A LABORATORY STUDY OF THE ATMOSPHERIC CORROSION OF METALS.

PART I.--THE CORROSION OF COPPER IN CERTAIN SYNTHETIC ATMOSPHERES, WITH PARTICULAR REFERENCE TO THE INFLUENCE OF SULPHUR DIOXIDE IN AIR OF VARIOUS RELATIVE HUMIDITIES.

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The results of a previous series of investigations on the atmospheric corrosion of metals have been communicated to the Faraday Society in the form of three reports to the Atmospheric Corrosion Research Committee of the British Non-Ferrous Metals Research Association, under whose auspices the work was conducted. The first two reports,¹ for which the present author was responsible, were concerned with the systematic examination of the behaviour of the common metals on exposure to several types of indoor atmosphere and to the open air; in particular, the properties of thin (sometimes invisible) films of reaction product were studied, and their influence in determining the rate of attack was established. Methods of determining the rate of attack included measurement of loss of reflectivity and of change in weight, supplemented by micrographic examination and analysis of the products of corrosion, including, in the case of open air exposure, both the residual (" surrosion ") product adhering to the metal, and the soluble ("erosion") product removed by rain.

The Third Report,² by Dr. J. C. Hudson, was concerned exclusively with field tests in the open air and recorded the results (after a period of exposure, in most cases, of twelve months) of a comprehensive series of tests on a wide range of non-ferrous metals and alloys, at five representative stations in this country. For the purpose of these tests Hudson developed a method whereby the change in electrical resistance of thin wires was utilised as a measure of the rate of corrosion ; this was supplemented by determinations of changes in weight, by micrographic examination, and by tensile tests; the results of the tensile test experiments have been published as a separate and later communication.³

Since the publication of the Second Report, the open air corrosion of copper has been dealt with in two papers 4 by the present author, in collaboration with Mr. L. Whitby, chiefly from the point of view of the

¹ Trans. Faraday Soc., **19**, 839, 1924; **23**, 113, 1927. ² Ibid., **25**, 177, 1929. ³ J. Inst. Metals, **44**, 409, 1930. ² *Ibid.*, **25**, 177, 1929. ³ *J. I* ⁴ *Ibid.*, **42**, 181, 1929; **44**, 389, 1930.

composition of the green patina that characterises copper surfaces after prolonged exposure.⁵

All the foregoing communications have one characteristic in common, in that they deal with the behaviour of the metal during exposure to ordinary everyday atmospheres. In connection with the First and Second Reports, some work was done with the object of associating certain effects with specific atmospheric constituents; for the most part, however, the experiments were "analytic" in character, i.e. they depended upon the removal of the constituent under investigation. Experiments in which additions were made to an otherwise pure atmosphere (*i.e.* the "synthetic" (i.e. the "synthetic" method) were admittedly limited, and the opinion was expressed that "much more work remains to be done in the field represented by these experiments." It is with the object of exploring this field, and more particularly with the object of investigating atmospheric corrosion under strictly defined conditions in the laboratory, that the present series of investigations has been instituted. The subject is thus approached from an entirely different angle from that represented in the previous researches. Instead of taking atmospheres as they are found, subject to the usual fluctuations in meteorological conditions, atmospheres will be prepared synthetically, and will be subjected to rigorous control with respect to composition, temperature, and relative humidity; in this way, it will be possible to investigate one factor whilst others are kept constant.

In the present communication a technique is described which it is hoped will form the basis of an extended programme of research. The earlier investigations, whilst they did not altogether neglect the corrosion of iron, necessarily had a non-ferrous bias. Although this bias no longer obtains, it has been thought expedient to conduct the first series of experiments upon copper, more especially as it was desired to throw further light upon recent results obtained in the study of the open air corrosion of that metal. Synthetic atmospheres have been employed containing various concentrations of sulphur dioxide at various controlled relative humidities. Besides the main experiments at constant temperature, other experiments have been included to represent "supersaturated" conditions at fluctuating temperatures. The effect of carbon dioxide, and to a lesser extent hydrogen chloride, has also been investigated.

Experimental.

General Procedure.—The main experiments have dealt with the behaviour of copper towards atmospheres in which definite amounts of sulphur dioxide and of water vapour have been added to purified air; concentrations of sulphur dioxide of 0.01, 0.1, 0.5, 1.0, 2.0 and 10.0 per cent.; and relative humidities of 50, 63, 75, 99 and 100 per cent. at a uniform temperature of 25° C., have been investigated. Other experiments in which these conditions have been departed from in respect to the nature of the added constituent, temperature, hygrometric conditions, or purity of the metal, will be noted in their appropriate place.

An experiment consists normally in exposing eight small copper specimens to the atmosphere under investigation, in a bell-jar which is

⁵ The predominant constituent was found to be basic copper sulphate, except under purely marine conditions, when basic copper chloride predominated; basic copper carbonate was present only in minor proportion. Complete agreement with the formula of the corresponding mineral (e.g., Brochantite, $CuSO_4 . 3Cu(OH)_2$) was found in products after 70 years' exposure and upwards; after shorter periods the basicity of the product was less than that of the mineral.

itself contained in an air-thermostat at 25°. At intervals, the atmosphere is replenished and, usually, a specimen is replaced at the same Typical intervals are as follows: 1, 4, 7, 11, 15, 20, 25, and 30 days. time. After the first withdrawal (when a similarly-treated specimen is added) each specimen is replaced by the one previously removed, so that the full complement is maintained. Between the removal of a specimen and its replacement its weight-increment is determined; the rate of attack is thus measured by the rate of formation of the corrosion product and a time corrosion curve is plotted for each experiment.⁶

Specimens.—Square specimens of 5 cm. edge (i.e. total area 0.5 sq. dm.) cut accurately to dimensions, with a single hole (0.3 mm. diam.) for suspension, have been used throughout the experiments. Unless otherwise stated, they have been taken from high-grade electrolytic copper sheet, 0.53 mm. in thickness; in some cases, for the purpose of comparison, similar specimens of arsenical copper, of B.E.S.A. specification, containing 0.45 per cent. arsenic, have been employed. The sheet has first been polished for the purpose of removing all surface defects; the final surface has been obtained by polishing each specimen separately with Hubert No. I emery paper; this has been followed by rubbing with pure cotton wool and, finally, immersion in pure carbon tetrachloride for removal of The specimens have then been transferred to a vacuum traces of grease. desiccator in which, after immediately evacuating, they have been allowed to remain overnight for weighing and exposure the following day.

Weighing.—The system of weighing employed throughout is based upon the work of Conrady 7; this permits of specimens employed in the investigation (average weight II grams) being weighed correct to 0.001 In most cases this degree of accuracy has not been required, since mgm. the maximum error has been imposed in other ways; nevertheless, the specimens have usually been weighed correct to 0.01 mgm.

Suspension of Specimens.-The specimens in any given experiment are suspended on a stand constructed of glass rod (see Fig. 1). This carries eight projecting arms in two rows of four, each arm terminating in a hook from which the specimen is directly suspended; opposite specimens are 10.0 cm. apart. The arms are staggered, so that a specimen in the upper row is immediately over a gap between two specimens in the lower row. The specimens are placed on the stand immediately after weighing and the full complement is transferred to the bell-jar to be used in the experiment; this is at once evacuated and placed in position in the air-thermostat in readiness for filling with the atmosphere under investigation.

Bell-Jar and Accessories.—Each bell-jar (see Fig. 1) has a capacity of approximately 10,000 c.c.; height, approximately 14 ins.; internal diameter, $8\frac{1}{2}$ ins.; the base-plate is of thoroughly annealed glass, $\frac{1}{2}$ in. in thickness, underneath which is placed a rubber mat $\frac{1}{4}$ in. in thickness. The stopper is fitted with a three-way tap; one of the side tubes is of normal diameter and is for the purpose of connecting to the air-pump for rapid evacuation; the other is of capillary (I mm.) bore, and is for the purpose of connecting to the appropriate apparatus for filling. A mixture of vaseline and graphite is used as lubricant, vaseline having no dele-

⁶ Each curve given in the paper has been checked by means of at least one duplicate experiment. The degree of reproducibility is shown by typical figures in Table I. (Appendix), p. 274. ⁷ Proc. Roy. Soc., 101A, 211, 1922.

terious influence upon the composition of the atmosphere, whilst graphite prevents any seizing of surfaces under pressure.

The air-pump is a "Cenco Hyvac" pump, capable of giving a vacuum of 0.001 mm.

Preparation and Introduction of Atmosphere.—The development of a suitable method of preparing atmospheres of any desired relative humidity is dealt with in a supplementary paper ⁸ to which reference may be made for more precise details. The air is first led through a purification train in which incidental impurities are removed, together with, it should be noted, the whole of the normal content of carbon dioxide. It next passes alternatively, either through a desiccating train (a tower of concentrated sulphuric acid followed by three towers of phosphorus pentoxide) or through the saturating apparatus. From this point each branch is similar, and includes a long "grid" of



glass tubing immersed in a water thermostat at 25° (in which the airstream is thoroughly thermostated), a fine-adjustment metal tap for regulating the rate of flow, and finally (inside the air-thermostat) a Jena glass filter tube, from which connection is made to the bell-jar. At this point the two branches are connected by a three-way tap whereby either branch may be put into communication both with the bell-jar and with a mercury barometer tube.

The evacuated bell-jar containing the specimens having been allowed to remain sufficiently long in the air-thermostat, the appropriate amount of dry air is admitted, as noted by the reading on the barometer tube, so that when the filling is completed with saturated air the desired relative humidity is obtained. Whilst there is still a negative pressure in the bell-jar of approximately 6 cm., passage of air is suspended whilst the addition is made, from a Hempel burette, of a mixture containing the

⁸ "The Quantitative Humidification of Air in Laboratory Experiments." This volume, p. 248.

appropriate amount of special constituent (usually sulphur dioxide) or constituents necessary to bring the composition of the atmosphere in the bell-jar to that desired. This mixture is previously prepared in a separate bell-jar using (normally) pure dry air; the sulphur dioxide is obtained from a syphon, and is either passed through several tubes containing phosphorus pentoxide or bubbled through water at 25° in the case of a completely saturated atmosphere. The mixture is brought to atmospheric pressure after standing in the air-thermostat, and the pressure of the withdrawn portion (usually 100 c.c. in volume) is adjusted in the Hempel burette before being added to the main bell-jar. Passage of the saturated stream (or the desiccated stream in the case of an atmosphere of zero humidity) is then resumed until the pressure in the bell-jar has reached atmospheric. Experience has shown that the diffusion of sulphur dioxide, or other gas, when introduced in this way into the partially evacuated bell-jar is extremely rapid.9

Air-Thermostat .- The two air-thermostats that have been used in the course of the research are described in a supplementary paper ¹⁰; the temperature control in the later of these is such that the maximum variation in point of time is less than 0.01° in several weeks, whilst spatial variation over the working space of the cupboard does not exceed 0.015° . The position of a bell-jar in the thermostat is shown in elevation in Fig. 2 (supplementary paper, p. 243). The delivery tubes from the humidifying apparatus are not shown in the diagram; actually these extend right across the cupboard, so that a bell-jar may be filled on either side of the regulator, connection being made either to the desiccating or saturating branch by means of a side tube with stop-The positions of a full complement of twelve bell-jars are shown cock. in plan in Fig. 3 (supplementary paper, p. 243).

DISCUSSION OF RESULTS.

I. Unsaturated Atmospheres.

A. Atmospheres Containing no Added Impurity.--Experiments in which copper specimens were exposed to purified air, in the desiccated and saturated condition respectively, for periods up to forty days, revealed no visible change upon the metal. Gravimetric results are plotted in Fig. 3 (curves A and B only). In the case of the dry atmosphere the true values are excessively small and experimental error has naturally its greatest effect. A definite weight-increment was invariably obtained after one day's exposure, but no further measurable change was observed during the period of the experiment. The curve (A) is plotted according to the maximum values obtained, and represents a weight-increment of 0.015 mg. (actual) or 0.03 mg. per sq. dm. In the light of previous work,¹¹ in which a study was made of the oxidation of copper at temperatures above, but not far removed from normal (the values thus permitting extrapolation) this figure is in appreciable excess of the true value and the difference must therefore represent experimental error; nevertheless, considering the series of experiments as a whole this curve may be accepted as the "datum" curve-any

⁹See, for example, results obtained with hydrogen sulphide. Appendix, Table II., p. 275. ¹⁰ "An air thermostat for quantitative laboratory work"; p. 241.

¹¹ W. H. J. Vernon, J. Chem. Soc., 128, 2273, 1926.

departure from which may be definitely attributed to the conditions imposed in the particular experiment.

Curve B in Fig. 3 represents the action of purified air at relative humidities of both 99 and 100 per cent. relative humidity, complete saturation bringing about no measurable difference as compared with conditions just below saturation. There is, however, an appreciable difference between the action of these atmospheres and that of the desiccated atmospheres, corresponding with an increase in the weightincrement of 0.05 mg. per sq. dm.

B. Atmospheres Containing Sulphur Dioxide. — Atmospheres containing sulphur dioxide in concentration ranging from 0.01 to 10.0



per cent. have been investigated. The results are discussed in three groups, according to the relative humidity of the atmosphere.

(i) Atmospheres of Zero Relative Humidity.—Exposure to desiccated atmospheres, at all concentrations of sulphur dioxide, has had no visible effect upon the metal; systematic weighings have also failed to show any effect due to the presence of sulphur dioxide, even at the highest concentration. The curve representing the action of these atmospheres is thus identical with the "datum" curve for pure dry air (curve A in Fig. 3).

(ii) Atmospheres of 50 per cent. Relative Humidity.-The introduction

of water vapour brings about an immediate differentiation among the atmospheres of various concentrations of sulphur dioxide, in respect to their action upon copper. This is shown in Fig. 3, where curves C to H represent the effects of atmospheres of 50 per cent. relative humidity, at the respective concentrations of sulphur dioxide. The curves are all similar in type, being exponential in form over the first part, and then "flattening" toward the time axis. The exponential portion persists for the longer time the higher the concentration of sulphur dioxide, but the (approximate) equilibrium value, represented by the nearly horizontal portion of the curve, is reached in all cases after about thirty days' exposure.

In Fig. 4 the various equilibrium values are plotted against concentration of sulphur dioxide. Whilst there is a general increase in corrosivity with increasing concentration, there is a marked break in the



curve toward a minimum corrosion value at a concentration of 1.0 per cent. sulphur dioxide. This break will be referred to later in discussing the higher relative humidities.

All the corrosion values at 50 per cent. relative humidity (Figs. 3 and 4) are of a relatively low order, the specimens undergoing no more than a slight darkening after thirty days' exposure.

(iii) Atmospheres of 75, 99, 100 per cent. Relative Humidity.—At relative humidities of 75 per cent. and upwards the rate of attack is of a definitely higher order of magnitude than is the case with the atmospheres of 50 per cent. R.H. Accordingly, in Figs. 5 to 10, where the corrosion-time curves are grouped according to the sulphur dioxide content, a smaller vertical scale (equal to 1-50th that in Fig. 3) is employed. In each case, the curve for 50 per cent. R.H. is repeated, so that the difference in scale may be appreciated. The curves are similar in type

to those representing the lower rates of attack, except that a rather longer time (usually from thirty to forty days) is taken for the nearly flat portion to be reached. The appearance of the specimens after exposure varies from a darkening or clouding of the surface at the lower rates of attack to a definite coating of bluish corrosion product in the more corrosive atmospheres. At the highest rate of attack (10 per cent.



sulphur dioxide, 100 per cent. R.H.) the characteristic clouding of the surface is observed within ten minutes from the start; the specimen is appreciably attacked after a day's exposure (when traces of sulphate appear) and in the course of a week is covered with a bluish film. In cases where a comparison has been made between the action of atmospheres of 99 and 100 per cent. R.H., no difference whatever has been

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observed in the appearance of the specimens, whilst any difference in weight-increment has been extremely small. In the case of the atmosphere containing 10 per cent. sulphur dioxide the influence of 63 per cent. relative humidity was investigated. In appearance after exposure the specimens from atmospheres of 50 per cent. and 63 per cent. relative humidity are indistinguishable; the difference gravimetrically (see curves A and B, Fig. 10) is also extremely small. There is, however, a relatively enormous difference between the effects of the atmospheres of 63 per cent. and 75 per cent. relative humidity.



In Fig. 11, the final weight-increments, representing the nearly horizontal portion of each corrosion-time curve, are plotted against concentration of sulphur dioxide. Values for 99 per cent. and 75 per cent. R.H. are represented in the two main curves; values for 50 per cent. R.H. (plotted to larger scale in Fig. 4) are again included for comparison. Although atmospheres of 63 per cent. relative humidity are represented only at the highest concentration of sulphur dioxide, there is little doubt that the close proximity to the 50 per cent. R.H. curve would also

obtain at intermediate concentrations. Two points of major interest are represented by these curves. First, the great disparity between the effects of atmospheres of 50 and 63 per cent. and those of 75 and 99 per cent. relative humidity. The results point clearly to the existence of a *critical humidity* lying between 63 per cent. and 75 per cent., below which relative humidity has comparatively little, and above which it has a profound effect. Below the critical humidity, even at high concentrations of sulphur dioxide, specimens may be exposed without undergoing appreciable attack beyond a slight general darkening; above the critical humidity the metal undergoes relatively severe corrosion at a rate which increases greatly with increasing concentration of sulphur dioxide. The conception of critical humidity was introduced in the Second Report ¹² in connection with experiments upon the atmospheric



corrosion of iron. The principle was carried to a further stage in the Third Report,¹³ particularly in connection with the behaviour of specimens exposed in Stevenson screens. The present experiments leave little doubt concerning the importance of critical humidity in the corrosion of copper, whilst the work of Hudson suggests that it may be of even greater importance in the case of other metals.

A second point of interest presented by Fig. II is the marked break in the corrosion-concentration curves toward a minimum corrosion value at 1.0 per cent. sulphur dioxide. This break is shown clearly in the curves for the higher relative humidities (75 and 99 per cent. R.H.), the two curves following an approximately parallel course. It is re-

¹² W. H. J. Vernon, Trans. Faraday Soc., 23, 140, 162, 1927.
¹³ J. C. Hudson, Trans. Faraday Soc., 25, 204, et seq., 1929.

markable, moreover, that the same break also occurs in the curve for 50 per cent. R.H.; although the scale of Fig. 11 does not permit this to be seen, the effect is brought out clearly on the larger scale of Fig. 4. The experimental data are sufficiently definite; although the interpretation of the phenomenon is not obvious, the matter is rendered clearer by a consideration of the following analytical results.

A series of experiments was conducted with the object of determining the composition of the reaction products. Atmospheres were employed, each of 99 per cent. relative humidity, containing sulphur dioxide in the following proportions, 0.5, 1.0 per cent. (eight specimens exposed in each), 2.0 per cent., 4.0 per cent. (four specimens exposed in each). The experiment was continued for 30 days, the atmosphere being replaced at the usual intervals, the specimens, however, being allowed to remain until the Immediately on the conclusion of each experiment the specimens end. were weighed and the product was removed from them by immersion in standard N/100 sulphuric acid. The specimens were then dried and reweighed. SO_4'' was estimated as barium sulphate, and copper¹⁴ as the coordinate compound of copper and salicylaldoxime $(C_7H_6O_2N)_2Cu$. The precipitate in each case was centrifuged and weighed in the centrifuge tube, all usual precautions being taken. The amount of $[SO_4]''$ in the product was obtained as the difference between the total $[SO_4]''$ determined and that due to the sulphuric acid used for removing the product. The results are given below. (Previous tests had shown the complete absence of sulphite $[SO_3]''$ from the products.)

0.5 per cent. SO₂ Atmosphere.

Weight of copper in product	=	35 [.] 87 mg.
[Loss in weight of specimens	=	35.72 mg.]
Weight in SO ₄ " in product	==	41.64 mg.
Calculated formula of product	=	$CuSO_4 + 0.32 Cu(OH)_2$.

1.0 per cent. SO₂ Atmosphere.

Weight of copper in product	= 17.31 mg.	
[Loss in weight of specimens	= 17.27 mg.]	
Weight of SO_4'' in product	= 28.26 mg.	
Calculated formula of product	$t = CuSO_4 + 0.07 H_2SC$)4.

2.0 per cent. SO₂ Atmosphere.

Weight of copper in product	=	15.82 mg.
[Loss in weight of specimens	-	15.96 mg.]
Weight of SO_4'' in product		36.37 mg.
Calculated formula of product	=	$CuSO_4 + 0.34 H_2SO_4$.

4.0 per cent. SO₂ Atmosphere.

Weight of copper in product = 3.63 mg. (A portion only of the total product was examined.) Weight of SO₄" in product = 15.73 mg. Calculated formula of product = CuSO₄ + 0.65 H₂SO₄.

The foregoing results appear to be of considerable significance. In the case of atmospheres containing less than 1° per cent. sulphur dioxide, copper sulphate in the product is associated with excess of base ; atmospheres containing more than 1° per cent. sulphur dioxide, on the other hand, yield products associated with excess of sulphuric acid. The product from

¹⁴ Ephraim, Ber., 63, [B], 1928, 1930.

the atmosphere containing $r \circ per$ cent. sulphur dioxide shows fairly close agreement with the composition of normal copper sulphate. The slight excess of sulphuric is very probably due to the critical concentration of sulphur dioxide occurring at a point not exactly coincident with $r \circ per$ cent.; it appears reasonable to assume that at the critical concentration the product would consist entirely of normal copper sulphate.

The further suggestion emerges that in atmospheres containing less than the critical concentration of sulphur dioxide (approximately 1.0 per cent.) oxidation of SO_2 to SO_3 is catalysed at the surface of the specimen by metallic copper, and, in the presence of oxygen, copper sulphate is formed; in the presence of water vapour copper hydroxide is formed concomitantly to an extent that is dependent upon the concentration of sulphur dioxide. In atmospheres containing more than 1.0 per cent. sulphur dioxide, oxidation of the excess of SO_2 is catalysed with the formation of free sulphuric acid. It seems most probable, therefore, that the characteristic shape of the



Atmospheres containing Sulphur Diaxide.

time-corrosion curves (Fig. 3 and Figs. 5 to 10) is due to the catalytic oxidation of sulphur dioxide, the rate of attack falling off as the active centres on the surface of the specimen become exhausted.

C. Atmospheres Containing Carbon Dioxide (with Sulphur Dioxide).—The influence of carbon dioxide when present in the atmosphere together with sulphur dioxide was investigated by comparing the effects of an atmosphere containing 0.01 per cent. sulphur dioxide with those produced by the same atmosphere to which I per cent. carbon dioxide had been added, the experiments being duplicated at relative humidities of 50 per cent. and 99 per cent. The results are shown in Fig. 12. At the lower relative humidity, no difference could be detected in the effects due to the two atmospheres and the two groups of results are plotted in one curve (A). At the higher relative humidity, the atmosphere containing no carbon dioxide gave a rather higher corrosion rate than the atmosphere to which carbon dioxide had been added; the restraining influence of carbon dioxide appears to be connected essentially with the presence of a very thin film of moisture at the surface.

D. Atmospheres Containing Hydrogen Chloride (with Sulphur Dioxide).—The effect was tried of adding a small amount (0.01 per cent.) of hydrogen chloride gas to an atmosphere containing 1.0 per cent. sulphur dioxide at a relative humidity of 50 per cent. For the first time in the series of experiments, interference colours, in their characteristic order, were developed upon the specimens. The curve is plotted at B in Fig. 13, whilst the straight line at C, derived from squares of points on the main curve, shows this to be a parabola. This is in agreement with previous work (First and Second Reports) in which the development of interference colours was invariably associated with a parabolic curve. The curve for the atmosphere of 1.0 per cent. sulphur dioxide in the absence of hydrogen chloride is plotted at A.

The curve for hydrogen chloride alone is similar to that shown at B, but not so regular. It is probable that sulphur dioxide, in presence of free hydrogen chloride, acts merely as a reducing agent, and serves to maintain the film of reaction product in the cuprous condition. That the



FIG 13 INFLUENCE OF HYDROGEN CHLORIDE ON CORROSIVITY OF UNSATURATED ATMOSPHERE CONTAINING SULPHUR DIOXIDE

film of product consists of cuprous chloride is confirmed by its photochemical properties; thus, on subsequent exposure to light, an impression of the glass supporting stand was produced upon some of the specimens, corresponding with the shadow thrown by the stand. The foregoing results are of interest as showing that, although sulphur dioxide in the atmosphere normally plays a primary part, in exceptional circumstances it may play a secondary part, depending upon the nature of the added constituent.

2. Saturated and Supersaturated Atmospheres.

In the following experiments, for the purpose of obtaining conditions of complete saturation which would be maintained indefinitely, the modified form of Hempel desiccator shown in Fig. 2 was employed. The specimens were supported on stands similar to those already described (Fig. 1) except that they were smaller, and in some cases carried four specimens only. The cleaned and weighed specimens having been introduced, the vessel was evacuated and refilled with purified air.

Before atmospheric pressure was reached, either distilled water (conductivity water ¹⁵ was used in some experiments) or a solution of sulphur dioxide of appropriate concentration was introduced through the stopcock into the annular reservoir. The vessel was either kept in the thermostat at 25° or was allowed to remain on the laboratory bench (protected from direct sunlight) according to the particular experiment.

A. Atmospheres Containing no Added Impurity, --- A " blank " experiment was conducted (in thermostat) in which H.C. copper specimens were exposed in the corrosion vessel with conductivity water in the annular reservoir. A definite film of moisture was observed upon the specimens within a few days which persisted throughout the period of exposure. Nevertheless, only a very slight general darkening of the specimens was observed, to appreciate which, comparison with a freshlycleaned surface was necessary. Weight-increments at seventy-eight and 140 days' exposure respectively were 0.215 and 0.325 mgm. per sq. dm. In a similar experiment at ordinary room temperature, employing specimens of both H.C. and arsenical copper, a greater darkening of the arsenical copper was observed after only one day's exposure.

B. Atmospheres Containing Sulphur Dioxide.-In the following experiments, a saturated solution of sulphur dioxide has been contained in the annular reservoir. The much greater rate of attack (due to the high concentration of sulphur dioxide) as compared with the experiments in Section I, has permitted relatively large amounts of corrosion product to be removed for examination; the justification for this procedure will appear below.

Visual and Analytical Results .-- Within several days the specimens become covered with a film of moisture which collects in drops of pale green liquid at the lower edge. On the upper parts of the specimen very fine crystals (apparently of normal copper sulphate) gradually appear, particularly round the suspension hole, where definite crystals have been observed within three days. In about a week, at which stage the specimens deliquesce freely, the whole surface is covered with a finely crystalline film. The foregoing description applies fairly generally both to H.C. and arsenical copper, except that arsenical copper is characterised by a very rapid darkening in the early stages,¹⁶ resulting in about three days in a nearly black background on which the crystalline film develops.

In an experiment in which four specimens of H.C. copper were contained in the corrosion vessel (the experiment was conducted during the month of July, with the vessel on the laboratory bench, screened from direct sunlight), at the end of twenty-eight days the specimens were covered with a pale blue deposit, whilst 23 c.c. of green liquid had collected at the bottom of the vessel. The specimens were dried in vacuo ; the film was removed and analysed with the following result. Copper, 36.5per cent. (Cu in $CuSO_4 = 39.6$ per cent.); sulphate $[SO_4]$, 50.5 per cent.; sulphite, nil. The green liquid, after boiling with 2N hydrochloric acid with simultaneous passage of a stream of nitrogen to remove any SO₂, was found to contain [SO4] 0.2005 gram; Cu 0.0760 gram. This represents an excess of $[SO_4]$ over that required for normal copper sulphate

 ¹⁵ Prepared by a routine method in the Corrosion Section of the Chemical Research Laboratory (see Bengough, Stuart and Lee, J. Chem. Soc., 129, 2156, 1927; Stuart and Wormwell, *ibid.*, 132, 85, 1930).
¹⁶ This confirms earlier observations in connection with the open-air tests at South Kensington (First Report, Vernon, *loc. cit.*, p. 875).

of 0.0855 gram, showing the presence of free sulphuric acid. This result confirms the observation already made that, at the higher concentrations of SO_2 , oxidation of sulphur dioxide to sulphuric acid is catalysed at the surface of the specimen independently of the formation of copper sulphate.

Gravimetric Results.—An experiment with H.C. and arsenical copper two specimens of each, exposed in the corrosion vessel with saturated sulphur dioxide solutions, was conducted in the thermostat for twenty days. Weight-increments of the specimens were determined after vacuum desiccation over concentrated sulphuric acid for one week; the products were then completely removed and the loss in weight of the specimens was determined. The results were as follows :—

Weight-increments (grams per sq. dm.).	Weight-losses (grams per sq. dm.).
H.C. copper. (I) 0.62414 0.64300	H.C. copper. (1) 0.21504 0.22612
(2) 0.66184 0 0.4300	(2) 0.23722) 0 22022
Arsenical copper. (1) 0.53862 0.51456	Arsenical copper. (1) 0.19720 0.19734
(2) 0.49050 - 3-13-	(2) 0.17748)

Further experiments were conducted in which specimens of H.C. and arsenical copper were exposed to the saturated atmosphere, both at 25° and at room temperature, for periods of fifty-one and forty-nine days respectively; four specimens of each material were exposed in each case. The specimens were removed at intervals; the figures given below are those yielded by the specimen last to be removed; intermediate values, however, showed approximately the same ratio between H.C. and arsenical copper.

Thermostat. 51 days. 2 Weight-increments.	Temperature 25°. H.C. copper.	0·7464 gram	per	sq. dm.
Weight looper	Arsenical copper.	0.5912	,,	,,
weight-losses.	Arsenical copper.	0.3070	,, ,,	,, ,,
Room. 49 days. Temp	erature range 10-23°	. Mean Ten	ipera	uture 16°.
Weight-increments.	H.C. copper. Arsenical copper.	1·1914 gram 1·4392	s pei	sq. dm.
Weight-losses.	H.C. copper.	0.94058	,,	,,
	Aisemear copper.	0.7120	,,	,,

In the foregoing examples, arsenical copper, with one exception, has yielded a lower weight-increment than has H.C. copper, and in all cases it has yielded an appreciably lower loss in weight. (In experiments of this type, greater significance attaches to loss in weight figures than to weight-increments, owing to the large amount of looselyadhering product.) These results confirm the results of field tests in the Second and Third Reports,¹⁷ in which the greater resistance of arsenical copper to atmospheric corrosion was shown.

Behaviour of Corrosion Products.—The corrosion products were removed from the specimens by careful scraping with a horn spatula, supplemented occasionally with a nickel spatula. In no case was there any evidence of appreciable pitting of the metal. Underneath the layer of corrosion product, and adhering firmly to the metal, there was a red film, presumably of cuprous oxide, on the H.C. specimens, and a dark brown film on the arsenical specimens. This, again, confirms earlier observations in connection with the open-air tests.¹⁸

¹⁷ Second Report (Vernon, *loc. cit.*), p. 178; Third Report (Hudson, *loc. cit.*), p. 288.

¹⁸ Second Report (Vernon, loc. cit.), p. 177.

The products from the second series of experiments ("thermostat" and "room") were carefully collected and divided into four groups as follows :----

(1)	"Thermostat Experiment	t."		J		·,		/ · · · ·
(-)	"Thermentet Development	, s da	ys	and	21 0	lays	exposure	(mixed).
(2)	i nermostat Experimen	τ.						
	Products from 3	36	,,	,,	51	,,	,,	
(3)	"Room Experiment."							
,	Products from	7			T.A			
(Λ)	" Room Experiment "	4		,,	- 7	,,	,,	,,
(4)	Products from a	-			10			
	1 Toducts Hom 2	./	,,	"	49	,,	,,	,,

In each group the products from the H.C. and arsenical specimens were kept separate, so that altogether there were eight separate collections of



FIG 14 - Hygroscopicily of Corrosion Products. Weight-increments of (previously desicculed, products in almosphere of 100 per cent relative humidity.

bottles were then placed (the stoppers being removed during the actual experiment) in a large flat-bottomed "crystallising basin" in which they were ranged round a similar, smaller vessel, placed in the middle. The whole was then placed within a bell-jar similar to those used in the main experiments, except that a delivery tube with stopcock passed through the stopper and terminated just above the middle dish. The bell-jar

19 Vernon and Whitby, J. Soc. Chem. Ind., 47, 255T (1928).

products. Each of these was placed in a weighing bottle and submitted to vacuum desiccation over concentrated sulphuric acid, in a Hempel desiccator at 25°, with occasional shaking of the product and periodical weighing. The desiccation was continued (the vacuum being maintained by frequent re-evacuation of the desiccator) until approximate constancy of weight was obtained, for which a period of five months was required. (The tenacity with which associated moisture is retained by atmospheric corrosion products from actual field tests, even at a temperature of 100°, has been discussed in a previous paper,¹⁹ in which a characteristic curve was reproduced). A portion of each product was then transferred to a clean dry weighing bottle in sufficient quantity (from 0.2 to 0.3 gram) just to cover the bottom of the bottle. The

was placed in the thermostat and, after evacuation, was filled with an atmosphere of 50 per cent. relative humidity by the method already described; just before the filling was completed, a solution of sulphuric acid (sp. gr. 1.329) was run into the middle dish by means of the delivery tube; the vapour pressure of this solution was such as would maintain a relative humidity of 50 per cent. and hence compensate for water vapour removed by the desiccated products. After two hours' exposure of the products the bottles were removed for weighing. Subsequently they were replaced, and the experiment was repeated for further periods,

the weight of the products being determined after two, six, twelve and twenty-eight hours' exposure. The whole experiment was repeated, with a further batch of dry products, employing an atmosphere of 75 per cent. relative humidity (with sulphuric acid solution of sp. gr. 1.22; and again repeated with a final batch of products exposed to an atmosphere of 100 per cent. relative humidity, with distilled water in the middle dish. Typical curves, showing the rate of absorption of water vapour by the desiccated products in an atmosphere of 100 per cent. relative humidity, are given in Fig. 14, where the percentage weightincrements of products from H.C. and arsenical copper are plotted against time. The curves represent the behaviour of products from the first period of corrosion (groups I and 3) and the lower curves the be-



FIC 15 CRITICAL HUMIDITY AS SHOWN BY INTEROSCOPICITY OF CORROSION PRODUCTS (CURVES A& B) AND BY THE CORROSION OF THE METAL (CURVE C) AT A SERIES OF RELATIVE HUMIDITIES

haviour of those from the second period (groups 2 and 4). The results from the "thermostat" and "room" experiments are thus taken together and mean values plotted; the curves yielded by individual experiments, however, are closely similar. In each case, the product from H.C. copper shows an appreciably greater hygroscopicity than that from arsenical copper; furthermore, the difference is more marked in the products representing the longer period of corrosion.

In Fig. 15 (curves A and B) the "final" weight-increments (after twenty-eight hours' exposure at each relative humidity) yielded by the

products from H.C. and arsenical copper, are plotted against relative (This method is similar to that employed by Hudson²⁰ in humidity. the case of corrosion products collected from various specimens in his field tests, except that his products were not subjected to a previous desiccation.) For the purpose of comparison, results obtained in Section I with an atmosphere containing IO per cent. sulphur dioxide (the highest concentration there employed) are replotted on the same diagram (curve C); the values in this case represent the final weightincrements undergone by the metal at each relative humidity (including, in this case, an atmosphere of 63 per cent. R.H.), the very great step between 63 per cent. and 75 per cent. relative humidity representing the "critical humidity" which has already been discussed. It is noteworthy that the curves from the present experiments exhibit quite definite breaks in approximately the same position; the magnitude of these breaks is not so great as that in curve C; nevertheless, there can be little doubt that they are again determined by the critical humidity, the value for which coincides with that in the previous experiments. It is significant, moreover, that the influence of critical humidity, as shown by curves A and B is more marked in the case of high-conductivity than in the case of arsenical copper.

Reference has already been made to the greater resistance to atmospheric corrosion exhibited by arsenical copper, as compared with high conductivity copper, as shown by exposure tests in the field. Samples of old copper roofings, quite sound after upwards of 100 years' exposure, have been found ²¹ to be definitely arsenical. In the Second Report it was suggested that the superiority of arsenical copper is due to the presence of a protective film, the development of which in the early stages of exposure to the open-air, had actually been followed by reflectivity measurements. A supplementary factor is now revealed by the present experiments in respect to the greater hygroscopicity of the product from H.C. copper, and the greater susceptibility of the purer material to changes taking place at the critical humidity. The experiments also suggest that the influence of arsenic is likely to become more marked with increasing period of exposure. This is confirmed by the observation, first made by Hudson,²² that arsenic actually accumulates in the product during corrosion in the field thus, Hudson found that after a year's exposure (at Birmingham) the ratio of arsenic to copper was four times greater in the product than in the metal.

Atmospheres Containing Carbon Dioxide (with Sulphur С. Dioxide) .--- In order to ascertain the influence of carbon dioxide, three parallel experiments were carried out in the thermostat with the Hempel desiccator apparatus, as follows: (I) The liquid in the reservoir consisted of one volume of a saturated solution of sulphur dioxide, mixed with 400 volumes of distilled water, yielding a solution having only a "faint smell" of sulphur dioxide; the vessel was previously evacuated and filled with purified air in the usual way. (2) The reservoir contained one volume of saturated solution of sulphur dioxide, mixed with 400 volumes of saturated solution of carbon dioxide. In addition, 1.0 per cent. carbon dioxide was added to the atmosphere, so that a large excess of carbon dioxide over sulphur dioxide was ensured. (3) The

 ²⁰ Third Report (*loc. cit.*), p. 207.
²¹ Vernon and Whitby, J. Inst. Metals, 42, 189, 202, 1929.
²² Third Report (*loc. cit.*), p. 237. See also Vernon and Whitby, J. Inst. Metals, 42, 202, 1929.

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reservoir liquid consisted entirely of a saturated solution of carbon dioxide, whilst 1.0 per cent. carbon dioxide was added to the atmosphere as in (2). In each experiment, four specimens of H.C. copper were exposed to the atmosphere on the usual type of stand, and at intervals up to 320 days, a specimen was removed and its weight-increment determined. The results from experiments (1) and (2) showed an agreement that is somewhat remarkable, as will be seen from Fig. 16, the two series of values lying closely on a single curve. In contrast with



the relatively thick, dark green coating produced on the specimens in these experiments, the specimens from experiment (3) had suffered no change in appearance beyond the slight general darkening that is characteristic of exposure in pure saturated atmospheres; the weight-increment at 245 days was 0.77 mg. per sq. dm. a value too small to be shown on the vertical scale of Fig. 16 (compare 192.4 and 191.9 mg. per sq. dm. in the other experiments). It is evident that the influence of carbon dioxide, in relation to the influence of very much lower concentrations of sulphur dioxide, is quite negligible.

Appendix.

Influence of Surface Condition upon Rate of Attack.

Experiments have been carried out in which, instead of the usual treatment with fine emery paper (see p. 257), specimens have been prepared by the method of sand-blasting.²³ White Calais sand was employed for this purpose and was ejected from the nozzle (7/16'' diam.) at a pressure of 7 lbs./sq. inch, the specimens being held at a distance of approximately 12 ins. from the nozzle. The specimens were exposed to an atmosphere containing 1.0 per cent. sulphur dioxide at a relative humidity of 99 per The results are plotted in Fig. 17 (Curve B) together with (Curve A) cent. the results yielded by specimens prepared with fine emery paper (see also It will be seen that the sand-blasted specimens have curve C in Fig. 8). undergone a profoundly greater attack as compared with the emeried Nevertheless, satisfactory reproducibility is yielded, as shown specimens. by the duplicate figures in Table I. (these are given for a period of 11 days The weight-increments yielded by duplicate experiments with only). emeried specimens, for a similar period, are also included.

¹³ Through the kind offices of Mr. C. R. Clark, Central Technical College, Eirmingham.

TABLE I.-ATMOSPHERE CONTAINING 1'O PER CENT. SO2; 99 PER CENT. RELATIVE HUMIDITY.

Surface	Evet	Time in Days, with Weight-Increment in Mgs. (Actual). ²⁴					
of Specimen.	I.	4-	7.	11.			
Sand-blasted	A	26·3	39 . 9	43°5	46•6		
	B	25·9	38.8	43°6	47•2		
Emeried	A ²⁵	2·42	2·85	2•70	3°27		
"	B ²⁵	2·38	2·73	2•88	3°37		



The experiment described above was repeated with an atmosphere

cent. sulphur dioxide as before, but having a relative humidity of only 50 per cent. (i.e. less than the critical humidity). In this case the disparity between emeried and sandblasted specimens was not so pronounced, equilibrium values being 0.32 and 1.56 mg. sq. dm. respectively (compare 8.0 and 101'0 mg./sq. dm. for the atmosphere of 99 per cent. relative humidity). This suggests that the effects due to critical humidity, as described in the text, would have been greatly intensified had the experiments been conducted upon sand-blasted specimens.

containing 1.0 per

In order to ascertain the influence of surface under entirely different conditions of

35

30



15

Armosphere; emeried specimens

(Curve C. Fig 8)

Time in Days (Curves A and B)

20

²⁴ To convert to mg. per sq. dm. (as plotted), figures should be doubled. ²⁵ Expt. A was started on 9th January, 1930. Expt. B on 5th February, 1931.

25

20

0

5

10

Weighl

attack, experiments were conducted in an atmosphere containing o'or per cent. of hydrogen sulphide at a relative humidity of 50 per cent. Four specimens were employed in each experiment; they were withdrawn from the bell-jar precisely five minntes after the admission of hydrogen sulphide. This period was sufficient to produce a uniform tarnish of purple colour on the emeried specimens; in all cases there was appreciable excess of hydrogen sulphide in the bell-jar when the specimens were withdrawn. The results of duplicate experiments on both emeried and sandblasted specimens are given in Table II.

	Weight-Increments, Mgs. (actual), of Individ Specimens after 5 Minutes' Exposure.					
Sand-blasted specimens	<i>Expt. A.</i> 0'10 0'09 0'11 0'11	Expt. B. 0'10 0'09 0'09 0'11				
Mean value	0.	10				
Emeried specimens	Expt. A. 0°06 0°06 0°06 0°07	Expt. B. 0.06 0.06 0.05 0.07				
Mean value	0.	06				

TABLE II.—Atmosphere	CONTAINING O'	OI PER	CENT.	H ₂ S;	50	Per	CENT.
	RELATIVE HU	MIDITY			-		

The mean weight-increments are 010 and 006 mg. respectively. These values are plotted in Fig. 17 on the assumption that the process is controlled by film formation, and, hence, that the characteristic curve is the parabola; this assumption, in the case of tarnish films showing interference colours, is amply justified by the results of previous work.²⁶ Nevertheless, a consideration of the isolated points alone is sufficient to show that surface condition has a far smaller effect upon the "hydrogen sulphide type" of attack than upon the "sulphur dioxide type."

The foregoing results provide an interesting sequel to those recorded in the text. Thus, it was concluded that in an atmosphere containing sulphur dioxide and moisture, the corrosion process is controlled by the catalytic oxidation of sulphur dioxide at the metal surface, the actual rate of attack depending upon the number of active centres that are available. It can readily be understood that a specimen in the sand-blasted condition will present a greater number of such active centres than a specimen that has been polished with fine emery, to an extent that is quite disproportionate to the increase in total surface area. On the other hand, in the hydrogen sulphide type of attack, where the process is controlled by gaseous diffusion through an initially formed film, the reaction product, from the outset, takes the form of a continuous envelope; hence the magnitude of the attack would be expected to be in simple proportion to the surface area.

26 See, for example, " First and Second Reports," loc. cit.

Summary and Conclusions.

A technique is described for studying the atmospheric corrosion of metals in the laboratory by exposure of specimens to synthetic atmospheres. The corrosion of copper, in air containing sulphur dioxide, at various relative humidities, has been investigated. At zero relative humidity, the action of air containing various concentrations of sulphur dioxide, from 0.01 to 10.0 per cent., is indistinguishable from that of purified air; no visible effect is produced upon the specimens and the weight-increment is in the neighbourhood of the lowest limit of measurement by the methods employed. The introduction of water vapour brings about an immediate differentiation among the various concentrations of sulphur dioxide. Corrosion-time curves have been plotted for relative humidities of 50, 63, 75 and 99 per cent. The curves are exponential in form in the early stages, and then flatten toward the time axis, with which they become nearly parallel in from thirty to forty days. The process is controlled by the catalytic oxidation of sulphur dioxide at the metal surface, the rate of attack falling off as the active centres are used up. At 50 per cent. relative humidity the relationship of the atmospheres among themselves in respect to their action upon copper is similar to that which obtains at the higher relative humidities, but the magnitude of the attack is of a definitely lower order. Between 63 per cent. and 75 per cent. relative humidity there is, in most cases, a profound increase in the rate of attack, pointing to the existence of a critical humidity lying between these values. The curves connecting rate of corrosion with concentration of sulphur dioxide show, in all cases, a break toward a minimum value at approximately 1.0 per cent. sulphur dioxide. In atmospheres of this critical concentration, the reaction product consists of normal copper sulphate; at lower concentrations of sulphur dioxide it is accompanied by excess of base, and at higher concentrations by excess of sulphuric acid. Carbon dioxide, when present in large excess over sulphur dioxide, is without appreciable influence. Hydrogen chloride, on the other hand, when present in considerably lower concen-tration than sulphur dioxide, pursues an independent and (in atmospheres of relatively low humidity) much greater attack upon the metal; the attack, however, is of a different type, being represented by a parabolic corrosion-time curve (similarly for copper in atmospheres containing hydrogen sulphide), and consisting in the production of a series of inter-ference colours due to a film of cuprous chloride. The surface condition of the metal has a pronounced effect upon the first type of attack (controlled by catalytic oxidation of sulphur dioxide), but a comparatively small effect upon the second type (controlled by gaseous diffusion through a continuous envelope of reaction product).

Experiments have also been carried out with saturated and supersaturated atmospheres containing sulphur dioxide. A greater rate of attack has been observed upon high conductivity than upon arsenical copper, confirming the results of earlier field tests, and the development of a dark film upon the arsenical copper in the initial stages has also been confirmed. The hygroscopicity of the corrosion products, after prolonged desiccation, has been studied at relative humidities of 50, 75, and 100 per cent.; there is a marked increase between 50 and 75 per cent. relative humidity, corresponding with the critical humidity previously observed. The influence of critical humidity is more marked upon the products from H.C. copper than upon those from arsenical copper; the products from H.C. copper, moreover, are definitely more hygroscopic than those from arsenicat copper. This provides an additional explanation for the greater corrosion resistance of arsenical copper as observed in open-air exposure.

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