Electrode Potentials in Fused Systems. VIII. Oxidation

Kinetics of Silver in Sodium Chloride

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The oxidation rate of metallic silver in molten sodium chloride has been studied as a function of oxygen partial pressure and temperature $(800-900^{\circ})$. The rate of appearance of silver ions was followed by an e.m.f. method. These ions are formed by: (A) the reaction of O₂ with silver and (B) the reaction Ag + Na⁺ = Ag⁺ + Na. The rate of (A) is a linear function of p_{0_2} in the range $0 < p_{0_2} \le 1$ atm. For $p_{0_2} = 1$ at 870°, $r_A = 11.9 \times 10^{15}$, $r_B = 0.35 \times 10^{15}$ atoms cm.⁻² sec.⁻¹. With increasing time d[Ag⁺]/dt decreases because of the reverse of reaction A—the formation of metallic silver from Ag⁺ and O⁻² ions—for which $r_A^{-1} = (r_A + r_B)/K_A p_{0_2}^{1/2}$, where K_A , the equilibrium constant for (A), is 8.3 × 10^{-7} on the mole fraction scale. The general differential equation for this system is derived and numerically integrated. It is concluded that the rate-determining step for (A) is the chemisorption of O₂, which is hindered by an adsorbed layer of chloride ions, and that for (B) charge transfer is rate-determining.

Introduction

As the result of previous studies^{1,2} the general features of the oxidation of metallic silver in molten sodium chloride in the presence of oxygen are fairly well established. The appearance of silver and oxide ions is accounted for by the following two reactions occurring on the metal surface

$$2Ag(s) + \frac{1}{2}O_2 = (2Ag^+ + O^{-2})$$
 (in NaCl) (A)

$$Ag(s) + Na^+(l) = Ag^+ + Na$$
 (in Ag) (B)

Most or all of the sodium metal formed in reaction B diffuses into the silver.^{1b} Reaction A was found to be reversible, however, so that when $[Ag^+]^2[O^{-2}]$ becomes large, the formation of metallic silver occurs throughout the melt from the reaction

$$2Ag^{+} + O^{-2} = 2Ag(s) + \frac{1}{2}O_2$$
 (C)

Since (B), in general, does not come to equilibrium (the solubility of sodium in silver is usually not exceeded), it follows that when $[Ag^+]^2[O^{-2}] = K_A p_{O_2}^{1/2}$ the oxide ion concentration decreases as $[Ag^+]$ increases by reaction B. For a high metal surface–salt ratio this has been observed.^{1b} The relative rates of (A) and (B) depend on the partial pressure of oxygen. When p_{O_2} is high, (A) predominates, when it is low, (B) does.

Previous rate measurements^{1b} have shown that oxygen partial pressure has considerable effect on the rate although the thermodynamic equilibrium concentration of silver ion depends only on $p_{0,1}^{1/6}$.

An additional complication discovered during this work (see Experimental part) is that the passage of O_2 gas through NaCl displaces the equilibrium ($K_{eq} = 4.5 \times 10^{-5}$)

$$2NaCl(l) + \frac{1}{2}O_2(g) = Na_2O(l) + Cl_2(g)$$
 (D)

to the right. The chlorine thus produced may react with the silver according to

$$Ag + \frac{1}{2}Cl_2 = Ag^+ + Cl^-$$
 (E)

However, since the partial pressure of Cl_2 in the effluent gas was found to be approximately 1 part in 10⁵ of O_2 , its effect on the rate of formation of Ag⁺ compared to that of O_2 , its effect on the rate of formation of Ag⁺ compared to that of O_2 is negligible. Reaction E has therefore been neglected in the kinetic analysis.

The purpose of the present work was to study certain kinetic aspects of this system, in particular the

 ⁽a) K. H. Stern, J. Phys. Chem., 62, 385 (1958);
 (b) ibid., 66, 1311 (1962).

⁽²⁾ J. Kruger and K. H. Stern, J. Electrochem. Soc., 109, 889 (1962)

dependence of the rate of appearance of Ag^+ on the oxygen partial pressure in reaction A, the rates of reactions B and C, and the over-all kinetic behavior of the system, and also to determine the mechanism of reactions A and B. In order to gain more insight into the mechanism of (A) and (B), it proved useful to study the initial stages of the reaction where (C) does not occur.

Principle of the Experimental Method. The general experimental procedure consisted of placing a silver rod into molten NaCl at various fixed temperatures and measuring the rate of appearance of Ag^+ ions for various environmental conditions.

Since previous studies with radioactive silver^{1a} had shown that silver ions appear in the melt almost immediately after immersion of the Ag specimen it was necessary to use a simple method to follow the very low silver ion concentrations accurately and continuously without disturbing the system, as it would be by sampling.

Assuming only that silver is reversible to its ions at very low concentrations in AgCl–NaCl melts, some form of concentration cell appeared to be ideally suited to this method. After preliminary experiments³ with simple concentration cells had established such reversibility and the feasibility of carrying out kinetic studies by this method, it was found that membrane reference electrodes⁴ permitted a considerable simplification of the experimental arrangement. In this method the unknown concentration (strictly, the activity) is directly calculable from a cell e.m.f.

For the system under study we used the cell

$$\operatorname{Ag}|\operatorname{AgCl}(X_{\mathrm{R}}), \operatorname{NaCl}(1 - X_{\mathrm{R}})|\operatorname{Vycor}|\operatorname{AgCl}(X),$$

 $\operatorname{NaCl}(1 - X)|\operatorname{Ag}(F)|$

where the left compartment represents the reference electrode. The e.m.f. of this cell is^4

$$E = (RT/F)t_{Na^+} \ln\left[\left(\frac{X}{X_R}\right)\left(\frac{1-X_R}{1-X}\right)\right] \quad (1a)$$

 t_{Na^+} , the sodium ion transport number in the glass, is 0.95, independent of temperature in the range of this study (800–900°). To determine the unknown silver concentration X, eq. 1a is more conveniently written

$$\log X \simeq \log \left(\frac{X}{1-X}\right) = \frac{E}{2.303t_{\mathrm{Na}^+}(RT/F)} - \log \left(\frac{1-X_{\mathrm{R}}}{X_{\mathrm{R}}}\right) \quad (1b)$$

where the approximate equality sign holds for low concentrations, and the last term on the right is a constant for a fixed reference composition. Since e.m.f. measurements can easily be made to ± 0.1 mv., concentrations can be calculated to three significant figures even near $X = 10^{-5}$. It should also be noted that because of the form of eq. 1 a given change in e.m.f. corresponds to a relatively larger concentration change when X is small, so that the method is particularly sensitive in very dilute solutions.

Reference Electrode Preparation. A batch of a suitable AgCl-NaCl mixture ($X_{\rm R} = 0.0720$) was prepared by melting together the appropriate quantities of AgCl and NaCl. The cold melt was ground, analyzed several times by electrodeposition, and stored in a dark bottle in a desiccator. In each run 2–3 g. of this material was placed in fresh 9-mm. o.d., 20-cm. long Vycor tube. These tubes had previously been cleaned by soaking both their inside and outside surfaces in concentrated nitric or chromic acid and distilled water; they were dried at 130°.

To test the applicability of eq. 1 to cell F these reference electrodes were placed in synthetic AgCl-NaCl mixtures. In the concentration range of this study $(10^{-5} < X < 10^{-3})$, calculated X values were within 1.5% of prepared ones.

Cell Construction and Procedure. A heavy-walled 3.4-cm, i.d., 20-cm, long alumina crucible, placed into the outer alumina crucible, constituted the cell container. The hot junction of the measuring chromelalumel thermocouple was placed in a Vycor protection tube inside the container. The reference electrode and 75 g. of dried NaCl were placed in the cell. A tightfitting Vycor tube with a standard taper, ground female joint at its upper end was slipped over the crucible. In this position the top of the crucible was even with the top of the furnace, and the joint protruded above it. The upper part of the cell, consisting of the male joint and a length of tubing terminating in four narrow tubes accommodating the two silver electrodes, gas flow tube, and thermocouple, was placed into the lower joint. The Ag specimen, a mint silver cylinder, 3 cm. long and 1 cm. in diameter (area = 10.99 cm.²), attached to a heavy silver wire sheathed in a ceramic tube, was positioned by a clamp above the furnace inside the glass envelope. A thinner silver wire, also sheathed in ceramic for mechanical rigidity, was lowered into the reference electrode. Heating was started. When the NaCl had melted, a ceramic two-hole gas flow tube (hole diameter 1 mm.) was lowered into the melt. The de-

⁽³⁾ K. H. Stern and E. A. Richardson, presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962. Part of this work was done at the University of Arkansas, supported by the U. S Air Force Research and Development Command under Contract AF 49(638)-653.
(4) K. H. Stern, J. Phys. Chem., 67, 893 (1963).

sired gas (He–O₂ mixtures were obtained in tanks) was passed through a calibrated flow meter, $CaSO_4$ and Ascarite, and through the tube into the melt. After the gas had bubbled through the melt for 5–10 min., the Ag specimen was lowered into the melt and positioned with the bottom of the cylinder 1–2 cm. from the crucible bottom.

For approximately the first 5 min. the e.m.f. was usually steady or increased slightly, after which a regular decrease began. The time at which the decrease began was taken to be t_0 . Each run was continued for 1-3 hr. Potentials were read on either a Leeds and Northrup Type K-3 potentiometer or on a Sargent recording potentiometer. In some cases data at more than one temperature and/or flow rate were obtained from the same run. The silver specimens could be used a number of times since their dimensions remained virtually unchanged during any experiment. They were cleaned before each run by washing in NH₄OH, concentrated HNO₃, and distilled water. Although this etching procedure revealed an increase in grain size with time, the reaction rate was independent of grain size, as expected.²

The Reaction of NaCl with O₂ and NaCl Thermal Decomposition. Separate experiments were carried out to assess the importance of reaction D and of direct thermal decomposition, NaCl = $Na^0 + \frac{1}{2}Cl_2$. The equilibrium constant of the latter is very small (K = 8×10^{-13} at 850°), but it is conceivable that, when a carrier gas is bubbled through the melt, the equilibrium is significantly displaced to the right. To study these reactions, a test tube filled with NaCl was heated to 870° in the Vycor apparatus described previously.^{1b} The desired gas mixture was bubbled through the melt and the effluent gas was passed through a gas wash bottle containing 200 ml. of o-toluidine solution to absorb Cl₂ and was collected over water for ameasurement of gas volume. Thus, the amount of Cl_2 produced by the NaCl per liter of gas could be determined. This experimental method is sensitive to 0.1 p.p.m. Cl₂ in solution.

When helium, passed over hot copper to remove residual oxygen, was passed through the melt, no Cl_2 was detected. Hence, direct thermal decomposition is insignificant. When various O₂-He mixtures were used, however, Cl₂ was evolved, p_{Cl_2} increasing with oxygen content. For 0.007 $\leq p \leq 1$ atm., the ratio $p_{\text{Cl}_2}/p_{\text{O}_2}$ remained constant at $\sim 10^{-5}$.

If we assume that every molecule of O_2 and Cl_2 adsorbed on silver reacts, the correction to reaction A due to (D) is 1 part in 10⁵ and, therefore, negligible.

Results

In all the experiments no silver ion concentration $<10^{-5}$ mole fraction (m.f.) was ever observed. This is apparently the concentration which is established initially near the silver surface. Since this same numerical result was also obtained when deoxygenated helium was used, it is attributable to reaction B.

The rate of this reaction was determined separately by outgassing the melt for more than an hour with helium (initial O_2 content 5×10^{-5} atm.) which had been passed through a long tube filled with copper wool at 500° to remove residual oxygen. Four separate runs were carried out, each consisting of rate measurements at three temperatures in random sequence. Since the silver surface area and melt volume are constant during the experiment and since, in the very dilute melts, the sodium ion concentration remains virtually constant, zero-order behavior would be expected and was found; *i.e.*

$$(\mathrm{d}[\mathrm{Ag}^+]/\mathrm{d}t)_{\mathrm{B}} = k_2 \tag{2}$$

At 870° $k_2 = 3.0 \times 10^{-7}$ m.f. min.⁻¹, and the Arrhenius activation energy $E_2 = 45.4 \pm 11.4$ kcal. (1 cal. = 4.1840 joules).

In studying reaction A with He–O₂ mixtures, it was found that, particularly at high p_{O_2} values, $d[Ag^+]/dt$ was quite dependent on the gas flow rate. Consequently a number of runs were carried out to determine



Figure 1. Dependence of k_1' on flow rate: upper curve, $p_{O_2} = 1.00$; lower curve, $p_{O_2} = 0.0228$ atm. at 870°.

this rate dependence for p_{0_2} values of 1.00 and 0.0228. The results are shown in Fig. 1 where $d[Ag^+]/dt$ has been plotted as a function of flow rate F. Since reaction B occurs simultaneously and independently of (A) the rate shown is the sum of the two reactions. The dependence on F is clearly due to (A) alone since the rate of (B) is very small and independent of F. At both pressures there is a flow rate F_{\max} above which $d[Ag^+]/dt$ depends only on p_{0_2} , *i.e.*, is independent of flow rate, but F_{\max} increases with decreasing p_{0_2} . Consequently the pressure dependence of the rate was studied at flow rates $>F_{\max}$.

In all the experiments the silver ion concentration was a linear function of time, *i.e.*, reactions A and B are zero order at constant p_{0_2} . We therefore write for these reactions

$$d[Ag^+]/dt = k_1'(p_{O_2}) + k_2 = k'$$
 (3)

 $k_1'(p_{O_2})$ represents the pressure-dependent rate of reaction A and was determined from eq. 3 in two ways: (a) k_2 was determined in a separate experiment in the absence of O_2 (see above) and subtracted from the experimental rate k' measured in the presence of O_2 ; (b) k'was measured at a number of p_{O_2} values (cf. Table I) and extrapolated to $p_{O_2} = 0$. The extrapolated value is k_2 . Both methods give the same result for $k_1'(p_{O_2})$. Moreover, the value of k_2 obtained from method b is the same as that determined separately in the absence of O_2 , showing that reactions A and B occur independently. This implies either that the diffusion of sodium into silver is rapid compared to the rate of arrival of O_2 molecules at the surface or that the two reactions occur at fairly widely separated sites on the surface.

The dependence of $k_1'(p_{O_2})$ and k' on p_{O_2} is shown in Fig. 2 on a logarithmic plot. The dashed lines for nvalues of 0.5, 1, and 2 represent possible dependences of these rate constants on p_{O_2} in the equation

$$k_1'(p_{0_2})$$
 and $k' = (\text{const.})(p_{0_2})^n$ (4)

The determination of n is of course a useful tool for determining the mechanism of reaction A. It is clear from the plot that the data for $k_1'(p_{O_2})$ (filled circles) are best fitted to the n = 1 line and $k_1'(p_{O_2})$ is therefore a linear function of p_{O_2} as written in eq. 3.

In Table I are listed the values obtained. These rate constants represent the actual change per minute in the ion fraction of silver in the particular melt used. To convert these to the more significant units of g. atoms of Ag cm.⁻² min.⁻¹, these values must be multiplied by 75.0/(58.5)(10.99) = 0.117.

Some idea of the reaction velocity on the atomic level can be gained by a simple calculation. The highest rate measured, at $p_{\text{O}_2} = 1$, is 67.2×10^{16} atoms cm.⁻² min.⁻¹.

Since there are 1.2×10^{15} atoms/cm.², the number of atomic layers disappearing is $67.2 \times 10^{16}/1.2 \times 10^{15} = 562$, or one layer disappearing every 0.11 sec. This corresponds to a change in thickness of 0.1 mm. in 10.3 hr.

The rate constant for reaction C cannot conveniently be obtained experimentally because (a) it is very large, and (b) the deposition of silver occurs in the form of fine crystals^{1,2} so that the surface area changes greatly. It was therefore assumed that, when the solubility product $[Ag^+]^2[O^{-2}] = K_A p_{02}^{1/2}$ is reached, the driving force is represented by $k_3[Ag^+]^2[O^{-2}]$. This assumption is valid, independent of the mechanism of formation of metallic silver by reaction C. k_3 can then be calculated from the rate equations for reactions A, B, and C, viz.

$$d[Ag^+]/dt = k_1'(p_{O_2}) + k_2 - k_3[Ag^+]^2[O^{-2}]$$
 (5)

and the steady-state condition $d[Ag^+]/dt = 0$. Then

$$k_3 = \frac{k_1'(p_{O_2}) + k_2}{K_A p_{O_2}^{1/2}} \tag{6}$$

At 870° $K_{\rm A} = 8.3 \times 10^{-7.1 \rm b}$

 k_3 values calculated from eq. 6 are given in Table I.

Table I: Rate Constants for Reactions A-C at 870°				
p_{O_2}	$k' \times 10^{7},$ m.f. min. ^{-1a}	$k_{1}' \times 10^{7} (p_{O_{2}}),$ m.f. min. ^{-1a}	ks	
1.00	98.5	95.5	11.9	
0.65	45.0	42.0	6.8	
0.21 (Air)	31.8	28.0	8.4	
0.10	15.2	12.2	5.8	
0.0547	8.74	5.74	4.5	
0.0228	5.70	2.70	4.9	
0.007	3.60	0.60	5.2	
<0.00005	3.00			

 a To convert these values to atoms cm. $^{-2}$ sec. $^{-1}$ multiply by $1.172 \times 10^{21}.$

For a change in p_{0_2} over more than two orders of magnitude k_3 is virtually constant, as expected, since the rate of reaction C should be independent of p_{0_2} . The last line in Table I represents $d[Ag^+]/dt$ in the absence of O_2 , *i.e.*, it is the rate of reaction B ($k_2 = 3.00 \times 10^{-7}$ m.f. min.⁻¹ at 870°).

k' values were also determined for four p_{0_i} values at 830°. From these and from the data in Table I, the Arrhenius activation energy for reaction A could be calculated. The results of two methods of calculation are shown in Fig. 3. In the first method (closed circles) $k_1'(p_{0_i})$ values are calculated from eq. 3 at both 870 and 830°, and E_1 is determined in the usual way. In



Figure 2. Test for the pressure dependence of the rate constants at 870°: \bullet , $k_1'(p_{0_2})$; \bullet , $k' = k_1'(p_{0_2}) + k_2$. Dashed lines represent theoretical slopes for log $k = \text{constant} + n \log p_{0_2}$.



Figure 3. Activation energy as a function of oxygen pressure: Δ, E' ; • and O, E_1 . For method of calculation see text.

the second method (open circles) E_1 is calculated from E' (which is obtained from k' values at 870 and 830°) using the relation⁵

$$E' = \frac{E_1 k_1'(p_{0_2})}{k'} + \frac{E_2 k_2}{k'}$$
(7)

Both methods of calculation give essentially the same results for E_1 . The E_1 value at the lowest pressure

 $(p_{0_2} = 0.023 \text{ atm.})$ is subject to the greatest uncertainty since a small error in k_2 could greatly affect $k_1'(p_{0_2})$.

The increase in E_1 at low pressure is similar to the behavior of heats of chemisorption and is associated with a variety of surface sites. This will be discussed in the next section.

Discussion

In the previous section the expression for the rate of appearance of Ag^+ was deduced (eq. 5). From this, reactions A, B, C, and the experimental results it also follows that

$$d[O^{-2}]/dt = k_1'(p_{O_2}) - k_3[Ag^+]^2[O^{-2}]$$
(8)
$$d[Na^0]/dt = k_2$$
(9)

By combining eq. 8 and 9 with (5), the over-all corrosion rate of the silver can be expressed in terms of $[Ag^+]$ alone. In this form $[Ag^+]$ can be predicted for large t from our own measurements on relatively short time intervals at the beginning of the reaction. If the concentrations are given in terms of equivalents

$$d[Ag^+]/dt - d[O^{-2}]/dt = k_2$$
 (10)

from which

$$[O^{-2}] = [Ag^+] - k_2 t \tag{11}$$

Substitution of (11) into (5) gives

$$d[Ag^+]/dt = k_1'(p_{0_2}) + k_2 - k_3[Ag^+]^3 + k_3k_2[Ag^+]^2t \quad (12)$$

Equation 12 is the general differential equation which applies to the over-all rate of formation of silver ion in solution.

Equation 12 is in general agreement with experimental observations: (a) the initial kinetics (small $[Ag^+]$, t) are zero order; (b) for larger $t d [Ag^+]/dt$ decreases as the negative term becomes more important, but does not become zero, as long as reaction B continues—the rate does, however, go through a minimum; (c) eq. 11 implies that [O⁻²] goes through a maximum. Although eq. 12 cannot yet be integrated explicitly, the results of a numerical integration for the rate constants in Table I carried out on an IBM 7094 computer are shown in Fig. 4 for 10⁵ min.; in Fig. 5 the first 10⁴ min. have been shown on an expanded scale. One-half of the average value of k_3 in Table I (3.4) was used since $[O^{-2}]$ is expressed in equivalents. Figure 5 is in good agreement with the general results previously obtained for much higher metal surface area-salt ratios.^{1b} A

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⁽⁵⁾ Cf. A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1962, p. 375.



Figure 4. $[Ag^+]$ and $[O^{-2}]$ concentrations for $p_{O_2} = 1.0$ and 0.007 calculated from eq. 4 and 5 and the rate constants in Table I.



Figure 5. $[Ag^+]$ and $[O^{-2}]$ concentrations for $p_{O_2} = 1.0$ and 0.007 calculated from eq. 4 and 5 and the rate constants in Table I.

previous interpretation for rates at $p_{0_2} = 1$, in terms of a diffusion-controlled process,^{1b} is, thus, in error. The decrease in the rate at higher [Ag⁺] is merely the result of reaction C. Although the initial rate of silver ion formation is very strongly dependent on oxygen pressure, the silver ion concentrations for large t become nearly equal at all pressures (cf. Fig. 4). This is because, at large t, [O⁻²] is nearly zero at both high and low p_{0_2} , and the rate of reaction is primarily due to (B). Thus, at high p_{0_2} reaction A comes to equilibrium at long times, and the subsequent rate is due to (B) alone; at low p_{0_2} the rate of (A) is small and (C) is negligible, and the over-all rate is again primarily due to (B). At higher pressures the [O⁻²] maximum occurs sooner, and, of course, at much higher values.

We consider next reactions A and B from a more mechanistic viewpoint.

Reaction A. The general course of this reaction, as of any heterogeneous reaction, can be discussed in terms of a number of consecutive steps, *viz*.

- A_1 transport of O_2 molecules to the surface
- A₂ O₂ adsorption
- $A_3 \quad O_2 \rightarrow 2O$ possible rearrangements on the surface
- A₄ $O + 2Ag \rightarrow 2Ag^+ + O^{-2}$ (surface)
- A_5 desorption of products
- A_6 transport of products into the bulk liquid

Since the rate constant $k_1'(p_{O_2})$ is a linear function of p_{O_2} , *i.e.*, $k_1'(p_{O_2}) = ap_{O_2}$, it follows from simple considerations, based on the Langmuir adsorption theory,^{6,7} that A_2 , adsorption of molecular oxygen, is the ratedetermining step in the sequence. Moreover, even at the highest pressure studied, 1 atm., the metal surface is only sparsely covered with O2. The flow rate experiments indicate that, at F_{max} values or above, the O₂ in the melt and on the surface are in a steady-state condition since one would expect the fraction of the surface covered by O_2 , θ , to be proportional to the pressure. Under these conditions the rate of O_2 transport to the surface (A_i) equals the rate of the slowest step subsequent to A_2 . At lower flow rates, A_1 decreases relative to these steps so that the steady-state concentration is no longer maintained on the surface. The increase of F_{max} with decreasing partial pressure is consistent with this mechanism. Rates of A₃-A₆ are independent of partial pressure and flow rate whereas A_1 and A_2 depend on both. Therefore, at the lower pressures an increased flow rate is the only mechanism whereby A_1 can be sufficient to maintain a steady-state concentration of the surface. The effect is rather small (a change in p_{O_2} by a factor of 50 changes F_{max} by a factor of 3) because the steady-state coverage θ is much less at lower pressures, and, thus, $d[Ag^+]/dt$ is limited primarily by low θ rather than low F. It is quite possible that the melt may be supersaturated with O_2 (entrapment), but in any case, since the solubility (or supersolubility) is proportional to p_{O_2} , it follows that at any particular partial pressure when $F < F_{max}$ the melt does not hold the maximum possible concentration of O_2 , and $\theta < \theta_{max}$.

Since the magnitude of the activation energy of reaction A exceeds 5 kcal. (*cf.* Fig. 3) and increases with decreasing pressure, it is clear that the adsorption of O_2 is chemical rather than physical. This conclusion is also supported by a number of studies⁸⁻¹¹ of oxygen adsorp-

⁽⁶⁾ I. Langmuir, J. Am. Chem. Soc., 38, 2221 (1916).

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⁽⁸⁾ F. H. Buttner, E. R. Funk, and V. Hilldin, J. Phys. Chem., 56, 657 (1952).

⁽⁹⁾ A. F. Benton and L. C. Drake, J. Am. Chem. Soc., 56, 255 (1934).

⁽¹⁰⁾ W. W. Smeltzer, E. L. Tollefson, and A. Cambron, Can. J. Chem., 34, 1046 (1956).

tion on silver. Although only one of these⁸ lies in the temperature range of this work, all of the cited results above 200° are consistent with chemisorption; also, the properties of the adsorbed film are different from those of bulk Ag₂O. Near 200° two consecutive rates of adsorption, rapid and slow, have been found¹⁰ and interpreted in terms of two kinds of adsorption sites, but no relevant data exist at high temperatures. Surface tension measurements of silver⁸ in helium–oxygen mixtures at 930° in the range $10^{-4} \leq p_{O_2} \leq 0.2$ give a surface concentration of 1.98×10^{15} atoms of oxygen/cm.². Since the number of silver atoms is approximately ($r_{Ag} = 1.44 \text{ Å}$.) 1.2×10^{15} , this gives 1.65 atoms of O/atom of Ag.

As seen in Fig. 2, the rate of reaction is still increasing at $p_{O_2} = 1$. Hence, θ must be considerably less than unity, even at this pressure and for all $p_{O_2} \leq 1$ since the surface coverage of O_2 on the metal surface is controlled by the solubility of O_2 in the molten salt (and by the possible preferential adsorption of chloride ions) and is proportional to the pressure through Henry's law.

This conclusion is also consistent with steps A_2 , A_3 , and A_4 of the proposed mechanism. Each adsorbed O_2 molecule is adsorbed on two surface Ag sites. After its dissociation each resulting oxygen atom must exchange electrons with two adjacent Ag atoms. This requires that the surface be only sparsely covered with oxygen.

To gain some insight into possible reasons for the slowness of this reaction we write, from absolute reaction-rate theory

$$k_{\rm R} = \frac{kT}{h} c_{\rm Ag} c_{\rm O_2} e^{\Delta S^*/R} e^{-\Delta H^*/RT}$$
(13)

If the rate-determining step is the chemisorption of O_2 on silver, ΔS^* in eq. 13 should then correspond to the entropy of chemisorption. The maximum value of ΔS^* would be obtained for complete coverage, *i.e.*, c_{O_4} = 10¹⁵ molecules cm.⁻². $k_{\rm R}$ is the rate constant at 870° in atoms cm.⁻² sec.⁻¹, and $c_{\rm Ag} = 1.2 \times 10^{15}$ atoms cm.⁻². Changes of an order of magnitude in these concentrations hardly affect ΔS^* . The results of the calculation of ΔS^* are shown in Table II, where the Arrhenius activation E_1 (cf. Fig. 3) energy has been identified with ΔH^* since $\Delta H^* \approx E_1$ for reaction A.

It is immediately apparent that these entropies are impossibly large. The total molar entropy of O_2 at 870° is 53 e.u. The translational part of this is 43 e.u., and, normally, the loss of translational entropy is less, typically 30–35 e.u., because, even in immobile layers, the molecules possess configurational entropy.¹² The above model, together with the values of Table II, implies that reasonable entropy values can only be obtained if the concentration terms are drastically re-

3	7	6	3

	$k_1 \times 10^{-16}$,	
p_{O2} ,	atoms cm. ⁻²	ΔS^*
atm.	sec1	(e.u.) ^a
0.65	4.92	-134
0.21	3.37	-137
0.10	1.43	-158
0.0228	0.316	-222

duced. Even if we assume that the entire translational entropy is lost on chemisorption, we obtain from eq. 13 the product $c_{Ag}c_{O_2} = 10^{21}$, or, assuming equal concentrations, 3×10^{10} sites/cm.², covered with $p_{O_2} = 0.65$, *i.e.*, $\theta = 2.5 \times 10^{-5}$. Such an extremely small coverage suggests that the chloride ions in the system undoubtedly are strongly adsorbed and thus interfere with the adsorption of oxygen.

Reaction B. By analogy with reaction A we write reaction B as a sequence of steps, viz.

- B_1 transport of Na⁺ to surface
- B_2 adsorption
- B_3 electron exchange
- B_4 desorption of Ag⁺
- B_5 removal of Na atoms from the surface, *e.g.*, by diffusion into silver

The magnitude of $E_2 \simeq \Delta H^* = 45.4$ kcal. rules out adsorption of sodium metal or diffusion of sodium into silver as rate-determining steps. For the latter process activation energies would be expected to be 2–5 kcal.¹³ Assuming that a lattice of NaCl is laid down on the silver, ΔS^* can be estimated from eq. 13. We obtain $c_{\rm Na^+} = 7.6 \times 10^{14}$ ions/cm.². Again taking $c_{\rm Ag} =$ 10^{15} atoms/cm.² gives, for $\Delta H^* = 45.4$ kcal., $\Delta S^* =$ -92 e.u., a very large negative value.

The large values of ΔH^* seem to rule out any step except B₃ as rate-determining. The work function of clean silver is 4.3 e.u. = 99 kcal., but this value decreases on adsorption of foreign species on the metal surface.^{14,15} The large negative ΔS^* indicates that the same process

(14) M. Boudart, J. Am. Chem. Soc., 74, 3556 (1952).

(15) J. H. de Boer in "Chemisorption," W. E. Garner, Ed., Butterworth Scientific Publications, London, 1955, pp. 209-213.

⁽¹¹⁾ R. G. Meisenheimer, A. W. Ritchie, D. O. Schissler, D. B. Stevenson, H. H. Voge, and J. N. Wilson, "Second International Congress of Surface Activity," Vol. II, Academic Press, New York, N. Y., 1957, pp. 299-308.

⁽¹²⁾ Cf. B. M. W. Trapnell in "Chemisorption," W. E. Garner, Ed., Butterworth Scientific Publications, London, 1955, pp. 209-213.

⁽¹³⁾ D. Lazarus in "Metallic Solid Solutions," J. Friedel and A. Guinier, Ed., W. A. Benjamin, New York, N. Y., 1963; pp. xxxiv-7.

which accounts for the slowness of reaction A also affects (B) in a similar manner. Thus, if a layer of chloride ions is preferentially adsorbed on the metal, the concentration product $c_{Ag}c_{Na^+}$ will be considerably less than for complete coverage.

From this viewpoint both reactions A and B must be characterized as slow; *i.e.*, they would go much faster if the reactants could come into contact. In this model we then have a charged double layer on the surface, with sodium ions largely excluded from the metal side. This view is also consistent with the observation that when silver is briefly immersed in NaCl and withdrawn, the adherent salt is high in AgCl.

We next examine the reaction in more detail, particularly with respect to events occurring in the double layer. Initially the electrochemical potential of the silver (\mathcal{E}_1) is greater than that of the sodium chloride (\mathcal{E}_2) . When the two are placed in contact, the difference $\mathcal{E}_1 - \mathcal{E}_2$ decreases. This decrease occurs most easily through the formation of a charged double layer at the surface of the silver which is positive on the metal and negative on the sodium chloride side. As electrons are transferred from the silver to the sodium ions to establish equal electrochemical potentials for the two phases, the silver surface becomes positively charged, and sodium ions are reduced to metallic sodium. If the system remained in this condition, reaction B would cease after the initial formation of the double layer. A driving force for the experimentally observed continuation of the reaction is provided for by the formation of AgCl ion pairs, *i.e.*, the reaction, $Ag^+ + Cl^- \rightleftharpoons AgCl$, continues until this equilibrium is reached. The equilibrium constant for this reaction in NaCl has not been measured, but values are available in KNO₃ solvent.¹⁶ At 402°, K = [AgCl]/ $[Ag^+][Cl^-] = 396$; K values for AgBr and AgI in this solvent are 932 and 5420, respectively. The addition of the ion-pair formation reaction to reactions A-C would require a modification of eq. 5. The net effect is to decrease $d[Ag^+]/dt$ at large $[Ag^+]$. Previous studies^{1b} of reaction B over long periods of time showed that the concentration of Na in the silver is, at most, only a small fraction of that possible under equilibrium conditions.¹⁷ This indicates that alloy formation is, thus, only a secondary effect and that the ion-pair equilibrium is the factor which determines the eventual equilibrium state of this system.

The kinetic model used here predicts that $[Ag^+]$

increases indefinitely after reactions A and C have come to equilibrium due to the continuation of reaction B. It is known, however, that silver electrodes are quite stable in AgCl–NaCl melts containing more than 7–8% AgCl.^{1a} The rate of appearance of [Ag⁺], after reactions A and C have reached equilibrium and $[O^{-2}]$ has reached an approximately constant low value, would be of the form

$$d[Ag^+]/dt = k/[AgCl] = k/K[Ag^+][Cl^-] = k'/K[Ag^+]$$
(14)

where k is the rate constant for reaction B and K is the ion-pair formation constant for AgCl. Equation 14 indicates a gradual decrease of $d[Ag^+]/dt$ through (B) as $[Ag^+]$ increases. In the absence of oxygen the initial rate is approximately 10^{-7} m.f. min.⁻¹ (Table I) for $[Ag^+] \simeq 10^{-5}$. This gives for $k_2/K \simeq 10^{-12}$. Thus, when $[Ag^+]$ is increased to 10^{-2} , $d[Ag^+]/dt$ is decreased by a factor of 10^3 , e.g., a change in $[Ag^+]$ which initially takes 1 min. will then require 16 hr. This undoubtedly accounts for the stability of Ag– AgCl reference electrodes.

Unfortunately, it is not yet possible to determine K separately since it cannot be assumed that its value is the same in a pure chloride as in a nitrate environment. In any case, however, the k_2 values given earlier in the paper should be regarded as rates $(d[Ag^+]/dt)$ in the absence of oxygen which include an ion-pair equilibrium constant.

Ion-pair formation provides a plausible mechanism for the removal of positively charged silver formed on the silver side of the double layer. It implies that initial rates of both reactions A and B should increase with increasing covalent character of the silver-anion pair, *i.e.*, with increasing ion-pair formation constants. For example, rates should be greater in bromide and iodide melts and less in sulfates. Experimental tests of this conclusion are in progress.

Acknowledgments. We wish to thank Dr. H. Oser and Mr. J. D. Waggoner for the numerical integration of eq. 12 and for other mathematical assistance, and Mrs. J. L. Stiff for various analytical determinations. We are grateful to Drs. Margaret A. Reid and Jerome Kruger for helpful discussions.

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⁽¹⁷⁾ E. Quercigh, Z. anorg. Chem., 68, 301 (1910).