

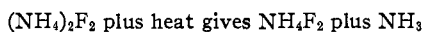
The time required for the expulsion of silica and excess reagents need not exceed twenty minutes, for both evaporations.

The residue is preponderantly oxides of iron, aluminum and titanium, with but negligible amounts of alkali and alkali earth oxides, and the loss can safely be attributed to silica in this particular case.

The data in Table I are typical of the results obtained.

Discussion

As ammonia fumes are given off copiously on heating ammonium fluoride, and a more fusible compound seems to be formed, it is suggested that the following reaction takes place



Experiments with the technical grades of the bifluoride lead to the conclusion that previously fused pieces of this flux would probably afford prompter fusion, greater fluidity, a more acid nature and an even quieter melt than the normal salt.

Summary

Molten ammonium fluoride rapidly decomposes powdered quartz and silicates. This reaction has been proved to be quantitative, in the case of glass sand, and shows the possibility of opening silicates preliminary to determining other constituents therein, particularly the alkali metals.

URBANA, ILLINOIS
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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]
**OXYGEN FILMS ON TUNGSTEN. I. A STUDY OF STABILITY BY
MEANS OF ELECTRON EMISSION IN PRESENCE OF
CESIUM VAPOR**

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RECEIVED NOVEMBER 26, 1930

PUBLISHED FEBRUARY 9, 1931

In this paper we wish to describe a powerful method of studying the properties and detecting the presence of adsorbed films of oxygen on a tungsten surface. This method, not in general use, seems to us to be capable of much wider application than we are making of it here, and for that reason we wish to call it to the attention of chemists. We shall, at the same time, present evidence obtained by it to show that adsorbed oxygen films are held on a tungsten surface by enormous binding forces,¹ very much greater even than those corresponding to the heat of dissociation of the oxygen molecule.

The experimental work on which this paper is based was done by Dr.

¹ Cf. Langmuir, Chandler Lecture, *Ind. Eng. Chem.*, **22**, 393 (1930).

K. H. Kingdon; a part has already been published elsewhere.² In that article it was shown that minute traces of cesium vapor have a remarkable effect on the electron emission from a tungsten surface. Some of the most important data are summarized quantitatively in Fig. 1, which is Langmuir and Kingdon's Fig. 1. Consider, for example, the curve labeled 20°. This shows that the electron emission in the presence of cesium vapor saturated at 20° (0.001 barye) at low filament temperatures (the right side of the diagram, subsequently to be referred to as Region I) varies with increasing temperature according to the Richardson equation

$$i = AT^2e^{-b/T} \quad (1)$$

up to about 640°K.,³ but is many billionfold greater than that from pure tungsten. Thus at 590° ($10^3/T = 1.7$) the emission is $10^{-6.2}$ amp. cm.⁻², whereas that from pure tungsten would be the unmeasurable quantity 10^{-31} , if Dushman's⁴ values of $A = 60.2$ and $b = 52,600$ are taken.

On increasing the temperature from 640 ($10^3/T = 1.56$) to 715° ($10^3/T = 1.4$), the emission is found to pass through a maximum (Region II) and decrease with further increase in temperature (Region III). This drop in emission is due to an evaporation of the cesium from the surface. Finally, when all the cesium has evaporated off, the points on the curve bend upward again (with decreasing $1/T$) and the emission follows Equation 1.

The most remarkable phenomenon, however, was the effect of oxygen on these composite surfaces. Ordinarily, a layer of oxygen decreases the

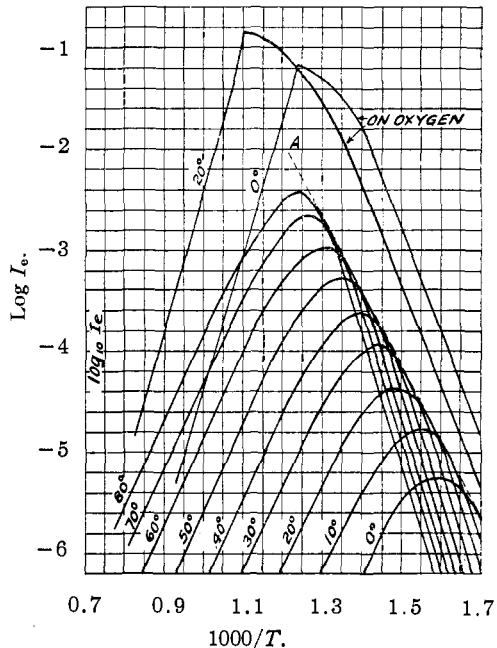


Fig. 1.—Electron emission from tungsten filaments in cesium vapor at various pressures (amps. cm.⁻²).

² I. Langmuir and K. H. Kingdon, "Thermionic Effects Caused by Vapors of Alkali Metals," *Proc. Roy. Soc. (London)*, A107, 61-79 (1925).

³ All temperatures, unless otherwise stated, will be given in absolute degrees, K. For the method of measuring temperature, the reader is referred to the article of Jones and Langmuir, *Gen. Elec. Rev.*, 30, 310-319, 354-361, 408-412 (1927).

⁴ S. Dushman, H. N. Rowe, J. Ewald and C. A. Kidner, *Phys. Rev.*, 25, 338 (1925).

emission from a pure tungsten surface. Thus, from Kingdon's data,⁵ $A = 5 \times 10^{11}$ and $b = 107,000$, we calculate that the emission from an oxygen-coated surface should be 10^{-33} at 910° ($10^3/T = 1.1$) as compared with $10^{-17.4}$ from pure tungsten. If, now, cesium vapor is admitted to the oxygen-coated filament, the emission at all temperatures is increased so that at 910° it is $10^{-0.9}$, according to the curve in Fig. 1, marked "On Oxygen 20° ." The general shape of the curve is the same as before, but now it obeys the Richardson equation up to much higher temperatures. The oxygen increases the stability of the cesium film, holding it much more firmly than tungsten does.

In all of these regions there is a balance between the rates of evaporation and of condensation of cesium on the surface, so that we may assume

$$\frac{k\theta e^{-H_\theta/RT}}{\text{Rate of evaporation}} = \frac{\alpha p(1-\theta)}{\text{Condensation}} \quad (2)$$

Here θ is the fraction of surface covered by the cesium atoms, H_θ is the heat of evaporation, and p the vapor pressure of cesium. The transition Region II thus occurs close to the temperature at which the equilibrium value of θ begins to be less than unity by a perceptible amount. Region I is that in which $(1-\theta)$ is very small or θ practically equal to unity. That this is true is also indicated by the fact that increasing the cesium vapor pressure affects the emission only slightly; in fact, decreases it instead of increasing it. Region III gives us the course of evaporation with the temperature.

Oxygen present on the surface produces two effects. One is a slight alteration of the work function, φ , through the cesium layer. The average work necessary to remove an electron from a surface is approximately a linear function of the fraction of the surface covered.

$$\varphi = \varphi_W + \theta_{Cs}(\varphi_{W-Cs} - \varphi_W) \quad (3)$$

where φ_W is the work function from a pure tungsten surface, φ_{W-Cs} is the corresponding work function from a tungsten surface covered with a complete layer of cesium, and θ_{Cs} is the fraction of the surface covered with cesium. Evidence supporting this hypothesis has been discussed elsewhere.⁶ From Equations 1 and 3 it follows that $\log i$ is a linear function of θ in view of the relation connecting b of equation 1 with φ

$$b = \varphi e/k = 11600 \varphi \quad (4)$$

if φ is given in volts. Although the work function from a Cs-O-W layer need not be exactly the same as that from Cs-W, this distinction is not very important, as may be seen from a study of Region I of the Cs-O-W and Cs-W curves (Fig. 1). The difference in $\log i$, which, by Equation 1, depends principally upon the work function, is only 0.7 (at 590°), a small fac-

⁵ K. H. Kingdon, *Phys. Rev.*, **24**, 510 (1924).

⁶ I. Langmuir, *ibid.*, **22**, 357-98 (1922).

tor indeed when compared with the enormous differences we shall make use of later.

The other effect of the presence of an oxygen film is to hold cesium atoms which would otherwise evaporate under the same conditions of temperature and pressure. This effect comes to light in Region III where we no longer have the surface completely covered with cesium. Every oxygen molecule which strikes a bare tungsten surface is held so strongly that it cannot be dislodged at the low temperatures which are sufficient to evaporate cesium. These adsorbed atoms are, moreover, capable of holding cesium atoms much more tightly than the bare tungsten surface. A relatively high temperature is required therefore to bring about the evaporation of these cesium atoms to produce any given value of Θ_{Cs} . It is this effect which allows us to go to much higher temperatures on the Cs-W curve of $\Theta_{Cs} = 1$, without evaporating off all the cesium layer. This is the reason that oxygen can increase the emission 10^6 fold.

On first thought it is natural to assume that the curves labeled "Oxygen" in Fig. 1 correspond to $\Theta_O = 1$, where Θ_O is the fraction of surface covered with oxygen. On the other hand, when we consider that, in the checkerboard arrangement of the surface, one oxygen adatom⁷ may hold more than one cesium atom, perhaps as many as three to seven, our first hypothesis does not seem likely.

We may think of the total fraction of the surface covered by cesium, Θ_{Cs} , to be made up of two parts, one of which is the fraction, Θ'_{Cs} , which would naturally be present in equilibrium at that temperature if no oxygen were there, and the other of which is the additional fraction, Θ''_{Cs} , held by the oxygen present.

$$\Theta_{Cs} = \Theta'_{Cs} + \Theta''_{Cs} \quad (5)$$

It is then to be expected that the additional fraction held, Θ''_{Cs} , should be directly proportional to the amount of oxygen present, up to a certain limit. For example, if the number of cesium atoms held by an oxygen atom were n , we would have

$$\Theta''_{Cs} = n\Theta_O \quad (6)$$

up to the point where $\Theta_{Cs} = n\Theta_O + \Theta'_{Cs} = 1$. Beyond this value, the emission should be nearly constant, although Θ_O might continue to increase to values all the way up to unity. For this reason we might expect the work function in Region III (where cesium is more or less evaporated off) to vary linearly with Θ_O from 0 to about 0.33 (if $n = 3$), and be little affected by subsequent addition of oxygen to the surface. Notwithstanding this uncertainty in our knowledge of Θ_O , we can probably be certain of one thing. Electron emissions of definite value below the maximum (at a

⁷ Becker, "The Life History of Adsorbed Atoms and Ions," *Trans. Am. Electrochem. Soc.*, 55, 153-175 (1929), has suggested using the term "adatom" for an adsorbed atom.

fixed comparison temperature and cesium pressure) will correspond to a definite θ_0 , no matter what evaporation procedure we have chosen to bring about this state.

Method of Procedure.—In this way, we have been able to develop a method of studying oxygen films on tungsten. First, a well-aged tungsten filament is flashed in vacuum for two seconds, at a temperature of 2700° , to clean its surface completely. It is then allowed to cool to room temperature, and cesium vapor at a pressure of 0.0024 barye (saturation pressure at 28°) is admitted.⁸ This instantly (within about one second)⁹ forms a complete layer on the tungsten surface and increases the electron emission from values too small to measure to those easily measured in the temperature range $550\text{--}900^\circ$ (see Fig. 1). To produce the film of oxygen which we propose to study, we raise the temperature of the filament to around 2000° , thus evaporating off all the cesium, surround the bulb with liquid air to lower the cesium vapor pressure to an infinitesimal amount, and admit oxygen, at 0.1 mm. pressure, covering the surface with a complete layer of the latter. The filament is then allowed to cool to room temperature, any residual oxygen is pumped out and cesium vapor is again admitted by simply removing the liquid air from the bulb. On now heating the fila-

⁸ This may be readily done in one of two ways. If a high frequency induction outfit is available, a nickel capsule containing a mixture of cesium dichromate and silicon may be placed in a side arm of the tube (pyrex). The whole may be baked out at as high a temperature as desirable, after which the cesium is liberated by bringing the nickel to a red glow by means of the high frequency coil. If the latter is not available, a second method is to use a mixture of metallic calcium and cesium chloride. The tube (lime or hard glass) may not be baked out at temperatures above 350° as the calcium would begin to react. When ready to drive over the cesium, the temperature is increased by heating with a Bunsen flame. This method has disadvantages over the first one in that the baking temperature may not be as high, and that the reagents, being hygroscopic, are apt to become contaminated while being handled.

⁹ We calculate that a fraction of cesium on the surface of $\theta_{Cs} = 10^{-5}$ may be readily detected by using a galvanometer ballistically and determining the positive ion emission while flashing the filament to 1500° . (All atoms on the filament pass off instantaneously as positive ions during the flashing if submitted to sufficient accelerating potential, say, 45 v.). An ordinary galvanometer has a sensitivity such that 10^{-9} coulombs will give a kick of 1 cm. This is equivalent to 6.3×10^9 positive ions. A surface completely covered with cesium contains 4×10^{14} atoms cm.^{-2} . Thus, the fraction readily detected is $\theta_{Cs} = 6.3 \times 10^9 / 4 \times 10^{14} = 1.57 \times 10^{-5}$. If n cesium atoms were held by each oxygen atom present, one could readily detect $\theta_0 = 1.57 \times 10^{-5} / n$. This suggests that an extremely powerful method of studying surfaces of low θ is to choose a cesium pressure low enough for the constant positive ion current to be small, and a filament temperature such that $\theta'_{Cs} = 0$. By making the filament positive with a sufficient voltage, all cesium atoms striking the surface will be instantaneously changed to cesium ions and flow to the cathode. This current should be balanced out of the galvanometer. If there were a small trace of oxygen on the filament, θ'_{Cs} would have a definite value, which could be determined by flashing the filament. The ballistic kick then will tell one how great is θ'_{Cs} and the relative value (although not absolute) of θ_0 .

ment to temperatures from 600 to 1200°, with positive voltage on the anode, no measurable electron emission is detected. To get the typical electron emission from the adsorbed cesium film, it is first necessary to "activate" the oxygen film. The maximum activation is produced by flashing the filament for a few seconds at temperatures from 1600 to 1800°, the exact temperature and time being of little importance.

After activation, the filament, in the presence of cesium vapor at 20°, gives at 650° an emission which is roughly only five times as great as before the oxygen film was produced. The activated oxygen film, however, allows us to raise the filament temperature to 850° or even 900° before losing enough of the adsorbed cesium to cause a decrease in emission. Under these conditions, the currents are 10^5 or 10^6 times greater than in the absence of the oxygen film.

We propose to use this increase as a measure of the amount of adsorbed oxygen and in this way study the rate of evaporation of these oxygen films.

In the absence of cesium vapor, the effect of oxygen is to decrease greatly the electron emission from tungsten. This change in emission can also be used to detect and study oxygen films, and has been used in the work to be described in the second paper of this series. The method has, however, the disadvantage that even at 1700° the emission from an ordinary filament is less than 10^{-8} ampere and at temperatures as high as this the films may evaporate somewhat even during the measurements. With cesium vapor, not only can much smaller amounts of oxygen be detected, but the tests for the oxygen are made at such low temperatures that no evaporation occurs.

This qualitative test becomes quantitative as soon as we know the law by which θ''_{Cs} depends on θ_O (Eq. 6). Until then we may reproduce at will particular values of θ_O without having more than approximate knowledge of their absolute magnitude.

In our studies of the evaporation of the films, the oxygen-covered filament was heated at a definite "evaporation temperature" for successive time intervals. After each heating to the evaporation temperature, the filament was cooled and the condition of its surface was then determined by measuring its electron emission¹⁰ at a series of "test temperatures" ranging from 802 to 1092°.

Similar data were obtained at other temperatures. By comparing the rapidity of the deactivation at various evaporation temperatures, as revealed by the changes in emission at any given test temperature, we can obtain the relative temperature coefficients of the rates of evaporation.

It was shown by Langmuir¹¹ that the rate of evaporation m is related to

¹⁰ This method is similar to that used by Langmuir in his study of thoriated tungsten filaments, *Phys. Rev.*, **22**, 357-398 (1923).

¹¹ I. Langmuir, *ibid.*, **2**, 329 (1913).

the vapor pressure, p , of a substance by the equation

$$m = (1 - r) (M/2\pi RT)^{1/2} p \quad (7)$$

where M is the atomic or molecular weight and r is the reflection coefficient of incident atoms. In the present case, from evidence that will be discussed in later papers of this series, we believe that r is small and has no appreciable temperature coefficient. Thus the temperature coefficient of the rate of evaporation is approximately the same as that of the vapor pressure (neglecting the factor $T^{1/2}$). In this way by the Clapeyron equation we may determine the heat of evaporation of adsorbed oxygen from the temperature coefficient of the rate of evaporation.

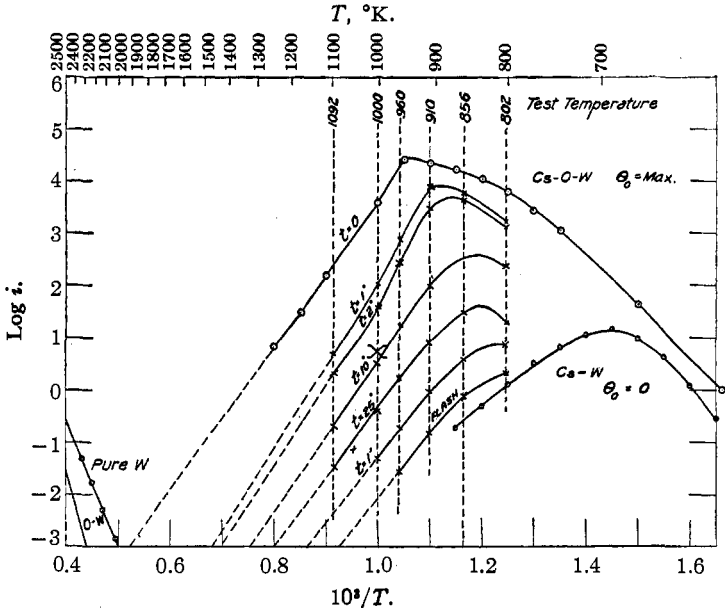


Fig. 2.—Electron emission from Cs-O-W surfaces of varying oxygen and cesium content. Total emission from 50-mm. 4-mil wire (0.01016 cm. diam.) in microamperes. O, Values from other data² calculated to wire of area used (0.1598 sq. cm.). X, Experimental values. Cesium vapor pressure, 0.00246 baryes (28°C.). t is time of oxygen evaporation at 2070°K.

Experimental Data.—The experimental data on the electron emission from Cs-O-W surfaces of varying θ_0 for one characteristic evaporation temperature are given in Fig. 2. Each of these curves corresponds to a definite time of evaporation of oxygen at 2070°. A similar set of curves was obtained for two lower evaporation temperatures, 1978 and 1856°. As these curves have the same appearance as those in Fig. 2, we shall not reproduce them here. To get the temperature coefficient of the rate of evaporation, and from it the heat of evaporation, one might pick the point X

in Region III, half-way between the top and bottom curve, and compare the evaporation time which gives a surface of that electron emission at that particular test temperature, with the evaporation time at the next evaporation temperature (1978°) which gives the same electron emission at the same test temperature. From what has been said above, it is reasonable that the surface is the same in both cases. As may be seen from Fig. 2, this arbitrary half-way curve was not among those determined experimentally. The time which would give this curve may be determined by any method of interpolation. That method which gives a straight line is, however, always the most convenient. From the logarithmic¹² form of Equation 2.

$$-\frac{d \ln \Theta}{dt} = k e^{-H_{\Theta}/RT} = k' \quad (8)$$

we see that if H_{Θ} is constant, a plot of $\log \Delta$, where $\Delta \equiv \log i - \log i_0$ and i_0 is the emission from the cesiated surface of $\Theta_0 = 0$, against evaporation time, t , should give us this straight line, in view of the relation between Δ and Θ (Equations 1, 3 and 4).

$$\frac{d \ln \Delta}{dt} = \frac{d \ln \Theta}{dt} \quad (9)$$

The "half life"¹³ may then be determined from the curve by inspection. Plotting $\log t_{1/2}$ against $1/T$ would now give us a curve the slope of which is a measure of the heat of evaporation.

Figure 3, in which is plotted $\log \Delta$ against t for four different test temperatures, shows that these curves are essentially straight, at least in the Θ region studied in these experiments. The velocity constant k' is then related to the time of half evaporation by the equation

$$t_{1/2} = (\ln 2)/k' \quad (10)$$

¹² In this and following papers we shall follow the customary notation in which log designates the common logarithm and ln the natural logarithm.

¹³ This "half life," in view of the consideration involved in Equation 6, does not necessarily mean the time it takes for Θ_0 to reach 0.5. It is the evaporation time it takes to obtain surface conditions such that, at the particular test temperature used, the sum $\theta'_{C_s} + \theta''_{C_s} = 0.5$.

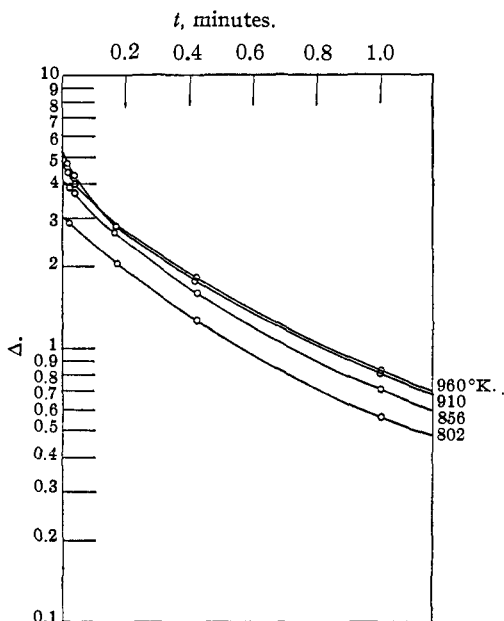


Fig. 3.—Course of evaporation with time at 2070°K., as measured at test-temperatures indicated. $\Delta \equiv \log i - i_0$ and is proportional to the covering fraction, Θ_0 .

A closer inspection of Fig. 3, however, reveals the fact that the half times obtained at different test temperatures are slightly different. In this example they are 0.27, 0.23, 0.32 and 0.33 minutes at the test temperatures 960, 910, 856 and 802°, respectively. It is obvious that some method of averaging must be resorted to if we are to get the best value of the temperature coefficient of evaporation. In doing this we have not limited ourselves to determining the half time, but have compared the times it takes for the surface to reach other stages of evaporation as well. Table I gives these evaporation times in minutes for different evaporation temperatures, test temperatures and Δ (proportional to Θ). We might next proceed to plot $\log t$ against $1/T$ for each separate set of times to reach the same stage of evaporation and find the average slope of all of these straight lines, but it is much simpler to reduce all times to values relative to that at the evaporation temperature 1978° as unity, average them, and plot the single set of three points. We have chosen the latter procedure.

TABLE I
EVAPORATION TIMES
Test temp., 802°K. ($A_a = 0.15$)

Δ	Evaporation temp., °K.			t_{1856}/t_{1978}	t_{2070}/t_{1978}
	1856 Minutes	1978 Minutes	2070 Minutes		
0.8	81.8	6.90	0.714	11.85	0.1034
.9	66.9	5.42	.632	12.34	.1166
1.0	55.9	4.29	.561	13.03	.1308
1.2	38.5	3.12	.454	12.34	.1455
1.5	29.1	2.07	.327	14.06	.1590
2.0	13.2	1.15	.181	11.48	.1574
Test temp., 856° ($A_a = 0.175$)					
0.9		7.52	0.811		0.1078
1.1	78.0	4.76	.664	16.39	.1395
1.5	40.7	2.81	.457	14.48	.1626
2.0	24.7	1.74	.304	14.19	.1652
2.5	13.1	1.17	.192	11.20	.1641
Test temp., 910° ($A_a = 0.20$)					
1.3	76.4	4.61	0.636	16.57	0.1379
1.5	53.8	3.52	.533	15.28	.1514
2.0	32.2	2.07	.352	15.56	.1701
2.4	19.9	1.47	.245	13.54	.1667
Test temp., 960° ($A_a = 0.225$)					
1.3	72.2	5.08	0.653	14.22	0.1286
1.5	50.7	3.53	.447	14.36	.1266
1.9	33.7	2.28	.384	14.78	.1684
2.3	19.9	1.63	.273	12.21	.1675
				Mean 13.77	0.1458

$\Delta = \log i_0 - \log i$, where i = electron emission from Cs-O-W surface of $\Theta_0 = x$, and i_0 = emission from Cs-W surface of $\Theta_0 = 0$. A_a = amperes at which filament a

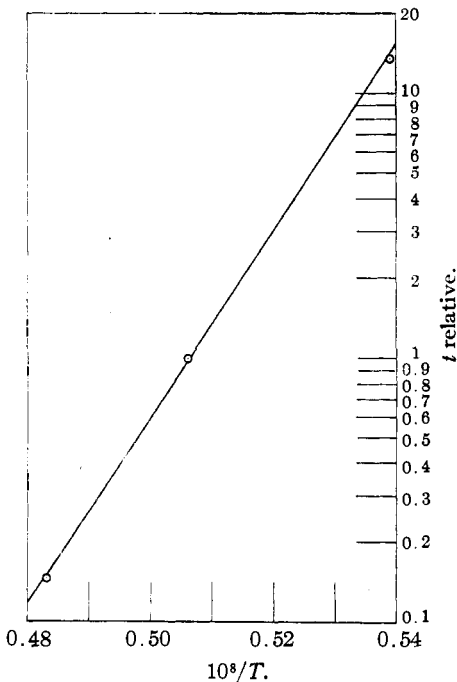
was run during emission readings. t_{1856}/t_{1978} = evaporation time relative to that at temperature 1978°.

TABLE II
TEMPERATURE COEFFICIENT OF EVAPORATION

T , °K.	$t_{1/2}$, min.	$t_{relative}$	$10^4/T$
1856	27	13.77	5.39
1978	2	1.00	5.06
2070	0.3	0.146	4.83

Thus Columns 5 and 6 of Table I give the relative times for each determination. These are averaged and given in Table II.

The heat of evaporation corresponding to the slope of the $\log t_{av}$. versus $1/T$ plot (Fig. 4) is 162 kg. cal. This is the heat per gram molecule of the substance dissociated. If the oxygen comes off in the form of atoms, as we have reason to believe, it is the heat per gram atom of oxygen. This is some 2.5 times the heat of dissociation of oxygen¹⁴ (per gram atom). It is no wonder, therefore, that a bare tungsten surface has such a power of taking up oxygen. The practically constant slope of the curves in Fig. 3 indicates that we are taking our measurements in a region where H_θ is independent of θ . We conclude therefore that 162 kg. cal. is most probably the heat of evaporation from a surface almost bare ($\theta_0 \sim 0.15$). In a later paper we shall present data from a θ region between 0.35 and 0.7 which show that H is less than 162 kg. cal., and decreases with increasing θ .



Slope equivalent to $H = 162$ kg. cal.
Fig. 4.—Relative evaporation time.

Concluding Remarks.—In the foregoing pages we have presented a method of studying the rate of loss of adsorbed oxygen from tungsten. Since this consists primarily in detecting the *amount* of oxygen on the surface, it may be used equally well for studying

¹⁴ Taking the heat of dissociation of oxygen per gram molecule to be 131 kg. cal., Rodebush and Troxel, THIS JOURNAL, 52, 3467 (1930); Copeland, Phys. Rev., 36, 1221-1231 (1930).

the *accumulation* of oxygen. As an illustration in this connection, we refer to the difficulty of Rodebush¹⁵ and his co-workers in finding a suitable method of detecting beams of oxygen molecules or atoms. We suggest that these could be readily identified by an adaptation of the above procedure. A beam of molecules impinging on a hot (1600°) clean (by preliminary flashing to 2700°) tungsten filament will deposit with almost one hundred per cent. efficiency until the surface has received its maximum sensitivity. The deposition of oxygen molecules on a cold surface does not affect the emission in the presence of cesium vapor. It is almost certain (it has not been tried) that a beam of oxygen atoms impinging on a cold surface will modify its subsequent emission in cesium vapor to the same extent as a molecular beam hitting a hot surface. If this is true, we have a method of distinguishing between atomic and molecular oxygen.

If a layer of $\Theta_0 = 0.33$ ($n = 3$ in Equation 6) gives the maximum emission ($10^6 \times$ the Cs-W emission), then a layer of $\Theta_0 = 0.33 \times (\log 2)/(\log 10^6) = 0.017$ will cause a doubling of the emission, which certainly can be readily detected. A beam of the density ordinarily used in molecular ray experiments will deposit a complete layer in about one second.¹⁶ It therefore would take only 0.017 second to deposit out of such a ray enough oxygen to be readily detected. These rays usually originate from enclosures in which the pressure is 0.1 mm. It may be seen that with such a sensitivity much lower pressures may be used, with the consequence that the beam can be better resolved. Hitherto, the most hopeful method of detecting oxygen beams seems to have been that of Knauer and Stern,¹⁷ who have a small box with an entrance consisting of a slit which may be moved back and forth across the beam. By measuring the pressure change in the box, the distribution of intensity in the beam may be determined. Up to now this is the only practical method invented to detect beams of inert gases, but this need no longer apply to the case of oxygen. The use of a movable tungsten wire in detecting beams is not only a much more simple method, but is also practical, as has been demonstrated by Taylor,¹⁸ who detected cesium beams by the positive ion current from a wire mounted on a contrivance capable of moving it across the beam.

We wish to acknowledge our indebtedness to Dr. K. H. Kingdon for the experimental data which we have used and to Mr. Saunders MacLane, who gave valuable assistance in analyzing these data.

¹⁵ Rodebush and Nichols, *THIS JOURNAL*, **52**, 3864-3868 (1930).

¹⁶ Pressures as low as 10^{-7} baryes would bring about the deposition of a layer of $\Theta = 1$ in about five hours. On account of this extreme sensitivity, all stray oxygen would have to be removed from the apparatus. This would be readily done, we believe, by the cesium vapor present under the conditions of the experiment.

¹⁷ F. Knauer and O. Stern, *Z. Physik*, **53**, 766 (1929).

¹⁸ J. B. Taylor, *ibid.*, **57**, 242-248 (1929).

Summary

A method is presented of studying the rate of loss of oxygen from an adsorbed film on tungsten, as well as of detecting its presence in a gas. This consists in observing its effect on the electron emission of a tungsten filament, sensitized by the presence of minute traces of cesium vapor (10^{-6} mm.). Under properly chosen conditions a monatomic oxygen film makes its presence known by increasing the emission a millionfold.

Using this method, the heat of evaporation of oxygen from the adsorbed layer was found to be 162 kg. cal. (7.0 v.) per gram atom.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 69]

THE ADSORPTION OF GAS MIXTURES BY SILICA

BY E. C. MARKHAM AND ARTHUR F. BENTON

RECEIVED NOVEMBER 28, 1930

PUBLISHED FEBRUARY 9, 1931

Introduction

Studies of the adsorption of gases by catalytically active solids, particularly in the last decade, have contributed greatly to a qualitative understanding of the kinetics and mechanism of contact catalysis. Frequently, however, more than one of the reactants or products are simultaneously adsorbed, and in such cases it is obviously necessary to have information concerning the adsorption of one gas in the presence of a second. Such data should also be useful in connection with the practical problem of separating the components of a mixture of gases or vapors. In addition, the behavior of mixtures may be expected to furnish a deeper insight into the nature of adsorption.

Comparatively little is known about the adsorption of the individual constituents of gas mixtures. Richardson and Woodhouse¹ studied the adsorption of carbon dioxide-nitrous oxide mixtures on charcoal. With their static method, however, the composition of the gas phase and of the adsorbed layer can be estimated only approximately. Klosky and Woo,² employing the flow method, have studied the adsorption of sulfur dioxide-butane and sulfur dioxide-methyl chloride mixtures on titania gel. Their results indicate that the presence of a second gas decreases the amount of the first gas adsorbed. Other recent studies on the adsorption of gaseous mixtures are those of Putnoky and Szélényi³ on ethanol-ether-air mixtures with various silica gels, and of Frolich and White⁴ on mixtures of methane and hydrogen at elevated pressures in contact with charcoal.

¹ Richardson and Woodhouse, *THIS JOURNAL*, **45**, 2638 (1923).

² Klosky and Woo, *J. Phys. Chem.*, **32**, 1387 (1928).

³ Putnoky and Szélényi, *Z. Elektrochem.*, **34**, 805 (1928); **36**, 10 (1930).

⁴ Frolich and White, *Ind. Eng. Chem.*, **22**, 1058 (1930).