

used in gas thermometers at room temperatures. It was thought worth while to see whether the gases could be detected after they had passed through the quartz glass.

A piece of clear quartz glass was drawn to an internal diameter of about 1.0 mm. and a wall thickness of about 0.5 mm. This tube was closed at one end and sealed by an internal seal into a second silica tube of about 5 to 6 mm. bore. The open end of the larger tube was then constricted; the whole tube was thoroughly heated, evacuated and sealed. On wrapping the two ends of the evacuated tube with tin foil, no discharge could be excited with a 25mm. induction coil.

The open end of the capillary tube was then sealed to a supply of helium under a pressure of 100 atmospheres. After a period of time varying with different tubes from two to four hours, the spark coil used above was able to excite a luminous discharge in the evacuated tube. At first, the discharge was greenish in color, characteristic of discharges in low pressure helium, but soon changed to the better known yellow color as the pressure presumably increased. The spectrum was photographed in several cases and no lines could be detected other than those of helium.

After finding the tubes permeable to helium, in most cases the evacuated tube was opened, re-evacuated, sealed as before and the capillary tube filled with hydrogen under 100 atmospheres' pressure. In no case was it possible to excite a discharge in the system when the capillary was filled with hydrogen. One tube, into which sufficient helium diffused in four hours to permit exciting a discharge, when tested with hydrogen showed no discharge after the hydrogen pressure had been maintained in the capillary for a period of 11 days.

Longer runs were not made with hydrogen because of the difficulty in keeping the apparatus tight. The special sealing wax used to join the quartz glass to the metal supply cylinder seemed to be affected by the hydrogen, and sooner or later the gas would work through and quickly release the pressure. Possibly, longer runs would be successful with hydrogen.

Conclusion.—Quartz glass is permeable to helium at room temperature under a pressure of 100 atmospheres.

Negative results were obtained for hydrogen under the same conditions.

CONTRIBUTION FROM THE CHEMICAL LABORATORY
UNIVERSITY OF KANSAS
LAWRENCE, KANSAS

HOWARD M. ELSEY

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McCulloch's Observations Regarding the Rapid Corrosion of Metals by Acids within Capillaries.—A recent Note in THIS JOURNAL by McCulloch¹ records an instance of marked localized corrosion set up where a

¹ McCulloch, THIS JOURNAL, 47, 1940 (1925).

rubber band had been wrapped around an iron rod and the whole immersed in dil. hydrochloric acid. McCulloch interprets the intense corrosion of the iron within the capillary channels between rubber and metal by supposing that hydrogen can escape from such places with special facility. The observation is of interest, but the explanation is not very easy to accept. The present writer² has recorded numerous cases of intense localized corrosion within similar capillary channels under conditions where the expulsion of hydrogen as a gas is out of the question. Thus the corrosion of zinc, cadmium, iron and lead in solutions of salts such as sodium or potassium chloride has been shown to be accelerated where inert substances such as glass, porcelain, thread or rubber are pressed close against the metallic surface. These cases are undoubtedly due to differential aeration currents. The parts shielded by the inert substances are comparatively inaccessible to dissolved oxygen and become anodic towards the better "aerated" regions, thus suffering local attack. Since it has also been demonstrated by the writer³ that differential aeration currents can be generated even in liquids sufficiently acid to cause the evolution of hydrogen, it seemed worth while to ascertain whether McCulloch's case might not be due to differential aeration.

Accordingly, four pieces cut from the same iron rod were wrapped with rubber in the way described by McCulloch. Two were placed in flasks containing 1.4 *N* hydrochloric acid which had been shaken with air, the space in the flask above the liquid being filled with air. The other two were placed in flasks containing similar acid which had been freed from dissolved oxygen by boiling, the space above the liquid being filled with carbon dioxide. After five days, the specimens were removed and examined. The two specimens exposed under "aerobic" conditions showed the McCulloch phenomenon admirably; there were clean grooves cut into the iron, as though with a tool, where the rubber had pressed against it. The two specimens exposed under "anaerobic" conditions were much less corroded and did not show the effect. Other experiments continued for 16 days gave similar results; the anaerobic specimens were, on the whole, *less* corroded below the rubber than on the uncovered portion. It would seem that the effect described by McCulloch is not conspicuous except in the presence of oxygen.

Although dilute acids can attack iron and steel in the absence of oxygen, yet the rate of attack is generally found to be greatly increased when oxygen is present. Whitman and Russell,⁴ for instance, found that the attack on mild steel by 4% hydrochloric acid was increased 15 times by the presence of oxygen. My own results agree with those of Whitman and Russell,

² Evans, *J. Inst. Met.*, **30**, 239 (1923).

³ Evans, "The Corrosion of Metals," Arnold, **1924**, p. 91.

⁴ Whitman and Russell, *Ind. Eng. Chem.*, **17**, 349 (1925).

the attack being enormously enhanced by oxygen. When iron rods (not provided with rubber bands) were immersed in the acid in the presence of oxygen, corrosion penetrated longitudinally from the two ends along the center of the rods, producing an effect like a hollow tree; if pressed between the fingers after this treatment, the sides of the rod could be caused to collapse, so that the whole crumbled.⁵ This penetration of corrosion along internal paths, causing rottenness of the material even when the outer parts are apparently little changed, is of course a special feature of differential aeration attack. It would seem that in McCulloch's experiment the intense attack in the capillary channel below the rubber band is also due mainly to differential aeration, the attack being localized at the anodic points relatively inaccessible to oxygen, while the aerated surface outside the band forms the cathode. The present writer would be the last to deny the importance of capillary forces in some types of corrosion, having indeed attributed to such causes the localized corrosion of iron in chloride-chromate and chloride-carbonate mixtures,⁶ which cause attack to be concentrated mainly at the water line or at the margins of drops. However, capillary action appears to play but little part in the case described by McCulloch.

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ULICK R. EVANS

The Rapid Corrosion of Metals by Acids within Capillaries. Reply to Ulick R. Evans.—In the note on "Corrosion of Metals by Acids within Capillaries"¹ it should have been made clear that the effect described was believed not to be due at all to differential aeration, but to differ from the well-known cases of pitting from the latter cause.

The writer has repeated the procedure described by Evans in the preceding note, using the same test-pieces (rivets), wrapped with rubber bands, as shown in the first note.¹ (These were first cleaned from scale by a short dip into concd. hydrochloric acid.) Three 1-liter bottles were used, each containing about 250 cc. of 1.4 *N* hydrochloric acid, which had been previously boiled and cooled in a vacuum. One bottle was left exposed to the air, one had the air replaced by hydrogen, and the third by carbon dioxide. The latter two were sealed with rubber stoppers, through which glass tubes permitted the escape of gas beneath the surface of mercury. The test was continued for four days.

In a later experiment, the conditions were made more completely air-free by letting boiled acid flow from an evacuated flask into another evacu-

⁵ The "hollow-tree phenomenon" was not caused by the protective action of scale, since the rods were abraded with emery just before immersion.

⁶ Evans, *J. Soc. Chem. Ind.*, **43**, 315T (1924); **44**, 163T (1925).

¹ McCulloch, *THIS JOURNAL*, **47**, 1940 (1925).