CLXVI.—*The Validity of the Interference Method for the Measurement of the Specific Area of a Copper Surface.*

By FREDERICK JAMES WILKINS.

THE surfaces of all solids are rough, and possess irregularities of both microscopic and macroscopic dimensions: even optically plane surfaces probably contain roughnesses of a molecular order. In general, therefore, the specific area of a surface will be very different from its apparent area. Of the methods proposed for the measurement of the specific area, those due to Bowden and Rideal (*Proc. Roy. Soc.*, 1928, *A*, **120**, 80), Constable (*ibid.*, 1927, *A*, **115**, 570), and Wilkins (*Nature*, 1930, **125**, 236) are particularly suitable for use with metals. Bowden and Rideal calculate the specific area from the amount of hydrogen which must be deposited upon an electrode in order to bring about a given change of potential, as compared with the amount required to bring about the same change of potential at a liquid mercury electrode. Wilkins has pointed out that the specific area may be measured if the vapour pressure and rate of vaporisation of the surface are known. Constable's method is entirely different, however; having shown that the colour of the oxide film formed on metals, such as nickel, copper, and iron, is due to interference and is consequently determined uniquely by its thickness, he calculates the volume of a film from its weight and the density of the oxide, and combines this with its thickness, as determined by its colour, to estimate the specific area of the surface.

It is difficult to compare results obtained by these three methods. Bowden and Rideal measure the area accessible to hydrated hydrogen ions, and Wilkins measures that accessible to condensing atoms of the vaporising solid; thus these two methods should give similar results, and although the experimental evidence to which the latter method can be applied is at present scanty, yet the respective results are not contradictory. The relation between the results obtained by these methods and that of Constable is much more complex. In the particular case of an activated nickel surface, the results obtained by Constable and by Bowden and Rideal are widely different. The former (*Proc. Roy. Soc.*, 1928, *A*, **119**, 196) finds that the ratio (A) of the specific to the apparent area is 1·3—4·5, depending upon the degree of activation of the surface, while the other workers obtain the much higher value of 46 for a recently activated surface, and 29 for the same surface after it has been allowed to " age." Bowden (*Nature*, 1928, **122**, 647), discussing the difference between these figures, has pointed out that the interference method is unable to take account of irregularities which are of an order less than 10^{-5} cm. It would appear, therefore, that these minute irregularities are able to increase the specific area by a factor of at least 10.

During the course of a study of the kinetics of the oxidation of copper, an opportunity arose for the application of the interference method to this metal. Constable, while providing the necessary optical data for this case, has studied only nickel in detail. It is clearly important that the values of A obtained for nickel should be confirmed (as far as order of magnitude is concerned) by experiments on another metal, so that the reality of the ten-fold factor may be substantiated.

EXPERIMENTAL.

The copper was used as pieces (1 sq. dm. in area) of pure electrolytic foil which had been carefully cleaned by abrasion first with emery paper of gradually increasing fineness and finally with Hubert 000. It was further cleaned by rubbing with cotton-wool dipped in alcohol and then with dry grease-free cotton-wool. The oxidations were carried out by heating either in air or in a closed system of known volume containing pure oxygen. In the first case, the amount of oxide formed was determined by weighing the copper before and after oxidation on a Sartorius microbalance; in the second, the weight of oxide was determined from the fall of pressure in the system. The pressures were determined accurately by measuring the movement of a mercury column with a travelling microscope. Activation of the copper was brought about by reduction with hydrogen. A detailed account of the experimental technique will appear in a forthcoming paper.

Results.

(1) *Values of* A *for Copper Surfaces which have not been activated.*—The first series of experiments refers to the oxidation of copper foil at 183°. The results are shown in Table I in the order of increasing film thickness. In all the tables, weights of oxide are given as mg. per sq. dm. The figures of column 2 were determined from the colour of the oxide film, Constable's data being used to correlate this with the thickness (see *Proc. Roy. Soc.*, 1928, *A*, **119**, 196).

TABLE I.

Wt. of oxide.	Wt. of oxide, from colour.	Ratio, *A*.
2·22	5·01	0·443
2·54	5·18	0·490
3·64	5·76	0·632
3·82	5·88	0·65
4·56	7·23	0·63

TABLE II.

Temp. of oxidation.	Wt. of oxide.	Wt. of oxide, from colour.	Ratio, *A*.
125°	0·843	2·47	0·341
150	1·73	2·82	0·614
175	3·37	5·41	0·623
200	5·68	7·41	0·767

All the experiments give anomalous values of *A*, a value of less than unity being physically impossible, since it suggests that the specific area is *less* than the apparent area.

In order to confirm the result, Vernon's data (J., 1926, 2273) were used for the calculation of *A* (see Table II). The figures of Tables I and II are in complete agreement, showing that over the experimental range *A* is always less than unity, and increases as the temperature of oxidation and the thickness of the oxide film increase. The thickness of the surface film containing oxide does not, therefore, determine uniquely the colour of the film. In an attempt to obtain further information, a few determinations of *A* were made with activated copper surfaces, for all Constable's work has been carried out on activated metallic surfaces.

(2) *Values of* A *for Activated Copper Surfaces.*—The first experiments were made with a sample of copper which had been oxidised and reduced many times until it had reached a state of maximum activation. The results were :

Temp. of oxidation	183°	305°
Wt. of oxide	3·61	5·00
,, , from colour	2·24	2·53
A	1·62	1·98

The change in the value of *A* given by the experiment at 305° is particularly interesting. The reduction after the first experiment was carried out at 183°. Since the subsequent oxidation at 305° required only a few minutes, the deactivation accompanying it must have been slight. The increase in *A* is therefore to be attributed solely to the increase in the temperature of oxidation. This phenomenon was confirmed in a second series of experiments in which A was determined for a specimen of copper during a period of gradually increasing activation (see Table III). The value of A seems to be dependent chiefly upon the temperature of oxidation—at least, to such an extent as to mask any changes due to activation.

TABLE III.

No. of expt.	Temp. of oxidn.	No. of oxidns. after reduction.	Wt. of oxide.	Wt. of oxide, from colour.	A.
1	305°	2	5·79	2·71	2·14
2	305	3	5·39	2·53	2·13
3	183	4	4·92	3·44	1·43
4	183	6	4·01	2·94	1·37
5	183	20	4·35	2·53	1·72
6	183	21	4·47	2·53	1·76

Expt. 1 was carried out on a piece of copper which had been already oxidised once and reduced at 305°. The activation of the surface gives a value of A greater than unity and of the order of those obtained by Constable in his work. The oxide film formed in this experiment was reduced at 305°. Notwithstanding the increase of activation (as measured by the increased rate of oxidation) between Expts 1. and 2, any change in the value of A was smaller than the experimental error, which is about 0·1 unit. Even more striking is the value of the ratio obtained from Expt. 3. Before this oxidation, the oxide film had been reduced at 183°, and reduction at this low temperature should be accompanied by a considerable increase in area owing to the decrease in the sintering of the surface. Instead of an increase in A, however, an unexpected decrease was obtained. Subsequent activation at 183° gave at the terminal state (see Expts. 5 and 6) values in reasonable agreement with that of the first experiment in the previous series (p. 1306).

Discussion.

The experimental results may be summarised by saying that copper which has not been activated gives anomalous values for A, which are dependent upon the temperature and the thickness of the oxide film; further, while the values of A given by activated copper are greater than unity, they are also very largely dependent upon the temperature of heating, and are scarcely affected by the activation of the surface.

The interference theory of the colours of thin films of oxide on metals seems to be well established qualitatively (see, *e.g.*, Evans, J., 1925, **127**, 2484; *Proc. Roy. Soc.*, 1925, *A*, **107**, 228; *Chem. and Ind.*, 1926, **45**, 213). Constable's work provides the chief quantitative evidence in its favour, in that he has shown that if the quantity of oxide determined directly is corrected by an area factor ($A > 1$) it is equal to the quantity of oxide given by the colour of the film.

This work has shown, however, that in the case of copper, the nature of the correcting factor A is not so simple as Constable has supposed. In order to interpret the anomalies two courses are open, *viz.*, (*a*) to reject the interference theory as an explanation of the colours; (*b*) to amend the calculations of Constable. In view of the qualitative evidence in favour of the interference theory, the second course would seem to be the more hopeful.

Experiments on the kinetics of the low-temperature oxidation of copper (shortly to be published; compare also Wilkins, *Z. Elektrochem.*, 1929, **35**, 500) have shown that oxygen diffuses through the oxide film to the underlying copper along the grain boundaries of the oxide. The oxidation of copper appears, therefore, to proceed grain by grain; and it is to be expected, in consequence of this granular oxidation, that the oxide film will contain appreciable quantities of unchanged copper. Further, one would expect the proportion of unchanged copper in the film to be the greater the larger the grain size of the copper and the thinner the film. Direct experimental evidence demonstrating the existence of this unchanged copper has been recently obtained by Evans and Stockdale (J., 1929, 2651), who heated a square sheet of copper along one edge, obtaining a film of oxide of thickness gradually decreasing as the distance from the hot edge is increased. They found that the thin oxide films formed at the low-temperature points contained "much residual metallic copper"; the proportion of metallic copper to oxide gradually diminished as the high-temperature edge was approached.

An explanation of the experimental results is now possible on the basis that the colour of the oxide films is an interference phenomenon. Copper which has not been activated is made up of large grains. The film which gives rise to the colour will not, therefore, be pure oxide, but will contain large amounts of unchanged metal. The volume of the film as calculated by Constable's method will consequently be much too great, and values of A will be obtained which are less than unity. The gradual increase in A with increasing film thickness is in perfect agreement with this interpretation.

Activated copper, on the other hand, has a much smaller grain size, and the oxide films formed by it will contain less unchanged copper. Further, the proportion of unchanged copper will, as before, be smaller the higher the temperature.

We therefore conclude that, as far as copper is concerned, Constable's interference method possesses very narrow limitations; for it is clear that, if results of accuracy are to be obtained, one must determine the optical properties and the density of each film.

This restriction will not apply to nickel, for Evans and Stockdale (*loc. cit.*) have shown that its oxide films are remarkably free from metallic occlusions. The values of A for this metal determined by the interference method are trustworthy. Further, although the values of A found in this work for activated copper are not a true indication of the specific area, they are of such a nature that they may be said to confirm, as far as order of magnitude is concerned, the results of Constable for activated nickel. The remarkable increase of A when determined with the hydrogen-ion method is therefore real; and the irregularities of dimensions less than 10^{-5} cm. would appear to increase the specific area by as much as ten times.

Summary.

It is shown that, when Constable's interference method for the measurement of the specific area of a surface is applied to oxide films formed on copper which has not been activated, the values obtained for the ratio (A) of the specific to the apparent area are anomalous in that they are always less than unity. Further, A is not a constant for a given surface but increases with the thickness of the oxide film and the temperature of oxidation. Activation of the copper surface by oxidation and reduction gives values of A which are greater than unity but are still dependent upon the temperature of oxidation. The interference method, therefore, does not give trustworthy values for the specific area when applied to the measurement of copper surfaces.

It is suggested that these results may be explained by assuming that the oxide film contains unchanged metallic occlusions, the proportion of unchanged metal to oxide varying with the conditions and extent of oxidation. Experimental evidence is cited in favour of this interpretation.

My thanks are due to Dr. W. H. Mills for the use of his microbalance, and to the British Non-Ferrous Metals Research Association for a grant. I should, further, like to express my indebtedness to Dr. E. K. Rideal for his constant interest and advice during the progress of this research.

LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE.

[*Received, March 20th*, 1930.]