phan.[6] The medium of Stokes, *et al.*,[7] was employed with *Streptococcus faecalis* R which was incubated for thirty-seven hours at 31°. The tests were conducted at a number of levels of tryptophan, and the results obtained are shown in Fig. 1.

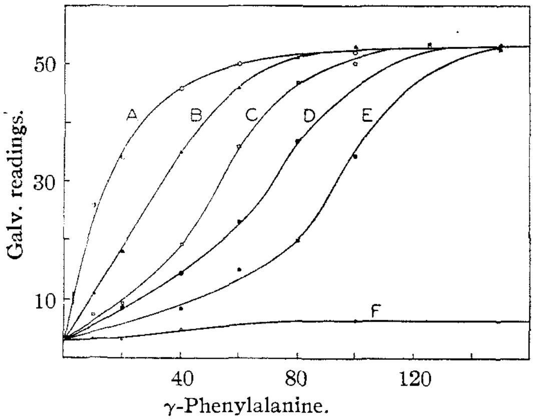

Fig. 1.—Prevention of the toxicity of *dl*-tryptophan for *Streptococcus faecalis* R by *dl*-phenylalanine: Curve A, 2000 γ *dl*-tryptophan per 10 cc. of culture medium; Curve B, 4000 γ; Curve C, 6000 γ; Curve D, 8000 γ; Curve E, 10,000 γ; Curve F, 0 γ. Galvanometer readings, a measure of culture turbidity; distilled water reads zero, an opaque object 100. γ-Phenylalanine, quantity of phenylalanine per 10 cc. of culture medium.

As shown, *dl*-tryptophan prevented growth of *Streptococcus faecalis* R when relatively low concentrations of phenylalanine are present, and the inhibition was competitive in nature; *i. e.*, it became apparent only when the *ratio* of tryptophan to phenylalanine exceeded a certain value and was independent of the absolute amount of inhibitor over the range of concentrations of the tests. Over this range of concentrations, a ratio of *dl*-tryptophan to *dl*-phenylalanine of about 100:1 was sufficient to cause a 50% inhibition of growth as measured turbidimetrically. Such an effect indicates that tryptophan competes with phenylalanine for an enzyme, the functioning of which is essential for growth of the organism. Similar effects may be observed with *l*-tryptophan in place of the racemic form and with *Lactobacillus casei* and *Staphylococcus aureus* as well as with *Streptococcus faecalis* R.

While it is admittedly improbable that ratios of tryptophan to phenylalanine of the magnitude of 100:1 would ever actually exist in nature, it is of importance to realize that such natural analog-metabolite pairs do exist, and that they may by cumulative effects constitute a complex system of biological balances and controls.

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(6) E. Beerstecher, Jr., and W. Shive, *J. Biol. Chem.*, **164**, 53 (1946).

(7) J. L. Stokes, M. Gunness, I. M. Dwyer and M. C. Caswell, *ibid.*, **160**, 35 (1945).

THE CLAYTON BIOCHEMICAL INSTITUTE
AND THE DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF TEXAS
AUSTIN, TEXAS
RECEIVED SEPTEMBER 30, 1946

Surface Area of Chrome-Plated Nickel

BY CALLAWAY BROWN AND HERBERT H. UHLIG*

In studies of reaction rates on apparently plane metal strips, the area available for reaction is an important undetermined factor. Bowden and Rideal,[1] from studies of electrolytic hydrogen deposition on metal electrodes, conclude that the interfacial area may be very much higher than the apparent or projected area even on apparently smooth surfaces such as polished silver, and annealed, electroplated or rolled nickel. Although these results appear entirely consistent, the method is indirect and the significance of the "accessible" areas obtained has not been clarified by independent measurements.

Quantitative determination of the area of a gas-solid interface by low-temperature adsorption of inert gas[2] has been applied largely to powdered materials because of the large ratio of surface to volume available. However, by use of an adsorption reagent at very low temperature and pressure, surface areas smaller than 100 sq. cm. may be measured.[3] We have applied this low-pressure adsorption technique to strips of chrome-plated nickel and find a large ratio of accessible to apparent area, sensitive to the previous history of the sample. This result confirms a similar conclusion[4] based on studies of the quantity of passive iron adsorbed on electrodeposited chromium.

Preliminary tests with ethylene showed that large quantities of this gas were sorbed by chrome-plated nickel at room temperature and at low pressure. The sorption was irreversible and increased slowly for many hours, typical of activated adsorption. This complication made ethylene unsuitable for surface area determination by physical adsorption at low temperature, but it is of interest that the quantity of ethylene ultimately sorbed at room temperature and at very low pressure was sufficient to cover in a unimolecular layer an area about 20 times the apparent area. Sample 3 in Table I, taken from the same lot of chrome plate, was later found to have a ratio of accessible to apparent area of 49, so that the ethylene sorbed actually covered less than one half the accessible area.

Ethane at −183° was chosen for the low temperature work as it was practically unadsorbed at room temperature and equilibrated rapidly and reversibly at −183°. Nickel strips 5 cm. wide, 15 cm. long, and approximately 0.6 cm. thick were chrome-plated by standard commercial practice. A single strip was usually cut in half, cleaned with fine silica sand, washed with

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* Present address: Dept. of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.

(1) F. Bowden and E. Rideal, *Proc. Roy. Soc.* (London), **A120**, 59, 80 (1928).

(2) S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).

(3) L. A. Wooten and C. Brown, *ibid.*, **65**, 113 (1943).

(4) H. H. Uhlig, unpublished data.

distilled water, and the two halves were placed in a bulb of approximately 120-ml. capacity. The sample bulb was then sealed to the low-pressure adsorption apparatus[3] with special care to avoid heating the metal strips in the glass-blowing operation. The sample was baked at 400° with continual pumping for several hours until the pressure fell below 5×10^{-5} mm. A large quantity of gas was evolved during the bake-out, presumably hydrogen from the electroplating process.

It was necessary to cool the sample to bath temperature (liquid oxygen) in the presence of several mm. of helium, after which the helium was pumped out and ethane admitted. Typical BET plots[2] are shown in Fig. 1. The limited pressure range covered was due to the large amount of gas adsorbed relative to the capacity of the apparatus, but since the intercept is ordinarily close to the origin, the slope of the lines is reasonably well established. The vapor pressure of ethane at −183° was 8.9×10^{-3} mm. The effect of thermal transpiration on all pressure readings remains undetermined so detailed analysis of the adsorption isotherms is unjustified, but the main conclusions of the present work can hardly be affected.

Results for three samples are summarized in Table I.

TABLE I

SURFACE AREA OF CHROME-PLATED NICKEL STRIPS

Apparent area is 150 sq. cm.

Sample	Treatment	V_m, cc. 1 mm., 25°	Surface area, sq. cm.	Accessible area / Apparent area
1	Plated	35	2300	15
	Plated-etched	60	4000	27
2	Plated	28	1800	12
	Plated-etched	21	1400	9.4
3	Plated	110	7300	49
	Plated-etched	120	8000	53

The V_m column was calculated in the usual way[2] from the slope of the BET plots and then corrected for the comparatively small adsorption (10%) on the walls of the sample bulb. The conversion factor, 67 sq. cm. per cc. (1 mm., 25°) of ethane adsorbed in a monolayer is based on an average cross section of 20.5×10^{-16} sq. cm. from X-ray data on solid ethane.[5] This factor has been found to give the correct area within 10% for fused quartz beads with an average diameter of 0.144 mm. determined microscopically.[6]

The thickness of chromium plate in sample 1, measured using micrometers, was about 0.5 mil. compared with 1.5 mils. for sample 3. The thicker plate on sample 3 may account for the greater accessible area of the specimen, since a porous structure appears to be necessary to account for the large area. Samples 1 and 2 were cut in half after plating in order to use a sample bulb of moderate size, but sample 3 was run as a single strip with the electroplate intact. After the result for the plated sample was obtained, the sample was removed from the bulb and sprayed with warm 1.5 N hydrochloric acid until hydrogen was evolved over all the surface. The hydrochloric acid was washed off with distilled water and the sample rerun to obtain the "plated-etched" result.

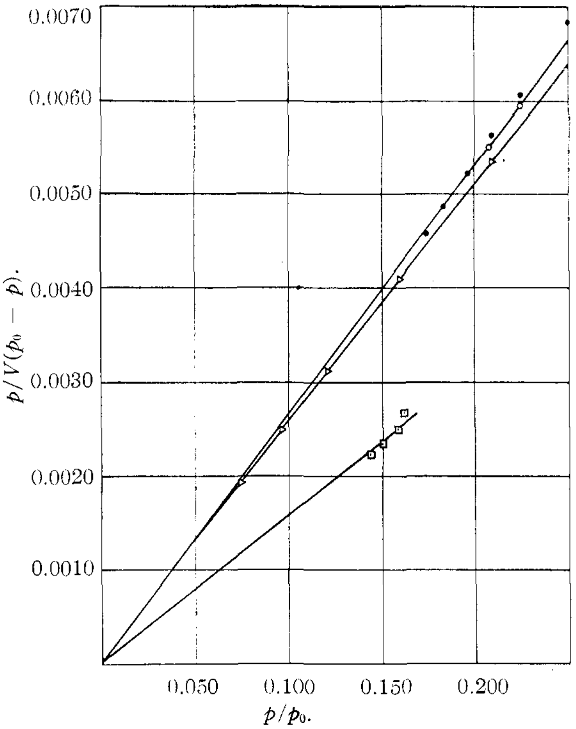

Fig. 1.—BET[2] plots for ethane at −183° on chrome-plated nickel: ⊙, initially; □, after hydrochloric acid etch; △, glass bulb only—ordinate × 10.

Photomicrographs of the etched surfaces also show differences in the two plates (Figs. 2 and 3) although it is not certain that the appearance in any way is related to the measured surface. The surface cracks and fissures are typical of chromium electroplates.[7] The cracks plus a net work of protuberances and deep valleys visible at higher magnification, or with the electron microscope as illustrated by etched copper,[8] are consistent with the large measured accessible surface.

The present results show that a large ratio of accessible to apparent area exists for electrodeposited chromium and that the magnitude of the accessible area is sensitive to the previous history of the surface. Further work is necessary to relate the accessible area to the thickness and age of the plate as well as conditions under which the electroplating was carried out. Our results make

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[5] S. B. Hendricks, *Chem. Rev.*, **7**, 431 (1930).

[6] C. Brown and L. A. Wooten, unpublished data at Bell Telephone Laboratories.

[7] N. Hackerman and D. I. Marshall, "Electrochemical Society Preprint 89-15," April 15, 1946.

[8] C. S. Barrett, "Structure of Metals," McGraw-Hill Book Co., New York, N. Y., 1943, p. 223.

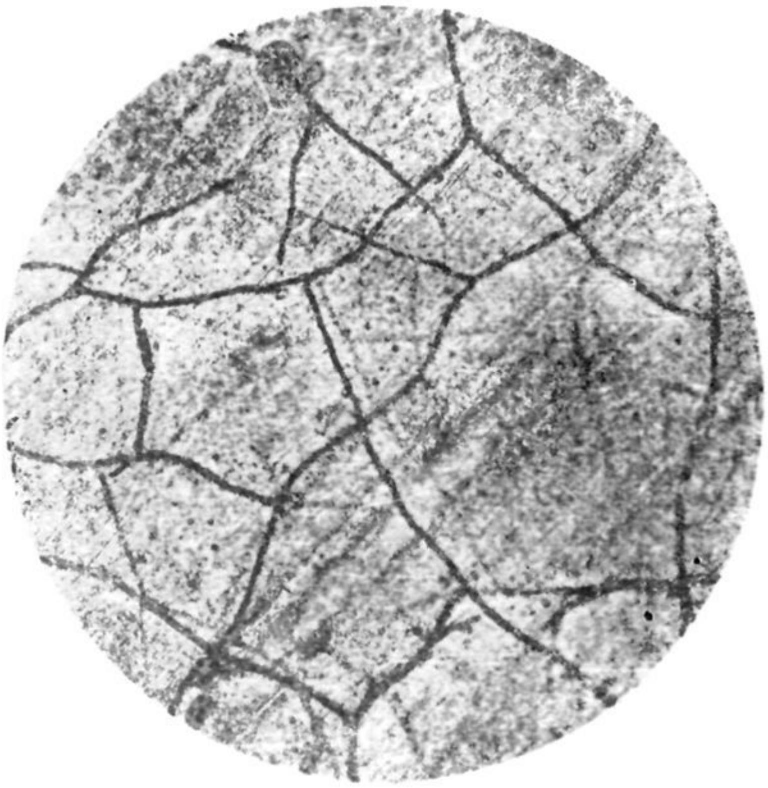

Fig. 2.—Photomicrograph (375×) of chrome-plated nickel; sample 1, thickness 0.5 mil., surface ratio—27.

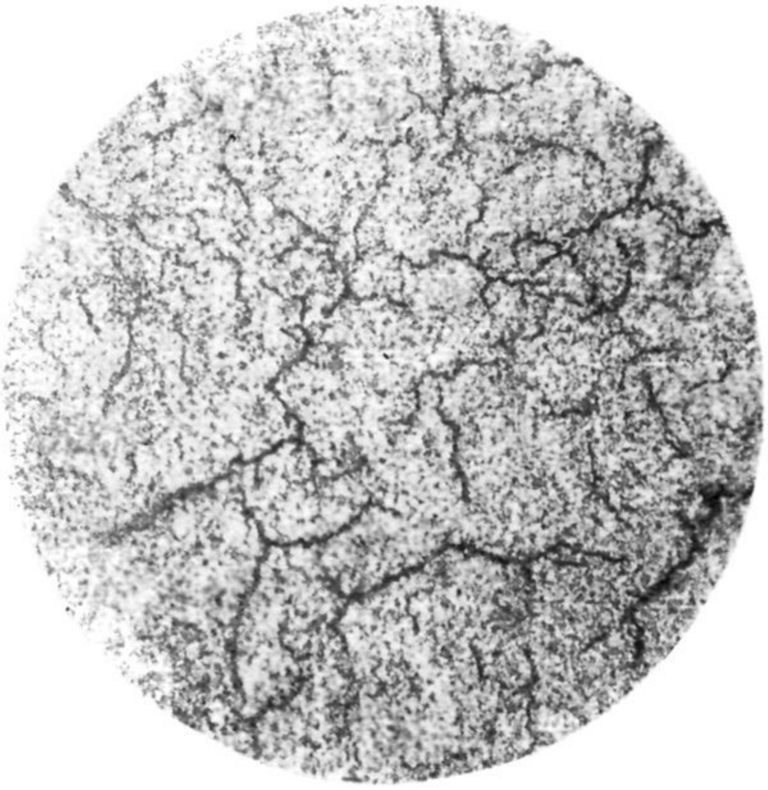

Fig. 3.—Photomicrograph (375×) of chrome-plated nickel; sample 3, thickness 1.5 mil., surface ratio—53.

plausible the previous claims of Bowden and Rideal pointing to a ratio as high as 50 of accessible to apparent area for etched silver, and a surface ratio of 12 for electrodeposited nickel, and furthermore indicate that these high ratios may apply to metals in general with similar preparation.

RESEARCH LABORATORY
GENERAL ELECTRIC CO.
SCHENECTADY, NEW YORK

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Reaction of Some Furan Derivatives with Formaldehyde and Amine Hydrochlorides

BY R. F. HOLDREN

A recent communication[1] described the reaction of 2-methylfuran with formaldehyde and various amine hydrochlorides. A further study of this reaction as applied to other furan derivatives is reported herein.

Marini[2] has reported that the sulfuric acid condensation of ethyl 2-furoate and methylolphthalimide gave ethyl 5-phthalimidomethylfuran-2-carboxylate. In the present work no reaction was observed with compounds which contained a negative group attached to the furan nucleus, *e. g.*, 2-furoic acid and ethyl 2-furoate.

Although furfuryl acetate reacted slowly with formaldehyde and ethyl amine hydrochloride at 60°, no simple product could be isolated from the mixture. Apparently the ester first hydrolyzed to furfuryl alcohol which then reacted to give polymeric substances. That this is the case is inferred from the fact that furfuryl alcohol gave only resins under the same conditions. In contrast to this it was found that furfuryl acetate reacted readily with benzylamine hydrochloride at 30°. However, the product decomposed on distillation *in vacuo,* thus preventing the isolation of any pure material.

Furfuryl cyanoethyl ether reacted readily with formaldehyde andethylamine hydrochloride. Again the product was found to decompose on vacuum distillation. In these last two cases all attempts at purification by crystallization of the hydrochlorides from the reaction mixture were of no avail.

Furfuryl alcohol reacted with formaldehyde and dimethylamine hydrochloride at 30° to yield 5-dimethylaminomethylfurfuryl alcohol. Morpholine hydrochloride behaved in the same manner to give 5-N-morpholinomethylfurfuryl alcohol. The acidic nature of the hydrochlorides caused considerable polymerization of the furfuryl alcohol in both instances. Only resins could be isolated on reaction of furfuryl alcohol with ammonium chloride and ethylamine hydrochloride.

Experimental

All melting and boiling points are uncorrected. Hydrochloride salts were prepared as described in the previous communication.[1]

Furfuryl Cyanoethyl Ether.—This compound was prepared in 95% yield by the method of Bruson and Riener,[3] using 40% potassium hydroxide as a catalyst. No reaction occurred if benzyltrimethylammonium hydroxide was used as a catalyst. Since the ether has been reported only in the patent literature,[4] some physical constants are given below: b. p. 100–101° (1 mm.), $n^{30}{}_{D}$ 1.4742; b. p. 109–110° (2 mm.), d_{30} 1.090.

The reaction product of the ether with formaldehyde

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(1) Holdren and Hixon, THIS JOURNAL, **66**, 1198 (1946).

(2) Marini, *Gazz. chim. ital.*, **69**, 340 (1939) [*C. A.*, **33**, 8607 (1939)]. The author is grateful to the referee for calling his attention to the prior work.

(3) Bruson and Riener, THIS JOURNAL, **65**, 23 (1943).

(4) Bruson, U.S. Patent 2,280,790 (1942).