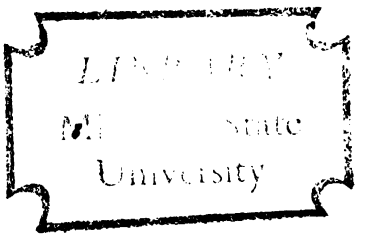
THE DIFFUSION OF HELIUM, HYDROGEN, NITROGEN, AND AIR THROUGH ELECTROLYTIC NICKEL

Thesis for the Degree of Ph. D

MICHIGAN STATE COLLEGE

Russell H. Fay

1954



THE DIFFUSION OF HELIUM, HYDROGEN, NITROGEN, AND AIR THROUGH ELECTROLYTIC NICKEL

By

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THESIS

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1954

ACKNOWLEDGMENTS

The author wishes to express his sincere thanks to Dr. Dwight T. Ewing under whose inspiration, constant supervision, and unfailing interest these investigations were undertaken. He is also deeply indebted to Mr. Bernard C. Case for many helpful suggestions as well as to Dr. Otto Kardos. The assistance of Dr. Austin J. Smith in critically reviewing the thesis is greatly appreciated. A grant from the Hanson-Van Winkle-Munning Company under which these studies were made is also gratefully acknowledged.

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TABLE OF CONTENTS

INTRODUCTION

Discontinuities or pores in electrodeposited metals have been held responsible for the failure of these metals to protect adequately the base metal which they cover. In the present work this porosity was studied by measuring the rate of diffusion of gases through thin electrolytic nickel foils at overpressures of one atmosphere or less. The effect of different gases, air, hydrogen, helium, and nitrogen was studied and their rate of diffusion correlated with Grahams Law.

Corrosion of electrolytic foils had been previously reported to greatly increase the permeability of these foils to gases after a brief initial period in which the permeability was affected very little. This effect of corrosion was evaluated in two corrosive media.

The diffusion of ions in liquid media through electrolytic nickel foils was investigated to attempt to determine the size of the pores which were present in the electrodeposit.

HISTORICAL BACKGROUND

Diffusion of Gases Through Metals

The first recorded observation of the diffusion of gases through metals was that of Cailletet (1) in 1863. He found that nascent hydrogen, produced by immersing an iron vessel in dilute sulfuric acid would, in part, pass through the iron vessel and appear on the inside of the vessel. If the vessel was made cathodic in an electrolytic cell the rate of diffusion was increased and the diffusion would proceed even with a pressure inside the vessel of twenty atmospheres. However, if the vessel was surrounded by molecular hydrogen there was no noticeable diffusion at room temperature. At 350°C. diffusion could be measured and the rate of diffusion increased rapidly with further temperature increases. Subsequent investigations (2,3) have shown that the rate of diffusion of molecular gases through metals is proportional to the square root of the overpressure at high and intermediate overpressures. However these extrapolated isotherms would not pass through the origin, but rather, intersect the abscissa at a value which is less, the greater the temperature. Careful measurements indicate that at low overpressures the rate of diffusion departs from its dependency on the square root of the overpressure and the values do pass through the origin. This indicates that there is no "threshold overpressure" necessary to initiate the diffusion process.

The differing permeabilities, which various metals exhibit when exposed to gases, was ascribed by Fast (4) to the property of the gas to form a compound with the metal, the diffusion rate of the gas being high if compound formation were possible. Rhines (5) postulated that a gas would diffuse through a metal in those instances in which it was soluble in the metal. The behavior of the halogen gases which react readily with most metals, but do not diffuse through any metal to any great extent, disprove Fast's statements. The rare gases cannot, of course, form compounds with any metal. It has been reported (6) that the rate of diffusion of helium through copper, nickel, or molybdenum, if it proceeds at all, must be at least 10^5 times slower than the rate of diffusion of common gases.

Characteristics of Electrodeposited Metals

It was recognized as early as 1887, that one metal deposited upon a second metal, did not cover the second metal continuously until it had reached a considerable thickness. Oberbeck (7) investigated the thickness of a metal necessary before a platinum electrode would assume the electromotive potential of the deposited metal. This thickness was computed from the weight of the deposit and found to be two to three millimicrons for zinc, one to two millimicrons for cadmium, and one millimicron for copper; hence it appears that several atomic layers must be built up before the base metal is completely covered.

Electrodeposited metallic coatings can be divided into two types depending on their relative position in the electromotive series, in relation to the base metal which they are protecting. If the coating is less noble than the base metal, the protection is of a sacrificial nature; the base metal is protected because the coating is preferentially attacked, hence the base metal is protected despite minor discontinuities in the coating.

However, in the case of coatings more noble than the base metal, if there are any discontinuities in the coating, the presence of the coating may actually be detrimental, since this will restrict the anodic areas to those areas where discontinuities exist and thus greatly increase the corrosion of the base metal at these locations. The two dissimilar metals form a galvanic cell. The potential existing between these metals is dependent only upon the two metals and the electrolyte with which they are in contact. This potential is, of course, independent of the relative areas of the two metals. Any current flow, as a result of this potential, must obey Ohm's Law. If the anodic reaction is the dissolution of the base metal, with large anodic areas the loss of metal might not be objectional. In the case of a restricted anode area, in which the same amount of current must flow and hence the same amount of metal removed but from a smaller area, a rapid failure of the base metal at this particular point may occur. These electrochemical reactions may be altered if polarization occurs.

Such discontinuities have been held accountable for the failure of electrodeposited nickel coatings. It is characteristic of such coatings

that they fail in localized areas, the base metal then corroding rapidly from this position while the larger portion of the electrodeposited nickel coating is not visibly affected. It has not been proved that such localized failure is related to discontinuities in the original deposit but it is not unreasonable to expect that they are. Attempts to link the two have been carried on for a considerable length of time. The early attempts were mainly by the use of some chemical reagent, considered noncorrosive to the metallic coating, but which gave a characteristic color reaction with the base metal. Such methods have been severely criticized (8) since it cannot be proved that all pores may be thus identified or that the reagent is noncorrosive to the metallic coating.

Another suggested method is that of photographing nonadherent deposits (9). Obviously this method is limited by the fact that tortuous pores may not allow light to pass, and by the size of the pore which can be determined.

Thon and Kelemen (10) have reported an apparatus for the measurement of the porosity of nonadherent deposits by means of gas permeability. A similar apparatus was used in this work.

A consideration of the manner in which an electrodeposit is formed makes it appear altogether reasonable that these deposits should be more porous than similar sheets obtained from the same metal cast and then rolled to similar dimensions. It is characteristic of an electrodeposit that it does not form uniformly over the base metal but appears to start at discrete points and then grows laterally from these positions.

The reason for this is not clear; it may be due to the presence of "active centers" in the base metal, to the presence of points or projections (perhaps on a microscopic scale) in the base metal, or to the presence of atomic planes having a preferred orientation such that it is easier for the electrons to move to the surface of the base metal at that point. Since the formation of the deposit is in a direction toward the anode it would be expected that discontinuities would develop when these laterally growing grains meet. Electrodeposits are formed at temperatures considerably below the freezing point of the metal and the mobility of the metallic atom at the moment the solid is formed must be considerably less than when the solid metal is formed from a melt; hence it is less likely that the electrodeposited metal will be formed with the atoms in their most stable configuration.

The codeposition of hydrogen has been considered as a factor in the formation of pores. Wood (11) found from x-ray diffraction patterns that electrodeposited nickel had the same lattice constants as metallurgical (i.e., cast and worked) nickel. He observed that the lines were broader for electrodeposited nickel and attributed this to the concentration of hydrogen at the interfaces between crystallites. He calculated these crystallites to be 10^{-5} to 10^{-6} cm in size. Other investigators (12,13,14) attributed this diffuseness of the lines to the crystal size. Crystal sizes ranging from 10^{-3} to 10^{-5} cm were reported.

EXPERIMENTAL

Electrolytic nickel foils were produced from a Watts type nickel solution operated at a pH of 2.2. Four liters of the solution were prepared having the following concentration:

Nickel sulfate	240 grams/liter
Nickel chloride	45 grams/liter
Boric acid	30 grams/liter

The materials were dissolved in distilled water. Sufficient nickel carbonate was added to the solution to raise the pH to about 5.2, fifteen milliliters of 30% hydrogen peroxide per liter of solution was added and the solution allowed to stand overnight. The solution was filtered through #2 Whatman filter paper and the pH lowered to 2.2 by the addition of concentrated sulfuric acid. Seven and one-half grams of activated charcoal (Nuchar) per liter of solution was added, the solution kept overnight with agitation and again filtered through #2 Whatman filter paper. Excess hydrogen peroxide was destroyed by heating the solution. The solution was electrolyzed ten ampere-hours per liter to remove metallic impurities. A corrugated cathode with an average current density of 0.5 amperes per square decimeter was used. The solution was stored in sealed bottles holding two liters each.

Foils were formed electrolytically on panels of rolled steel, the total surface area being about one-tenth of a square foot. The first size panel used measured two by three and one-half inches. Strip

deposits from these panels gave three foils, each large enough for the first permeability apparatus. The foils were taken, one above the other, from the center of the strip deposit. The panel size was subsequently changed to two and seven-sixteenths by three and one-sixteenth inches. With this size panel, six foils, each large enough for the first permeability apparatus, could be obtained. An entire strip deposit of this size was used by the second permeability apparatus.

Both sides of the panel to be used for producing strip deposits were covered with a deposit of electrolytic nickel from the same solution from which strip deposits were subsequently to be produced. In some instances the surface was buffed, in others it was left as deposited. A few foils were electroformed directly on the surface of stainless steel (18-8) panels without an intermediate deposit of electrolytic nickel.

Panels which had been buffed were wiped off with carbon tetrachloride to remove any adhering buffing compound. The panels were cleaned electrolytically using an alkaline cleaner and given an acid dip. The alkaline cleaner was prepared daily with the following concentration:

Sodium hydroxide	21 grams/liter
Sodium metasilicate	15 grams/liter
Trisodium phosphate	18 grams/liter
Sodium carbonate	6 grams/liter

Two liters of this cleaning solution were used. The panel to be cleaned was made anodic, the cathode employed being of rolled steel designed to just fit within the two liter beaker holding the cleaning solution. The cleaning solution was operated at 90 to 95°C.

The acid, also prepared daily, consisted of 20 per cent (volume) hydrochloric acid and was used at room temperature. The timing of the cleaning cycle was varied to produce nonadherent deposits. A typical cycle would be: 20 seconds in the alkaline cleaner, the panel being anodic with a current density of 40 amperes per square foot, rinse in running water, 20 seconds acid dip, rinse in running water, 20 seconds in the alkaline cleaner (anodic, 40 amperes per square foot), rinse in running water, 5 seconds acid dip, rinse in distilled water and deposition immediately started. For thinner foils and foils from unbuffed surfaces it was necessary to increase the time of the electrolytic cleaning and/or the current density (80 to 100 amperes per square foot) and to reduce the time of the acid dip.

The deposition of the nickel foil took place in a one liter rectangular glass jar. Deposition was carried out at a pH of 2.2 $\pm$ 0.05, temperature 55 $\pm$ 2°C. The pH was checked with a Beckman model G pH meter which was tested daily against a standard buffer. At no time was it found necessary to raise the pH; when necessary to lower the pH additions of concentrated acid were made near the anode. For all solutions except "D" concentrated hydrochloric acid was used. For solution "D" a mixture of concentrated hydrochloric acid and concentrated sulfuric acid with the same ratio of chloride to sulfate ions as existed in the original solution was used.

The panel was held in place by an alligator type clip attached to a piece of nickel wire. The panel was placed against the back of the jar so that the deposition of nickel took place predonderantly on one

side of the panel. The solution was agitated with a glass stirrer having two blades, each 1 centimeter by 0.75 centimeter, set 45° to the horizontal (90° with respect to each other). The stirrer was driven at 525 ± 25 revolutions per minute by a variable speed stirring motor. The stirrer was set near the level of the bottom of the panel and nearer the cathode than the anode. Bubbles which formed on the panel but were not removed by the stirrer were dislodged by jarring the panel.

A graph of the efficiency of the plating solution was prepared giving the time necessary to deposit a given thickness of nickel. When sufficient time had elapsed to give the desired thickness of deposit the panel was removed from the solution and rinsed with distilled water. The deposit was then cut with a razor blade about one-quarter of an inch from the edge of the panel. If the surface of the base panel was properly passivated the strip deposit could be removed with no difficulty. For deposits of about five microns or less the strip deposit was removed under distilled water to reduce the likelihood of tearing. The strip deposit was then dried on a sheet of absorbent paper, marked in one corner with its identifying number (pencil), placed in an envelope, and stored in a desiccator over calcium chloride. The thickness of the strip deposit was determined using a micrometer caliper equipped with a ball attachment and reading to the nearest ten-thousandth of an inch. Five or six measurements were taken for each strip deposit and the results indicated that the geometry of the plating cell gave quite uniform deposits. For this reason the thinner foils (eight microns or less) were measured by weighing the foil and computing their thickness.

Each foil was identified by an individual group of characters. The first character (a letter) indicated the liter of solution, as drawn from the stock solution, from which the strip deposit was produced, e.g., A, B, C, D. The second character (a number) indicated the particular panel used as a base plate. The letter "S" preceding the number indicated that the panel was of stainless steel. The third character (a letter) indicated the strip deposit from a particular panel in the sequence in which they were produced, i.e., A, B, C, etc. For the second permeability apparatus an entire strip deposit was used at once. With the first permeability apparatus six test foils could be cut from one strip deposit. These were further identified by the side of the deposit from which they were taken, i.e., with the side of the deposit which was removed from the base plate away from the observer, the left side of the strip deposit was designated as 1 the right side as 2. A final letter indicated the vertical position, the foil taken nearest the bottom of the strip deposit being A, the one from the center B, and the one from the top C.

The strip deposits were checked visually using a thirty-five power binocular microscope and photographed to locate any gross imperfections. The foils were photographed placed in a printing frame. A piece of glass between the strip deposit and the photographic film served to diffuse any light which passed through the strip deposit, thus making any gross pores more easily identified. Aluminum foil was used to mask the remainder of the photographic film. Both Kodak spectrum analysis No. 1 plates exposed 15 minutes and Kodak ortho contrast film exposed

five minutes, twelve inches from a 100 watt filament lamp gave good results.

The permeability apparatus consisted of a vacuum tight system which could be divided into two portions by an electrolytic nickel foil in a special holder. If, then, an overpressure was applied to one side of the foil, the rate at which the gas passed through the foil could be measured on the opposite side of the foil by a McLeod gauge.

A number of foil holders were constructed before one was obtained which was satisfactory. The first holder (Figure 2-/) was constructed of mild steel. A circular foil five-eights of an inch in diameter was held between the two pieces of the holder in such a manner than an exposed area of three-eights of an inch in diameter separated the two portions of the system. The two pieces of the holder were joined by a threaded collar. Each piece of the holder was joined to the permeability apparatus by means of a ground glass joint.

The ground glass joint was sealed to the holder with plicene cement. The ground glass joint connected to the system was attached to glass arms with double bends to give sufficient flexibility to the system so that the holder could be inserted and removed (Figure 1). The foils placed in this holder soon developed concentric cracks under the bearing surface of the holder. Polishing the ends of the holder did not remove the difficulty. A variety of gasketing materials were tried including copper, lead, and nylon, but the same trouble persisted. The holder had been constructed with two graphited rings to prevent twisting of the two parts when the holder was tightened; however, it

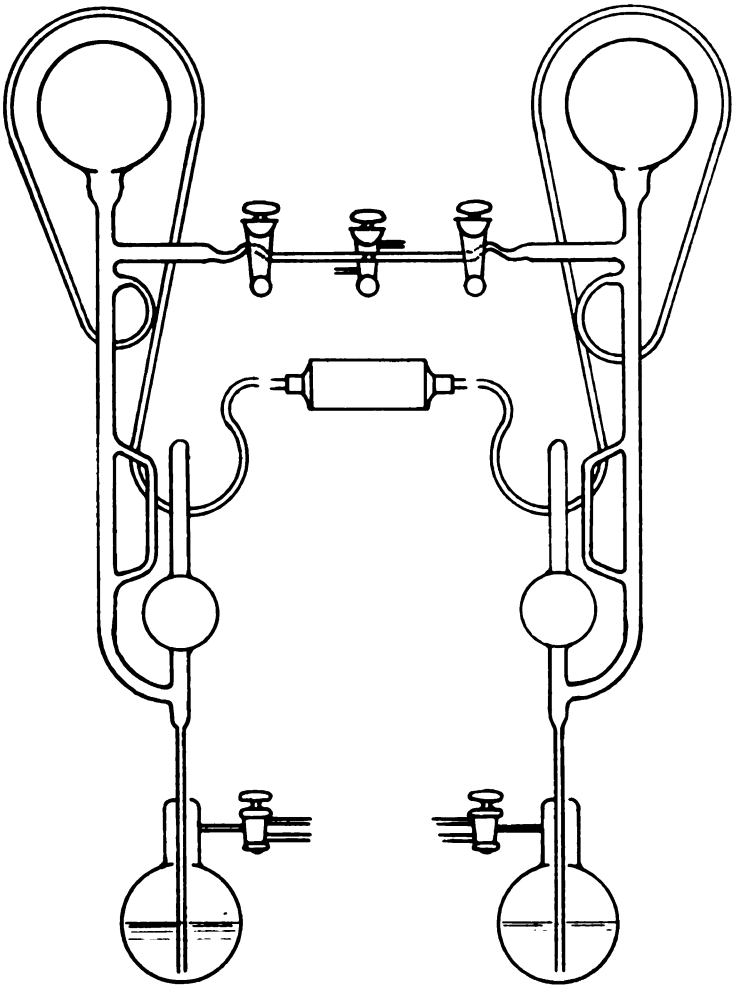

FIGURE 1.

FIRST PERMEABILITY APPARATUS

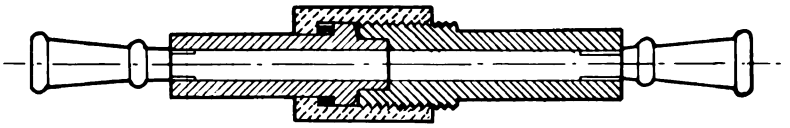

FIGURE 2-A

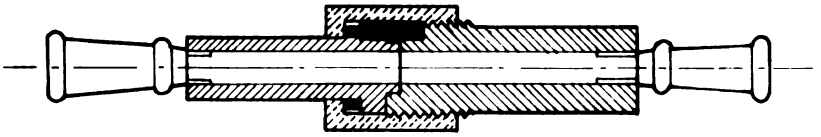

FIGURE 2-B

was felt that there might still be enough twisting action between the two parts to produce the concentric cracks. A second holder (Figure 2-B) was constructed with a keyway so that all twisting of the two pieces could be eliminated. After a few measurements on a foil the concentric cracks still developed.

A third holder (Figure 3-A) was constructed of glass. The foil was sealed to the end of a glass adapter. Silicone high vacuum stopcock grease was used between the foil and the glass adapter. A lucite ring placed over the foil, was sealed, under pressure, to the glass adapter. A number of cements were tried; the one finally selected was glyptal, which did not require heating, that might change the characteristics of the foil, and did not wet the foil, thus it would not creep into the capillaries of the foil and seal them. This holder was later discarded to avoid the use of stopcock grease on the foils.

The first holder was then redesigned, enlargening the cavity into which the foil was placed. The foils were sealed between two lucite rings which had been ground flat. The rings were sealed under pressure using glyptal cement. This method worked satisfactorily and another similar holder (Figure 3-B) was constructed of aluminum. Instead of sealing with a twisting action the two pieces of this holder were joined by six cap screws.

The second permeability apparatus (Figure 4) employed ball and socket joints rather than the flexible glass arms for inserting and removing the foil holder. Manometers were added for measuring the over-pressure used.

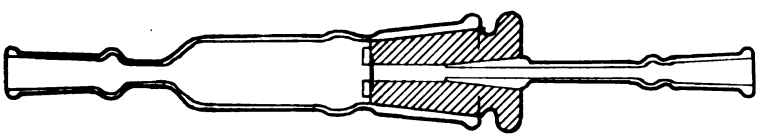

FIGURE 3-A

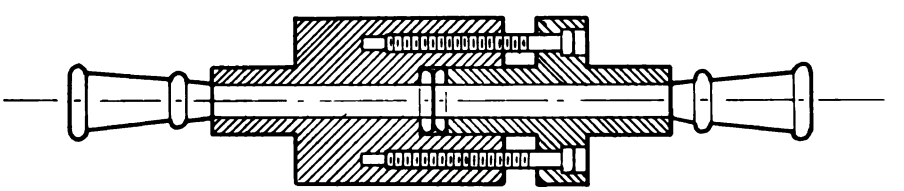

FIGURE 3-B

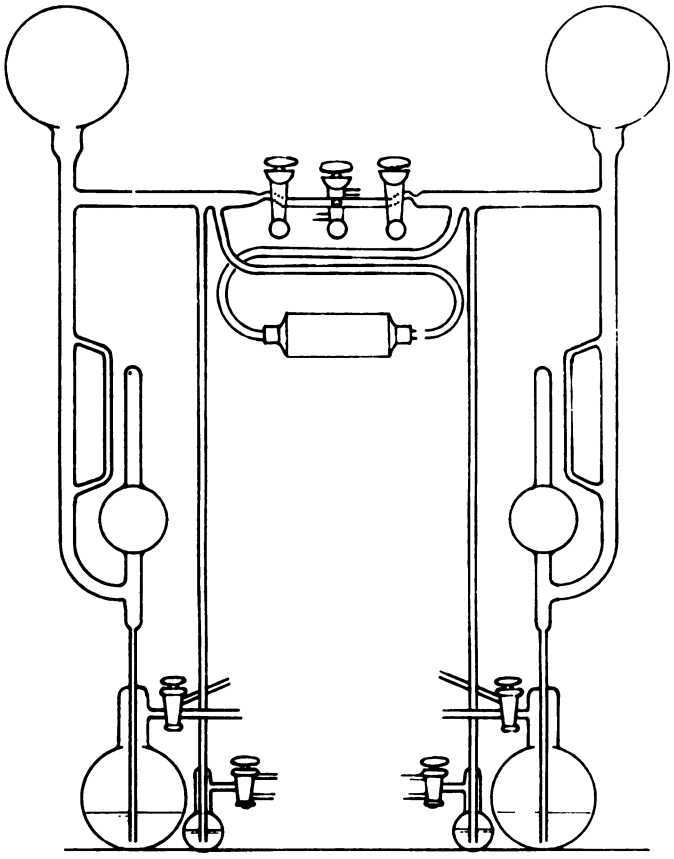

FIGURE 4.

SECOND PERMEABILITY APPARATUS

The foil holder was of a type described by Dr. Thon of Princeton University in unpublished work (Figure 5). Rubber "O" rings stretched the foil taut, eliminating any wrinkling of the foil. The vacuum tight seal was supplied by the raised collar of the aluminum holder. No trouble was encountered with concentric cracks under the bearing surfaces, probably due to the aluminum being a much softer metal.

With the first apparatus, measurements of the pressure increase were made every five minutes for fifteen minutes. After observing an initial lag in the rate of diffusion, the frequency of readings and the interval of time was increased. When the second apparatus was used, readings were taken every minute for twenty-five minutes. The results were plotted on a graph (increase in pressure versus time) and the pressure increase from the five minute reading to the twenty minute reading used to calculate the permeability constant "k". This constant was calculated from the formula developed by Thon and Kaleman (15):

$$k = V/F \times l/\Delta P \times p/t \qquad \text{where}$$

V	is the volume of the low pressure side of the system in liters
F	is the area of the exposed foil in cm^2
ΔP	is the overpressure across the foil in mm of Hg
p	is the increase in pressure (mm of Hg) on the low pressure side of the foil in time interval
t	for which a 15 minute interval was used

the units of this "k" are liters-cm^{-2}-min^{-1}.

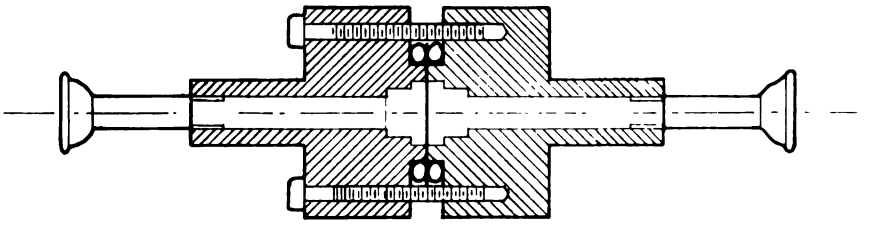

FIGURE 5.

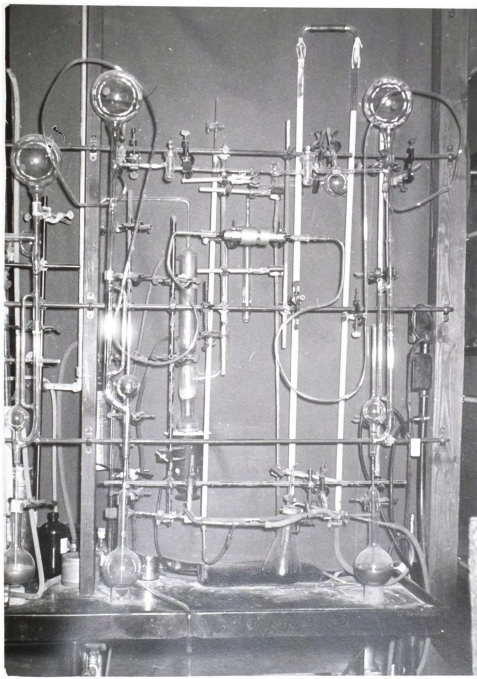

FIGURE 6

FIRST PERMEABILITY APPARATUS

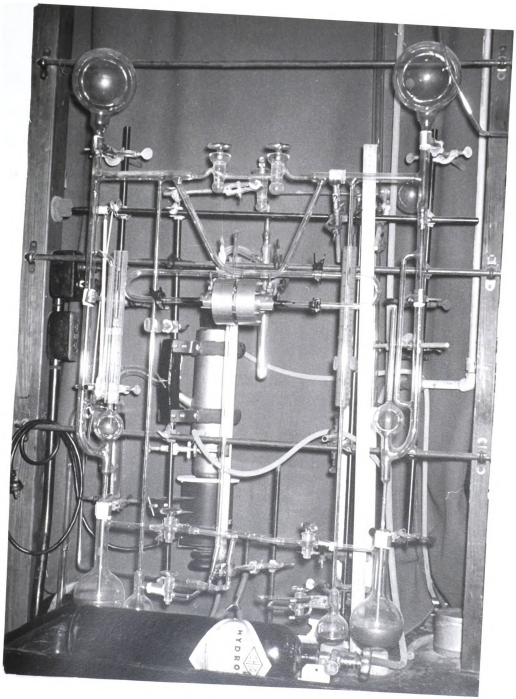

FIGURE 7

SECOND PERMEABILITY APPARATUS

RESULTS

The first electrodeposits obtained from a nickel solution were found to have a much higher permeability than those which were produced subsequently during any continuous period of electrolysis. It was found that three to four hours of continuous electrolysis at 4.3 amperes per square decimeter of cathode area was necessary before the solution would produce deposits with a permeability constant of about 10^{-6} which was considered to be about the limit of the sensitivity of the first apparatus. Smallers "k's" were in some instances determined but since they represented a pressure change of the order of one micron of mercury in fifteen minutes their accuracy was questionable. A typical curve is illustrated in Figure 8.

The same effect was noted subsequently when the solution was again used to produce foils. However, each time the solution was used to produce foils the initial foil was of a lower permeability than the initial foil electroformed the previous time the solution was used, and a shorter period of electrolysis was required to reduce the permeability. After nearly a hundred hours of electrolysis at 4.3 amperes per square decimeter (cathode) uniformly good ($k \approx 10^{-6}$) foils could be produced from the first.

Figure 9 (Table I) illustrates the effect of two types of corrosive media on the permeability of electrodeposited foils. All of these foils were 25 $\pm$ 1 microns in thickness and were cut from the same strip

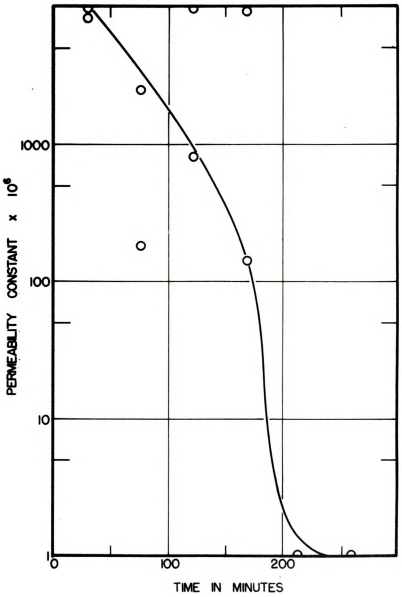

FIGURE 8. EFFECT OF ELECTROLYSIS ON THE PERMEABILITY

TABLE I

EFFECT OF CORROSIVE MEDIA ON PERMEABILITY CONSTANT

Time (hrs)	11.5 N HCl Vapor		10% H_2SO_4		
	(1-B)	(2-A)	(1-A)	(2-B)	(1-C)
0	1.0×10^{-6}	1.0×10^{-6}	5×10^{-7}	2.0×10^{-6}	7×10^{-7}
4	1.0×10^{-6}	5×10^{-7}			
8	5×10^{-7}	9×10^{-7}			
10	4.7×10^{-6}	2.0×10^{-6}			
12	2.1×10^{-6}	3.8×10^{-6}			
13			1.2×10^{-4}	1.6×10^{-6}	2.0×10^{-6}
14	4.2×10^{-4}	3.0×10^{-5}			
18			1.0×10^{-3}	1.5×10^{-6}	3.0×10^{-6}
20			2.6×10^{-4}	1.8×10^{-5}	7.0×10^{-6}
22			5.8×10^{-4}	2.1×10^{-4}	4.4×10^{-5}

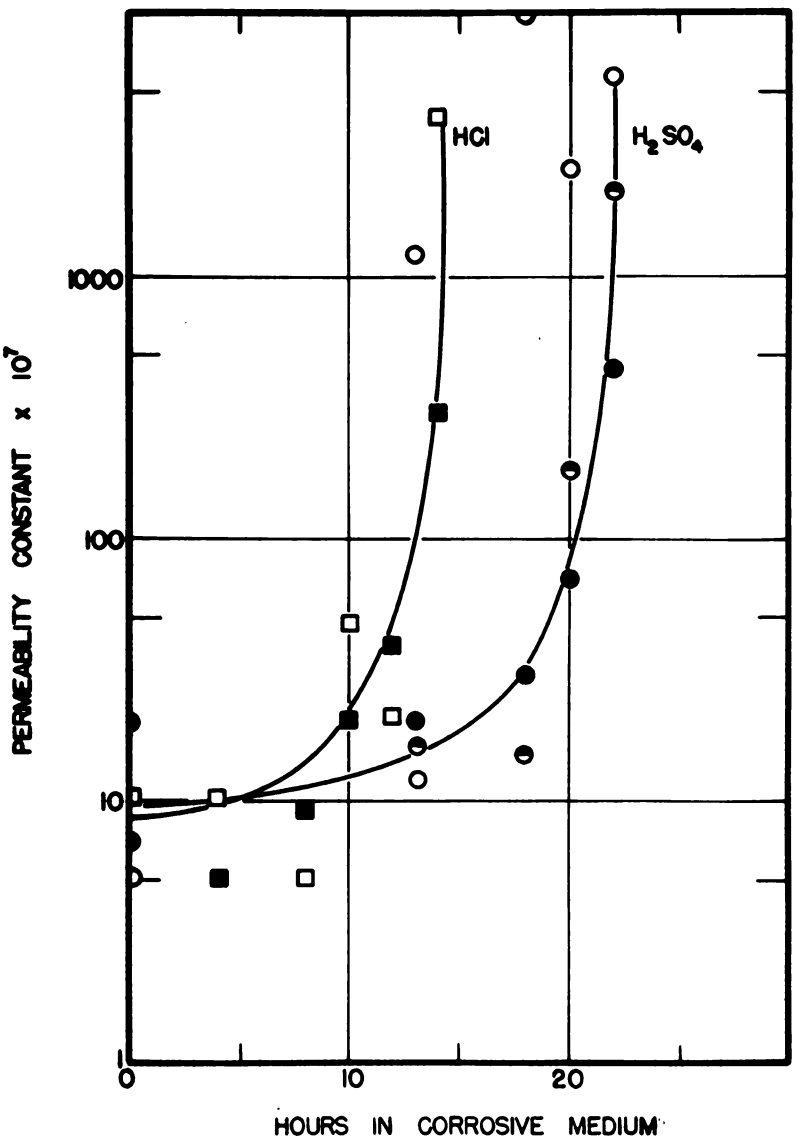

FIGURE 9. EFFECT OF CORROSIVE MEDIUM ON PERMEABILITY

deposit (C-Sl-E), produced on a buffed stainless steel (18-8) panel. The corrosive media were kept in a constant temperature bath (25.0 ± 0.5°C.). To remove corrosion products, which might clog pores, the foils were rinsed with water which had been adjusted to a pH of 3.0 by the addition of hydrochloric acid. Exposure to the vapor of 11.5 N hydrochloric acid was found to be about twice as corrosive as immersion in ten per cent (volume) sulfuric acid. The shape of the curves was characteristic of the effect of a corrosive media on the permeability. The initial exposure produced very little change in the permeability. After a few hours exposure there was a sudden and abrupt increase in the permeability. After this increase had started it increased rapidly to a point where the permeability was too great to be measured by the apparatus. When this portion of the curve, where the permeability was rapidly increasing, was extrapolated to the point where the permeability was 10^{-6}, the corresponding hours in the corrosive medium was referred to as the "breakdown time" for the foil. If the very low results are rejected as due to defects in the foil, the relationship is nearly linear when the breakdown time for the foils is plotted against the thickness. These results (Figure 10, Table II) were obtained using 11.5 N hydrochloric acid as the corrosive medium.

After employing a mercury vapor diffusion pump, in addition to the rotary oil pump, it was noted that the pressure increase during the first five minutes of a run was less than that during any succeeding five minute interval. It had been the practice to evacuate both sides of the system to about 0.0005 mm of mercury or less, then to admit an

TABLE II

RELATIONSHIP OF THICKNESS TO THE BREAKDOWN TIME OF ELECTROLYTIC NICKEL FOILS IN 11.5 N HCl VAPOR

Thickness (microns)	Breakdown Time (hrs)	Thickness (microns)	Breakdown Time (hrs)
10	3.0	23	7.0
10	3.5	23	7.0
18	5.5	23	7.0
18	8.5	24	11.0
18	10.5	25	8.0
20	9.0	25	8.0
20	9.5	25	11.0
		25	12.0

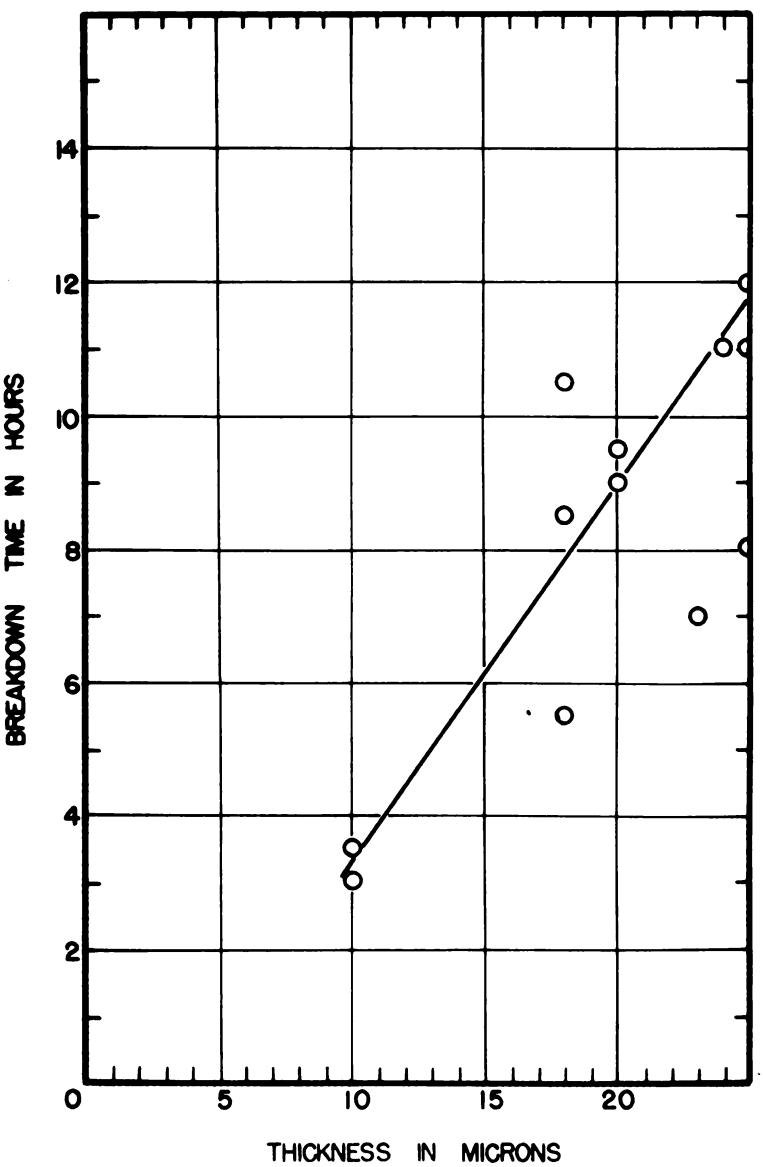

FIGURE 10. RELATIONSHIP BETWEEN BREAKDOWN TIME AND FOIL THICKNESS

atmosphere of overpressure to one side and measure the subsequent increase in pressure on the opposite side of the system. To determine if this initial lag was caused by the adsorption of the gas on the surface of the foil, an overpressure of one atmosphere was left on one side of the foil while the opposite side was evacuated to as low a value as possible (usually a few microns of mercury), the vacuum pumps were then shut off and the increase in pressure noted. The increase in pressure was, in this case, linear with respect to time, the slope of the curve being about the same as that for the previous run (in which both sides of the system were evacuated), after the initial lag during the first few minutes. Typical results are illustrated in Figure 11 and Tables III, IV and V.

A change in the permeability of the foils over a period of time is observed; for foil C-S1-D-1-B the permeability increased, for foil C-S1-D-1-A the permeability decreased. For foil C-S1-D-1-B; Runs I, II, III and IV were made the same day, Run V was made four days later, Run VI twenty-six days after the first four runs, and Run VII twenty-eight days after the first four runs. Runs I and II for foil C-S1-D-1-A were made the same day. Runs III and IV were made eighteen days later, and Runs V and VI were made thirty days after the first two runs. Both runs for foil C-S1-D-2-C were made the same day. All foils were from the same strip deposit, 25 microns in thickness. When originally produced, about six months previous to this series of tests, all foils had an initial permeability of about two microns of mercury in fifteen minutes. All permeability tests were made with one atmosphere

TABLE III

INITIAL LAG IN THE DIFFUSION OF AIR THROUGH FOIL C-S1-D-1-B

Time (min)	Pressure at Outgoing Side of Foil in mm of Hg						
	Run I	Run II	Run III	Run IV	Run V	Run VI	Run VII
0	0.000	0.002	0.003	0.000	0.000	0.002	0.003
1		.005					
2		.007		.001		.003	.012
3		.011		.002			
4		.013					
5	.003	.016	.016	.004	.004	.010	.023
6				.006			
7		.022		.007		.016	.031
10	.007	.031	.030	.013	.011	.027	.043
12						.035	.048
15	.025	.043	.044	.025	.021	.045	.060
17						.052	.068
20	.036			.038		.060	.076
22						.068	.082

Run I — Both sides of system evacuated
Run II — Evacuated only one side of system
Run III — Evacuated only one side of system
Run IV — Both sides of system evacuated
Run V — Evacuated only one side of system
Run VI — Both sides of system evacuated
Run VII — Evacuated only one side of system

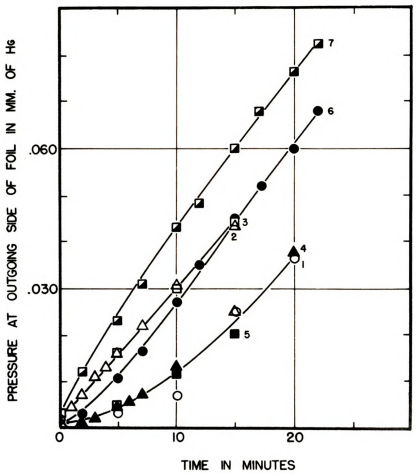

FIGURE 11. INITIAL LAG IN SETTING UP STEADY STATE OF FLOW THROUGH FOIL C-SI-D-I-B

1.	EVACUATED	BOTH	SIDES
2.	"	ONE	SIDE
3.	"	"	"
4.	"	BOTH	SIDES
5.	"	ONE	SIDE
6.	"	BOTH	SIDES
7.	"	ONE	SIDE

TABLE IV

INITIAL LAG IN THE DIFFUSION OF AIR THROUGH FOIL C-S1-D-1-A

Time (min)	Pressure at Outgoing Side of Foil in mm of Hg					
	Run I	Run II	Run III	Run IV	Run V	Run VI
0	0.000	0.011	0.002	0.005	0.001	0.001
1	.002		.004			
2	.005	.022	.007	.015	.002	.003
3	.010					
4	.015					
5	.020	.040	.018	.026	.004	.007
7	.031	.048	.025	.034	.006	.010
10	.044	.072	.038	.046	.011	.013
12	.060	.080	.046	.048		.016
15	.078	.100	.054	.066	.018	.020
17	.088	.110	.062	.072	.020	.023
20	.108	.130	.074		.023	.026
22	.120	.136	.084		.026	.030

Run I — Both sides of system evacuated
Run II — Evacuated only one side of system
Run III — Both sides of system evacuated
Run IV — Evacuated only one side of system
Run V — Both sides of system evacuated
Run VI — Evacuated only one side of system

TABLE V

INITIAL LAG IN THE DIFFUSION OF AIR THROUGH FOIL C-S1-D-2-C

Time (min)	Pressure at Outgoing Side of Foil in mm of Hg	
	Run I	Run II
0	0.000	0.004
2	.001	.012
5	.004	.023
7	.007	.029
10	.013	.040
12	.018	.046
15	.025	
17	.031	.060
20	.040	.072
22	.046	.080

Run I Both sides of system evacuated
Run II Evacuated only one side of system

overpressure (741 ± 5 mm of Hg). There was no correlation between the variation in overpressure and the variation in permeability. Foil C-Si-D-1-A had been stored exposed to laboratory atmosphere but protected from dust particles by cheesecloth. Foils C-Si-D-1-B and C-Si-D-2-C had been stored in a dessicator over calcium chloride.

Attempts were made to determine if ions in solution as well as gases would pass through the foils. Using a foil to separate solutions which contained, respectively, chloride ions on one side and silver ions on the other; chromate ions on one side and lead ions on the other; in neither instance was there any indication of any precipitation on either side of the foil after twenty-four hours.

It was possible, however, to measure the diffusion of hydrogen ions through a foil 25 microns thick under similar conditions. The foil was used to separate a solution of ten per cent (volume) sulfuric acid from distilled water. The volume of distilled water was approximately twenty milliliters, the volume of ten per cent sulfuric acid was about 2.75 milliliters for trials 1 and 2, and 2.0 milliliters for trials 3 and 4. In trial 3 a little 0.1 N sodium hydroxide was added to the distilled water in an attempt to get a longer period of diffusion before an equilibrium was reached. The previously determined "k" for this foil was 8×10^{-3}. The results are illustrated in Figure 12 and Table VI.

The remainder of the data was obtained using the second permeability apparatus. The rate of diffusion at different overpressures for foil C-1-F (13 microns thick, deposited on a buffed electrolytic nickel surface) is shown in Figure 13 and Table VII. There was a linear increase

TABLE VI

CHANGE OF pH DUE TO THE DIFFUSION OF HYDROGEN IONS THROUGH ELECTROLYTIC NICKEL

Time (min)	Trial 1	Trial 2	Trial 3	Trial 4
0	7.97	6.48	9.88	8.60
2			10.00	
5		6.34	10.20	7.72
6	7.68			
7	7.61			
9	7.50			
10		6.32	10.35	
11.5				7.32
13	7.33			
15	7.25	6.34	10.45	7.10
19	7.08			
20			10.35	6.98
23	6.70			
25			10.57	
26.5				6.88
28	6.44			6.86
30	6.30			6.86
34	6.23			
35	6.19		10.50	
40	6.06			
45				6.80
65				6.79
75				6.80
100		6.32		
155	5.85			
195	5.70			
245	5.80			
315	5.75			
1200	5.75			

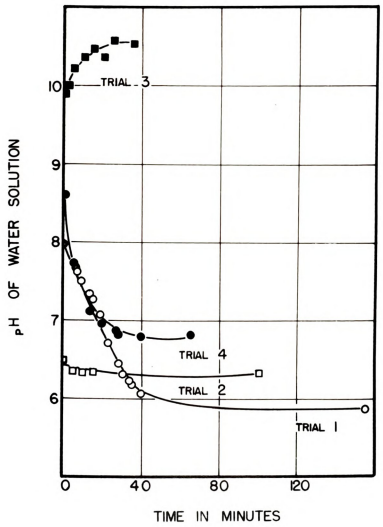

FIGURE 12. DIFFUSION OF HYDROGEN IONS THROUGH ELECTROLYTIC NICKEL

TABLE VII

EFFECT OF OVERPRESSURE ON THE RATE OF DIFFUSION OF AIR THROUGH FOIL C-1-F

Overpressure mm Hg	Rate of Diffusion		k x 10^6
	mm Hg/15 min	cc/cm²/15 min	
4.0	0.006	0.001	10
23	.021	.0034	7.6
37	.034	.0056	7.6
105	.098	.016	7.6
300	.323	.0531	8.9
741	6.30*	1.04	71
293	1.45	.239	41
99	.571	.0938	48
51	.258	.0424	42
18	.131	.0215	60
9.0	.123	.0204	110
4.0	.076	.0124	160
3.0	.044	.0072	120

* Extrapolated reading

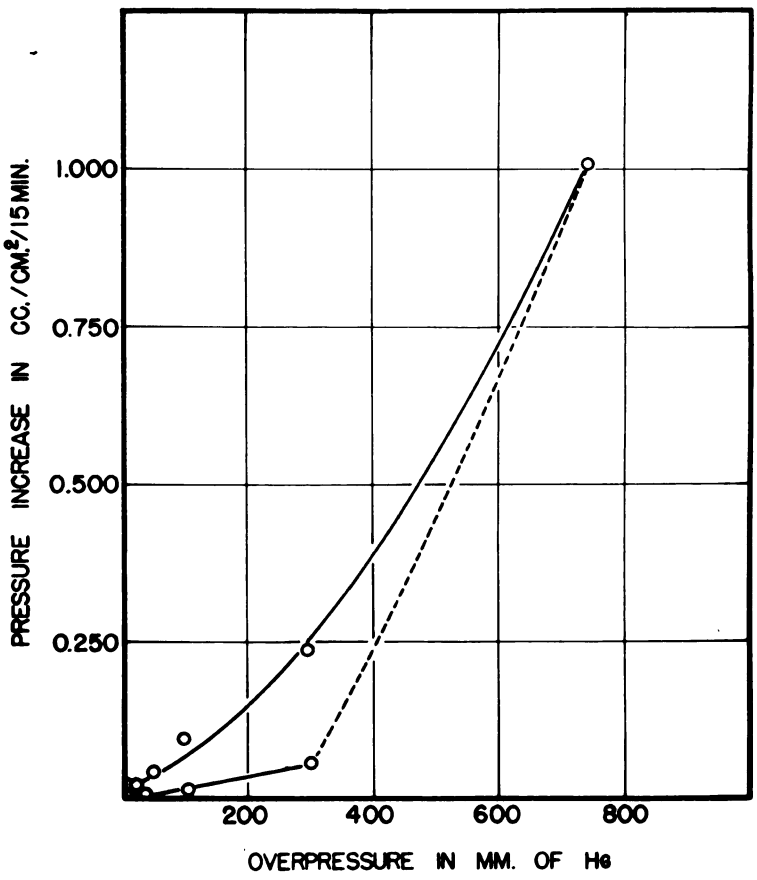

FIGURE 13. EFFECT OF OVERPRESSURE ON THE RATE OF DIFFUSION OF AIR THROUGH FOIL C-I-F

in the rate of diffusion as the overpressure was increased up to 300 mm of mercury. When the overpressure was further increased to one atmosphere (741 mm of mercury) the rate of diffusion increased sharply. The rate of diffusion increased about twenty times while the overpressure was increased by a factor of about two and one-half. When the rate of diffusion was again tested at successively lower overpressures the rate of diffusion was consistently greater than it had been previously for a similar overpressure. When the foil was removed from the holder and examined visually a small crack was apparent where the holder had gripped the foil. Since it was apparent that the permeability characteristics of the foil could be changed by high overpressures it was decided to work with overpressures of the order of 100 mm of mercury or less.

Foil C-2-B (13 microns thick, deposited on a buffed electrolytic nickel surface) had a nearly linear increase in the rate of diffusion as the overpressure was increased from one to one hundred mm of mercury as shown by Figure 14 and Table VIII. However, in view of subsequent results, it should be noted that there was only one reading taken between twenty-three and sixty-five mm of mercury overpressure and that this reading was below the straight line.

The rate of diffusion of hydrogen through foil D-02-C (8 microns thick, deposited on a buffed electrolytic nickel surface) is illustrated in Figures 15 and 16 (Table IX). Previous to this dry air had been used as the diffusing gas. At very low overpressures the rate of diffusion increased very little as the overpressure was increased, at

TABLE VIII

EFFECT OF OVERPRESSURE ON THE RATE OF DIFFUSION OF AIR THROUGH FOIL C-2-B

Overpressure mm Hg	Rate of Diffusion mm Hg/15 min	Rate of Diffusion $cc/cm^2/15$ min	$k \times 10^6$
3.0	0.061	0.010	170
4.0	.119	.0194	250
9.9	.258	.0423	220
34.0	.720	.118	180
98.6	2.66	.436	220
65.4	1.76	.290	220
22.7	.580	.0958	210
7.8	.207	.0340	220
3.0	.071	.011	200
2.22	.048	.0079	180
1.43	.028	.0046	160
.88	.018	.0030	170

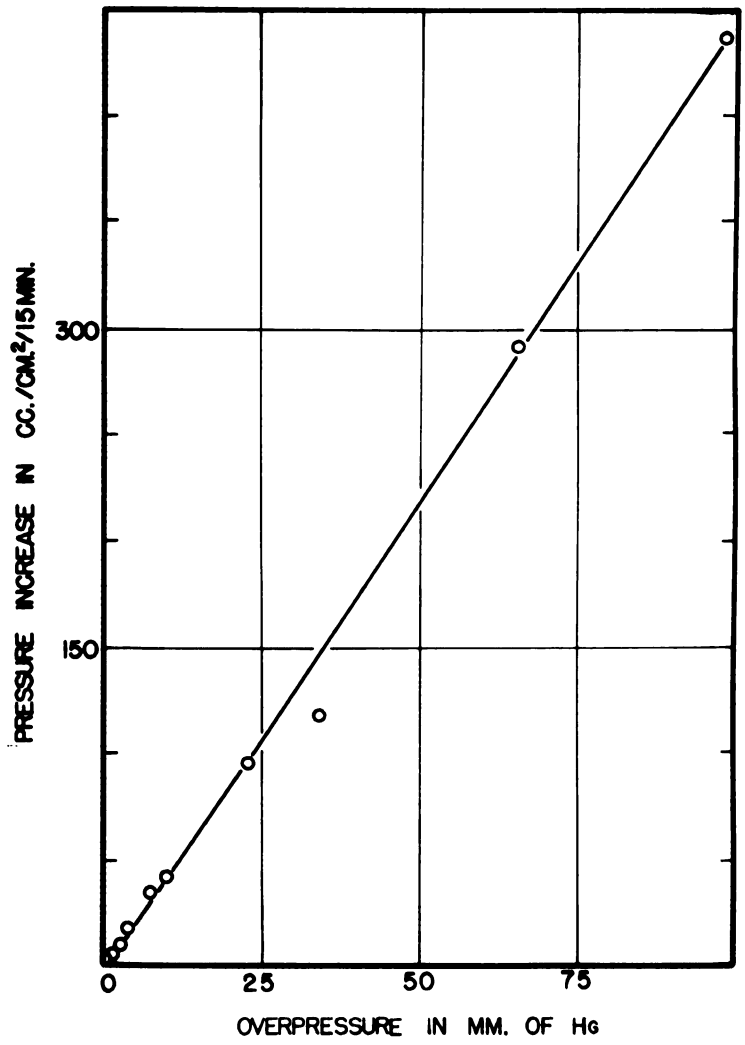

FIGURE 14. EFFECT OF OVERPRESSURE ON THE RATE OF DIFFUSION OF AIR THROUGH FOIL C-2-B

TABLE IX

EFFECT OF OVERPRESSURE ON THE RATE OF DIFFUSION OF HYDROGEN THROUGH FOIL D-02-C

Overpressure mm Hg	Rate of Diffusion mm Hg/15 min	Rate of Diffusion $cc/cm^2/15$ min	$k \times 10^6$
3.5	0.0022	0.00036	5.2
6.8	.0071	.0011	8.7
13.5	.0100	.0017	6.1
38.1	.0150	.0025	3.3
58.1	.0270	.0045	3.9
64.8	.0440	.0072	5.6
84.7	.0570	.0094	5.7
76.7	.0480	.0079	5.2
69.9	.0190	.0032	2.3
51.2	.0330	.0054	5.4
36.7	.0280	.0046	6.3
22.1	.0150	.0025	5.6
32.7	.0140	.0023	3.6
.011	.0010	.00017	760
.033	.0012	.00019	300
.125	.0010	.00017	66
1.58	.0034	.00055	18
.65	.0020	.00032	26
.070	.0008	.00013	90
.008	.0003	.00005	300
.023	.0005	.00008	180
1.95	.0016	.00026	6.4
1.31	.0016	.00026	10
1.34	.0010	.00017	6.2

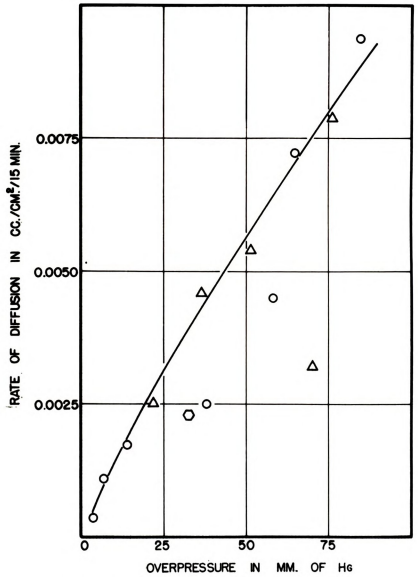

FIGURE 15. EFFECT OF OVERPRESSURE ON THE RATE OF DIFFUSION OF H_2 THROUGH FOIL D-02-C
○ FIRST RUN △ SECOND RUN ⬡ OTHER READINGS

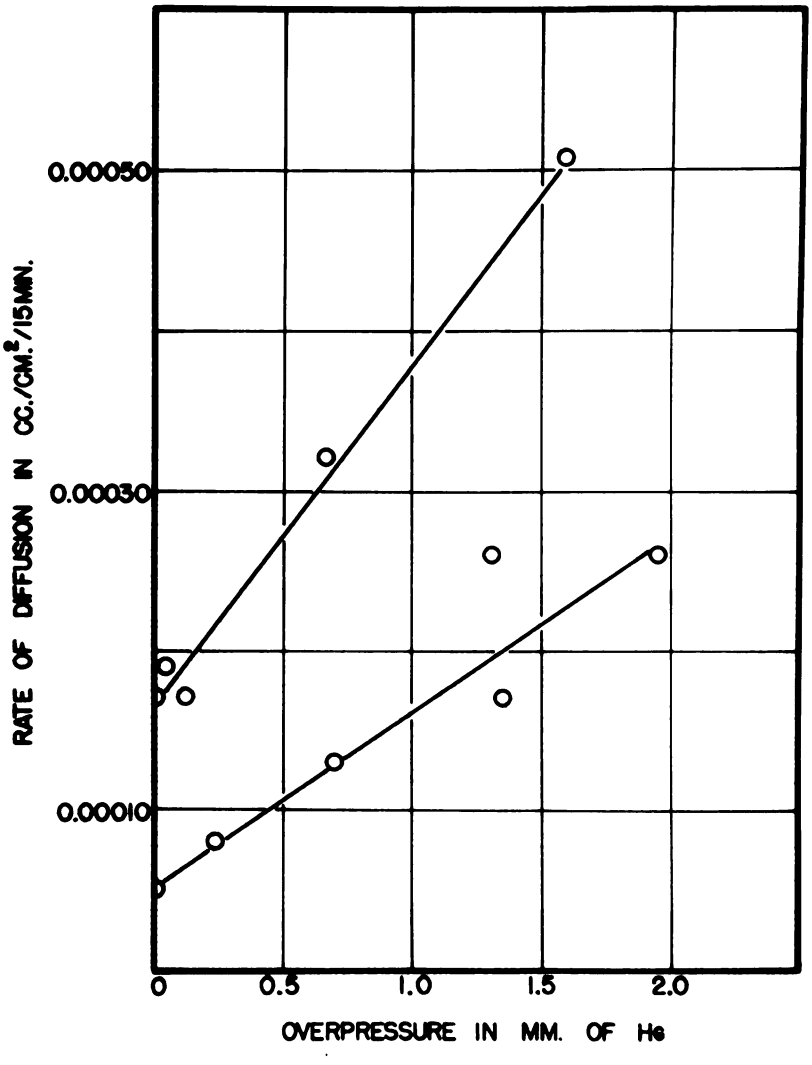

FIGURE 16. EFFECT OF OVERPRESSURE ON THE RATE OF DIFFUSION OF H_2 THROUGH FOIL D-02-C

overpressures from three to one hundred mm of mercury the rate of diffusion increased more rapidly and linearly. The circles indicate the first readings, taken in the order of increasing overpressures, the triangles represent readings taken in the order of decreasing values of the overpressure, hexagons are other readings taken. Readings which are low are probably due to contamination of the hydrogen by air. The readings below two mm of mercury overpressure can be divided into two sets, one set indicating a rate of diffusion about twice that indicated by the other set.

The data from foil D-02-B (15 microns thick, deposited on buffed electrolytic nickel) had the least variation from a smooth curve of any foil tested. There was a sharp break at 36 mm of mercury overpressure. When the rate of diffusion of hydrogen is plotted against the overpressure only two points fall off a smooth curve. The point at 65 mm of mercury overpressure could be interpreted as another break (Figure 17, Table X). If the rate of diffusion is plotted against the square root of the overpressure two straight lines are obtained with a break at 36 mm of mercury overpressure.

The first gas to be used with foil D-03-A (8 microns thick, deposited on an unbuffed electrolytic nickel surface) was hydrogen. The first two series of readings were made starting at low overpressures and increasing the overpressure for successive readings as indicated by the circles and squares. The third series of readings was made starting with the highest overpressure and decreasing the overpressure for successive readings as indicated by the triangles. Hexagons are, again,

TABLE X

EFFECT OF OVERPRESSURE ON THE RATE OF DIFFUSION OF HYDROGEN THROUGH FOIL D-02-2

Overpressure mm Hg	Rate of Diffusion mm Hg/15 min	Rate of Diffusion cc/cm²/15 min	k x 10^6
0.04	0.0002	0.00004	40
3.3	.0010	.00016	2.4
8.1	.0016	.00026	1.6
16.7	.0023	.0038	1.1
30.5	.0030	.00049	.82
52.7	.0059	.00097	.93
65.5	.0070	.0011	.91
85.5	.0090	.0015	.87
109.9	.0110	.0018	.83
73.6	.0080	.0013	.90
41.2	.0044	.00072	.89
26.6	.0042	.00069	1.3
38.9	.0038	.00062	.81
36.0	.0032	.00053	.74
1.38	.0005	.00008	3
1.58	.0004	.00006	2
.150	.0003	.00005	2

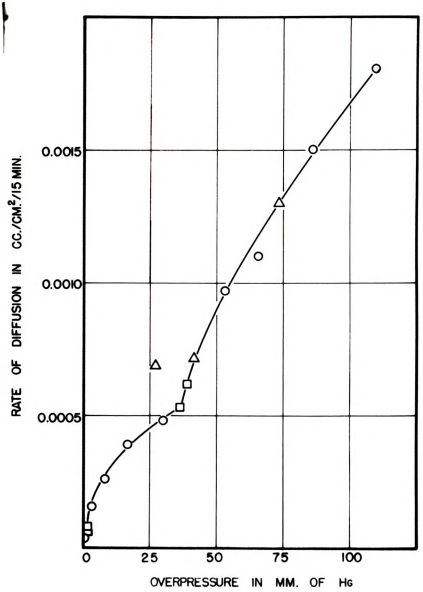

FIGURE 17. EFFECT OF OVERPRESSURE ON THE RATE OF DIFFUSION OF H_2 THROUGH FOIL D-02-E
○ FIRST RUN △ SECOND RUN □ OTHER READINGS

extra readings. The data (Table XI) as plotted in Figure 18 shows a break at 45 mm of mercury overpressure. Figure 19 (Tables XI, XII and XIII) compares the results of diffusing hydrogen, helium, and nitrogen through foil D-03-A. Helium displays the same pronounced break as hydrogen; nitrogen, when plotted to the same scale as the other two gases does not have nearly so pronounced a break and might be interpreted as a linear function.

Foil D-03-B (8 microns thick, deposited on an unbuffed electrolytic nickel surface) was first tested with nitrogen. The first series of readings gave a typical curve with a break at about 53 mm of mercury overpressure. After the last (highest) reading was made a stopcock was inadvertently turned in the wrong direction and an overpressure of 250 mm of mercury was momentarily placed on the foil. When subsequent readings were made, the rate of diffusion had increased and the second curve was obtained. At this time, due to a leak in the connection to the rotary oil pump, which was not discovered until later, it was necessary to use the mercury vapor pump to obtain pressures low enough to make permeability measurements. In this instance the mercury vapor pump was operated continuously for five hours after which the rate of diffusion was found to have increased again and the third curve was obtained. These results are shown in Figure 20 and Table XIV. The foil was also tested using hydrogen and helium, both gases exhibiting a break between 40 and 50 mm of mercury overpressure (Figure 21, Tables XIV, XV and XVI). When examined visually there was no apparent damage to the foil

TABLE XI

EFFECT OF OVERPRESSURE ON THE RATE OF DIFFUSION OF HYDROGEN THROUGH FOIL D-03-/

Overpressure mm Hg	Rate of Diffusion mm Hg/15 min	Rate of Diffusion cc/cm²/15 min	k x 10^6
1.02	0.0056	0.00088	46
1.30	.0055	.00088	35
2.15	.0063	.0011	24
4.90	.0739	.0121	130
6.00	.0670	.0110	93
10.00	.0590	.00968	48
17.70	.132	.0217	62
26.15	.190	.0312	60
54.30	.308	.0506	47
79.30	.500	.0820	52
95.80	.620	.102	54
62.00	.435	.0713	58
62.10	.460	.0755	61
83.50	.604	.0991	60
3.15	.0243	.00398	63
10.30	.0870	.0143	72
22.20	.169	.0277	63
32.70	.220	.0362	56
43.30	.285	.0468	55
50.90	.327	.0536	53
58.50	.420	.0688	60
70.30	.507	.0832	60
86.50	.590	.0965	57
.098	.0010	.00017	85
42.30	.242	.0398	48
42.80	.261	.0428	51
71.00	.375	.0615	44
97.00	.634	.104	54
81.10	.540	.0896	55
71.10	.464	.0761	54
61.80	.428	.0702	57
52.70	.382	.0626	60
40.40	.269	.0443	55
33.40	.265	.0435	66
24.70	.160	.0263	54
16.50	.125	.0205	63
6.70	.0590	.00968	73

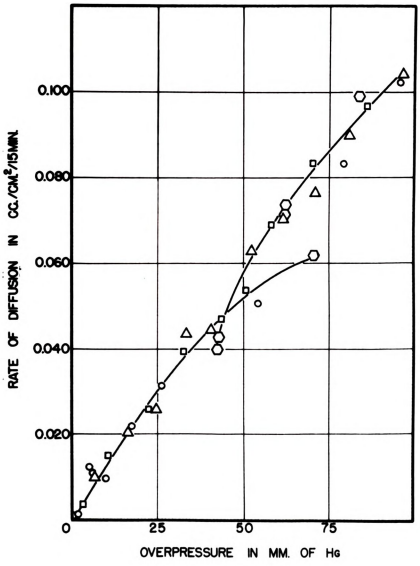

FIGURE 18. EFFECT OF OVERPRESSURE ON THE RATE OF DIFFUSION OF H_2 THROUGH FOIL D-03-A
○ FIRST RUN □ SECOND RUN △ THIRD RUN
⬡ OTHER READINGS

TABLE XII

EFFECT OF OVERPRESSURE ON THE RATE OF DIFFUSION OF HELIUM THROUGH FOIL D-03-A

Overpressure mm Hg	Rate of Diffusion		k x 10^6
	mm Hg/15 min	cc/cm^2/15 min	
0.060	0.0009	0.0002	100
1.13	.0074	.0012	54
3.50	.0321	.0053	76
7.50	.0574	.0094	64
11.8	.0900	.0147	63
23.7	.131	.0215	46
36.2	.205	.0337	47
45.4	.236	.0387	43
52.9	.284	.0465	45
61.8	.344	.0565	46
75.1	.400	.0651	44
92.4	.438	.0720	39
89.5	.450	.0739	42

TABLE XIII

EFFECT OF OVERPRESSURE ON THE RATE OF DIFFUSION OF NITROGEN THROUGH FOIL D-03-A

Overpressure mm Hg	Rate of Diffusion		$k \times 10^6$
	mm Hg/15 min	$cc/cm^2/15$ min	
3.20	0.0086	0.0014	22
10.1	.0294	.00482	24
22.4	.0550	.00903	20
34.3	.0800	.0132	19
51.3	.118	.0194	19
62.4	.140	.0230	19
72.6	.160	.0263	18
92.6	.216	.0354	19

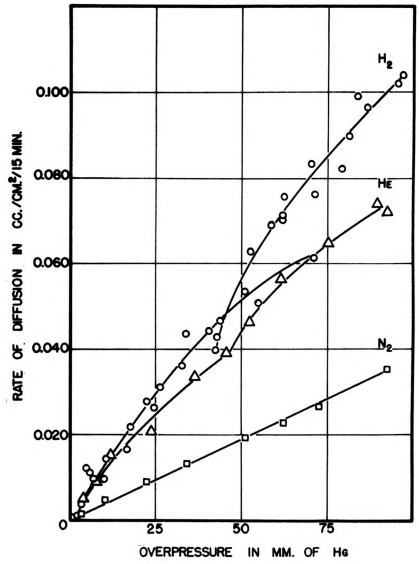

FIGURE 19 EFFECT OF OVERPRESSURE ON THE RATE OF DIFFUSION OF GASES THROUGH FOIL D-03-A

TABLE XIV

EFFECT OF OVERPRESSURE ON THE RATE OF DIFFUSION OF NITROGEN THROUGH FOIL D-03-B

Overpressure mm Hg	Rate of Diffusion		$k \times 10^6$
	mm Hg/15 min	cc/cm^2/15 min	
3.20	0.0070	0.0011	18
10.4	.0169	.00277	13
21.2	.0462	.00757	18
31.2	.0620	.0102	16
42.9	.0800	.0132	15
53.1	.0950	.0156	15
62.0	.121	.0198	16
70.5	.146	.0240	17
81.0	.171	.0281	18
91.6	.189	.0311	17
56.4	.142	.0233	21
1.41	.0035	.00057	15
6.40	.0174	.00286	23
18.5	.0430	.00707	22
50.7	.131	.0215	21
76.3	.175	.0287	19
41.4	.097	.0159	20
33.9	.139	.0228	34
3.0	.0156	.00256	43
15.4	.0710	.0117	38
25.7	.102	.0168	33
36.3	.154	.0252	35
42.2	.178	.0292	35
44.1	.172	.0282	32
46.7	.200	.0328	36
51.3	.216	.0354	35
51.6	.212	.0347	34
55.7	.217	.0356	32
56.9	.225	.0368	33
60.2	.241	.0394	33
62.0	.244	.0400	33
65.1	.252	.0413	32
72.5	.285	.0468	33
88.5	.355	.0583	33

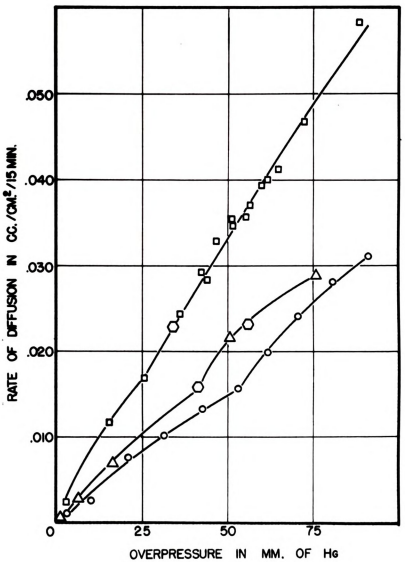

FIGURE 20 EFFECT OF OVERPRESSURE ON THE RATE OF DIFFUSION OF N_2 THROUGH FOIL D-03-B

○ FIRST RUN △ SECOND RUN □ THIRD RUN

⬡ OTHER READINGS

TABLE XV

EFFECT OF OVERPRESSURE ON THE RATE OF DIFFUSION OF HELIUM THROUGH FOIL D-03-B

Overpressure mm Hg	Rate of Diffusion		$k \times 10^6$
	mm Hg/15 min	cc/cm^2/15 min	
1.97	0.0160	0.0026	68
9.00	.0960	.0160	89
27.0	.281	.0460	86
43.7	.424	.0696	81
47.3	.440	.0721	77
50.9	.478	.0785	78
54.2	.500	.0820	77
61.8	.576	.0947	77
71.9	.655	.108	76
85.2	.766	.125	75

TABLE XVI

EFFECT OF OVERPRESSURE ON THE RATE OF DIFFUSION OF HYDROGEN THROUGH FOIL D-03-B

Overpressure mm Hg	Rate of Diffusion		$k \times 10^8$
	mm Hg/15 min	cc/cm^2/15 min	
3.06	0.200	0.0328	470
10.3	.146	.0239	120
20.5	.270	.0443	110
25.8	.315	.0518	100
33.0	.395	.0648	99
39.4	.465	.0755	98
45.1	.530	.0869	98
46.1	.555	.0913	100
49.5	.625	.103	100
55.5	.693	.114	100
66.1	.830	.136	100
76.3	.940	.154	100
87.6	1.12	.184	110

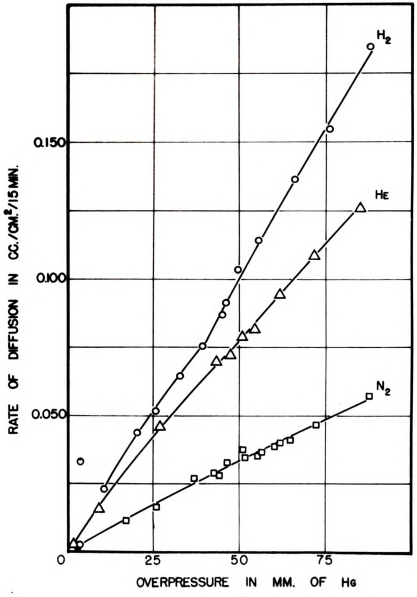

FIGURE 21 EFFECT OF OVERPRESSURE ON THE RATE OF DIFFUSION OF GASES THROUGH FOIL D-03-B

to account for the increase in the rate of diffusion found when the foil was being tested with nitrogen.

The last graph (Figure 22) and Table XVII illustrates how closely the behavior of nitrogen and hydrogen corresponded to Grahams Law when diffusing through the electrolytic nickel foils over a range of over-pressures. As compared to helium, nitrogen diffused faster than would be expected while the hydrogen diffused slower than would be expected. The dotted lines indicate the theoretical rate (as compared to helium) that the gases should diffuse to correspond to Grahams Law.

TABLE XVII

CORRELATION OF THE RATE OF DIFFUSION TO GRAHAMS LAW

Foil	Overpressure mm Hg	Nitrogen		Helium	Hydrogen	
		Rate of Diffusion	Ratio to Helium	Rate of Diffusion	Rate of Diffusion	Ratio to Helium
D	5.0	0.0026	0.330	0.0078	0.0078	1.00
'	10.0	.0043	.360	.0118	.0129	1.09
0	20.0	.0080	.400	.0200	.0240	1.20
3	30.0	.0117	.430	.0275	.0347	1.26
'	40.0	.0152	.440	.0346	.0445	1.29
A	50.0	.0191	.454	.0420	.0555	1.32
	60.0	.0229	.454	.0505	.0660	1.31
	70.0	.0268	.455	.0590	.0770	1.31
	80.0	.0305	.455	.0670	.0890	1.33
	90.0	.0342	.450	.0760	.0990	1.30
D	5.0	.00385	.433	.0089		
'	10.0	.00740	.433	.0171	.0237	1.39
0	20.0	.0140	.400	.0350	.0440	1.26
3	30.0	.0206	.434	.0475	.0595	1.25
'	40.0	.0270	.433	.0625	.0765	1.22
B	50.0	.0335	.435	.0770	.0990	1.29
	60.0	.0390	.429	.0910	.121	1.33
	70.0	.0460	.430	.107	.143	1.37
	80.0	.0520	.437	.119	.167	1.40
	90.0	.0590	.444	.133	.190	1.43
Grahams Law			.374			1.41

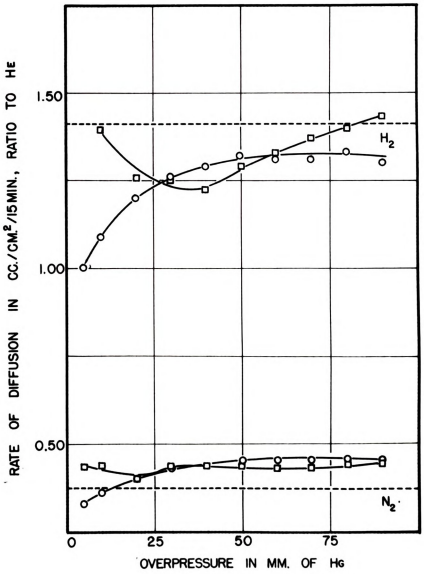

FIGURE 22 CORRELATION TO GRAHAM'S LAW

○ FOIL D-03-A

□ FOIL D-03-B

DISCUSSION

The observation that an initial period of electrolysis is necessary before a nickel solution will produce electrodeposits of optimum quality has been made before (12). In this study it was found that after the optimum condition had been reached, this character of the solution could be lost on standing and subsequent electrolysis was necessary to again bring the nickel solution to a condition where it would produce optimum quality (less permeable) deposits.

The effect of corrosion on the permeability of electrolytic nickel foils was characteristic of that which had been previously reported (15). Both types of corrodant had the same ultimate effect; a rapid increase in the permeability of the foil before any visible sign of failure (e.g., visible holes) appeared.

Most of the experimentation on the corrodibility of nickel foils was performed using 11.5 N hydrochloric acid vapor as the corrosive medium. The low results are probably due to defects in the foils. The effect of increasing the thickness of the foil is nearly linear. The effect of doubling the thickness of the foil is to slightly more than double the breakdown time. This is in accord with other reports (16) which indicate that the rate of corrosion of nickel (both electrolytic and metallurigal) is linear with respect to time in 11.5 N hydrochloric acid vapor.

An initial lag in setting up a steady state of flow of gases through porous material has been noted in other studies (17). This was believed to be due either to the penetration of the gas into the material, which included some blind pores, or adsorption of the gas on the surface of the foil. It was observed repeatedly that evacuating both sides of the system with a mercury vapor pump (to less than 0.5 microns of mercury) then admitting an atmosphere of overpressure to one side, would produce an initial lag in the rate of diffusion. If, an overpressure of one atmosphere was left on one side, while the opposite side was evacuated, it was noted (with one exception), that the rate of diffusion was linear, as soon as evacuation was stopped.

The initial lag amounted to about 0.02 $\pm$ .01 mm of mercury. Since the foil area for these runs was 0.375 cm^2 and the volume of the apparatus into which the gas was diffusing, 1.45 liters, this amounted to 1.0×10^{-4} liter-atmospheres/cm^2 of foil area. The Watts type solution is known (14) to yield deposits such that the 100 plane is parallel to the substrate metal. The closest interatomic distance in this plane is 2.48×10^{-8} cm, hence a one centimeter row would contain 4×10^7 nickel atoms. A square centimeter would not contain over 1.6×10^{15} atoms. Therefore, even if the gaseous molecules (oxygen or nitrogen) were adsorbed in a one to one ratio the geometric surface of the foil could not account for more than one-thousandth of the observed lag. Measurements of the true surface area of nickel foils by the gas adsorption method (18) indicate that the true surface area of electrolytic nickel foils is at least twice the geometric area. The surface

area may, in fact, be much higher, since the foils in this study (18) were heated at 450°C. for thirty to forty hours, sintering may have occurred, sealing off small capillaries.

When the second permeability apparatus was constructed the foil holder was made much larger so that this phenomenon could be studied more closely. There was no instance, while using the second permeability apparatus, in which there was an initial lag in the rate of diffusion. The phenomenon may have been due to the surface on which the foil had been deposited. An initial lag was observed only with foils deposited on a buffed stainless steel (18-8) panel. The first layers of an electrodeposit are known to be greatly influenced by the substrate upon which they are deposited (19,20).

The only ion which was found to diffuse through the electrolytic nickel foil in liquid media was hydrogen. It will be observed that the diffusion of hydrogen ions reached an equilibrium value after a short period of diffusion. An attempt to extend this period of diffusion by adding 0.1 N sodium hydroxide to the solution into which the hydrogen ions were diffusing was unsuccessful. The equilibrium value (pH) increased for successive runs. The failure to detect the diffusion of ions other than hydrogen may have been due to the precipitation of silver chloride or lead chromate within the pores blocking further diffusion.

It has been reported (15) that the rate of diffusion of gases through electrolytic nickel varies directly with the overpressure. Results obtained with the first permeability apparatus indicated that

this was true from atmospheric pressure (740 mm of mercury) to about 50 mm of mercury overpressure. Below this overpressure the rate of diffusion appeared to decrease more slowly than the overpressure decreased, however, these readings at low overpressures were near the limit of accuracy of the first permeability apparatus. The second apparatus was designed to increase the accuracy of these readings at lower overpressures. The size of the foil, exposed for permeation by gases, was increased about sixty times. The lower limit of the readings possible with the McLeod gauge was decreased ten times by adding an additional scale to the capillary.

Employing the second permeability apparatus it was again observed that the rate of diffusion varied linearly with the overpressure only at overpressures of about fifty mm of mercury or over. High overpressures (one atmosphere) were found to damage the foil. This was probably due to the increased foil size since no trouble was encountered with the first apparatus. If the data is plotted employing log-log coordinates that portion of the curve above fifty mm of mercury had a slope of unity (if the overpressure were doubled, the rate of diffusion was doubled) which is indicative of molecular flow. Since molecular flow occurs only when the mean free path of the gas molecule is large compared to the diameter of the capillary this would indicate that the size of the pores was of the order of magnitude of about 10^{-5} cm. or about 0.1 microns. At higher overpressures the gases diffuse through capillaries by viscous flow. In this type of flow the rate of diffusion is a linear function of the overpressure squared.

Adzumi (21) found that the rate of flow of gases through porous diaphrams could be interpreted by the formula:

$K = A \bar{b} P + \gamma B F$ where

K is the rate of flow of gas in mm-cc/second
A is $5.230 \times 10^{2}(1/\eta)$ (η is the viscosity of the gas)
B is equal to (r^4/l) where r is the radius of the capillary, l the length in cm.
P is the mean pressure across the diaphram
γ is the coefficient of slip assumed to be 0.9
B is $3.043 \times 10^{4}(T/M)^{-1/2}$ where T is the absolute temperature, M the molecular weight of the gas
F is equal to (r^3/l)

Any data on the diffusion of gases which give a linear function when the rate of diffusion is plotted against the overpressure could be similarly interpreted. If the pores are assumed to be of uniform radius and normal to the surface the ratio of F/F will give the pore radius. By this method Adzumi determined that the pore size in a series of earthenware plates were of the order of magnitude of 10^{-6} cm. Applying this equation to the data of diffusion of gases through electrolytic nickel gives less plausible results.

Foil B-02-L is illustrative of this fact. The gas used was hydrogen, the temperature about 25°C. The ordinate intercept is equal to BF, if the best straight line is drawn through the points the ordinate intercept is about 0.0001 cc/15 minutes or 6.4×10^{-5} cc-mm/second, hence F is equal to 3.8×10^{-8}. At an overpressure of 100 mm of mercury (mean pressure 50 mm of mercury) the rate of diffusion is 0.0017 cc/15 minutes from which ΔP is equal to 1.1×10^{-4} cc-mm/second. The viscosity of hydrogen at 25°C. is 8.92×10^{-5} hence the value of A is 4.6×10^{-12}. The calculated radius of the pores is the ratio F/F or the order of one

micron, obviously much too high since a pore of such size would be readily visible when the foil was examined under a microscope. Calculations from the data of other foils gave similar results.

In the study of adsorbed films of gases Harkins (22) observed that these films undergo phase changes. If the pressure of the gas is plotted against the volume of gas adsorbed a second order phase change will produce a characteristic "kink" similar to the break noted in the plot of rate of diffusion versus overpressure. If such a mechanism were responsible for the diffusion of gases through the electrolytic nickel foils it would explain why the calculated size of the pores is much too large. It would not be necessary for the gas molecule to strike a pore opening in order to diffuse through the foil. If the molecule struck the foil and was adsorbed, it could then diffuse over the surface of the foil, through a pore, and evaporate from the other side of the foil which is under negligible pressure. The surface diffusion of nitrogen and hydrogen was reported (21,22,23,24) but helium was reported as not undergoing surface diffusion. The surface was found to be a very critical factor in this diffusion. The materials reported included glass spheres, aluminum oxide, calcium carbonate, and silica.

Throughout these studies it was apparent that the permeability of the foils was affected by some factor(s) of much greater influence than the foil thickness. Often foils 25 microns thick and having no visible or photographic porosity had much greater permeabilities than similar foils 8 microns thick. The permeability was independent of the direction

in which the gas passed through the foil. Three of the foils produced from solution "D", D-02-C, D-03-B, and D-03-A, were of similar thickness (8 microns); foil D-02-E was about twice as thick (15 microns). The two from an unbuffed surface (D-03-A, D-03-B) had a much greater permeability than the other two which were from a buffed surface. The correlation of the permeability of D-03-A and D-03-B was very good until D-03-B was damaged by high overpressure.

Moore and Smith (25) found that rolled nickel foils could be cathodically impregnated with a greater volume of hydrogen if the surface of the foil consisted of a buffed layer of metal than if this layer was etched away before the foil was charged with hydrogen. They postulated that the buffed layer of disturbed metal acted as semipermeable membrane, perhaps by allowing the hydrogen ions to diffuse through, but preventing hydrogen atoms from diffusing out.

Nickel deposited on a mechanically buffed nickel surface has a random orientation until considerable thickness of metal (up to 0.1 microns) has been formed. Such a layer could have a greater effect on the permeability than the total thickness of the deposit. This is probably the reason that deposits from unbuffed surfaces gave more reproducible results and a more permeable deposit than deposits from an unbuffed surface.

CONCLUSIONS

The diffusion of gases through electrolytic nickel differs from the diffusion of gases through metallurgical (i.e., cast and worked) nickel in at least three respects:

1. Diffusion of gases through electrolytic nickel is initiated at much lower temperatures and overpressures.
2. The effect of overpressure on the rate of diffusion of gases through electrolytic nickel is more nearly a linear function of the overpressure, while with metallurgical nickel the rate of diffusion is more nearly a linear function of the square root of the overpressure.
3. Rare gases (e.g., helium) diffuse through metallurgical nickel very much slower than ordinary gases or not at all; hydrogen, helium, and nitrogen all diffuse through electrolytic nickel at relative rates comparable to those predicted by Grahams Law.

The diffusion of gases through metallurgical nickel is recognized as "lattice diffusion" or"activated diffusion". The diffusion of gases through electrolytic nickel corresponds more nearly to molecular flow through capillaries. However, this correspondance is not exact. Particularly at low overpressuresthere is considerable departure from Grahams Law. Calculations from the rate of flow indicate pores of a greater size than could be present. The rate of corrosion of nickel

in hydrochloric acid vapor is known to be linear with respect to time. The rate of molecular flow increases as the cube of the radius of the capillaries. Yet it was observed that the initial exposure to hydrochloric acid vapor had little effect on the rate of diffusion.

It appears that the initial permeability is due to a combination of molecular flow through capillaries and surface flow. The initial corrosion of the foils does not attack the internal surfaces of the pores but rather starts at an outer surface and corrodes through the foil. This explains the approximately linear relationship of breakdown time to thickness of the foil and the sharp increase in permeability of the foil at breakdown time. At breakdown time the foil has corroded through so that the internal surfaces of the pores may be attacked. The sharp increase in permeability is due to the rate of flow then increasing as the cube of the capillary radius and the fact that more pores are continually corroding through.

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