monovalent and colorless. When the third level or shell is incomplete, 2–8–17, it is bivalent and colored. Iron may have the kernel 2–8–13, or the kernel 2–8–14; both states are incomplete and the ions are colored. Possibly, the non-existence of color in elements with incomplete kernels is due to the fact that absorption bands lie outside the visible spectrum. This is known to be true for the rare earth gadolinium which has a number of bands in the extreme ultraviolet. The explanation of the source of color given by Stieglitz[5] accounts for the color of ions having a variable valence as "by the proximity of a strong reducing atom to a strong oxidizing atom," but makes no mention of the color of the rare earth ions which have, in most cases, a fixed valence.

Another interesting feature of the chart is that a fairly uniform curve may be drawn through the following bands: Nd 1606, Il 1719, Sm 1788, Eu 1902, Tb 2049, Dy 2103 and Ho 2198. Europium has only two bands, very close together, and terbium only one in the region covered by the chart. The most prominent band of illinium also lies close to the curve. The fact that these bands occur in such regularity and are of increasing frequency with increasing atomic numbers, as may be expected from analogy with X-ray and spark spectra, would indicate a basic similarity in the electron shift causing the band.

It is probably accidental that so many absorption bands do fall within the narrow limits of the explored spectrum. An extension of the study to the ultraviolet and the infra-red should, in many cases, reveal the presence of many more bands and aid in the study of atomic structure.

Summary

1. The presence of color in the rare earths and some common elements seems to be due to an incomplete kernel.
2. A relationship among the spectra of some of the rare earths is pointed out.

URBANA, ILLINOIS

NOTES

The Diffusion of Helium and Hydrogen through Quartz Glass at Room Temperature.[1]—The permeability of silica glass to helium and other gases at high temperatures has long been known[2] and its permeability to helium and hydrogen at room temperatures has been suspected, various observers[3] having reported the apparent loss of these gases from quartz glass bulbs

[5] Stieglitz, "A Theory of Color Production," The Franklin Institute, **1924.**

[1] Presented at the New Haven Meeting of the American Chemical Society, April, 1922.

[2] Jacquerod and Perrot, *Compt. rend.*, **139**, 789 (1904). Williams and Ferguson, THIS JOURNAL, **44**, 2160 (1922).

[3] Keyes and others, *J. Math. Phys.*, **1**, 289 (1922). Henning, *Z. Physik*, **5**, 264 (1921).

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
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McCulloch's Observations Regarding the Rapid Corrosion of Metals by Acids within Capillaries.—A recent Note in This Journal by McCulloch[1] records an instance of marked localized corrosion set up where a

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[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 writer[2] 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 writer[3] 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,

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[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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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-

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[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).

ated flask (300 cc.) containing four of the rivets. When the latter flask was completely filled, a rubber tube dipping beneath mercury was cut to make a way for hydrogen to escape. A parallel test was made with some of the same acid to which air was admitted.

The writer agrees with Evans that the grooving about the rubber bands is less distinct in the air-free acid than it is when air is present, but he does not find that the effect ceases to exist at all. The fact that the grooves are less distinct is attributed to a more rapid attack of the surface as a whole, rendering the action within the capillary spaces less only by comparison.

It is admitted that differences in oxygen concentration, where such exist, may be a contributing cause, but not the principal cause of the capillary corrosion. There may be electrolytic action due to the lowering of hydrogen concentration in the neighborhood of bubbles resting upon an oxygen-free surface. Further work should be done to find out how important this effect may be.

There is a marked difference in the manner in which the air-free acid acts upon the iron surfaces. The air-free acid attacks the surface smoothly and uniformly, while the aerated acid acts more strongly within the pores of the metal. Measurement was made of the decrease in thickness of the exposed portions of the rivets under the two conditions. The average decrease in the aerated acid was in the two experiments 0.025 mm. and 0.05 mm. In the air-free acid the losses were 0.25 mm. with carbon dioxide, 0.175 mm. and 0.10 mm. with hydrogen. The losses in weight were not concordant, however, for in the first experiment, five rivets in aerated acid lost 1.68 g., and five under hydrogen, 2.59 g., while in the second experiment, four in aerated acid lost 4.14 g., and four in air-free acid 4.03 g. These erratic weights may be explained by variations in structure of the iron, rendering it easier for the acid to attack between the fibers in some pieces than in others. It is plain that there is much room for further work upon these problems.

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An Improvement of the Cobalt Aluminate Test for Aluminum.—When a supposed precipitate of aluminum hydroxide is dissolved in nitric acid, treated with a few drops of cobalt nitrate and then reprecipitated and ignited on a platinum wire according to the method given by Noyes[1] great dexterity is required to prevent the precipitate, which shrinks on ignition, from falling off the wire. The foregoing procedure is a modi-

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[1] Noyes, "Qualitative Chemical Analysis," MacMillan, **1922**, 9th ed., p. 99.

fication of that recommended by Noyes, Bray and Spear[2] in that the hydroxide of aluminum is reprecipitated with cobalt hydroxide adsorbed onto it before ignition instead of a piece of filter paper dipped into a solution of the mixed nitrates being ignited. In each procedure the ignition of the filter paper with the precipitate is specified.

On attempting to surmount the difficulty described above, it has been found that the decrepitation can be prevented by moistening the lump of precipitate with a small drop of concd. sulfuric acid before heating it. The presence of a small amount of filter paper mixed with the precipitate is immaterial, but an attempt should be made to take up as little paper is possible; this eliminates its subsequent oxidation. The drop of acid as added best by means of a stirring rod, not by dipping. The acid dissolves the combined aluminum and cobalt precipitate, forming sulfates which remain on the wire when the water and excess acid are evaporated and, when strongly heated, become a dull, dark blue mass.

Precipitated silicic acid, which is the substance usually mistaken for aluminum hydroxide, does not dissolve readily in the concd. sulfuric acid. When evaporated and strongly heated this yields a fusible, shiny blue mass easily distinguished from the former. When a mixture of approximately equal amounts of silica and aluminum hydroxide is treated in this way the cobalt and aluminum hydroxides dissolve immediately in the acid. The silicic acid, being slow to dissolve, remains segregated and on strong heating gives a bead of fusible cobalt silicate while the rest of the wire is coated with the dull, dark blue of cobalt aluminate.

The delicacy of the test by this procedure is about the same as that by the method of Noyes, but the manipulation is easier for students to execute. It has been tried by a class in qualitative analysis and has given results more satisfactory than the usual method.

CONTRIBUTION FROM THE CHEMICAL LABORATORY
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A Boiling-stirring Rod to Prevent Bumping.—The prevention of bumping in boiling liquids has been the subject of much study, and many devices have been suggested to effect it. The one most often advocated is some adaptation of the capillary tube, which functions fairly well in some cases but cannot be used under all conditions, especially in quantitative work, and it has many limitations.

The rod here described possesses all of the advantages and none of the limitations of the capillary tube; it is suitable for quantitative work, functions satisfactorily, even when a precipitate is present, and it is

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[2] Noyes, Bray and Spear, THIS JOURNAL, **30**, 544 (1908).

quite easily made, either from a piece of glass tube or a solid glass rod, as may be preferred.

When made from a piece of tube, the end is closed by rotating in the flame and is slightly blown out. It is then reheated at the extreme tip and when the pressure on the inside is reduced, a small dimple, or bellshaped depression is formed in the end. When made from a glass rod the depression may be formed with a piece of pointed hard carbon, care being exercised in either case to form the depression exactly in the end of the rod, the size and depth of the depression being rather unimportant. For quantitative work it should be of such size that any adhering precipitate can be easily removed with a small piece of filter paper.

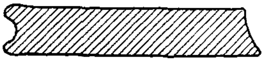
Fig. 1.—A boiling-stirring rod to prevent bumping.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
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[CONTRIBUTION FROM THE UNIVERSITY OF VERMONT]

NORMAL BUTYLBENZENE

BY R. R. READ AND L. S. FOSTER

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During a study[1] of certain derivatives of normal butylbenzene it became necessary to prepare a considerable quantity of that material. Of the two methods available for the preparation, the Fittig and the Grignard, the former was chosen due to the more readily available materials.

Descriptions and comments regarding this reaction found in the literature do not encourage attempts to conduct the operation on a moderately large scale in the laboratory, yet it may be so carried out that the high yield and simplicity of operation leave little to be desired.

Experimental.—A copper kettle, the size of a gallon (3.8 liter) pail, was made of heavy material and fitted with the tinned iron friction ring and cover of such a pail. Three holes were cut in this cover and connections about 2 cm. in length and diameter soldered in place. The outlets were fitted with a dropping funnel, a thermometer well, and a reflux condenser (preferably an all-metal one) and the kettle was placed in a bath of running water so that it was immersed to within 5 cm. of the top.

Four hundred and sixty g. of sodium was prepared by rolling under a cement lawn roller, or slicing into pieces 2 mm. thick, and placed in the

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[1] This study is directed towards the determination of the disinfectant power of phenol as influenced by groups placed in the various positions about the ring. The writers are indebted to Treat B. Johnson of Yale University for opening the field to them.