a)^2} dv.$$

The total number of electrons which reach the surface with a velocity perpendicular to it exceeding a certaiu value v_0 is therefore

$$(23) \qquad n = \frac{\mathbf{N}}{a\sqrt{\pi}} \int_{v_0}^{\infty} e^{-(v/a)^2} v dv = \frac{a\mathbf{N}}{2\sqrt{\pi}} e^{-(v_0/a)^2}.$$

By combining this with (20) and (21) we obtain,

$$(24) \qquad n = \mathbf{N} \sqrt{\frac{RT}{2\pi M}} e^{-Mv_0^2/2RT}.$$

[1] *Phil. Trans.*, **201**, 516 (1903).

The velocity v_0 is the velocity which the electron must have in order that it can combine with an oxygen molecule. As the temperature of the metal varies, the number of electrons having this necessary velocity will increase according to equation (24). Therefore, ε, which measures the rate of the reaction of oxygen with the tungsten, would be proportional to n. We may assume that N and v_0 do not vary with the temperature and thus obtain from (24) a relation of the form

(25) $$\varepsilon = B\sqrt{T}\ e^{-b/T}$$

where

(25a) $$b = Mv_0{}^2/2R.$$

Taking the logarithm of (25), we get

(26) $$\ln \varepsilon = -b/T + \ln B + \tfrac{1}{2}\ln T.$$

Differentiating:

(27) $$\frac{d \ln \varepsilon}{dT} = \frac{b}{T^2} + \frac{1}{2T}.$$

This equation differs from Arrhenius' equation (11) only by the addition of the term $\dfrac{1}{2T}$. For all ordinary chemical reactions this term is very small compared to the first term.

The data for ε in Table IV were compared with this equation. By taking $B = 0.85$ and $b = 12830$, equation (26) gives the results in the fourth column of Table IV. These agree as well with the observed values of ε as do the results in column 3 obtained from Arrhenius' equation.

We are thus able to derive a correct form of equation for the reaction velocity from Maxwell's distribution law.

Knowing now the numerical value of b, we can calculate the actual velocity v_0 of the electrons necessary to bring about a reaction. From

(25a) $$v_0 = \sqrt{2bR/M}.$$

Substituting $b = 12830$, $R = 83.2 \times 10^6$, $M = 0.00055$, we find

$$v_0 = 62.4 \times 10^6 \text{ cm. per sec.}$$

This velocity is small compared to that of cathode rays.

It is of interest to know through what voltage drop an electron would have to pass in order to attain this velocity. We have, if $P =$ drop in potential,

$$P = \tfrac{1}{2}(m/e)v_0{}^2.$$

For electrons $e/m = 18.0 \times 10^6$ e. m. units.

Whence the potential drop is 108.0×10^6 e. m. units or 1.08 volts. It is probably significant that this is the order of magnitude of the voltage necessary to decompose most chemical compounds.

Let us now calculate what proportion of all the electrons reaching the

surface do so with a velocity exceeding v_0. If we place $v_0 = 0$ in (24),
we find that the total number of electrons reaching the surface is

(26) $$n_0 = N \sqrt{RT/2\pi M}.$$

The proportion of these which have a velocity exceeding v_0 is therefore
equal to $e^{-Mv_0^2/2RT}$ or, in other words, to $c^{-b/T}$. This ratio is given in
column 3, Table V.

<div align="center">TABLE V.</div>

I. Temp.	II. ε observed.	III. n/n_0.	IV. $\varepsilon n_0/n$
1270° K.	0.0011	0.000041	27
1470	0.0053	0.000162	33
1570	0.0094	0.000282	33
1770	0.0255	0.000715	36
2020	0.049	0.00173	28
2520	0.12	0.0062	19

The relative number n/n_0 of electrons striking the oxygen molecules
which actually combine with them is very small. For example, if we
consider a filament at 1270° being struck by 910 oxygen molecules, we
see from the value of ε that on the average only one of these will combine
with the tungsten.

On the other hand, we see from the value of n/n_0 that in order for one
electron to combine with an oxygen molecule $1/0.000041$ or about 24,400
electrons must collide with oxygen molecules without combining. This
leads us to the conclusion that each oxygen molecule striking the filament
will, on the average, be struck by about 27 electrons. The number of
electrons striking each oxygen molecule is equal to $\varepsilon n_0/n$ in the fourth
column. The average is about 30 and up to 1800° does not vary much
with the temperature.

The number of electrons which strike each oxygen molecule depends
on the number of electrons per unit volume in the metal, on their velocity,
and on the forces the electron has to overcome in moving from the interior
of the metal to the point where it collides with the oxygen molecule.
If we assume that these forces are negligible, we may roughly calculate
the number of electrons per unit volume.

Let us assume provisionally that the average distance between the
electrons in the metal is about the diameter of an oxygen molecule. Since
there are six possible directions perpendicular to each other in which an
electron may move, we may consider that only one-sixth of all the mole-
cules are moving towards the surface at any one time. If the velocity
of the electrons and oxygen molecules were the same, then the chance
that an electron would strike a molecule during a collision of the latter
with the metal would be one-sixth. We can therefore readily see that
the number of electrons which would strike the oxygen molecules during
a single collision would be equal to $^1/_6 v_2/v_1$ where v_2 is the average veloc-

ity of the electrons and v_1 the average velocity of the oxygen molecules. The mass of an oxygen molecule is about 58,000 times as great as that of an electron. If the temperature of the oxygen and metal were the same, the velocity of the electrons would be $\sqrt{58,000}$ or 240 times that of the molecules. As the temperature of the oxygen is lower than that of the metal, this ratio would be somewhat larger—probably in the neighborhood of 400. In this case $^1/_6 v_2/v_1$ becomes 67. This represents the number of electrons which would strike an oxygen molecule if the average distance between the electrons in the metal were equal to the diameter of the oxygen molecule. The atomic volume of tungsten is about one-third of the molecular volume of oxygen. If we should assume that there is one free electron for each atom of metal, then we should expect 3×67 or 200 electrons to strike each oxygen molecule during a collision. The results of our experiments have already led us to conclude that the number of collisions is about 30. This would indicate that there are about one-seventh as many free electrons as there are tungsten atoms. It must be remembered, however, that this conclusion has been reached by assuming that no work is required to move an electron from the interior of the metal to the surface where it can collide with the oxygen molecule. If such forces do exist opposing this motion, then there must be more than one-seventh as many electrons as tungsten atoms. In any case, it is significant that we find the number of electrons so nearly equal to that of the tungsten atoms.

The question arises as to whether the impact from a smaller number than 30 electrons might not be sufficient to drive away an oxygen molecule. The momentum of a molecule moving with a velocity corresponding to the temperature T is proportional to $\sqrt{MT}$. If we take the momentum of the electrons in the metal at 1600° as unity, we find for the momentums of

Electrons in metal.................................   1
Tungsten atoms in metal.......................... 570
Oxygen molecules at 300°......................... 100
Oxygen molecules at 1600°........................ 240

The average momentum taken up by the oxygen is $100 + 240$ or 340. The collision of one electron against an oxygen molecule is only capable of giving it the momentum $2 \times 1 = 2$. It would require, therefore, the impact from 170 electrons to give the oxygen molecule the velocity it must have when it leaves the surface of the metal. This would indicate that about 85% of its momentum is obtained by impact against tungsten atoms and only about 15% from collisions with electrons.

We see, then, that our conclusion that each oxygen molecule is struck by 30 electrons, does not lead us into any inconsistencies, but leads to results which are in themselves probable.

Summary.

1. In order to obtain a vacuum so free from water vapor that a heated

tungsten filament will not produce appreciable quantities of hydrogen by the decomposition of the water vapor, it is necessary during exhaustion to heat the bulb to 360° for about an hour and to employ either phosphorous pentoxide or liquid air as a drying agent.

2. By this heating, about 300 cu. mm. of water vapor, 20 cu. mm. of carbon dioxide and 4 cu. mm. of nitrogen are evolved from a 40 watt lamp bulb which could not be removed from the bulb at room temperature by ordinary means.

3. A tungsten wire heated in oxygen at low pressures begins to oxidize at about 800° K, the oxide forming a brown or blue coating on the metal. By heating to about 1200° the oxide volatilizes without dissociation and leaves the wire clean and bright.

4. Above 1200° oxygen at pressures below 0.02 mm. acts on a tungsten wire at a rate which is strictly proportional to the pressure of oxygen and is proportional to the surface of tungsten exposed. The rate increases as rapidly with the temperature as do the rates of most chemical reactions at similarly high temperatures. No fatigue effect can be observed and the past history of the wire does not influence the results. There is much evidence that no film of oxide remains on the metal, but that the oxide distils off to the bulb as fast as formed.

5. The composition of the oxide produced is WO_3.

6. The velocity of the reaction is not affected by varying the temperature of the bulb.

7. The conditions under which this reaction was studied differ in several important respects from those that prevail with reactions at ordinary pressures. Because of the fact that the normal free path of the molecules of the gas is of the same order of magnitude as the dimensions of the bulb, the following unusual conditions prevail:

(a) A molecule of oxygen can strike the filament only once before returning to the surface of the bulb.

(b) The velocity of the oxygen molecules is not affected by the temperature to which the filament may be heated. Hence we may say that the metal is made to react with a gas at a totally different temperature from itself—a thing impossible at atmospheric pressure.

(c) The product of the reaction, WO_3, in diffusing away cannot influence the rate at which the oxygen comes in contact with the metal, as would be the case at higher pressures.

These facts make it much easier to study the mechanism of the reaction.

8. The rate at which the oxygen molecules come into contact with the surface of the filament was calculated. This rate gives the maximum possible rate of the chemical reaction. The ratio of the actually observed rate to this maximum rate is called ε. The values of ε at different tem-

peratures are given in Table IV. They range from 0.0011 at 1270° K to 0.15 at 2770° K.

9. Applying the principles of the kinetic theory to an analysis of the experimental data, we are led to the following conception of the mechanism of the reaction.

The oxygen molecules that strike the filament do not react directly with tungsten atoms, but as a first step become negatively charged by taking up an electron from the metal. On the average, about 30 electrons in the metal collide with the oxygen molecule during the time that it is in contact with the metal. Only those electrons which have a velocity of 62×10^8 cm. per sec. or more, succeed in charging the oxygen atoms. When we say that 30 electrons collide with each oxygen molecule, we mean that 30 electrons reach such positions with respect to the oxygen molecule that they would combine with it if their velocities were greater than 62×10^6 cm. per sec. The number of electrons in the metal that have velocities as high as this is so small that only a few of the oxygen molecules that strike the tungsten become negatively charged. For example, with the tungsten wire at 1270°, only one electron out of about 24,400 has a velocity as high as 62×10^6. Therefore the number of oxygen molecules that receive a charge is only 30/24400, or only about one out of a thousand.

The number of electrons in the metal must be at least one-seventh as great as the number of tungsten atoms.

The oxygen molecule, after taking up a negative charge, is held by electrostatic forces to the positively charged tungsten atoms and soon, by secondary reactions, combines with the tungsten and with oxygen atoms to form WO_3. The present experiments do not throw much light on the nature of these secondary reactions.

This theory accounts quantitatively for the observed values of ε between the temperatures 1270 and 1770° K, and for the fact that ε does not depend on the temperature of the oxygen. It also leads to several interesting deductions which do not appear to be inconsistent with known facts.

The writer wishes to express his indebtedness to Mr. S. P. Sweetser, who has carried out most of the experimental part of this investigation.

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SEBACATES AND CACODYLATES OF THE RARE EARTHS.

BY C. F. WHITTEMORE AND C. JAMES.

The sebacates appeared to be worthy of special consideration, inasmuch as they afford a separation of the rare earths from thorium in a faintly