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Sorption of Oxygen and Krypton by Evaporated Silver Films

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The sorption of oxygen at 473°K and the adsorption of krypton at 77.8°K by evaporated silver films of different specific surface areas has been studied. The results of the krypton adsorption fitted the BET isotherm and by making some assumptions about the type of packing on the surface, the average number of surface atoms, and the number of broken surface bonds associated with each adsorbed krypton atom was determined. The initial uptake of oxygen was fast and was taken to be adsorption on the surface, giving a maximum coverage when the number of adsorbed oxygen atoms equals the number of krypton atoms in the monolayer at 77.8°K. Adsorption of oxygen appears complete at or before 10^{-2} mm Hg; "slow" sorption was observed between 10^{-2} and 2×10^{-1} mm Hg and this "slow" sorption was taken to be dissolution into the bulk.

It seems very probable that the adsorption is dissociative and some speculations are made about the type of bonding to the surface.

INTRODUCTION

Apart from its intrinsic interest, the study of the sorption of oxygen by silver, at temperatures and pressures where silver oxide is unstable, is of importance in understanding the oxidation of organic compounds catalyzed by silver. A multitude of studies has been carried out on chemically prepared powders or surface-treated foils, but only a few workers (*1–4*) have utilized evaporated films and, of these only one (*3*) has worked in the temperature range near that of catalytic processes or used any means of measuring the surface area. It is well accepted that oxygen dissolves in massive silver in measurable amounts (*5*) at and above 473°K and several cm Hg pressure. The aim of this work was to measure the rate and extent of sorption on a clean surface (namely an evaporated film), at 473°K and in the pressure range 5×10^{-3} to 2×10^{-1} mm Hg; these measurements were related to the krypton adsorption at 77.8°K on the same films. By preparing films of different specific surface area, the separation of adsorption from solubility was attempted.

METHOD

Materials

(a) Silver. Johnson Matthey spectroscopically pure silver was used.

(b) Krypton. Krypton was supplied by the British Oxygen Co. and the purity was quoted as better than 99%, the remainder being inert gases.

(c) Oxygen. Oxygen was prepared from potassium permanganate (A.R.) in the manner described by Hoge (*6*).

Apparatus

The adsorption apparatus was based upon that of Rosenberg (*7*). Mercury cutoffs were used in the gas manipulation and a liquid nitrogen trap made from "Veridia" precision capillary leads, 2 mm diameter, protected a spherical adsorption vessel from mercury vapor. The connecting tubing between the trap and the adsorption vessel was also made of the same capillary.

The temperature of the gas burette and the thermistor Pirani gauge was kept constant at 29.5 ± 0.2°C by a water thermostat; the temperature of the adsorption vessel was kept constant to ±1.0°C by a Cambridge controller and measured by a mercury thermometer; an oxygen vapor pressure thermometer was used to measure the temperature of the liquid nitrogen bath.

In order to follow pressure changes over fairly long periods of time the Pirani gauge was operated in a constant potential bridge; in the case of oxygen an altered bridge ratio enabled higher pressures to be measured than was possible with Rosenberg's (7) original design. The dead space in the apparatus was ascertained by measuring the volumes of the various parts before they were sealed together.

Film Preparation

A platinum filament (0.02 inch diameter) was attached by nickel clips to 2 mm diameter tungsten leads inserted through the walls of the adsorption vessel. In the absence of an evaporated film this filament assembly gave no detectable sorption of oxygen after 60 min at 473°K in the presence of 1.5×10^{-1} mm Hg oxygen. Silver was melted on to the filament at 10^{-5} mm Hg in an auxiliary apparatus and outgassed by passing 12 amp for 90 min. The filament assembly was then sealed into the adsorption vessel which was pumped and baked under vacuum for 12 hr at 673°K. The vessel was surrounded by liquid nitrogen and the silver evaporated by passing a current of 15–20 amp through the filament for 25–45 min to give film weights varying from 30–150 mg. In some experiments the evaporation was carried out in a krypton atmosphere of 1 mm Hg, the krypton being pumped out when the evaporation was complete. The film was then annealed at 473°K for 60 min before oxygen was admitted.

Sorption Measurements

Oxygen sorption at 473°K was generally measured first before the krypton adsorption. A dose of oxygen was admitted and pressure measurements taken at intervals of time until the pressure changed only very slowly, then a second dose was admitted and followed in the same way; further doses were admitted until the pressure in the system reached 2×10^{-1} mm Hg. The vessel was then pumped out for 2 hr, the temperature lowered to 77.8°K and the adsorption of krypton measured in the same way.

The krypton results at 77.8°K were corrected for thermomolecular flow using Rosenberg's (7) data. For oxygen at 473°K and at pressures less than 5×10^{-3} mm Hg the pressure in the adsorption vessel was calculated, from Knudsen's equation, to be 1.25 times greater than that in the system at room temperature; the correction at 3×10^{-1} mm Hg pressure was assumed to be negligible and for intermediate pressures an interpolated value was used.

RESULTS

Structure of the Films

Films deposited in the presence of krypton were blue-black immediately after deposition but changed to a yellow-brown after being annealed at 473°K. Films deposited in vacuum had a bright mirror-like appearance which was unchanged after annealing at 473°K.

It was possible to examine the thinnest part of the film by transmission electron microscopy which showed that the film consisted of a tangled mass of aggregates which appeared to have been formed by the fusion of smaller particles. Examination of the films by electron diffraction

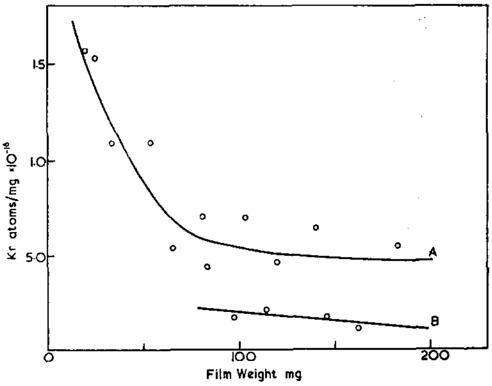

FIG. 1. Specific surface area (krypton monolayer per mg) vs. film weight. A. Films deposited in krypton. B. Films deposited in vacuum.

indicated that no preferred orientation existed.

The variation of specific surface area with film weight, for deposition in vacuum or krypton, is shown in Fig. 1. The specific surface area is taken to be proportional to the monolayer coverage of krypton per mg. It can be seen that for films deposited in krypton the specific surface area decreases as the film weight increases until a weight of 70 mg is reached when there is a trend towards constant specific area. The large scatter in this region is probably due to uncontrollable variations in the evaporation conditions.

The Adsorption of Krypton

The Pirani gauge and gas-dosing burette were separated by capillary tubing from the adsorption vessel so that it was necessary to wait an appreciable time after the admission of a dose for equilibrium pressure to be reached. If it is assumed that the flow is molecular and that the adsorption of krypton by silver is rapid, it is possible to calculate the rate of pressure decrease at the gauge. The calculated curves fitted experimental points well for the initial doses showing that, as has generally been assumed, physical adsorption was rapid and that the low conductance of the tubing was the rate-governing factor.

The pressure at the gauge fell from 10^{-1} mm to 5×10^{-3} mm Hg in 5 min for the initial doses; if no adsorption took place the pressure in the system reached to within 5% of the equilibrium value in 19 min; the pressures used in the isotherms were therefore measured at least 20 min after the admission of a dose.

The adsorption isotherms of krypton on films of varying specific surface areas, before or after oxygen sorption, were all similar in shape; a typical isotherm is shown in Fig. 2. All the results fitted the BET equation up to the highest pressures measured, 6×10^{-1} mm Hg; the results of Fig. 2 are replotted in Fig. 3 to show the fit to the BET equation. The value of p_0, the saturation vapor pressure, was taken as the value for solid krypton at 77.8°K and was determined as 1.81 mm in good agreement with other determinations (*8, 9*).

In order to obtain the best fit to the BET equation and thus the best value of n_m, the monolayer coverage, the results were treated by the least squares method; the reproducibility was ±3% for successive determinations, i.e., the bulb was allowed to reach room temperature, the krypton pumped off, and then the bulb cooled again to 77.8°K and a second run performed. On some films identical values for n_m, within experimental error, were obtained both before and after oxygen sorption at 473°K and 2×10^{-1} mm Hg.

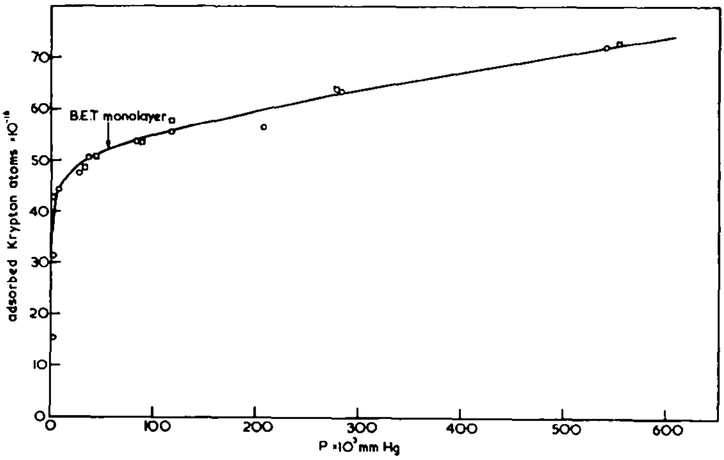

FIG. 2. Number of krypton atoms adsorbed at 77.8°K vs. pressure; ○, initial run; ☐, repeat run after warming film, pumping off krypton, and then cooling back to 77.8°K.

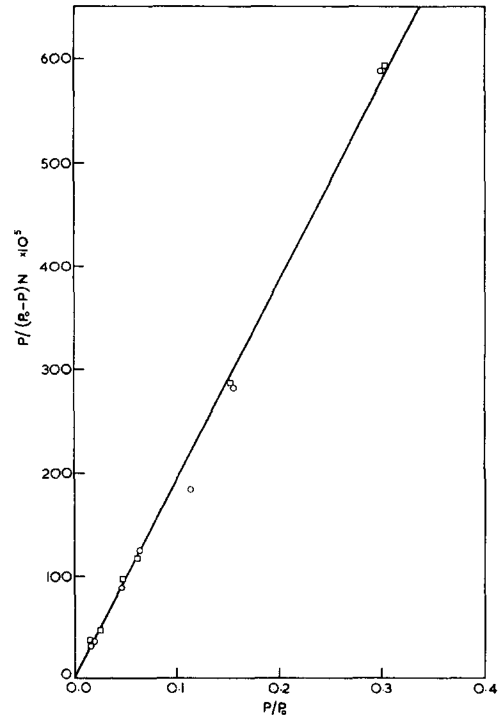

FIG. 3. Results of Fig. 2 replotted as $P/(P_0 - P)N$ vs. P/P_0 where P = pressure, P_0 = saturation vapor pressure, N = number of krypton atoms adsorbed. ○, Initial run; □, repeat run.

The Sorption of Oxygen

(a) The sorption rate. Figure 4 shows the decrease of pressure at the gauge with time after the admission of successive doses of oxygen to a film at 473°K. Calculations similar to those carried out previously for krypton showed that the sorption rate for the first four doses was very fast and the fall in pressure was governed by flow through the capillary connections. For the subsequent doses, when the residual pressure exceeds about 10^{-2} mm, "slow" sorption is occurring and the fall in pressure is not governed only by capillary flow.

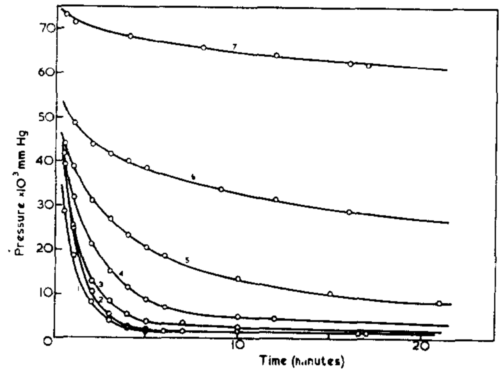

FIG. 4. Oxygen sorption. Pressure vs. time for a number of doses admitted in the order given by the number on the curves.

Similar rate curves were found for all the films examined, although the proportion of "fast" to "slow" sorption increased as the specific surface area of the film increased.

(b) Sorption isotherms. Isotherms were plotted of the quantity sorbed 20–30 min after the admission of a dose when the sorption rate was very slow; the isotherms were probably not true equilibrium isotherms. The curves in Fig. 5 show the oxygen sorbed per mg as a function of pressure for films of different specific surface areas, i.e., different krypton monolayers, n_m, per mg. A large number of films was examined and the pressure at which the number of sorbed oxygen atoms at 473°K equalled the number of krypton atoms in the monolayer at 77.8°K (indicated by an arrow in Fig. 5) was about 10^{-2} mm Hg in all cases. This

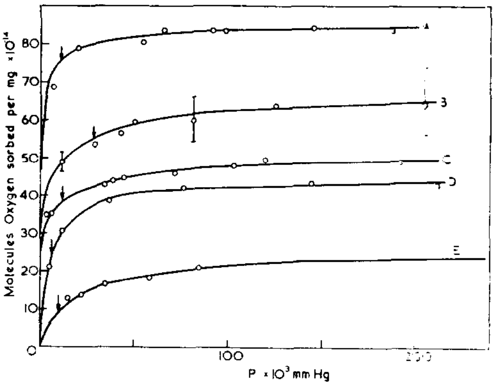

FIG. 5. Number of oxygen molecules sorbed per mg vs. pressure for films of different specific surface areas. Krypton monolayer per mg, atoms $\times 10^{-16}$. A, 1.53; B, 1.10; C, 0.71; D, 0.46; E, 0.18. The limits shown on curve B indicate the 95% confidence limits. The arrow indicates the pressure at which an O/Kr atom ratio of 1.0 is reached.

pressure also corresponded to the change from "fast" to "slow" sorption.

An examination of Fig. 5 shows that the oxygen sorbed per mg at 10^{-2} mm Hg, the "fast" sorption, increased with specific area but that the additional oxygen sorbed between 10^{-2} and 2×10^{-1} mm, the "slow" sorption, is approximately independent of the surface area per mg.

(c) **Desorption.** At 473°K after 30 min pumping at 10^{-6} mm Hg no uptake of oxygen could be detected by admitting further oxygen. However, after 12 hr pumping at 10^{-6} mm and 473°K further oxygen could be sorbed, the additional oxygen sorbed being about 16% of the initial sorption at 2×10^{-1} mm Hg.

(d) **Reaction of sorbed oxygen with carbon monoxide.** The object of this experiment was to distinguish between oxygen adsorbed on the surface and oxygen absorbed in the bulk, on the assumption that there would be a difference in reactivity between oxygen held in these two positions.

Oxygen was admitted to a film and allowed to come to equilibrium at 473°K, then the vessel was pumped out rapidly, the temperature lowered to 423°K and carbon monoxide at several cm Hg pressure admitted for 60 min. The vessel was pumped out rapidly, the temperature raised to 473°K, and oxygen re-admitted. The krypton monolayer value was the same before and after the treatment with carbon monoxide. The results are given in Table 1.

TABLE 1
REACTION OF SORBED OXYGEN WITH CARBON MONOXIDE[a]

	Oxygen sorbed per mg molecules $\times 10^{-16}$	Equil. pressure (mm Hg)
Before CO treatment	0.41	7.4×10^{-2}
After CO treatment	0.30	6.3×10^{-2}

[a] Film wt, 119.4 mg; krypton monolayer, 0.46×10^{16} atoms/mg.

In view of the fact that pumping for a short time does not cause any measurable desorption, the oxygen sorption after the carbon monoxide treatment must mean that oxygen has reacted and left the film in a condition to sorb more oxygen. However, only 75% of the original amount of sorbed oxygen could be taken up after the carbon monoxide treatment so that complete restoration of the sorption capacity did not occur.

(e) **Sorption at 433°K and 300°K.** In both cases the films were deposited at 77.8°K in krypton, annealed 60 min at 473°K and then cooled to the appropriate

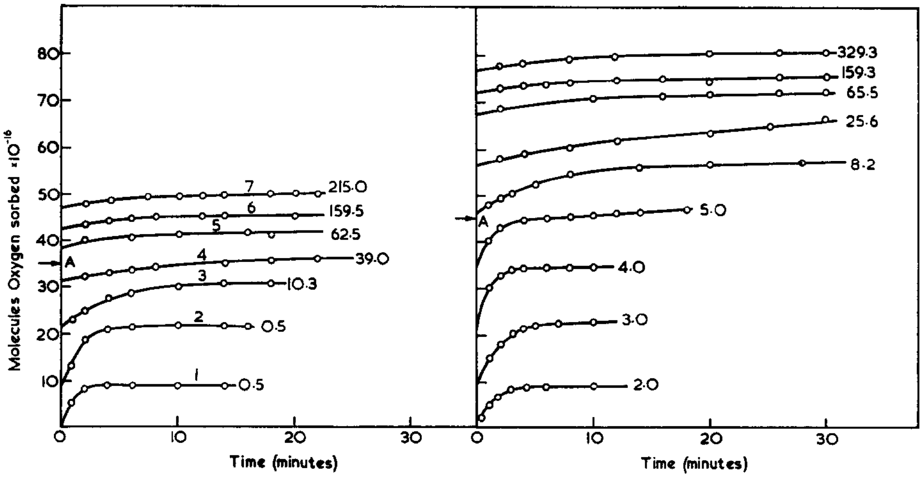

FIG. 6. Number of oxygen molecules sorbed vs. time for a number of doses. The numbers on the curves show the pressures (mm Hg $\times 10^3$) reached before the next dose was admitted. Point A indicates the O/Kr atom ratio of 1.0. (a) 433°K; film wt, 102.5 mg. (b) 473°K; film wt, 139.7 mg.

lower temperature. In Fig. 6a the sorption rates at 433°K are plotted; it shows that the first two doses are sorbed rapidly but that "slow" sorption occurs after an oxygen/krypton atom ratio of 0.6 is reached. For comparison the sorption at 473°K on a film of similar specific surface area is shown in Fig. 6b and the "fast" sorption up to an oxygen/krypton ratio of 1.0 is readily apparent. The shape of the isotherm at 433°K is very similar to that at 473°K. The amount sorbed at 2×10^{-1} mm is given in Table 2. At 300°K even the initial dose is sorbed slowly but the amount being small, the accuracy is low. The uptake was constant between 7×10^{-2} and 2×10^{-1} mm Hg and the value at 2×10^{-1} mm Hg is given in Table 2.

TABLE 2
OXYGEN SORBED AT 433°K AND 300°K

	A	B
Film wt (mg)	102.5	53.5
Kr monolayer atoms/mg $\times 10^{-16}$	0.70	1.10
O_2 adsorbed molecules/mg $\times 10^{-16}$		
at 300°K	—	0.2
433°K	0.5	—
473°K[a]	0.5	0.7

[a] Values at 473°K, estimated.

DISCUSSION

1. Structure of Film

It has been reported (*10*) that "black" films of metals deposited in inert gases consist of a collection of small particles formed originally in the gas phase. The evaporation conditions in this work (high krypton pressure and steep temperature gradient) are very favorable for the formation of such films. Annealing at 473°K would be expected to sinter the smaller particles, thus accounting for the color change and the structure seen by transmission electron microscopy.

From their mirror-like appearance, the films deposited in vacuum would be expected to have a larger particle size than the films deposited in krypton and, in fact did have considerably lower specific surface areas than the films deposited in krypton.

2. Adsorption of Krypton

The conditions for the application of the BET equation have been considered recently by Cannon and Gaines (*11*) who came to the conclusion that the equation can best be applied when a monolayer is almost complete before multilayer formation starts, i.e., the constant C in the BET equation should be large. The value 500 ± 100 was found for C in this work so that this condition is fulfilled.

Haynes (*12*) has shown that when C is large the influence of the choice of p_0 on the value of n_m derived from the BET equation becomes relatively unimportant. One set of results in this work was plotted using in one case 1.81 mm as p_0 and in the other case, 2.80 mm (the value for supercooled liquid krypton) and the value of n_m derived in the first case was only 3% greater than in the second case. In view of the above considerations, it seems that the value of n_m represents with some confidence the monolayer value. Later in the discussion the average number of surface atoms and the average number of surface bonds associated with each adsorbed krypton atom will be required and these values have been obtained on the basis of the following assumptions.

The first assumption was that krypton was adsorbed on sites and not in a close-packed array which was independent of the underlying structure. Calculations (*13*) have been made of the binding energy of an atom held by dispersion forces to various planes of a body-centered cubic structure and these calculations show that the positions where the atom is embedded in the surface with the maximum number of close neighbors have greater binding energies than other positions and so constitute preferred adsorption sites. Experimental evidence to support the above conclusion comes from adsorption studies of inert gases on tungsten (*14*) in the field emission microscope.

Many workers have found that in order

to obtain agreement between the areas found by krypton and nitrogen adsorption a larger area than the close-packed area must be assigned to krypton. Anatase has been carefully studied (*15*) and effective areas for krypton and xenon of 19.5 Å^2 and 27.5 Å^2 were derived by comparison with nitrogen adsorption; these results should be compared to 14.0 Å^2 and 16.5 Å^2, the close-packed values. Anderson and Baker (*16*) have calculated for the natural cleavage plane (001) of anatase that, assuming xenon is adsorbed in positions of maximum contact with neighboring atoms, an area of 28.3 Å^2 is obtained for xenon, in good agreement with experimental values.

The second assumption is that in the film crystals of all orientations have an equal probability of being present.

The final assumption is that nearly complete coverage of all planes is reached during the measurements.

Having made these assumptions, ball models of various atomically flat surfaces of silver were then constructed in the manner described by Moore and Nicholas (*17*) and balls of the appropriate diameter for krypton (Ag:Kr diameter-ratio 0.72) were placed on the surface, assuming site adsorption. On the (111) and (100) surfaces these sites were the centers of triangular and square arrays, respectively; on all the other surfaces there were in addition corner and edge sites having a larger number of close surface neighbors. These more complex sites were filled first and then the simpler types of site mentioned above, giving the maximum coverage possible consistent with site adsorption. In the interior of the metal each atom has twelve nearest neighbors, and a surface atom will be defined as a silver atom with less than the full coordination number twelve; a surface atom has from eleven to six nearest neighbors depending upon its position. An examination of the ball models gives a value for the number of krypton atoms which can be adsorbed per unit cell of surface and from this value the average number of surface atoms associated with each adsorbed krypton atom can be found. Although not of primary interest, the average area of occupation per krypton atom was also calculated.

A surface silver atom has a degree of unsaturation in its bonding and, crudely, we can say that it has from one to six broken bonds depending upon its position. Mackenzie, Moore, and Nicholas (*18*) have shown how to calculate the total number of surface atoms per unit area and the total number of broken bonds associated with these atoms. Thus, for a given surface, the average number of broken bonds per surface atom, i_{AV}, can be calculated. For the (*hkl*) surface with $h \geqslant k \geqslant l \geqslant 0$ in a face-centered cubic crystal we have:

$$i_{\text{AV}} = \frac{4h + 2k}{h + k}$$

Having found the average number of surface silver atoms associated with an adsorbed krypton atom from the ball model, and knowing i_{AV}, it is possible to calculate the average number of broken bonds associated with a krypton atom adsorbed on a given surface. The value of i_{AV} has been calculated for fourteen surfaces chosen to be representative of all surfaces. In deter-

TABLE 3

THE ADSORPTION OF KRYPTON ON SILVER ASSUMING SITE ADSORPTION ON VARIOUS ATOMICALLY SMOOTH SURFACES

Plane (*hkl*)	Av. no. of surface Ag atoms per Kr atom	Av. no. of broken bonds per surface Ag atom, i_{AV}	Av. no. of broken bonds per Kr atom	Av. area (Å^2) occupied by Kr atom
100	2	4	8.00	16.65
110	4	3	12.00	23.50
111	3	3	9.00	21.63
210	3	10/3	10.00	19.65
311	8/2	7/2	14.00	20.71
321	5	16/5	16.00	31.15
331	9/2	3	13.50	27.23
431	14/3	22/7	14.67	28.30
432	7/2	22/7	11.00	22.42
731	5	17/5	17.00	31.97
851	13/4	42/13	10.50	19.74
10,21	12/5	11/3	8.80	17.06
10,92	19/4	58/19	9.67	23.83
10,98	19/6	58/19	9.67	21.73
Grand average	3.62	3.24	12.11	23.36

mining the grand average values, the appropriate weighting factor for the multiplicity of the planes has been used. The results for the fourteen surfaces are given in Table 3. It can be seen from the table that this model leads to an average value of 3.6 surface silver atoms per krypton atom, or in terms of broken bonds, 12.1 bonds per krypton atom.

The average area occupied by a krypton atom is given by this method as 23.4 Å^2 which is rather higher than the value 19.5 Å^2 adopted by other workers to obtain agreement with nitrogen results on other adsorbents, but is of the same magnitude and suggests that the above model is not unreasonable.

Using the value 23.4 Å^2, film areas of 200–2000 cm^2 were obtained, compared to 40 cm^2, the geometrical area of the adsorption vessel wall.

3. Oxygen Sorption

The observation that the ratio of "fast" to "slow" sorption increases as the specific surface area increases, suggests that both adsorption on the surface and absorption into the bulk are occurring. Assuming that the amount of adsorbed oxygen is proportional to the surface area, and the amount of absorbed oxygen to the volume, leads to the following expression for the total sorption

$$n_p = K_1 A \theta + S_p \qquad (1)$$

where

n_p = number of molecules oxygen sorbed per mg at pressure p,
A = surface area per mg,
= $K_2 \times$ (krypton atoms in monolayer at 77.8°K per mg),
θ = surface coverage at pressure p,
S_p = number of molecules of oxygen absorbed per mg at pressure p,
K_1 = number of adsorbed oxygen atoms per unit area,
K_2 = surface area per adsorbed krypton atom,

To test Eq. (1), the oxygen sorbed per mg at a constant pressure was plotted against the monolayer krypton value per mg for a series of films with different specific surface areas. Figure 7 shows the results for the sorption at 2×10^{-1} mm Hg and as would be expected from the above equation, a straight line with a positive intercept was found. The results at various pressures were tested in the same way, using the least squares method to obtain the best fit, and at each pressure the above equation was obeyed. The slope ($K_1K_2\theta$) and intercept (S_p) are given in Table 4 as a function of the oxygen pressure.

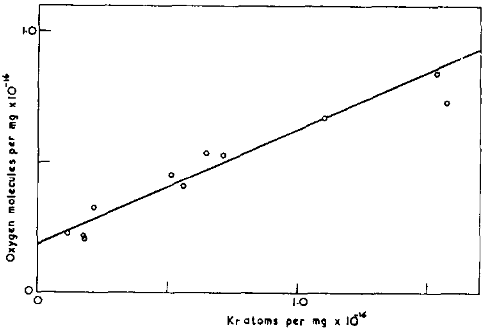

FIG. 7. Number of oxygen molecules per mg sorbed at 2×10^{-1} mm Hg vs. krypton monolayer per mg.

TABLE 4

TEST OF EQ. (1) AT DIFFERENT OXYGEN PRESSURES

Oxygen pressure (mm Hg)	Slope ($K_1K_2\theta$) (Oxygen atoms/ krypton atoms)	Intercept (S_p) (Molecules $\times$ 10^{-16}/mg)
1.0×10^{-2}	0.90 ± 0.16^a	0.05 ± 0.04
3.0×10^{-2}	0.88 ± 0.16	0.11 ± 0.04
7.0×10^{-2}	0.90 ± 0.16	0.15 ± 0.04
1.0×10^{-1}	0.92 ± 0.12	0.16 ± 0.04
1.5×10^{-1}	0.92 ± 0.12	0.17 ± 0.04
2.0×10^{-1}	0.90 ± 0.12	0.18 ± 0.04

[a] The limits shown are the 95% confidence limits.

The above equation was obeyed from 10^{-2} to 2×10^{-1} mm Hg. Increase in pressure from 10^{-2} to 7×10^{-2} mm Hg appreciably increased the amount absorbed, but at still higher pressures the amount absorbed only increased slightly.

The experiment in which carbon monoxide was admitted to the film provided a check on the oxygen absorbed in the interior; if the oxygen which did not react with the carbon monoxide is the absorbed gas, then this amount should agree with the amount derived by the above method. The quantity left after carbon monoxide treatment was $0.10 \pm 0.01 \times 10^{16}$ molecules/mg compared to $0.15 \pm 0.04 \times 10^{16}$ molecules/mg found from the intercept at the corresponding pressure, in reasonable agreement, considering the experimental error. The finding that only about 70% of the total sorbed oxygen reacted with carbon monoxide has also been observed on silver powders (*19*).

From Table 4, it is apparent that $K_1K_2\theta$ is constant at oxygen pressures from 10^{-2} to 2×10^{-1} mm Hg which means that adsorption is complete at or before 10^{-2} mm Hg and that the surface coverage is constant at pressures above this value. It has been shown (*20*) that if the surface concentration on a particle of regular shape is constant and the concentration of the absorbate in the interior is very low, then the initial uptake should be proportional to $(\text{time})^{1/2}$. To test this dependence upon $(\text{time})^{1/2}$, the results for Fig. 6b in the pressure region of 2.5×10^{-2} mm and higher were plotted in Fig. 8 as a function of $(\text{time})^{1/2}$ and a straight line was obtained. The sorption rate was almost independent of pressure until the highest pressures were reached, when it did decrease. This decrease would be expected as the concentration of oxygen in the interior increases.

The change from rapid uptake to slow uptake of oxygen at 10^{-2} mm and the completion of adsorption at this pressure must mean that the adsorption of oxygen by silver is fast. Maximum coverage corresponds to 0.90 ± 0.10 atoms of oxygen per krypton monolayer atom, suggesting that the adsorption is dissociative.

Indirect evidence for the dissociative adsorption of oxygen by silver comes from diffusion measurements (*21*) and from studies of the catalytic oxidation of ethylene (*22, 23*).

There is evidence that oxygen is adsorbed preferentially on sites where it can interact with as many surface atoms as possible in the same way as has been suggested for krypton. Germer (*24*) found the sticking coefficient for oxygen on nickel, a face-centered cubic metal, was low on the smooth, close-packed planes (111), (100), and high on the (110), the atomically rough plane, where an oxygen atom could

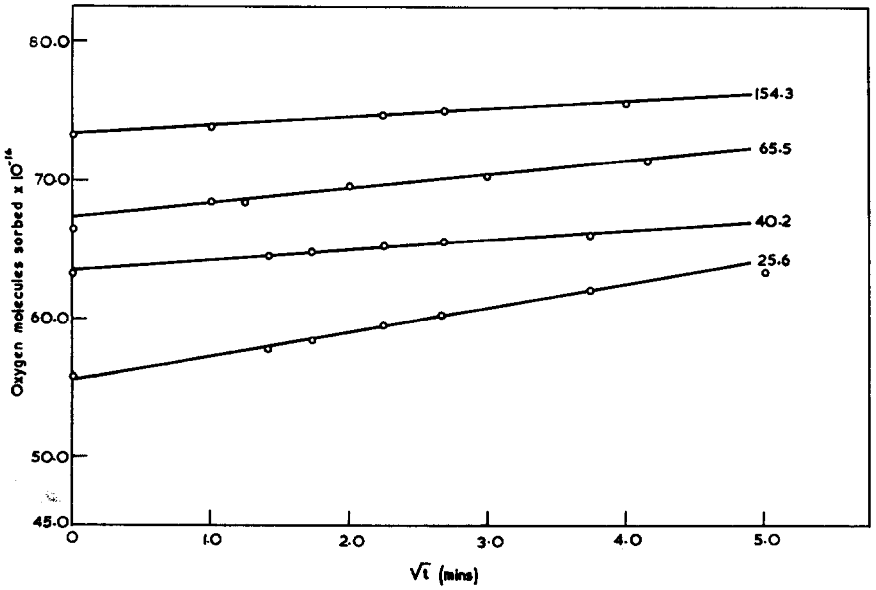

FIG. 8. The results of Fig. 6(b) replotted as number of oxygen molecules sorbed vs. $(\text{time})^{1/2}$. The numbers on the lines show the pressures (mm Hg $\times 10^3$) reached before the next dose was admitted.

embed itself more deeply in the surface. Adsorption with dissociation would favor the closer interaction of oxygen with surface atoms because the smaller atom could approach more closely than the molecule.

In view of the difference in atomic diameter and the type of bonding, it does seem surprising that there should be almost a one to one correspondence between krypton and oxygen atoms, i.e., that one oxygen atom is associated with the same average number of silver atoms as one krypton atom. It follows from the earlier part of the discussion that each oxygen atom is associated on the average with 3.6 surface silver atoms (see Table 3) and with 12.1 broken bonds. It is generally considered that in a metal like silver the outermost valency electron takes part in the binding of one atom to its twelve nearest neighbors. On the simplified picture presented here, therefore, each adsorbed oxygen atom is associated on the average with one electron.

Measurement of the change in work function of silver films after oxygen sorption (*25*) showed that a dipole was formed with a negative charge on the adsorbed oxygen. Measurement of the change in electrical resistance of a silver film after oxygen sorption showed (*26*) that the resistance increased, supporting the view that electron transfer from silver to adsorbed oxygen took place.

Although it is unlikely that a completely ionic bond is formed, consideration of the formation of an O^- ion from oxygen ($\Delta H_f^0 = -13.1$ kcal mole) (*27*) shows that it is not an unfavorable change from a thermodynamic viewpoint.

The simple picture of adsorption proposed in this discussion is an attempt to put into semiquantitative terms the ideas that adsorption arises from the saturation of surface bonds, and that the strongest bonding occurs when an adsorbed atom can interact with as many surface atoms as possible. Although undoubtedly oversimplified, it does lead to a picture which is not at variance with the experimental results.

The sorption experiments at 433°K suggest that some of the "fast" adsorption may have an appreciable activation energy, because at 433°K sorption with a measurable rate is observed before the pressure at which an oxygen/krypton ratio of one is reached. After a film has been pumped for 12 hr at 473°K, it is possible to take up further oxygen; it is not possible to decide from this single experiment whether oxygen has desorbed or whether some surface oxygen has diffused into the interior, but in view of the experiments at 433°K, it does suggest that at the higher coverages, some oxygen is more weakly adsorbed. This suggestion would be in keeping with the general finding that the heat of adsorption of gases on metals decreases with coverage.

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