



8-1957

Some Properties of Surface Films Formed by Adsorption of *n*-Nonadecanoic Acid on Mechanically Activated Metal Surfaces

Tomlinson Fort Jr.
University of Tennessee - Knoxville

Follow this and additional works at: https://trace.tennessee.edu/utk_graddiss

 Part of the [Chemistry Commons](#)

Recommended Citation

Fort, Tomlinson Jr., "Some Properties of Surface Films Formed by Adsorption of *n*-Nonadecanoic Acid on Mechanically Activated Metal Surfaces. " PhD diss., University of Tennessee, 1957.
https://trace.tennessee.edu/utk_graddiss/3076

This Dissertation is brought to you for free and open access by the Graduate School at TRACE: Tennessee Research and Creative Exchange. It has been accepted for inclusion in Doctoral Dissertations by an authorized administrator of TRACE: Tennessee Research and Creative Exchange. For more information, please contact trace@utk.edu.

To the Graduate Council:

I am submitting herewith a dissertation written by Tomlinson Fort Jr. entitled "Some Properties of Surface Films Formed by Adsorption of *n*-Nonadecanoic Acid on Mechanically Activated Metal Surfaces." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Hilton A. Smith, Major Professor

We have read this dissertation and recommend its acceptance:

David A. Shirley, John C. Dean, D. D. Williams, M. J. Joncich

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

July 19, 1957

To the Graduate Council:

I am submitting herewith a dissertation written by Tomlinson Fort, Jr., entitled "Some Properties of Surface Films Formed by Adsorption of *n*-Nonadecanoic Acid on Mechanically Activated Metal Surfaces." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Hilton A. Smith
Major Professor

We have read this dissertation
and recommend its acceptance:

David A. Shirley

John G. Dean

D. D. Uicker

W. J. Fouch

Accepted for the Council:

Salv. Wantling
Dean of the Graduate School

SOME PROPERTIES OF SURFACE FILMS FORMED BY ADSORPTION
OF n-NONADECANOIC ACID ON MECHANICALLY ACTIVATED
METAL SURFACES

A DISSERTATION

Submitted to
The Graduate Council
of
The University of Tennessee
in
Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

by
Tomlinson Fort, Jr.

August, 1957

ACKNOWLEDGMENT

The author would like to express his most sincere thanks to Dr. Hilton A. Smith for his friendship and counsel during the course of this work, and to the Office of Ordnance Research, United States Army, for the funds which made this research possible.

He would also like to very humbly thank his Mother and Father who have always encouraged and helped him in anything worthwhile he set out to do, and his wife, Martha, for her love and understanding which have helped him so much during his years in graduate school.

TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION	1
A. The Problem	1
B. Previous Work	1
1. Adsorption on Metal Powders	1
2. Adsorption on Gross Metal Surfaces	3
a. Lubricating Layers	3
b. Oleophobic Layers	6
c. Direct Measurement of Adsorbed Material	7
3. Theoretical Aspects of Adsorption on Metal Surfaces	8
a. Adsorption Cross Section of Fatty Acids	8
b. Mechanism of Adsorption from Solution onto Metal Surfaces	9
4. Adsorption and Reaction on Metal Surfaces Prepared under an Inert Solvent	11
a. Work of Smith and Allen	11
b. Work of McGill	14
II. EXPERIMENTAL METHOD	20
A. Surface Preparation	20
1. Technique	20
2. Equipment	22
a. Lathe	22

CHAPTER

PAGE

II. (continued)	
b. Cutting Tool	22
c. Machining Cups and Holders	24
d. Metal Samples	24
B. Adsorption of Fatty Acid	28
1. Technique	28
2. Equipment	29
a. Adsorption Cups	29
b. Stirrers	31
c. Temperature Control	31
3. Reagents	31
a. Solvent	31
b. Solute	34
c. Acid Solutions	34
C. Counting Apparatus and Measurement Techniques	37
1. Technique	37
2. Equipment	38
III. EXPERIMENTS ON FRESH METAL SURFACES	39
A. Introduction	39
B. Radiochemical Standardization	40
1. The Problem	40
2. Experimental Technique and Results	42
3. Notes	44
C. Experiments on Solution Machined Metals	46

III. (continued)

1. Tests of Proposed Reaction Mechanism	46
2. Adsorption Experiments	47
3. Desorption Experiments	51
4. Free Energy Calculations	51
5. Results	53
a. Cobalt	53
b. Indium	56
c. Tin	57
D. Discovery of Soap Desorption and Monolayer	
Replenishment	57
1. Inconsistent Data	57
2. Hypothesis of "Exchange" Adsorption	59
3. Tests of Hypothesis	60
a. Choice of Metal	60
b. Effect of Soap Solubility	60
c. Proof of "Exchange"	63
E. Factors Influencing "Exchange"	69
1. Effect of Fatty Acid Solution Concentration	69
2. Effect of Different Metals	73
a. Radiochemical Studies	73
b. Analytical Experiments	73
IV. RESULTS AND DISCUSSION	77
A. Mechanism of Monolayer Replenishment	77

IV. (continued)	
B. Nature of the Exchange Phenomenon	78
C. Correlation of Experimental Results	86
D. The Kramer Effect	91
E. Suggestions for Further Work	93
V. SUMMARY	94
APPENDIXES	98
APPENDIX I. ELECTRON EMISSION FROM CLEAN METAL SURFACES . .	99
A. New Experimental Methods	99
B. Electron Emission from Newly Prepared Surfaces	100
1. Emission Due to Abrasion	100
a. Emission Decay	100
b. Effect of Temperature	101
2. Emission Due to Phase Changes	102
3. Emission Due to Sample Irradiation	102
4. Emission from Etched Specimens	104
5. Possible Explanations for the Kramer Effect	104
C. Formation of Hydrogen Peroxide at Fresh Metal Surfaces	107
1. Experimental Evidence	107
2. Theoretical Explanation	107

CHAPTER

PAGE

APPENDIX II.	PREPARATION OF THE <u>n</u> -NONADECANOIC ACID	110
	A. Preparation of the Grignard Reagent	110
	B. Synthesis of the Unlabeled Acid	112
	C. Synthesis of the Labeled Acid	113
	1. Carbonation	113
	2. Product	116
	3. Notes	116
APPENDIX III.	PREPARATION AND PROPERTIES OF THE HEAVY	
	METAL SOAPS	119
	A. Preparations	119
	1. General Procedures	119
	2. Iron III Nonadecanoate	119
	3. Cobalt II Nonadecanoate	120
	4. Iron II Nonadecanoate	120
	B. Properties	121
	1. Melting Points	121
	2. Solubilities	121
APPENDIX IV.	MICROANALYTICAL TECHNIQUES	122
	A. Cobalt	122
	1. Analytical Method	122
	2. Procedure	122
	B. Iron	126
	1. Analytical Method	126
	2. Procedure	127

CHAPTER

PAGE

APPENDIX IV. (continued)

C. Copper	131
1. Analytical Method	131
2. Procedure	133
3. Notes	135
D. Silver	137
1. Analytical Method	137
2. Procedure	138
E. Aluminum	140
1. Analytical Method	140
2. Procedure	141

APPENDIX V. THERMODYNAMIC CALCULATIONS	144
A. Method of Calculation	144
B. Metal-Acid Reactions	144
1. Reaction of Cobalt with <u>n</u> -Nonadecanoic Acid	144
2. Reaction of Iron with <u>n</u> -Nonadecanoic Acid	146
3. Notes	147
C. Standard Free Energies of Formation of the Metal Soaps	149
APPENDIX VI. COUNTING STATISTICS	150
BIBLIOGRAPHY	152

LIST OF TABLES

TABLE	PAGE
I. Spectrographic Analyses of Metal Samples	26
II. Working Concentrations of <u>n</u> -Nonadecanoic Acid Solutions . .	36
III. Acid Standardization Counts	43
IV. Standardization Factors	45
V. Activation Energy Factors and Free Energy Changes for the Soap Formation Reactions	54

LIST OF FIGURES

FIGURE	PAGE
1. Allen's Adsorption Isotherms	13
2. McGill's Adsorption Isotherms	18
3. Machining Apparatus	21
4. The Cutting Tool	23
5. Details of Sample Mounting	25
6. Details of Solution Stirring Apparatus	30
7. Thermostated Sample Mount and Adsorption Cup Jacket . . .	32
8. Adsorption Isotherms on Cobalt	48
9. Adsorption Isotherms on Indium	49
10. Adsorption Isotherms on Tin	50
11. Desorption Isotherms on Cobalt and Indium	52
12. Influence of Desorbing Solutions on Desorption Rate . . .	62
13. Fatty Acid - Soap Exchange on Copper Surfaces	64
14. Adsorption Isotherms at Elevated Temperatures	68
15. Decay of Exchange Rate with Age of Metal Surfaces	70
16. Exchange as a Function of Fatty Acid Solution Concentration	72
17. Exchange Rates Determined from Radiochemical Measurements	74
18. Exchange Rates Determined from Analytical Measurements . .	76
19. Kinetic Treatment of the Radiochemical Results	79
20. Kinetic Treatment of the Analytical Results	81
21. Carboxylation Apparatus	114

FIGURE

PAGE

22. Cobalt Analyses	125
23. Iron Analyses	130
24. Copper Analyses	132

CHAPTER I

INTRODUCTION

A. The Problem

The work reported here is concerned with the adsorption of n-nonadecanoic acid onto freshly machined metal surfaces. The work done is a direct continuation of that begun by Smith and Allen¹ and continued by McGill² whose experimental techniques have largely been adopted. The investigation involves the adsorption of a typical polar organic molecule onto "clean" metal surfaces, prepared under rather rigidly controlled and unique conditions in a system from which the usual surface contaminants are believed to be absent. The purpose of these studies is to gain some insight into the properties of metal surfaces themselves, the nature of adsorption onto these surfaces, and the nature of the resulting adsorbed surface layers. The long chain fatty acid chosen for the adsorption studies is a typical lubricant. Therefore, the results are of particular value in the study of metal wear and corrosion inhibition. Adsorption is, of course, the first step in any heterogeneously catalyzed process. It is, therefore, expected that the results obtained will be of more than academic interest.

B. Previous Work

1. Adsorption on Metal Powders

Historically, much of our knowledge of metal surfaces has come from adsorption studies. The majority of this work has been part of

an attempt to explain or determine the catalytic activity of the metal in question, and consequently, the studies have usually been carried out with the metal in powder form. Working with metal powders has several inherent advantages, as well as some disadvantages. Powders have a very large surface area; so adsorption and reaction on them can be studied by ordinary macro or semi-micro means. The surface area of catalyst powders is always uncertain, however. Determination of this area has usually been done by nitrogen adsorption,³ but there is never any guarantee that the surface available for adsorption of a nitrogen molecule is the same as that available for adsorption of a reacting species. Further, obtaining reproducible surface areas with different batches of catalyst is very difficult.

Catalyst powders are always contaminated by coatings of oxide, hydroxide, etc., due to prior treatment of the catalytic material. As this previous treatment is never exactly the same for any two batches of catalyst, the surface conditions vary, and results obtained with one batch do not necessarily apply to another.

There are two rather different techniques used for studying adsorption on metal powders. Probably the most used for fundamental work has been the adsorption of gases onto metals under rather high vacuum conditions. The techniques involved are rather specialized and are of little applicability to the present problem and so will not be discussed further here. Reference may be made to the text by Brunauer⁴ who considers the subject at some length.

The second technique involves adsorption from solution. Allen⁵ has made an adequate summary of work done in this laboratory⁶ and

elsewhere^{7,8,9} on the adsorption from solution of long chain fatty acids, esters, amines, and alcohols onto metal powders. Results of experiments of this type are sometimes contradictory due to the difficulty of preparing catalytic materials having the same surface properties. Any new technique which would give more reproducible results would be of value.

2. Adsorption on Gross Metal Surfaces

a. Lubricating layers. The principal impetus for the study of adsorption onto smoothly machined metal surfaces has come not from catalysis, but from interest in the causes and prevention of friction, corrosion, and wear.

The mechanical engineer applies the term "boundary lubrication" to that effected by a layer of the lubricating material only a few molecules in thickness. This type of lubrication does not reduce friction to the degree that a large excess of the lubricant does, and the lubricating layer is removed much more rapidly in the wearing process than in the more usual "hydrodynamic" lubrication. However, boundary lubrication offers a unique method of studying adsorption on gross metal surfaces because the coefficient of friction is influenced here not only by the properties of the lubricant but also by those of the underlying metal. Factors are the thickness of the adsorbed film, the type of molecule adsorbed as well as its molecular weight, the smoothness of the underlying metal, the speed at which the metal surfaces are passed over each other, and the force between the metal surfaces. Since these variables can be controlled, friction measurements provide one method of measuring the extent and nature of adsorption of the lubricating film.

The effect of temperature on boundary lubrication is striking. Generally, it is found that as temperature is raised there is little increase in friction until some well-defined point is reached where a sudden increase is noted. The effect is reversible when the lubricant is cooled. It has been shown that this temperature is the same as that of the bulk melting point of the solid lubricant.¹⁰ Fatty acids are an exception to this rule. They maintain their lubricating properties to temperatures far above their melting points. The reason for this seems to be that the fatty acids react with the metal atoms of the sliding surfaces to produce soaps, which have much higher melting points than the acids themselves. This idea is substantiated by the fact that with inert metals like gold and platinum which would not be expected to form soaps, the lubricating properties of fatty acids disappear just at their bulk melting points. With more active metals, the temperature of the onset of friction increase has been shown to be identical to the melting point of the appropriate metal soap.

The formation of such soaps on metal surfaces has been tested by a tracer technique.¹¹ A metal surface made radioactive by neutron bombardment was immersed in a fatty acid solution. It was then removed, and the adsorbed material desorbed into hot benzene. Radioactive metal was desorbed indicating chemical reaction had occurred. The quantity of metal desorbed was evidence that several molecular layers of soap had formed, except on the most noble metals where no reaction was indicated. Probably, where reaction occurs, the fatty acid diffuses through the soap layer and reacts with the underlying surface. The rate of diffusion of this soap back into the solvent is slower, and, hence, there is a build up of soap on the surface.

The detailed behaviour of the metal soap depends on how it is deposited on the metal surface. If there is a weak attachment between the soap and the metal surface, the soap may desorb back into the excess lubricant. This tendency is, of course, increased as temperature is raised so the breakdown of the lubricating film may take place at a lower temperature than the theoretical. Adsorbed soap applied from water solution breaks down at about 100°, due to ebullition of occluded water. Fatty acids which react in situ to form adsorbed soaps are better lubricants than are soaps formed elsewhere and then used as lubricants because of their stronger attachment to the surface.

Finally, experiments have been performed¹² to try to determine the optimum metal surface state for most efficient lubrication. In particular, the effect of mild oxidation of the metal surface on the efficiency of lubricating films has been studied. Results indicate that the most efficient lubrication is attained with surfaces which have been allowed to oxidize for a short period, preferably in the presence of water. The explanation given for this is that the free energy requirements of the reaction of the metal oxide with the fatty acid are more favorable than those of the reaction of the metal itself. This leads to more complete surface reaction. The additional soap formed on the oxidized metal surface makes a more efficient lubricating layer. Quantitative measurements to correlate the extent of oxide formation with reaction of fatty acid had not been undertaken at the time the present series of investigations was begun.

Studies of boundary lubricants have shown, then, that adsorption of fatty acids by metals is a chemisorptive process leading to soap

formation, that the stability of the adsorbed layer is dependent on the conditions of its formation, and that soap formation is favored by oxidation of the metal surface.

b. Oleophobic layers. Another property of adsorbed films which, like friction, has been used to study adsorption on macroscopically smooth metal surfaces is the ability of certain adsorbed films to repel the approach of molecules of solvent. Such films, which show an unusual degree of resistance to wetting, are called oleophobic.

Oleophobic layers were first discovered in 1946 by Bigelow, Pickett, and Zisman.¹³ Metal specimens dipped into a solution of eicosyl alcohol in hexadecane could be removed dry, while if immersed in solvent only they retained an oily layer. These investigators reasoned that the oleophobic property must be caused by oriented close-packing of monolayers of adsorbed material on the surface, and making use of contact angle measurements, they were able to calculate the cross-sectional area of the film molecules. Oleophobic layers were formed from a variety of solvents and polar solutes, the general requirements being the presence of a polar group at the end of a hydrocarbon chain of at least eight and preferably fifteen or more carbon atoms, and a low solubility in the solvent used. It is interesting to note that for every compound studied a characteristic temperature was found, above which the oleophobic property disappeared. This temperature has been used to calculate the heats of adsorption of several long chain compounds.¹⁴

Study of oleophobic layers, then, has furnished information about the orientation, dimensions, and heats of adsorption of adsorbed layers of fatty acids on metals.

c. Direct measurement of adsorbed material. A more fundamental technique for measuring adsorption on gross samples of metal than either of those mentioned above is the direct determination of the quantity and character of the adsorbed material. This method would surely have come into wider use than it has were it not for the experimental difficulties attendant to it. These are due to the fact that the surface area available for adsorption is very small so that extremely sensitive micro-analytical techniques are necessary in detecting adsorbed material, and to the extreme difficulty of obtaining a smooth surface of measurable and known area.

The first difficulty has been attacked in at least two ways: by the use of radioactive tracers as an analytical method, and by the use of micro balances. Dobry¹⁵ used this latter technique to determine the amount of chemisorbed stearic acid on copper and on copper oxide surfaces. After measuring weight increases of the metal due to exposure to the acid in benzene solution, he desorbed the adsorbed films into fresh benzene and subjected the desorbate to a copper analysis. In this way, he was able to determine what part of the acid was physically adsorbed and what part chemically adsorbed. He found usually about 30 per cent reaction on the oxidized surfaces and none on the unoxidized copper metal.

Probably a better method than this is the radioactive tracer technique. As mentioned above, Bowden and Moore¹¹ used a tagged metal surface onto which ordinary stearic acid was adsorbed in the form of Langmuir-Blodgett layers. The film was then desorbed, and the amount of metal removed was measured by a counting technique. Reaction amounted

to approximately 25 per cent.

Beischer¹⁶ used a tracer technique in which the fatty acid labeled with carbon-14 was adsorbed from Langmuir troughs onto the metal. The active layer was then pressed against a piece of X-ray film for a standard time interval, and the activity was determined by measuring the degree of darkening of the film.

After forming the film, physically adsorbed material was removed by benzene rinsing and vacuum evaporation, and the remaining material was assumed to be chemisorbed. It was found that layers adsorbed on glass surfaces where no reaction could occur were removed completely in this manner. However, solubility of the soap in benzene always led to somewhat low results. It was estimated that reaction amounted to approximately 30 per cent. No attempt was made to prevent oxidation of the copper surface.

The second problem, that of smooth and reproducible surfaces, has not yet been satisfactorily solved. The usual polishing, etching, and degassing always leaves contaminants on the surface. High temperature outgassing is applicable to few adsorption systems. It is thought that the method used in the present investigation may prove more satisfactory than those previously employed.

3. Theoretical Aspects of Adsorption on Metal Surfaces

a. Adsorption cross section of fatty acids. The manner in which fatty acid molecules become adsorbed on metal surfaces, and the properties of the adsorbed films, are influenced by the shape of the individual adsorbed molecules, and the manner in which they are aligned on the metal.

Most of our knowledge of the alignment of molecules in ~~Langmuir~~-Blodgett type films has come from the study of these films on water surfaces. ~~Langmuir~~¹⁷ has substantiated the old idea that the polar parts of the molecules are attracted into the aqueous phase, with the nonpolar hydrocarbon tails oriented normal to it and extending out from it, by showing that the area occupied per molecule of saturated fatty acid in such films is independent of chain length of the acid.

A large number of experiments with surface balances on such films has shown that abrupt increases in the film pressure occur at points which are characteristic of the species of which the film is composed. This resistance to further compression is thought to occur at the points where close-packed molecular layers are formed, with further compression made possible only by crumpling the film. From data determined from this type of experiment plots of area per molecule vs. film pressure can be made, and the region due to close packing extrapolated to zero pressure to obtain the area occupied per molecule in the ideal uncompressed film. Using this method, Adams¹⁸ found that the cross-sectional area of fatty acids of from fourteen to twenty-two carbon atoms was approximately 20 \AA^2 .

b. Mechanism of adsorption from solution onto metal surfaces. Adsorption must occur through diffusion of the adsorbable material in the solution to the metal surface. It is known¹⁹ that fatty acids exist in solution in hydrocarbon solvents at least partly in the form of dimers, held together at the carboxyl position by hydrogen bonds. Frewing^{20,21} has suggested that the dimerized state is maintained

after adsorption, but later work¹³ seems to indicate this is an error. One of the first steps in adsorption is then the splitting of the dimer pair, and whatever energy is necessary for this is furnished at the expense of the heat of adsorption.

From their work on oleophobic monolayers, Bigelow, Pickett, and Zisman¹³ and Bigelow, Glass, and Zisman¹⁴ determined that the adsorbed molecules are vertically oriented on the surface in a close-packed state with the polar parts of the molecules attached to the surface, and that only monomolecular layers are formed. These can sometimes bridge small proclivities in the metal due to the lateral attraction of the carboxyl groups and carbon chains. If the chains are unsaturated, adsorption may occur at the double bond as well as at the carboxyl group, which leads to horizontal orientation of the adsorbed molecules.

These ideas are probably an oversimplification, because later electron diffraction studies²² have shown that the molecules of stearic acid in oleophobic layers are tilted an average of 5° from the vertical. Epstein²³ interpreted his electron micrographic studies as indicating the presence of surface clusters which he thought were circular and had a diameter of approximately 100 \AA . He suggested that the reason for the presence of these clusters was probably the difference in cross section of the carboxyl groups and hydrocarbon chains. The central molecules are vertically oriented with the peripheral ones leaning toward the center due to the lateral attraction of the hydrocarbon tails.

The energetic processes leading to the formation of a two dimensional array of molecules on a surface has been considered by

Roberts²⁴ and Topping.²⁵ Energy is involved in the alignment of the molecular dipoles among themselves as well as with the mirror images of these dipoles which are induced in the metal surface. Here again, a homogeneous uncontaminated surface for adsorption would greatly simplify theory and calculations.

4. Adsorption and Reaction on Metal Surfaces Prepared under an Inert Solvent

a. Work of Smith and Allen. As stated above, various investigators have studied adsorption from solution onto metal powders as part of studies of heterogeneous catalysis by metals. However, many of the catalyst powders were contaminated with oxide, etc., due to previous exposure to the air. The extent of oxide formation on these surfaces, and the effect of this contaminant on surface area and adsorptive and catalytic behaviour was largely unknown. A knowledge of what this effect is would be very valuable since the knowledge could be used to help interpret and better understand the behaviour of almost all catalytic materials.

Smith and Allen¹ undertook to study this problem. Due to the difficulty of preparing "clean" catalyst powders they worked with gross samples of several typical metals. Their method of preparation of surfaces was unique. Using a modified, hand-operated bench lathe, fresh surfaces were prepared on a variety of metal cylinders by machining them under an inert cover liquid containing carbon-14 labeled n-nonadecanoic acid. After machining, the metal cylinders were transferred, while wet, to stirred cups which contained the same fatty acid

solution used for machining. The acid was allowed to adsorb onto the metal surfaces for measured time intervals after which the cylinders were removed, allowed to drain, and the extent of adsorption determined with a Geiger counter. If the adsorption onto an oxidized surface was to be determined, the cylinder was cut in air and allowed to oxidize, after which it was placed under the solution containing the labeled acid and treated as described.

Results of Smith's and Allen's experiments on copper, nickel, iron, and aluminum metals are shown graphically in Figure 1. The adsorption isotherms for all four metals are markedly different, depending upon whether the adsorption was onto the oxidized or unoxidized surfaces. For the unoxidized metals, adsorption quickly reached a maximum value, while for the oxidized surfaces adsorption continued to increase even after several days exposure to the labeled acid solution. In every case, adsorption was higher on the oxidized than on the unoxidized surfaces.

Smith and Allen explained their results by hypothesizing a reaction between the metal surface atoms and fatty acid which led to formation of chemisorbed metal soap. The higher adsorption on the oxidized surface was explainable, as the free energy requirements of the reaction



are known to be more favorable than those of the reaction



They made no effort to control the properties of the oxide layer.

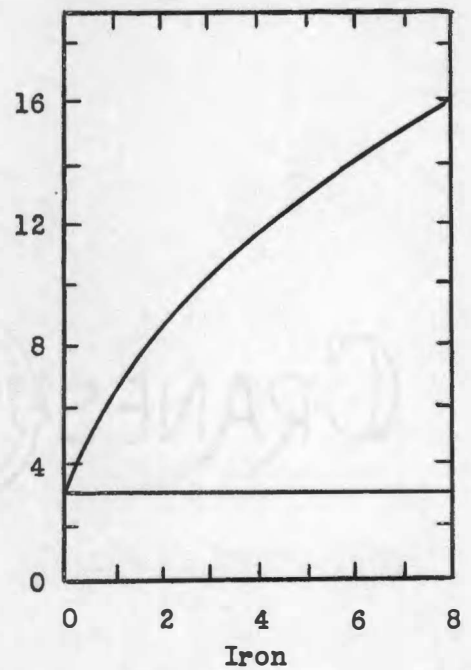
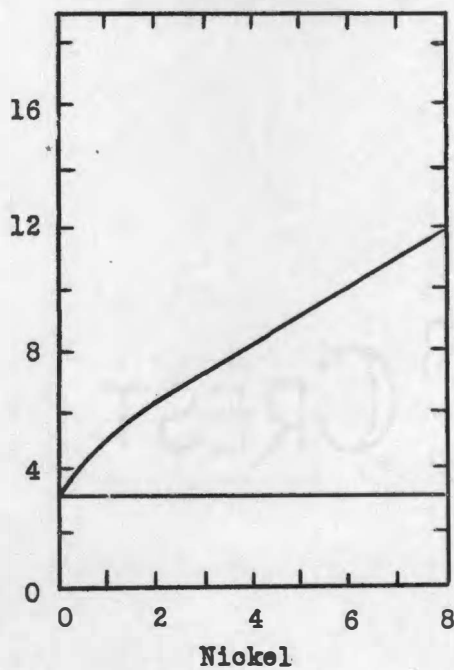
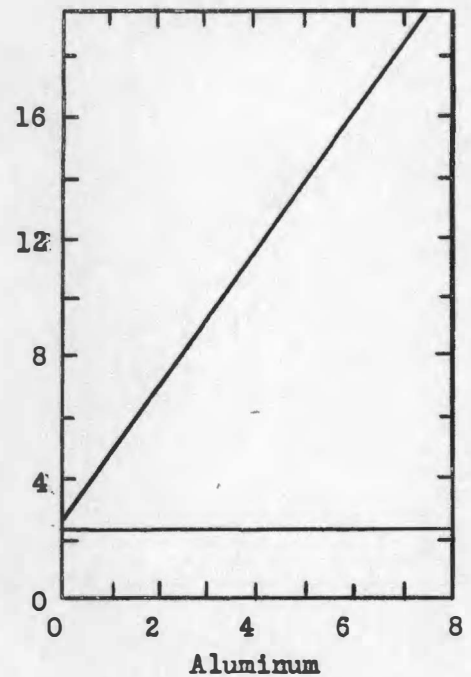
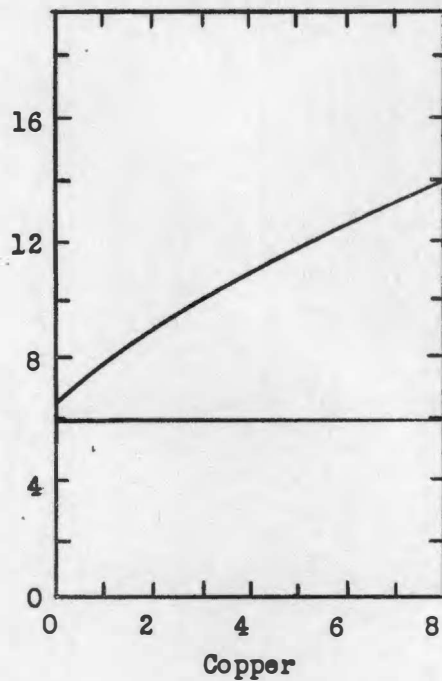


FIGURE 1 - ALLEN'S ADSORPTION ISOTHERMS

Adsorption (ordinate) in units of molecules per 100 \AA^2 is plotted as a function of acid exposure time in days. For each metal, the higher curve represents adsorption on an oxidized surface and the lower curve adsorption on an unoxidized surface.

Smith and Allen suggested that complete coverage of the surface was responsible for the adsorption plateau on the unoxidized surfaces, while pitting of the surfaces in the oxidation process led to increased surface area and sites available for reaction for the oxidized metals. Attempts were made to estimate heats of adsorption by determining adsorption isotherms at various temperatures, but results were inconclusive.

b. Work of McGill. McGill² continued the work begun by Allen, using the same general techniques and equipment. He studied the adsorption behaviour of n-nonadecanoic acid onto eight different metals when they were machined under the labeled acid solution and never exposed to the air. Of the metals studied, he found that magnesium, lead, copper, nickel, and aluminum quickly reached adsorption plateaus and that these plateaus indicated an identical population density of adsorbed acid. The value obtained, 4.17 molecules per 100 Å², was exactly that which Langmuir obtained¹⁷ from force-area measurements on compressed fatty-acid films spread on water, and corresponds to close-packed monomolecular layers based on the cross section of the carboxyl groups as the limiting factor. This implies that the metal surfaces produced were, so far as adsorption is concerned, perfectly flat.

Silver showed a small deviation from monolayer coverage while gold and platinum gave characteristically different isotherms. Silver was considered as being a limiting case for chemisorption, with all metals more active reacting completely to give the saturated adsorption layer and gold and platinum reacting little or not at all. What little

adsorption there was on these metals was considered due purely to physical attraction to the surface.

Comparative experiments were also run on oxidized and unoxidized surfaces. The experimental technique was varied from that of Allen to allow control of the thickness of the oxide layer. In contradistinction to the results of Allen, McGill found that adsorption on unoxidized surfaces was higher, not lower, than that on surfaces which were exposed to the air for short, measured time intervals. This was considered very significant, as it had always been found previously that adsorption was favored by oxidation of the surface.

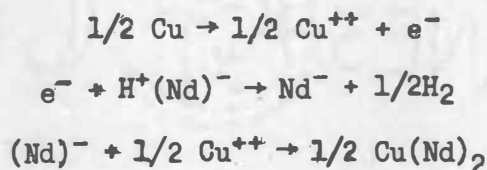
McGill was able to find some precedent for his work in the results of Shaw²⁶. This investigator, making a fundamental study of cutting fluids, had found that the combination of high local temperatures and pressures existing in the neighborhood of the cutting edge, and the nascent metal surface produced by the cutting process were often able to promote chemical reactions. He was able to prepare a variety of metal-organic compounds in this manner under conditions which would normally be very unfavorable for reaction.*

McGill suggested that the seemingly anomalous results he had obtained, as well as Shaw's "mechanical activation", were explainable in terms of a newly discovered phenomenon, the Kramer effect. This is the name applied to the low energy electron emission observed from freshly prepared or "clean" metal surfaces which occurs for short

*The Cincinnati Milling Machine Company, by whom Shaw was employed, have patented an apparatus for carrying out such reactions. This they call the "Cimmac Reactor".²⁷

periods after such surfaces are prepared. Energy of these electrons has been estimated to be of the order of a few electron volts. Emission decays rapidly, according to a hyperbolic law. This emission is almost certainly responsible for the hyperactivity of such surfaces which has been mentioned earlier.*

McGill reasoned that nascent metal surfaces, from which low energy electrons were being emitted, might well be sufficiently energetic so that their reaction with the fatty acid would be favored over that of the metallic oxide from which emission was absent. He hypothesized a reaction mechanism for the chemisorption, involving the Kramer electron, as follows. Copper is used as an example.



The net reaction is



McGill went to considerable pains to show that chemisorption was indeed occurring and that this chemisorption was influenced by the Kramer effect. He showed that the adsorptive ability of the various surfaces declined with increasing aging time under the pure inert solvent before exposure to the fatty acid solution, and that this decline paralleled that of the Kramer effect. He was also able to correlate adsorptive ability with ability of the fresh surfaces to expose photographic

*The cause of the Kramer effect is still in dispute. Most of the significant work done concerning it together with the various explanations proposed for the electron emission are summarized in Appendix I.

plates. This latter phenomenon, known as the Russell effect, is possibly another manifestation of the Kramer effect, and is discussed in Appendix I.

Thermodynamic calculations showed that the free energy changes involved in the soap formation reaction were unfavorable for several of the metals studied, but that additional energy on the order of an electron volt could make reaction possible. McGill hypothesized that this energy was supplied by the Kramer electron.

The effect of machining the various metals under progressively more dilute solutions is shown in Figure 2. As the metals become more noble, more and more concentrated solutions are necessary for complete surface coverage. This McGill explained as being due to the Kramer effect also. As solution concentration decreases, it takes longer and longer for sufficient fatty acid to diffuse to the surface to form the saturated adsorption layer. Since the Kramer effect is decaying as this diffusion to the surface is occurring, the more noble metals would be expected to be affected first because chemisorption on their surface requires more energy. Aluminum is clearly an anomalous case, as monolayer coverage is attained on it only with the highest acid concentration, in spite of the activity of the metal.

McGill also showed by another type of experiment that adsorption was accompanied by chemical reaction. He desorbed the adsorbed fatty acid from the metal surface and then subjected the desorbed material to an analysis for the metal in question. His thought was that if a soap were formed on the surface the desorbing fatty acid should carry with

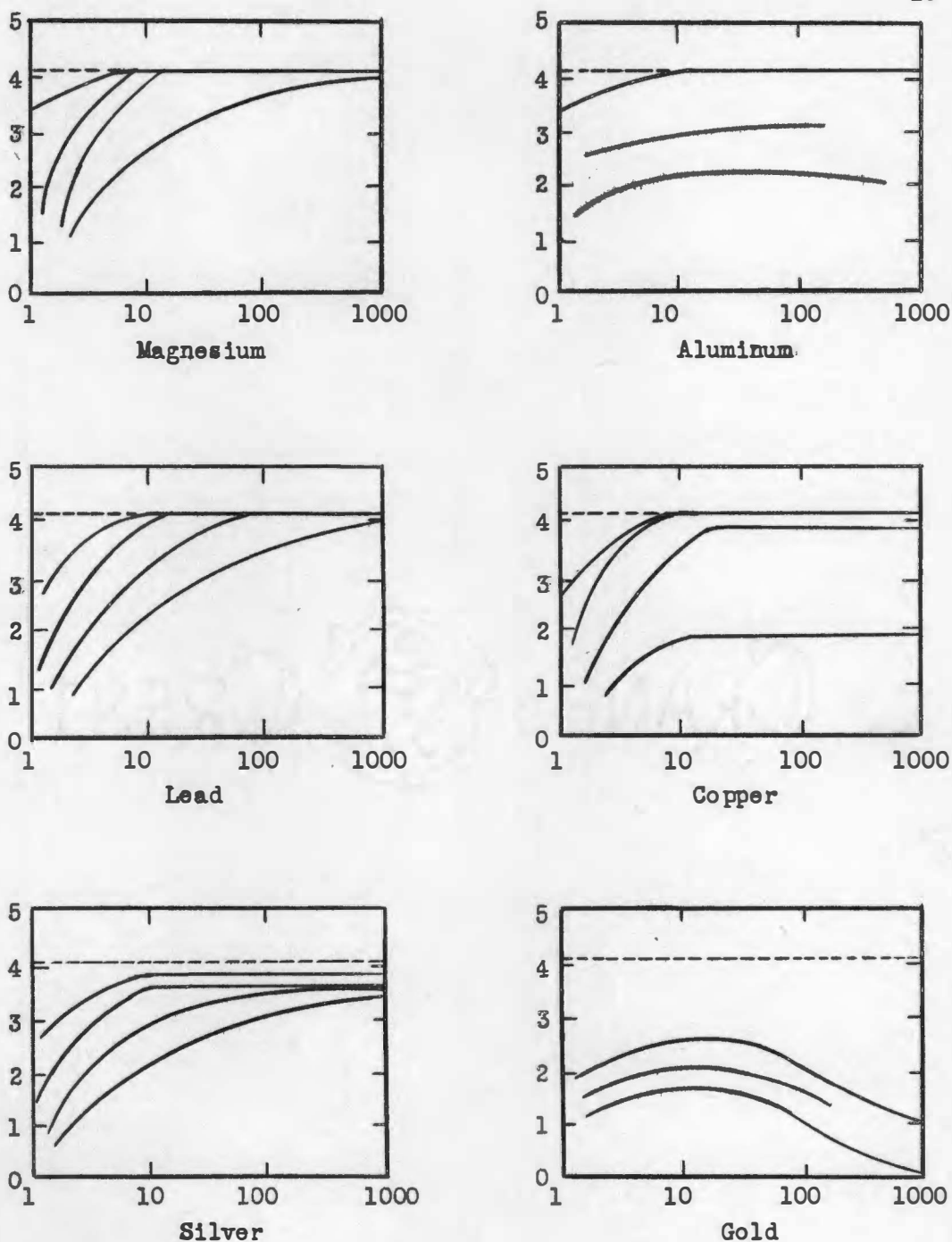


FIGURE 2 - MCGILL'S ADSORPTION ISOTHERMS

All the metals were machined under solutions "A", "A/2", "A/4", and "A/8" which accounts for the progressively lower adsorption isotherms. Adsorption (ordinate) in units of molecules per 100 Å² is plotted as a function of acid exposure time in minutes. The dotted lines indicate monolayer surface coverage.

it an atom of the metal, while if the adsorption were merely a physical phenomenon, the process should be completely reversible. In every case, except that of gold and platinum, it was found that adsorption was accompanied by quantitative chemical reaction, and that when two different soaps could be formed on the metal surface due to several valence states, the amount of metal desorbed was characteristic of only one of these. Rates of desorption were also shown to be characteristic of the solubility of the soap, and not of the fatty acid itself, in the solvent.

CHAPTER II

EXPERIMENTAL METHOD

A. Surface Preparation

1. Technique

The experimental techniques used in this work are largely those of Smith and Allen¹ as modified by McGill.² The apparatus is pictured in Figure 3. The metal samples on whose surfaces adsorption was to be measured were mounted in specially designed machining cups. These machining cups were in turn mounted on a modified bench lathe so that the cup and cylinder assembly could be transposed in both horizontal directions beneath a stationary, specially designed cutting tool mounted vertically over the ways of the lathe by means of a section of angle iron attached to the lathe bed.

To prepare a fresh metal surface, the stationary cutting tool was lowered by adjustment of the compound feed micrometer, to which it was attached, until lateral movement of the sample and cup assembly resulted in a thin slice of metal being removed from the top of the sample cylinder. Depth of the cut was usually from 0.1 to 0.2 mils, and cut width was 100 mils.* Fifteen "passes" were thus necessary to bare

*The position of the cuts was fixed by the tool carriage cross-feed micrometer and the cut depth by the compound feed micrometer. Because of a small amount of "play" in the cross-feed micrometer mechanism, it was found necessary that the setting always be approached from the same direction (either clockwise or counterclockwise). It was also found that the cutting tool could be lowered most effectively in the immediate neighborhood of the metal surface by lightly tapping the lowering control arm with a small wrench, and noting the amount of lowering effected.

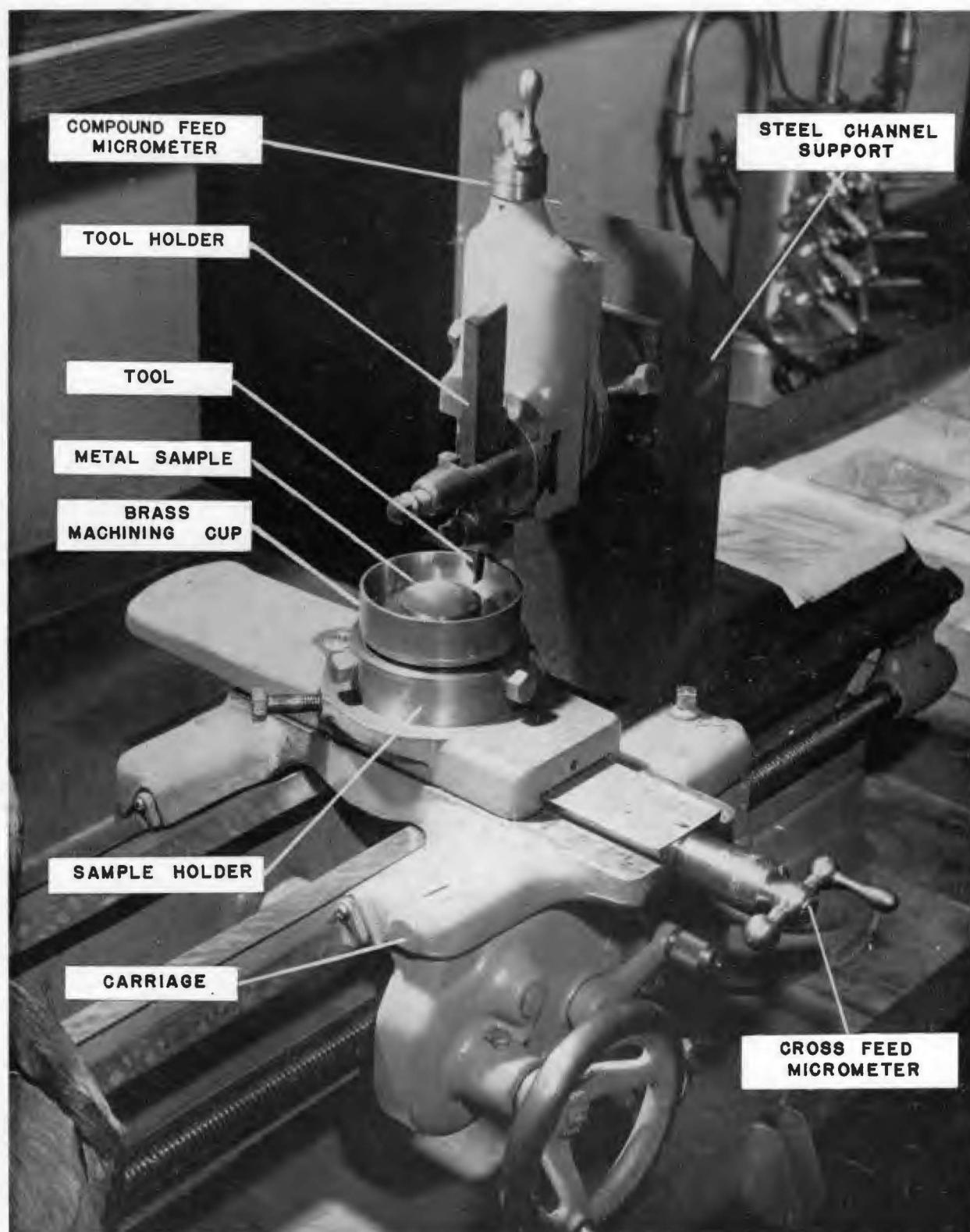


FIGURE 3
MACHINING APPARATUS

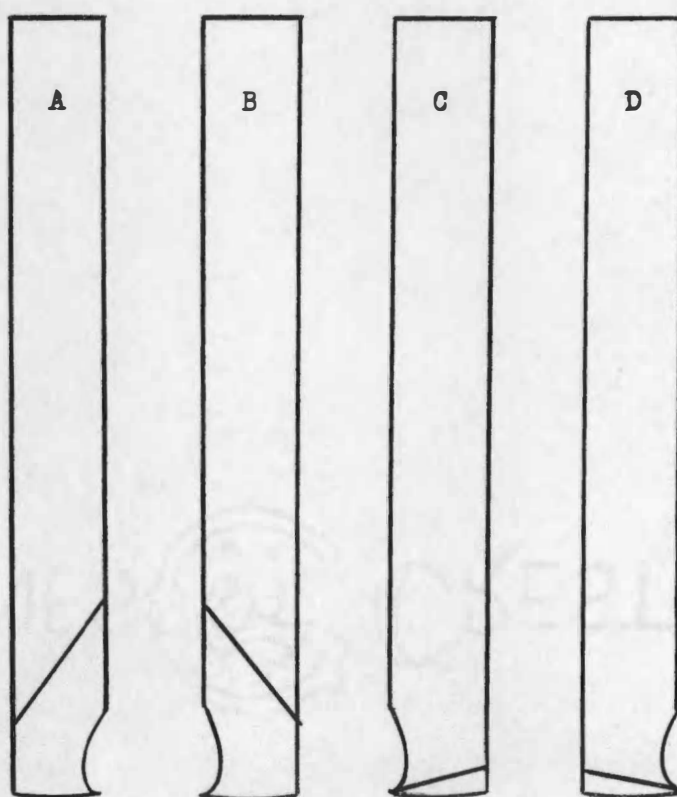
completely the top of a 1.5-inch sample cylinder. The cutting tool was never dragged a second time over a fresh surface but instead, between cuts, the sample and cup assembly was transposed around the cutting tool to position it for a new cut. All cutting was done manually, as this procedure was found to give the best results. A standard total machining time of one hundred seconds was established, which was essentially the same as that of McGill. This could be reproduced to plus or minus five seconds.

2. Equipment

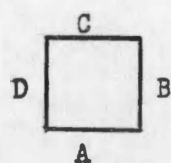
a. Lathe. The lathe which was adapted to perform the planing operation described above was the same as that used by Allen and McGill, and is pictured in Figure 3. A South Bend 24-inch metal turning lathe was actually used, but similar equipment could be similarly adapted.

b. Cutting tool. The cutting tool was of the same type as that employed by McGill² which was a modification of that employed by Allen.¹ The tool is shown in Figure 3, and is diagrammed in Figure 4. It was formed to the specifications given from a quarter-inch square Rex AAA blank by a fine grinding wheel, and was then hollow ground to a 3/16-inch radius. The bottom was ground slightly convex to produce a shallow rounded cut. The tool was resharpened before such new metal surface was prepared by stroking the bottom of the cutting edge on an oilstone, and the top of the cutting edge on a piece of # 400 carborundum paper wrapped around a 3/16-inch dowel. This preserved the hollow ground edge. After having been sharpened, the tool was washed twice with acetone, and then wiped thoroughly with a tissue soaked with cyclohexane.

FIGURE 4
THE CUTTING TOOL



Side Views
(twice actual size)



Top View

c. Machining cups and holders. These cups held the inert solvent, or the solution, which covered the metal sample cylinders as new surfaces were being cut on them. They also served as mounts for the sample cylinders. These cups were identical to those employed by McGill, and are diagrammed in Figure 5. They were machined in the Departmental Shop from standard brass stock to the specifications given. The cup sides were machined to a 2° taper to fit the cup bottoms, and so were removable. A very thin film of Nonaq brand stopcock grease spread over the taper joint effectively prevented solvent leakage.

The machining cups were mounted in specially constructed holders made to fit the lathe bed. They were held in place by three 3/8-inch machine bolts mounted equidistantly around the periphery of the holders. These holders were so marked that they could be removed from the lathe bed and then replaced exactly in the original position. Thus, when a new surface was to be prepared, the former cuts were always exactly parallel to the lathe bed.

d. Metal samples. In the course of this work, experiments were run on copper, magnesium, silver, aluminum, tin, indium, and cobalt metals. The first four of these were used for other experiments by Allen and/or McGill. The latter three have not been previously investigated. All metals were machined to 1.5-inch cylinders and then mounted on the base of the machining cups in the manner indicated. The spectrographic purity of all the samples is presented in Table I.

The copper was a bar of commercial electrolytic copper. Very smooth surfaces could be cut on it by making very shallow cuts. Surface

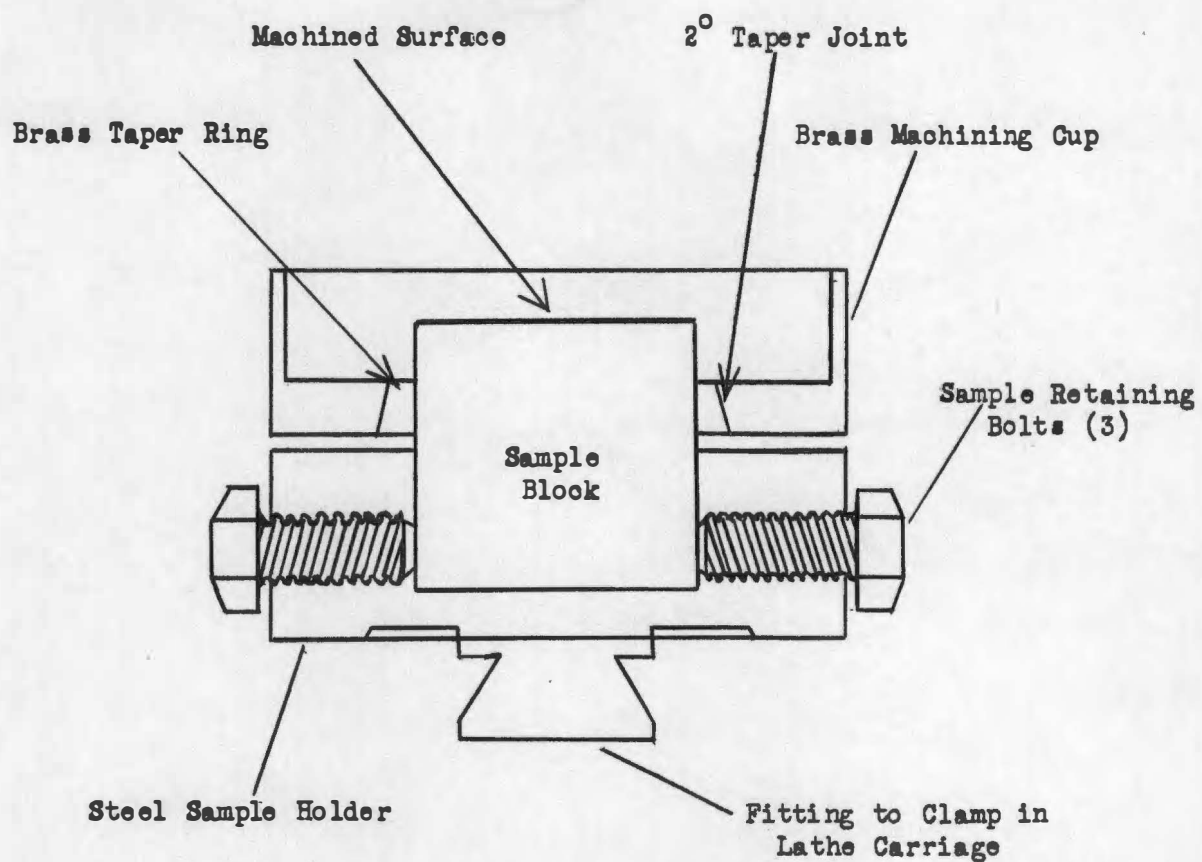


FIGURE 5

DETAILS OF SAMPLE MOUNTING

TABLE I

SPECTROGRAPHIC ASSAYS OF THE PURITY OF THE METAL SAMPLES*

Impurity	Metal Sample						
	Sn**	Cu	In	Cu	Ag	Mg	Al
Ag	0.001	-	-	0.002	Strong	-	-
Al	-	0.005	-	0.001	0.001	0.001	Strong
Bi	0.01	-	-	-	-	-	-
Co	-	Strong	-	-	-	-	-
Cr	-	-	-	-	-	-	0.02
Cu	0.03	0.1	0.001	Strong	0.01	0.002	0.03
Fe	0.03	0.1	-	0.05	0.03	0.02	0.5
In	-	-	Strong	-	-	-	-
Mg	-	-	-	0.0005	-	Strong	0.5
Mn	-	1.0	-	-	-	0.002	0.05
Ni	0.002	1.0	-	0.003	-	-	0.2
Pb	2.5	-	-	-	-	-	-
Si	-	0.1	-	0.002	-	-	0.4
Sn	Strong	0.2	-	-	-	-	-
Ti	-	-	-	-	-	-	0.03

*The concentrations of the impurities are given in per cent. All unlisted metal impurities were undetectable. All the impurity levels listed are correct to a factor of three.

**The per centage of lead in the tin sample was redetermined by a more sensitive method and found to be 1.17 per cent (plus or minus 0.1 per cent).

quality varied considerably with cut depth. The copper was soldered to the base of the machining cup.

The magnesium was obtained from the Dow Chemical Company. Although highly machinable, this particular sample contained some large single crystals. These made the machined surfaces not quite as homogeneous as they might otherwise have been. The magnesium was attached to the machining cup with a film of ordinary Duco household cement.

The silver was obtained from the A. T. Wall Company, Inc. It was highly machinable and very smooth surfaces could be cut on it. It was attached to the brass machining cup with soft solder.

The aluminum was cut from commercial aluminum stock. Some slight crystallinity was noted in the sample, as with magnesium. The metal was easy to machine and was attached to its machining cup with special aluminum solder.

The tin was obtained from the Division Lead Company. The metal was very soft and easily cut, producing very smooth surfaces. It was soldered to the machining cup.

The indium was obtained from the American Smelting and Refining Company. It was very soft, easy to machine, and produced smooth surfaces. However, the metal shavings formed in the machining process adhered to the cut surface whenever they came in contact with it. They were removed from the surface with a pair of tweezers, but the shavings appeared to form a true weld when they adhered and their removal left somewhat pock-marked regions on the surface. The areas so marked were small compared to the total surface area, however. The indium was attached to the machining cup base with Duco cement.

The cobalt was found to be quite hard and was most difficult to machine. The cut depth could not exceed 0.15 mils and cutting at all was only possible with a very sharp tool. The metal tended to powder rather than come off as smooth shavings, but surfaces appeared fairly smooth. The sample was attached to the machining cup with ordinary solder.

B. Adsorption of Fatty Acid

1. Technique

The method of preparation of a new metal surface has been described above. When adsorption measurements on such a surface were to be carried out the machining operation was done, not in air, but under an inert solvent which served as a cover liquid and protected the nascent surface from exposure to the air. The solvent contained in solution the fatty acid whose adsorption was to be measured. This solution was contained by the machining cups previously described. Volume of the solution was sufficient to cover the face of the metal sample cylinder to a depth of $1/4$ inch.

Although all the metal surfaces were machined in the manner described, they were transferred immediately after cutting from the machining cups to specially designed glass adsorption cups which contained the same solution. Here most of their actual exposure to the fatty acid solutions occurred. This was done for two reasons. First, it seemed desirable to rid the solution of the metal shavings produced by the machining process as these would, of course, adsorb fatty acid

and unnecessarily deplete the solution. Second, the metal machining cups offered no ready method of stirring the acid cover solutions. Such stirring was deemed necessary to prevent formation of a diffusion barrier to further adsorption which might limit surface coverage. Accordingly, as soon as machining was completed the bolts which held the sample holder to the lathe bed were loosened and the cutting tool was raised to permit removal of the sample and cup assembly from the lathe. The solution was then poured off, the machining cup removed from its base, and the sample, cup base, and cup holder quickly inverted over the glass adsorption cup which was equipped with a magnetic stirrer. With practice, this whole operation could be carried out in only a few seconds and the transfer made so quickly that the metal surface was always kept wet and never exposed to the air. Figure 6 is a diagram of the sample, holder, adsorption cup, and stirring apparatus. All acid exposure times were counted beginning with the initial cut on the metal surfaces. A constant stirring rate of 140 rpm. was adopted and used for all the experiments carried out.

2. Equipment

a. Adsorption cups. These were constructed from ordinary 150-ml. beakers by cutting off the beaker bottoms, some at 1-inch and others at 2.5-inches, and then flanging the cut edges. The sample holders rested on the flanged lips of these cups when the samples were inverted over them. These flanged lips were ground on emery paper to make a tight seal with the sample holders, which effectively prevented solvent evaporation over long acid exposure times.

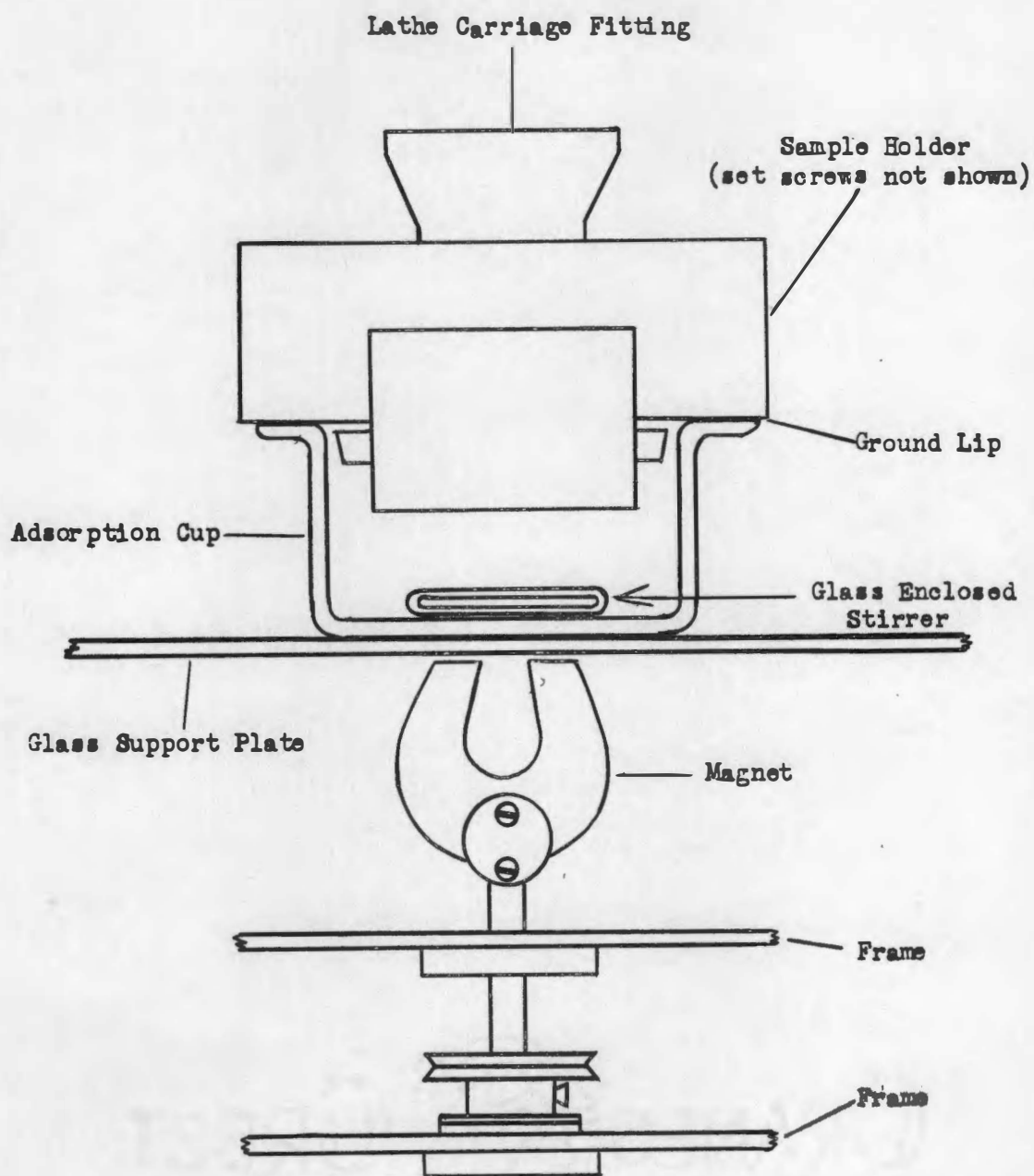


FIGURE 6
DETAILS OF SOLUTION
STIRRING APPARATUS

b. Stirrers. The stirring assembly is diagrammed in Figure 6. The magnetic stirring bars were made by sealing 5/8-inch pieces of ordinary steel paper clips in sections of small diameter glass tubing. These stirring bars were turned by small Alnico magnets attached to a variable speed motor.

c. Temperature control. Most of the adsorption experiments were carried out at room temperature (23-28°), but several of the adsorption measurements on copper were made under controlled temperature conditions, as were all the exchange measurements. McGill² has described a thermostated sample mounting which he used for some elevated temperature adsorption measurements on copper, and this is diagrammed in Figure 7. By use of this apparatus, machining could be carried out while water from a constant temperature reservoir was circulated through the sample block. A thermostated jacket for the glass adsorption cups was also constructed which permitted the solutions in these cups to be stirred while adsorption measurements were being made. This jacket is also shown in Figure 7.

Water was circulated through the cup and jacket assemblies by a centrifugal pump from a reservoir maintained at constant temperature within plus or minus 0.1°.

3. Reagents

a. Solvent. Cyclohexane was used exclusively as the solvent in the present work. This is the same solvent as that used by Allen and McGill, but differs from that of most other investigators who have usually employed benzene.

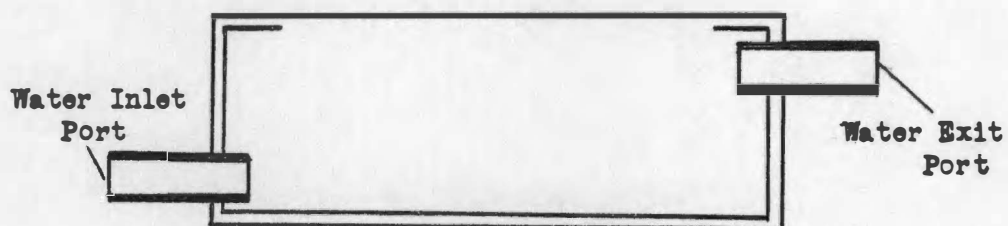
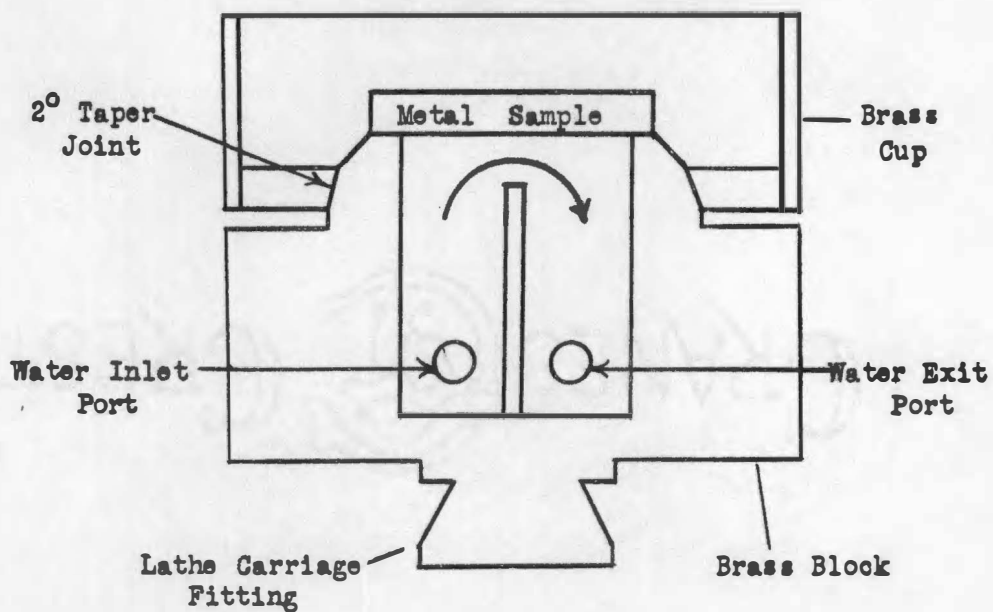


FIGURE 7
THERMOSTATED SAMPLE MOUNT AND
ADSORPTION CUP JACKET

The choice of solvent was dictated by the features desired. First, it had to be strictly nonpolar as any polarity would interfere with the adsorption which was to be studied. Secondly, it had to be absolutely nonreactive with the metal and solute. Third, it was desirable that solubility of oxygen be as low as possible, as any dissolved gas would react with the nascent metal surfaces. Fourth, it was desirable that the solvent have a fair volatility. Fifth, as large quantities of solvent were to be used, it was desirable that it be nontoxic, inexpensive, and fairly easily purified.

Cyclohexane was felt superior to benzene on both the second and third counts. The double bonds in the benzene molecule were considered possible reaction sites and, although the solubility of oxygen in cyclohexane has not been determined it is thought to be very low, and lower than that in the unsaturated hydrocarbon.*

McGill² has summarized most of the commonly employed methods of purifying cyclohexane. He chose a nitration procedure followed by extraction with alkali to remove the benzene which is the principal cyclohexane contaminant. He followed this by refluxing over sodium amalgam to remove water and, finally, passed the solvent through an activated alumina column to remove the last traces of polar material.

This procedure was found unnecessarily involved, however. It was found that very pure cyclohexane could be prepared by fractionating

*Allen purged several of his solutions with argon to prove that dissolved oxygen did not significantly affect his results. He found no difference in adsorption. Boiling the solvent was also without effect.

the drum grade material to remove most of the water and other contaminants; then passing the fractionated solvent through a 4-ft. adsorption column 25 mm. in diameter. The upper half of the column was packed with Davidson 100-200 mesh silica gel, and the lower half with Alcoa F-20 grade activated alumina. Solvent was collected at the bottom of the column at the rate of one drop every six seconds.

The quantity of adsorbent in a column of these dimensions is sufficient to purify several liters of cyclohexane. The silica gel effectively removes any unsaturated organic compounds, including benzene, and the alumina removes any traces of other polar materials. The columns' efficiency can be conveniently checked from time to time by examining the purified material for the characteristic ultraviolet absorption maxima of benzene.

b. Solute. Nonadecanoic acid was used exclusively as the solute in the present work. This is the same long chain fatty acid as that studied by Allen and McGill, and was chosen to make the results obtained as nearly comparable to theirs as possible. It was originally chosen by Allen because it was a representative long chain fatty acid, had but one polar group which could become adsorbed on the nascent metal surfaces, and because it was easily synthesizable, incorporating an atom of carbon-14 via octadecyl bromide and the Grignard reaction. Details of this synthesis are given in Appendix II.

c. Acid solutions. All of the fatty acid solutions under which the metals were machined and from which adsorption occurred were prepared by dissolving the appropriate quantity of the acid in a measured quantity of cyclohexane. Because the fatty acid was labeled to the

extent of 1.44 mole per cent with carbon-14, and because the working solutions were extremely dilute, the preparation of solutions of accurately known concentration and activity required some care. Carbon-14 is a weak beta emitter, and has been extensively used as a tracer for organic compounds. Because of the long half-life of the isotope, 5568 years,²⁸ the loss of activity due to radioactive decay is negligible over a period of a few years. However, the energy of disintegration may be sufficient to decompose other molecules of fatty acid resulting in a serious loss. To minimize this effect, the acid is best stored as a solution in which the energy of disintegration is largely absorbed by large quantities of inert solvent.

Accordingly, at the beginning of the present study 67.75 mg. of the purified labeled fatty acid was dissolved in 500 ml. of cyclohexane freshly passed through a new adsorption column. The solution was stored in a 500 ml. volumetric flask which had been cleaned with hot chromic acid, rinsed repeatedly with distilled water, and finally, steamed and thoroughly dried. This solution of concentration 135.5 mg./l. was designated solution "S", following the nomenclature of Allen. Another standard was also prepared identical to "S" except that it was prepared using unlabeled acid. This was designated solution "50 U".

From these two standards, working solutions were prepared by appropriate dilution. In the table shown below, solutions designated "A" are radioactive, while those designated "U" are not radioactive.

In an attempt to minimize adsorption on the walls of the volumetric flasks used to contain the working solutions, whenever a new flask was put into use a solution was made up in it, allowed to stand

TABLE II

WORKING CONCENTRATIONS OF n-NONADECANOIC ACID
SOLUTIONS IN CYCLOHEXANE

Acid Designation	Acid Concentration	
	$\mu\text{g.}/\text{ml.}$	$M \times 10^{-6}$
2U and 2A	5.26	17.7
U and A	2.63	8.83
A/2	1.32	4.41
A/4	0.66	2.20
A/8	0.33	1.10

for a week, discarded, and the flask filled with a new stock solution. This was done to allow the establishment of equilibrium between adsorbed fatty acid and acid in solution.

C. Counting Apparatus and Measurement Techniques

1. Technique

At the end of the desired exposure time of the metal to the fatty acid solution, the sample was removed from the adsorption cup and adsorption determined with the aid of a Geiger counter. When the sample was withdrawn the machined face was always wet with a small amount of solvent. This, of course, carried with it some non-adsorbed radioactive acid which, if not corrected for, would lead to erroneous adsorption measurements. Allen¹ corrected for this source of error by making what he called a drainage count. He immersed in the solution a clean metal sample which had been machined in air, then quickly removed it, before any reaction could occur on the surface. He then inclined the sample and allowed it to drain. He then counted the sample, and added the count obtained to the background of the Geiger tube. This procedure was somewhat erratic because results depended on room temperature, air currents, etc.

McGill found that such draining was unnecessary and that very reproducible counts could be obtained by blotting the surface with a clean photo blotter as soon as it was removed from the solution and before any solvent evaporation could occur. The solution was absorbed by the blotter leaving only the adsorbed acid on the surface. This

procedure was used throughout the present work, except that a clean tissue was usually substituted for the photo blotter.

McGill's counting technique was also adopted and used throughout this work. An aluminum mask, 1 mm. thick, having a 1.0-inch hole in its center was constructed to fit over the Geiger tube window. The active surface could then be butted directly against the mask which gave a constant counting geometry without risking contamination of the tube window. As the one-inch diameter opening in the mask was considerably smaller than the 1.5-inch diameters of the metal samples, the area counted was limited to the center of the samples, and any anomalous edge effects were eliminated. A sponge rubber pad placed beneath the metal sample holders while the counting was taking place acted as a spring and kept the sample surfaces pressed flush against the mask. A standard counting time of fifteen minutes was established and used for making all adsorption measurements.

2. Equipment

All measurements were made with a Nuclear Instrument Company Model 165 scaler. The Geiger tube was a Tracerlab TGC-2 end window tube having a mica window thickness of 1.8 mg./cm.^2 and was filled with helium and a quench gas at 720-mm. pressure. Operating voltage was 1300 volts. The tube was shielded with a 1/8-inch lead jacket. No detectable change in tube characteristics was noted over the course of the investigation.

CHAPTER III

EXPERIMENTS ON FRESH METAL SURFACES

A. Introduction

It has been stated that the work reported here is a direct continuation of that begun by Allen and carried on by McGill. Therefore, the most logical place to start was an extension of McGill's work to other metals. This both familiarized the investigator with the experimental techniques used, and added to the knowledge Allen and McGill had gained about the adsorption behaviour of n-nonadecanoic acid on machined, activated metal surfaces.

Accordingly, samples of cobalt, indium, and tin metals were obtained. Sources and spectrographic assays of these materials have been previously given. Choice of the latter two specimens was not arbitrary. It has been stated above that McGill found the adsorption behaviour of aluminum to be anomalous (Figure 2). In spite of its high activity, he observed the saturated monolayer adsorption on this metal only when it was machined under the highest acid concentration he used, solution "A". In an attempt to explain this behaviour, McGill stated that aluminum was normally a trivalent metal and consequently would be expected to form the trivalent soap. However, at the time he completed his work no such aluminum soap had ever been prepared.* The reason given for

*Since that time, preparation of aluminum III soaps has been reported.^{29,30} The third fatty acid molecule adds to the aluminum atom only with difficulty, and so McGill's explanation is in no way compromised.

this was that aluminum is a small atom, and that steric limitations prevent the approach of three fatty acid molecules to the metal. Consequently, if such a trivalent soap were formed on the machined metal surface it would probably be rather unstable, particularly as an aluminum surface atom can present only one "face" for reaction with the fatty acid.

Indium is also a trivalent metal but has a considerably greater atomic weight than does aluminum, as well as a larger atomic diameter. It is less electropositive. Consequently, if adsorption were observed to be higher on indium than on aluminum, McGill's postulate would be substantiated.

Similarly, tin lies directly above lead in the periodic table, is usually divalent, but has a smaller atomic diameter. Hence, it was thought that some steric limitation of adsorption might be observed on this material. There was also the possibility that the tin tetravalent soap would be formed on the metal surface, in which case a strong steric effect would be expected.

B. Radiochemical Standardization

1. The Problem

In all this work, the extent of adsorption of the fatty acid on the metal surfaces was measured with a Geiger counter. To obtain the desired information about surface coverage it was necessary to convert the counts per minute into population density of adsorbed acid.

This determination is somewhat complicated by the fact that the same amount of tagged fatty acid adsorbed on the different metals does

not yield the same count rate. The principal reason for this is the different backscattering ability of the various metals. The direction of the soft beta radiation emitted by the carbon-14 tagged acid is originally isotropically distributed. Some of the beta particles are directed to the window of the Geiger tube, others toward the metal. The various metals are more or less able to reflect the radiation back to the Geiger tube, and this reflection is called "backscatter". Backscatter is a function both of surface roughness^{31,32} and of atomic number.³³ Generally speaking, a rough surface has a higher backscatter than a smooth one does, and reflecting ability increases with increasing nuclear mass.

Also, another factor may influence count rate. All the collisions of the beta particles with the metal surfaces are not completely elastic, and thus the reflected electrons strike the tube window with less energy than do those which come directly from the fatty acid. With low energy radiation such as that emitted by carbon-14, this may diminish the fraction of the reflected electrons which are able to penetrate the tube window and be counted. Consequently, the effect of backscatter on count rate of adsorbed acid may be somewhat decreased.

Because of the different reflecting ability of the various metals toward electrons, and because differently prepared surfaces of the same metal have different backscattering ability, the relation between count rate and population density had to be determined for each different metal. Surfaces were prepared under as nearly duplicate conditions as possible to those on which adsorption was to be measured.

The method involved pipetting a known quantity of fatty acid solution onto a metal surface which had been machined under cyclohexane, letting the solvent evaporate, then counting the sample surface. From these data, the desired information was obtained.

2. Experimental Technique and Results

Determination of the relation between count rate and acid population density was made as follows.

The metal to be calibrated was machined under pure cyclohexane, which was then poured off. The fresh surface was blotted dry. With the sample holder resting on a steady, level bench, exactly 0.50 ml. of solution "A" was pipetted onto the top of the sample cylinder. The solution quickly spread to cover completely the fresh surface. It was prevented from spilling over the edge by the sharp edges produced on the sample in the machining process. A glass plate was then laid over the top of the machining cup, which made a fairly air-tight seal and so prevented solvent evaporation.

After an hour the glass plate was removed and the solvent allowed to evaporate. The sample was then counted. Results of a series of these determinations made in identical fashion on indium, tin, and cobalt are given in Table III.

The method of calculating the standardization factors for the three metals was as follows. A 1.5-inch diameter circular "face" was cut on each of the sample cylinders. The area of each face was 11.4 cm.² Onto this area was pipetted 0.50 ml. of solution "A", which had a fatty acid concentration of 2.63×10^{-6} g./ml. The molecular weight of the fatty acid is 298. Now assuming even distribution of the fatty acid

TABLE III

ACID STANDARDIZATION COUNTS

Counts per Minute per 0.50 ml. of Solution "A" Evaporated on Metal Surfaces		
Cobalt	Indium	Tin
643	622	571
620	709	622
725	635	626
689		608
701		
676	655	607 Average

over the metal surface, the population density of adsorbed acid was, in units of molecules per 100 \AA^2 ,

$$0.50 \times \frac{2.63 \times 10^{-6}}{298} \times 6.02 \times 10^{23} \times \frac{100}{11.4 \times 10^{16}} = 2.33 .$$

Now, consider cobalt as an example. The 0.50 ml. of solution "A" pipetted onto the surface of cobalt yielded a count rate of 676 c/m. The standardization factor for this material was then

$$2.33 \times \frac{1000}{676} = 3.44 \text{ molecules/} 100 \text{ \AA}^2 \text{ per } 1000 \text{ c/m.}$$

This means that a monolayer of fatty acid adsorbed on cobalt metal should yield a count rate of 1210 c/m.

The acid standardization factors calculated for cobalt, indium, and tin as part of this work, together with similar calculations made for magnesium, copper, aluminum, and silver by McGill are listed in Table IV. A short treatment of counting statistics, applicable to measurements made throughout this work, is given in Appendix VI.

3. Notes

All of the metal surfaces to be used for acid standardizations were prepared by machining under cyclohexane. With several of the metals studied, surfaces machined in air appeared to have a different roughness than those machined under the inert solvent.

The assumption that the fatty acid pipetted onto the metal surfaces distributes itself uniformly is, of course, an error. Lack of uniform distribution is responsible for most of the variance in count rate on different surfaces of the same metal noted in Table III.

It was felt, however, that by running a series of such measurements

TABLE IV

STANDARDIZATION FACTORS

Metal	Population Density* per 1000 c/m.	Counts per Minute per Monolayer
Cobalt	3.44	1210
Indium	3.56	1171
Tin	3.83	1088
Magnesium	3.37	1240
Copper	3.07	1357
Aluminum	4.05	1030
Silver	2.43	1716

*Population density in units of molecules per 100 Å².

and averaging the count rates obtained, the error was at least partially nullified.

It was desirable to pipette larger portions of the fatty acid onto the metal surfaces than 0.50 ml., as the higher count rate which would be obtained would make results more precise. However, this was the largest volume of acid solution which the metal surfaces could consistently support. Larger volumes resulted in spills.

C. Experiments on Solution Machined Metals

1. Tests of Proposed Reaction Mechanism

McGill subjected the adsorbed fatty acid on the metals which he studied to a series of tests which were designed to prove or disprove soap formation on the metal surfaces as well as to indicate, if reaction did occur, whether this reaction was influenced by the Kramer effect.

These tests were:

- (1) A study of the effect of acid concentration on adsorption.
- (2) Measurement of the rates of desorption of the adsorbed fatty acid.
- (3) Determination of the free energy changes involved in the soap formation reaction.
- (4) Chemical analyses of the solution containing the desorbed fatty acid.

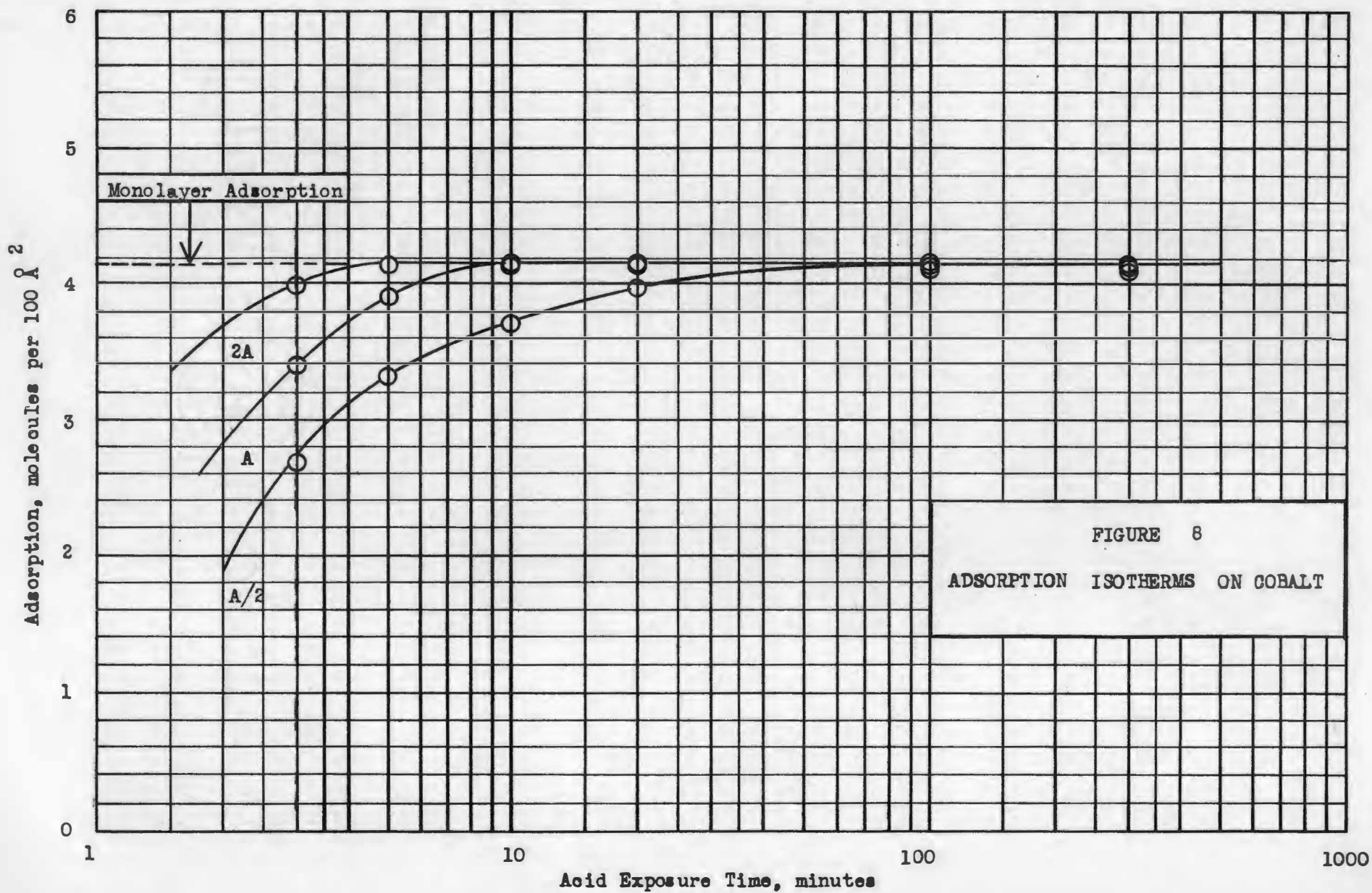
Most of these tests were also applied to the metals studied here.

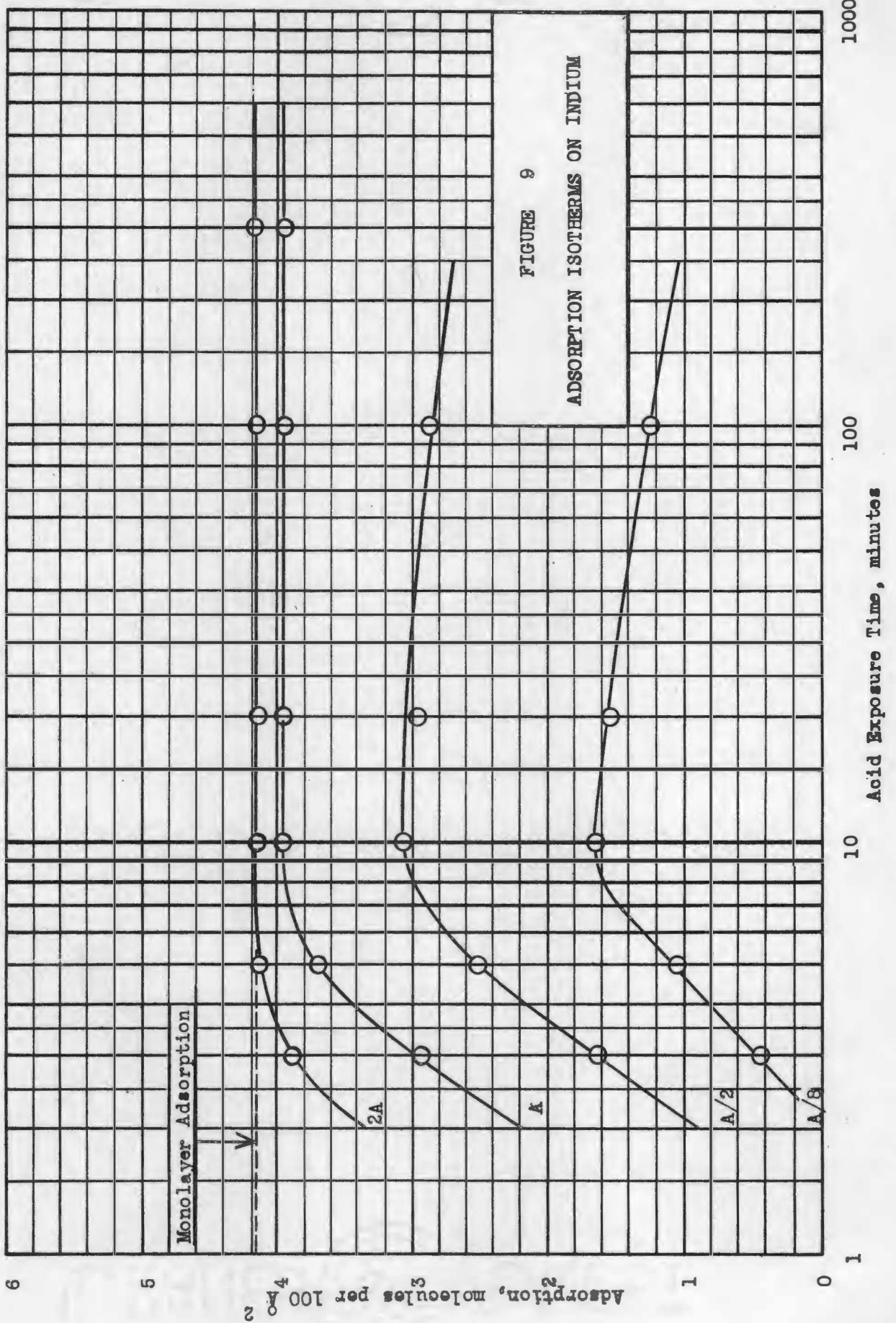
2. Adsorption Experiments

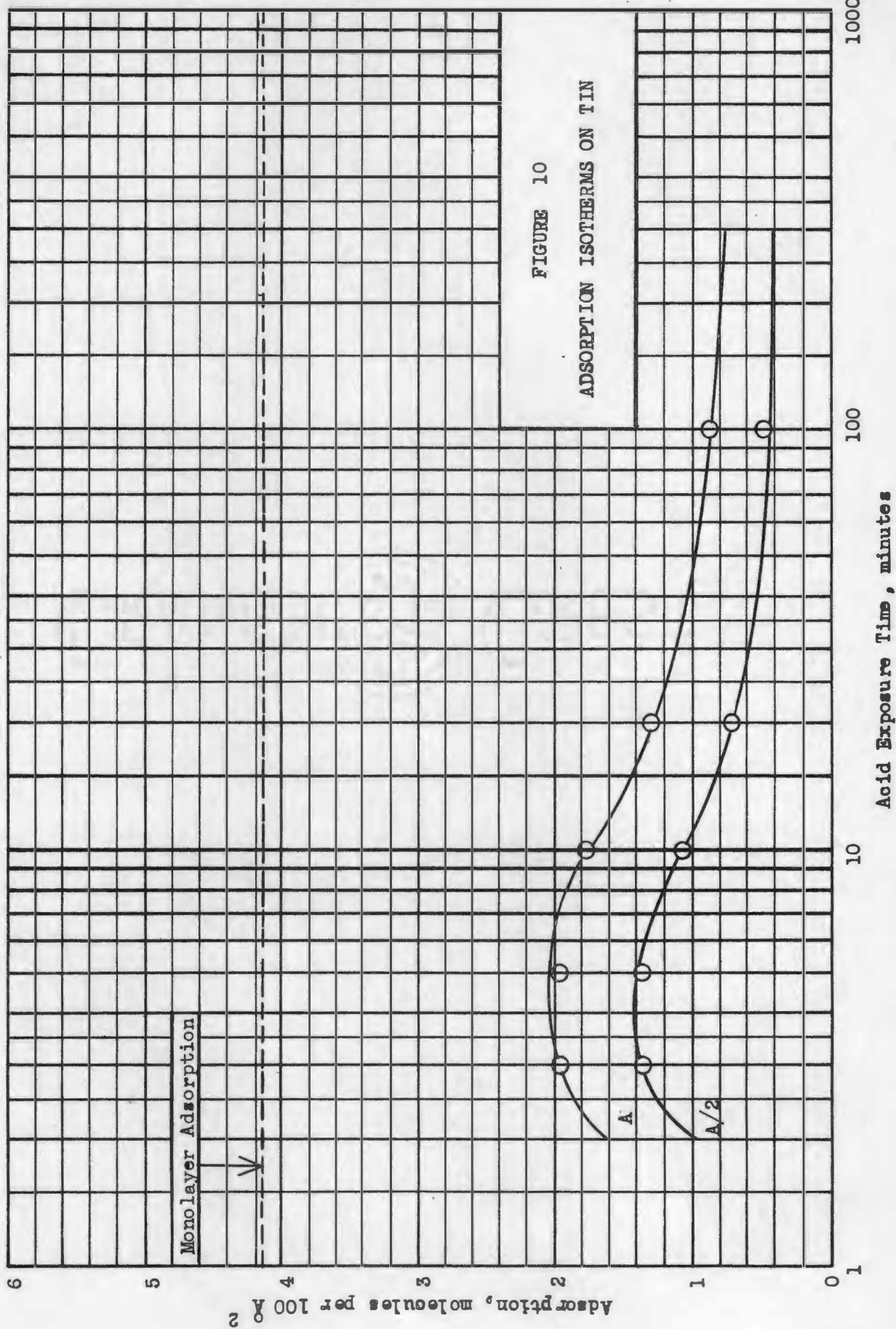
Adsorption experiments were carried out on the cobalt, indium, and tin metals using the techniques described. The samples machined under the fatty acid solutions were quickly transferred to stirred, 25 ml. adsorption cups where they were exposed to the acid solution for various time intervals, removed, blotted dry, and counted. All this series of experiments was run at room temperature (23-28°). Acid exposure times were counted from the initial cuts on the metal surfaces, and the acid solutions were stirred in the adsorption cups at the rate of 140 rpm.

Results of these adsorption experiments carried out under progressively more dilute solutions are presented graphically in Figures 8, 9, and 10. Cobalt eventually attained the saturated population density of 4.17 molecules per 100 Å² when machined and exposed to solutions "2A", "A", and "A/2". Indium attained monolayer coverage only when adsorption occurred from solution "2A", and showed progressively larger departures from this value when machined under solutions "A", "A/2", and "A/8". Some decay in adsorption was noted for indium metal at the higher acid exposure times, when it was machined under the most dilute solution.

Adsorption on tin metal under solutions "A", and "A/2" showed a wide departure from that calculated for the adsorbed monolayer, and the adsorption isotherms had a characteristically different shape from those of cobalt and indium.







3. Desorption Experiments

Desorption experiments were run on the two metals which had been found to adsorb a monolayer of the tagged fatty acid. A re-determination of the desorption rate of the fatty acid from a machined copper surface which had been previously made by McGill was also made for purposes of comparison.

The metals were machined under solution "A",* then quickly transferred to stirred, 25 ml. adsorption cups for fifteen minutes total fatty acid exposure time. It was assumed that during this period a monolayer of fatty acid was adsorbed on each metal surface.

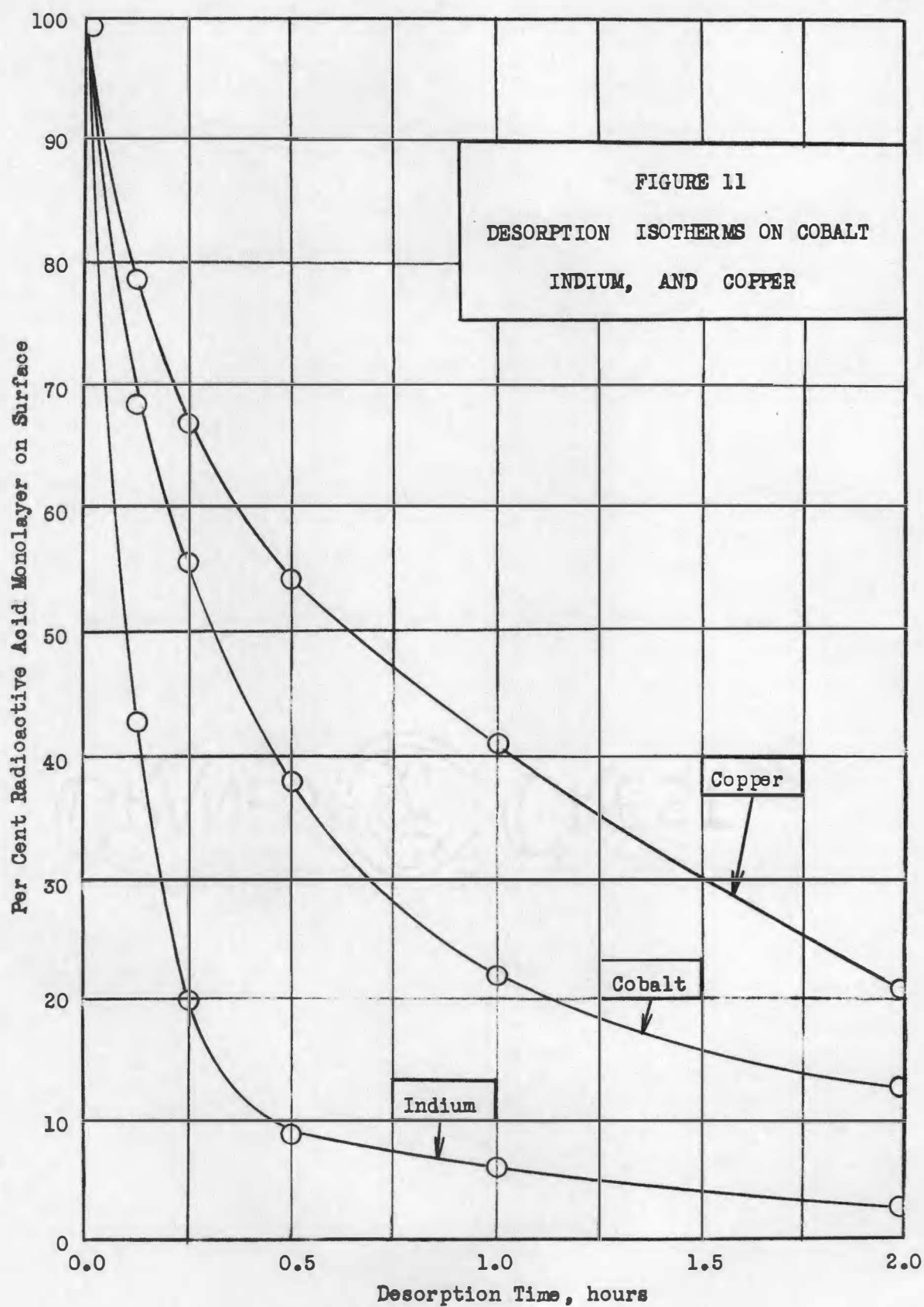
The samples were then quickly transferred to stirred, 75 ml. desorption cups which contained pure cyclohexane and the fatty acid allowed to desorb for measured time intervals after which the samples were removed, blotted dry, and counted. The transfers from adsorption to desorption cups were made very quickly so that the metal surface was always kept wet with solvent. These experiments were also carried out at room temperature of from 23-28°.

The results of the desorption measurements are given graphically in Figure 11.

4. Free Energy Calculations

A determination was made of the free energy change involved when cobalt reacts with n-nonadecanoic acid to form the cobalt II soap.

*Indium was machined and equilibrated under solution "2A", as this acid concentration was necessary for the monolayer adsorption on this metal.



Details of the calculation, preparation of the soap and method of obtaining the necessary data are given in Appendixes III, IV, and V.

A similar calculation was also made for the reaction of iron metal to form the iron III soap. The tin and indium soaps could not be prepared by the method described because of their extreme tendency toward hydrolysis.

Results of the iron and cobalt calculations, together with the results of similar calculations made by McGill for copper, lead, and silver are summarized in Table V. It is interesting to note that for all five metals, the main contributing factor to the free energy change accompanying the soap formation reaction is the free energy of formation of the metal ion. The order of free energy changes exactly parallels the order of activity of the metals. This being the case, it is probably unnecessary to determine free energy changes for reaction of other metals with nonadecanoic acid. For all metals more active than cobalt the change will almost surely be negative; for all metals less active than lead, the change will be positive.

5. Results

a. Cobalt. The adsorption results given in Section 2 point up quite different behaviours for each of the three metals studied. Each concentration of nonadecanoic acid solution under which cobalt was machined yielded a monolayer of the adsorbed acid, given sufficient time. The differences in times required to attain the saturated adsorption layer may be attributed simply to a concentration effect; it takes longer for enough acid molecules to form the monolayer to diffuse to the metal surface with the more dilute solutions.

TABLE V

ACTIVATION ENERGY FACTORS AND FREE ENERGY
CHANGES FOR SOAP FORMATION REACTIONS*

Metal Ion	$\Delta F^\circ_{\text{ion}}/n^{**}$	Soap Formed	ΔF of Soap Formation Reaction
Co^{+2}	-6.40	Cobalt II	-3.2
Pb^{+2}	-2.90	Lead II	1.28
Fe^{+3}	-0.84	Iron III	1.6
Cu^{+2}	7.76	Copper II	6.70
Ag^{+1}	18.43	Silver I	18.48

*All free energy values and activation energy factors given in kcal. per mole.

** $\Delta F^\circ_{\text{ion}}$ is the standard free energy of formation of the metal ion, and n is the valence of the ion. Values are taken from Latimer, "Oxidation Potentials." 34

This is just the behaviour for this metal which would be predicted from McGill's results and the position of cobalt in the electrochemical series. McGill suggested that adsorption of the fatty acid on the various metals was the result of a surface reaction between acid and metal surface atoms, leading to formation of the appropriate metal soap. Cobalt is more active than lead and copper, both of which McGill found attained monolayer coverage and formed soaps when machined under the solution concentrations used for cobalt (see Figure 2).

Desorption from the surface of this metal occurs at a considerably faster rate than does desorption from silver, copper, and lead, but much slower than from gold and platinum. McGill suggested that desorption rate should be a function of the solubility of the desorbing species in the desorbing solvent. If this is so, the material desorbed from the cobalt surface was certainly not nonadecanoic acid. If it were cobalt II nonadecanoate the solubility of the soap in cyclohexane should be greater than that of the corresponding copper, silver, and lead soaps. Determination of the solubility of this soap in cyclohexane (see Appendix IV) showed that this was indeed the case.

The free energy change involved in the reaction leading to the formation of the cobalt soap was found to be negative (see Appendix V). This is a more favorable situation than that which McGill found for copper, lead, and silver where it was necessary to make use of the additional energy furnished by the Kramer electron to make reaction possible at all. In view of these various facts, it is felt quite certain that cobalt does react with n-nonadecanoic acid to form a close-packed monolayer of cobalt II nonadecanoate on the metal surface.

b. Indium. Indium was found to attain monolayer adsorption only when machined under the most concentrated acid solution used, "2A". Progressively wider departures from this value were noted as the concentration of the acid solutions was decreased. A definite decline in surface coverage was noted with the most dilute acid solution, "A/8", at the higher acid exposure times.

It has been stated that experiments on indium were carried out to try to prove or disprove McGill's idea that steric factors were responsible for the anomalous results he obtained for aluminum metal. It was hoped that adsorption would be higher on indium than on aluminum for a given acid concentration, because indium is a larger atom than aluminum and steric requirements should consequently not be as severe.

Results, viewed from this standpoint, were disappointing. Whereas aluminum adsorbed a monolayer of acid when machined under solution "A", indium had to be machined under "2A". Departures from the saturated layer were in every case greater for indium than for aluminum. In view of these facts, McGill's idea of steric limitation is open to serious question. It still seems fairly certain that adsorption of fatty acid on indium is due to soap formation, however, as indium is a rather active metal and free energy requirements for this reaction should be less severe than for several other metals on whose surfaces soap formation has been proved.

Desorption of fatty acid from an indium surface occurs at a faster rate than does desorption from any metal yet studied excepting only gold and platinum. The high desorption rate from indium probably

indicates a relatively high solubility of the indium soap in cyclohexane, compared to that of the other metals.

c. Tin. The adsorption isotherms on tin were quite different from those of both cobalt and indium. Adsorption did not approach the monolayer value and the shape of the adsorption-time curves were similar in form to those which McGill obtained on gold and platinum (see Figure 2).

This behaviour was quite unexpected, as tin has a fair activity and thus should form a soap fairly readily. Steric effects, if present at all, should not have lowered adsorption to the degree noted, particularly if the expected tin II soap were formed on the metal. An explanation for the observed behaviour was not immediately apparent.

D. Discovery of Soap Desorption and Monolayer Replenishment

1. Inconsistent Data

The results of the experiments described in Section C are interesting and were readily reproducible. It was apparent, however, that the "anomalous" behaviour noted for aluminum, indium, and tin required some explanation. There were two possibilities. Either the picture of the whole adsorption mechanism built up by McGill was in error, which seemed very unlikely, or some yet unconsidered variable which was somehow masked for adsorption on most metals was influencing adsorption on aluminum, indium, and tin. In an effort to discover this variable, a close scrutiny was made of McGill's data, as well as that of the present work. The following points may be pertinent.

(1) Adsorption on aluminum, indium, and tin is not as great as would be predicted from the activities of these metals.

(2) The solubility of the indium soap in cyclohexane, judging from desorption measurements, is higher than that of any of those yet determined. Probably, the aluminum soap is also relatively soluble in this solvent.

(3) McGill ran a single elevated temperature experiment on copper metal. He found that although adsorption was initially higher than on the metal machined at room temperature, adsorption steadily declined with increasing acid exposure time. Unlike the metal machined at room temperature, no adsorption plateau was noted. A slight decline in adsorption was noted from indium and aluminum at the higher acid exposure times when these metals were machined under the most dilute acid solutions.

(4) For all adsorption measurements made with solutions more dilute than "A", McGill exposed the machined surfaces to the fatty acid solution in the large, 75 ml. adsorption cups. His stated reason for doing this was that "the 25 ml. of these dilute acids did not supply sufficient acid to form the saturated adsorption layer." He found this to be so in spite of the fact that a calculation shows that 25 ml. of the most dilute acid used, "A/8", contains a fourfold excess of acid required to form the monolayer.

(5) McGill showed that once a monolayer had been adsorbed onto a metal surface, the saturated coverage of the surface was maintained for acid exposure times of at least one thousand minutes. This fact has been verified several times in the present work. However, McGill

also showed that a copper surface loses 80 per cent of its activity (adsorbed monolayer) if it is exposed to pure, stirred cyclohexane for half an hour. Similarly, a cobalt surface loses 60 per cent of its activity and an indium surface 90 per cent. Evidently, maintenance of the monolayers of adsorbed acid on the metal surfaces is strongly dependent on the medium surrounding the adsorbed acid layer. It seemed of interest to determine what it was that caused this difference with the hope of gaining an insight not only into what caused the low results on aluminum, indium, and tin, but into the whole adsorption process.

2. Hypothesis of "Exchange" Adsorption

All of the inconsistencies mentioned in Section 1 can be explained if it is assumed that when a monolayer of fatty acid is adsorbed on the metal surfaces it is not static there but that there is continual desorption of metal soap. Additional fatty acid then diffuses to the surfaces and reacts with the newly bared metal surface atoms to form more soap. This may also later desorb.

If this assumption is correct low adsorption on indium, aluminum, and tin may be due to an exceptionally fast rate of soap desorption. This desorption may be so fast that at the lower acid solution concentrations rate of diffusion of fatty acid to these metal surfaces is not sufficient to maintain a surface monolayer. It has been stated that the rate of desorption from an indium surface is very fast due probably to a soluble indium soap.

If solubility of the soaps in cyclohexane is the factor that makes for faster and slower desorption, McGill's failure to obtain a

monolayer of adsorbed acid on copper at 45° is not surprising. Solubility of copper II nonadecanoate in cyclohexane would be expected to be higher at the higher temperature.

The larger acid adsorption cups McGill used, when machining the various metals under the lower concentration cyclohexane solutions, were necessary because the solutions had to contain fatty acid sufficient to form not one, but several monolayers of adsorbed soap.

A fatty acid solution is essential to maintain a monolayer of adsorbed acid on the metal surfaces because replenishment of the material adsorbed on the metal surfaces is continually necessary.

3. Tests of Hypothesis

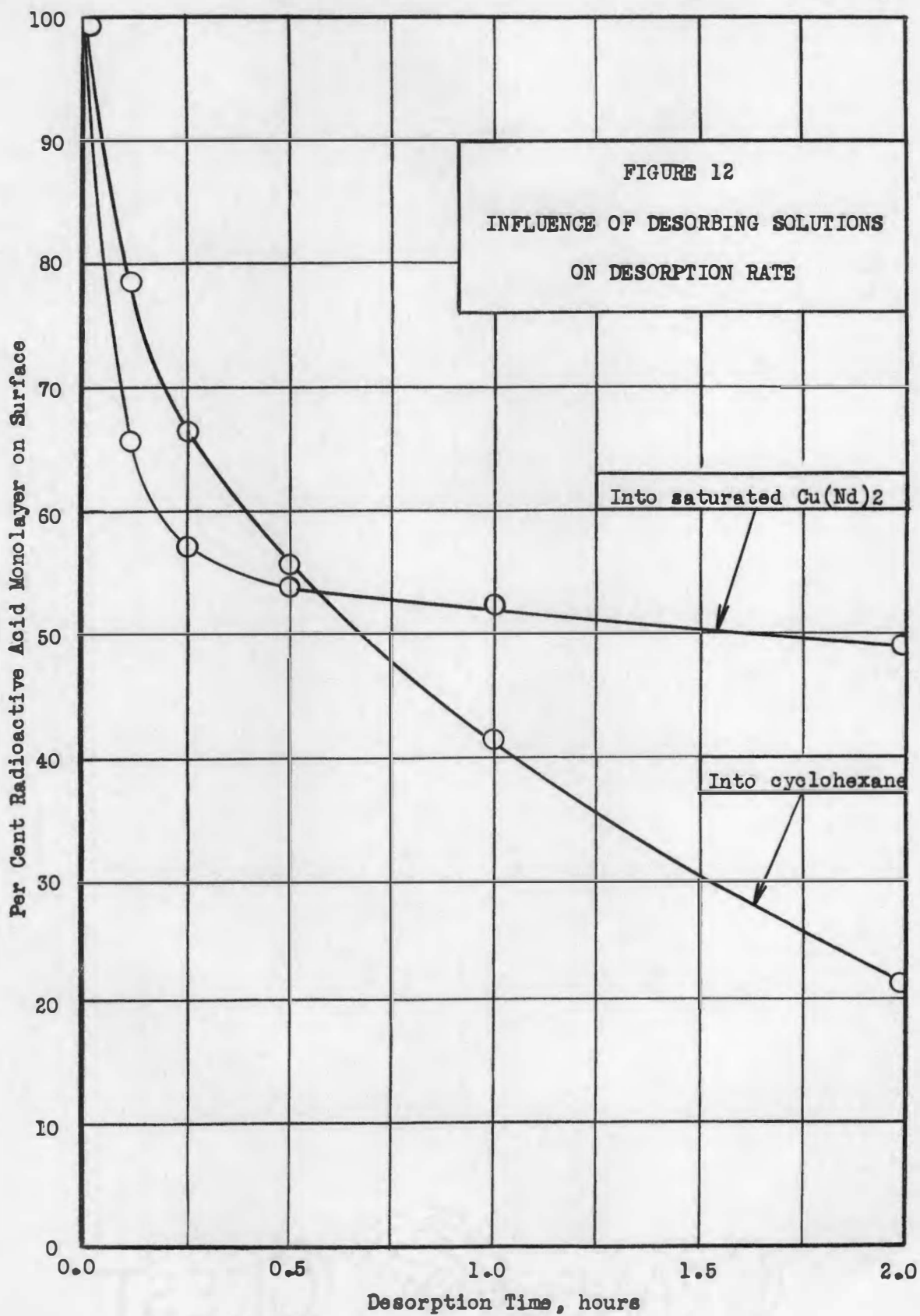
a. Choice of metal. Several tests were run to determine whether the ideas advanced in the previous section were correct. Copper was chosen for these experiments as it is an easily machinable metal, adsorbs a monolayer of fatty acid readily, shows no oleophobic property with regard to the solution at any fraction of surface coverage, and because solubility measurements had already been made on the copper II soap in both water and cyclohexane.

b. Effect of soap solubility. It was thought most likely that the rates of desorption of the various metal soaps were functions of the solubilities of these soaps in cyclohexane. If this were so, "exchange" would only continue until the solution in the adsorption cups became saturated with respect to the soaps, when further desorption should cease. Now, the copper soap formation reaction has been shown to have a positive free energy change (see Table V). If monolayer

coverage of the surface were to be maintained, then, it was necessary that the Kramer effect remain operative until this solution saturation was accomplished.

As a test of this idea, a copper surface was machined under solution "A", transferred to an adsorption cup and allowed to remain there for an hour to let the activating Kramer effect decay. The metal surface was then transferred, while wet, to a new equilibration cup containing fresh solution "A". It was left there for ten minutes, removed, blotted dry, and counted. It was hoped that some decrease in adsorption would be noted due to the inability of the decaying Kramer effect to activate metal-fatty acid reactions sufficiently to keep pace with the desorption of the copper soap until this new adsorption cup was saturated with the metal soap. No appreciable drop in count rate was noted although the experiment was repeated several times.

This first experiment seemed to indicate that saturation of the solution with the metal soap was not necessary for maintaining a monolayer on the metal surface. To prove this, a saturated solution of copper II nonadecanoate was prepared as described in Appendix IV. The copper surface was then solution machined, transferred to a stirred adsorption cup containing solution "A", and exposed for fifteen minutes. It was known that under these conditions a monolayer of the radioactive acid was adsorbed. The surface was then transferred, while wet, to a stirred 75-ml. cup which contained the saturated solution of the non-radioactive soap. It was exposed to this soap solution for measured time intervals, removed, blotted dry, and counted. Results of these experiments are shown graphically in Figure 12.

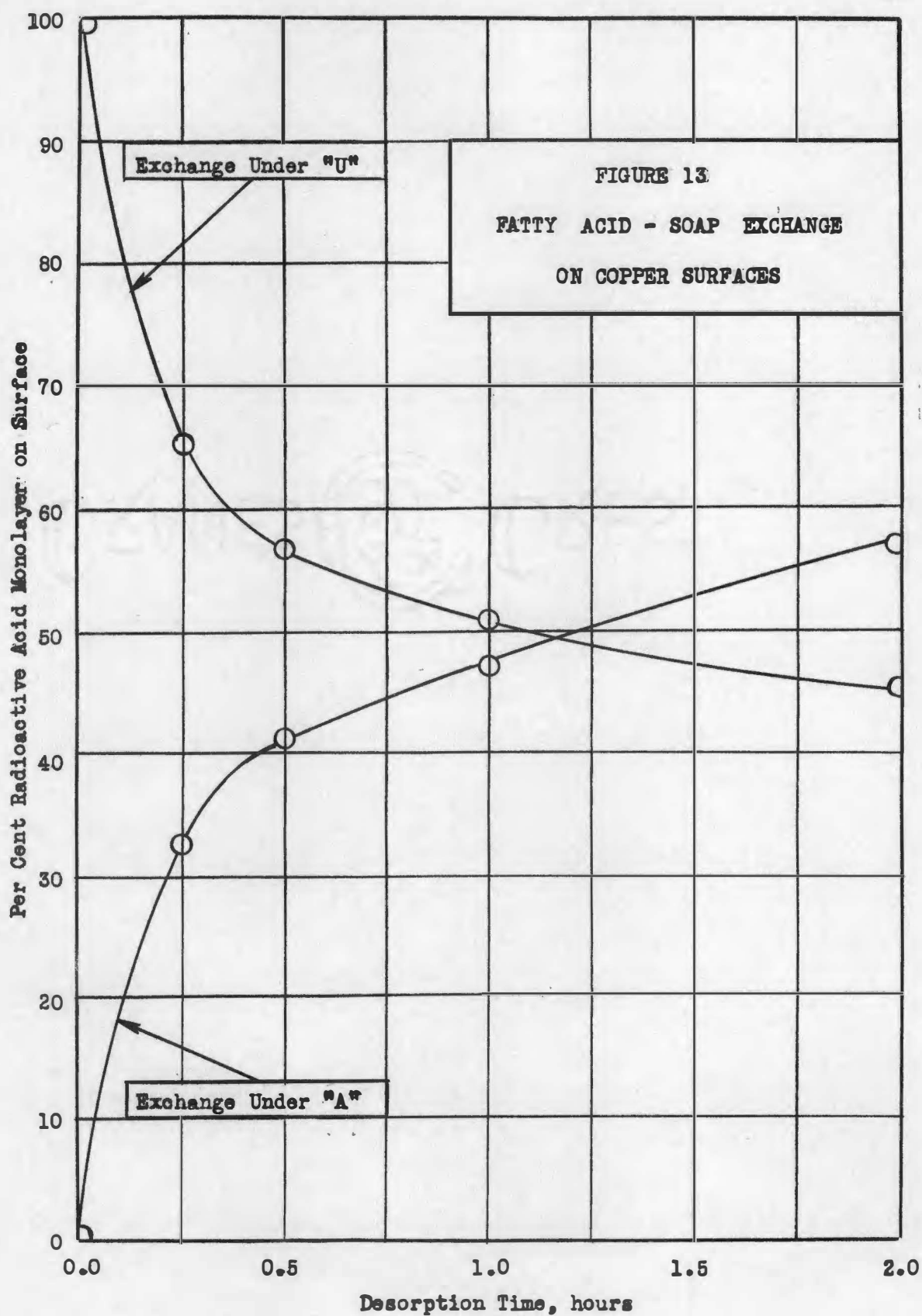


This experiment verified the fact that a solution saturated with the copper soap could not prevent desorption of this same soap from the metal surface, although desorption rate was somewhat slower than that into pure cyclohexane. Data were checked by preparing new saturated soap solutions and repeating the experiments, always with the same results.

c. Proof of "exchange". The question which now presented itself was whether desorption was actually taking place at all from the metal surfaces during the time an adsorbed monolayer was maintained or whether a given monolayer, once adsorbed, remained on the surface due to some property of the acid solution to which it was being exposed. To study this, the following experiments were designed.

(1) A solution of nonadecanoic acid in cyclohexane was prepared of the same concentration as solution "A", and differing from this solution only in that the acid molecules were not radioactive. This solution was designated solution "U".

Copper was machined under solution "A", then transferred to a stirred adsorption cup for fifteen minutes total acid exposure time to adsorb a monolayer of acid. The metal surface was then transferred, while wet, to another stirred cup which contained solution "U". It was exposed to this second solution for various time intervals, removed, blotted dry, and counted. Results of these experiments are given graphically in Figure 13. A new metal surface was cut for each experimental point. All solutions were stirred at 140 rpm. and were thermostated at 25°.



(2) The reverse experiment to that just described was also performed. The metal was cut under solution "U", allowed to form a saturated layer of the nonradioactive acid, and transferred to a new stirred adsorption cup containing solution "A" for various time intervals. Except for inversion of order of exposure of the metal to the fatty acid solutions, the two experiments were identical. Results of these experiments are also given in Figure 13.

These two experiments showed conclusively that "exchange" adsorption was indeed taking place on the copper surface. The metal surfaces treated as described in (1) showed a sharp departure from complete coverage with the radioactive acid after short exposures to the nonradioactive acid solution. Similarly, surfaces on which a monolayer of the nonradioactive acid was adsorbed, (2), showed a regular pick-up of radioactive acid when they were exposed to solution "A". As the experiment described in Section b showed that total adsorption was not affected by transferring a copper surface from one adsorption cup to another, the changes noted could only have come from desorption of soap from the metal surface and filling of the resulting vacancy in the adsorbed layer by other molecules of fatty acid.

It is interesting to note that the per cent coverage of the copper surface by the radioactive acid, as given in Figure 13, always adds up to 100 for a given acid exposure time. This means that there is no preferential adsorption or desorption of the fatty acid from the surface due to part of it being radioactive and part not. Desorption data were not as precise as the adsorption data obtained previously.

However, most of the determinations were run at least twice and it is felt that the values indicated are good to plus or minus 2 or 3 per cent.

(3) To further verify that "exchange" adsorption was taking place the acid solutions under which the copper metal was machined were subjected to copper analyses. The reasoning was that if the "exchange" were occurring copper metal should be desorbed from the metal surfaces into the acid solutions. The concentration of copper in the solutions should increase with increasing exposure times of the metal to the fatty acid. The procedure used for this analysis is described at some length in Appendix IV. Results of the analysis are given graphically in Figure 18 (page 76). The expected increase in copper concentration with exposure time was verified, which further confirms the desorption hypothesis.

(4) Still another experimental confirmation of the desorption was obtained. It has been stated that in the single adsorption experiment which he ran on copper at 45° McGill found considerably different adsorption behaviour than that observed on the metal at room temperature. High temperature was found to suppress the adsorption, although initial adsorption rate was increased. The amount of adsorbed acid decreased with increasing acid exposure time.

This adsorption decrease with time appeared to be another confirmation of the "exchange". A monolayer can only be retained on the metal surface if acid molecules migrate there and react at least as fast as soap molecules are desorbed, and it did not seem illogical that this desorption should occur at a faster rate at the higher temperature.

It appeared that McGill did not stir his solutions during the 45° experiments, however. All exposure of the metal surfaces to the fatty acid took place in the brass machining cup. For this reason his data at this temperature are really not comparable to those at room temperature. In the present work, an additional thermostating cup was constructed so that the sample could be stirred at 45°. Machining of the metal sample was carried out in the thermostated cup described by McGill (see Figure 7). Twenty minutes was allowed for the attainment of temperature equilibrium before the machining process. During this period, the solutions were covered with glass cover plates to prevent solvent evaporation.* The samples had to be transferred very quickly from the machining cup to the thermostated adsorption cup to prevent evaporation of the solvent from the hot surfaces. The solutions were stirred at the usual 140 rpm.

Results of a series of these experiments at 48° and at 60° are given in Figure 14, along with adsorption data for copper obtained at room temperature and the results McGill obtained for his unstirred solutions at 45°. The necessity of stirring all solutions is clearly shown. Instead of decreasing, adsorption at 48° increases to a value of almost a monolayer which remains constant for some forty minutes, after which a sharp drop is indicated. Adsorption at 60° is less, attaining a much lower plateau which also drops off after about forty minutes acid exposure time.

*Details of the thermostating technique and equipment have been given above.

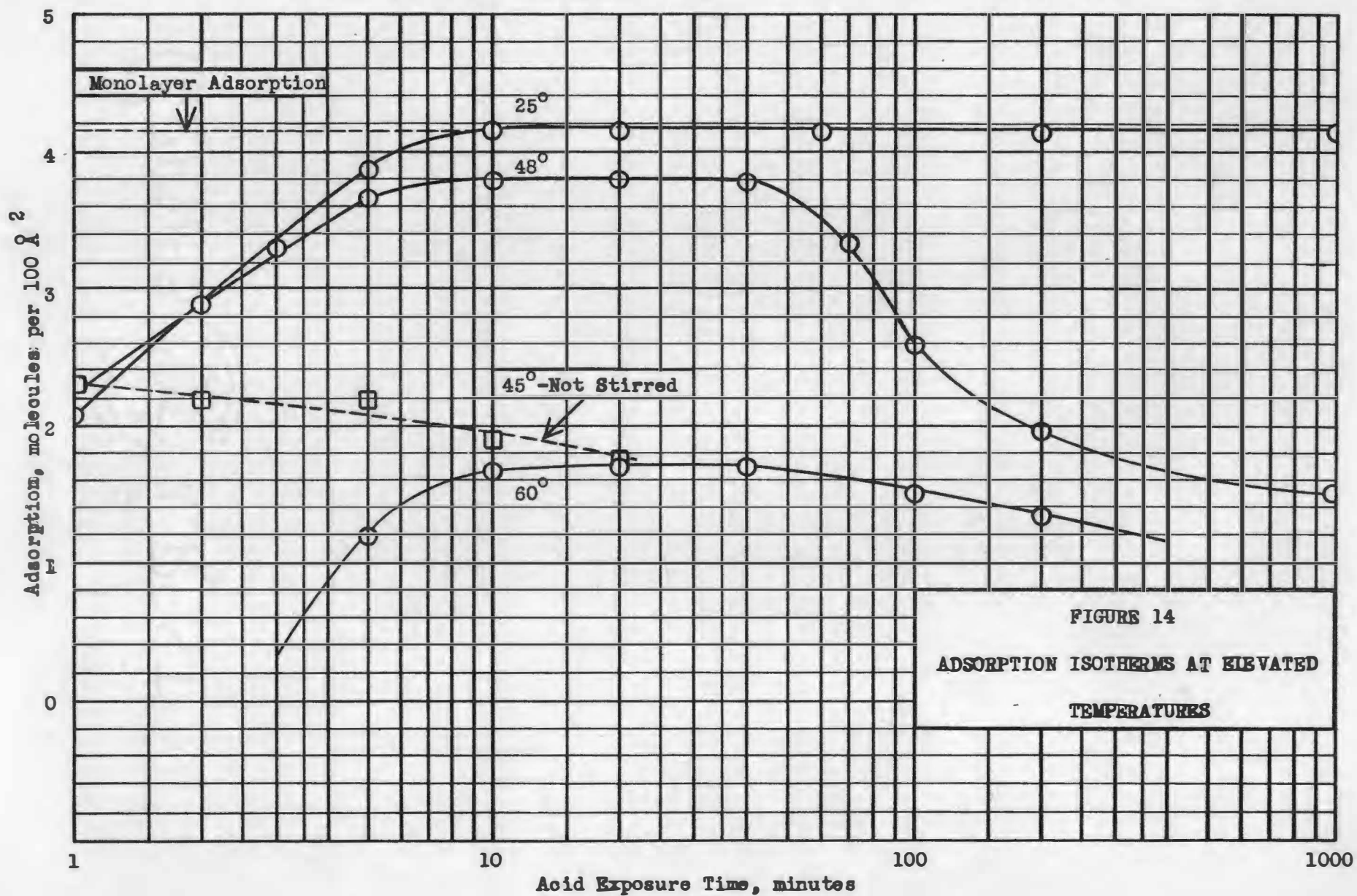


FIGURE 14
ADSORPTION ISOTHERMS AT ELEVATED
TEMPERATURES

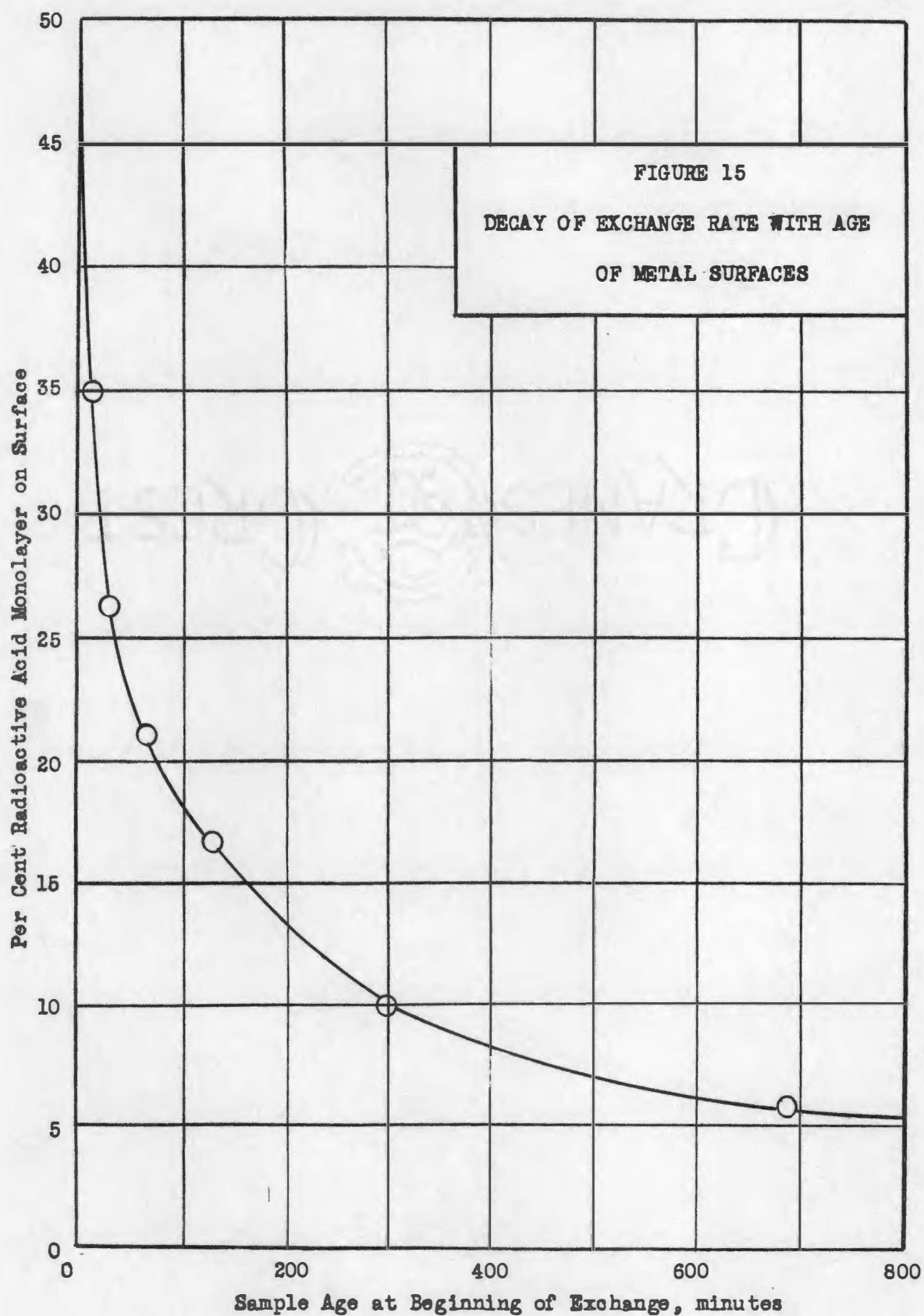
The difference between the results of this study at 48° and McGill's results at 45° provides additional evidence that desorption of adsorbed soap is occurring. In the unstirred solutions a diffusion barrier is set up which limits fatty acid adsorption. As these acid molecules which are adsorbed themselves eventually leave the metal surface, total surface coverage declines. In the stirred solution the diffusion barrier is not present and adsorption approaches monolayer coverage.

(5) A final experiment was performed which, though designed to furnish data about exchange rate as a function of age of the metal surface, also indicated that the hypothesized desorption and adsorption from the metal surfaces was correct. A copper surface was machined under solution "U" and exposed to this same solution in an adsorption cup for various time intervals. After measured exposure times to this solution it was transferred while wet to a stirred adsorption cup containing solution "A", and allowed to equilibrate for thirty minutes. It was then removed, blotted dry, and counted. Results of this experiment are given in Figure 15. The pick-up of radioactive acid noted is another confirmation of the hypothesis of exchange. The shape of the isotherm of Figure 15 will be discussed in some detail below.

E. Factors Influencing "Exchange"

1. Effect of Fatty Acid Solution Concentration

A series of "exchange" experiments was run on copper metal to determine the effect, if any, of different concentrations of acid



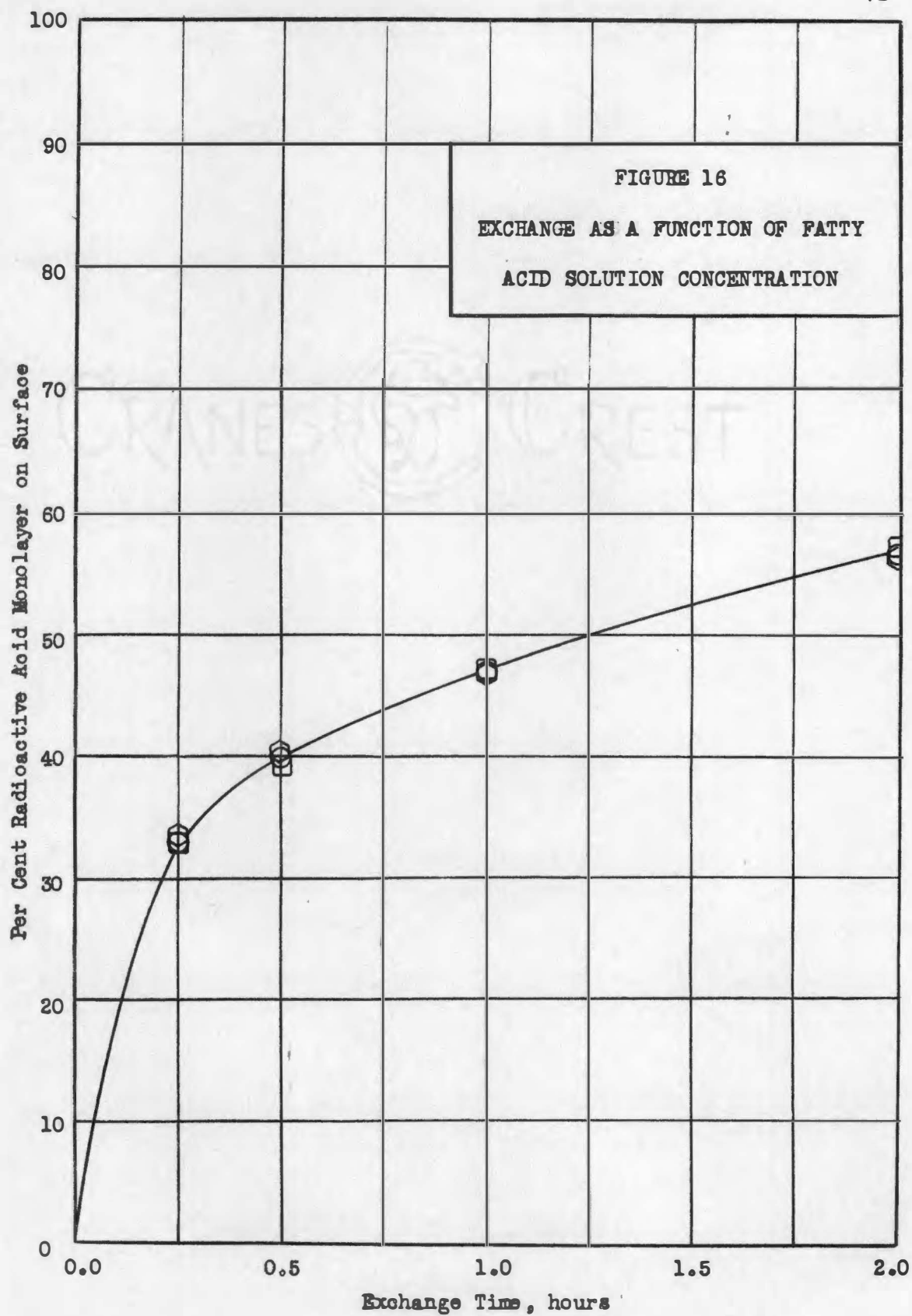
solutions on the exchange rate. All these experiments were carried out in the thermostated adsorption equipment at 25°. The 25 ml. adsorption cups were used, and stirring was at the constant rate of 140 rpm. The experiments were as follows:

(1) Copper was machined under solution "U", then transferred to an adsorption cup containing this same solution for a total acid exposure time of fifteen minutes. The metal sample was then transferred to a new adsorption cup which contained solution "A". It was exposed to this second acid solution for various time period, removed, blotted dry, and counted.

(2) This same procedure was repeated, except that after fifteen minutes exposure of the fresh surface to solution "U" the sample was transferred to a cup containing solution "A/2" instead of "A". After varying exposure times to this second acid solution the sample was again removed, blotted dry, and counted.

(3) The sample was machined under solution "2U", transferred to a stirred cup where it was exposed to this acid solution for a total of fifteen minutes, then transferred to a new cup which contained solution "A". After varying time periods the sample was removed, dried, and counted to determine pick-up of radioactive acid.

The results of these three experiments are all given in Figure 16. It is evident that there is no difference in "exchange" rate. Acid concentration does not affect the rate of desorption, and hence exchange, as long as this concentration is sufficient to maintain a saturated monolayer on the surface of the copper metal.

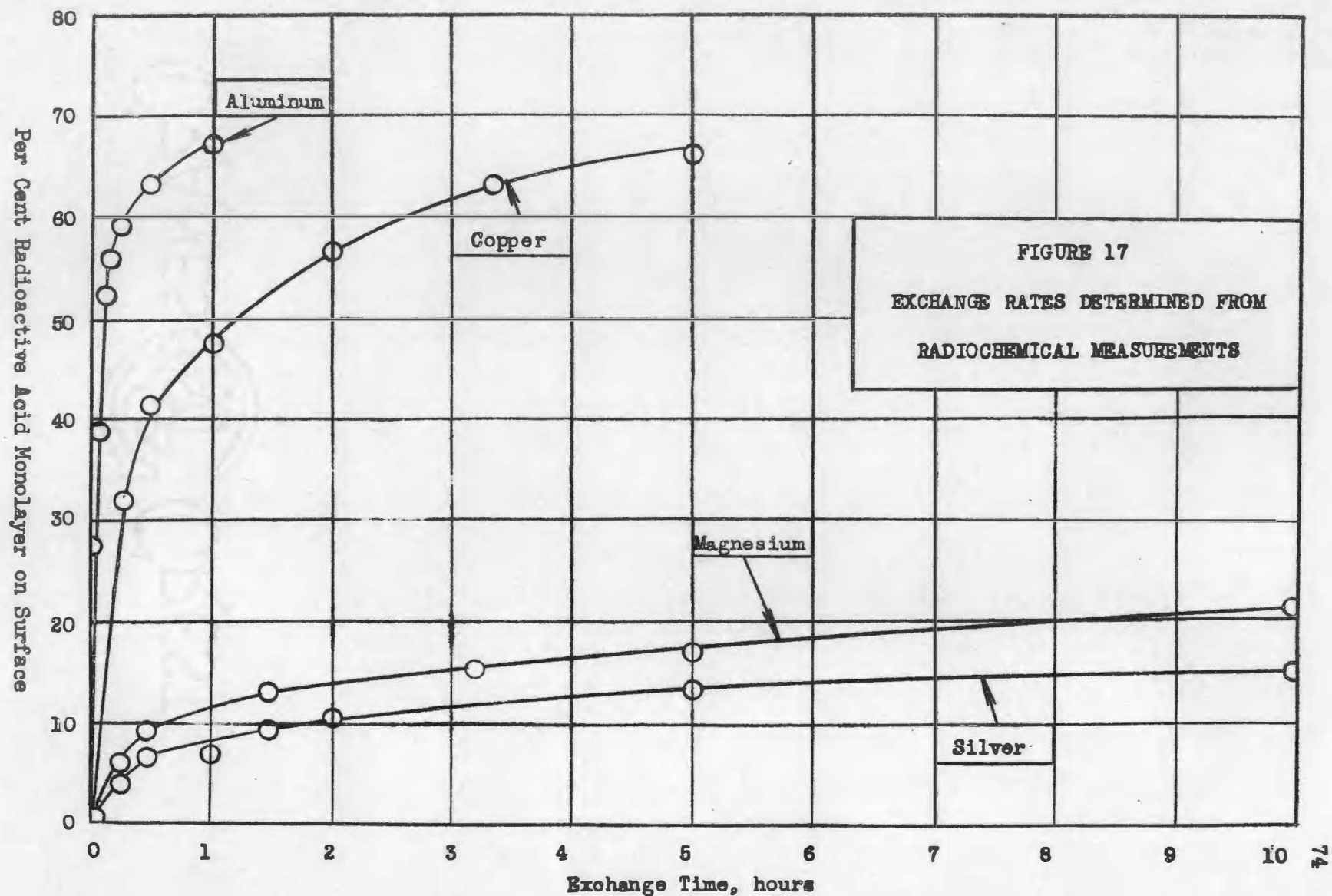


2. Effect of Different Metals

a. Radiochemical studies. "Exchange" experiments were run on magnesium, silver, and aluminum in an identical manner to one of those run on copper metal. The metal surfaces were machined under solution "U", transferred to a stirred adsorption cup containing this same acid solution and exposed for a total time of fifteen minutes. They were then transferred, while wet, to new adsorption cups which contained solution "A". They were exposed to this solution for varying times after which they were removed, blotted dry, and counted. Experiments were run in the thermostated equipment at 25°, and all solutions were stirred at 140 rpm.

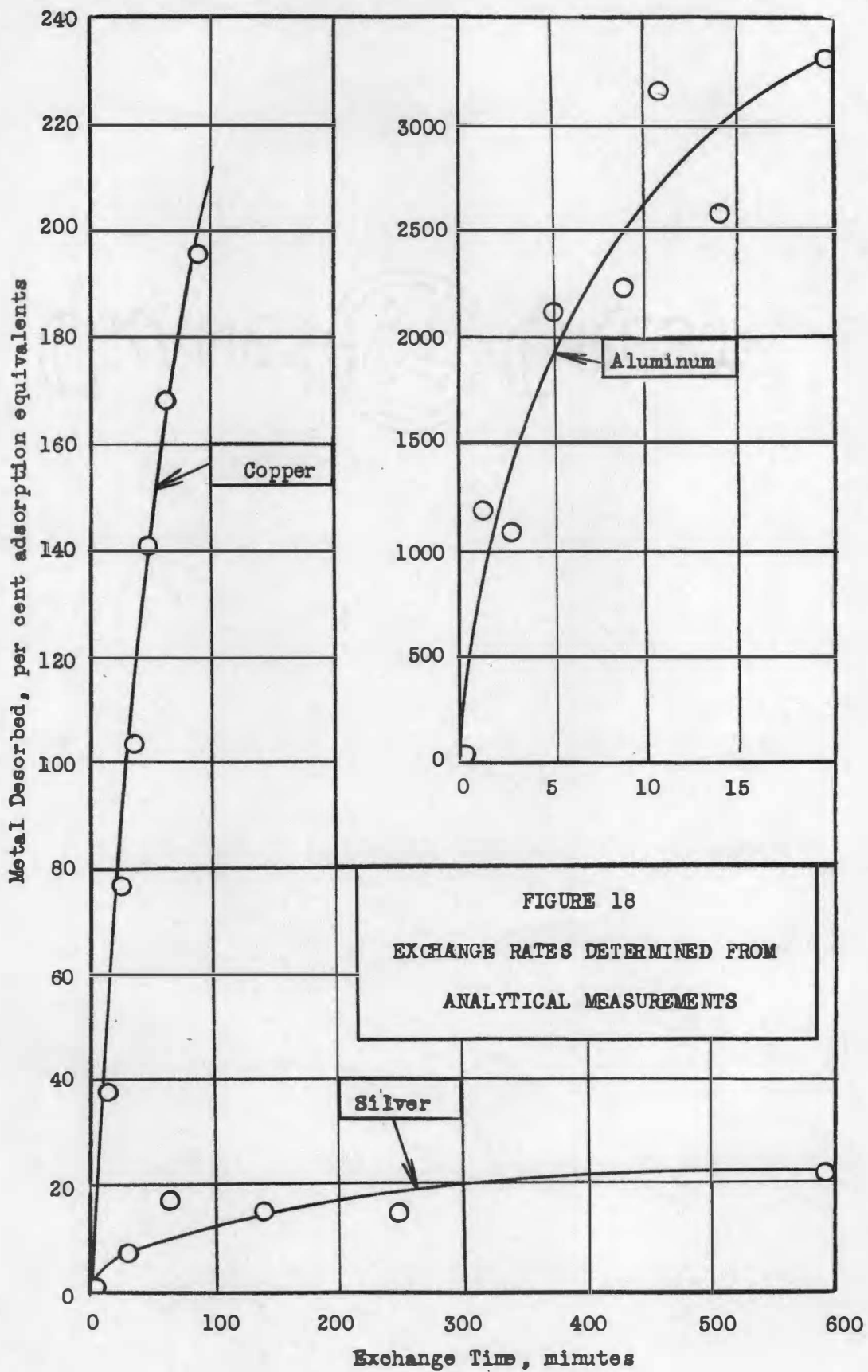
Results of these experiments are shown in Figure 17. A large difference in exchange rate was noted for the four metals. Aluminum exchanged much the fastest, copper had an intermediate rate, and magnesium and silver exchanged relatively slowly.

b. Analytical experiments. Analytical experiments were run on the acid solutions beneath which aluminum and silver were equilibrated which paralleled similar experiments run on the copper solutions. The metals were machined beneath solution "U", transferred to stirred adsorption cups which contained this same acid solution, and left there for a total acid exposure time of fifteen minutes. It was assumed that a monolayer of fatty acid was adsorbed by each metal during this period. The metal surfaces were then transferred to other adsorption cups which also contained solution "U". After varying exposure times to the acid solution they were removed and the solutions subjected to analyses for the desorbed metals. Details of the analytical methods



used are given in Appendix IV. Desorption of the soaps into the acid solutions resulted in an increase in concentration of the metal in the solution with increasing solution exposure times.

Results of these experiments are given graphically in Figure 18. The aluminum concentration increases faster than that of copper, which is in turn faster than silver. The copper results are more precise than those of aluminum, which are more than those of silver. This is due partly to the analytical methods used (see Appendix IV) and partly to the very small amount of silver which was present for determination. These experiments were not run in the thermostated equipment, but room temperature was not far from 25°.



CHAPTER IV

RESULTS AND DISCUSSION

A. Mechanism of Monolayer Replenishment

The following picture can now be presented for the "exchange" of position of fatty acid and soap molecules on the various metal surfaces. The monolayer of adsorbed soap is not static on the surface, but molecules of metal soap are continually being desorbed. As this desorption occurs new fatty acid molecules migrate to the surface, react with the newly exposed metal surface atoms, and fill the vacancies in the adsorbed monolayers created by the desorbed soap molecules. These new soap molecules may themselves be later desorbed, and the whole process repeated.

The number of vacancies existing in the adsorbed monolayer at any given moment is very small relative to the number of adsorbed molecules as the radiochemical analytical method detects no departure from complete surface coverage over long time periods. This implies that the limiting factor in the exchange is the rate of desorption of soap and not adsorption of fatty acid. This is verified by the fact that exchange rate is not a function of acid solution concentration as long as this concentration is sufficient to maintain a monolayer of adsorbed material on the surface.

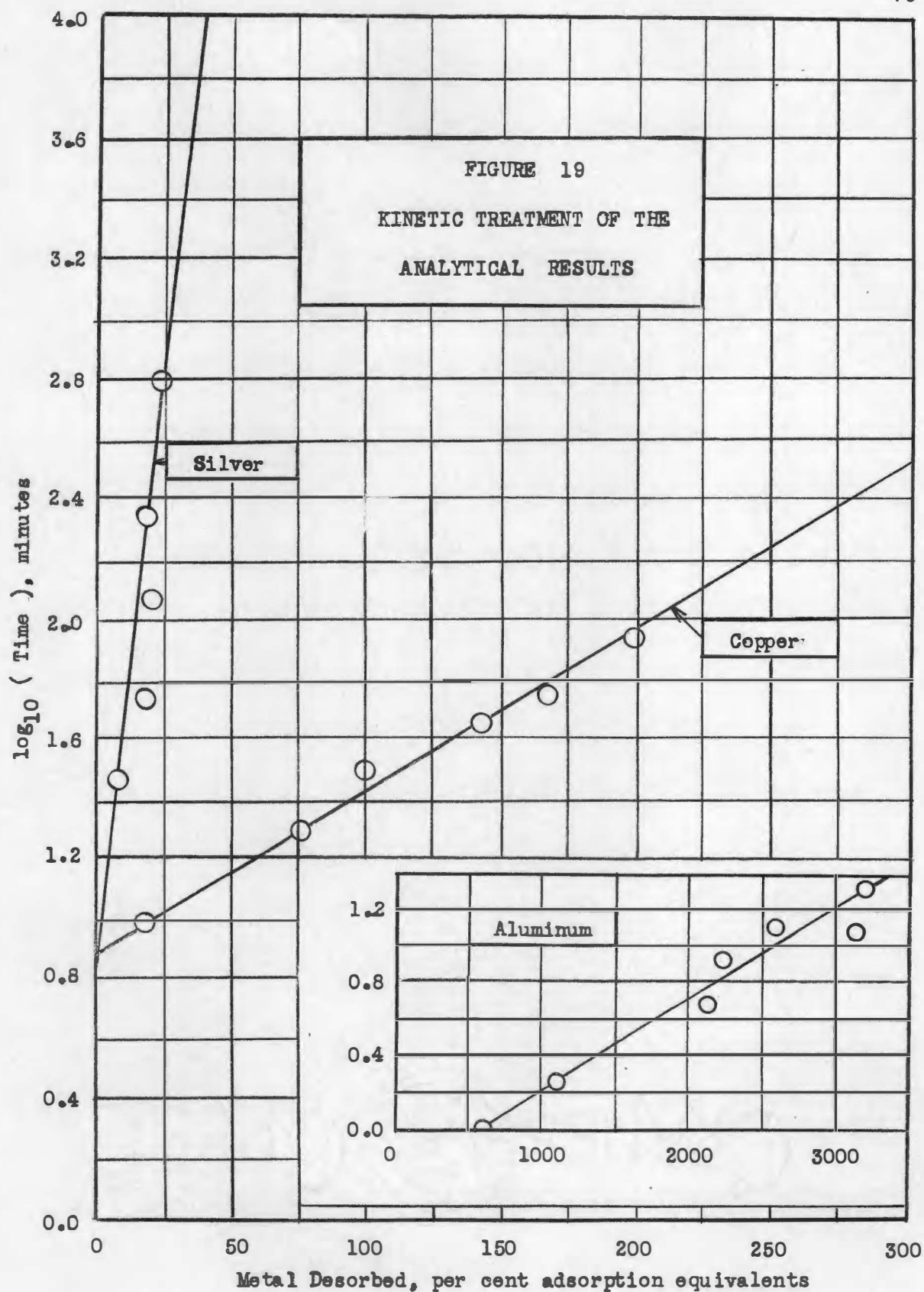
B. Nature of the Exchange Phenomenon

When the exchange phenomenon was first postulated it was thought that exchange rate was a function principally of the solubility of the desorbed metal soap in the desorbing solvent. The experiments described in section D3b of the previous chapter showed that this was not true. A copper surface desorbed half of its adsorbed soap layer into a saturated solution of this same soap in which the solubility of more soap was nil, although desorption rate was somewhat slower than the rate of desorption into pure solvent.

Desorption does not occur at a constant rate. Both the radiochemical experiments (see Figure 17) and the analytical experiments (see Figure 18) indicate that exchange is at first very fast, but rapidly slows as the age of the metal surface from which it is occurring increases. After several hours the soap monolayer does become essentially static on the surface.

It was found that the exchange on all the different metals studied did occur in a regular and predictable manner. Plots of log exchange time vs. log per cent of the surface covered by the non-radioactive acid gave good straight lines. This relationship is summarized in Figure 19 for magnesium, copper, silver, and aluminum.

An attempt was made to find a similar relationship between total amount of metal desorbed and exposure time to the fatty acid solutions, working from the results of the analytical experiments described in section E2b of the previous chapter. The data was not as precise as that from the radiochemical experiments, but reasonably straight lines

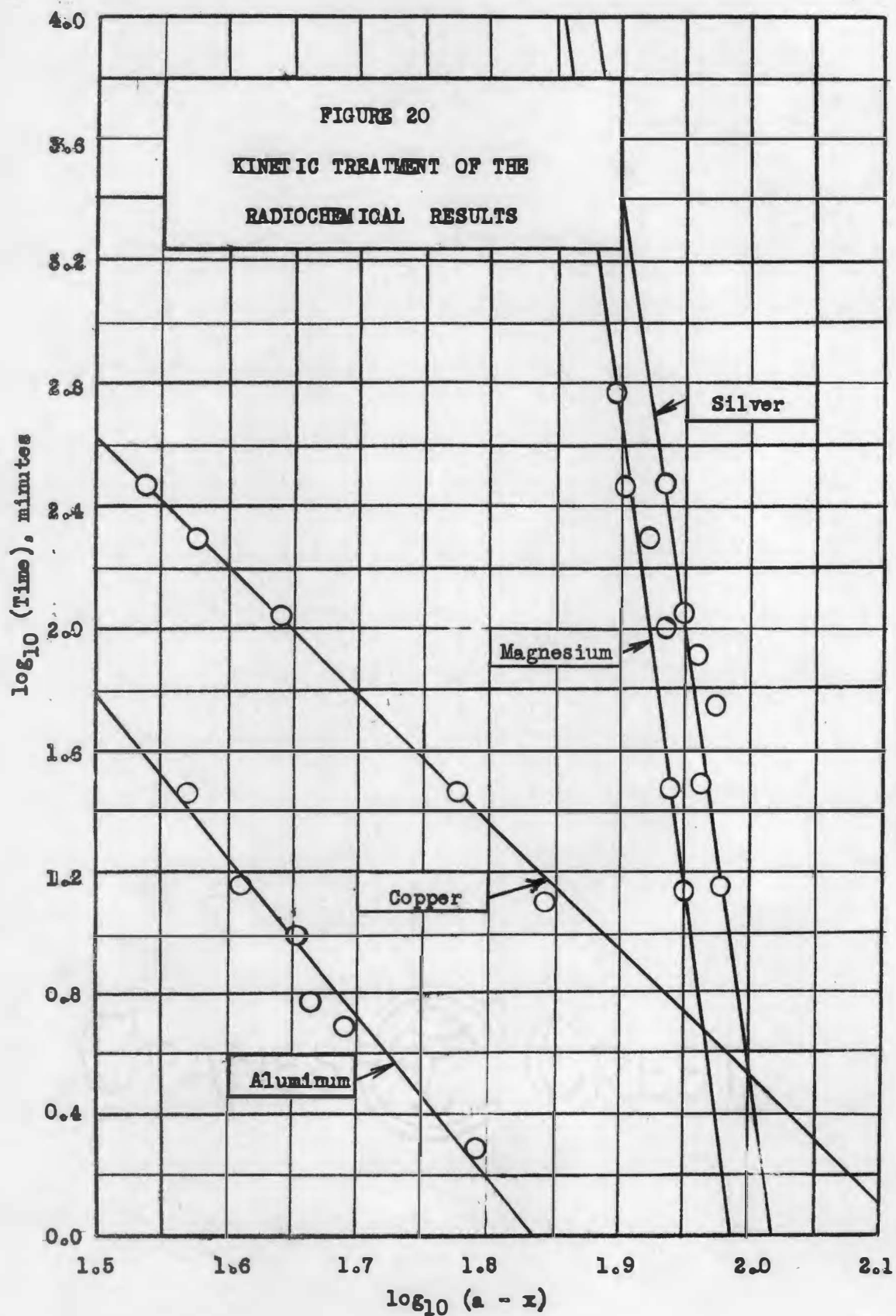


were obtained when log of exchange time was plotted as a function of fatty acid desorbed. These relations are summarized in Figure 20 for copper, silver, and aluminum.

Both the measurements of pick-up of radioactive acid by the metal surfaces and the measurements of total amounts of soap desorbed from these surfaces indicate the same qualitative behaviour for the exchange phenomenon, a fast initial exchange rate which rapidly declines. The rate of exchange of soap was always found to be faster than the rate of pick-up of radioactive acid. This was as expected. It has been stated that a single surface site is probably covered, bared, and recovered several times in the course of the exchange process. As individual sites on the metal surfaces which were originally covered by a nonradioactive layer of acid were allowed to exchange under a radioactive acid solution only the first such desorption and readsorption contributes anything to a pick-up of radioactivity by the surface.* Further desorption and readsorption only replaces one radioactive acid molecule by another, which contributes no additional activity to the surface. It is very unlikely that any desorbed soap is readsorbed onto the metal surfaces, however, and so each molecule which is desorbed is detected by analysis of the cyclohexane solutions.

Because it had been found possible to express both per cent exchange and amount of soap desorbed as functions of time, it was

*Throughout this section it is assumed, for the sake of simplicity, that every fatty acid molecule in the radioactive solutions is tagged with carbon-14 of lower specific activity. Because of the very large number of fatty acid molecules involved, this assumption introduces no error into the results.



possible to make a quantitative comparison of the results of the two types of experiments. The reasoning which follows is predicated on the following two premises.

(1) Rate of desorption is the limiting factor in exchange from all metal surfaces where monolayer coverage is maintained.

(2) The activity of the metal is equal across its face. Making use of these premises, the following equation can be written:

$$\frac{dx}{dt} = (R) \frac{(a - x)}{(a)} \quad (1)$$

where

x = Radioactive acid on metal surface (in terms of per cent adsorption equivalent)

a = Total acid on metal surface (always 100 in terms of per cent adsorption equivalent)

$a - x$ = Total nonradioactive acid on metal surface (in units of per cent adsorption equivalents)

t = Time (minutes)

R = Rate of desorption from surface (per cent adsorption equivalents per minute).

To integrate this expression R must be evaluated. It has been shown that a plot of quantity of desorbed metal as a function of log time yields a straight line. Therefore

$$\text{Metal desorbed} = b \ln(t) + c \quad (2)$$

where b and c are constants and the quantity of metal desorbed is expressed in units of per cent adsorption equivalents. Now, differentiating Equation (2)

$$\frac{d(\text{Metal desorbed})}{dt} = \frac{b}{t} = R . \quad (3)$$

Now, inserting this expression for (R) in Equation (1) there is obtained

$$\frac{dx}{dt} = \frac{(b)}{(t)} \frac{(a - x)}{(a)} \quad (4)$$

or

$$\frac{dx}{(a - x)} = \frac{(b)}{(a)} \frac{(dt)}{(t)} . \quad (5)$$

This may be easily integrated to yield

$$- \ln (a - x) = \frac{b}{a} \ln (t) + \text{constant} . \quad (6)$$

Equation (6) implies that a plot of $\log (a - x)$ vs. $\log (t)$ should be a straight line with a slope of $-(b/a)$. It is significant that such plots were found to give straight lines for all the metals studied (see Figure 19).

The comparison between the results of the two types of experiments was made as follows. Graphs of quantity of metal desorbed as functions of log time are straight lines and have slopes of 2.303 (b). Similarly, graphs of $-\log (a - x)$ plotted as functions of $\log (t)$ are also straight lines with slopes of (b/a) . The value of (a) is constant, and in the units used to measure adsorption and desorption here, equal to 100. Therefore

$$\text{from Equation 2, } b = (\text{slope})/(2.303) ;$$

$$\text{from Equation 6, } b = (\text{slope}) (100) .$$

Calculation and comparison of the (b) values were made for the three metals on which both the analytical and radiochemical experiments had been performed. Results were as follows:

<u>Metal</u>	<u>b(Equation 2)</u>	<u>b(Equation 6)</u>	<u>Ratio</u>
Aluminum	929	18.7	49.7
Copper	76.4	22.8	3.35
Silver	App. 4	3.30	1.2
Magnesium	-	5.10	-

It is obvious that the results obtained by use of the two different analytical methods do not check. The value for b obtained from equation (2) is always larger than that obtained from equation (6). The value of the ratio decreases in the order aluminum, copper, silver.

The lack of correspondence of the results indicate either incorrect results derived from one or both types of experimental measurements, or an incorrect premise for the mathematical derivation which correlated the two types of data. Although the analytical experiments did not give as precise results as was desired, it did not seem possible that the whole series of analyses could have been in error by a factor of fifty, which would have been necessary to bring the two b values in line for aluminum metal. Results of the radiochemical experiments were precise for all the metals studied. Accordingly, it appeared that the cause of difficulty must lie in the assumptions of the mathematical treatment.

The two sets of data can be brought into line if the second premise, on which the mathematical correlation is based, is discarded. In other words, it is necessary to postulate regions of unequal activity on the metal surfaces. This idea is by no means new. As early as 1925, Taylor^{35, 36} suggested the presence of active sites on catalytic materials. His original idea was that even the most polished surfaces are not

perfectly smooth and, therefore, consist of atoms of varying degrees of unsaturation. Adsorption would be expected to take place preferentially at the highly unsaturated peaks on this surface and these would then have the highest catalytic activity.

A far stronger argument than this for the presence of active centers on freshly machined metal surfaces is supplied by the Kramer effect. The following points can be made:

(1) Exchange rate on none of the metal surfaces remains constant with time. Always, initially fast exchange is followed by a rapid decrease in exchange rate. This general type of behaviour is characteristic of the Kramer effect.

(2) McGill's experiments showed rather conclusively that the Kramer effect is operative and responsible for chemisorption on surfaces prepared in the manner described.

(3) It has been postulated³⁷ that the Kramer electrons are not emitted from the entire metal surface but from certain "sites" or "centers". Thus, these electron emission sites may be the active spots on which most chemisorption and reaction occurs.

(4) It has been stated that the general form of the curve relating pick-up of radioactive acid and time is as predicted by equation (6) of the previous section. Plots of $-\log(a - x)$ vs. $\log(t)$ do give straight lines. This would be predicted if active sites were responsible for exchange and the activity of each site were different but decayed according to the same rate law. The actual curves obtained then would represent a summation of the exchange ability of all sites across the surface.

In view of these four points, it may be tentatively stated that all portions of the metal surfaces are not activated to the same degree by the machining process. The more energetic surface sites are not only able to activate more chemical surface reactions than are the less energetic ones but also desorb adsorbed metal soap at a faster rate. This implies that energy is required to separate the adsorbed molecules from the metal surfaces, and that this energy is of the order of magnitude (1 e.v.) which can be furnished by the Kramer effect. This must be so because it is desorption and not adsorption which is the limiting factor in the exchange equilibrium.

C. Correlation of Experimental Results

By making use of the Kramer effect and its hypothesized influence on adsorption, desorption, and metal surface activity several other pieces of experimental data may be explained. These then serve further to substantiate the proposed adsorption picture.

(1) For each of the metals studied, a very considerable exchange rate was noted ten minutes after machining (see Figure 17). In spite of this, McGill found that a copper surface aged ten minutes after machining under pure cyclohexane was able to chemisorb less than half a monolayer of fatty acid. Now, immediately after machining there are a large number of active centers on the metal surface and copper is able to adsorb a saturated monolayer of nonadecanoic acid. The sites are of unequal initial energy and decay at different rates. Ten minutes after machining, a large number of the low energy sites have decayed to

an extent that they can no longer activate surface reaction and consequently, monolayer formation is no longer possible. Many of the initially high energy sites still have more than sufficient energy for chemisorption, however, and on these, adsorption, reaction, and desorption occur to the extent indicated by the analytical experiments. There is, of course, a difference between the two experiments; McGill's aging was carried out under pure solvent while here the metal surfaces were always exposed to the fatty acid solution. It may then be possible that adsorbed fatty acid is able to "protect" a surface from Kramer decay. Choice between these two possibilities will have to await further experiments on the nature of the Kramer effect.

(2) The difference in the ratios of observed to calculated change decreases in the order aluminum, copper, silver. This indicates either that more active centers are produced on copper than are produced on silver, but less than are produced on aluminum, or that the sites produced on aluminum have more energy than those on copper, etc. Probably, both of these ideas are partly true. Aluminum is considerably more active than the other two metals. Consequently, one would expect that active centers would be easier to produce on aluminum than on either copper or silver. Once produced, these centers are more easily able to desorb the aluminum soap because of the strained state of this material when adsorbed on the metal surface. The silver soap formation reaction requires 18.48 kcal. per mole of energy to proceed, the copper requires 6.70 kcal. per mole, and although similar calculations have not been made for aluminum one would expect that the reaction would be actually exothermic (see page 54). Hence, for this last metal, soap

formation may even increase the energy or number of the active centers.

(3) The results of the elevated temperature adsorption measurements made on copper (see Figure 14) are striking. Adsorption at 48° increased to a value of almost a monolayer after about ten minutes acid exposure time. This adsorption level was maintained for thirty minutes. A sharp decline in adsorption was then noted. Behaviour was similar at 60°, but the adsorption plateau was much lower.

The effect of temperature on the metal-acid reactions is complex. There are at least four variables which must be considered as influencing adsorption: the effect of temperature on the Kramer effect and, hence, the availability of active sites, the effect of temperature on the free energy changes associated with the soap formation reaction, and the effect of temperature on the rates of migration of fatty acid molecules to the metal surfaces and of desorption of soap from them.

Now, if it can be assumed that the centers which are responsible for adsorption and reaction are affected in the same manner by temperature elevation as is the Kramer effect, there are, immediately after machining, a higher number of such centers at the higher temperature. The decay rate is greatly increased for these centers, however (see Appendix I). Consequently, a short time after machining, the number of centers on the surface is less than on the same metal machined at room temperature.

As the copper-nonadecanoic acid reaction is endothermic to the extent of 6.7 kcal. per mole, temperature elevation should favor reaction.

Increased temperature increases the number of collisions of fatty acid molecules with the metal surface per unit time, and, hence, the number of potential reaction sites.

Increased temperature increases the rate of desorption of the soap molecules from the copper surface, both because solubility of the copper soap almost surely increases with temperature, and because less Kramer energy is required to detach the adsorbed molecules from their positions on the metal surface.

The results of the experiments at 48° and 60° show that adsorption is always lower than at the corresponding acid exposure time at room temperature. The furthest departure from monolayer coverage is at 60° , indicating that this 35° temperature increase with its more favorable free energy change and number of collisions of fatty acid with the metal is not able to compensate for the more rapid decay of the Kramer effect and/or desorption from the surface.

A clue to the actual situation can be found in the shape of the adsorption isotherms. At both 48° and 60° adsorption plateaus were noted at less than monolayer coverage. These were maintained for some minutes. To explain these plateaus, as well as the similar adsorption plateaus noted on almost all metals when they are machined under the more dilute acid solutions, it is necessary to assume that a portion of the metal surfaces is inactive so far as adsorption is concerned. These "dead areas" are the result of the decaying of the Kramer effect.

Now, at the elevated temperatures where Kramer activity is initially very high the low energy sites quickly emit all their electrons and become inactive for adsorption. This occurs before sufficient fatty acid can diffuse to the surface to form the saturated layer, and, hence, adsorption is lower at 48° and at 60° than at room temperature. It is, of course, also possible that a very high desorption rate at the

elevated temperature, due to increased solubility of the soap and high activity of the desorption sites, is responsible for the low adsorption noted.

As time passes, both the desorption rate and the energy of the active centers decline. These rates are different. At forty minutes acid exposure time the Kramer effect has decayed to such an extent that it is no longer able to activate enough sites to keep pace with the desorption, which requires a smaller amount of energy. As soon as this happens, the sharp departures from the adsorption plateaus are noted.

(4) The adsorption results which were obtained for aluminum and indium metals, and which served as the starting point in the present investigation, can now definitely be ascribed to a very fast desorption rate of the metal soaps from the surfaces. This desorption rate is high, both because these soaps are relatively soluble in cyclohexane and because they are extraordinarily easily dislodged from their positions on the metal surfaces. This is because of the strained state of the soap molecules.* Because of this strained condition, energy requirements for soap formation are relatively high in spite of the activities of the metals and a large number of energetic active sites are necessary to make monolayer adsorption possible. The fact that indium is a larger atom than aluminum does relieve steric crowding to some extent, but the distorted bond angles which are principally

*The "F" and "B" strains popularized by H. C. Brown³⁸ are referred to.

responsible for fast desorption rate are present with both adsorbed soaps. Consequently, it is not surprising that indium shows a departure from monolayer adsorption as readily as aluminum does, when acid solution concentrations are decreased.

(5) The very low adsorption isotherms obtained on machining tin metal beneath solutions "A" and "A/2" are as yet unexplained although they may be due to an extremely rapid desorption of soap from the metal surface. No experiments have been performed to determine whether such soap formation actually occurs on tin. In spite of the activity of this metal its adsorption behaviour is like that of gold and platinum, on which McGill showed that no reaction occurred. This low adsorption is clearly anomalous and merits further work.

D. The Kramer Effect

In all of the preceding discussion, correlation of the Kramer effect with adsorption has been emphasized. However, the Kramer effect is only one of several factors which influence adsorption, and these other factors may be partly or wholly responsible for some of the adsorption behaviour noted. Consequently, results obtained from adsorption studies can be used to draw conclusions about the Kramer effect only with the greatest caution. Several inferences may be drawn, however, which may be significant.

(1) If the active centers on which most exchange occurs are the same as the centers from which the Kramer electrons are emitted, the Kramer centers have definite positions on the metal surface, are

not mobile, and are of different energies. All experiments point to the fact that some centers on the metal surfaces have sufficient energy to activate many molecular soap formation reactions, and do so, while others have sufficient energy to activate only a very small number of such reactions.

(2) The generally accepted temperature dependence of Kramer electron emission seems to be verified. Adsorption results are consistent with the thesis that raising the temperature temporarily increases electron emission, but that emission then falls to a lower level than emission at room temperature, due to more rapid emptying of the electron emission centers. The total number of electrons releasable from a metal surface by temperature elevation is constant and independent of the manner of such elevation.³⁹

(3) It is most difficult to reconcile the idea that exothermic surface oxidation of the metals is responsible for the electron emission with the conditions under which the adsorption studies were performed. Solubility of oxygen in cyclohexane has been stated to be very low. Further, experiments have repeatedly shown that the adsorptive ability of the metal surfaces is highest immediately after machining, before slow diffusion of oxygen through the solvent could occur. Neither can adsorption of the fatty acid furnish the energy necessary for electron emission because, for several metals on which the Kramer effect has been shown to influence adsorption, chemisorption is an endothermic process. It would appear then that Kramer emission is characteristic of the freshly prepared metal surfaces themselves, and not of adsorption or occlusion of foreign materials on these surfaces.

E. Suggestions for Further Work

In all the work reported here it has been implied that the various metals studied emit Kramer electrons which are responsible for adsorption. Studies have shown (see Appendix I) that the number of electrons emitted varies widely with the metal, finishing procedure, etc. However, no carefully controlled comparative experiments have ever been run under conditions anything like those present in the adsorption experiments. If an apparatus could be designed which would enable this type of measurements to be made it would add greatly to an understanding of the adsorption results. For instance, if tin emits no Kramer electrons its adsorption behaviour is as would be predicted.

Studies of adsorption and exchange at other temperatures than 25° should add greatly to knowledge of the adsorption picture and activating Kramer effect.

A modification of the machining techniques to allow cutting of some of the harder metals, especially iron, would allow adsorption measurements to be made on these commercially important materials.

Studies of adsorption on alloys would be very interesting. These would be especially so on alloys of varying percentages of tin and lead because of the markedly different adsorption behaviour of these materials, and results obtained would aid in understanding the whole adsorption picture.

CHAPTER V

SUMMARY

The study of the adsorption of n-nonadecanoic acid onto freshly machined metal surfaces begun by Smith and Allen¹ and continued by McGill⁵ has been extended to three additional metals: cobalt, indium, and tin. The adsorptive ability of cobalt was found to be entirely as predicted from the results of McGill's experiments and the position of this metal in the electrochemical series. The results of the adsorptive studies on this material were correlated with data obtained from desorption experiments and from free energy calculations.

The adsorptive abilities of indium and tin were not as predicted, however. Like aluminum, which was studied by McGill, indium adsorbed a monolayer of fatty acid only when machined under the most concentrated acid solutions and wide departures from this saturated adsorption coverage were noted as acid solution concentrations were decreased. Tin showed a wide departure from monolayer coverage and the adsorption isotherms on this metal resembled those of the noble metals gold and platinum rather than those of other metals with activity comparable to that of tin.

To explain this "anomalous" adsorption behaviour for aluminum, indium, and tin, it was necessary to extend the adsorption picture proposed by McGill. It was hypothesized that the adsorbed soaps were continually being desorbed from the metal surfaces at a rate which was a function both of the solubility of the soap in the desorbing solvent and the Kramer activity of the metal. Monolayer coverage was maintained

by diffusion of additional fatty acid to the surfaces which reacted there to form the metal soaps, under the activating agency of the Kramer effect. Various experiments were designed to test this hypothesis, all of which substantiated the postulated "exchange".

To correlate the results of several of these latter experiments it was found necessary to make the additional hypothesis that metal surfaces prepared in the manner described do not have uniform adsorptive ability across their "faces". It was suggested that the active centers on these metal surfaces were identical with the centers from which the Kramer electrons were emitted. Using this idea, several conclusions were drawn relative to the cause and nature of the Kramer effect itself.

In the light of the experiments which have been described the following statements can be made with regard to adsorption of nonadecanoic acid onto freshly machined metal surfaces.

(1) Adsorption on most metals which have been studied is the result of reaction of a fatty acid molecule with a metal surface atom to produce a soap. Platinum, gold, and possibly tin are exceptions to this. Adsorption on these three metals is much less than on all the others, and the adsorption isotherms have a characteristically different shape.

(2) The saturation level of adsorption on the metals prepared in the manner described with the possible exceptions noted above is the same, 4.17 molecules of fatty acid per 100 \AA^2 of geometric metal surface area. This is the value which would be calculated, assuming a close-packed monolayer of adsorbed acid on a perfectly smooth surface with a

unit roughness factor, and assuming that the limiting factor is the cross section of the carboxyl groups.

(3) Adsorption and chemical reaction on the various metals is due to the activating agency of the Kramer effect. Thermodynamic calculations show that the additional energy supplied by this phenomenon is necessary for reaction to occur at all on several of the metals, and greatly speeds reaction on the others by helping overcome the activation energy required in the chemisorptive process.

(4) The adsorbed soap molecules do not remain on the metal surface. They are continually desorbed and their places in the adsorbed monolayer almost immediately filled by other fatty acid molecules which diffuse to the surface and react there under the activating influence of the Kramer electron. Desorption is the limiting step in this replacement of adsorbed material as the analytical method is unable to detect departures from 100 per cent surface coverage over long time periods.

(5) The rate of exchange decays with time. Immediately after machining, exchange rate on the metal surfaces is very fast but rapidly declines with time until, after several hours, the adsorbed material is essentially static on the surface.

(6) Exchange does not occur at the same rate from all points across the metal surface but occurs principally at the active centers which are responsible for the Kramer effect. These centers have different energies and decay at different rates, though all according to the same kinetic law. Decay rate of these centers is greatly increased by raising the temperature and the activity of the surface temporarily

increased in the process.

The adsorption picture as outlined is able to satisfactorily explain the experimental data which has been obtained for adsorption of n-nonadecanoic acid onto the various metals which have been studied in this, and the preceding work.

APPENDICES

APPENDIX I

ELECTRON EMISSION FROM CLEAN METAL SURFACES

A. New Experimental Methods

A more fundamental approach to both catalysis and to lubrication and wear than that of adsorption is the study of clean metal surfaces. It has been known for a long time that such surfaces are unusually reactive. If placed in contact they may even be energetic enough to produce a weld. Because of this extremely high reactivity they are very difficult to prepare and keep clean for study, and so until recently the cause of this hyperactivity was unknown.

During the last few years, however, several new experimental techniques have been worked out to enable the properties of clean or freshly prepared metal surfaces to be studied independently of adsorption, and by their use, knowledge of the true nature of such surfaces has been greatly increased. The new methods may be listed: (1) Use of a Geiger counter to detect electron emission from worked or abraded metal surfaces. (2) Study of electron emission from metals during phase changes. (3) Use of the photoelectric effect to determine electron emission from surfaces excited by incident radiation. (4) Study of electron emission from annealed and then etched metal specimens. (5) Study of the formation of hydrogen peroxide at active, freshly prepared metal surfaces when these are exposed to moist air. (6) Study of the chemical reactivity of surfaces machined under a solvent or solution, so that the environment of the freshly prepared

surface is controlled.

There is at present considerable doubt that the phenomena detected by use of the techniques listed are all manifestations of the same thing. A knowledge of all of them contributes to the over-all knowledge of the properties of metal surfaces and why they act the way they do. The first five techniques listed will be discussed briefly. The sixth technique is, of course, that of the present investigation, and is discussed at considerable length above.

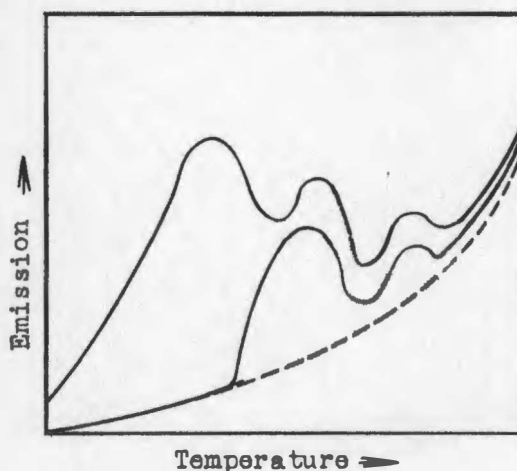
B. Electron Emission from Newly Prepared Surfaces

1. Emission Due to Abrasion

In 1947 the German physicist Kramer⁴⁰ discovered that abraded surfaces of a variety of metals gave off negatively charged particles which could be detected in a Geiger point counter tube. Emission-time curves showed a rapid decay, with emission intensity varying with finishing procedure, and with the gas charge of the counter tube. Unabraded specimens showed no such emission. This phenomenon has since become known as the Kramer effect.

a. Emission decay. Special attention has been paid to the form of the emission curve by Haxel, Houtermans, and Seeger³⁹ and others,⁴¹ who have shown that the product of particle frequency and time remains nearly constant. In other words, the subsidence of emission follows a hyperbolic law. Plots of emission vs. time on double logarithmic coordinates give straight lines.

b. Effect of temperature. The effect of temperature on the electron emission from abraded surfaces is striking. The plot below is a schematic example given by Lintner and Schmid⁴² to illustrate typical behaviour. Curve 1 is obtained if heating and observation are begun shortly after finishing. Curve 2 is obtained if subsidence of the emission at room temperature is allowed to occur before heating, and Curve 3 if the abraded sample is allowed to age for a long time before heating is begun. Experiments indicate that the maxima occur at the same temperature for the same metal, and gas medium for the counter tube.



Kramer³⁷ has shown that if the abraded sample is allowed to age for a sufficient time interval the first maximum disappears completely; the temperature at which emission is first detected is characteristic of the metal and independent of the method of finishing the sample and the gas in the counter tube. Kramer calls this temperature the "Umwandlungstemperatur" or turning point, and has determined it for a variety of metals.³⁷ An abraded specimen becomes exhausted on heating,

so far as electron emission is concerned, and a second heat treatment produces no further electrons. The total number of electrons releasable from a surface-treated metal specimen by temperature elevation is constant, and independent of the manner of such elevation.³⁹

2. Emission Due to Phase Changes

Electron emission from metal surfaces has also been noted as the result of various other treatments. Kramer³⁷ showed that molten Wood's metal emitted a large number of electrons as it solidified. Similar behaviour has been more recently noted for mercury.⁴³ Kramer was even able to determine the transition temperature of chromium from the hexagonal to the space-centered cubic modification and the transition of antimony from the amorphous to the crystalline form by noting discontinuities in the electron emission curves of these metals as they were cooled.

3. Emission Due to Sample Irradiation

Quantitative measurement of subsidence of after-current in counter tubes following glow discharge^{44,45} and ultraviolet irradiation⁴⁶ has revealed the same type of logarithmic decay as noted for electron emission following abrasion. Intensive electron bombardment will produce delayed electron emission from some metals.⁴⁷ Kramer^{41,48,49} has noted similar effects from nonmetals.

Seeger⁵⁰ has more recently made a study of the subsidence of after current with time and temperature after excitation by X rays, ultraviolet and visible light, and glow discharge. Constancy of the product of emission and time was confirmed. The effect of temperature

on the electronic emission was also found to be similar in character to that of surface finished specimens.

On repetition of heating, electron emission again fails to occur. If excited by visible light, the first maximum in the heating curve (see plot, page 101) is absent, but it appears if the specimen is subjected to ultraviolet irradiation.

In the case of aluminum it was found that oxide layers of increasing thickness have a marked effect on the emission produced by ultraviolet irradiation. With increasing thickness of the oxide layer emission passes through a maximum, then decreases. For specimens with essentially no oxide layer emission is low.

Kramer⁴⁸ and later Lintner and Schmid⁴² observed that abraded metal surfaces gave photoemission at wave lengths much longer than those necessary for photoemission from the clean metal without abrasion. The decline in emission of the unilluminated specimen, linear on double logarithmic coordinates, shows a different type of subsidence curve than that of emission from an illuminated specimen. Grunberg and Wright⁵¹ found that evaporated metal films gave the same results as did abraded specimens. These latter authors also found that as the wave length of the incident light was increased, photoemission passed through maxima at definite wave lengths. All metals they investigated gave emission in the ultraviolet, but only aluminum, magnesium, and zinc gave emission in the visible range. They found that if the outer layer of metal were etched away after such emission had subsided new layers of high activity were found which extended 5 to 10 μ below the surface.

4. Emission from Etched Specimens

Emergence of electrons has been noted from annealed aluminum specimens after careful etching.⁵² Subsidence of emission again follows a hyperbolic law. No such behaviour has been found for iron, copper, or nickel.

5. Possible Explanations for the Kramer Effect

Numerous explanations have been advanced to account for the phenomena which are known as the Kramer effect. In his original papers on the subject, Kramer⁴⁰ based his suggestions on observations of antimony. The coincidence of electron emission with the temperature at which he had previously shown⁵³ that amorphous antimony passed over into the crystalline state led him to the opinion that the emission of electrons is related always to a conversion of the metal in question from a nonmetallic to a metallic state. He cited the existence of the Beilby layer, supposed to be formed in cold finishing the metals, as a possibility for this "nonmetallic" phase. According to this interpretation, the heat liberated in the spontaneous transition back to the metallic phase is the source of the energy for electron emission.

Haxel, et al.³⁹ object to this proposal for two reasons. First, experiments have shown that all of a partially converted piece of antimony can darken a photographic plate and not just the phase boundary. Second, very high heats of transformation have to be assumed for the observed emission to be possible. For a work of emergence of the electrons of one electron volt, a heat of transformation of 23 kcal. per mole is necessary. This value exceeds the heat of fusion of the metals. Haxel suggests instead that the energy necessary is furnished

by oxidation of the fresh surface exposed in the abrasion process. The energy liberated in the oxidation is of the same order of magnitude as the work of electron emergence. The gradual decay of emission is explained by assuming an activation energy for the chemisorption which is furnished by the heat motion of the atoms involved. This energy would be expected to decrease as the number of potential reaction sites decreases.

Kiepenheuer,⁵⁴ on the other hand, suggests that the emission may really be regarded as a field emission, the electric field necessary being due to an insulating layer on the metal surface which adsorbs positive ions close to the metal substrate, with resulting field strengths of up to 10^5 volts per centimeter. This is the same type of phenomenon as that known as the Malter effect.⁵⁵ Roggen and Scherrer⁵⁶ consider that the setting up of the positive space charge which they agree creates the field is due to an internal photoelectric effect caused by X-ray or ultraviolet irradiation. According to this idea, the gradual subsidence of emission can be explained by gradual neutralization of the field.

Grunberg⁵⁷ takes the view that the abrasion produces structures in the surface of the metal from which electrons can be emitted by the action of light in the visible wave length range. These areas of low work function are produced by the intimate mixing of the metal oxide and metal in the abrasion process. He cites as evidence of this the fact that the decay of emission is greatly accelerated by the presence of oxygen, which would be expected to destroy such centers. The high wave length emission peaks noted above were found mainly with aluminum,

magnesium, and zinc, which are all known to form excess metal oxides.

A similar idea is advanced by Nassenstein⁵⁸ who suggests a two step mechanism for electron emission, the first being the promotion of electrons to high lying energy levels by the abrasion process. From these high lying centers the electrons are emitted thermally even at room temperature.

It is apparent that the cause of the electron emission known as the Kramer effect is still in considerable doubt. Unfortunately, many of the experiments performed thus far have not been adequately controlled; so that interpretation of the results obtained is very difficult. For example, it has recently been shown that particles of emery used for abrading the metal surfaces become embedded in the metal during the abrasion process and that these emery particles are themselves excellent electron emitters. Consequently, it is very difficult to determine whether the observed emission is due to the metal, the abrasive, or a combination of the two.

Also, most of the metal surfaces after being abraded in air have been placed in a counter tube charged with some ionizing gas. These gases certainly react with the exposed metal surfaces, and the effect of such reaction should certainly influence electron emission. It is even uncertain at present whether the observed emission is due to the metal itself, or to chemisorption and/or occlusion of other materials on its surface. More, and more rigidly controlled experiments are much needed to resolve these questions.

The use of new experimental methods should aid in obtaining more reliable experimental results. Recently, the Kramer electrons have been

counted by means of a secondary electron multiplier⁵⁹ and by a vibrating reed electrometer.⁶⁰ These instruments should obviate at least some of the difficulties attendant to use of the Geiger counter.

C. Formation of Hydrogen Peroxide at Fresh Metal Surfaces

1. Experimental Evidence

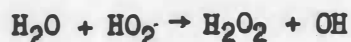
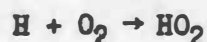
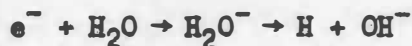
The ability of freshly prepared metal surfaces to blacken a photographic plate has been recognized for a long time. The phenomenon is known as the Russell effect, because of Russell's classic series of experiments dating to 1897.^{61,62,63,64,65} By passing a current of air between the active surface and the photographic plate, and noting that the image produced was distorted, Russell was able to show that the darkening of the image was due to a gas and not a true radiation. He suggested that the gas responsible was hydrogen peroxide.

In 1939 Churchill⁶⁶ confirmed and extended Russell's work and proved the presence of hydrogen peroxide by chemical means. Neither Russell nor Churchill was able to explain what caused the formation of hydrogen peroxide at the fresh surface.

2. Theoretical Explanation

It has been assumed that the formation of hydrogen peroxide at a nascent metal surface is related to the presence of electrons there,⁶⁷ and dependent on the surface being abraded or otherwise excited so that it gives off electrons. Recently, Grunberg⁶⁸ has suggested that the presence of such free electrons at the surface could initiate a series

of free radical reactions between water and oxygen leading to the production of hydrogen peroxide.



Grunberg found that aluminum, zinc, magnesium, and nickel, when cut under water containing oxygen produced measurable amounts of hydrogen peroxide, while copper and iron, which are catalysts for the decomposition of hydrogen peroxide, did not. He found, however, that the amount of hydrogen peroxide formed was proportional to the total metal surface area exposed by cutting, and that all the metal surface atoms reacted. All solutions became turbid, indicating formation of substantial amounts of metal hydroxides in the cutting process.

Becker and Wolff⁶⁹ found no correlation between the number of electrons emitted and the amount of hydrogen peroxide formed.

McGill² showed that water very quickly quenched the Russell effect. It was also completely quenched by chemisorption of a long chain fatty acid onto a freshly machined surface. However, a surface aged after machining under an inert solvent in which oxygen was not soluble showed a uniform activity, in spite of a finite finishing time.

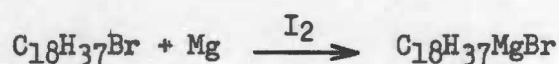
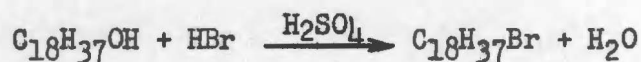
In view of these somewhat conflicting data, it is not possible to state unequivocally that the electrons which are responsible for the Kramer effect are the cause of the production of hydrogen peroxide at clean metal surfaces. However, the Kramer effect is probably the most

reasonable explanation advanced so far which can explain the phenomenon known as the Russell effect. Again, more and better controlled experiments are much needed.

APPENDIX II

PREPARATION OF THE n-NONADECANOIC ACID

A. Preparation of the Grignard Reagent



Both the unlabeled and the carbon-14 labeled n-nonadecanoic acid used in this work were prepared via octadecyl bromide and the Grignard reaction. This method was chosen both because octadecyl bromide forms the Grignard reagent very smoothly, and because the Grignard reaction affords a convenient way of incorporating an atom of carbon-14 into the fatty acid molecule. The procedure outlined by Lehto⁷⁰ was employed to prepare the octadecyl bromide, and that described by Allen¹ was used to prepare the Grignard reagent. This reagent was synthesized as follows.

Several hundred milliliters of reagent grade hydrobromic acid was fractionated in a 4-ft. Vigreux column to rid the acid of decomposition products. A middle fraction which represented the azeotropic acid composition was collected at 125.6°/742 mm., and used in the synthesis which follows.

To 120 g. (80.7 ml.) of the purified hydrobromic acid in a 500-ml. round-bottomed flask was added 38 g. (21 ml.) of concentrated sulfuric

acid* and 100 g. of Mathieson reagent grade n-octadecyl alcohol. The flask was then fitted with a condenser and refluxed over an open flame for six hours. Two phases were present in the flask during the refluxing period, the lower one composed of water and the two inorganic acids, and the upper of n-octadecyl alcohol and bromide.

After refluxing the mixture for six hours 100 ml. of water was added to dilute the acids, and the mixture was poured into a separatory funnel. The water layer was discarded. The organic layer was then extracted five times with 25-ml. portions of concentrated sulfuric acid, then twice with water, and finally, once with a dilute solution of sodium carbonate. Because the layers were very viscous and slow to separate the mixture was centrifuged during each extraction.

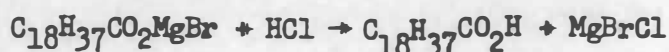
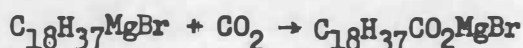
The crude octadecyl bromide was then distilled from a Claisen flask at a pressure of 3 mm. The fraction boiling from 160-163° was collected and used for synthesis of the Grignard reagent. The yield was 42 g., or 34 per cent, of theoretical.

Approximately 22.5 g. of the alkyl bromide was refluxed with 300 ml. of dry ether in a 500-ml. round-bottomed flask which was fitted with an efficient reflux condenser. One and four-tenths grams of freshly cut magnesium turnings was added, followed by a small crystal of iodine. The reaction soon started and in five hours all the magnesium had disappeared. A slow stream of dry nitrogen was passed through the

*The initial mixing of hydrobromic and sulfuric acids must be done very cautiously and preferably under the hood, as it is accompanied by evolution of some heat and considerable bromine vapor.

flask throughout the refluxing period. If kept tightly stoppered, the Grignard reagent could be stored for several days with no detectable decomposition.

B. Synthesis of the Unlabeled Acid

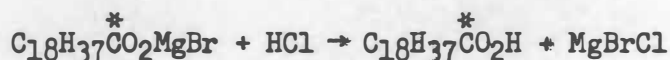
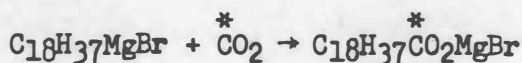
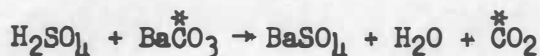


One-half of the solution of octadecyl magnesium bromide obtained as the product in Section A was poured into a 500-ml. beaker about one-fourth full of a slurry of Dry Ice, and ether which had been dried over sodium. The slurry was stirred until all the Dry Ice had sublimed. The product was hydrolyzed by shaking the resulting solution in a separatory funnel with three 50-ml. portions of 10 per cent hydrochloric acid. The aqueous extracts were discarded.

The ether solution of the fatty acid and alcohol was extracted with 50 ml. of 10 per cent sodium hydroxide. The ether layer which contained non-acidic impurities formed by hydrolysis of the Grignard reagent was set aside, and the aqueous phase was extracted twice more with 100-ml. portions of ether.

The aqueous layer was then acidified and extracted three times with ether. The ether was evaporated and the nonadecanoic acid recovered as a white powder. Melting point was 68.6-68.7°. Yield was 6.95 g. which was 69 per cent of theoretical.

C. Synthesis of the Labeled Acid

1. Carbonation

Carbonation of a Grignard reagent to produce an ordinary unlabeled fatty acid by a technique such as has been described above is a very simple process. When it is desired to produce a carbon-14 labeled product, however, the technique becomes considerably more involved. This is due to the limited amount of tagged carbon dioxide which is usually available, and to the desirability of working in a closed system, which saves contaminating the working area with the radioactive gas.

Carbon-14 is available from the United States Atomic Energy Commission in the form of labeled barium carbonate. Carbon dioxide can be easily generated from this reagent by treating it with sulfuric acid. Dauben, Reid, and Yankwich⁷¹ have described an apparatus for preparing fatty acids from tagged carbon dioxide generated in this manner. Their apparatus was improved by Allen⁵ who used it successfully for the fatty acid synthesis to be described. McGill² made a few minor changes in the technique which slightly improved the yield of fatty acid. The apparatus used in the present synthesis is pictured in Figure 21.

Two hundred milligrams of dry barium carbonate which was tagged to the extent of 1.44 mole per cent with carbon-14 was weighed into the

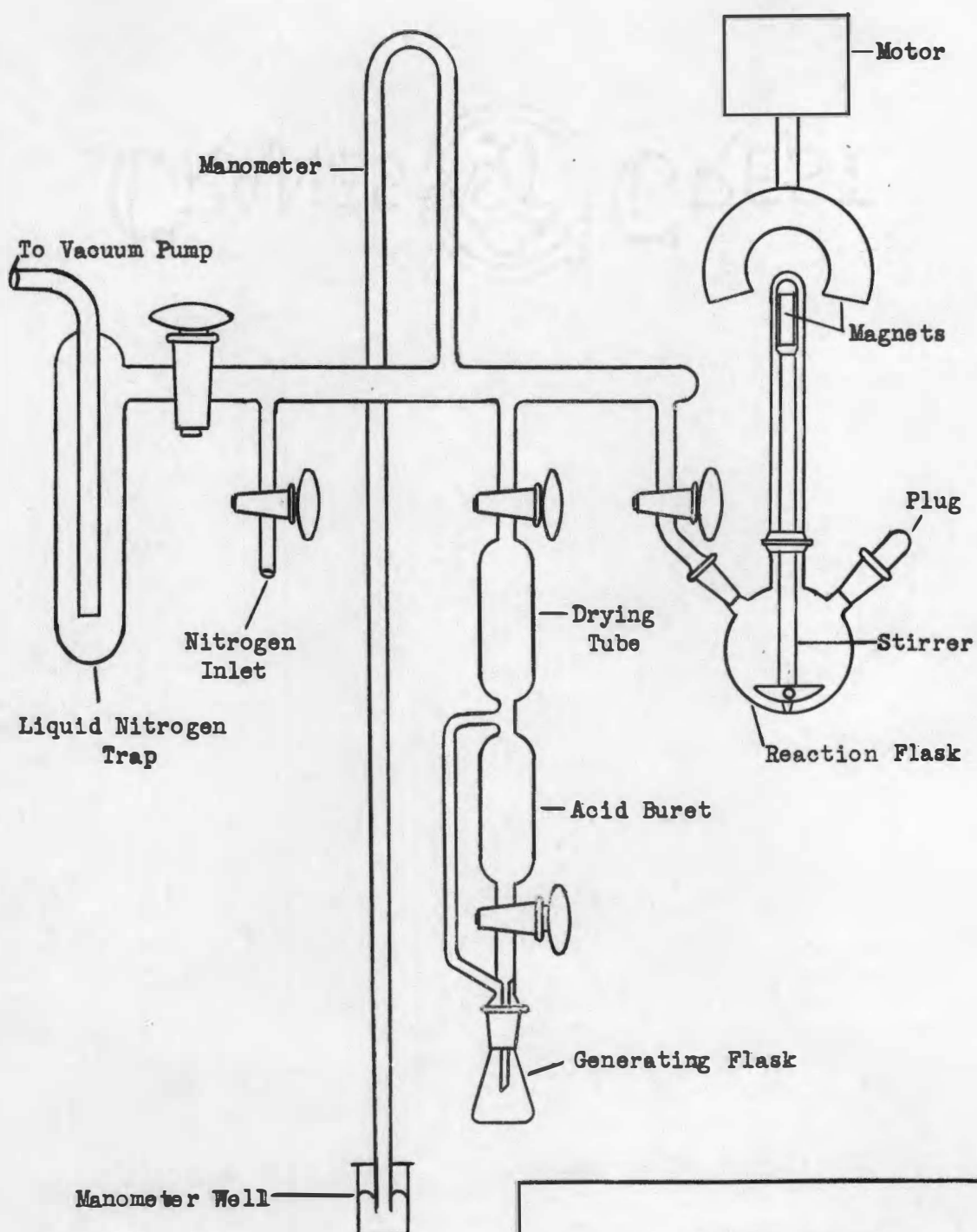


FIGURE 21
CARBOXYLATION APPARATUS

small gas generating flask pictured in Figure 21 and distributed in a ring on the bottom by swirling the flask. Then, 5.0 ml. of concentrated sulfuric acid was pipetted into the acid burette and the entire system assembled, evacuated, and tested for leaks. The system was then alternately filled with dry nitrogen and evacuated three times. When the system came to atmospheric pressure the third time the plug on the reaction flask was removed, and with dry nitrogen flowing through the system and out through the reaction flask, 7.0 ml. of the octadecyl magnesium bromide reagent prepared as described in Section A was pipetted into the flask.

The system was sealed, and the Grignard reagent frozen with a Dewar of liquid nitrogen. The system was then completely evacuated. The Dewar flask containing the liquid nitrogen was replaced by one which contained acetone which had been cooled with Dry Ice to a temperature of about -20° . The reaction mixture melted and nitrogen which was dissolved in the frozen Grignard reagent was liberated. This procedure was repeated twice more. On melting the reagent for the third time, no further gas evolution was noted.

The magnetic stirrer was then started, and carbon dioxide was liberated from the barium carbonate by allowing sulfuric acid to drop slowly upon it from the acid burette. The gas was generated at as uniform a rate as possible by regulating the drop rate of the sulfuric acid. When all the acid had been added the barium sulfate was dissolved in the excess sulfuric acid by heating the bottom of the flask with a low flame.

When the manometer showed that no more carbon dioxide was being evolved or absorbed the stirrer was stopped, and the reaction flask contents were again frozen with liquid nitrogen. A full vacuum was obtained, which indicated that all of the carbon dioxide gas had either been absorbed by the Grignard reagent or frozen in the reaction flask. This flask was then isolated from the rest of the system, the contents again melted with the cooled acetone, and the contents vigorously stirred for fifteen minutes. The flask was then opened to the system and the reaction product worked up.

2. Product

The reaction flask contents were transferred to a 500-ml. separatory funnel, after which the flask was rinsed successively with ether, hydrochloric acid, and ether again. The washings were added to the funnel. The reaction product was then hydrolyzed by shaking it with four portions of 10 per cent hydrochloric acid. The organic layer contained the radioactive acid along with some octadecyl alcohol produced by hydrolysis of the unused Grignard reagent. This solution was next suspended in a 10 per cent solution of sodium hydroxide which was extracted three times with ether to remove the octadecyl alcohol. The water layer was acidified with 10 per cent hydrochloric acid, and the precipitated acid taken in several portions of ether. These ether extracts were evaporated in a small beaker, and the fatty acid recrystallized from acetone.

Yields of fatty acid produced in this manner average 192 mg., which is 62 per cent of the theoretical based on the amount of carbon

dioxide which was used. The product was obtained as thin plates having a melting point of from 67-68° which compares favorably with the published value of 68.65°.

3. Notes

Some difficulty was experienced in making the stopcock, which regulated the flow of sulfuric acid from the acid burette absolutely leak proof. The acid appeared to react with all of the more usual stopcock greases, in spite of the fact that they are supposed to consist only of saturated hydrocarbons. A very thin film of a silicone type lubricant was finally adopted, but even this was not completely satisfactory.

Distributing the barium carbonate in a ring around the bottom of the generating flask was a suggestion of McGill, and was done to prevent the dusting and initial violent gas evolution which occurred if the sulfuric acid were allowed to drop directly onto the barium carbonate.

It was advisable to keep the temperature of the cooled acetone as nearly constant as possible, because even at -20° ether has a considerable vapor pressure which, of course, changes with temperature. These changes can complicate manometer readings and make it uncertain whether gas evolution had ended or whether the system was leaking, etc.

On several trial runs when the reaction product was being worked up and the fatty acid was suspended in 10 per cent alkali a considerable amount of white material precipitated at the water-ether interface. This was an emulsion of the sodium soap of the fatty acid, the presence of which complicated the extraction. The separation could be successfully

carried out, nevertheless, by including this emulsion as part of the aqueous phase, but the number of extractions had to be increased and this always decreased the yield.

APPENDIX III

PREPARATION AND PROPERTIES OF THE HEAVY METAL SOAPS

A. Preparations

1. General Procedures

The soaps of iron and cobalt were prepared by use of the general procedure outlined by Elliott⁷² and by Whitmore and Lauro.⁷³ This involves the addition of a solution of an inorganic salt of the heavy metal to an aqueous solution of the sodium soap of the fatty acid. The soaps were then purified by recrystallization from benzene.

2. Iron III Nonadecanoate

A 1.0-g. sample of unlabeled n-nonadecanoic acid was dissolved in a solution of 50 ml. of 95 per cent ethanol and 50 ml. of distilled water. The solution was warmed to about 60° on a hot plate, and two drops of bromthymol blue indicator was added. The solution was then titrated with approximately 0.1 N sodium hydroxide to the indicator's green neutral point. The neutral solution was then boiled to expel most of the alcohol.

A slight excess of ferric chloride hexahydrate (0.31 g.) was weighed into a 50-ml. Erlenmeyer flask and dissolved in a small amount of water. This solution was heated to about 70° and added to the warm solution of the sodium soap. The iron III soap precipitated as a salmon-colored solid. This was allowed to cool to room temperature, was filtered, suspended in hot water, and filtered again in order to get rid of any inorganic contaminant. It was then dried in an

evacuated desiccator over Drierite, and finally recrystallized from benzene.

3. Cobalt II Nonadecanoate

A 1.0-g. sample of unlabeled n-nonadecanoic acid was dissolved in a solution of 50 ml. of 95 per cent ethanol and 50 ml. of distilled water. This solution was warmed to about 60° on a hot plate and two drops of bromthymol blue indicator was added to it. The solution was then titrated with approximately 0.1 N sodium hydroxide to the indicator's green neutral point. The neutral solution was boiled to expel most of the alcohol.

Exactly 0.486 g. of cobaltous nitrate hexahydrate was then weighed into a 50-ml. Erlenmeyer flask. This is a slight excess over the amount of this salt required to react with the acid. The salt was dissolved in a small amount of water and heated on the hot plate to approximately 70°, when it was added to the warm solution of sodium nonadecanoate. The cobalt soap precipitated as a lavender-colored solid. The solution was cooled and filtered, and the precipitate was washed thoroughly with water to remove any inorganic cobalt contaminant. The sample was then dried in an evacuated desiccator over Drierite, and finally recrystallized from benzene.

4. Iron II Nonadecanoate

A preparation of iron II nonadecanoate was also attempted using the same general techniques as those described. This preparation was unsuccessful because of the strong tendency of the ferrous iron to oxidize in the air to the ferric state. It was not felt that the

data which would have been obtained from this soap justified building an apparatus which would allow the soap to be prepared in pure form, and so the preparation was abandoned.

B. Properties

1. Melting Points

Iron III nonadecanoate melted at 112-113°. Cobalt II nonadecanoate decomposed when heated above about 200°.

2. Solubilities

The solubilities of the two soaps were determined in cyclohexane and in water. Details of these determinations are given in Appendix IV. The values found are given below, and are compared with the solubilities McGill found for similar soaps in these same solvents.

<u>Soap</u>	<u>Solubility in Water</u>		<u>Solubility in Cyclohexane</u>	
	<u>g./ml.</u>	<u>moles/l.</u>	<u>g./ml.</u>	<u>moles/l.</u>
Iron III	4.75×10^{-8}	5.01×10^{-8}	3.92×10^{-5}	4.13×10^{-5}
Cobalt II	6.83×10^{-7}	1.04×10^{-6}	3.16×10^{-5}	4.83×10^{-5}
Silver I	1.27×10^{-6}	3.2×10^{-6}	1.90×10^{-8}	4.69×10^{-8}
Copper II	7.1×10^{-9}	1.1×10^{-8}	1.00×10^{-7}	1.52×10^{-7}
Lead II	2.61×10^{-6}	3.2×10^{-6}	2.1×10^{-7}	2.62×10^{-7}

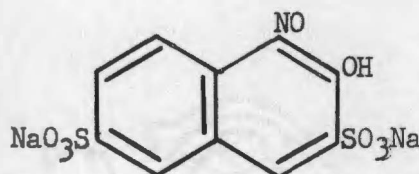
APPENDIX IV

MICROANALYTICAL TECHNIQUES

A. Cobalt

1. Analytical Method

The method used for the cobalt analysis was based on that outlined by Dean,⁷⁴ simplified somewhat because of the lack of interfering ions. Cobalt reacts with nitroso-R salt,



which is yellow in aqueous solution, to give a soluble red complex salt. This salt, unlike the nitroso-R salt complexes of most other metals, is stable in mineral acid solutions. This stability is the basis of the specificity of the reagent for cobalt, because most similar complexes, if present, can be destroyed by suitably lowering the pH of the sample solution.

2. Procedure

Reagents were prepared as follows:

a. Cobalt-free water. This was prepared by passing distilled water through a 4-ft. column which contained Amerlite MB-3 ion exchange resins. The purified water was collected at the bottom of the column at the rate of one drop every ten seconds.

b. Primary cobalt standard. A standard cobalt solution of concentration 100 ppm. was prepared by dissolving 0.0404 g. of reagent grade cobalt chloride hexahydrate in deionized water, adding 1 ml. of concentrated hydrochloric acid and diluting to 100 ml.

c. Secondary cobalt standard. A standard cobalt solution of concentration 10 ppm. was prepared by diluting 10 ml. of the primary standard to 100 ml. with deionized water which contained 1 ml. of concentrated hydrochloric acid. This secondary standard was always made up just before use.

d. Cobalt working solutions. Standard cobalt solutions of concentration 0.05, 0.10, 0.30, 0.50, and 0.80 ppm. were prepared by pipetting 0.5, 1.0, 3.0, 5.0 and 8.0-ml. aliquots of the secondary standard solution into 100-ml. volumetric flasks, and eventually diluting them to 100 ml.

e. Nitroso-R salt. A 0.1 per cent solution of nitroso-R salt was prepared by dissolving 0.1 g. of the salt in 100 ml. of the cobalt-free water.

f. Sodium acetate buffer. A 10 per cent solution of sodium acetate was prepared by dissolving 100 g. of the reagent grade chemical in 1 l. of cobalt-free water.

g. Sulfuric acid. An approximately 0.1 N solution of sulfuric acid was prepared by diluting 2.66 ml. of the concentrated acid to 1 l. with cobalt-free water.

The purpose of this analysis was to determine the solubility of cobalt II nonadecanoate, prepared as described in Appendix III, in water and in cyclohexane at 25°. Accordingly, saturated solutions of

the soap were prepared by heating several hundred milliliters of the two solvents to approximately 60° , adding an excess of the cobalt soap, and then allowing the two solutions to cool slowly and with frequent agitation to near room temperature. They were then poured into Erlenmeyer flasks and equilibrated for three days in a 25° thermostat.

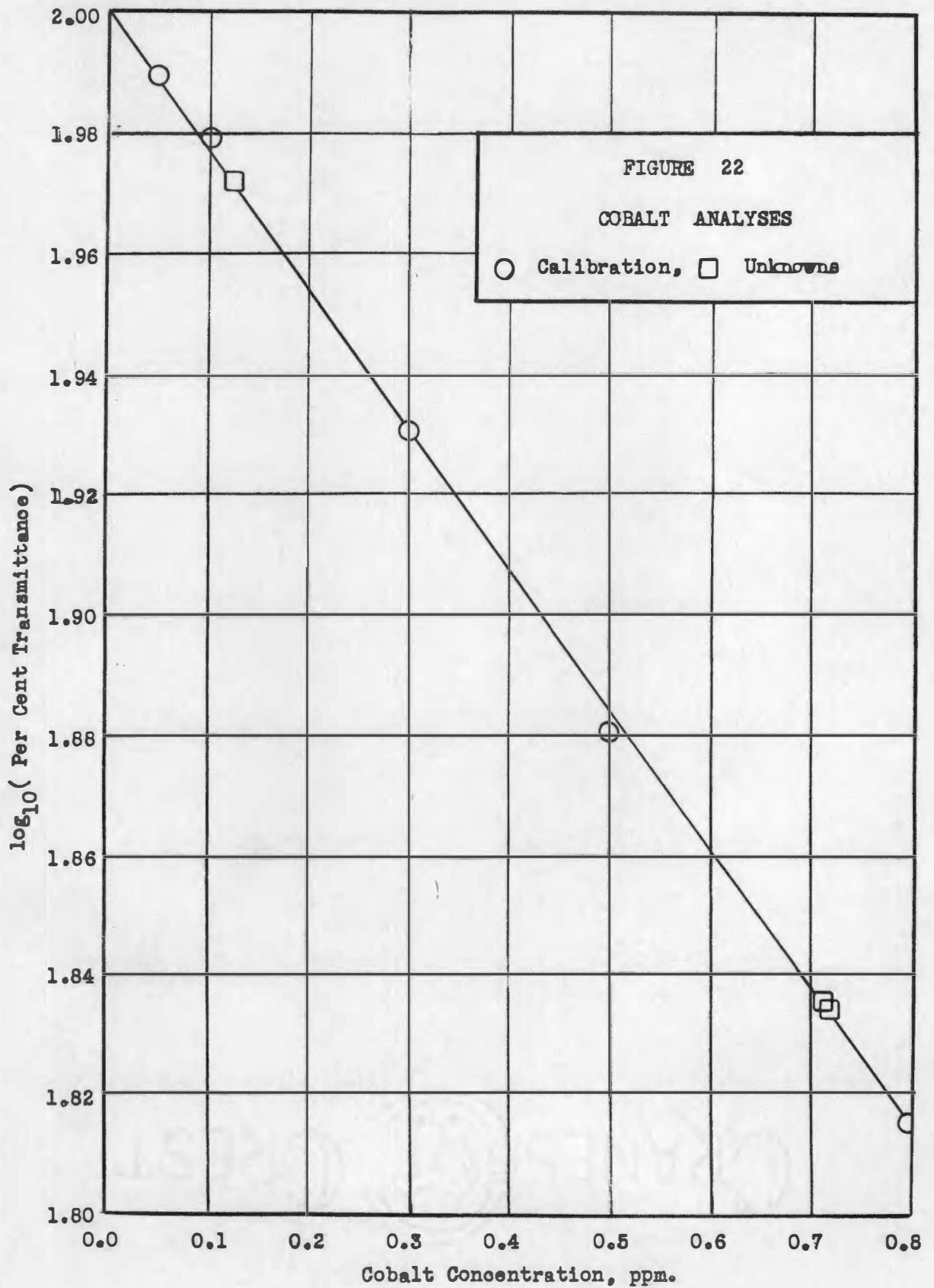
The saturated water solution of the cobalt soap then was filtered, and a 200-ml. aliquot was evaporated to about 30 ml. and washed into a 100 ml. volumetric flask.

Two 25-ml. portions of the cyclohexane solution of the cobalt soap were admitted to ~~small~~ separatory funnels, extracted three times with 5-ml. portions of approximately 0.1 N sulfuric acid, and the aqueous extracts combined and admitted to 100-ml. volumetric flasks.

These unknowns, and the cobalt standards prepared as described, were diluted to approximately 50 ml. with cobalt-free water and buffered to pH 5-5.5 with 10 per cent sodium acetate. Two milliliters was usually sufficient. The pH was checked with bromcresol green external indicator.

Two milliliters of the nitroso-R salt solution was added, the flasks shaken, 1.5 ml. of concentrated hydrochloric acid added, and then the flasks were diluted to the mark with cobalt-free water.

The solutions were examined at 510 m μ with the aid of the Beckman Model DU spectrophotometer and 5 cm. absorption cells. All results were obtained using a blank sample as a reference standard. These results are shown graphically in Figure 22. A strict Beer's law dependence was found for the cobalt complex, and concentrations of the saturated



cobalt solutions taken from the graph were:

- | | |
|--------------------|------------|
| (1) In water | 0.123 ppm. |
| (2) In cyclohexane | 0.708 |
| (3) In cyclohexane | 0.715 |

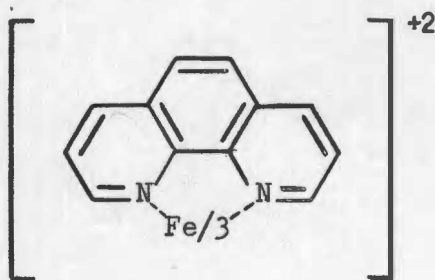
Correcting for the dilution of the saturated solutions before the actual analyses took place, the actual values found are:

<u>Solubility in Water</u> of $\text{Co}(\text{Nd})_2$	<u>Solubility in Cyclohexane</u> of $\text{Co}(\text{Nd})_2$
6.83×10^{-7} g./ml.	3.16×10^{-5} g./ml.
1.04×10^{-7} moles/liter	4.83×10^{-5} moles/liter

B. Iron

1. Analytical Method

The method used for the determination of iron is based on that described by Sandell.⁷⁵ It makes use of the formation of an orange-red complex,



between 1,10-phenanthroline and ferrous iron. Sandell states that color intensity is independent of the acidity in the pH range of 2-9. The complex is very stable and solutions show no change in color after many months. Beer's law is closely followed. Ferric iron present in the sample is reduced to the ferrous state with hydroxylamine hydrochloride.

prior to the analysis.

2. Procedure

Reagents were prepared as follows:

a. Iron-free water. This was prepared by passing distilled water through a 4-ft., 25-mm. diameter column which contained Amberlite MB-3 ion exchange resin. The purified water was collected at the bottom of the column at the rate of one drop every ten seconds.

b. Primary iron standard. A standard iron solution was prepared by weighing out exactly 1.000 g. of pure iron wire, and dissolving it in a mixture of 50 ml. of concentrated nitric acid, 50 ml. of concentrated sulfuric acid (spec. g. 1.84), and 50 ml. of iron-free water. This was boiled until fumes of sulfur trioxide appeared, then diluted to 1 l. with water which had been passed through the ion exchange column. The result was a solution of iron of concentration 1000 ppm.

c. Secondary iron standard. A standard iron solution of concentration 100 ppm. was prepared by diluting 10 ml. of the primary standard to 100 ml. with water which had been passed through the ion exchange column. This secondary standard was made up just before use.

d. Tertiary iron standard. A tertiary iron standard of concentration 10 ppm. was prepared by diluting 10 ml. of the secondary standard to 100 ml. with the iron-free water. This tertiary standard was always prepared just prior to use.

e. Hydroxylamine hydrochloride. A 10 per cent solution of hydroxylamine hydrochloride was prepared by dissolving 10 g. of the reagent in iron-free water, and diluting the solution to 100 ml.

f. Sodium acetate. A 10 per cent solution of sodium acetate was prepared by dissolving 100 g. of the reagent grade chemical in 1 l. of iron-free water.

g. 1,10-Phenanthroline. A saturated solution of 1,10-phenanthroline was prepared by adding an excess of the reagent to approximately 100 ml. of iron-free water which had been warmed to approximately 60° on a hot plate, then allowing the solution to cool slowly to room temperature with frequent agitation.

h. Sulfuric acid. An approximately 0.1 N solution of sulfuric acid was prepared by diluting 2.66 ml. of the concentrated acid to 1 l. with iron-free water.

The purpose of this analysis was to determine the solubility of iron III nonadecanoate, prepared as described in Appendix III, in water and in cyclohexane. Accordingly, saturated solutions of the soap were prepared by heating several hundred milliliters of the solvents to about 60°, adding an excess of the iron soap, and then allowing the two solutions to cool slowly, with frequent agitation, to room temperature. They were then poured into glass-stoppered Erlenmeyer flasks and equilibrated for three days in a 25° thermostat.

Three-hundred milliliters of the filtered aqueous soap solution was evaporated to approximately 40-ml. volume and washed into a 100-ml. volumetric flask with approximately 0.1 N sulfuric acid.

A 25-ml. aliquot of the saturated cyclohexane solution of the soap was filtered and passed from a burette into a small separatory funnel. This solution was extracted three times with 5-ml. portions of approximately 0.1 N sulfuric acid. The aqueous extracts were

combined and admitted to a 100-ml. volumetric flask.

Standard iron solutions of concentration 0.01, 0.05, 0.10, 0.30, and 0.50 ppm. were prepared by pipetting 0.10-ml., 0.50-ml., 1.00-ml., 3.00-ml., and 5.00-ml. aliquots into 100-ml. volumetric flasks which were subsequently brought up to a total volume of 100 ml.

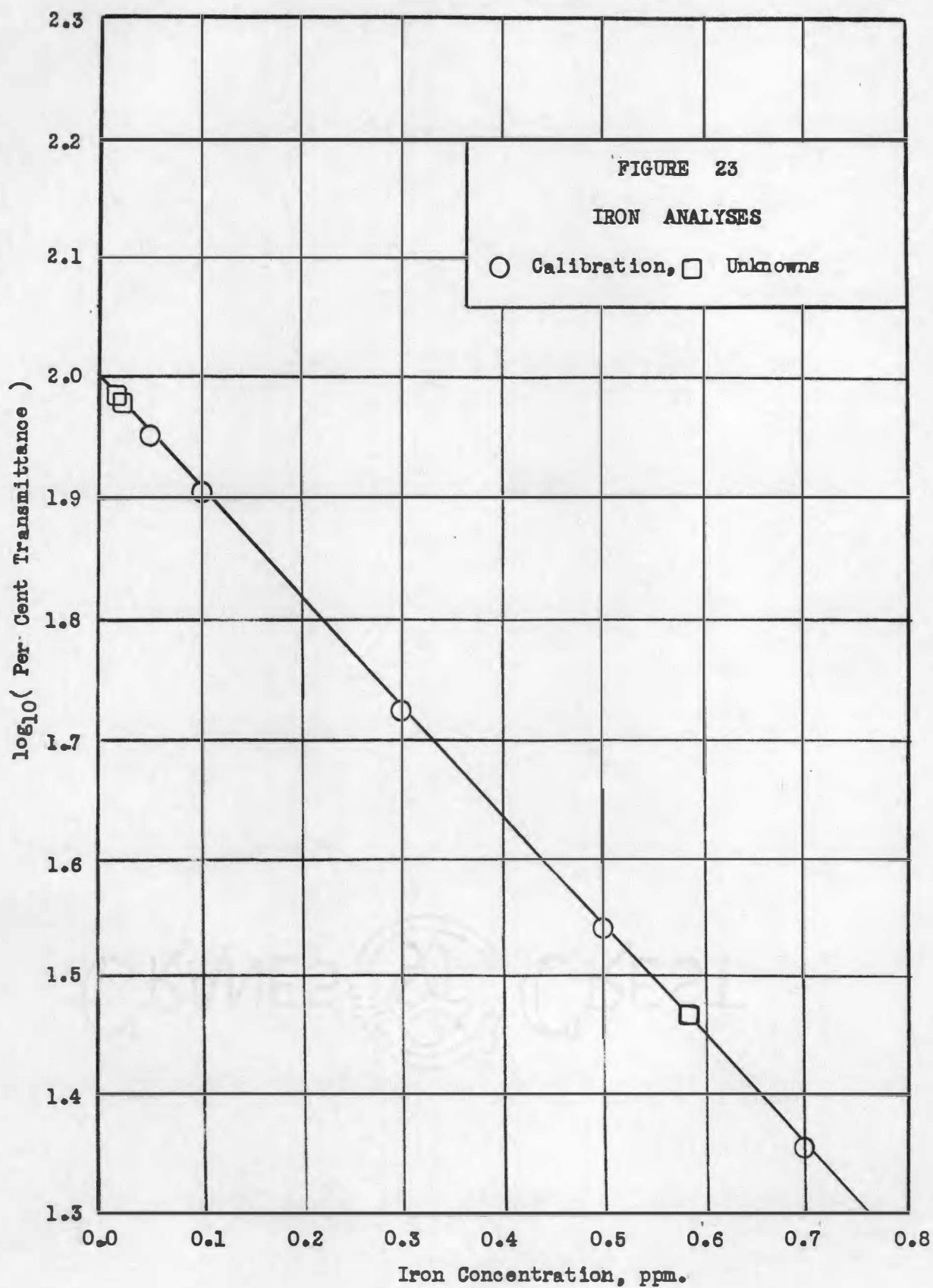
Eight-tenths milliliters of the 10 per cent solution of hydroxylamine hydrochloride was pipetted into each flask.

Three milliliters of the saturated solution of 1,10-phenanthroline was then added, followed by 8 ml. of the 10 per cent sodium acetate. The flasks were then diluted to the mark with iron-free water.

The transmittance of all the solutions was determined at a wave length of 490 mμ with the aid of the Beckman Model DU spectrophotometer. Special 5 cm. absorption cells were employed for the measurements which were made using a blank sample as reference solution. The results of these measurements are given graphically in Figure 23. A strict Beer's law dependence was found for the iron complexes, and concentrations of the saturated iron solutions taken from the graph were:

(1) In water	0.0085 ppm.
(2) In water	0.0085
(3) In cyclohexane	0.563
(4) In cyclohexane	0.561

Correcting for the concentration and dilution of the saturated solutions before the actual analyses took place, the values found are:

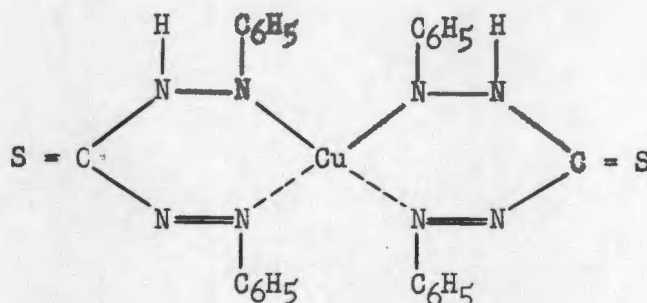


<u>Solubility in Water</u> of $\text{Fe}(\text{Nd})_3$	<u>Solubility in Cyclohexane</u> of $\text{Fe}(\text{Nd})_3$
4.75×10^{-8} g./ml.	3.92×10^{-5} g./ml.
5.01×10^{-8} moles/liter	4.13×10^{-5} moles/liter

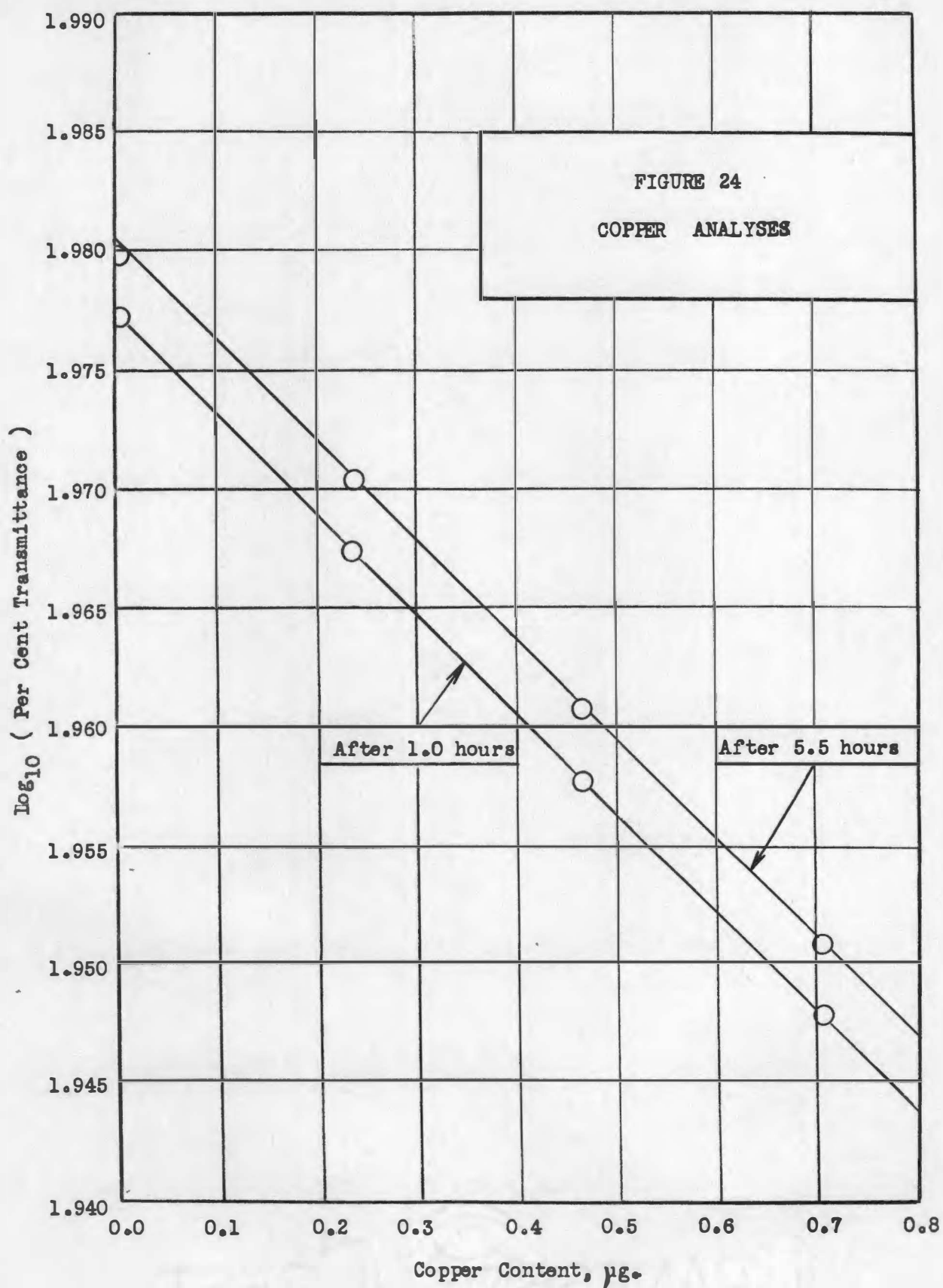
C. Copper

1. Analytical Method

The analytical method used for the determination of copper in cyclohexane solutions employs the much used reagent, dithizone, for the development of the intensely red-violet colored cupric keto dithizonate.



It is believed that the method of color development used is unique with this work, and so it will be discussed in detail. It involves the very simple procedure of shaking the cyclohexane solution of the copper soap with a dilute solution of dithizone. It was found that the chelating agent was strong enough to react quantitatively with the copper in this aprotic solvent, giving precise results with a minimum of trouble and the possibility of error attendant to a more involved method. Typical calibration curves obtained are shown in Figure 24, which also shows the stability of the color produced as a function of time between color generation and measurement. The only difficulty attendant to use



of the technique described is that the reagent, when used in the aprotic solvent, loses all specificity for copper. This was no handicap in the present determination, however.

2. Procedure

Reagents were prepared as follows:

a. Cyclohexane. The purification of the cyclohexane used throughout this work has been described in some detail above. It is very unlikely that even the practical grade material contained anything which would interfere with the copper analyses.

b. Carbon tetrachloride. Practical grade carbon tetrachloride was fractionated through an 8-ft. still, and a middle fraction was used for preparing the solutions described.

c. Chloroform. Reagent grade chloroform was used without further purification.

d. Primary copper standard. Use of this method necessitated the preparation of cyclohexane solutions of the copper soap of known concentration. The solutions cannot be prepared directly, as the saturation solubility of the soap in this solvent is only 0.1 mg./l., too low for accurate weighing. However, Koenig⁷⁶ states that the solubility of copper stearate is "fair" in chloroform at 25°. Accordingly, 4.89 mg. of the purified copper II nonadecanoate prepared by McGill² was weighed on a semimicro balance and dissolved in 100 ml. of chloroform. This gave a solution containing 4.71×10^{-6} g./ml. of copper.

e. Secondary copper standard. Five milliliters of the primary copper standard was diluted to 500 ml. with chloroform. This solution

had a copper concentration of 0.0471×10^{-6} g./ml.

f. Primary dithizone. Ten milligrams of purified dithizone was weighed on a semimicro balance and dissolved in 100 ml. of purified carbon tetrachloride. The solution was kept in a brown glass bottle under refrigeration to retard decomposition of the reagent.

g. Secondary dithizone. Twenty-five milliliters of the primary dithizone solution was diluted to 250 ml. with cyclohexane. This solution was always made up immediately before use.

Zero, 5, 10, and 15-ml. aliquots of the secondary copper standard solution were pipetted into four 50-ml. mixing cylinders equipped with ground glass stoppers, and then the solvent was completely evaporated from each by partially immersing the cylinders in a water bath kept at a temperature just below the boiling point of the chloroform. About 25 ml. of cyclohexane was then added to each cylinder. The copper unknowns were cyclohexane solutions of the soap contained in the 25-ml. adsorption cups which have been previously described.

Two milliliters of the secondary dithizone solution was pipetted into each of the unknown copper solutions and into the mixing cylinders containing the standards, all of which were equipped with small magnetic stirring bars. The solutions were then vigorously stirred for one hour. A definite color change was usually detectable in one or two minutes and some tests seemed to indicate that even here, the rate determining step was the desorption of the adsorbed soap from the cup walls.

At the end of an hour the unknown copper solutions were poured into other mixing cylinders and the volume of each was made up to 40 ml. with cyclohexane. Each cylinder was then thoroughly shaken and examined

as quickly as possible in the Beckman Model DU spectrophotometer. A magnifying glass was found helpful in determining small differences in optical density. All determinations were run using 5-cm. absorption cells at a wave length of 510 m μ against a cyclohexane blank. This is the wave length of minimum absorption of dithizone but maximum absorption of cupric dithizonate, so optical density increases with increasing copper concentration. Results with the standards were fairly precise, indicating that the chelating agent is strong enough to pull the copper from the cup walls into the solution. The results obtained with the unknowns have been given in Figure 18.

3. Notes

The particular problem encountered in the analysis described above was that of analyzing for minute amounts of copper which was partly dissolved in cyclohexane, and partly precipitated on the walls of the container. It was fairly certain that at least part of the desorbed copper was not in solution, since McGill's determination of the solubility of copper II nonadecanoate indicated that the saturation solubility of the soap in cyclohexane was only 1.0×10^{-7} g./ml. Thus, one monolayer of desorbed soap was sufficient to completely saturate the 25 ml. of solvent in the adsorption cup. It was thought that several such monolayers would be desorbed. This being the case, it appeared that there were two analytical possibilities. Either the copper analyses could be run in the same adsorption cups into which the soap was desorbed, all desorbed copper would be determined, or some rinsing and extracting technique could be attempted which would pull all the copper present into the aqueous phase as some inorganic

salt, where solubility would no longer be a problem.

As no analytical method could be found which would permit analyses in the cyclohexane solutions, the latter technique was tried first. The analytical method of Lambert⁷⁷ as modified by McGill² was tested. It was found unsuitable, however, as wide deviations from Beer's law, accompanied by increasingly erratic results, were noted if the total copper present exceeded about 0.3 μg .

Sandell⁷⁵ spends considerable time discussing the application of dithizone to the determination of very small quantities of copper. The method involves shaking an aqueous solution of controlled pH, containing the cupric ion with a carbon tetrachloride solution of dithizone. A small amount of dithizone enters the aqueous phase where it reacts by an ionic mechanism to give the cupric dithizonate which then re-enters the organic layer. Although excellent in principle, when it was tried it was found that the two extractions necessary to first pull the copper from the cyclohexane into the water and then back into the carbon tetrachloride, plus the difficulty of removing all the copper from the walls of the adsorption cups, made the results rather erratic with the minute amounts of copper which were to be determined.

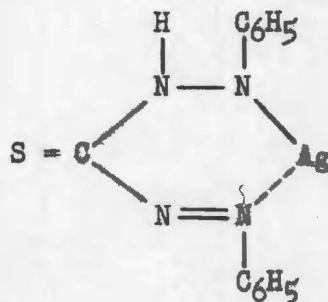
This difficulty led to the development of the method finally used. It was uncertain whether a quantitative reaction between copper and dithizone would occur under these conditions, as the aprotic cyclohexane could furnish no solvation energy to help drive the reaction to completion. However, the precise results shown in Figure 24 suggest that quantitative reaction did indeed occur. To make absolutely certain

that partial reaction did not lead to erroneous results, the standards used were prepared from a purified sample of the same compound whose solutions were to be analyzed for copper. Also, all analyses were begun with the copper soap of the standards adsorbed on the walls of the mixing cylinders, which duplicated as nearly as possible the situation of the unknowns.

D. Silver

1. Analytical Method

The method used for the determination of silver is a modification of those described by Sandell⁷⁵ and by McGill.² It is based on the greater stability of yellow silver keto dithizonate



than that of the red-violet copper keto dithizonate, a solution of which is used as the complex forming agent in the analysis. The method involves a mixed color comparison of the hues of the unknown solutions with those of the knowns. Colors range from yellow to violet, depending on the amount of silver present.

Because the stability of the cupric dithizonate itself is considerably greater than that of the dithizonates of almost all common

interfering metals, no special purification of water, acids, etc., is required to remove traces of contaminants which would interfere if dithizone itself were used as the reagent. Only gold, palladium, and mercury interfere with the silver determination if it is carried out as described. These metals form stronger complexes with dithizone than silver does. However, they are rarely present and normally pose no problem in the analysis.

2. Procedure

Reagents were prepared as follows:

a. Sulfuric acid. An approximately 0.1 N solution of sulfuric acid was prepared by diluting 2.66 ml. of the concentrated acid to 1 l. with distilled water.

b. Primary silver standard. A primary silver standard of concentration 10 mg./ml. was prepared by dissolving 1.575 g. of dried silver nitrate in 0.1 N sulfuric acid, and making the solution up to a volume of 100 ml.

c. Secondary silver standard. A secondary silver standard was prepared by diluting 2.5 ml. of the primary standard to 250 ml. with 0.1 N sulfuric acid. This solution had a silver concentration of 100 $\mu\text{g./ml.}$

d. Tertiary silver standard. One milliliter of the secondary silver standard was diluted to 1 l. with 0.1 N sulfuric acid. This gave a solution of silver concentration 0.1 $\mu\text{g./ml.}$

e. Primary dithizone. An approximately 0.01 per cent (w/v) solution of dithizone in carbon tetrachloride was prepared by dissolving

10 mg. of the purified dithizone in 100 ml. of the fractionated solvent. This solution was kept in a brown glass bottle and under refrigeration to retard decomposition of the reagent.

f. Secondary dithizone. Ten milliliters of the primary dithizone solution was diluted to 100 ml. with purified carbon tetrachloride. This solution was prepared fresh just before use.

g. Cupric dithizonate reagent. Twenty-five milliliters of the secondary dithizone solution was shaken with an excess of an aqueous solution of reagent grade copper sulfate. The water layer was then discarded, and the organic phase thoroughly washed three times with 0.1 N sulfuric acid to get rid of any suspended copper. The carbon tetrachloride solution of cupric dithizonate was then diluted to 50 ml.

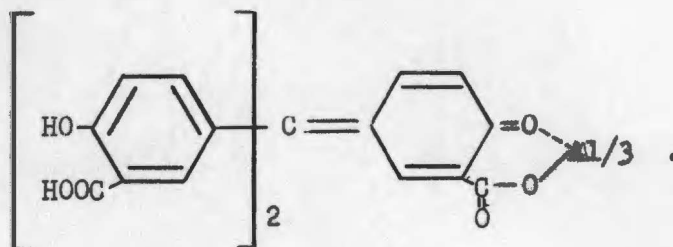
The purpose of this analysis was to determine the quantity of silver nonadecanoate desorbed from a surface of silver metal when this was exposed for varying time intervals to a cyclohexane solution of nonadecanoic acid. To begin the analytical procedure, it was necessary to bring the desorbed silver into the aqueous phase. Accordingly, the soap solutions were extracted three times with 5 ml. portions of 0.1 N sulfuric acid, and the aqueous extracts combined and admitted to a set of small flat-bottomed glass vials equipped with snap-on polyethylene lids. A set of standard silver solutions was also prepared by pipetting 0, 0.5, 1.0, 1.5, and 2.0 ml. of the tertiary silver standard into similar vials. These contained 0.05, 0.10, 0.15, and 0.20 μg of silver. The volume of each of the known solutions was then made up to 15 ml. to correspond with those of the unknowns.

Exactly 0.2 ml. of the cupric dithizonate reagent was pipetted into each of the vials which were then capped and shaken for two minutes. The droplets of carbon tetrachloride were shaken down in the tubes to form one large drop at the bottom. Color comparison of the standards and unknowns was made visually. Standards only 0.05 μg different in silver content could be clearly distinguished, but these approached the limit of surety about color differences.

E. Aluminum

1. Analytical Method

The method used for the aluminum analyses is described by Sandell.⁷⁵ It is based on the formation of a deep red-colored lake when aluminum is treated with a weakly acid solution of ammonium aurintricarboxylate (aluminon). The color has been ascribed by Feigl as being due to an internal complex salt between aluminum and the reagent, having the formula,



The color has also been credited to colloidal aluminum hydroxide on which the organic compound is adsorbed with a pronounced color change. The reagent is very sensitive. As little as 0.01 μg of aluminum has been detected in 10 ml. of sample in a column of solution with a 1-cm.²

cross section. As the reagent is itself colored, Beer's law is not generally followed except when large excesses of aluminon are present. The color development of the lake does not take place immediately, but is reasonably complete within fifteen minutes.

2. Procedure

Reagents were prepared as follows:

a. Aluminum-free water. This was assured by passing distilled water through a 4-ft. column which contained Amberlite MB-3 ion exchange resins. The purified water was collected at the bottom of the column at the rate of one drop every ten seconds.

b. Hydrochloric acid. A standard hydrochloric acid solution was prepared by diluting 7.4 ml. of the concentrated reagent to 1 l. with the aluminum-free water.

c. Primary aluminum standard. A standard aluminum solution was prepared by dissolving 0.176 g. of potassium aluminum sulfate dodecahydrate in the hydrochloric acid, and diluting the solution to 100 ml. This gave a solution of aluminum concentration 0.1 mg./ml.

d. Secondary aluminum standard. This was prepared by diluting 1 ml. of the primary standard to 100 ml. with the hydrochloric acid solution. The resulting solution had an aluminum concentration of 1 μ g./ml.

e. Tertiary aluminum standard. A tertiary standard aluminum solution was prepared by diluting 20 ml. of the secondary standard to 100 ml. with the hydrochloric acid solution. This had an aluminum concentration of 0.2 μ g./ml.

f. Ammonium acetate. A 10 per cent ammonium acetate solution was prepared by dissolving 100 g. of the reagent grade chemical in aluminum-free water, and diluting the solution to 1 l.

g. Ammonium aurin tricarboxylate. A 0.2 per cent (w/v) solution of the aluminon reagent was prepared by dissolving 0.2 g. of the reagent in 100 ml. of aluminum-free water.

The purpose of this analysis was to determine the amount of aluminum III nonadecanoate desorbed from a machined aluminum surface when this surface was exposed for varying time intervals to a cyclohexane solution of the fatty acid. To begin the analytical procedure, the aluminum was brought into the aqueous phase. Accordingly, the cyclohexane solutions were extracted twice each with 5-ml. portions of the hydrochloric acid solution. These extracts were combined and poured into a specially prepared set of color comparison tubes. The tubes were made by sealing the bottoms of 15-inch sections of 11 mm. Pyrex tubing. The tops of these tubes were flanged.

Aluminum standards were also prepared containing 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.4, and 2.6 ug of aluminum by pipetting suitable quantities of the tertiary aluminum standard into other color comparison tubes. The volume of each of the known samples was made up to 10 ml. with the hydrochloric acid solution to match the volume of the unknowns.

Exactly 0.2 ml. of the aluminon reagent was pipetted into each of the color comparison tubes, and the reagent was carefully washed down the tube walls with a small amount of the acid solution.

Five milliliters of the ammonium acetate solution was then pipetted into each of the tubes, and the volume of each solution was made up to 20 ml. The solutions were then stirred with a long glass rod.

Colors of the samples and unknowns were compared after half an hour. It was found convenient to mount the sample tubes in holes drilled in a section of two-inch by four-inch board, and then view the sample tubes from the top. The tubes were supported on the bottom by a piece of frosted glass over a fluorescent light bulb. This gave excellent even illumination and the differences in hue of the various sample solutions could be clearly distinguished. The results of these analyses have been given in Figure 18.

APPENDIX V

THERMODYNAMIC CALCULATIONS

A. Method of Calculation

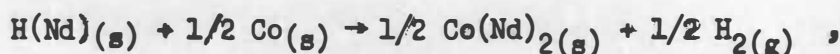
This section is concerned with the derivation of the free energy changes involved when n-nonadecanoic acid reacts with metallic cobalt and metallic iron to form the appropriate metal soaps. The results obtained, added to the calculations of similar quantities made by McGill,² are so far as is known the only free energy data available for any of the heavy metal nonadecanoates, and should also add to the very meagre thermodynamic data available for derivatives of any of the long chain fatty acids.

The free energy changes involved in the net soap formation reactions were determined by summation of the series of reactions listed below, whose free energy changes were either known or could be calculated. The only necessary experimental data which were not already available were the water solubilities of the two metal soaps. These were determined as part of this work in the manner described in Appendix IV.

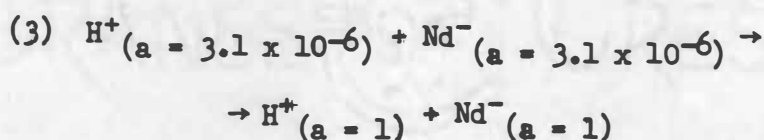
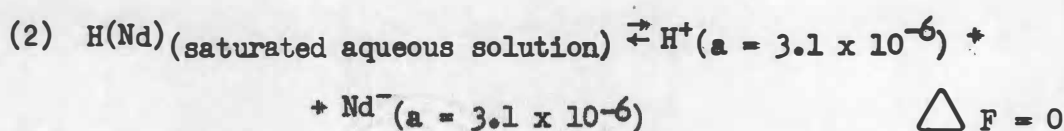
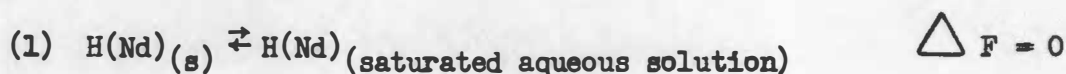
B. Metal-Acid Reactions

1. Reaction of Cobalt with n-Nonadecanoic Acid

It was desired to calculate the free energy change associated with the reaction of cobalt with n-nonadecanoic acid to form the cobalt soap. This reaction,



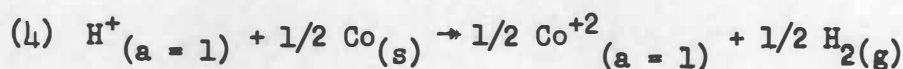
has the same free energy change associated with it as does the following sequence of reactions.



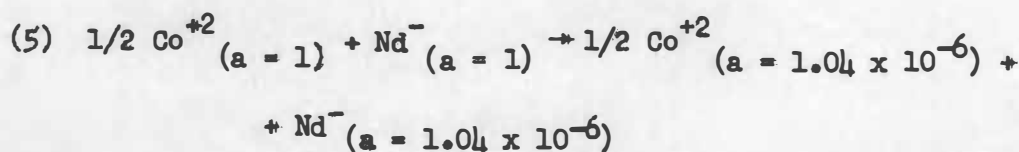
$$\Delta F = (2) RT \ln (a_2/a_1)$$

$$\Delta F = (2)(1.986)(298.1)(2.303) \log \frac{1}{(3.1 \times 10^{-6})}$$

$$\Delta F = 15 \text{ kcal. per mole}$$



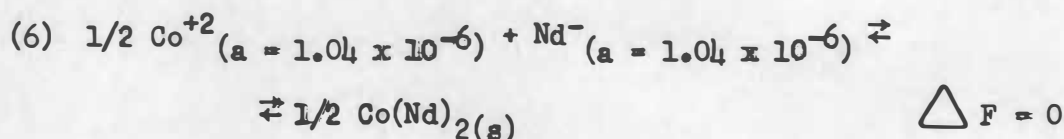
$$\Delta F = (1/2)(-12.8) = -6.4 \text{ kcal. per mole}$$



$$\Delta F = (1/2) RT \ln (\text{Co}^{+2}) + (1/2) RT \ln (\text{Nd}^-)^2$$

$$\Delta F = (1/2)(1.986)(298.1)(2.303)(\log_{10} 1.04 \times 10^{-6}) + (1/2)(1.986)(298.1)(2.303)(\log_{10} 2.08 \times 10^{-6})^2$$

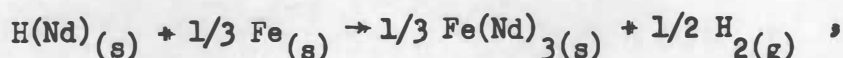
$$\Delta F = -11.8 \text{ kcal. per mole}$$



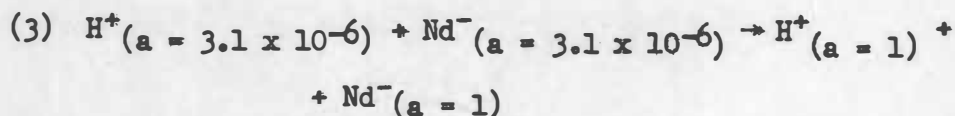
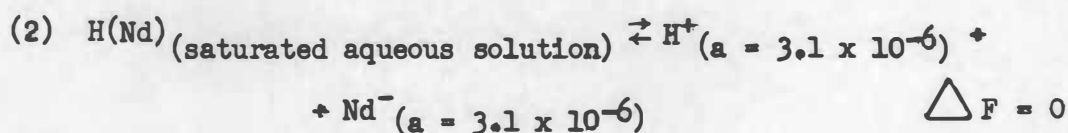
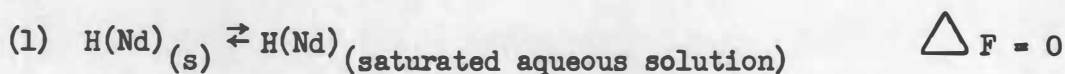
By summing these reactions and the free energy changes involved in each, a total free energy change of -3.2 kcal. per mole was obtained for the net reaction.

2. Reaction of Iron with n-Nonadecanoic Acid

It was desired to calculate the free energy change associated with the reaction of iron with n-nonadecanoic acid to form the iron III soap. This reaction,



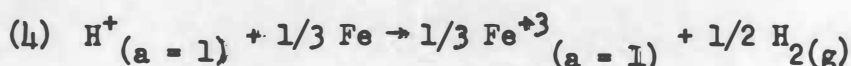
has the same free energy change associated with it as does the following sequence of reactions.



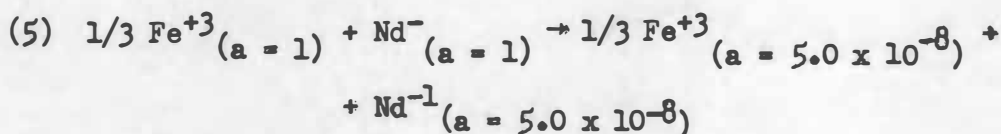
$$\Delta F = 2 RT \ln (a_2/a_1)$$

$$\Delta F = (2)(1.986)(298.1)(2.303) \log \frac{1}{(3.1 \times 10^{-6})}$$

$$\Delta F = 15 \text{ kcal. per mole}$$



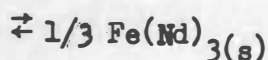
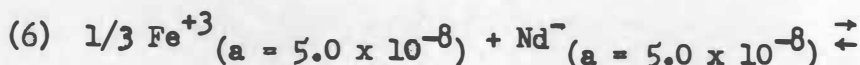
$$\Delta F = (1/3)(-2.53) = -0.84 \text{ kcal. per mole}$$



$$\Delta F = (1/3) RT \ln (\text{Fe}^{+3}) + (1/3) RT \ln (\text{Nd}^-)^3$$

$$\Delta F = (1/3)(1.987)(298.1)(2.303)(\log_{10} 5.0 \times 10^{-8}) + (1/3)(1.987)(298.1)(2.303)(\log_{10} 15.0 \times 10^{-8})^3$$

$$\Delta F = -12.6 \text{ kcal. per mole}$$



$$\Delta F = 0$$

Summing the above reactions and the free energy changes involved in each, a total free energy change of +1.6 kcal. per mole was obtained for the net reaction.

3. Notes

In both the case of the cobalt and the iron reactions, reaction (1) has a zero free energy change associated with it. This is because it represents an equilibrium process in which the saturated aqueous solution of the fatty acid is in equilibrium with the solid acid.

Reaction (2) for both metals also has a zero free energy change associated with it, because it also represents an equilibrium process. The concentrations of the hydrogen and nonadecanoate ions which are in equilibrium with the saturated aqueous solution of the fatty acid were obtained by McGill.² He obtained these from solubility determinations

made on the acid in aqueous solution and the known value of the dissociation constant of stearic acid at 25°, which was assumed to be the same as that of nonadecanoic acid at this temperature.

In reaction (3), the hydrogen and nonadecanoate ions are concentrated to unit activity from the concentration at which they are in equilibrium with the saturated solution of the fatty acid. The free energy change involved is calculated in the usual manner.

In reaction (4), the cobalt and iron metals, both in their standard states, are made to react with the hydrogen ion to form the cobaltous and ferric ions, plus hydrogen gas. The only species involved which do not have zero free energies of formation and hence contribute to the free energy change of the reaction are the two metal ions. Latimer³⁴ gives the free energy of formation of the cobalt ion as being -12.8 kcal. per mole, and that of the ferric ion as being -2.53 kcal. per mole.

In reaction (5), the metal ions produced in reaction (4), plus the nonadecanoate ions, are diluted from unit activity to the concentration at which they exist when in equilibrium with the saturated solutions of the metal soaps. To obtain the correct values for these latter concentrations, the solubilities of both soaps were determined in water at 25°. Details of these determinations have been given in Appendix IV.

In reaction (6), the cobaltous and ferric ions are combined with the nonadecanoate ions by an equilibrium process to form the solid metal soaps. The free energy changes involved in these processes is again zero.

C. Standard Free Energies of Formation
of the Metal Soaps

The standard free energy of formation of n-nonadecanoic acid may be estimated to be about -75.5 kcal. per mole, using the approximation method of Parks and Huffman.⁷⁸ This value may be combined with the free energy changes involved in the soap formation reactions to calculate the standard free energies of formation of the two metal soaps. Making this calculation, the values obtained were: cobalt II nonadecanoate, $\Delta F^\circ_f = -157.4$ kcal. per mole; iron III nonadecanoate, $\Delta F^\circ_f = -221.8$ kcal. per mole.

APPENDIX VI

COUNTING STATISTICS

The following treatment of counting statistics is similar to that given by Allen⁵ which was taken from the considerably more detailed discussion given by Taylor.⁷⁹

The standard deviation of the sum or difference of two values is the square root of the sum of the squares of the standard deviations of the values. For any radioactive count n , the number of samples may be considered to be infinite, and the square root of n gives the standard deviation of the count. Therefore, for

n_1 = counts with sample plus background

n_2 = counts obtained for background alone

t_1 = observation time for sample plus background

t_2 = background observation time

the activity A and the standard deviation association with it are given by

$$A = \left[\frac{n_1}{t_1} - \frac{n_2}{t_2} \right] \pm \left[\left(\frac{n_1}{t_1} \right)^2 + \left(\frac{n_2}{t_2} \right)^2 \right]^{\frac{1}{2}}$$

or

$$A = \left[\frac{n_1}{t_1} - \frac{n_2}{t_2} \right] \pm \left[\frac{n_1}{t_1^2} + \frac{n_2}{t_2^2} \right]^{\frac{1}{2}} .$$

The standard deviation, Δ , in per cent is obtained by dividing the second term on the right by the first and multiplying by 100;

$$\Delta = \left[\frac{100}{\frac{n_1}{t_1} - \frac{n_2}{t_2}} \right] \left[\frac{n_1}{t_1^2} + \frac{n_2}{t_2^2} \right]^{\frac{1}{2}} .$$

That deviation which will be encountered no more than 10 per cent of the time is called the reliable error, E , and is obtained by multiplying the standard deviation by 1.65, the factor for a normal distribution;

$$E = \left[\frac{1.65}{\frac{n_1}{t_1} - \frac{n_2}{t_2}} \right] \left[\frac{\frac{n_1}{t_1^2}}{+} \frac{\frac{n_2}{t_2^2}}{+} \right]^{\frac{1}{2}} .$$

Now, in this work all samples were counted for fifteen minutes, and the lowest count rates obtained were of the order of 500 c/m. Thus, total counts detected were approximately 7500. Background averaged 80 c/m., or in fifteen minutes 1200 counts. Therefore, under these conditions

$$E = \left[\frac{1.65}{\frac{8700}{15} - \frac{1200}{15}} \right] \left[\frac{\frac{8700}{225}}{+} \frac{\frac{1200}{225}}{+} \right]^{\frac{1}{2}} .$$

$$E = (.33)(.44)^{\frac{1}{2}} = 2.1 \text{ per cent.}$$

This value represents a maximum error, because as count rates increase the results become increasingly precise. In any case, it is felt that any error due to counting statistics is well within the other experimental errors inherent in the measurement techniques.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. H. A. Smith and K. A. Allen, J. Phys. Chem., 58, 499 (1954)
2. R. M. McGill, "The Adsorption of n-Nonadecanoic Acid on Mechanically Activated Metal Surfaces," Doctoral Dissertation, The University of Tennessee, Knoxville, Tennessee, December 1955.
3. P. H. Emmett, "Catalysis," Volume I, Reinhold Publishing Co., New York, N. Y., 1954, pp. 31-74.
4. S. J. Brunauer, "The Adsorption of Gases and Vapors," Volume I, Princeton University Press, Princeton, N. J., 1943.
5. K. A. Allen, "The Adsorption of n-Nonadecanoic Acid on Smooth Metal Surfaces," Doctoral Dissertation, The University of Tennessee, Knoxville, Tennessee, August 1953.
6. H. A. Smith and J. F. Fuzek, J. Am. Chem. Soc., 68, 229 (1946).
7. E. L. Cook and N. Hackermen, J. Phys. and Colloid Chem., 55, 549 (1951).
8. E. B. Greenhill, Trans. Faraday Soc., 45, 625 (1949).
9. S. C. Daniel, Trans. Faraday Soc., 47, 1345 (1951).
10. F. P. Bowden and D. Tabor, "Friction and Lubrication," Methuen and Co., Ltd., London, England, 1956, p. 123.
11. F. P. Bowden and A. C. Moore, Trans. Faraday Soc., 47, 900 (1951).
12. F. P. Bowden and D. Tabor, "Friction and Lubrication," Methuen and Co., Ltd., London, England, 1956, p. 126.
13. W. C. Bigelow, D. L. Pickett, and W. A. Zisman, J. Colloid Sci., 1, 513 (1946).
14. W. C. Bigelow, E. Glass, and W. A. Zisman, J. Colloid Sci., 2, 563 (1947).
15. A. Dobry, Lubrication Eng., July-August 1954, taken from Research Report R-94603-2-H, Westinghouse Research Laboratories, March 1954.
16. D. E. Beischer, J. Phys. Chem., 57, 134 (1953).
17. I. Langmuir, J. Am. Chem. Soc., 39, 1848 (1917).

18. N. K. Adams, "The Physics and Chemistry of Surfaces," 2nd Ed., Oxford University Press, London, England, 1938, pp. 47 et. seq.
19. A. W. Ralston, "The Fatty Acids and Their Derivatives," John Wiley and Sons, New York, N. Y., 1948, pp. 398, 400, 401.
20. J. J. Frewing, Proc. Roy. Soc., A 181, 23 (1942).
21. J. J. Frewing, Proc. Roy. Soc., A 182, 270 (1944).
22. K. C. Brummage, Proc. Roy. Soc., A 191, 243 (1947).
23. H. T. Epstein, J. Phys. and Colloid Chem., 54, 1053 (1950).
24. J. K. Roberts, "Some Problems in Adsorption," Cambridge University Press, Cambridge, England, 1939.
25. J. Topping, Proc. Roy. Soc., A 114, 67 (1927).
26. M. C. Shaw, J. Applied Mechanics, 15, 37 (1948).
27. M. C. Shaw, U. S. Patent 2,416, 717 (March 4, 1947).
28. W. F. Libby, "Radioactive Dating," University of Chicago Press, Chicago, Illinois, 1952.
29. R. C. Mehrota and K. C. Pande, J. Inorg. and Nuclear Chem., 2, 60 (1956).
30. A. Gilmour, A. Jobling, and S. M. Nelson, J. Chem. Soc., 1972 (1956).
31. L. Yaffe and K. L. Justus, J. Chem. Soc., 341 (1949).
32. R. G. Baker and L. Katz, Nucleonics, 11, No. 2, 14 (1953).
33. L. R. Zumwalt, Atomic Energy Commission Unclassified Publication No. 567 (1950).
34. W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," 2nd. Ed., Prentice-Hall, Inc., New York, N. Y., 1952.
35. H. S. Taylor, Proc. Roy. Soc., A 108, 105 (1925).
36. H. S. Taylor, J. Phys. Chem., 30, 145 (1926).
37. J. Kramer, "Der Metallische Zustande," Vandenhoeck and Ruprecht, Gottingen, 1950.

38. J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1956, page 79.
39. O. Haxel, F. G. Houtermans, and K. Seeger, Z. Phys., 130, 109 (1951).
40. J. Kramer, Z. Phys., 125, 739 (1949).
41. J. Kramer, Z. Phys., 133, 620 (1952).
42. K. Lintner and E. Schmid, Z. Metallkunde, 45, 276 (1954).
43. F. Futschik, Unpublished dissertation, University of Vienna, 1954.
44. W. Christoff, Ann. Phys., 23, 747 (1935).
45. H. Paetow, Z. Phys., 111, 770 (1939).
46. K. H. Lauterjung and H. Neuert, Z. Phys., 122, 266 (1944).
47. M. Tanaka, Proc. Phys. Math. Soc. Japan, 22, 899 (1940).
48. J. Kramer, Z. Phys., 128, 538 (1950).
49. J. Kramer, Z. Phys., 129, 34 (1951).
50. K. Seeger, Z. Phys., 135, 152 (1953).
51. L. Grunbert and K. H. R. Wright, Proc. Roy. Soc., A 232, 403 (1955).
52. O. Bruner, K. Lintner, H. Muller, and E. Schmid, Z. Phys., 136, 605 (1933).
53. J. Kramer, Ann. Phys., 19, 37 (1934).
54. K. O. Kiepenheuer, Z. Phys., 107, 145 (1937).
55. L. Malter, Phys. Rev., 50, 48 (1936).
56. F. Roggen and P. Scherrer, Helv. Phys. Acta, 15, 497 (1942).
57. L. Grunberg and K. H. R. Wright, Nature, 170, 456 (1952).
58. H. Nassenstein, Naturwissenschaften, 41, 329 (1954).
59. K. Seeger, Z. Phys., 141, 221 (1955).
60. R. M. McGill, private communication.
61. W. J. Russell, Proc. Roy. Soc., 61, 424 (1897).

62. W. J. Russell, Proc. Roy. Soc., 63, 102 (1898).
63. W. J. Russell, Proc. Roy. Soc., 64, 409 (1899).
64. W. J. Russell, Proc. Roy. Soc., 78, 385 (1906).
65. W. J. Russell, Proc. Roy. Soc., 80, 376 (1908).
66. J. R. Churchill, Trans. Electrochem. Soc., 26, 341 (1939).
67. H. Golbrecht and G. Barsch, Z. Phys., 132, 129 (1952).
68. L. Grunberg, Proc. Roy. Soc. (London), B 66, 153 (1953).
69. M. Becker and H. Wolff, Z. Metallkunde, 44, 570 (1953).
70. E. Lehto, private communication.
71. W. G. Dauben, J. C. Reid, and P. E. Yankwich, Anal. Chem., 19, 828 (1947).
72. S. B. Elliott, "The Alkaline-Earth and Heavy-Metal Soaps," American Chemical Society Monograph No. 103, Reinhold Co., New York, N. Y., 1946.
73. W. F. Whitmore and M. Lauro, Ind. Eng. Chem., 22, 646 (1930).
74. J. A. Dean, Anal. Chem., 23, 1096 (1951).
75. E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience, New York, N. Y., 1944, pp. 201, 218, 270, 397.
76. A. E. Koenig, J. Am. Chem. Soc., 35, 951 (1914).
77. R. H. Lambert, Anal. Chem., 24, 868 (1952)
78. G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," American Chemical Society Monograph No. 60, Chemical Catalog Co., New York, N. Y., 1932.
79. D. Taylor, "The Measurement of Radio Isotopes," John Wiley and Sons, Inc., New York, N. Y., 1951.

VITA

Tomlinson Fort, Jr., was born in Sumter, South Carolina, on April 16, 1932. He attended elementary schools in Bethlehem, Pennsylvania, and was graduated from high school at Athens, Georgia, in 1948. The following fall he entered the University of Georgia from which he was graduated in 1952 with a B.S. degree and major in chemistry.

In September 1953 he entered the Graduate School of the University of Tennessee holding a Graduate Assistantship which supported him for two years and through the completion of his Master's research work. Since that time his research has been financed by very generous grants from the Office of Ordnance Research, United States Army, and from the United States Atomic Energy Commission.

The author is a member of Alpha Chi Sigma, Gamma Sigma Epsilon, and the Society of the Sigma Xi. He is married to the former Martha Kirby of Crossville, Tennessee.