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Kinetics of Reaction and Adsorption in the System Silver-Oxygen

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Since finely divided silver "sorbs" oxygen strongly, but not hydrogen or carbon monoxide, it was considered to provide a particularly suitable substance with which to study the relation of adsorption to the kinetics and absolute rates of catalyzed oxidation reactions.¹ More recently it was found² that such silver is capable of reacting with oxygen to form silver oxide at ordinary pressures and at temperatures as low as 170°, at rates which were slow but still sufficiently great to permit accurate measurement of the equilibrium pressures. This finding indicated the possibility that the catalytic activity of the silver may depend on oxide formation rather than adsorption. The answer to this problem has been obtained from a study of the rates of adsorption and of oxide formation at different temperatures and pressures, the results of which are here reported. The data also provide new information regarding the nature of the so-called "activated" adsorption, and its relation to "physical" adsorption and to compound formation.

Apparatus and Materials

The apparatus used for all experiments with Ag_I (see below) was the same as that already described in connection with the measurements on the silver oxide equilibrium.² Ag_{II} was studied in a separate apparatus, functioning on the same principle as the former. The only important difference was that the mercury trap connecting the ad-

sorption bulb with the manometer and Töpler pump and the trap leading to the buret were combined into one. The "free space" not occupied by the adsorbent, determined with purified helium, amounted to 34.7 and 39.3 cc. for Apparatus I and II, respectively. Constant temperatures were ordinarily produced by use of vapor baths, sometimes under regulated pressure. The liquids mainly used were: oxygen, water, chlorobenzene, xylene, turpentine, *o*-dichlorobenzene, ethylene glycol, diphenyl oxide and diphenylamine.

Materials.—Both samples of silver were prepared by reduction of precipitated silver oxide with hydrogen at a low temperature. Ag_I (39.4 g.) was the sample used in our equilibrium measurements.² Ag_{II} (45.86 g.) was the same, except for a slight loss in transferring to a new bulb, as that employed by Benton and Elgin.^{1b} Both samples had been heated for many hours at 300° in hydrogen and in vacuum before any of the experiments here described were undertaken.

In addition to the usual purification, the oxygen employed was carefully freed from possible traces of hydrogen by repeated passage over platinized asbestos and "Dehydrite," between the buret and a mercury-sealed reservoir.

All volumes are at 0° (760 mm.) and all pressures in mm. at 0°.

Kinetics of Formation and Decomposition of Silver Oxide.—Lewis³ studied the rate of decomposition of small samples of silver oxide at temperatures of 327–353°. Under the conditions employed the reaction was strongly autocatalytic, a maximum rate being reached when about half the oxide was decomposed. In the present experiments a large sample of reduced silver was oxidized

(1) Benton and Elgin, *THIS JOURNAL*, (a) **48**, 3027 (1926); (b) **51**, 7 (1929); and unpublished observations.

(2) Benton and Drake, *ibid.*, **54**, 2186 (1932).

(3) Lewis, *Z. physik. Chem.*, **52**, 310 (1905).

to the desired extent (0–10%) at 170–180°, whereupon the rate at which small quantities of oxygen were taken up or evolved was measured at different temperatures and pressures, by observing the rate of rise or fall of pressure in the closed system at constant volume.

All the data relating to silver oxide were obtained with Ag₁. Complete oxidation would have required 2047 cc. of oxygen (N. T. P.).

Rate of Decomposition.—Some of the data of a typical experiment are recorded in Table I. The amount of oxygen on the sample in the form of oxide was about 200 cc. initially, and 191 cc. at the end. Each mm. change in pressure at 174° corresponded to 0.0286 cc. of oxygen.

TABLE I
RATE OF DECOMPOSITION AT 174°

Time, hr.	Press., mm.	Rate, cc./hr.	k_2 , cc./hr.
0.0	6
.25	12	0.69	0.70
.75	22.5	.60	.62
1.50	37	.55	.59
2.50	56	.54	.60
4.00	84	.53	.63
6.00	118	.49	.63
10.00	175	.41	.61
23.75	300	.26	.56
25.75	312	.17	.55

It is evident from the values in Column 3 that the rate decreases as the pressure builds up toward the equilibrium value,² which is 443 mm. at 174°. Since, as shown below, the rate of the reverse reaction is proportional to the oxygen pressure, the kinetics of decomposition should be representable by the equation

$$\frac{d(\text{O}_2)}{dt} = k_2 - k_1 p = k_2 \left(1 - \frac{p}{P}\right)$$

where p is the actual pressure of oxygen and P is the pressure at equilibrium. The values of k_2 thus calculated, on the basis of average rates and pressures from point to point, are seen from Column 4 to be substantially constant. In most of the measurements the decomposition, starting from zero pressure, was followed only up to 10 to 30% of the equilibrium pressure; thus the correction for the reverse reaction was usually small. The average deviation of k_2 in an individual experiment was approximately 5%.

A survey of the measurements on rate of decomposition is given in Table II. The values in Column 2 are the amounts of oxide present in equivalent cc. of oxygen (200 cc. = 10% oxida-

tion). The experiments are listed in the order in which they were made. In the six-month interval between the two series the sample was subjected to repeated oxide formations and adsorptions.

TABLE II
RATE OF DECOMPOSITION OF SILVER OXIDE
 $E_2 = 35.6$ kcal.

Temp., °C.	O ₂ present, cc.	k_2 , cc./hr.	Log A_2 , cc./hr.
First Series			
174.0	200	0.63	17.19
189.1	47.8	2.53	17.22
182.0	47.8	1.30	17.19
189.0	46.4	2.33	17.19
175.0	44.6	0.71	17.20
182.0	43.2	1.37	17.22
188.9	41.9	2.23	17.18

Av. 17.199

Second Series			
179.2	21.0	1.26	17.29
198.3	19.7	6.16	17.28
179.4	17.3	1.25	17.28
198.2	16.0	6.51	17.31

Av. 17.290

It will be seen that the results are reasonably reproducible. Further, the fraction oxidized, within the limits 0.8 to 10%, exerts little effect, if any. This result would not be unexpected if the sample had been thoroughly oxidized superficially before each run. This was the procedure, however, only in the first three experiments of the First Series; in the other cases the sample was used just as it was at the end of the preceding decomposition.

From the equation, $k_2 = A_2 e^{-E_2/RT}$, the following values of the activation energy E_2 in kcal. are obtained: Series 1, 175–182°, 36.4; 182–189°, 34.3; Series 2, 179–198°, 36.2. With the average $E_2 = 35.6$, the calculated values of log A_2 , as given in Column 4 of Table II, are approximately constant.

Rate of Formation.—An experiment showing the effect of pressure on the rate of formation is detailed in Table III. There were about 190 cc. of oxygen in form of oxide at the start and 195 cc. at the end. The values of k_1 in the last column have been calculated from the equation, $-\Delta(\text{O}_2)/\Delta t = k_1 p_{\text{av.}} - k_2 = k_1(p_{\text{av.}} - P)$. The equilibrium pressure P has been taken as 365 mm. Over a range of 14:1 in rate, k_1 is substantially constant. Other measurements, except those made in the immediate neighborhood of equilibrium where uncertainty in $p - P$ becomes very

great, confirmed the proportionality of rate to distance from equilibrium.

TABLE III
RATE OF FORMATION OF OXIDE AT 168°

Time, hr.	Press., mm.	Rate $\times 10^3$ cc./hr.	$p_{av.} - P$, mm.	$k_1 \times 10^3$ cc./hr./mm.
0	542.8
1.1	536.8	161	174.8	0.92
12.5	482.6	135	144.7	.93
21.5	454.2	92	103.4	.89
24.0	447.7	75	86.0	.87
36.8	420.8	60.5	69.3	.87
47.0	405.9	42.0	48.4	.87
61.8	391.4	28.2	33.7	.84
72.8	383.5	20.8	22.5	.92
94.7	375.0	11.2	14.3	.78

A summary of the results at different temperatures is given in Table IV. The experiments are listed in the order in which they were made.

TABLE IV
RATE OF FORMATION OF SILVER OXIDE
 $E_1 = 22.0$ kcal.

Temp., °C.	O ₂ present, cc.	$k_1 \times 10^3$, cc./hr./mm.	Log A_1
Series 1			
141	3.6	0.62	8.39
161	4.1	2.40	8.45
141	4.5	0.45	8.25
179	4.7	5.59	8.38
161	3.8	2.57	8.48
139	4.1	0.70	8.51
161	3.9	2.53	8.47
100	3.4	0.034	8.41
			Av. 8.418
Series 2			
179.8	10.5	1.73	7.85
139.0	10.9	0.146	7.82
160.0	11.4	.635	7.89
139.0	12.4	.159	7.86
139.0	14.1	.149	7.83
160.2	15.1	.610	7.88
160.7	20.5	.621	7.87
			Av. 7.857

Series 2 followed immediately after Series 1, and immediately preceded the Second Series of decompositions in Table II. In Series 2 there was no intervening treatment of the sample between runs; in Series 1 the oxide formed in a given run (0.6 to 1.0 cc.) was partially decomposed before the succeeding run. The quantity of oxygen present at the start is shown in Column 2.

Comparison of Series 2 with the values of k_1 in Table III indicates that the extent of oxidation, in the range 0.5 to 10%, exerts no appreciable effect on the rate of formation. However, with

smaller amounts of oxygen present (Series 1), the rates are considerably faster. It will be shown below that this sample *adsorbs* at these temperatures approximately 3.5 cc. of oxygen in the form of activated adsorption, and does so at a rate which is large compared to that of oxide formation. Accordingly, of the amounts of oxygen present in Series 1, 3.5 cc. is adsorbed, and only the remainder (0 to 1 cc.) is present as oxide. Thus these results represent as nearly as possible the *initial* rate of oxide formation. It is noteworthy that this initial rate is only about four times as great as the constant rate observed in presence of oxide equivalent to 10 to 190 cc. of oxygen.

From the equation $k_1 = A_1 e^{-E_1/RT}$ the following values of the energy of activation E_1 in kcal. were obtained: Series 1, 100–140°, 21.7; 140–161°, 24.2; 161–179°, 17.4; Series 2, 139–160°, 23.6; 160–180°, 20.5. The average is 21.5, but in view of the larger number of experiments in the range 140–160°, we have given this range more weight and taken E_1 as 22.0. It will be seen from the fourth column of Table IV that the values of A_1 calculated on this basis are fairly constant.

Comparison of Rates with Equilibrium.—The magnitude of the energies of activation for the formation and decomposition of the oxide shows clearly that these processes are not controlled by diffusion factors, at least in the ordinary sense. If the rates in each direction refer to the actual chemical reaction itself, it follows that $E_2 - E_1 = Q$, the heat of the reaction. The Q thus obtained is $35.6 - 22.0 = 13.6$ kcal. per mole of oxygen, or 6.8 per mole of Ag₂O. The heat of formation obtained from the equilibrium measurements² in the same temperature range was 7.0 ± 0.2 .

The equilibrium pressure should be given by the equation

$$P = k_2/k_1 = \frac{A_2}{A_1} e^{-(E_2 - E_1)/RT}$$

Values of P thus calculated (Table II, Series 2 and Table IV, Series 2) are 596 mm. at 173.0° and 1090 mm. at 191.2°, which may be compared with 422 and 790 mm. observed at the same two temperatures. In view of the very great effect of small changes in the E values, agreement as to order of magnitude is probably all that can be expected.

Adsorption of Oxygen by Ag₁

At temperatures above about 140° it was possible to study the adsorption of oxygen which

occurs at pressures less than those at which silver oxide can form. Below 100° adsorption could be investigated even at pressures above the dissociation pressure of the oxide (21 mm. at 100°), since here the rate of oxide formation by Ag_2O is negligibly small. Thus the maximum rates of oxide formation at 760 mm., based on the data of Table IV, Series 1, are 0.027 cc. of oxygen per hour at 100° , and 5×10^{-7} at 0° .

It was found that adsorbed oxygen could not be removed completely even by long-continued evacuation at 300° . Accordingly, before each new experiment the sample was twice subjected to gradual heating in hydrogen to 300° , allowed to stand for one-half hour, and then evacuated. It was found that adsorbed oxygen is completely removed in this way, and it was already known^{1a} that hydrogen is not retained in significant quantity under these conditions.

All volumes are cc. (0° , 760 mm.) taken up by the whole weight of sample employed.

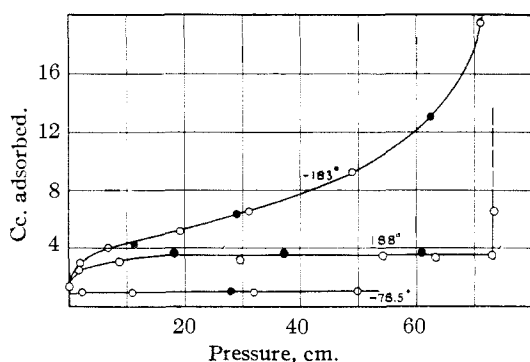


Fig. 1.—Adsorption of oxygen by AgI .

Previous Work on Adsorption of Oxygen by Silver.—Adsorption of various gases by silver has been investigated by Durau,⁴ Nikitin and Sharkov,⁵ and Reyerson and Swearingen.⁶ A brief study of the adsorption of oxygen was reported by Benton and Elgin.^{1a} Taylor⁷ measured the rate at which oxygen was taken up by silver in the range 0 – 184° . The apparent energy of activation decreased with increasing adsorption from 17 to 13 kcal. It is not certain to what extent, if any, these measurements were affected by oxide formation or by physical adsorption, but in view of our own results it is probable that activated adsorption was alone involved.

(4) Durau, *Z. Physik*, **37**, 419 (1926).

(5) Nikitin and Sharkov, *J. Russ. Phys.-Chem. Soc.*, **58**, 1095 (1926).

(6) Reyerson and Swearingen, *J. Phys. Chem.*, **31**, 88 (1927).

(7) Taylor, *Z. physik. Chem.*, Bodenstein Festband, 475 (1931).

Adsorption Isotherms.—Adsorption equilibria of Ag_2O at pressures up to one atmosphere are shown in Fig. 1 for -183 , -78.5 and 188° . Open circles represent points obtained from the side of lower pressure, solid circles the reverse. At the two lower temperatures equilibrium was reached practically instantaneously, except at the first point (see below), and no change occurred during the one-half to one hour of observation at each pressure. At 188° , on the other hand, equilibrium was approximated only after several hours. That the constant values finally reached in the temperature range 180 – 200° do correspond to equilibrium is shown by the close agreement ordinarily obtained when equilibrium was approached from higher and from lower pressures. (When an intervening formation and decomposition of oxide had occurred, as in Fig. 1, 188° , subsequent adsorptions were somewhat higher than before. The formation and decomposition of oxide presumably results in an increase in surface, but, if so, the process of burning off with hydrogen must restore the sample to what may be regarded as a standard condition, since check runs, even at wide intervals, were in excellent agreement.)

At -183° the adsorption is of the characteristic physical type, increasing rapidly with increasing pressure as the vapor pressure of liquid oxygen is approached. At -78.5° the flatness of the isotherm shows clearly that here the physical adsorption has become almost negligibly small, and that nearly the whole adsorption of 1 cc. is of the "chemical," or activated type. This conclusion is supported by the fact that the first portion of gas admitted did not come to equilibrium immediately, but required ten to fifteen minutes. At 0° there was a very rapid activated adsorption of 1.0 cc., followed by an extremely slow further adsorption. Thus the first cc. of activated adsorption is sharply differentiated as to rate from the further 2.5 cc. A similar behavior was observed in the case of hydrogen on iron⁸ at -78.5 and 0° .

All the isotherms obtained in the range 179 – 197° were essentially identical with the one at 188° shown in Fig. 1, except that the point of abrupt change at the dissociation pressure of the oxide naturally varied with the temperature. The limiting adsorption was always very close to 3.5 cc. At temperatures between 0 and 170°

(8) Benton and White, *THIS JOURNAL*, **54**, 1820 (1932).

equilibrium was never reached. Some of the adsorptions obtained after long times of observation are given in Table V. In no case was the final rate greater than 0.01–0.02 cc. per hour. On the assumption that down to 139° the results are not far from equilibrium, the activated adsorption would appear to be roughly independent of temperature over the range 140–200°.

TABLE V
ADSORPTION AT INTERMEDIATE TEMPERATURES

Temp., °C.	Adsorption, cc.	Final <i>p.</i> , mm.	Time, hr.
0	1.86	556	96
100	3.63	680	56
100	2.99	506	14
139	3.46	87	15
179	3.63	417	4

Conclusions cannot safely be drawn at the lower temperatures, since at 0° the rate curves showed that equilibrium was not even approached, and at 100° the rate of formation of oxide is appreciable. (The pressure shown at 139° is about 34 mm. less than the dissociation pressure.)

The evidence that solubility of oxygen in silver is not an appreciable factor in these measurements will be presented after the results with Ag_{II} have been described.

Rate of Desorption of Oxygen.—The bare surface was allowed to adsorb the desired quantity of oxygen at pressures below the dissociation pressure, then cooled to 100° and evacuated. From measurement of the gas thus pumped off, the amount remaining adsorbed was known. The silver was then rapidly heated to the temperature of the experiment and the rate of desorption determined by measuring at regular intervals the gas removed by frequent operation of the Töpler pump. Ordinarily the pressure in the bulb did not at any time exceed 0.1 mm.

Since the rate of desorption has been found to decrease very rapidly as gas is removed from the surface, the observed adsorptions were plotted against the time so as to provide by interpolation a comparison of rates over equal intervals of volume. Table VI summarizes the data obtained. The two experiments in a given set were made in immediate succession, but the two sets were separated by five months' use of the sample for other purposes. Throughout this paper values of *k* and *E* are averages over the *interval from each adsorbed volume to the next*.

Although the rates were much greater in the second set, the energy of activation *E*₂ is approxi-

TABLE VI
RATE OF DESORPTION OF OXYGEN FROM Ag_I
*E*₂ = 28.4 kcal.

O ₂ on, cc.	<i>k</i> ₂ , cc./hr.		<i>E</i> ₂ , kcal.	Log <i>A</i> ₂ , cc./hr.	
	189.2°	226.3°		189.2°	226.3°
2.30
1.97	0.157	1.32	26	12.61	12.54
1.93	.040	0.37	28	12.02	11.99
1.89	.019	.28	34	11.70	11.87
	179°	197°		179°	197°
2.10
2.00	0.75	2.4	27	13.59	13.57
1.90	.52	1.7	28	13.44	13.42
1.80	.27	1.1	33	13.15	13.23
1.70	.14	0.43	26	12.87	12.83
1.65	.08	.23	25	12.62	12.55

mately the same, the average of all values being 28.4 kcal. In a given set, with rates varying by a factor of nearly ten as the amount of adsorption changed, there is no definite trend in the values of *E*₂. However, the range over which these studies could be made was too narrow to give a positive decision on this point.

Shortly after the first set a desorption experiment was made at 295°. The rate in the range 1.97–1.89 cc. adsorbed, though too fast for exact measurement, gave a value of *E*₂ of about 30 kcal. when compared with the rate at 226°. On the assumption that *E*₂ = 28.4 over the whole range studied at 295°, the following values of log *A*₂ were obtained for each 0.2 cc. desorbed.

Initial ads., cc.	2.00	1.80	1.60	1.40	1.20
Log <i>A</i> ₂ , cc./hr.	12.00	11.82	11.56	11.35	10.92

Rate of Adsorption.—Reliable values of the energy of activation are not obtainable from the measurements in the range 180–200° since more than half of the adsorption occurred at rates too fast for measurement, and the last part is made uncertain by the near approach to equilibrium. In the range 0–100° the rates of adsorption were slow enough for measurement, yet in comparison the maximum rates of oxide formation were negligible. A pair of experiments is shown in Table VII. Values of time and *E*₁ refer to the adsorption *intervals* of Col. 1. The values given for 0° are observed points, those for 100° are

TABLE VII
RATE OF ADSORPTION BY Ag_I

O ₂ on, cc.	Time interval, min.		<i>E</i> ₁ , kcal.
	0°	100°	
0
1.55	1487	0.9	(15.0)
1.64	2987	2.3	14.1
1.82	4427	9.2	10.8
1.86	5732	11.2	13.1

interpolated. The range of pressure at the two temperatures was practically the same, 563–556 mm. at 0° and 548–539 mm. at 100°. The amount of oxide formed in the total time could not have exceeded 0.004 cc. in either case.

Another measurement at 0° compared with the same values at 100° gave the following (again with nearly equal pressures at the two temperatures)

O ₂ on, cc.	0–1.56	1.62	1.69	1.73
E ₁ , kcal.	(14.7)	13.7	13.0	14.0

Successive experiments at 139 and 179°, at equal pressures of 138–118 mm. where oxide formation cannot be a factor, gave the following

O ₂ on, cc.	1.90–2.10	2.24	2.50
E ₁ , kcal.	9.5	13.7	12.2

In all these measurements the rate of desorption was negligible. The energy of activation is nearly constant, the average being 12.7 kcal. In the range 1.5–2.5 cc., out of a total possible adsorption of 3.5 cc., there is no obvious trend in the values of *E*. The slightly higher values in the range 0–1.5 cc. are somewhat doubtful because of the usual uncertainty in kinetics as to the initial time.

Experiments at 179° with average pressures differing by a factor of five showed that the rate increases with the pressure and is probably proportional to it. (The uncertainty arises from the fact that "check" runs showed considerable variation.) Accordingly the rate of adsorption may be expressed by the equation $d(O_2)/dt = A_1 e^{-12,700/RT} p$. Representative values of log *A*₁ thus calculated for adjacent experiments at 0 and 100° are given in Table VIII. The enormous decrease in rate with increasing adsorption will be evident.

TABLE VIII

ABSOLUTE RATE OF ADSORPTION

O ₂ on, cc.	0.0	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4
Log <i>A</i> ₁ , cc./hr./mm.	8.75	6.78	6.00	5.26	5.06	4.64	4.21	3.83	

Heat of Adsorption.—In successive experiments at 188 and 197° with 3.04 cc. adsorbed, the equilibrium pressures were 161 and 224 mm., whence the Clapeyron equation gives *Q* = 16 kcal. Another pair of experiments at 188.2 and 197° yielded values decreasing from 23 to 15 kcal. for adsorptions from 2.5 to 3.0 cc. The apparent trend is probably within the limits of possible error. On the assumption that $Q = E_2 - E_1$ a value of 28.4 – 12.7 = 15.7 is obtained.

We conclude that the rates measured are the actual inverse rates of adsorption and desorption.

Adsorption of Oxygen by Ag_{II}

In spite of the nearly identical method of preparation and treatment of the two silver samples, remarkable differences in behavior were found. Thus Ag_{II}, studied under the same conditions as the former sample, never formed silver oxide in appreciable quantity. It can be stated definitely that the rate of formation was at least 100 times smaller.⁹ At a given fraction of the total adsorption the rates of adsorption and desorption were of the same order of magnitude as those found for Ag_I. However, the adsorption maximum was now 2.5 times as great, so that the time required to reach approximate equilibrium was much longer than with the other sample. Thus at 197°, after twenty to thirty hours at a given point, equilibrium was nearly but not quite attained, as judged by approaching it from higher and from lower pressures. At 178° even eighty to one hundred hours were insufficient. The rough isotherms obtained below 200° will be omitted; they show an exactly similar trend to those for Ag_I, but the adsorption at one atmosphere was about 9.0 cc. instead of 3.5. An effort was made to determine isotherms in successive experiments at 254 and 294°. Apparent equilibrium was attained at each point in about twenty hours at 254° and in less than one hour at 294°. Much sintering occurred, however, as shown by the fact that later points showed less adsorption than earlier points at the same pressure. At 254° and 650 mm. the decrease was about 15% in 200 hours, or 0.005 cc. per hour. At 294° the sintering caused a decrease of about 0.02 cc. per hour. When the adsorption at each point is thus corrected back to the initial state of the surface in each experiment, smooth isotherms are obtained from which the heat of adsorption in the range 4–6 cc. is 16 kcal. If the final state at 254° is compared with the initial state in the immediately following experiment at 294° the calculated heat of adsorption is almost zero. These facts support the conclusion previously mentioned, that the process of burning off with hydrogen before each experiment restores the surface to a fairly "standard" condition.

(9) Since this sample was the identical material used by Benton and Elgin,^{1b} it follows that oxide formation could not have affected their results or their conclusions as to the mechanism by which silver catalyzes the oxidation of hydrogen.

Adsorption at the Lower Temperatures.—

Isotherms at -183 and -78.5° are shown in Fig. 2. (In plotting the latter curve the adsorptions have been multiplied by five.) At both temperatures equilibrium appeared to be attained almost at once. Evidence that this was actually the case at -183° is given by the close agreement of points obtained on retracing the isotherms from higher pressures. The same procedure at -78.5° revealed that here true equilibrium was not reached. In the figure open circles represent the first ascent of the isotherm; the subsequent points, indicated by black circles, are numbered in the order obtained. Time of observation was ten to twenty minutes, except at Point 3 where in 11.6 hours the adsorption increased from 1.65 to 1.86 cc. Repetition of the experiments both at -78.5 and at -183° gave results essentially identical with those shown.

At -183° we have a typical physical adsorption, possibly combined with about 1 cc. of activated adsorption occurring at the first point. At -78.5° there is a rapid activated adsorption of 1 cc., followed by a very slow further adsorption. We estimate that at 650 mm. the (instantaneous) physical adsorption amounts to about 0.5 cc. If so, comparison with -183° gives for the order of magnitude of the heat of physical adsorption a value of 2–3 kcal. per mole of oxygen.

Rate of Desorption.—The observed rates of desorption are summarized in Table IX, which gives the values of $\log A_2$ on the assumption that the energy of activation is the same as for AgI , 28.4 kcal. The assumption is evidently supported by the data.

O_2 on, cc.	197°	$\log A_2$, cc./hr. 224°	295°
5.25–5.10	...	12.29	...
5.10–4.90	11.96	11.86	...
4.70–4.50	...	11.71	...
3.50–3.00	11.32

Rate of Adsorption.—Rates of adsorption under comparable conditions but at widely separated dates differed at most by a factor of two or three. The energy of activation E_1 in the range 140 – 200° was found to be in the neighborhood of 12 kcal. Table X gives the observed rates in terms of $\log A_1$, based on a value of $E_1 = 12.7$ kcal., the same as for AgI . The rates shown at 179.2° are the averages of three experiments at nearly equal pressures, in which the average deviation

TABLE X
RATES OF ADSORPTION BY Ag_{11}

O_2 on, cc.	139°	$\log A_1$, cc./hr./mm. 139°	179.2°	197.7°
0–4.0	6.22	6.22
4.2	5.29	5.38	5.12 ^a	...
4.4	5.25	5.29	4.99 ^a	...
4.6	5.05	5.18	5.09	...
4.8	4.84	5.03	4.89	...
5.0	4.73	4.88	4.73	...
5.2	4.59	4.77	4.60	...
5.4	4.39	4.57	4.40	4.34
5.6	4.27	4.46	4.25	4.21
5.8	4.21	4.36	4.10	4.07

^a One experiment only.

of $\log A_1$ from the mean was 0.13. The actual range of average pressures in the experiments of Table X, from left to right, were 231–126, 142–37, 217–180, 460–447 mm. For a given volume adsorbed the results are seen to be fairly consistent.

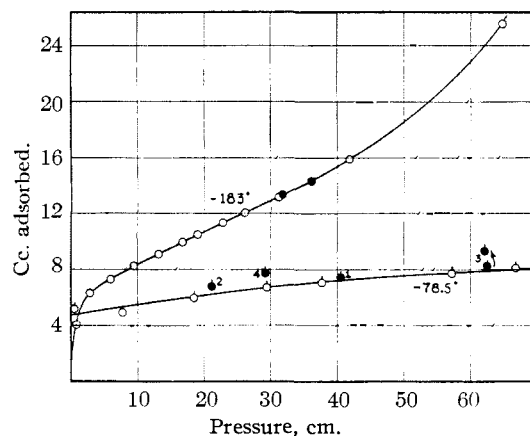


Fig. 2.—Adsorption of oxygen by Ag_{11} . In plotting the curve for -78.5° the actual adsorptions have been multiplied by 5.

As already mentioned, the rate of activated adsorption at -78.5° in the range 1.0–1.4 cc. was extremely slow. In the same range at 0° the rate was too fast for precise measurement. Analysis of the results shows that the energy of activation could not have been less than 10 kcal. The same conclusion could be drawn for the range 2.5–3.0 cc. from experiments at 0 and 100° . This evidence again indicates that the energy of activation does not vary greatly with the amount of gas adsorbed—at least not sufficiently to account for the rapid decrease in rate with increasing adsorption.

Solubility as a Possible Complication

While oxygen dissolves readily in liquid silver, the solubility in solid silver appears to be very

small. Steacie and Johnson¹⁰ found that at 800 mm. pressure 10.5 g. of silver foil took up 0.14 cc. of oxygen at 200°, 0.10 cc. at 300°, and 0.09 cc. at 400°. The sorption was proportional to the square root of the pressure. On the basis of these results the solubility of oxygen in our samples at 200° would be about 0.6 cc. at 800 mm. and 0.2 cc. at 100 mm. Reference to Fig. 1 will show that such solubilities are at most a minor factor in the adsorptions here reported, which at 100 mm. and 200° amount to about 3 and 7 cc., respectively, for Ag_I and Ag_{II}. Further, the flatness of the 188° isotherm shows that if any part of the total sorption is proportional to the square root of the pressure it must be relatively insignificant.

Behavior Following Temperature Changes.—When after many hours equilibrium was apparently reached at 160–180° and the temperature then quickly raised to about 200° (the pressure being always below the dissociation pressure of the oxide), the sorption gradually and continuously decreased toward the new value characteristic of the higher temperature. On the other hand, when the temperature was changed from a value in the range 160–180° to 294° the sorption at first rapidly decreased but later *increased* slightly. The increases might be considered to represent the difference in solubility over this range or possibly the whole solubility at 294° if the rate of solution at the lower temperatures was negligibly small. In either case the indicated solubilities are unimportant, since the observed increases amounted to only 0.1–0.2 cc. (at pressures of 100–400 mm.).

When equilibrium was attained in the range 160–170° and the sample then cooled to 0° there was no measurable change in sorption. On cooling further to –78.5° an increase of only 0.16 cc. was found (Ag_{II}, pressure 271 mm.). Clearly the physical adsorption, represented by such increases, is small down to –78.5°. Cooling from 0 to –183°, however, resulted in greatly increased adsorption. Thus for Ag_{II}, with 8.37 cc. adsorbed at 0° and 540 mm. (after cooling from 179°), the adsorption increased to 16.19 cc. at –183° and 134 mm. In another experiment with the same sample, the adsorption increased from 2.66 cc. at 0° and 543 mm. to 10.93 at –183° and 132 mm. In the former case the surface was

probably almost completely covered by the activated adsorption at 0°, and only about 30% covered in the latter case. The nearly equal increases on cooling to –183° show that the extent of physical adsorption on a given area of surface is only slightly affected by a drastic change in the nature of the surface—a relation for which much evidence exists for other systems also.

Extent of Surface of Samples Employed

Since each sample reached a limiting value for the activated adsorption which remained constant over a considerable range of temperature, we conclude that this limit represents complete covering of the surface with a unimolecular, or possibly monatomic, layer. The physical adsorption at –183° is undoubtedly multimolecular at the higher pressures, and probably at all pressures where the isotherm is convex downward (see Figs. 1 and 2). Both isotherms strongly suggest an adsorption which is tending toward a limiting value at pressures of 100–150 mm., but with the limit masked by increasing capillary condensation. These limiting values appear to be roughly 4.5 and 10–10.5 cc. for Ag_I and Ag_{II}, respectively. These may be compared with the limiting activated adsorptions, namely, 3.5 and 9 cc. If, as indicated above, 1 cc. of activated adsorption occurred in each case at –183°, the limiting values for the two types of adsorption would be practically identical for a given sample. We conclude that these values correspond to adsorption on the whole exposed surface and not merely on a few specially active spots.

On the assumption that each exposed silver atom adsorbs one molecule of oxygen, there are $6.06 \times 10^{23} \times 3.5/22,400$ silver atoms in the surface of Ag_I. Since a face of the unit face-centered cube of silver (edge = 4.06 Å.) contains the equivalent of two silver atoms, the area assignable to each is 8.24×10^{-16} sq. cm. Thus the surface area of Ag_I would be 7.8×10^4 sq. cm. Similarly the area of Ag_{II} would be 2.0×10^5 sq. cm. If the areas are calculated on the assumption of a single adsorbed layer of close-packed molecules whose diameter is that of ordinary oxygen molecules, essentially the same results are obtained. It is conceivable, however, that the adsorption involves one oxygen *atom* to each superficial silver atom, or even, if the adsorbed oxygen occupies the same positions relative to the silver atoms as in the silver oxide lattice, one

(10) Steacie and Johnson, *Proc. Roy. Soc. (London)*, **A112**, 542 (1926). See also Sieverts and Hagenacker, *Z. physik. Chem.*, **68**, 115 (1910).

oxygen atom to two silver atoms. Nevertheless there can be little doubt that the areas calculated above are of the correct order of magnitude.

Absolute Rates Compared with Rates of Collision

Oxide Formation.—Only the *initial* rate of oxide formation could logically be expected to have any relation to the rate of collision of oxygen molecules with the original surface. With Ag_I this initial rate is given by the expression, cc. reacting per hr. per mm. = $2.6 \times 10^8 e^{-22,000/RT}$. If the factor 2.6×10^8 be assumed to represent the total number of collisions with the surface, the area required is 6.6×10^8 sq. cm. The agreement of this value, within one order, with that calculated from the adsorption is suggestive but may well be accidental. The negligibly small rate of oxide formation by Ag_{II} means either a considerably higher activation energy for this sample or, if E is the same, the factor A multiplying the exponential term must be at least 10^8 times smaller than the rate of collision of oxygen with the surface. It seems probable that oxide formation involves as an intermediate step the relatively rapid process of activated adsorption.

Adsorption.—The rate of collision of oxygen with Ag_I (7.8×10^4 sq. cm.) at 1 mm. pressure and an average temperature of 100° is 3.3×10^9 cc. per hr. For the first cc. of adsorption an average value of A of 5.6×10^8 was observed. From the rapidity with which the rate subsequently decreases with increasing adsorption (Table VIII), it appears quite possible that the *initial* rate would furnish an A value close to the total rate of collision. For Ag_{II} (area = 2.0×10^5 sq. cm.) the rate of collision is 8.5×10^9 cc. per hour per mm. The average A for the first 4 cc., out of a total adsorption of 9 cc., is 1.7×10^6 . The initial rate was certainly several orders of magnitude higher.

Thus the evidence is consistent with the hypothesis that every collision with energy in excess of 12,700 cal. per mole results in activated adsorption. There is no satisfactory way to test the alternative possibility that activated adsorption results not from energetic collisions of molecules from the gas phase, but when the necessary activation energy is acquired by the few physically adsorbed molecules which are presumably always present on the surface. If gaseous collisions are alone responsible it is not easy to see why the A value decreases from about 10^9 initially to about

10^5 when only half the surface has been covered (Ag_I , Table VIII). The 50% increase in E necessary to account for these results certainly did not occur.

The bearing of these results on the mechanism of the catalytic action of silver in oxidation reactions will be considered in a forthcoming report.

Summary

Finely-divided reduced silver may react with oxygen to form silver oxide at ordinary pressures and at temperatures as low as 160° . The rate of formation, which is proportional to the pressure but practically independent of the extent of oxidation in the range 0.3 to 10%, is given by the expression, cc. reacting per hour per mm. pressure = $7.2 \times 10^7 e^{-22,000/RT}$. The initial rate in absence of oxide is about four times as great. The rate of decomposition, approximately constant over the same range of composition as the formation, is $1.9 \times 10^{17} e^{-35,600/RT}$. The difference between the energies of activation of the forward and reverse reactions is found to equal the heat of reaction and the equilibrium pressures calculated from the reciprocal rates agree fairly well with the directly measured values.

At pressures below the dissociation pressure of the oxide two types of adsorption occur, (1) a practically instantaneous physical adsorption which is large at -183° but decreases rapidly with increasing temperature, and which has already become small at -78.5° ; (2) an "activated" adsorption whose limiting value is nearly independent of temperature over the range 150 – 200° , and which proceeds very slowly at 0° but increases rapidly at higher temperatures. The energy of activation for this second process was found to be 12.7 kcal., and for the desorption process 28.4 kcal. These values show no definite variation for successive fractions of the surface, in spite of the fact that in each case the actual rates fall off very rapidly as the process continues. It is shown that solubility is not an appreciable factor in these measurements.

When the limiting activated adsorptions are used to calculate the surface areas of the two samples employed, it is found that the rate at which oxygen molecules collide with the surface with energy in excess of the required activation energy is roughly equal to the initial rate of adsorption.

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