

Official Notice.

THE FIRE AT THE BRUSSELS EXHIBITION.

On Sunday, August 14th last, the British Section of the Brussels Exhibition and all its contents, with the important exception of machinery, was totally destroyed by fire. With it perished the Chemical Industry exhibits. On Saturday, August 20th, the Royal Commission met and resolved to reconstitute the Section in the Salle des Fêtes.

As members of the Society form no inconsiderable portion of the Commission, Exhibitors, and Jury, it is hoped that they will respond without delay to the official invitation to form a fresh Exhibit of the British Chemical Industries. The offices of the British Commission are at Queen Anne's Chambers, Westminster.

Liverpool Section.

Meeting held at the University, on Wednesday,
January 12th, 1910.

DR. JAMES CONROY IN THE CHAIR.

THE SOLUBILITY OF OXYGEN IN MOLTEN SILVER.

BY F. G. DONNAN AND T. W. A. SHAW, M.Sc.

(From the Muspratt Laboratory of Physical and Electro-Chemistry, University of Liverpool.)

In 1820 Chevallot (*Annales de Chimie*, 13, 299, 1820) found that 8 grms. of melted silver saturated with air gave up 7.8 c.c. of oxygen on solidifying. Gay Lussac in 1830 found that 1 volume of silver evolves 22 volumes of oxygen on solidification. A careful determination with modern methods of the solubility of oxygen in melted silver possesses both a technical and a scientific interest. For the silver smelter and refiner is troubled with the "spitting," i.e. foaming over, of the silver in the moulds during a pour, and with the liability of the ingot to "blister" on rolling, due to still entangled oxygen; whilst the molecular condition of the oxygen dissolved in the molten metal presents an interesting scientific problem.

A knowledge of the amount of oxygen dissolved in a given mass of molten silver at a given temperature might prove useful to the refiner, in giving him some guide to the amount of oxidisable metal (aluminium, copper) required to be added to the melt in order to deoxidise it.

Of course the technical difficulty could be overcome by working in an atmosphere of some gas which is not appreciably dissolved by melted silver, but this procedure might offer certain inconveniences in practice.

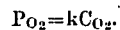
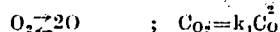
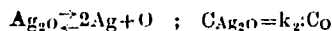
As regards the scientific interest of the problem, the dissolved oxygen may exist either in a state of "physical" solution, or in combination as dissolved oxide, Ag_2O . In the former case the oxygen may be dissolved either as molecules, O_2 , or as atoms, O .

Let us consider the case of physical solution first. From Henry's law, the concentration of the dissolved oxygen will be proportional to the pressure (or partial pressure) of the oxygen if the molecular condition of the oxygen dissolved in the silver is the same as in the gaseous state, i.e. if the oxygen exists in both cases as diatomic molecules. We may express that by the equation $P_{\text{O}_2} = kC_{\text{O}_2}$. Supposes however, that the oxygen dissolved in the silver consist, mainly of atoms and only to a very small extent as molecules. We shall then have an equilibrium between the molecular and atomic oxygen in the silver, expressed by the law of mass action $C_{\text{O}_2} = k_1 C_{\text{O}}^2$, since the chemical equilibrium is $\text{O}_2 \rightleftharpoons 2\text{O}$.

As Henry's law still holds for the dissolved molecular oxygen, we have still $P_{\text{O}_2} = kC_{\text{O}_2}$, so that $P_{\text{O}_2} = kk_1 C_{\text{O}}^2$ or $C_{\text{O}} = \text{const.} \times \sqrt{P_{\text{O}_2}}$.

But according to our supposition we may regard C_{O} as practically equal to the total concentration of dissolved oxygen, so that in this case the concentration of the dissolved oxygen will be proportional to the square root of the oxygen-pressure.

Consider now the case where the oxygen contained in the molten metal exists mainly as Ag_2O , and to only a very slight extent as O_2 and O ("chemical" solution). As before, the laws of mass-action and distribution lead to the equations



$$\text{Hence } P_{\text{O}_2} = kk_1 C_{\text{O}}^2 = \frac{kk_1}{k_2^2} C_{\text{Ag}_2\text{O}}^2 \text{ or}$$

$$C_{\text{Ag}_2\text{O}} = \text{const.} \times \sqrt{P_{\text{O}_2}}$$

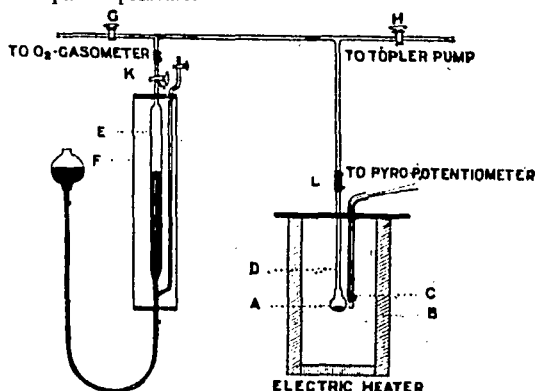
As by our assumption the oxygen of the Ag_2O constitutes the main bulk of the oxygen contained in the molten metal, the last equation shows us that the concentration of the dissolved oxygen will be proportional to the square root of the oxygen-pressure.

We cannot therefore distinguish in this way between oxygen "physically" dissolved in the atomic condition and oxygen "chemically" dissolved, i.e. contained in Ag_2O dissolved in the melted silver.

It is clear, however, that measurements of the solubility of oxygen in melted silver at different pressures and constant temperature will throw much light on the molecular condition of the solution.

With this object in view, and also in order to obtain data bearing on the technical question, the following apparatus was designed for the purpose of carrying out preliminary measurements. It was intended later to employ a more elaborate apparatus provided with compensating bulb and compensating leads, but the excellent work of Sieverts (see later), which was published after our first measurements had been made, appeared to us to render further work on this question unnecessary.

It will be evident from the following description and diagram that our preliminary apparatus was designed to measure the solubility at pressures equal to and below atmospheric pressure.



(A) is a small bulb of clear fused silica, provided with a long narrow stem (B). The silver is introduced into this bulb in the form of thin wire. The bulb is heated by the electric heater (H), which is wound with platinum wire and well insulated. The temperature is indicated by a Pt.-Pt. Rh. thermo-junction (shown at (c)), connected up with a suitable potentiometer. The stem of the silica tube is connected by means of the rubber joint (L) with the narrow tubing shown in the figure, which leads through the necessary taps to the Töpler pump, oxygen generator, and gas-burette (E) with water-jacket (F). The oxygen was produced by heating potassium permanganate and was purified from carbon dioxide and dried by passing through layers of soda-lime and phosphorus pentoxide respectively.

The silver employed was obtained as specially pure silver from Messrs. Sandars and Lees, Birmingham, and was not analysed.*

*The silver was not of course gas-free. The dissolved or entangled gases were removed as explained later.

The determination is carried out in the following way. The tap (κ) being shut (or the rubber connecting tube of the burette being compressed by a screw-clip), the apparatus (containing no silver in the silica bulb) is pumped out and then filled with pure oxygen to about atmospheric pressure. The taps (σ) and (η) being closed and (κ) open, the mercury levels are adjusted so that the gas is at the desired pressure (in our experiments, atmospheric pressure). Electric current is then passed through the coils of the heater (a controlling resistance and ammeter being in circuit) and the temperature gradually raised to the desired value. During the heating the pressure is maintained constant by lowering the mercury reservoir attached to the burette. When the temperature has become steady and no further increase in volume occurs, the burette-reading is taken and the atmospheric pressure and the air-temperature at various parts of the connecting tubing noted.

The apparatus is now allowed to cool down, the silica tube disconnected at (L), and a known weight of silver introduced into it. Connection is again made securely at (L), the tap (κ) closed, and the apparatus evacuated. The silver is then melted by heating up to about 1000°C ., and the Töpler pump kept in action until all the dissolved gases are pumped out. The silver is then allowed to cool and solidify *in vacuo*. When the apparatus has again attained room temperature, it is filled with oxygen by heating the permanganate, the tap (α) is closed, and the pressure adjusted to atmospheric as before. The silver is then heated up in the atmosphere of oxygen to the same temperature as in the initial blank experiment, the pressure being kept constant by adjustment of the mercury-reservoir. When the volume ceases to alter, indicating that the silver has become saturated with oxygen, the burette reading is taken, and the air-temperature at different parts of the apparatus noted as before.

It is very necessary that the varying temperatures at different parts of the "dead" connecting tubing should be the same in the absorption as in the blank experiment. In particular it is necessary that the distribution of temperature along the upper portions of the stem of the silica tubes should be practically the same in the two experiments.

The tap (κ) is now closed, and the apparatus entirely evacuated, after which the silver is allowed to cool and solidify *in vacuo* as before. It was found by experience that if melted silver containing dissolved oxygen was allowed to cool and solidify in the silica tube the latter invariably cracked. The solidified silver appeared to adhere strongly to the silica, the fracture being due to the very unequal contraction on cooling. If, however, the silver had been previously pumped free from gases when in the molten state and was allowed to cool *in vacuo*, it did not adhere to the silica, and no fracture ensued.

The results obtained are as follows:—

1.—(a) *Blank experiment* (no silver in tube):

Initial reading of gas-burette = 20.7.
Final reading of gas-burette = 37.2.
∴ Total expansion = 16.5 c.c.
Barometer = 766 mm.
Temperature of water in jacket of burette = 18°C .
Expansion reduced to 0° and 760 mm. = 15.6 c.c.
Temperature of furnace = 1020°C .

(b) *Absorption experiment* (15.07 grms. silver in silica tube):

Initial reading of gas-burette = 19.8.
Final reading of gas-burette = 1.9.
∴ Total contraction = 17.9 c.c.
Barometer = 751 mm.
Temperature of water in jacket = 16°C .
Contraction of volume reduced to 0° and 760 mm. = 16.4 c.c.
Temperature of furnace = 1020°C .

In order to calculate the results of this experiment, we have to correct for the volume occupied by the silver in the absorption experiment. This is done as follows:—Let v = volume occupied by the silver. A volume v of oxygen at pressure p and temperature 291° (absolute) would contain $\frac{vp}{291R}$ mols. (where R is the gas-constant). At a

temperature of 1293° (absolute) the volume v would contain $\frac{vp}{1293R}$ mols. Hence the corresponding increase of oxygen in the gas-burette is equal to $\frac{vp}{291R} - \frac{vp}{1293R}$ mols. But 1 mol of oxygen at pressure p and temperature 291° (absolute) occupies a volume $\frac{291R}{p}$. Hence the increase of volume in the gas-burette is equal to $v - \frac{v \cdot 291}{1293}$. For v we have to put the volume of 15.07 grams of melted silver. Taking the density of melted silver as 9.5 (Roberts and Wrightson, 1881), $v = 1.58$ c.c. Hence the increase of volume is 1.22 c.c. This is the expansion observed in the blank experiment corresponding to that volume of oxygen in the silica bulb which is occupied by silver in the actual absorption experiment. Reduced to 0°C ., it becomes 1.15 c.c. The corrected (reduced) expansion is therefore $15.6 - 1.15 = 14.45$ c.c.

The total absorption of oxygen is therefore $16.4 + 14.45 = 30.85$ c.c. This is for 15.07 grams of silver. The volume of oxygen (measured at 0° and 760 mm.) absorbed by 10 grms. of melted silver at 1020°C . and 751 mm. pressure is therefore $\frac{30.85}{15.07} \times 10 = 20.5$ c.c.

Sieverts and Hagenacker (Zeitschr.-physikal. Chem., 68, 115, 1900) give 20.56 c.c. as the volume of oxygen absorbed per 10 grms. of silver at 1024° and 760 mm.

II.—(a) *Blank Experiment* (new silica bulb):

Initial reading of gas-burette = 11.9.
Final reading of gas-burette = 29.1.
∴ Total expansion = 17.2 c.c.
Barometer = 753 mm.
Temperature of water in jacket = 16° .
Expansion reduced to 0° and 760 mm. = 16.04 c.c.
Temperature of furnace = 1020°C .

(b) *Absorption Experiment*:

Initial reading of gas-burette = 24.8.
Final reading of gas-burette = 5.5.
∴ Total contraction = 19.3 c.c.
Barometer = 753 mm.
Temperature of water in jacket = 17°C .
Contraction of volume reduced to 0° and 760 mm. = 18.05 c.c.
Temperature of furnace = 1020°C .

Correction:—Volume of 16.25 grms. of melted silver = 1.71 c.c. Amount of expansion which would correspond to that due to the volume of 1.71 c.c. of the silica bulb = $1.71 - 0.38 = 1.33$ c.c. at 17°C . and 753° . Reduced correction = 1.25 c.c. Hence absorption = $18.05 + 16.04 - 1.25 = 32.84$ c.c. Hence volume of oxygen (measured at 0° and 760 mm.) absorbed by 10 grms. of melted silver at 1020°C . and 753 mm. pressure = $\frac{32.84}{16.25} \times 10 = 20.2$ c.c. This result agrees very satisfactorily with the previous one. These preliminary results having been obtained, it was intended, as stated above, to proceed to more exhaustive experiments with an apparatus provided with a compensating bulb and compensating leads, the correction for the volume of the silver being eliminated if necessary by adding an equal volume of silica rod to the compensator.

In order to show the nature of the results obtained, we reproduce here a table from the paper referred to.

Solubility of oxygen in molten silver at 1075°C .

Oxygen pressure in mm. Hg. (P).	c.c. O_2 (reduced to NTP) absorbed by 10.87 grms. Ag (m).	$\frac{P}{m}$	$\frac{\sqrt{P}}{m}$
1203	26.01	44.7	1.20
760	21.01		1.31
488	17.02		1.30
346	14.63	23.8	1.28
209	11.75		1.23
150	10.00		1.21
128	8.87		1.28
39	4.75	8.2	1.31

It will be evident that the concentration of the oxygen in the molten metal is proportional to the square root of the oxygen-pressure over a very wide range of pressures. From this we can conclude, as shown previously, that the oxygen is either "physically" dissolved as atomic oxygen or exists in the form of dissolved silver monoxide. It cannot be physically dissolved as ordinary diatomic molecules corresponding to those which exist in the gaseous state.

The assumption that the oxygen exists in the silver as dissolved silver monoxide cannot be disproved by the fact that solid silver monoxide would exert an enormous oxygen dissociation-pressure at temperatures near 1000° C., for it must be remembered that in the present case the silver monoxide exists in the form of a dilute solution. From this point of view the "spitting" of silver would be due to the fact that on solidification of the silver the silver oxide (not being soluble to any extent in the solid silver) is thrown out of solution and hence explosively dissociates.

Possibly the "keying" of the solidified silver (saturated previously with oxygen) to the silica bulbs, noticed in some of our earliest experiments, may be explained by the presence of dissolved oxide of silver reacting with the silica to form a silicate of silver.

Returning now to the technical question, we see from the results of Sieverts and Hagenacker quoted above, that at 1075° and 150 mm. pressure, 10.87 grms. of silver absorb 10.09 c.c. oxygen. This is then the amount of oxygen which would be absorbed by this weight of silver saturated with air (since nitrogen is not appreciably soluble in melted silver). At the melting point of silver the amount of oxygen dissolved would be somewhat greater, about 11 c.c. (reckoned at 0° C. and 760 mm. pressure).

We shall be well within the mark if we allow 11 cc. of oxygen per 10 grms. silver. Now 11 c.c. of oxygen would weigh 11×0.00143 grms. To combine with this we should therefore require of, say, aluminium

$$\frac{11 \times 0.0043 \times 102}{48} = 0.1 \text{ gm.}$$

A kilogram of silver, therefore, would be deoxidised by 10 grms. of aluminium.

Another method would be to blow out the dissolved oxygen by a current of steam, or to use this to remove any excess of aluminium remaining dissolved in the silver. These operations would have to be carried out immediately before and during the pouring of the melted silver into the moulds, as the absorption of oxygen is very rapid.

As we know from the work of Sieverts and Hagenacker (*loc. cit.*) that the oxygen is contained in the molten silver in an atomic condition (whether as "free" atoms or in the form of Ag₂O), we can now attempt to calculate the initial freezing point of molten silver saturated with air at atmospheric pressure. To do this we have to employ the well-known van't Hoff equation, $\Delta t = \frac{RT^2 n}{\lambda M}$.

Where Δt = lowering of freezing point, R = gas-constant (in calories per degree centigrade per mol.).

λ = latent heat of melting of silver in calories per gram.

T = absolute temperature of melting point.

n = number of g-atoms oxygen dissolved.

M = mass of silver in grams.

We have T = 962 + 273 = 1235

$\lambda = 24.7$ (Pionchon, *Comptes Rendus*, 1887).

R = 1.985.

According to Sieverts and Hagenacker, 10 grms. silver absorb at 973° C. and 760 mm. oxygen-pressure, 21.35 c.c. of oxygen (measured at 0° C. and 760 mm.). We have, therefore, approximately

$$n = \frac{21.35 \times 0.001420}{16 \times \sqrt{5}}$$

$$M = 10$$

and hence

$$\Delta t = \frac{1.985 \times (1235)^2}{24.7} \times \frac{21.35 \times 0.001420}{16 \times 10 \times \sqrt{5}} = 10.4^\circ$$

The freezing-point of silver saturated with air is stated to be 955°, so that the observed value of Δt is 962 - 955 = 7°. The agreement is perhaps as good as could be expected, considering the uncertainty of several of the data available. The value of λ is not known with any degree of certainty, whilst it is doubtful if the initial freezing-point of silver in equilibrium with the atmosphere has been determined very exactly. The agreement between calculation and experiment is not, however, good enough (with the data at present available) to afford independent confirmation of the atomic condition of the dissolved oxygen.

It is interesting to compare the solubilities of oxygen in molten copper, silver, and gold. In the case of copper the solid oxide Cu₂O can separate from the solution, since the dissociation-pressure of Cu₂O at the melting-point of copper is quite low. In the case of silver the solid phase Ag₂O cannot separate owing to its very great oxygen dissociation-pressure, although Ag₂O can probably exist in dilute solution in molten silver. Finally, in the case of gold the affinity between this metal and oxygen has become so low that even a very dilute solution of oxide of gold in molten gold would correspond to an oxygen-pressure many times greater than that of the atmosphere. This comparison may perhaps lend some support to the view that the oxygen present in molten silver exists as dissolved silver monoxide.

In conclusion, we wish to express our best thanks to the Council of the University of Liverpool for a special Treasury grant, which enabled us to defray the considerable expenses of this investigation.

December, 1900.

Discussion.

Dr. J. T. CONROY said it was satisfactory that the figures of the several experimenters so closely agreed.

Mr. H. J. WATSON said that in the refining of silver industrially, silver absorbed oxygen very quickly, and there was considerable difficulty in ladling the silver in consequence. He had tried copper and found it to answer very well; the copper absorbed the oxygen which the silver had dissolved; but when they commenced to ladle the silver, while the surface was fairly free from slag, the first few bars did not spit upon cooling, but the later ones did, showing that oxygen was absorbed very rapidly, and unless the ladling operation was carried out very quickly, the later bars had in some cases to be returned to the furnace. He might add that their difficulties arose through having to remove tellurium; it was then that the silver began absorbing oxygen. Before that they had had no trouble. They blew the silver with steam.

Professor F. G. DONNAN, in reply to questions, stated that no experiments had been made on the deoxidising action of aluminium. There was no appreciable dissociation of oxygen gas at the temperatures in question.

He was very interested in the remarks made by Mr. Watson, who had a practical acquaintance with the subject from the refiner's point of view. It was clear from what he had said that copper was fairly efficient as a deoxidiser during the earlier stages of the pour, but that owing to the using up of the copper, spitting and foaming occurred in the moulds during the later stages. He would be much interested to know whether Mr. Watson could get better results by keeping a current of dry steam continuously passing through the molten silver. He would point out to Mr. Hill, who had enquired whether the steam would not have an oxidising action, that at the temperatures in question the dissociation of steam was far too small for that to occur. Dr. Basset had suggested that as cuprous oxide did not dissolve in molten silver, it was improbable silver oxide would do so. The analogy was not a very good one. Silver oxide stood in somewhat the same relation to molten silver as a hydrated compound did to water.

Mr. H. J. WATSON said that steam was used to oxidise the impurities in the silver. Steam did oxidise them, but not the silver. They did not blow the steam through during the ladling operation; they blew the steam on to the surface of the silver.