428. *The Effect of Sulphur Dioxide on the Oxidation of Copper.*

By T. Mills and U. R. Evans.

The effects of small additions of sulphur dioxide on the oxidation of copper were studied at temperatures from 88° to 172°. The growth laws observed in pure oxygen in this temperature range agreed with observations by recent workers, and were interpreted in terms of a mechanism which accounted for the transition from logarithmic growth at low temperatures to parabolic growth at high temperatures by means of a single theory. Sulphur dioxide accelerated the oxidation of copper, although it did not alter the mechanism of the film-growth laws. It also caused a controlled growth of cuprous sulphate in the film by a secondary reaction; the amount of sulphate was a linear function of the cuprous oxide in the film.

Sulphur compounds are known to accelerate oxidation of copper. Vernon [1] and Evans [2] showed that the presence of hydrogen sulphide produced colour changes on copper at room temperature in dry air. Vernon found that the increase in the rate of attack was proportional to the sulphide concentration. Hudson and his co-workers [3] found that 0·1% of sulphur dioxide increased twenty-fold the rate of oxidation of copper at 400°. Hallowes and Voce [4] observed a faster oxidation of copper with 0·1% of sulphur dioxide in air at 400°, and a more marked increase with 5%. Farber and Ehrenberg,[5] with 5% of sulphur dioxide and 95% of helium, obtained corrosion of copper at 1027°; they did not analyse the products, but postulated two competing reactions: $4Cu + SO_2 = 2Cu_2O + S$ and $2Cu + SO_2 = Cu_2S + O_2$.

The kinetics of the oxidation of copper in the presence of sulphur dioxide have not been studied, but the accelerating effect of both hydrogen sulphide and sulphur dioxide is undoubtedly due to the formation of sulphide in the oxide film.

In the present work the behaviour of copper was studied both in pure oxygen and with added traces of sulphur dioxide. An electrometric method of film analysis was developed.

Experimental

Preparation of Copper Specimens.—The specimens measuring 8 × 1·5 cm. were cut from rolled copper sheet 0·01 in. thick, supplied by Messrs. Harrington Bros. The copper was of electrolytic grade, containing: Cu, 99·93; O, 0·04%; with minor impurities. A hole 3 mm. in diameter was drilled at one end of the specimen to support it in the electrometric apparatus. To avoid irregularities due to variable surface conditions, a 5-cm. length of each specimen was anodically etched in 10% nitric acid at 20 mA/cm.^{2} for 10 min. After being rapidly washed with water and acetone, it was wiped dry with filter-paper, which removed a loose deposit of black oxide. Next, the specimen was cathodically treated for 10 sec. in 0·1N-sodium dihydrogen phosphate (in twice-distilled water) at 20 mA/cm.^{2}; vigorous evolution of hydrogen occurred. After being washed quickly in distilled water, then acetone, and dried on filter-paper, the untreated 3 cm., which had been used for handling and connection, was cut off; the specimen, placed in a glass rack, was introduced into the oxidation chamber. The cathodic treatment in the mildly acidic buffer reduced the films formed during and after the anodic etch; an air-formed film about 10 Å thick was still present, but was reduced by heating in hydrogen at 400°, in the oxidation chamber. The hydrogen was pumped off and the specimen was not exposed to oxygen again before the oxidizing atmosphere was admitted to the oxidation chamber.

Oxidation Apparatus.—A schematic diagram of the oxidation apparatus with the gas purification lines is shown in Fig. 1*A*. Fig. 1*B* shows in detail the more important working sections of the apparatus.

Oxygen atmospheres containing sulphur dioxide were prepared by proportioning a standard volume of sulphur dioxide between the volume *C* and the evacuated gas reservoir *B*. The

[1] Vernon, *Trans. Faraday Soc.*, 1923, **19**, 839.
[2] Evans, *Trans. Amer. Electrochem. Soc.*, 1924, **46**, 247.
[3] Hudson, Herbert, Ball, and Bucknall, *J. Inst. Metals*, 1929, **42**, 253.
[4] Hallowes and Voce, *Metallurgia*, 1946, **34**, 95.
[5] Farber and Ehrenberg, *Trans. Electrochem. Soc.*, 1952, **99**, 427.

reservoir was filled to atmospheric pressure with oxygen and the concentration of sulphur dioxide was calculated.

The main section of the oxidation chamber consisted of a 3-foot length of 40-mm. glass tubing. The volume of the oxidation chamber was 1·2 l. so that, when the working pressure of the oxidising atmosphere was 20 cm. Hg, 10 runs could be carried out with one filling of the reservoir *B*. With the sulphur dioxide concentrations and the specimen-size employed, the sulphur dioxide concentration did not significantly decrease during a run. Further, with the static atmosphere the concentration of sulphur dioxide near the specimen did not appreciably change, since, as shown below, the consumption of sulphur dioxide is independent of the sulphur dioxide concentration, and is a linear function of the thickness of the film of cuprous oxide.

FIG. 1A. *Gas-purification lines and pumping system.*

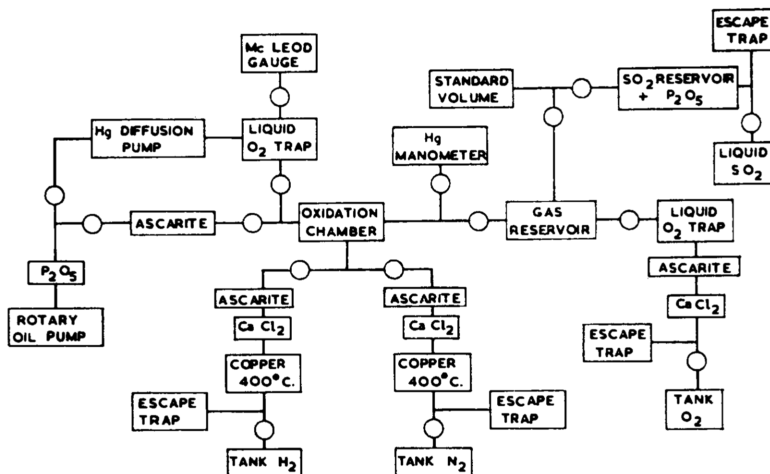
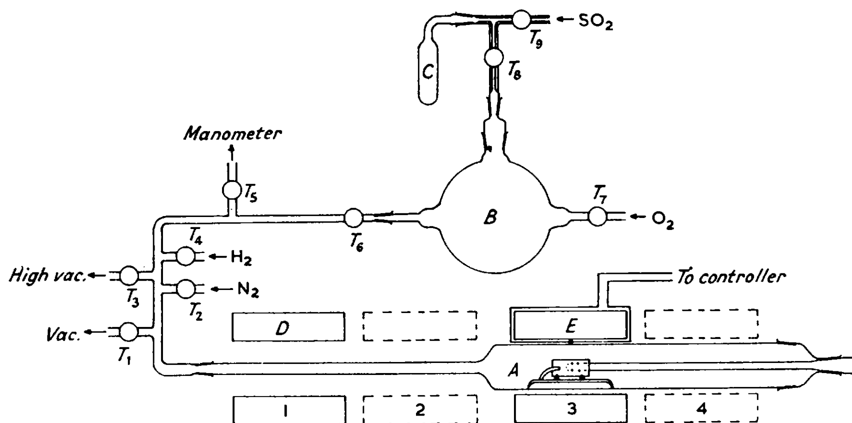


FIG. 1B. *Details of the oxidation chamber and vessels for mixing the oxidising atmosphere.*



The working section of the oxidation chamber could be heated by either of two furnaces. Furnace *D* operated with a 6-in. zone at 400° ± 5° and was used to reduce the specimens in hydrogen. Furnace *E* was used during the oxidation of the copper. It has a 4-in. zone with temperature uniform to ±1° over the temperature range 88—172°. The temperature was measured by a chromel–alumel thermocouple with the hot junction located in the centre of the oxidation chamber in a glass sheath.

Oxidation Procedure.—After two specimens had been placed in the oxidation chamber the air was pumped out as quickly as possible. A vacuum of pressure less than 5×10^{-5} mm. Hg was taken to indicate that there were no leaks in the system. The specimens were reduced in hydrogen at 400° for ½ hr., then cooled to the oxidation temperature. The hydrogen was

pumped out and the oxidation chamber was flushed with nitrogen. The oxidation was started by admitting the oxidizing atmosphere as quickly as possible to bring the pressure to the desired value as indicated by the mercury manometer. The period of oxidation was terminated by evacuating the oxidation chamber and cooling the specimens.

Measurement of Film Thickness.—Film thickness was measured in two ways. The electrometric procedure was mainly used, being the most accurate for thin films and capable of use in estimations of the various products separately in a complex film; it had been used on copper by Evans and Miley,[6] Campbell and Thomas,[7] Bouillon,[8] and Allen.[9] A gravimetric method based on an Oertling microbalance was used to verify the electrometric numbers, or to interpret them in the case of complex films; it was non-destructive. When the gravimetric method was employed, the specimens were reduced in hydrogen, weighed, and then given a second reduction in hydrogen before the start of the oxidation experiment.

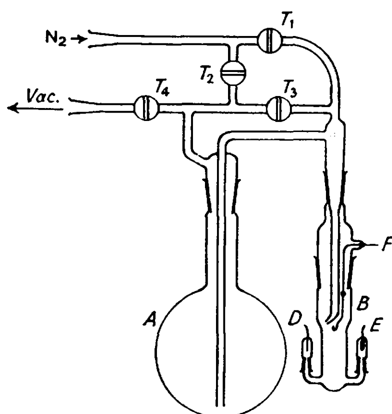
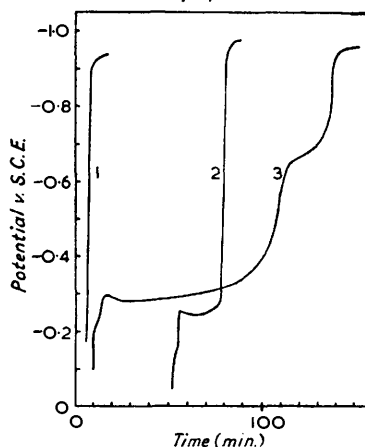


FIG. 2. *Cells for the electrometric reduction.*

FIG. 3. *Electrometric reduction curves of films on copper.*

1, *Copper reduced in hydrogen*; c.d. 1 μA/cm.^{2}
2, *Copper heated in oxygen at* 120° *for* 45 *min.*; c.d. 10 μA/cm.^{2}
3, *Copper heated in oxygen at* 150° *for* 440 *min.*; c.d. 20 μA/cm.^{2}



Electrometric Apparatus.—The apparatus for deoxygenating the solution and performing the cathodic reduction (Fig. 2) was a modified version of the apparatus used for a similar purpose by Mills and Willis.[10] The electrolyte was contained in the 1-l. reservoir flask *A*. The specimen was suspended on a platinum wire hook in cell *B* by means of the hole drilled near one end. The two side tubes on cell *B* contained severally the auxiliary platinum anode *D* and a silver–silver chloride reference electrode *E*.

The solution and cells were de-aerated by alternately evacuating and filling the apparatus with oxygen-free nitrogen. After four cycles, sufficient solution just to cover the copper specimen was forced over into cell *B*. The electrolyte was a 0·1N-phosphate buffer containing equimolar amounts of NaH_2PO_4 and Na_2HPO_4, made up in twice-distilled water, and had a pH of 6·9. A small amount of potassium chloride was added for the silver–silver chloride electrode.

For most of the reductions a current of 150 μA was used. After each experiment the area of the specimen was measured and the reduction time was expressed in terms of the time to reduce the film with a current density of 10 μA/cm.^{2}. The time of reduction, designated by T_w, was then directly proportional to the number of chemical equivalents of copper that had reacted to produce the film. T_r was used to refer to the various reduction times of the individual

[6] Evans and Miley, *Nature*, 1937, **139**, 283.
[7] Campbell and Thomas, *Trans. Electrochem. Soc.*, 1939, **76**, 303.
[8] Bouillon, *Bull. Soc. chim. belges*, 1951, **60**, 337.
[9] Allen, *Trans. Faraday Soc.*, 1952, **48**, 273.
[10] Mills and Willis, *Trans. Electrochem. Soc.*, 1953, **100**, 452.

constituents in the film. This method of measuring the film growth was the most convenient for the present work in view of the complex nature of the films encountered.

Oxidation in pure oxygen.

Analysis of Films.—The phosphate buffer, pH 6·9, was chosen so that the pH of the reduction of the oxides was controlled, thus making it possible to identify the product by its potential of reduction. Previous workers, using unbuffered solutions, found that cuprous oxide was reduced at potentials (dependent on current density) which were more negative than the reversible value. Experiments in borate and phosphate buffers of pH 6·9 showed that cuprous oxide was reduced at its reversible potential of $-0{\cdot}18$ v on the saturated calomel scale. In unbuffered 0·1N-potassium chloride or -potassium sulphate the reduction step was displaced several tenths of a volt. This was shown to be due to alkali formed at the copper cathode by observing a similar effect in a phosphate buffer at pH 9.

Even in the buffered neutral solution the reduction of cupric oxide was complicated. A sample of cupric oxide was prepared by rubbing cupric oxide powder into a film-free copper specimen, and on electro-reduction approximately 20% of the powder was reduced near the reversible reduction potential of $-0{\cdot}08$ v, and the remainder was reduced at $-0{\cdot}6$ v. The potential of the arrest at $-0{\cdot}6$ v was sensitive to current density, and the immediate response of the potential to very small changes in current density indicated that a resistance over-potential was causing part of the displacement.

Typical reduction curves for the electrometric determination of films are shown in Fig. 3. Curve 1 was obtained with a specimen reduced in hydrogen, cooled in vacuum, and transferred to the electrometric apparatus as quickly as possible. There is no evidence of any film on the copper. On successive anodic and cathodic polarizations a value of 60 μF/cm.^{2} was obtained for the capacity of the electric double-layer at the copper–solution interface. This low value of the capacity indicated that, after the hydrogen reduction, the copper had a small real surface area of the order of 2—3 times the geometric area. However, microscopic examination indicated a roughening of the surface, similar to that observed by Garner,[11] which was probably due to the evolution of steam formed by the reduction of intergranular cuprous oxide.

Curve 2 is that obtained on reduction of a film formed by heating in 20 cm. Hg pressure of oxygen for 45 min. at 120°. The film consisted mainly of cuprous oxide reduced at $-0{\cdot}2$ v. There is a small arrest at $-0{\cdot}1$ v, the reduction potential of cupric oxide, which was interpreted as being due to cupric oxide formed on the peaks of projections observed on the hydrogen-reduced copper. The arrest was not observed with thin films formed on specimens that had not been reduced in hydrogen. However, the arrest was obtained with specimens that had the loose black oxide deposit, formed during the anodic etching, left on the surface. In this case the cathodic reduction pre-treatment reduced the oxide particles and left a spongy copper deposit on the specimen. It would seem that, where the film becomes abnormally thick due to projections or a spongy deposit, the cuprous oxide first formed is oxidized to cupric oxide, the small deposit of cupric oxide then being reduced at its reversible potential. With thick films, formed at 120°, an arrest at $-0{\cdot}6$ v was obtained. The appearance of this arrest has been shown by Bouillon [8] and Halliday,[12] by electron diffraction, to be due to the presence of cupric oxide in the film. Table 1 (i) shows the analyses of 10 sets of duplicate specimens for oxidation experiments at 120°; similar analyses were obtained for films formed at 88°. At 150° and 172° the formation of cupric oxide was greater. The analyses of films formed at these temperatures are shown in Tables 1 (ii) and 1 (iii), respectively. Curve 3 in Fig. 3 shows the reduction curve for a film formed at 150°. T_w (calc.) in the tables was estimated from the gravimetric determination of the film.

Growth Laws.—The first series of experiments were carried out at 120°. An oxygen pressure of 20 cm. Hg was used, so that the reaction was carried out under conditions where Allen [13] found the rate to be independent of the oxygen pressure. Two specimens, supported on a glass rack, were used in each experiment and the mean was used in plotting the results. Throughout the experiments the mean deviation from the mean was $\pm 2\%$. The curve obtained, plotted in Fig. 4, gave two linear regions when plotted against the logarithm of the oxidation time. After 100 min. the initial slow logarithmic build up of film increased to give a second logarithmic relation. The curve in the second region was not so well defined as the first

[11] Garner, *Proc. Roy. Soc.*, 1949, *A*, **197**, 294.
[12] Halliday, *Trans. Faraday Soc.*, 1954, **50**, 171.
[13] Allen, *Research*, 1952, **5**, 487.

section. This was undoubtedly due to the fact that different specimens passed from the first to the second stage at different times. In order to obtain a well-defined curve for the second stage the procedure of intermittently heating and weighing a single specimen was employed. The curve obtained under these conditions is shown in Fig. 5, with the thickness plotted against log ($t^{\frac{1}{2}}$ + 10), where t is the oxidation time.

The initial slow logarithmic build up of the film was confirmed by experiments at 88°, where the heating times used were much longer and therefore were not subject to timing errors in the oxidation time. The results are plotted in Fig. 4.

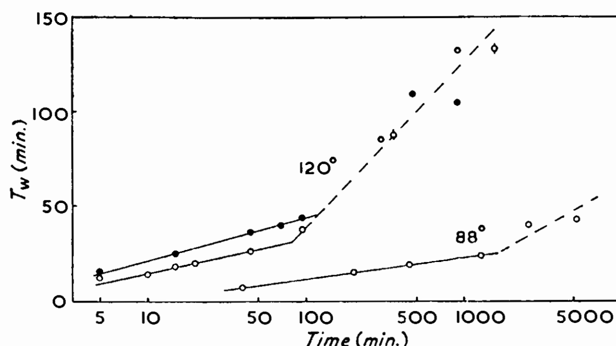


FIG. 4. *Growth of oxide films on copper showing the relation between thickness and log (oxidation time); with oxygen pressures of* 20 (-○-) *and* 50 (-●-) *cm.* Hg.

Experiments in 50 cm. Hg pressure of oxygen at 120°, plotted in Fig. 4, confirmed that the oxidation rate was independent of the oxygen pressure in the region 20—50 cm. pressure. The displacement of the first linear region was due to a more rapid initial oxidation rate with the higher oxygen pressure.

TABLE 1. *Copper oxidized in* 20 *cm.* Hg *pressure of oxygen.*

Oxidation time (min.)	T_r (min.) for arrest at: −0·2 v (Cu_2O)	−0·1 v (CuO)	−0·6 v (CuO)	T_w (min.) for whole film	T_w (min.) (calc.)	Oxidation time (min.)	T_r (min.) for arrest at: −0·2 v (Cu_2O)	−0·1 v (CuO)	−0·6 v (CuO)	T_w (min.) for whole film	T_w (min.) (calc.)
					(i) At 120°.						
5	12·1	0·5	—	12·6	—	95	36·7	2·0	—	38·7	—
	12·0	0·5	—	12·5	—		34·7	2·0	—	36·7	—
10	12·7	1·5	—	14·2	—	300	83·2	3·0	1	87·2	—
	12·2	1·5	—	13·7	—		80·2	3·0	1	84·2	
15	16·7	1·5	—	18·2	—	360	83·4	2·0	—	85·4	—
	16·4	1·5	—	17·9	—		87·3	3·0	0·5	90·8	—
20	19·1	1·0	—	20·1	—	920	130·2	3·5	—	133·7	—
	18·2	1·0	—	19·2	—		129·7	3·0	—	132·7	—
45	24·6	2·5	—	27·1	—	159	130·7	3·0	3·0	136·7	—
	23·3	2·0	—	25·3	—		125·8	3·0	3·0	131·8	—
					(ii) At 150°.						
10	60	2	—	62	67	50	129	2	12	143	129
	68	2	—	70	71	440	193	7	56	256	249
50	118	2	12	132	133		241	8	44	293	295
					(iii) At 172°.						
20	108	3	24	135	127	110	161	12	62	235	240
	119	4	18	141	139	440	203	18	76	297	280
110	*	12	*	247	245		*	*	70	343	339

* End-point not well defined.

At 150° the initial slow step was not obtained, and the plots of the results given by the intermittent heating and weighing of two specimens are shown in Fig. 5. The thickness was a linear function of log ($t^{\frac{1}{2}}$ + 3). Control experiments, in which a number of single heating periods were used, showed that the intermittent heating method did not affect the film growth, and enabled an electrometric analysis of the film to be obtained at various stages of the film growth. These results are shown in Table 1 (ii).

A similar technique was used for experiments at 172°, and the results, plotted in Fig. 6, were found to fit a parabolic law for heating times up to 200 min. At higher times the rate of oxidation decreased. Tabe 1 (iii) records the analysis of the film at various heating times. The results obtained at 150° are also plotted in Fig. 6; it is seen that the parabolic law is not obeyed.

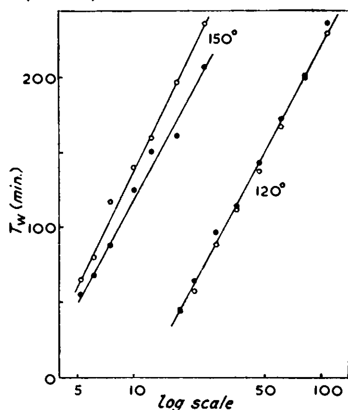


FIG. 5. *Growth of oxide films on copper, in* 20 *cm.* Hg *pressure of oxygen; the results at* 120° *were plotted against* log ($t^{\frac{1}{2}}$ + 10), *and the results at* 150° *against* log ($t^{\frac{1}{2}}$ + 3).

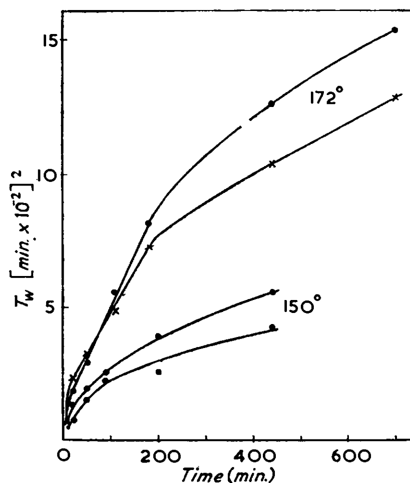


FIG. 6. *Growth of oxide films on copper: the square of* T_w *plotted against oxidation time.*

Discussion of Growth Laws.—Various growth laws have been reported for the oxidation of copper below 500°. Above this temperature the parabolic law is always obtained. Allen,[13] working with copper carrying initially a film 20 Å thick, obtained results agreeing with the parabolic law at 127°. However, in agreement with the present work, White and Germer [14] found a logarithmic law to be obeyed at room temperature with evaporated copper specimens which were initially film-free, and Lustman and Mehl [15] obtained the double logarithmic relation in the temperature range 88—150° with hydrogen-reduced specimens. Garforth,[16] working with hydrogen-reduced evaporated films, found that at 120° and 140° there was an initial rapid growth of the first 100 Å, then growth ceased for an induction period and suddenly started again. In agreement with the new results at 172°, Dighton and Miley [17] found that at 180° growth was initially parabolic and then slowed down to give a logarithmic relation. Campbell and Thomas [11] and Rhodin [19] reported a region of film growth obeying a cubic law; no evidence of such a law was obtained in the present work.

Cabrera and Mott [20] considered that the initial growth of 100 Å observed by Garforth was the formation of a pseudomorphic film, and that growth ceased owing to this film's being opaque to cuprous ions when the electric field arising from capture of electrons by adsorbed oxygen atoms became insufficiently strong, owing to the thickness having become too great. Growth started again after a time interval (40 min. at 120°) when the film recrystallized and became conducting to cuprous ions. The initial slow logarithmic growth (also obtained in the present work) was considered to be the continued growth of this pseudomorphic film. With the etched copper specimens used, it was to be expected that the film would contain cracks and flaws which would permit a continuation of the

[14] White and Germer, *Trans. Electrochem. Soc.*, 1942, **81**, 305.
[15] Lustman and Mehl, *Trans. Amer. Inst. Min. Met. Eng.*, 1941, **143**, 246.
[16] Garforth, quoted in *Rep. Progr. Physics*, 1948/9, **12**, 163.
[17] Dighton and Miley, *Trans. Electrochem. Soc.*, 1942, **81**, 321.
[18] Campbell and Thomas, *ibid.*, 1947, **91**, 623.
[19] Rhodin, *J. Amer. Chem. Soc.*, 1950, **72**, 5102.
[20] Cabrera and Mott, *Rep. Prog. Physics*, 1948/9, **12**, 163.

oxidation even though the intact, pseudomorphic, film was protective. In these circumstances a logarithmic growth law would be expected according to the theory advanced by Davies, Evans, and Agar.[21]

They considered that at temperatures too low for passage of ions through the main part of the film, passage of oxygen inwards can still occur at pores, but that the formation of voluminous oxide at any one pore provides a chance of sealing neighbouring pores. This leads to the equation

$$W = k_1 \log (k_2 t + k_3) \qquad (1)$$

where W is the weight of oxygen taken up in time t. If $k_3 \ll k_2 t$, it becomes

$$W = k_4 \log t + k_5 \qquad (2)$$

the equation actually obtained in the present work from 100 to 300 Å at 88° and 120°.

The break in the curve at film thickness of the order of 300—400 Å, where the second logarithmic relationship started at oxidation temperatures of 88° and 120°, may be attributed to the recrystallization of the pseudomorphic film. This view is supported by photomicrographs of films on electropolished specimens. When the tint advanced beyond the first-order brown, the grains exhibited a fine structure which suggests that recrystallization of the cuprous oxide film had occurred.

According to Cabrera and Mott,[20] the logarithmic relation after the breakdown of the pseudomorphic film should mean that the film was still opaque to cuprous ions and the oxidation once more continued at pores in the film. However, the logarithmic growth may be accounted for if the recrystallized film allows cations to pass outwards, leaving cavities at the metal–metal oxide interface and thus reducing the effective area undergoing oxidation. Dravnicks and McDonald [22] suggested that the consumption of metal owing to the outward diffusion of ions should lead to voids in the metal–metal oxide interface. On this basis the transition, with increasing oxidation temperatures, from (1) logarithmic growth (120°), (2) parabolic growth in the early stages followed by logarithmic growth (172°), and (3) parabolic growth over the entire range of oxidation (>500°) may be accounted for by a single theory.

Dunnington, Beck, and Fontana [23] showed that large cavities were formed between the metal and scale on strongly heated iron, and Caplan and Cohen [24] made the same observation on iron–chromium alloys. Bouillon [8] observed blisters of cupric oxide on copper heated for 1 hr. at 295°. He attributed their formation to the oxidation of the cuprous oxide film at zones where the cuprous oxide became isolated from the underlying metal owing to cavity formation. Dennison and Preece [25] observed a decrease in the rate of oxidation of copper alloys containing beryllium or aluminium which they attributed to a decrease in the effective area caused by the formation of insulating layer of either beryllia or alumina at the metal–metal oxide interface.

When a new metal cation passes outwards through the oxide film, a vacancy is left at the metal–metal oxide interface and it may do one of three things: (1) remain at a point where no cavity previously existed and thus result in a further decrease in effective area, (2) migrate to the bottom of an existing cavity, or (3) migrate to a dislocation which can act as a sink and destroy the vacancy.

Assuming that the chance of the occurrence of (1) is proportional to the number of sites still available for the vacancy, Evans [26] deduced:

$$W = k_6 \log (t^{\frac{1}{2}} + k_7) + k_8 \qquad (3)$$

an equation of which the ordinary logarithmic equation is a special case obtained when $k_7 \ll t^{\frac{1}{2}}$, (3) then becoming:

$$W = k_9 \log t + k_8 \qquad (4)$$

[21] Davis, Evans, and Agar, *Proc. Roy. Soc.*, 1954, *A*, **225**, 443.
[22] Dravnicks and McDonald, *Trans. Electrochem. Soc.*, 1948, **94**, 139.
[23] Dunnington, Beck, and Fontana, *Corrosion*, 1952, **8**, 2.
[24] Caplan and Cohen, *J. Metals*, 1952, **4**, 1057.
[25] Dennison and Preece, *J. Inst. Metals*, 1953, **81**, 229.
[26] Evans, *Rev. Pure Appl. Chem.*, 1955, **5**, 1.

The experimental results at 120° and 150° agree with the new equation (3), but not with the ordinary logarithmic equation.

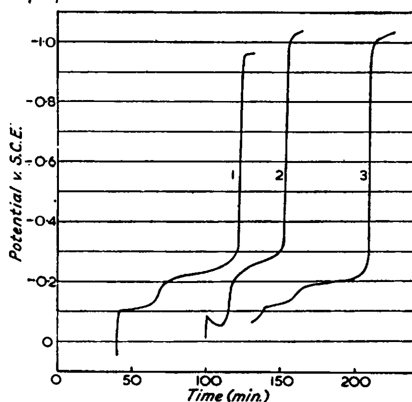
The decrease in cavity formation with decrease in effective area is probably more complex than that just suggested. When the area undermined by cavities has become large, a partial collapse of the undermined film by slip in the oxide would result in re-establishment of contact between oxide and metal at some points, thus increasing the effective area.

As the oxidation temperature is raised, the chance of relief of stress will increase and the probability of cavity formation will diminish. At 172° the formation of cavities only becomes appreciable at large film thicknesses, and at much higher temperatures the parabolic law has been obtained over the whole range of film growth by most investigators, suggesting that cavities are not formed under these conditions.

Oxidation in the presence of sulphur dioxide.

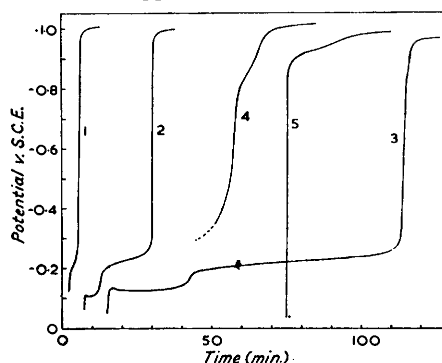
Analysis of the Film.—The film formed in the presence of sulphur dioxide produces a much greater weight increase than would be indicated by the electrometric determination if the film

FIG. 7. *Electrometric reduction curves of films formed on heating copper at* 120° *in oxygen containing* SO_2; c.d. 10 $\mu A/cm.^2$



1, *Electrolyte, phosphate buffer.*
2, *Electrolyte, borate buffer.*
3, *Electrolyte, borate buffer* + 0·041N-KBr.

FIG. 8. *Electrometric reduction curves of films on copper*; c.d. 10 $\mu A/cm.^2$



1, 3 *min. in* O_2 + 0·2% SO_2 *at* 120°.
2, 5 *min. in* O_2 + 0·2% SO_2 *at* 120°.
3, 45 *min. in* O_2 + 0·2% SO_2 *at* 120°.
4, 460 *min. in* O_2 + 0·2% SO_2 *at* 120°.
5, *Cuprous sulphide film treated in hydrogen at* 400°.

consisted of oxide alone. Chemical tests showed that this increase is due to the presence of sulphate in the film. The type of reduction curve obtained is shown in curve 1, Fig. 7. The arrest at −0·1 v is equivalent to the sulphate in the film, and that at −0·2 v is due to cuprous oxide. This interpretation is confirmed by the gravimetric estimation of the film for all film thicknesses, oxidation temperatures, and sulphur dioxide concentrations used in the investigation.

Weighing of the specimens after the electrometric determination showed that, when sulphate was present in the film, some loss of copper occurred—in amounts unrelated to the sulphate content of the film. This suggested that the sulphate was present as cuprous sulphate and underwent the reaction $Cu_2SO_4 = CuSO_4 + Cu$ when immersed in the solution. The loss of copper could reasonably be ascribed to some of the finely divided copper's being washed into the solution.

The cupric sulphate was evidently precipitated on the electrode as an insoluble phosphate and was electro-reduced as such. It was shown that the addition of a dilute solution of cupric sulphate to the phosphate buffer gave a precipitate. A similar test with a borate buffer of pH 6·9 gave no precipitate. When a specimen was cathodically reduced in a borate buffer, a curve such as that shown in curve 2, Fig. 7, was obtained. The cupric sulphate arrest was at −0·05 v, which corresponded to the reduction potential of cupric hydroxide. The electrometric result in the borate buffer was smaller than that in the phosphate buffer owing to the greater solubility of cupric hydroxide. That the first reduction step was due to the precipitation of insoluble

cupric salts formed by reaction with the solution was further confirmed by the use of an 0·1N-sodium carbonate solution. The first arrest in this solution occurred at the reduction potential of cupric carbonate.

The sulphate was shown to be present in the film as cuprous sulphate in the following way. Potassium bromide was added to the borate buffer. If soluble cuprous salts were present they would be stabilized by being precipitated as cuprous bromide. A bromide concentration of 0·041N was chosen so that the cuprous bromide, if formed, would be reduced at −0·12 v, a potential intermediate between that of the arrest due to cupric hydroxide and that due to cuprous oxide. Curve 3, Fig. 7, is the one obtained in this solution, and an analysis of the curve is given in Table 2, in which is also recorded the result of analyzing the film on a duplicate specimen, in phosphate buffer.

Part of the first arrest (equivalent to 8 min.) occurred at the cupric hydroxide potential, and the balance at the cuprous bromide potential. This showed that at least 70% of the sulphate

TABLE 2. *Electro-reduction data for copper heated in* 20 *cm.* Hg *pressure of* $O_2 + 1\%\ SO_2$, *at* 120° *for* 5 *minutes.*

Solution	Arrest due to sulphate (min.)	Arrest due to cuprous oxide (min.)	T_w, Total time of reduction of film (min.)
Borate buffer + 0·041N-KBr ...	8 + 22 = 30	51	81
Phosphate buffer	29	55	84

was present as cuprous sulphate. It is possible that the cupric hydroxide was formed in the interior of the film, where the solution was depleted of bromide by diffusion through the outer layers of cuprous sulphate. A similar effect was observed in the phosphate buffer, wherein, with extremely thick films, part of the sulphate salts were reduced as cupric hydroxide instead of cupric phosphate.

Typical reduction curves of films of different thicknesses, formed in the presence of sulphur dioxide, are shown in Fig. 8, and Table 3 shows the electrometric analysis of films formed at different heating times in $O_2 + 0{\cdot}2\%\ SO_2$ at 120°. In the initial rapid period of oxidation (up to a thickness of 30 Å at 120° and 750 Å at 172°) only cuprous oxide was formed, then on further heating the formation of cuprous sulphate started. With thick films an arrest at −0·8 v was obtained. The work of Price and Thomas [27] seemed to suggest that the arrest may have been

TABLE 3.

Oxidation time (min.)	T_r (min.), arrest at −0·1 v	T_r (min.), arrest at −0·8 v	T_w (min.), reduction time of total film	Oxidation time (min.)	T_r (min.), arrest at −0·1 v	T_r (min.), arrest at −0·8 v	T_w (min.), reduction time of total film
3	—	—	4·0	30	20·6	0·5	58·6
	—	—	4·1		26·0	0·5	66·2
5	4·8	—	20·7	70	43·3	0·5	121·3
	4·7	—	18·6		45·4	0·5	118·3
10	10·5	—	30·0	120	51·3	2·0	150·0
	9·7	—	27·5		55·9	3·0	155·2
20	17·0	1·0	47·0	360	78·0	3·5	208·5
	15·5	0·5	42·5		74·0	3·5	213·0

due to cuprous sulphide. However, a similar arrest was obtained with the air-formed film on copper after anodic etching in either 10% nitric or sulphuric acid, and also by Allen [9] with specimens electropolished in phosphoric acid. Therefore it seemed that it was due to the reduction of some product formed by the reaction of copper salts with the phosphate buffer. Curve 4, Fig. 8, recording the last section of a reduction curve with a total reduction time of T_w = 315 min., shows this arrest clearly. Curve 5 is the reduction curve of a thin cuprous sulphide film. Comparison of curves 4 and 5 suggests that the arrest on curve 4 at −0·8 v is not due to cuprous sulphide. Further, after the reduction which gave curve 5, hydrogen sulphide could be smelt in the electrometric cell, whereas after curve 4 was obtained no hydrogen sulphide could be detected. Thus it seemed that if any sulphide was formed in the film, the quantities were too small to be detected.

Film Composition as a Function of Film Thickness.—In Figs. 9, 10, and 11, the equivalent reduction time (T_r, min.) of the sulphate in the film is plotted against the equivalent reduction time (T_w, min.) of the whole film. It is seen that the amount of sulphate is a linear function of

[27] Price and Thomas, *Trans. Electrochem. Soc.*, 1939, **76**, 329.

the film thickness at each temperature studied. The curves do not pass through the origin because in the initial stages of the oxidation only cuprous oxide is formed. At each temperature the amount of sulphate formed is independent of the concentration of the sulphur dioxide.

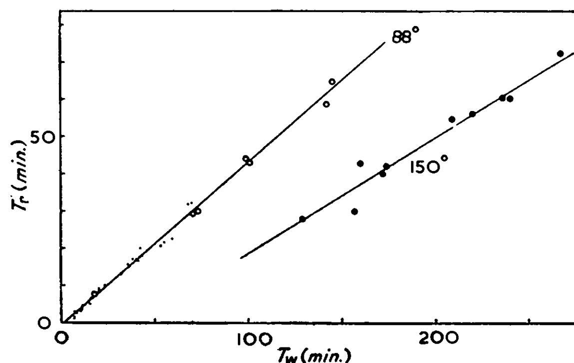


FIG. 9. *T_r, equivalent to the reduction of Cu_2SO_4 plotted against T_w for the total film.*

•, $O_2 + 0{\cdot}2\%$ SO_2 *at* 88°.
○, $O_2 + 2\%$ SO_2 *at* 88°.
●, $O_2 + 0{\cdot}2\%$ SO_2 *at* 150°.

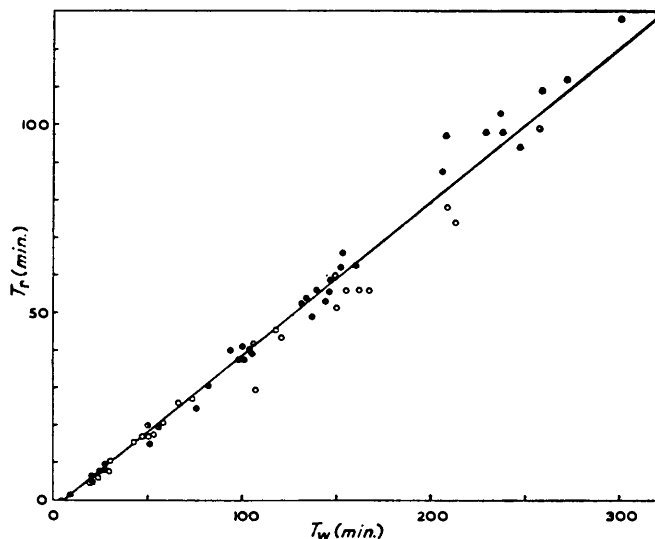


FIG. 10. *T_r equivalent to the reduction of Cu_2SO_4 plotted against T_w for the total film formed at* 120°.

○, $O_2 + 0{\cdot}2\%$ SO_2, 20 *cm.* Hg *pressure.*
◒, $O_2 + 1\%$ SO_2, 20 *cm.* Hg *pressure.*
◑, $O_2 + 2\%$ SO_2, 20 *cm.* Hg *pressure.*
●, $O_2 + 0{\cdot}2\%$ SO_2, 50 *cm.* Hg *pressure.*

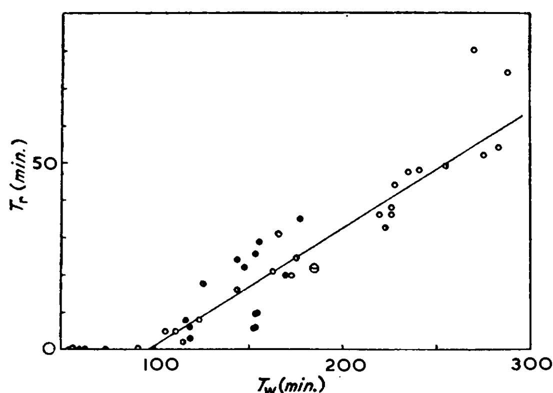


FIG. 11. *T_r equivalent to the reduction of Cu_2SO_4 plotted against T_w for the total film formed at* 172°.

● *and* ◑, $O_2 + 0{\cdot}1\%$ SO_2.
○, $O_2 + 0{\cdot}2\%$ SO_2.
⊖, $O_2 + 1\%$ SO_2.

At 172°, where the oxidation up to T_w = 200 min. took place in 5 min., the results are rather scattered, making interpretation of the kinetics difficult.

The controlled formation of cuprous sulphate, after the film had grown to a certain thickness, dependent on the temperature, suggested that the sulphate was the result of a secondary

reaction which did not take part in the accelerating effect of sulphur dioxide on the oxidation of copper. This was confirmed by experiments in which duplicate specimens were oxidized in air; one specimen was kept for film analysis whilst the second was oxidized in oxygen containing sulphur dioxide. The specimen carrying a cuprous oxide film on the surface did not undergo the usual acceleration in the atmosphere containing sulphur dioxide, although cuprous sulphate was duly formed. The analyses of two sets of experiments are shown in Tables 4 and 5.

TABLE 4.

Analysis of film on first specimen, formed in air at 120° in 75 min
Arrest at −0·1 v (CuO) : T_r = 3 min.
Reduction time of total film : T_w = 29 min.
Analysis of film on second specimen after further heating at 120° for 1030 min. in 20 cm. of $O_2 + 1\%$ SO_2.
Arrest at −0·8 v : T_r = 3 min.
Arrest at −0·1 v (Cu_2SO_4) : T_r = 90 min.
Reduction time of total film : T_w = 236 min.

$$(T_r \text{ for } Cu_2SO_4)/\Delta T_w = 0{\cdot}43$$

TABLE 5.

Analysis of film on first specimen, formed in air at 120° in 105 min.
Arrest at −0·1 v (CuO) : T_r = 2·5 min.
Arrest at −0·6 v (CuO) : T_r = 1·5 min.
Reduction time of total film : T_w = 51 min.
Analysis of film on second specimen after further heating at 120° for 180 min. in 20 cm. of $O_2 + 1\%$ SO_2.
Arrest at −0·1 v (Cu_2SO_4) : T_r = 17 min.
Reduction time of total film : T_w = 86 min.

$$(T_r \text{ for } Cu_2SO_4)/\Delta T_w = 0{\cdot}49$$

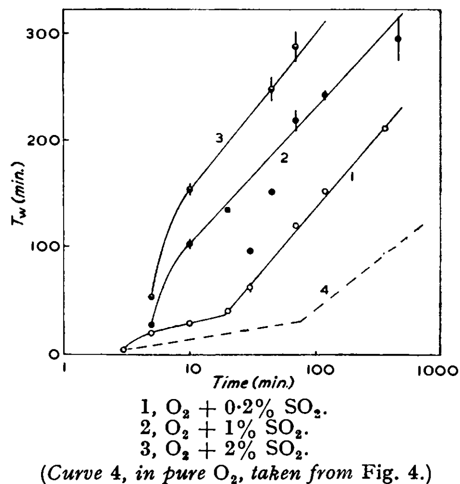
The values of 0·43 and 0·49 for $T_r/\Delta T_w$ are in reasonable agreement with the value of 0·41 for the slope of the curve at 120° in Fig. 10. A possible cause of the higher value with the comparatively thin sulphate film in Table 5 is the reaction of sulphur dioxide with cupric oxide in the film. Cupric oxide was detected at −0·6 v on the first specimen, whereas on the second there was no arrest between −0·4 v and the potential of the evolution of hydrogen. It is possible that the sulphur dioxide reacted with the cupric oxide to form cupric sulphate. This reaction would introduce a small error in the calculations based on the assumption that T_w gave a measure of the amount of cuprous ions formed in the film.

Electro-polished specimens were oxidized in $O_2 + SO_2$ atmospheres and examined under the microscope. The films showed the same characteristics as those formed in pure oxygen, *i.e.*, brown-tinted grains appeared smooth, and grains with more advanced tints exhibited a fine structure. No information was obtained regarding the nature of the sulphate deposit in the film. Although, in the next section, the growth laws have been interpreted in the same way as those obtained in pure oxygen, it is possible that, when more information is available regarding the structure and electrical properties of the sulphate in the film, it will be found that its formation insulates part of the surface and contributes to the decrease in the effective area undergoing oxidation.

Growth Laws.—The effect of 0·2, 1, and 2% of sulphur dioxide on the rate of oxidation at 120° is shown in Fig. 12. The film growth was plotted against the logarithm of the oxidation time and it is seen that a linear relation was obtained in the later stages of the oxidation. With 0·2% of sulphur dioxide the oxidation was initially slow, as it was in pure oxygen; however, the transition to the second stage occurred at a shorter oxidation time, suggesting that the recrystallization of the pseudomorphic film occurred earlier in the presence of sulphur dioxide. With 1 and 2% of sulphur dioxide the initial oxidation, once started, was rapid and then decreased to give a logarithmic relation. The broken curve shown is that obtained in runs in pure oxygen.

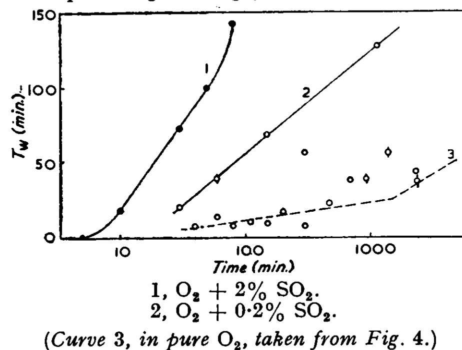
At 88°, with 2% of sulphur dioxide, there was an induction period of 5 min. in which no detectable oxidation occurred, then oxidation proceeded rapidly, without the appearance of the initial slow step. With 0·2% of sulphur dioxide a mixed set of results was obtained, as can be seen from the plot in Fig. 13. In some experiments there was no acceleration of the oxidation, the results following the curve obtained in pure oxygen. Four results, fitted to curve 2 in Fig. 13, indicated accelerated oxidation without the appearance of the initial slow step. Some results fell in intermediate positions, suggesting that, although the pseudomorphic film formed, it recrystallized earlier than it did in pure oxygen.

FIG. 12. *Results of oxidation experiments at 120° plotted against* log (*oxidation time*).



1, O_2 + 0·2% SO_2.
2, O_2 + 1% SO_2.
3, O_2 + 2% SO_2.
(*Curve* 4, *in pure* O_2, *taken from* Fig. 4.)

FIG. 13. *Results of oxidation experiments at* 88° *plotted against* log (*oxidation time*).



1, O_2 + 2% SO_2.
2, O_2 + 0·2% SO_2.
(*Curve* 3, *in pure* O_2, *taken from Fig.* 4.)

FIG. 14. *Results of oxidation in* O_2 + 0·2% SO_2 *at* 150° *and* 172° [T_w *plotted against* log (*oxidation time*)].

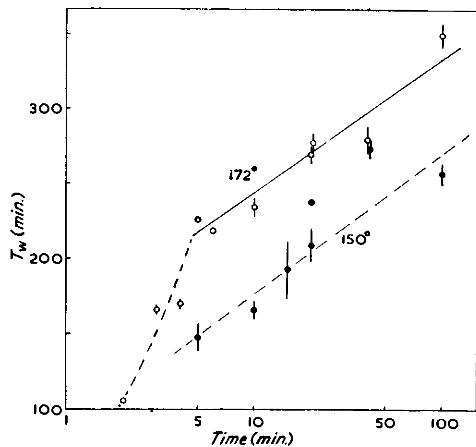


FIG. 15. *Results of oxidation in* O_2 + 0·2% SO_2, *at* 172° (T_w *plotted against oxidation time*).

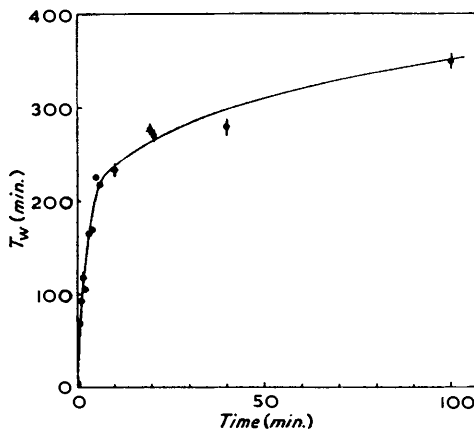


FIG. 16. *Results of oxidation at* 172° *in* O_2 + 0·2% SO_2 (○, *curve* 1), *and* O_2 + 0·04% SO_2 (●, *curve* 2). (*Square of* T_w *plotted against oxidation time.*)

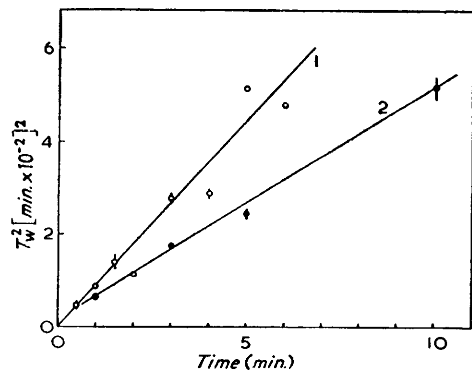
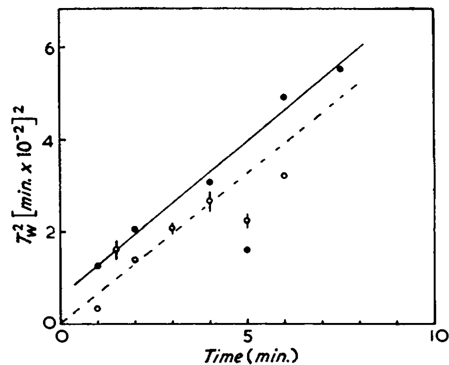


FIG. 17. *Results of oxidation in* O_2 + 0·1% SO_2, *at* 172°. ○, *from first series of experiments*; ●, *from second series of experiments.* (*Square of* T_w *plotted against oxidation time.*)



At 150°, with 0·2% of sulphur dioxide, the oxidation in the first 5 min. was very rapid, and a rather scattered set of results obtained at higher heating times fitted a logarithmic relation. The plot is shown in Fig. 14.

The plot of film thickness against oxidation time for the results obtained at 172° with 0·2% of sulphur dioxide is shown in Fig. 15. The results obtained for film-growth above $T_w = 200$ min., plotted in Fig. 14, fitted a logarithmic relation and the results for film growth up to $T_w = 200$ min., plotted in Fig. 16, fitted the parabolic relation in the same way as was observed in pure oxygen.

The parabolic region of oxidation at 172° was studied at two other concentrations of sulphur dioxide (0·04 and 0·1%), and the results are plotted in Figs. 16 and 17. With 0·1% of the dioxide difficulty was experienced in obtaining reproducible results. This was attributed to the difficulty in obtaining standard initial conditions of admitting the oxidizing atmosphere, for at 172° the gas momentarily chilled the specimens—an important matter since the entire range of heating times was only 5 min. Two series of experiments were carried out. In Series I, shown as open circles in Fig. 17, the gas was admitted very quickly until the pressure was 15 cm. Hg., and then as quickly as possible until it reached 20 cm. In Series II, shown as filled-in circles, the gas was admitted slowly, 30 sec. being required to reach 20 cm. In a 5-min. oxidation, the first procedure was found to give a low result. Two linear curves were obtained from the two sets of results. The similar slopes of the curves indicate that the rate constant in each case was the same. The displacement of the second curve was due to the different initial conditions.

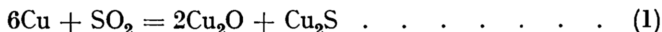
The effect of the concentration of sulphur dioxide on the parabolic rate constant at 172° is shown in Table 6. The last value was the result from a single oxidation experiment with an oxidation time of 2½ min.; the curve was assumed to pass through the origin. It is seen that the rate constant increased with the sulphur dioxide concentration; however, the increase was not a linear function of the concentration, as might be expected from Vernon's work,[28] but the effect decreased with increasing sulphur dioxide concentrations.

TABLE 6.

Oxidizing atmosphere (20 cm. press.)	Rate constant ($\Delta T_w^2 \times 10^{-3}$/5 min.)
Pure O_2	9·6
O_2 + 0·04% SO_2	24·8
O_2 + 0·1% SO_2	32·4
O_2 + 0·2% SO_2	42·0
O_2 + 1% SO_2	68·4

Discussion.—Sulphur dioxide has two effects on the oxidation. The first is dependent on the sulphur dioxide concentration and increases the reaction rate. The second is independent of the concentration and affects the composition of the film.

(i) *Effect of sulphur dioxide on the rate of oxidation.* Sulphur dioxide causes accelerated oxidation only when the $O_2 + SO_2$ mixture reaches a bare copper surface. Thus the reaction only occurs only in the early stages of oxidation, before the oxide film has grown and limited the rate of supply of cuprous ions to the sulphur dioxide adsorbed on the surface. The reaction taking place was undoubtedly



$$6Cu + SO_2 = 2Cu_2O + Cu_2S \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The free-energy change of reaction (1) at 120° is of the order of 16 kcal., which is much less than the free energy of formation of cuprous sulphate (approx. 78 kcal.). Reaction (1) has been shown [5] to proceed at 1027°, and the analogous reaction has been shown [29] to proceed on iron at 300°. It is reasonable to assume that defects introduced into the oxide lattice by reaction (1) are responsible for the accelerated oxidation, since, even at room temperature, sulphide is known greatly to accelerate the oxidation of copper.

The importance of introducing the sulphide into the first layers of oxide was shown by Vernon [28] and Constable; [30] the latter observed that preliminary exposure of copper to air slowed down the subsequent rate of oxidation when exposed to a 1 : 1 mixture of dry oxygen and hydrogen sulphide at room temperature.

The increase in the rate constant at 172°, when the parabolic law is obeyed, shows that

[28] Vernon, *Trans. Faraday Soc.*, 1927, **23**, 113.
[29] Tolly, *J. Soc. Chem. Ind.*, 1948, **67**, 369.
[30] Constable, *Proc. Roy. Soc.*, 1929, *A*, **125**, 630.

the amount of sulphide introduced into the film increased with the sulphur dioxide concentration. At 120°, in the later stages of the oxidation, there is obedience to the logarithmic law. The results, plotted in Fig. 12, show that with increasing sulphur dioxide concentrations the curves are displaced so that corresponding film thicknesses are reached in shorter times. With 0·2% of sulphur dioxide an initial slow step indicates that the pseudomorphic film was formed. With 1 and 2% of sulphur dioxide the initial oxidation was rapid, and the rate decreased with time to give the logarithmic relation. This behaviour is consistent with the theory already advanced, which attributes the logarithmic relation to a deviation from the parabolic law caused by cavities producing a decrease in the area undergoing oxidation.

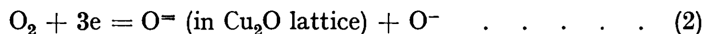
At 88°, at a concentration of 0·2% of sulphur dioxide, the conditions seemed to be a critical region between the observed accelerated film growth due to sulphur dioxide at higher temperatures, and the conditions at room temperature where Vernon [31] found that 10% of the dioxide did not affect the rate of oxidation of copper in dry air. Thus at 88°, with 0·2% of sulphur dioxide, if the reaction with oxygen forms a protective oxide film before appreciable reaction of sulphur dioxide with the copper surface has occurred, the pseudomorphic film will grow until it recrystallizes in the normal way observed in pure oxygen. In some experiments it would seem that the pseudomorphic film was not formed with sufficient speed to prevent the formation of sulphide, so that there was almost immediate accelerated oxidation. Some intermediate points in Fig. 13 indicate that, although the pseudomorphic film was formed, sufficient defects were introduced to cause an earlier breakdown of the film.

With 2% of sulphur dioxide at 88°, the adsorption of sulphur dioxide must have been sufficient to allow reaction to occur with the copper to produce an immediate accelerated rate of oxidation.

(ii) *Mechanism of sulphate formation.* The second effect did not influence the rate of oxidation; it was only observed when the reaction occurred on a copper surface carrying cuprous oxide, and it resulted in the formation of a controlled amount of cuprous sulphate in the oxidation product.

The results can be interpreted in terms of the mechanism proposed by Garner, Grey, and Stone [32] for the adsorption of oxygen on cuprous oxide. They found that when this cuprous oxide was then treated with carbon monoxide, 50% of the adsorbed oxygen reacted to give carbon dioxide. They suggested that the two oxygen atoms of an adsorbed molecule were not exactly equivalent. One oxygen atom, O_L, occupied a favourable adsorption site in the cuprous oxide lattice, and the other, O_M, was left in a reactive, and possibly mobile, state. This view was further supported by the work of Stone and Tiley,[33] who found that with $O_2 + CO_2$ mixtures, equal volumes of the gases were adsorbed on cuprous oxide; apparently one oxygen atom was adsorbed at a favourable site in the cuprous oxide lattice, and the other reacted with the carbon dioxide to form a carbonate ion. Carbon dioxide alone was not adsorbed on a bare cuprous oxide surface. Garner, Grey, and Stone considered that the mobile oxygen atom was trapped as O^- by the process $Cu^+ + O_M = Cu^{2+} + O^-$, creating a positive hole in the cuprous oxide.

If the growth of sulphate occurs through the reaction of the sulphur dioxide with this mobile oxygen, one would expect the following equations for the reaction :



$$O_2 + 3e = O^{=} \text{ (in } Cu_2O \text{ lattice)} + O^- \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$2O^- + SO_2 = SO_4^{=} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From equations (2) and (3) a slope of 0·33 would result for the plot of T_r (Cu_2SO_4) against T_w. The experimental results are listed in Table 7.

TABLE 7.

Oxidation temp.	88°	120°	150°	172°
Slope of T_r (Cu_2SO_4) $-T_w$ curve	0·44	0·41	0·31	0·32

[31] Vernon, *Trans. Faraday Soc.*, 1931, **27**, 255, 582.
[32] Garner, Grey, and Stone, *Discuss. Faraday Soc.*, 1950, **8**, 246.
[33] Stone and Tiley, *ibid.*, p. 254.

When the growing film was thin, sulphate was not formed. This was due to the mobile oxygen's being incorporated in the cuprous oxide lattice when the rate of supply of cuprous ions was high. The importance of film thickness on the course of the surface reaction was shown by van Cleave and Rideal,[34] who studied the catalytic reaction of hydrogen and oxygen on copper wires at 170—250°. With thin films the gases were consumed in the ratio 1 : 1, and with thick films on the copper in the ratio 2 : 1.

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Department of Metallurgy, The University, Cambridge.
Department of Supply, Australia.
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[34] van Cleave and Rideal, *Trans. Faraday Soc.*, 1937, **33**, 635.