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The Chemisorption of Oxygen on Group IB Metals and Their Surface Oxidation

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The modern views on the kinetics and mechanism of the chemisorption of oxygen on group IB metals and their surface oxidation (up to the appearance of an oxide phase) are described. Processes occurring in the temperature range from 0° to 300-400°C, which are of interest in connection with problems of catalysis and radioelectronics, are mainly considered. The bibliography includes 123 references.

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I. INTRODUCTION

Group IB metals are catalysts of mild, partial oxidation[1,2]. Catalytic oxidation processes are usually regarded as occurring in stages and it is believed that one of the stages is chemisorption of oxygen[1-4]. The overall rate of the catalytic process on metallic catalysts in general and on group IB metals in particular usually depends significantly on the rate of adsorption of oxygen[5]. This is one of the reasons why much attention is being devoted to the study of the kinetics and mechanism of the chemisorption of oxygen on copper, silver, and gold. Another reason is the requirement for pure materials in the radioelectronics industry[6] and the consequent necessity for assessing the possible contamination of the metals by oxygen under various conditions and also for assessing the effect of the chemisorption of oxygen on the properties of the finished articles. The third reason for studying the above processes is the effect of small amounts of oxygen on various mechanical characteristics such as creep (see, for example, Ostrovskii et al.[7]), strength (see, for example, Gupta[8] and Ahlers[9]), the self-diffusion coefficient (see, for example, Cabane[10]), etc. The chemisorption of oxygen on gold is also of special importance in connection with the problem of reference electrodes in measurements of the changes in contact potentials during the adsorption of oxygen on various surfaces.

II. CERTAIN CHARACTERISTICS OF THE SURFACE INTERACTION OF COPPER, SILVER, AND GOLD WITH OXYGEN

The phase interactions of copper, silver, and gold with oxygen differ sharply in the thermodynamic sense. Table 1 presents the standard free energies of formation ΔG_{f_0} and the standard heats of formation ΔH_{f_0} of copper, silver, and gold oxides from the elements, both at 25°C.[11] It follows from the table that, in the temperature range considered, the metal-oxygen equilibrium involving copper is sharply displaced towards the formation of the oxide and in the case of gold towards the metal. The equilibrium position for silver depends on the oxygen pressure and temperature. Thus the equilibrium oxygen pressure over Ag_2O at 201°C is 1.526 atm, while at 174°C it amounts to 0.596 atm.[12] Nevertheless oxygen is chemisorbed on the pure surfaces of all the metals considered even at pressures much lower than 1 mmHg. The problem of the chemisorption of oxygen on gold remained open for a long time. It had been concluded[13] that oxygen is not chemisorbed, but subsequently it was shown[14] that the method of measurement used in the earlier study[13] was insufficiently sensitive. The widely held view that oxygen is not chemisorbed on gold was also supported by other results[15,16], where the degree of adsorption was not measured directly but it was observed that the electronic work function of gold does not change when the latter is in contact with oxygen at room temperature. However, it was shown later[17-22] and also in earlier studies[23,24] that gold in powder form[18,19,22-24] and in the form of a wire[17], films[20], and foil[21] can chemisorb oxygen.

Table 1. Thermochemical parameters of the oxidation processes.

Oxide	State	ΔH_{f_0}, kcal mole^{-1}	ΔG_{f_0}, kcal mole^{-1}	Remarks
CuO	crystalline	−37.1	−30.4	See also Refs.37 and 38
Cu_2O	ditto	−39.84	−34.98	See also Refs.37 and 38
Ag_2O	»	−7.31	−2.59	See also Ref.12
Ag_2O_2	»	−6.3	—	
Au_2O_3	»	19.3	39.0	

For many years it was not established reliably whether or not oxygen is chemisorbed on gold, since studies of the chemisorption of oxygen on group IB metals encounter a number of the difficulties described above, one of which is common to many metals and others are specific to the metals of the given Group.

1. The presence of admixtures of light elements, in the first place hydrogen and oxygen, and also of catalyst and

adsorption poisons such as sulphur, chlorine, etc. Oxygen may be present owing to the contact of the specimen with air before its introduction into the apparatus or as a result of its contact with the residual gas in the evacuated apparatus. In order to remove oxygen from copper[25], silver[26-28], or gold[19], prolonged treatment by heating with hydrogen or carbon monoxide is necessary. However, there is then a risk of the contamination of the surface layer of the specimen with hydrogen or carbon. At the same time the presence of oxygen on the surface lowers the degree and the initial rate of its adsorption and the presence of hydrogen can lead to an unduly high value of the observed degree of adsorption, since some of the oxygen is consumed in the oxidation of hydrogen. The presence of very small amounts of catalyst poisons as impurities on the surface can also alter its adsorption properties[29,30]. It is then necessary to take into account the ability of many non-metallic impurities in metals to migrate rapidly towards the surface[31-34].

2. The presence of small amounts of impurities comprising other metals. For example, it is known that the addition of very small amounts of nickel to copper sharply enhances its catalytic properties[35], while mercury vapour can alter sharply the adsorption and other properties of gold[36].

3. The possibility of the oxidation of lubricant vapour during the experiments on the adsorption of oxygen[19]. An impression may be created that oxygen is adsorbed to a greater extent than is in fact the case if one does not take into account the fact that part of it is consumed in the formation of water and carbon dioxide. The physical properties of the adsorbent such as the electron work function, electrical conductivity, etc. can also change as a result of the oxidation of the lubricant on the surface.

The need to work under the conditions of high purity leads to a sharp decrease of the specific surface. This imposes more stringent requirements for the purity of the adsorbant and gas employed and for the sensitivity of the method of measurement.

III. KINETICS OF THE PROCESSES

Here we shall consider mainly adsorption and surface oxidation, where the rate of absorption of oxygen is limited by adsorption and not by diffusion in the solid specimen. These processes can occur under different conditions. Such an approach makes it possible to assess the magnitude of the adsorption rate constants. These constants are needed in the derivation of kinetic equations for heterogeneous catalytic oxidation processes involving a mechanism comprising a number of stages and also for the calculation of the degree of contamination of the test metals by oxygen under the conditions of contact with the latter.

1. The Copper–Oxygen System

Above 0°C, copper can sorb irreversibly more than one monolayer of oxygen. Even at −195°C a very thin oxidised layer is formed on copper as a result of the chemisorption of oxygen[39]. This implies that the process is not limited to chemisorption alone, but that oxygen can penetrate also deeper layers of the metal. Thus the rate of sorption of oxygen can depend on at least two processes: the adsorption process proper as a result of which oxygen appears on the surface and another process leading to the generation of copper atoms on the surface capable of adsorbing new portions of oxygen. On contact between copper and oxygen, an induction period is initially observed, during which the formation of the oxide phase cannot be observed on the surface with the aid of the electron microscope[40]. During this period, oxygen is adsorbed and dissolved in the metal phase. The solubility of oxygen in the massive metal (s, in parts per million) up to 750°C is given by the equation[41]

$$\lg s = 2{,}2875 - (956.4/T). \qquad (1)$$

Solubilities close to those given by Eqn. (1) have been published[42]. The standard enthalpy of solution of oxygen in copper $\Delta H^{\circ}_{298} = -10$ kcal mole^{-1} [43] and the free energy of the process up to 750°C can be calculated from the equation $\Delta G = 4360 \pm 14.18\,T$.[41]

The appearance of nuclei of the oxide phase with dimensions less than 100 Å can be observed on the copper surface at the end of the induction period. Copper(I) oxide or Cu_2O_3, which has the structure of the former with a large number of defects, are mainly formed at temperatures up to 600–800°C.[44-47] At higher temperatures copper(II) oxide is also produced[48,49].

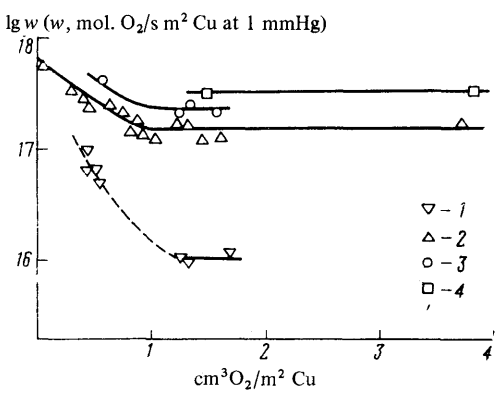


Figure 1. Variation of the rate of sorption of oxygen by copper with the degree of oxidation at different temperatures[18,50] (°C): 1) 55; 2) 105; 3) 125; 4) 135.

There have been comparatively few studies on the rate of adsorption of oxygen in the stages corresponding to the very beginning of the oxidation. Table 2 presents the results of those where measurements were made of the rate per unit surface of the specimen. It also includes the results of the determination of the activation energy. The kinetics of the earliest stage in the sorption of oxygen by copper have been investigated[18,50]. The preliminary reduction of the copper(II) oxide powder was carried out for 190 h at 300–330°C, with subsequent evacuation for 80 h at 350–400°C. Fig. 1 shows results from the study of the dependence of the rate of oxygen sorption on the degree of oxidation at different temperatures. Oxygen was admitted in portions at an initial pressure of 0.13 mmHg. The kinetics of the sorption of oxygen are described by the equation

$$r_{\cdot} = 4.1 \times 10^{23} \sqrt{\frac{T}{273}} \cdot P_{O_2}\, e^{-11800/RT} \qquad (2)$$

Table 2. Kinetic data for the copper–oxygen system.

Temp., range, °C	Rate constant: k, mol. O_2 s^{-1} m^{-2} $mmHg^{-1}$	Rate constant: degree of oxidation σ, cm^3 O_2/m^2 Cu	Activation energy E, kcal $mole^{-1}$	Kinetic equation	Rate of sorption of oxygen, 10^{-15} mol. O_2/s m^2 Cu mmHg	References
50—110[a]			15.5	$r = kP_{O_2}e^{-E/RT}$		61
55—135	$4{,}1\cdot10^{23}\sqrt{\frac{T}{273}}$	1—4	11.5	ditto	10 (55°), 330 (135°), 2000 (extrapolation to 200°), 45 (55°)[c] 350 (125°)[c]	18
55—135	$4{,}6\cdot10^{21}\sqrt{\frac{T}{273}}$	0.6	7.5	»[b]		50
25—200	$1{,}1\cdot10^{22}\sqrt{\frac{T}{273}}$	$0.25 < \sigma < 0.8$	7.3	»	52 (25°)[d] 1900 (150°)[d] 4800 (200°)[d]	51
50—400			5.6 — 5.9		500 (150°)[e]	62
300—600			21.8			44
150—800			21[f]			40
25—200			3.5 [(110)face]			53

[a] Pressure 76 torr. Copper sheet specimen subjected to preliminary oxidation to give a content of about 10 cm^3 O_2/mm^2 Cu.
[b] With decrease of σ from 1.0 to zero, the activation energy and k both fall.
[c] In the range $\sigma < 1.0$ cm^3 O_2/m^2 Cu the rate of adsorption decreases with increase of σ.
[d] In the range $\sigma < 0.2$ cm^3 O_2/m^2 Cu the rate of adsorption decreases with increase of σ.
[e] The average rate of adsorption for adsorption from zero to about 20 cm^3 O_2/m^2 Cu.
[f] Specimen oxidised to give a content of about 35 cm^3 O_2/m^2 Cu.

for degrees of oxidation in the range 1–4 cm^3 O_2/m^2 Cu. On further sorption of oxygen, the kinetics change sharply. When the degree of oxidation σ is less than 1 cm^3 O_2/m^2 Cu, the activation energy and the pre-exponential factor diminish with decrease of the degree of oxidation in such a way that the rate of sorption of oxygen increases at the same time (Fig. 1). Qualitatively similar behaviour was observed in another investigation[51]. The quantitative discrepancies between the results of the two studies[50,51] are probably due to the fact that in the investigation of Shakhovskaya et al.[51] the copper was cleaned in a different way before the oxygen sorption experiments (treatment for several hours at 250°C). The kinetic parameters obtained in the remaining studies whose results are presented in Table 2 are known to refer to surface-oxidised copper specimens which usually contained nuclei of the oxide phases.

The effective activation energies listed in Table 2 for such cases were influenced by diffusion phenomena; these results will be discussed in the section on the mechanism of oxygen sorption. At the end of the induction period the kinetics for the surface-oxidised specimens are no longer described by a simple equation of type (2) and as a rule the process is treated within the framework of the theory of Cabrera and Mott[52], although this does not account for a number of the observed phenomena and relations, for example the discontinuity of the oxidised layer, the differences between the rates of oxidation on different crystal faces, etc.[42] According to the kinetic measurements of Ostrovskii and Kalistratova[50], up to the sorption of 4 cm^3O_2/m^2 Cu (2.5×10^{19} mol./g Cu) the rate of sorption is proportional to the oxygen pressure (the specific surface of copper was 0.3 m^2g^{-1}). This suggests that in these experiments the diffusion of oxygen did not limit the rate of the process, i.e. oxygen was sorbed until the instant of the appearance of the oxide phase. In a study[40] on non-porous copper about 35 cm^3 O_2/m^2 (5×10^{16} mol./g Cu) was sorbed during the induction period at 150°C. This value is close to the solubility of oxygen in massive copper. Comparison of the results of Ostrovskii and Kalistratova[50] with those of Ertl[53] shows that porous copper can sorb (per unit weight of the metal) several orders of magnitude more oxygen than massive specimens. However, when the limiting degree of sorption of oxygen, occurring up to the formation of a new phase, is referred to unit surface area, this quantity differs much less. Although the specific surfaces differ by a factor of several thousands, in the case under consideration the degrees of sorption of oxygen referred to 1 m^2 differ by less than an order of magnitude. This is evidence for unusual properties of the surface layer of copper with respect to the sorption of oxygen. The main bulk of the oxygen dissolved in copper at low temperatures is probably located in the layer near the surface.

The rates of sorption of oxygen by different copper faces are different, but not as a rule by more than an order of magnitude. Gwathmey and Lawless[54] and later others[48,50] concluded that the (100) face sorbs oxygen fastest. Jardinier–Offergeld and Bouillom[56] observed the highest rate constant for the sorption of oxygen and the shortest induction period at 511°C for the (111) face. The induction period for the (110) face was longer than for the (111) face and for the (100) face it was longer still. The information available about the relative rates of sorption of oxygen by the (100) and (110) faces is contradictory[56–58]. Since the results were obtained at different temperatures, it may be that the discrepancies are due to marked differences between the activation energies for the sorption of oxygen on different faces[59].

2. The Silver–Oxygen System

Table 1 shows that the decrease of free energy in the oxidation of massive silver under standard conditions is small. In the oxidation of a cryptocrystalline powder the decrease of free energy may be somewhat greater, but, when the crystal size exceeds 10^{15} Å^3, which is usually the case for silver powders of films, comminution has little influence on the equilibrium position. At an oxygen pressure of the order of several mmHg or below only a two-dimensional adsorption structure is observed on the silver

surface[60], but no oxide phase. At temperatures above 0°C silver strongly sorbs considerable amounts of oxygen. Together with chemisorption, oxygen may dissolve in the bulk of the metal. The dissolution of oxygen in massive silver has been investigated[63-66]. The rate of dissolution and the solubility of oxygen are proportional to the square root of pressure. The heat of solution of oxygen in silver is about 12 kcal mole^{-1}.[67,68]

The formation of a monolayer adsorbed on non-porous specimens requires less oxygen than can dissolve in the specimen according to solubility data. However, the corresponding values have comparable orders of magnitude. The volume of oxygen corresponding to the formation of a monolayer on porous specimens can be much greater than the volume corresponding to the solubility, measured per unit weight of massive specimens. Nevertheless there are data[69] showing that, even at an oxygen pressure of about 0.2 mmHg, the decrease of oxygen pressure on contact with silver corresponds to the sorption of several oxygen monolayers. It is believed[69] that the surface layers of silver can sorb additional amounts of oxygen in the tetrahedral vacancies of the crystal lattice. Possibly the sorption of oxygen by the surface layers of copper described above is of the same type. The rate of the process described in the literature[69], which has been called "deep adsorption", is two-three orders of magnitudes lower than the rate of chemisorption of oxygen on silver. For this reason, the experimental rate of chemisorption should not be significantly influenced by this process.

The main results of the studies of the chemisorption of oxygen on silver are presented in Table 3. In selecting the studies quoted in the table the same criteria were applied as in the selection of the studies in Table 2. Comparison of the data in Tables 2 and 3 shows that the rate of sorption of oxygen by silver is two-three orders of magnitudes lower than the rate of sorption by copper. The rates of sorption of oxygen by silver obtained in different studies differ within the limits of a single order of magnitude when the comparison is made at the same temperature and degree of oxidation. Examination of the complete set of investigations of the chemisorption of oxygen on silver lead to the conclusion that three adsorption regions should be distinguished as a function of the degree of oxidation. The adsorption in these three regions is probably described by different kinetic equations. The first region corresponds to a change in the degree of oxidation σ up to 0.10–0.12 cm^3 O_2/m^2 Ag, i.e. within the limits of surface coverage by an oxygen monolayer constructed in such a way that an oxygen atom is bound to two silver atoms (AgS_2O, where Ag^S is a silver atom on the surface). The second region corresponds to $0.12 < \sigma < 0.22$–0.26, i.e. extends up to the adsorption of an oxygen monolayer in which an oxygen atom is bound to one silver atom (Ag^SO or $Ag^S{}_2O_2$). The third region corresponds to the adsorption of a greater amount of oxygen. The absorption in the first region was investigated in greatest detail in three studies[63,70,71], where measurements were made from σ = 0.05 cm^3 O_2/m^2 Ag. Other workers[71,72] described the results of studies on the kinetics in this region obtained at a pressure of about 10^{-2} mmHg, in terms of an equation of the type

$$r = Ce^{-b\Gamma}Pe^{-E/RT}, \qquad (3)$$

where $C = 10^{-9}$ mole s^{-1} cm^{-2} and $b \simeq 2.6 \times 10^{10}$ cm^2 mole^{-1} at 20°C. The rate of adsorption is proportional to the pressure. According to Temkin and Kul'kova[69], the activation energy for adsorption in this region is 7–8 kcal mole^{-1}, increasing to 10 kcal mole^{-1} when σ = 0.135 cm^3 O_2/m^2 Ag. According to other results[70], the activation energy depends in a complex way on temperature and on the degree of oxidation. The adsorption in the second region has also been studied[28,70]. According to the present author's results[28], the adsorption kinetics in the range $0.14 < \sigma < 0.21$ are described by the simple equation

$$r = kP(1-\theta)\cdot e^{-E/RT}, \qquad (4)$$

where $\theta = 0$ when σ = 0.13 cm^3 O_2/m^2 Ag and $\theta = 1$ when σ = 0.26 cm^3 O_2/m^2 Ag and $k = 7 \times 10^{11}$ mol. O_2 s^{-1} cm^{-2} mmHg^{-1} at 110°C. The activation energy for adsorption in this region, estimated[28] from the theory of the absolute rates of heterogeneous reactions[72], is 12 kcal mole^{-1}. In the third region the rate of adsorption is limited by surface diffusion[70] or diffusion in the surface layer[69]. The activation energy for the adsorption of oxygen is 22–29 kcal mole^{-1}.[70,73]

Table 3. Kinetic data for the silver–oxygen system.

Temp., range, °C	Rate constant: k, mol. O_2 s^{-1} m^{-2} mmHg^{-1}	Rate constant: Degree of oxidation σ, cm^3 O_2/m^2 Ag	Activation energy E, kcal mole^{-1}	Kinetic equation	Rate of adsorption of oxygen, 10^{-15} mol. O_2/s m^2 Ag mmHg	References
180—300			22 ÷ 29			73
100			3; 8; 22[a]		5 (100°, σ=0.10) 1 (100°, σ=0.18)	70
132—218			13[b]			79
23—200		0.03—0.08	8.2; 7.5; 10.2[c]	$r = Ce^{-ab}$ [d] (in the range $0.03 < \sigma < 0.08$)	6 (100°, σ=0.05) 1 (100°, σ=0.08) 0.25(100°, σ=0.25)	71
110	$7 \cdot 10^{15}$	0.13—0.21	12[e]	$r = kP(1-\theta)$[f] (in the range $0.145 < \sigma < 0.21$)	0.72(110°, σ=0.13) 0.36(110°, σ=0.18)	28
20		0.05—0.13		$r = Ce^{-ab}$ (in the range $0.05 < \sigma < 0.09$)	1 (20°, σ = 0.11)	80

a 3 kcal mole^{-1} is the activation energy for the adsorption of oxygen in the form of charged atoms, 8 kcal mole^{-1} is the activation energy for the adsorption of oxygen in the form of charged molecules, and 22 kcal mole^{-1} is the activation energy for surface migration.
b The activation energy for conduction in the silver film in contact with oxygen.
c 8.2 kcal mole^{-1} for σ = 0.09, 7.5 kcal mole^{-1} for σ = 0.10, and 10.2 kcal mole^{-1} for σ = 0.135.
d a and b are constants.
e Calculated using the theory of absolute reaction rates following Temkin[72].
f $0.1 < \theta < 1.0$; $\theta = 0.1$ when σ = 0.143 and $\theta = 1.0$ when σ = 0.26.

The rate of adsorption of oxygen and the maximum degree of adsorption are significantly influenced by the presence of electronegative elements as impurities in the silver. Thus 25% surface coverage of silver by chlorine reduces the rate of subsequent adsorption of oxygen[30] and surface coverage by sulphur even to the extent of several percent greatly reduces the degree and rate of adsorption of oxygen[29,74]. A theory of these phenomena has been discussed from the standpoint of the effect of mutual influence in chemisorption[75]. With the aid of added sulphur,

chlorine, selenium, and tellurium labelled with radioactive isotopes, it was established[31-33,76] that admixtures of electronegative elements (10^{-4}–10^{-1} at.%), uniformly distributed throughout the bulk of silver, diffuse to the surface during the pelleting of the catalyst at 200–300°C. Therefore, even when the concentration of the impurities is of the order of 10^{-3} at.% with respect to the specimen as a whole, the surface concentration can be of the order of several per cent, which, as stated above, influences significantly the adsorption of oxygen.

The total amount of oxygen which can be sorbed by pure silver per unit surface area is about one order of magnitude less than the amount of oxygen which can be sorbed by copper. At the same time oxygen hardly oxidises silver at pressures below 100–200 mmHg, but diffuses fairly rapidly through it. Therefore diffusion through silver can be used for the thorough separation of small amounts of oxygen[7] from hydrogen, nitrogen, and the inert gases, which are not adsorbed on silver.

Table 4. Kinetic data for the gold–oxygen system.

Temp., range, °C	Rate constant: k, mol. O_2 s^{-1} mm^{-2} $mmHg^{-1}$	Rate constant: degree of oxidation σ, cm^3 O_2/m^2Au	Activation energy E, kcal $mole^{-1}$	Kinetic equation	Rate of sorption of oxygen, 10^{-15} mol. $O_2/s\,m^2$ Au mmHg	References
50—400	$4.4\cdot10^{15}$ (120°)	0.015—0.083	3.2		7.3 (120°, σ=0.05) 0.94 (120°, σ=0.08)	17
25—150			~3			14
90—140	$22\cdot10^{15}$ (140°)	0.03—0.091	4.15[a] 10.5[c]	$r=kP(1-\theta)^4\left(\frac{2}{2-\theta}\right)^3$[b]	27 (140°, σ=0.05) 2.9 (140°, σ=0.09)	19
150—380			16÷20[d]		13 (150°, σ=0.06) 0.080(150°, σ=0.23)[e]	22

[a] Estimate obtained with the aid of the theory of absolute rates of heterogeneous reactions for the initial rate of adsorption.
[b] $\theta = 1$ when $\sigma = 0.13$ cm^3/m^2 Au and $\theta = 0$ when $\sigma = 0$; equation valid up to $\sigma = 0.09$.
[c] For $\sigma = 0.20$ cm^3/m^2 Au.
[d] Calculated from the results of the extrapolation of the experimental rates of adsorption for $\sigma = 0.06$–0.23.
[e] Result of the extrapolation of the relation between the rate and degree of adsorption.

3. The Gold–Oxygen System

The solubility of oxygen in gold at 300–900°C is only 5×10^{-4} cm^3 O_2 per gram of gold[78]. This is nevertheless more than the volume of oxygen required to adsorb a monolayer on the surface of 1 g of the massive metal. On the other hand, for porous gold with a specific surface of the order of 0.1 m^2g^{-1} the solubility is orders of magnitude smaller than the volume of oxygen needed to form a monolayer. The chemisorption of oxygen at 100–150°C corresponds to the formation of a surface monolayer with one oxygen atom for each gold atom[19]. Therefore in the study of the chemisorption of oxygen its dissolution can be virtually ignored. The results of the few studies on the kinetics of the chemisorption of oxygen on gold are presented in Table 4, which shows that similar rates of chemisorption are obtained in different investigations[14,19,22] at low surface coverages. The rate is two orders of magnitude lower than the rate of sorption of oxygen by copper at the same temperature and is close to the rate of sorption of oxygen by silver. With increase in the degree of adsorption, the rate of the latter decreases sharply. The adsorption of oxygen on gold containing not more than one silver atom for each 2000 gold atoms has been studied[19]. Thus the adsorption of oxygen on gold cannot be attributed to adsorption on the silver impurity. In order that gold can adsorb oxygen, it is very important to prevent contact with mercury vapour, since otherwise the capacity to adsorb oxygen is lost[36]. Preliminary treatment of gold before the study of the adsorption of oxygen is important, since the adsorbed oxygen and water, present apparently in the form of hydroxy-groups, are removed with much difficulty. Treatment with hydrogen for 100 h at 350°C and then evacuation at the same temperature and for the same period proved convenient for the purification of the adsorbant[19]. The treatment with hydrogen was carried out at low pressures to facilitate the diffusion of the resulting water to the trap where it was frozen out. The activation energy for the chemisorption of oxygen at a low degree of adsorption does not exceed 3–5 kcal $mole^{-1}$ as can be seen from the data in Table 4 and as has been shown by Endow et al.[21] With increase in the degree of adsorption, the activation energy rises[19,21,22]. The kinetics of the adsorption of oxygen up to the sorption of the amount corresponding to about 0.7 of a monolayer are described by the equation

$$r = kP(1-\theta)^4\left(\frac{2}{2-\theta}\right)^3, \qquad (5)$$

where $k = 2 \times 10^{16}$ mol. O_2 s^{-1} m^{-2} at a pressure of 1 mmHg, $\theta = 0$ when $\sigma = 0$, and $\theta = 1$ when $\sigma = 0.13$ cm^3 O_2/m^2 Au. Eqn. (5) was derived[81] for the case where the adsorbate molecule occupies four sites in adsorption on a homogeneous surface. In the adsorption of oxygen on gold this corresponds to the formation of Au_2SO. At a higher surface coverage the rate of adsorption is limited by the rate of rearrangement of the surface oxide layer, the observed activation energy for adsorption increases, and the reaction order with respect to oxygen pressure gradually falls. When the volume of the adsorbed oxygen approaches that corresponding to the formation of a monolayer of the surface oxide AuSO, the rate virtually ceases to depend on the pressure[19].

IV. CHANGES IN CERTAIN PHYSICAL PARAMETERS OF THE METALS DURING THEIR SURFACE OXIDATION

1. Heat of Adsorption

The heat of adsorption of oxygen on copper has been studied using powders[25,82] and films[83,84]. Russell and Bacon[82] observed a slow decrease in the heat of adsorption at 0°C in a Bunsen calorimeter from 92 kcal/mole O_2 with increased degree of adsorption. However, the portions of oxygen used were too large to determine the dependence of the differential heat of adsorption Q_d on the degree of adsorption. Later the variation of Q_d with surface coverage was investigated[83] with the aid of a Beeck calorimeter at 25°C and in another study[25] with the aid of a FOSKA calorimeter[85] at 100–130°C. The results obtained in these two studies[25,83] are presented in Fig. 2. The initial heat of adsorption at 25° and 100°C is about 115 kcal $mole^{-1}$. It then falls to the level of 82–90 kcal/mole O_2. At 25°C the decrease occurs at $\sigma = 0.08$ cm^3 O_2/m^2 Cu and 100°C at a degree of adsorption as low

as $\sigma = 0.04$ cm^3 O_2/m^2 Cu. After this the heat of adsorption remains almost constant both at 25° and 100°C up to the adsorption of a monolayer or a little more. Then at 25°C it falls to 58 kcal mole^{-1} when $\sigma = 1.0$ cm^3 O_2/m^2 Cu.

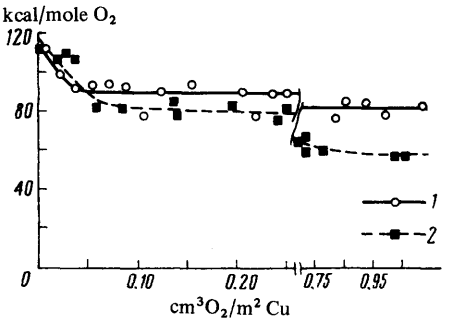


Figure 2. Variation of the heat of sorption of oxygen by copper with the degree of oxidation: 1) to the left of the discontinuity at 100° or 110°C; to the right of the discontinuity at 130°C according to Ostrovskii[25]; 2) at 25°C according to Starostina et al.[80]

It is believed[83] that the decrease is caused by the adsorption of oxygen on a surface layer of copper(I) oxide. At 100–110°C[25] the heat of adsorption decreases to only 82 kcal mole^{-1}, which is equal, within the accuracy of measurement, to the heat of oxidation of copper to the Cu_2O phase (Table 1). Thus at 100–110°C, where the rates of diffusion processes in the copper specimen undergoing oxidation are much higher than at 25°C, the region of enhanced heat of adsorption is narrower than at 25°C and after the oxidation of 1–2 copper monolayers the heat of reaction corresponds to the heat of oxidation to the oxide phase. It has been found that the heat of adsorption of oxygen on a copper film at room temperature is 110 kcal mole^{-1} regardless of the surface coverage[84]. The heat of adsorption of oxygen on silver has been determined calorimetrically[29,86,87] and also from the adsorption-chemical equilibrium involving water vapour[88,89], from the difference between the activation energies for adsorption and desorption[90], and from adsorption isosteres[73]. The results obtained in different studies agree. Fig. 3 presents the results of direct calorimetric measurements[87] at 110°C. Evidently the initial heat of adsorption is about 125 kcal mole^{-1}. Similar values were obtained in studies on the adsorption-chemical equilibrium involving water vapour: 108 kcal mole^{-1} [88] and 115 kcal mole^{-1}.[89] The heat of adsorption corresponding to almost complete monolayer coverage is about 15 kcal mole^{-1} according to Benton and Drake[90], which is close to the value obtained by Kul'kova and Temkin[89]. The isosteric heat of adsorption of oxygen on silver is 21 kcal mole^{-1},[91] and on silver containing 0.08% Ni and 0.13% Cu at oxygen pressures of several hundred mmHg it increases from 17 kcal mole^{-1} as the equilibrium pressure is reduced. For comparison, we may note that the heat of decomposition of Ag_2O is 14.7 kcal mole^{-1}.[12,92] It has been shown[87] that the heat of adsorption decreases appreciably in the presence of even small amounts (of the order of 1% of the monolayer) of a sulphur impurity on the surface of silver.

The heat of chemisorption of oxygen on gold has been determined in only two studies[18,19]. It was shown[19] that, in contrast to the heats of chemisorption on copper and silver, the heat of chemisorption of oxygen on gold is independent of the degree of surface coverage within the limits of experimental error (about 4%) and amounts to about 103 kcal/mole O_2.

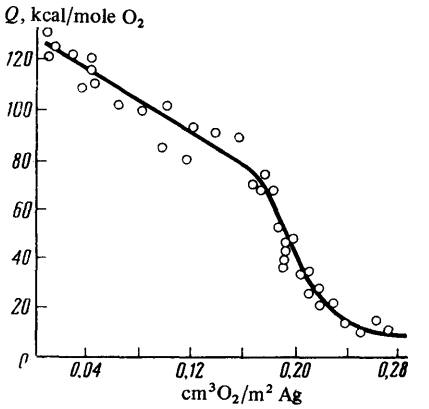


Figure 3. Variation of the heat of sorption of oxygen by silver with the degree of oxidation[84].

Thus almost all the oxygen adsorbed on a carefully cleaned gold surface is very firmly bound to the surface. It has been shown[19] that it can be removed only with much difficulty in the form of water after treatment by hydrogen with heating.

2. The Electronic Work Function

Table 5 presents the results of measurements of the maximum change in the electronic work function following the adsorption of oxygen on copper, silver, and gold. Evidently the electronic work function increases with adsorption or remains unchanged (on gold). The increase is evidence that the oxygen becomes negatively charged on adsorption. The maximum change in electronic work function after the adsorption of oxygen on this metal apparently depends on temperature, the amount of adsorbed oxygen, and to a large extent on the method of measurement employed. With increase of the amount of oxygen, the electron work function initially rises and then either remains unchanged or actually falls somewhat. If the oxygen is admitted onto the surface in portions, then after the introduction of each portion there is initially a rapid increase in the electronic work function and then a decrease. The decrease can actually amount to more than half of the initial rapid increase of the electron work function for the given portion of oxygen. The decrease in the electronic work function is usually explained by the diffusion of oxygen into the bulk of the specimen. However, one cannot rule out the possibility that it is partly due to the desorption from the surface of the water formed because the metals can contain hydrogen in the form of hydroxy-groups, owing to their previous history. Moreover the slow changes can be caused in many

instances by the processes occurring at the reference electrode. Table 5 shows that the smallest differences between the maximum changes in the electron work function on interaction with oxygen are observed for copper.

Table 5. Maximum increase in electron work function after the chemisorption of oxygen on Group IB metals.

Metal	Maximum increase in electron work function, V	Temperature of measurements, °C	Method	References
Copper	0.30	+20	d.	107
Copper	0.40[a]	+25	v.c.(Au)	108
	0.8[b]			
Copper	0.55	0—25	d.	109
Copper	0.27	+80	v.c.(Mo-gl.)	51
Silver	0.60	—	v.c.(Au)	110
Silver	0.20	+220	v.c.(Au)	97
Silver	0.30	+25	v.c.(Au)	93
Silver	0.75	+23		71
	0.75	+100		111
	0.65	+200	v.c.(Mo-gl.)	
Silver	1.04	+25	d.	95
Silver	0.90	+20,100		
	1.1	+200	v.c.(Au)	96
Silver	0.3	+20		
	0.7	+330	v.c.(Mo-gl.)	94
Gold	0.12	+25	d.	112
Gold	0	+25	v.c.(W)	16
Gold	0	+25	v.c.	113
	0.7	+400		
Gold	0	+25	ph.	99
Gold	0.30	+25	d.	20
Gold	(>0.35)	+150	v.c.(Mo-gl.)	22
	(>0.55)	+250		
	(>0.65)	+350		

a At a pressure below 1 mmHg.
b At a pressure of 50 mmHg.
Methods: d. = diode; ph. = photoelectric emission; v.c.(Au) = vibrating condenser with gold reference electrode; v.c.(W) = ditto with tungsten reference electrode; v.c.(Mo-gl.) = ditto with molybdenum electrode enclosed in glass.

In this case the electron work function amounts to 0.30–0.55 V close to room temperature when the oxygen pressure is below 1 mmHg. The increase in the electronic work function following an increase in oxygen pressure to 50 mmHg may be because at this high pressure and 25°C the surface is completely saturated by oxygen which cannot diffuse sufficiently rapidly into the bulk of the specimen and at low pressures part of the surface remains free as a result of the dissolution of oxygen. The results of measurements of the changes in the electron work function after the adsorption of oxygen on silver in different investigations differ very considerably. For example, when the adsorption of oxygen and the measurements of the change in electron work function were carried out at room temperature, the observed change in the electron work function ranged from 0.3 V in some studies[93,94] to about 1.0 V in others[95,96]. The results obtained at 100°C agree somewhat better, ranging from 0.65 to 1.1 V (except for the results of Enikeev et al.[93]). The measurements of the electronic work function of gold on contact with oxygen do not yet yield a final conclusion as to whether or not oxygen influences the electron work function. This is aggravated by the fact that the failure to take into account various experimental characteristics may have a decisive influence on the result for gold. For example, the formation of a gold film by atomising gold in an atmosphere of hydrogen[20], can lead to the occlusion of the gas by the film with subsequent formation of water when the film interacts with oxygen, whereas inadequate reduction of the initial gold hydroxide may lead to a distortion of the results for the adsorption of oxygen by the desorption of water, etc. According to the theory of the role of the surface electron gas in adsorption phenomena developed by Temkin and coworkers[27,98], the heat of adsorption being independent of the degree of surface coverage, as observed by Dobrovol'skii and Ostrovskii[19], should correspond to a constant electron work function in adsorption of oxygen on gold, which was in fact observed in careful investigations[16,19].

3. Electrical Conductivity and Other Properties

The electrical conductivity of thin copper, silver, and gold films decreases as a result of their contact with oxygen. The temperature coefficient of the resistance of copper decreases after the admission of oxygen[100-102]. At 0°C the introduction of oxygen into the space over degassed copper leads to a rapid increase of resistance. After some time the resistance ceases to change or begins to decrease. With increase of oxygen pressure above a certain limit, a slow increase of the resistance is again observed. The changes are irreversible, the electrical conductivity of the film is not restored after evacuation. Similar changes were observed also when oxygen was brought into contact with silver[102-104]. After a film 255 μm thick was exposed at 0°C to oxygen at a pressure of 0.1 mmHg, the resistance increased rapidly by 0.4% and then by a further 0.4% over 1 h.[104] At 200–300°C the resistance of a thin silver film increases in oxygen in proportion to the square of the time[103].

After the exposure of gold films 182 μm thick to oxygen at a pressure of 0.1 mmHg and 0°C, their resistance increases slowly to an extent reaching 2‰ after 1 h.[104] A decrease of the conductivity of gold in the presence of oxygen is observed also at higher temperatures (150–200°C)[105].

The adsorption of oxygen on copper or silver films about 50 Å thick alters the Hall potential[106]. As stated above, the oxygen impurity in copper and silver at a concentration of the order of 10^{-4}% greatly increases the self-diffusion coefficient of the metal[10].

V. THE MECHANISM OF THE PROCESSES IN THE SURFACE OXIDATION OF METALS

1. The Problem of Creating Clean Surfaces

A discussion of the problem of creating clean surfaces cannot be separated from a discussion of the oxidation mechanism, since the explanation of the phenomena observed in the sorption of oxygen is frequently determined by the presence of impurities in the specimens or at any rate depends significantly on them. The problem of the elimination from copper, silver, or gold of heavy element impurities which may influence the sorption of oxygen can now be solved comparatively readily because of the availability of sensitive and reliable analytical methods such as spectroscopic analysis, activation analysis, etc. Moreover, this is facilitated by the fact that,

in the storage and preparation of the specimens in vacuum apparatus, they are as a rule not subjected to additional contamination by heavy element impurities. It is much more difficult to determine the content of light element impurities, in the first place such as hydrogen, nitrogen, oxygen, and their compounds. In Group IB metals the problem is somewhat facilitated by the fact that these metals hardly sorb nitrogen and hydrogen. However, compounds of the above elements, including their oxides, can be adsorbed by Group IB metals.

Table 6. Heats of adsorption of the vapours of the principal impurities contaminating copper, silver, and gold.

Metal	Heat of adsorption, kcal mole^{-1}			
	CO	H_2O	CO_2	H_2S
Copper	16—17[83] 17.5[114] 9.3[115]	12[116]		
Silver		14.9[117]	17.5[118] (on Ag_2O)	78 ± 10*[29]
Gold	8.7[115]	14[19,36] 14.5[117]	14[19,36]	

* The interaction of the silver surface with hydrogen sulphide at 100°C proceeds in accordance with the equation $H_2S + (\ ) = H_2 + (S)$, where ( ) is a bivalent adsorption centre on the surface and (S) a chemisorbed sulphur atom[29].

Table 6 presents the heats of adsorption of certain substances contaminating the above adsorbents. Evidently the heats of adsorption are low and it would seem that *in vacuo* the surface should be rapidly cleaned. However, the problem is more difficult. Impurities in amounts greatly exceeding the volume of one monolayer can be present within the bulk of the crystals whence they can diffuse over a long period to the surface and contaminate it. Various sulphur- and chlorine-containing impurities, etc. diffuse rapidly to the surface on heating[32], but cannot be desorbed on heating *in vacuo*, since the bond energy between them and the surface is high (for example the bond energy of the sulphur atoms adsorbed on the surface of silver is 78 ± 10 kcal mole^{-1}).[29] The specimens obtained by reducing salts precipitated from aqueous solutions can contain considerable amounts of water and the acid residues of the salts undergoing decomposition, which are eliminated slowly owing to kinetic barriers which hinder their rapid diffusion to the surface. For example, the removal of residual water from gold obtained by the reduction of gold hydroxide at 350°C *in vacuo* takes place over hundreds of hours[19]. The elimination of oxygen present in the metal during the cleaning of the surface before the study of the adsorption of oxygen constitutes a special problem. Usually the metal is treated for this purpose with hydrogen or carbon monoxide and the water or carbon dioxide formed are evacuated. The cleaning of powdered copper in a static apparatus at 170°C requires treatment with hydrogen for hundreds of hours[25] and the cleaning of gold at 350°C requires many tens of hours[19]. The study of adsorption in an ultrahigh vacuum on sputtered metal films facilitates the solution of some of the problems enumerated above, but new problems are created because the surface of the films is very small compared with the surface of the powders and therefore very small amounts of impurities are sufficient to contaminate it (see, for example, Savchenko[119]). Nevertheless, the present review has shown that in those cases where sufficient attention was devoted to the cleaning of the specimens, the results obtained in the study of the oxidation of the surface of powders were analogous to those obtained in the study of the oxidation of the surface of thin films.

2. The Mechanism of the Sorption of Oxygen

The nature of the interaction of oxygen with copper, silver, and gold surfaces is in many respects similar, but each of the three systems has its specific features. The most striking common feature is that a definite amount of oxygen is sorbed by the metals above room temperature with a heat exceeding significantly the heat of formation of the corresponding oxides. Moreover, copper and silver can sorb considerable amounts of oxygen in their surface layers (deep adsorption) without the formation of an oxide phase. With increase of the specific surface, the maximum amount of such oxygen per unit weight of the metal increases and for specimens with a high surface area can be several orders of magnitude greater than the amount corresponding to the solubility of oxygen in the given metal determined for non-porous specimens. Even if the heat of deep adsorption exceeds that of the oxidation of the metal to an oxide phase, it does not do so by more than 10%. Most of the oxygen estimated in the determination of its solubility in such metals is probably concentrated in the surface layers. At the same time some oxygen can be present also in the bulk of the copper and silver, since its diffusion through a layer of the metal can be observed. The sorption of oxygen by porous gold is limited to a monolayer. The initial specific rates of sorption of oxygen on the metals under consideration have similar orders of magnitude when the comparison is made at 100–200°C. The initial heat of adsorption lies between 100 (gold) and 125 (silver) kcal/mole O_2 with an average error of the measurements in the range 5–7 kcal mole^{-1}. At the same time the variation of the rate of sorption of oxygen on copper, silver, and gold with the amount sorbed and the dependence of the heat of sorption on the amount sorbed on these metals are specific to each metal.

The sum total of the above results for the sorption of oxygen by copper shows that on clean copper oxygen is adsorbed and passes into the bulk of the metal. The collision of oxygen molecules with a surface coated by a layer of adsorbed oxygen probably stimulates an endothermic activated transfer of oxygen to the surface layer of the specimen with further adsorption on the liberated site. The heat of adsorption greatly exceeds the heat of oxidation to an oxide phase, while the heat of transfer of oxygen from the gas phase to the surface layer is close to the heat of oxidation of copper to an oxide phase. Therefore the initial heat of sorption of oxygen corresponds to the heat of adsorption, but, as the surface is covered, the heat of sorption approaches the heat of oxidation of copper to an oxide phase (Fig. 3). An increase of temperature increases the probability that the oxygen colliding with an unoxidised surface site is transferred directly to the surface layer. This explains why more oxygen is sorbed with a heat significantly exceeding the heat of oxidation of copper to an oxide phase at room temperature[83] than at 100°C.[25] Thus, in order to explain all the results obtained for the sorption of oxygen by copper up to the formation of nuclei of a new phase, it is necessary to assume that three processes can occur when oxygen molecules collide with the copper surface. In the collision

between an oxygen molecule and unoxidised surface sites there is a possibility of (1) the adsorption of the oxygen on the surface and (2) deep adsorption. When an oxygen molecule collides with oxidised surface sites, a third process is possible—the adsorption of the molecule with transfer of another molecule previously adsorbed to the surface layer. The rates of each of these processes are proportional to the oxygen pressure in the gas phase. The rates of the first two processes decrease with decrease of the fraction of unoxidised surface. The rate of the third process increases as the surface monolayer is oxidised and can fall slowly as oxygen is sorbed after the completion of the oxygen monolayer when diffusion in the surface layers begins to have an effect. The second process does not require an additional activation energy as compared with the first (the energy liberated in the adsorption step at any temperature is sufficient to transfer oxygen to the surface layer and the fate of a given species is determined solely by the direction of the impulse), since otherwise the decrease of the rate, illustrated in Fig. 1, would cease for different amounts of sorbed oxygen at different temperatures. The activation energy for adsorption is much lower than the activation energy for the third process. Thus on polycrystalline materials it amounts to 7.5 kcal mole^{-1} for the sorption of 0.6 cm^3 O_2/m^2 Cu [18,50] and to 7.3 kcal mole^{-1} for the sorption of between 0.25 and 0.80 cm^3 O_2/m^2 Cu [51]; on the (110) face, under the conditions of the formation of the adsorption layer, the activation energy is 3.5 kcal mole^{-1} [53]. Fig. 1 shows that, as oxygen is sorbed up to 1 cm^3 O_2/m^2 Cu, the activation energy rises. Extrapolation of the curves to the initial conditions yields very similar rates at different temperatures, i.e. the initial activation energy for adsorption is close to zero. The activation energy for the third process is 11.5 kcal mole^{-1} in the sorption of 1–4 cm^3 O_2/m^2 Cu [18,50] or 15.5 kcal mole^{-1} in the sorption of about 10 cm^3 O_2/m^2 Cu. [61] Under these conditions, the rate of sorption of oxygen is still proportional to the pressure. On further sorption of oxygen, the activation energy rises to 21.8 kcal mole^{-1} [44] or 21 kcal mole^{-1} [40] on sorption of about 35 cm^3 O_2/m^2 Cu. Within the limits of experimental error, these activation energies are equal to the activation energy for the diffusion of copper ions in the surface oxide film (20.1 kcal mole^{-1}). [120] The activation energies quoted in some studies [40,44,120] were obtained under conditions where the rate of sorption of oxygen is almost independent of its pressure in the gas phase. In other words, under these conditions, the rate of reaction is limited by diffusion in the solid. On further oxidation, nuclei of the oxide phase appear and an increased rate of sorption of oxygen characteristic of this stage is observed.

On silver as well as on copper, oxygen is adsorbed and passes into the bulk metal. As for copper, the heat of adsorption on silver greatly exceeds the heat of oxidation to an oxide phase and the heat of deep adsorption is close to the heat of oxidation of the metal. However, the difference between the initial heats of adsorption of oxygen on silver (about 125 kcal/mole O_2) and the enthalpy of formation of Ag_2O (about 15 kcal/mole O_2) is in this case much greater than the difference between the corresponding values for copper. The dependence of the differential heat of adsorption of oxygen on the degree of adsorption (Fig. 3) shows that the heat of adsorption of oxygen greatly exceeds the heat of oxidation to an oxide phase up to almost complete surface coverage, in which there is one oxygen atom for each surface silver atom (0.26 cm^3 O_2/m^2 Ag). An increase in the electronic work function of silver following the adsorption of oxygen is also observed up to virtually monolayer surface coverage [111]. The rate of deep adsorption of oxygen on silver at 250°C is three orders of magnitude slower than the average rate of monolayer adsorption [69] and deep adsorption should not affect the results of the study of the adsorption of oxygen up to the limit of one monolayer. At the same time deep adsorption can influence the catalytic properties of silver in oxidation reactions. The results of studies of the adsorption of oxygen on silver are described in terms of the hypothesis that adsorbed oxygen exists in two forms, one of which corresponds to the formation of a two-dimensional surface oxide Ag_2SO and the other to the formation of $AgSO$ (or Ag_2SO_2). Many workers have used ideas of this type [5,73,77,81]. In this connection we may point to the existence of the compound AgO, which is not a peroxide [121], and of the surface compound of silver and oxygen, which was identified as a superoxide [122]. Oxygen is adsorbed initially with formation of the surface oxide Ag_2SO. The adsorption of oxygen as Ag_2SO has the highest heat and involves the main change in the electronic work function. The adsorption of oxygen as $AgSO$ begins only after the surface has been largely covered by oxygen as Ag_2SO. The adsorption of oxygen on a reduced surface proceeds in accordance with the equation

$$4\,Ag^S + O_2 \rightarrow 2\,Ag^S\!\!\overset{O}{\diagup\diagdown}\!\!Ag^S, \qquad (6)$$

and on a surface coated by Ag_2SO according to the equation

$$2\,Ag^S\!\!\overset{O}{\diagup\diagdown}\!\!Ag^S + O_2 \rightarrow 4\,Ag^S(=O). \qquad (7)$$

In the intermediate range of coverages the following reactions can also occur:

$$2\,Ag^S + O_2 \rightarrow 2Ag^S \xrightarrow{+2Ag^S} 2\,Ag^S\!\!\overset{O}{\diagup\diagdown}\!\!Ag^S, \qquad (8)$$

$$Ag^S\!\!\overset{O}{\diagup\diagdown}\!\!Ag^S Ag^S + O_2 \rightarrow 3\,Ag^S(=O) \xrightarrow{+2Ag^S} 3\,Ag^S\!\!\overset{O}{\diagup\diagdown}\!\!Ag^S. \qquad (9)$$

The maximum degree of adsorption of oxygen on silver before the rate drops by 2–3 orders of magnitude corresponds to the saturation of a monolayer with one oxygen atom per surface silver atom. Thus it was possible to assume that oxygen is adsorbed in the form of $AgSO$ (or Ag_2SO_2). However, the heat of adsorption of oxygen on an oxygen-free surface differs from the heat of adsorption at monolayer coverage by more than 100 kcal mole^{-1}, a sharp decrease of the heat of adsorption being observed near the degree of adsorption corresponding to one oxygen atom per silver atom on the surface. Moreover, as adsorption proceeds until the attainment of the above surface coverage, the electronic work function of silver rises, but subsequent adsorption has little influence on it; the depolarisation of dipoles cannot explain this type of variation of electronic work function with surface coverage. Under conditions close to complete surface coverage by oxygen with one oxygen atom per two silver atoms, there is also a change in the kinetics of the adsorption of oxygen (Table 3). These findings can be explained by assuming that oxygen is adsorbed on the surface in the two forms indicated above. The existence of two forms of oxygen on silver was also postulated to account for its catalytic properties. The heat of adsorption of oxygen in the form of Ag_2SO is high, decreasing with surface coverage (Fig. 3). The rate of adsorption decreases exponentially under these conditions [71,80]. The bond between oxygen and silver in the surface oxide Ag_2SO is polar with the negative end of the

dipole directed to oxygen (Table 5). Further adsorption of oxygen, leading to the conversion of adsorbed oxygen from Ag_2SO into $AgSO$, involves a small heat change and the electronic work function of silver does not alter. Under these conditions, the rate of adsorption of oxygen falls linearly, to a first approximation, as the concentration of Ag_2SO on the surface decreases[28]. The adsorption terminates when the surface is covered by an $AgSO$ monolayer. Further sorption of oxygen proceeds slowly and is due to deep adsorption†. The introduction onto the surface of impurities comprising electronegative elements such as sulphur, selenium, etc. reduces the rate of adsorption of oxygen[29,30,74], and the heat of its adsorption[28], via the mechanism of the mutual influence of adsorbed species. Admixtures of the above elements, introduced into the bulk of the specimen, act similarly, since they can migrate rapidly to the surface[32].

The oxygen adsorbed on gold hardly penetrates into the bulk of the crystal lattice at temperatures below 150°C. The sorption of oxygen is limited to a monolayer. To describe the results of adsorption studies, it is assumed, as for the adsorption on silver, that the oxygen can exist in two forms on the surface: as Au_2SO and $AuSO$. The heat of adsorption of oxygen on a clean gold surface with formation of Au_2SO is equal, within the limits of experimental error, to the heat of adsorption of oxygen with formation of $AuSO$ on a surface coated by Au_2SO. A clean gold surface is homogeneous with respect to the adsorption of oxygen. The heat of adsorption is constant over a wide range of variation in the extent of surface coverage by a monatomic oxygen layer. It amounts to about 100 kcal $mole^{-1}$, while the enthalpy of oxidation of gold to an oxide phase is positive (Table 1). Up to 70% surface coverage by the Au_2SO species, the adsorption kinetics are described by Eqn. (5), which corresponds to the adsorption of each O_2 molecule on four adjacent atoms of the homogeneous gold surface. Subsequent adsorption involves mainly the formation of $AuSO$. Only two surface sites are required for the adsorption of an oxygen molecule in the form of $AuSO$. Therefore the rate of adsorption depends less strongly on the degree of surface coverage than the rate of adsorption in the form of Au_2SO. The rate of adsorption remains proportional to pressure, but Eqn. (5) does not hold. On further increase of the degree of adsorption, the order of the adsorption process with respect to oxygen pressure diminishes, since the observed rate of adsorption begins to depend on the rate of surface migration. Data on the electronic work function of gold in the adsorption of oxygen are contradictory, as can be seen from Table 5. In studies[16,99] carried out under the cleanest conditions using different methods for the measurement of the electronic work function, no changes in the latter were observed when gold came into contact with oxygen. The change in surface potential observed[20] on bringing gold into contact with oxygen can be attributed to the fact that the fusion of gold and the sputtering of the film were carried out in an atmosphere of hydrogen. The adsorbed oxygen might interact with the occluded hydrogen on the surface of the film, generating a charge on the latter.

† In a recently published study[123] the hypothesis of the existence of Ag_2SO and Ag_2SO_3 was used to explain the results of an investigation of the heteroexchange of oxygen on silver.

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