the fact observed by Posnjak and Merwin[12] that the compound present in the product of the cyanide process of nitrogen fixation is crystallographically different from ordinary sodium cyanide.

Acknowledgment.—The authors desire to express their indebtedness to Dr. J. M. Braham for suggestions and criticisms during the progress of this investigation.

Summary

The formation of sodium cyanide in a mixture of sodium carbonate, carbon and iron catalyst when heated in nitrogen takes place through (1) the reduction of sodium carbonate to metallic sodium, (2) the formation of sodium carbide from the elements, and (3) the absorption of nitrogen by (gaseous) sodium carbide to form sodium cyanide.

Iron has been shown to exert a marked catalytic effect on the absorption of nitrogen by sodium carbide, but does not appear to be essential for the reduction of sodium carbonate or for the formation of sodium carbide.

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NOTES

Rapid Corrosion of Metals by Acids within Capillaries.—About eight years ago the writer observed an interesting effect of hydrochloric acid upon iron surfaces in capillary spaces. So far as he is aware, this effect has not been previously described, so he feels that it may be well to present it at this time. The following simple experiment, which has been several times repeated, shows the nature of the effect. A rubber band is wrapped rather tightly about a piece of soft iron. The iron is immersed in dil. hydrochloric acid for a week or two. At the end of this time, the iron will be found to have been eaten away or pitted beneath the rubber. The acid has acted more rapidly within the capillary spaces between the rubber and the metal than it has upon the exposed surfaces. The experiment was modified, with the same result, by clamping two flat pieces of iron together and immersing them in acid. Also, the action was observed visually by using a glass slide attached to a flat piece of iron. Beneath the glass the capillary space was seen to be largely filled with greatly flattened bubbles, the boundaries of which were in slow but constant motion. The bubbles would extend till the edges of the slide were ap-

Original surface.

After pickling in HCl, showing pitting effected beneath a rubber band.

Fig. 1.

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[12] Posnjak and Merwin, *J. Wash. Acad. Sci.*, **9**, 282 (1919).

proached, when suddenly a break to the edge would occur, and small bubbles would be ejected with violence into the outer liquid. The contracted bubble would then resume its growth as before. There was thus a continual washing of the capillary surfaces, which may be partly responsible for the more rapid action there.

There is, however, a more important reason for this more rapid attack of the metal in the capillaries. This explanation is based on the belief that the rate of solution of a metal in a non-oxidizing acid is limited partly by the concentration of dissolved hydrogen at the metal surface. Solution of the metal may occur no faster than the hydrogen can escape from its surface. Now if the pressure of dissolved hydrogen is too low to cause bubbles to form, the escape of hydrogen must take place by diffusion and convection through the liquid into the atmosphere above, and will in general be very slow. When, however, a bubble lies upon the metal surface, an easy way of escape is offered the hydrogen, and the pressure in the solution is relieved at this point. This permits the metal beneath and about the bubble to dissolve at an increased rate, leaving a pit into which the bubble or its successors will sink. This may then be the explanation for the more rapid corrosion within the capillary spaces. The capillaries become filled with flattened or lengthened bubbles, while over the external surfaces small, round bubbles are scattered only here and there. The capillary surfaces are for this reason the more rapidly corroded.

This explanation is that of MacInnes and Adler[1] for hydrogen overvoltage, which they attribute to supersaturation of the surface with hydrogen, finding that a fall in overvoltage occurs when a bubble appears upon the cathode surface. Minute bubbles retained in capillaries may be the principal nuclei at which bubbles of hydrogen are liberated. A porous metal will then have a lower overvoltage than the same metal having a perfectly continuous surface.[2]

For this effect of acids in capillaries to be well observed two conditions are essential. First, the acid must not attack the metal with too great ease, else the solution within the capillaries will become rapidly exhausted, and the outer metal will be the more rapidly corroded. Second, the metallic product formed within the capillary must be soluble, else the capillaries will become clogged and the action cease from this cause, as is the case with dil. phosphoric acid and iron.

Such a capillary effect is encountered in the deep etching and pickling

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[1] MacInnes and Adler, THIS JOURNAL, **41,** 194, 2019 (1919).

[2] By this means also Whitman and others [*Ind. Eng. Chem.*, **15,** 672 (1923)] account for the greatly decreased rate of corrosion of a steel shaft in sulfuric acid when rotated rapidly. The evolution of hydrogen is rendered more difficult because the metal surface is washed free from hydrogen bubbles.

of metals with non-oxidizing acids. The pores and intergranular spaces of the metal may be enlarged, the action proceeding deep within the interior of apparently sound metals. Capillaries probably play their part, also, in the ordinary corrosion of unsound metals. Even when metals are apparently sound, pores too small to be detected with the microscope may be the obscure cause of deep penetration and pitting. This type of corrosion may be looked for in the case of metals submerged in the absence of oxygen. Wherever bubbles can be retained there may be more rapid action.[3]

It is believed that this type of corrosion is quite important and worthy of further study.

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A Simple Differential Air Thermometer for Use at Low Temperatures.—Having occasion recently to separate mixtures of nitric oxide, nitrous oxide, hydrogen chloride and nitrosyl chloride and to examine the mixtures for other possible gases boiling at intermediate temperatures, I have devised a simple air thermometer for the approximate determination of temperatures between the boiling point of liquid air and zero.

A bulb with a capacity of 2.5 to 5 cc. is blown at the end of a capillary tube 50 cm. in length and with an internal diameter of about 0.8 mm. A small globule of mercury, enough to occupy a length of about 5 mm. of the capillary, was introduced and, by cooling the bulb slightly, this was brought to a position about 100 mm. from the end, and the end was sealed. It is evident that if the temperature of the air in the capillary above the globule remains constant, and we disregard the small change in the volume of the air below the mercury and the transfer of air from the capillary to the bulb, the pressure in the bulb will vary directly as the absolute temperature. Taking the length of the column of air above the mercury as 1 at 0°, the length at any other temperature may be calculated, approximately, by the formula $273 \times 1/T$, in which T is the absolute temperature. The calculation gives the following values.

Temp., °C.	0	−10	−20	−30	−40	−50	−60	−70	−78.5	−80	−90
$273 \times 1/T$	1	1.039	1.079	1.123	1.172	1.224	1.282	1.345	1.404	1.414	1.492

Temp., °C.	−100	−110	−120	−130	−140	−150	−160	−170	−180	−190	−191.6
$273 \times 1/T$	1.578	1.674	1.784	1.908	2.052	2.219	2.415	2.649	2.936	3.286	3.351

With the temperature of the room at 25°, three points are fixed on the stem for the top of the mercury when the bulb is immersed in melting ice,

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[3] Shipley, McHaffie and Clare, *Ind. Eng. Chem.*, **17**, 381 (1925).