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DIFFUSION AND SOLUBILITY OF OXYGEN IN SILVER

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ABS: The diffusion and solubility of oxygen in Ag in the temperature range
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16. Abstract The rate of loss of oxygen from Ag samples led to the determination of the diffusion and solubility of oxygen in Ag in the temperature range between 412 and 862°C. The following interpolation formula was found for the solubility: $L = 8.19 \cdot 10^{-2} \cdot \exp(-11860/RT) \text{ Mol O}_2/\text{g} \cdot \text{At} \cdot \text{Ag} \cdot \text{at}^{-1/2}$ The process obeys the "Sieverts" square root law within the limits of error. The dissolution of oxygen in Ag is probably accompanied by the dissociation of the oxygen molecules into atoms. Our results do not agree with the data given by Steacie and Johnson which show a minimum in the solubility at 400°C. Tests on Ag-foils revealed that below a temperature of about 500°C a higher solubility is simulated by the adsorption of oxygen. The diffusion coefficient of oxygen in silver obeys the following equation: $D = 2.72 \cdot 10^{-2} \cdot \exp(-11000/RT) \text{ cm}^2/\text{s}$ The relatively low activation energy of 11 kcal/g·At suggests that the diffusion of oxygen takes place over interstitial sites.		
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DIFFUSION AND SOLUBILITY OF OXYGEN IN SILVER

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The temperature curve for the solubility L of a gas /321*
in a metal is given by the equation:

$$L = L_0 \exp\left(-\frac{H}{RT}\right) \quad (1)$$

where L is the solubility coefficient (expressed in moles of gas per gram-atom metal at a pressure of 1 atm), L_0 is an entropy factor, R is the gas constant, T the absolute temperature and H the heat of solution* referred to the standard state. Based on thermodynamic considerations, a monotonic function of temperature is expected for the heat of solution in the range considered here. Hence for the temperature-solubility curve one likewise gets a monotonic function. Metal-gas systems examined to date all fit this picture, with one exception: The system silver-oxygen.

Measurements conducted by E.W.R. Steacie and F.M.G. Johnson [1] on silver foils found a clearly marked minimum solubility of oxygen in silver at ca. 400°C. Later, an attempt was made to explain this minimum by the formation of silver oxide Ag_2O [2,3]. In our opinion the solubility minimum can be interpreted at least partly as a consequence of an additional adsorption of oxygen onto silver in the investigations of Steacie and Johnson [1]. The deviations of solubility values from the square-root law at low temperatures and lower pressures, as found by these authors, suggest the same origin. The apparatus and test method allowed no distinction between solubility and adsorption.

*Numbers in the margin indicate pagination in the foreign text.

*Editor's Note: heat of solution should be solution enthalpy

Our own orientation measurements with compact silver by our method, which only detects reversibly dissolved oxygen, yielded values as much as an order of magnitude below the data published by Steacie and Johnson [1]. This finding led us to repeat the determination of the solubility of oxygen in silver, while at the same time obtaining data on the diffusion of oxygen in silver, about which nothing was known but a single calculated value [4].

Experimental Method

The procedure we previously developed to determine the diffusion and solubility of gases in metals, already described in detail elsewhere [5,6], was also applied successfully to the system silver-oxygen. The method is based on observing the release of gas from a gas-charged metal body. The gas escaping from the metal is transferred to a collector vessel and the development over time is tracked with pressure measurements. The diffusion and solubility coefficients can be calculated from the resulting gas release curves.

The gas release from a metal follows the laws of volume diffusion, when this is the process that governs rate. However, in the many partial processes into which the escape of an atomically dissolved gas from a solid can be broken down, there is a risk that interface processes may govern or at least influence the gas release rate and hence cause misinterpretation of the results. If these processes are not known already from the found time law, using specimens of different dimensions and shapes makes it possible to find interference of this sort. Therefore our studies employed cylinders and various sizes of spheres.

Some experiments with refined silver (99.9 wt% Ag) did not yield reproducible results. Subsequent microscopic examination

revealed pores in the edge zone of the refined silver specimen.

The test specimens for the final measurement were produced as follows: Raw material was so-called crystallized silver, 99.995 wt% pure. It was melted in a vacuum (10^{-3} torr) in a quartz crucible, and poured into chills. Rolling and turning produced the following specimens:

Cylinders	0.53 cm ϕ and 29.85 cm long
Small spheres	0.98 cm ϕ
Large spheres	2.99 cm ϕ

To remove surface impurities, all specimens were pickled for 1 hr in a 10% aqueous solution of hydrochloric and tartaric acids. Precision determinations of density by the buoyancy method [7] yielded the following mean results:

Density before measurements

$$\rho(25^\circ\text{C}) = 10.4920 \pm 0.0008 \text{ g/cm}^3$$

Density after measurements

$$\rho(25^\circ\text{C}) = 10.4925 \pm 0.0008 \text{ g/cm}^3$$

Accordingly the dissolution of oxygen has no determinable effect upon the density of the silver we employed. For 322 for comparison, here we give the results obtained by T. Heumann and W. Wicke [8] with refined silver:

X-rays	$\rho(25^\circ\text{C}) = 10.507 \pm 0.01 \text{ g/cm}^3$
Buoyancy method	$\rho(25^\circ\text{C}) = 10.496 \pm 0.005 \text{ g/cm}^3$

(Heumann and Wicke [8] give the specific volumes for 20°C . Using the coefficient of thermal expansion of silver [9] we converted this data to the above densities at 25°C .)

The oxygen used for our studies was produced at 300°C from potassium permanganate (p.a.), condensed in a vessel chilled with liquid nitrogen, and purified by repeated distillation, freezing out all expectable impurities (water, carbon dioxide).

Results

In all, 38 measurements were performed in the range between 412 and 862°C at various pressures. The results are shown in the usual manner in Figs. 1 and 2. Measurements at constant temperature and different pressures had shown, in agreement with Steacie and Johnson [1], that the Sieverts square-root law also applies to the solubility of oxygen in silver. Within the error limits, the gas release curves of all specimens followed the law of volume diffusion. The low solubility and very slow development of diffusion below 400°C impede measurements in this range exceedingly, and prohibit expanding the investigation the temperature range where the compound Ag₂O is stable [10,11].

For the temperature function of the diffusion coefficient,

$$D = D_0 \exp\left(-\frac{E}{RT}\right) \quad (2)$$

from our measurements we get $D_0 = 3.66 \cdot 10^{-3}$ cm²/sec for the frequency factor, and $E = 11.00$ kcal/1/2 mol O₂ for the activation energy. For solubility one gets $L_0 = 3.34 \cdot 10^{-2}$ mol O₂/gr-atm Ag · atm^{-1/2} for the entropy term, and for heat of solution $H = 11.86$ kcal/1/2 mol O₂. This yields the amount of oxygen l (cm³NTP) dissolved in 100 g silver at temperature T (°K) and equilibrium pressure p (torr) as

$$\log l = 1.403 - \frac{2593}{T} + \frac{1}{2} \log p \quad (3)$$

Table 1 has the solubility values for an equilibrium pressure of 1 atm.

Fig. 1. Solubility coefficients for oxygen in silver

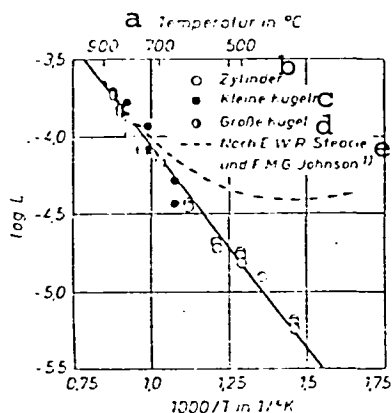
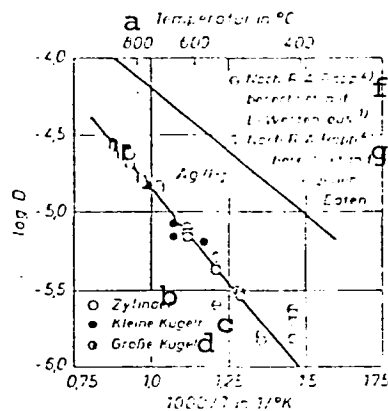


Fig. 2. Diffusion coefficients for oxygen in silver



Key to both figures:

- a. temperature
- b. cylinders
- c. small spheres
- d. large spheres
- e. after E.W.R. Steacie and F.M.G. Johnson [1]
- f. after R.A. Rapp [4], calculated with L values from [1]
- g. after R.A. Rapp [4], calculated with our own data

Table 1. Solubility of oxygen in silver at an equilibrium pressure of 1 atm, calculated with equation (3)

a Temperatur in °C	cm ³ O ₂ (NTP)/100 g Ag
200	0.0023
300	0.021
400	0.098
500	0.303
600	0.717
700	1.51
800	2.67
900	4.30

Key: a. temperature

Our estimates indicate the error limit of the diffusion coefficient above 500°C as ± 4%; at lower temperatures it rises to ± 6%. The error limit of the solubility coefficient is ± 8 in the entire range.

At higher temperatures the solubility data of Steacie and Johnson [1] coincide with our measurements (Fig. 1). The

deviations at lower temperatures, however, are clearly outside the error limits of the two studies.

Adsorption of Oxygen on Silver

Several passages in the literature report adsorption of oxygen on silver [12,13]. In the pressure and temperature range of interest to us, according to W.W. Smeltzer, E.L. Tollefson and A. Cambron [13], chemisorption of oxygen onto silver occurs. These authors' investigations were conducted with silver powder produced from a silver-calcium alloy. Since to us it seemed questionable to draw direct conclusions about the behavior of silver foil from the results from silver powder, we performed some experiments of our own, initially only for a qualitative determination of adsorption. The raw material was the same metal used to produce our specimens.

The apparatus we used, intentionally kept simple in structure, corresponds in principle to the test setup used in [13].

At a pressure of ca. 450 torr, a total of 14 measurements were performed between 240 and 400°C. Because of the broad spread of the individual results (error limit: $\pm 50\%$) no definite pronouncements are possible about the temperature dependence of adsorption. For the same reason we limit ourselves to reporting a value averaged over the whole temperature range: On the average, 0.085 cm^3 NTP oxygen were adsorbed on a silver surface measuring $2 \cdot 10^3 \text{ cm}^2$, equivalent to a coverage of $1.9 \cdot 10^{-9} \text{ mol O}_2/\text{cm}^2$. This value practically corresponds to a monomolecular layer, and given our rather coarse method is in satisfactory accord with the results of Smeltzer et al. [13], who found a coverage of $9.7 \cdot 10^{-10} \text{ mol O}_2/\text{cm}^2$ under similar conditions (270°C and 400 torr pressure). From this we conclude that concerning oxygen adsorption, our silver foil behaves similarly to the silver powder studied in detail by those authors.

Fig. 3. Oxygen uptake of silver foils (adsorption and solubility) referred to 1 atm.

Key:

- a. temperature
- b. after E.W.R. Steacie and F.M.G. Johnson [1]
- c. our own studies (adsorption and solubility)

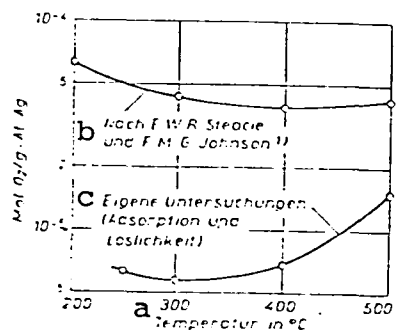


Figure 3 shows the calculated temperature curve for oxygen uptake (consisting of adsorption and solution) in our silver foil, compared to the solubility values of Steacie and Johnson [1]. The calculations were based on the data of Smeltzer et al. [13] for adsorption up to 300°C, and our own interpolation formula for solubility. The adsorption values above 300°C were obtained by extrapolation. Because of this imprecise procedure, naturally no quantitative agreement of the two curves can be expected. However, in our opinion their similarity confirms our initial view on the genesis of the solubility minimum found by Steacie and Johnson [1]

Comparison with Diffusion of Hydrogen in Silver

Our earlier investigations [6] found the following for the diffusion of hydrogen in silver between 388 and 600°C:

$$D = 2.82 \cdot 10^{-3} \exp(-7500/RT)$$

Using neutron deflection, it was found for the system palladium-hydrogen that the hydrogen atoms occupy the octahedral interstitial sites in the metal lattice [14]. We have no reason not to assume the same mechanism for the pair silver-hydrogen. The numerical values we found for the frequency factor and the activation energy for hydrogen diffusion in silver support this

assumption.

Moreover, observations concerning the diffusion of oxygen in this metal, particularly the relatively low activation energy for diffusion, suggest oxygen also behaves similarly. The low activation energy of oxygen diffusion rules out the assumption of diffusion via flaws in the silver.

Our measurements allow no far-reaching conclusions about the state of the oxygen or hydrogen dissolved in the metal. Hydrogen may very likely assume a state between an atom and a proton. There are no indications of the degree of ionization of oxygen atoms in the silver lattice.

A similar study of the systems gold-hydrogen and gold-oxygen only yielded conclusions about the diffusion of hydrogen in gold [15]. The solubility of oxygen in gold was below the detection limits of our equipment (under 10^{-7} mol O₂/gr-at gold).

Summary

From the course of oxygen release from silver specimens over time between 412 and 862°C, the diffusion and solubility of oxygen in this metal were determined. The following interpolation formula was obtained for solubility:

$$L = 8.19 \cdot 10^{-2} \cdot \exp(-11860/RT) \text{ Mol O}_2 / \text{g-At Ag-at}\bar{\alpha}^{1/2}$$

Within the error limits, this satisfies the Sieverts square-root law. Hence oxygen dissolves in silver very probably by splitting the molecule. We could not confirm the solubility curve with a minimum of 400°C, as given by E.W.R. Steacie and F.M.G. Johnson [1].

From some experiments with silver foils, we verified that

below ca. 500°C the adsorption of oxygen may simulate an increase in solubility.

The diffusion coefficients for oxygen in silver obey the following equation:

$$D = 2.72 \cdot 10^{-2} \cdot \exp(-11000 \cdot RT) \text{ cm}^2/\text{s}$$

The relatively low activation energy of 11 kcal/gr-at indicates a diffusion of oxygen via interstitial sites.

Our special thanks to Prof. H. Witte for discussions on this work. Our thanks to the Degussa company, Hanau, for supporting our investigations. The silver samples were kindly produced, finished and microscopically examined at the Metals Laboratory of the same company.

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