JOURNAL OF THE

Electrochemical Society

ELECTROCHEMICAL INDUSTRY

TVA Power Area

Courtesy Ethyl Corporation

Chlorine ...

for antiknock compounds

Ethyl chloride, ethylene dichloride and ethylene dibromide play an important part in the manufacture of antiknock compounds for combustion engine gasolines.

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TELEPHONE SCIENCE

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NO ENEMY CAN DODGE
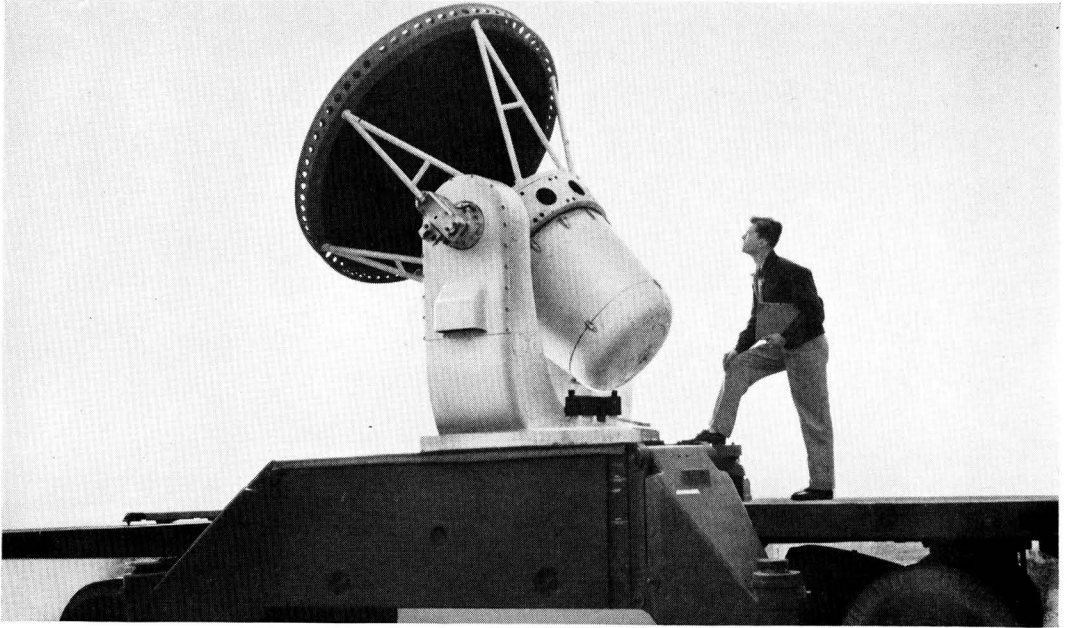
(Upper left) — Nike's missile climbs to destroy an enemy, under guidance of complex electronic controls. A radar is shown at right. Nike (pronounced Ny'kee) is named after the Greek goddess of Victory.

BELL TELEPHONE LABORATORIES

Is it possible to guide an anti-aircraft missile so that it will track down and destroy a rapidly maneuvering target? No one knew the answer for sure when the U. S. Army put this question to Bell Telephone Laboratories in 1945.

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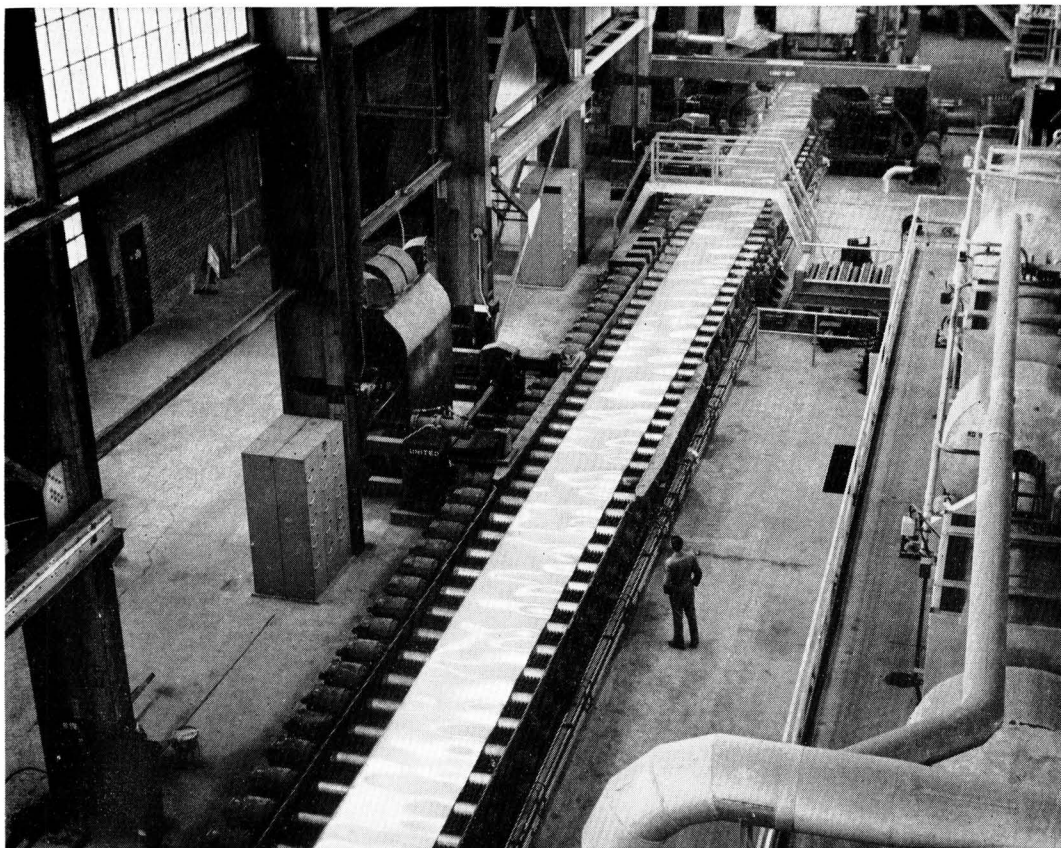
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Four G-E Micro-miniature Tantalytic
capacitors easily fit into small space
provided in this new all-transistor
hearing aid. Man above adjusts vol-
ume control.

**Other applications now being
investigated:**

> WALKIE-TALKIES
>
> WRIST RADIOS
>
> PAGING SYSTEMS

How Tantalytic Capacitors Are Used In Miniaturized Hearing Aids

Four G-E Micro-miniature Tantalytic capac-
itors are used in this new all-transistor hearing aid.
These high-capacitance, small-size units are
necessary due to the low-impedance characteristics
of transistors, as compared with the vacuum tubes
formerly used. Ceramic and paper dielectric
capacitors cannot supply sufficient capacitance in
the small size desired, according to hearing aid
design engineers.

Operating at a battery voltage of 2.5 volts,
this hearing aid uses two units rated at 2 micro-
farads each for by-pass, C_1 and C_2 (see diagram).
They give a low-impedance signal path from the
source to the input of the transistor. Two 1-micro-
farad units, C_3 and C_4, are used for coupling
and filtering respectively, where their low leakage
current of .18 microamperes/uf/volt at 25 deg.
C is especially important.

G-E Micro-miniature Tantalytics can be ob-
tained in ratings up to 20 volts, or, up to 8 uf in a
$\frac{5}{16}$-in. long by $\frac{1}{8}$-in. dia. case size, higher ca-
pacitance in a $\frac{1}{2}$-in. long by $\frac{1}{8}$-in. dia. case size.
Capacitance tolerance is -0% to $+100\%$.

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ture Tantalytic capacitors, contact your G-E
Apparatus Sales Office or write for bulletin
GEA-6065 to General Electric Company, Section
442-15, Schenectady 5, New York.

Pictures, circuit diagram, application information courtesy Sonotone Corp.
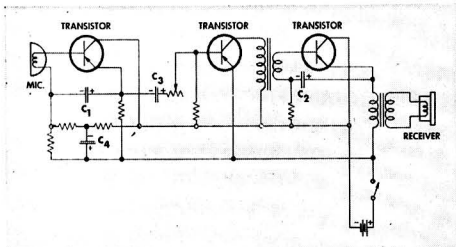
Simplified schematic diagram of Sonotone all-transistor
hearing aid, showing location of G-E Micro-miniature
Tantalytic capacitors.

GENERAL ⊕ ELECTRIC

"Bonnets" Off
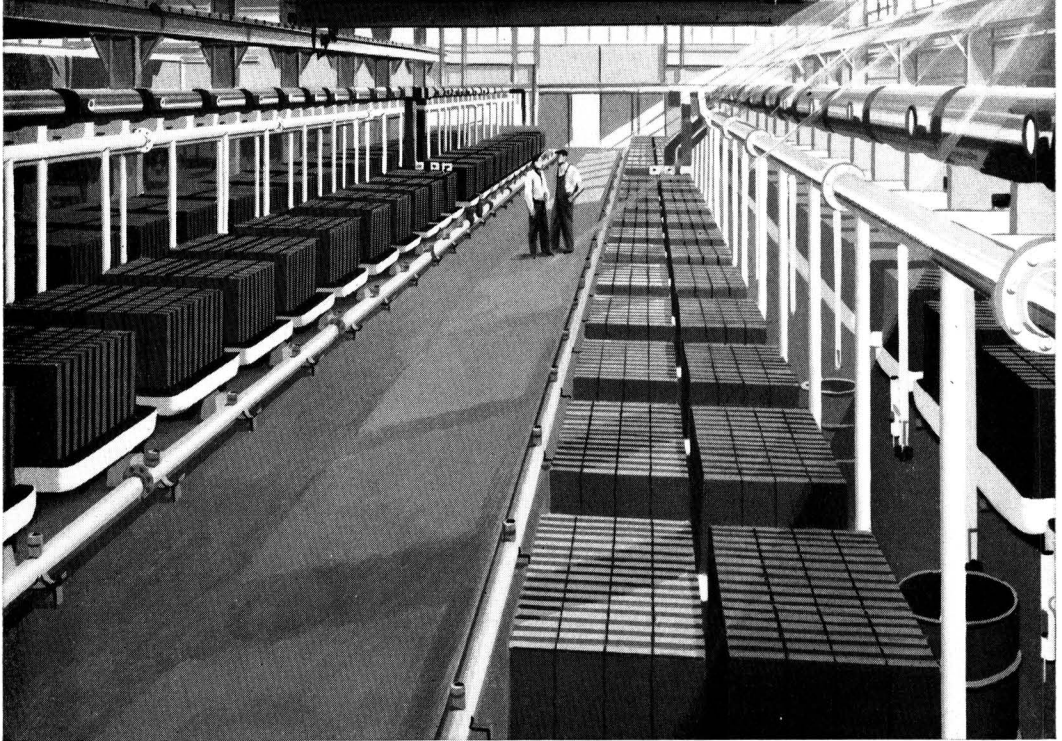
TO $12,000,000 NEW CHLORINE-CAUSTIC CAPACITY!

MONTAGUE, MICHIGAN is the scene of this sparkling Hooker Cell installation by Hooker Electrochemical Company. Part of a new $12,000,000 chlorine-caustic plant, it adds significantly to the demand for "Acheson" graphite anodes in this vital process.

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Editorial

Service

Our Government was founded on service by men of integrity, seeking better things from life. The fathers of our constitution gave freely of their service and sacrificed much materially to attain the form of government from which we have received so much in opportunity for the better things of life and opportunities to give service to our fellow men.

Likewise, all successful societies and organizations, technical or otherwise, should be founded on service of the individual to that society or organization. Only through service can we attain the highest standards and ideals and true enlightened fellowship.

It was service and sacrifice over the past few years by the able officers of your Society that has brought The Electrochemical Society to its high state of technical perfection. These officers, working with determination and unity of purpose, have brought the Society into well-being financially and technically. The JOURNAL of the Society has taken its place among the best in its field. Divisions have been revived, new Divisions added, and standards raised all along the line.

There is still much to do that demands the service, sacrifice, and devotion of all the members in order to maintain the standards we have attained through the service of our past officers.

Your Society has grown until it has taken on the character of big business. Like any business, costs of operation have risen these past years, yet our dues are low and within the reach of all worthy candidates. In order to maintain our position, the Society needs new members. It is the best way to keep the benefits of our Society within reach of all and still maintain our present high quality.

May we ask that in the coming year all Divisions and all Local Sections give service toward gaining new members. I am sure the field is ripe if we but give a little of our time to the task. There are many young technical men and scientists who are eligible to become members of The Electrochemical Society. The Society will benefit by having them, as active members, ready to take part and to give service to The Electrochemical Society that it may maintain its high prestige in the engineering and scientific field.

—MARVIN J. UDY
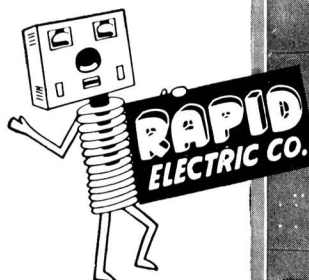
Remote control station for use with basic rectifier
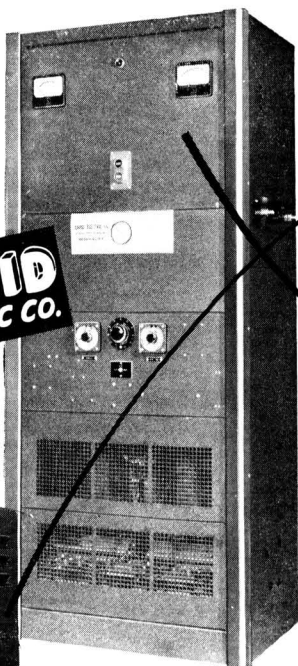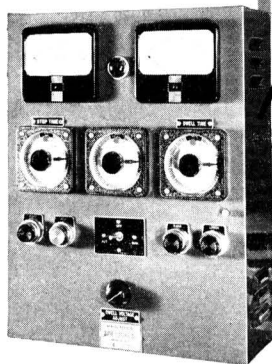
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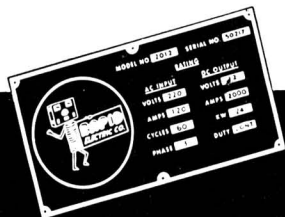
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ELECTROPROCESS PLANTS IN THE TVA POWER SERVICE AREA

Harry A. Curtis[1]

Introduction

The area served by the TVA power system is approximately twice that of the Tennessee River drainage basin. It does not include all of any one state, but covers most of Tennessee and some of the adjacent parts of Virginia, North Carolina, Georgia, Alabama, Mississippi, and Kentucky. The total power service area is approximately eighty thousand square miles.

Most the electroprocess plants in this area were built after 1933 when development of the power potential of the Tennessee River was undertaken by the TVA incident to control of the river. Relatively cheap power has no doubt been a factor, but by no means the only factor, in the rapid industrialization of the region in recent decades. The mild climate, abundant water supply, available man power, natural resources of the region, water transportation, location of expanding markets, and several other factors have also been favorable. Establishment of electroprocess industries has been part and parcel of the general industrial development now in progress.

The number of electroprocess industries locating in the region during the past twenty years is actually small in comparison with the number of other industries established in the region in the same period, i.e., less than a score of the former as against more than two thousand of the latter. In other words, the general industrial growth in the region is of much greater significance than is the establishment of a few relatively large electrothermal or electrolytic process plants. This is not to minimize the importance to the region of the large electroprocess plants, for, aside from the many other benefits they bring, the basic electric load at a high load factor that characterizes such plants makes possible lower electric energy rates for the small domestic users of power from the same power network.

Classification of Electroprocess Industries

The two types of electroprocess industries included in the title above differ from each other primarily in the functions served by the electrical energy consumed. For purposes of the present discussion, electrothermal processes are defined as those in which the electric energy is all converted to heat, and electrolytic processes as those in which at least a considerable part of the electric energy is used as such in the chemical reactions involved. Economically considered, this distinction is not significant since, so far as electrical energy consumption is concerned, the important consideration is the over-all quantity of electrical energy used per unit weight of product or products. Equipment required for a specific application of either process will be different for each application, and if the process be of the electrolytic type a part or all of the energy used must be in the form of direct current as contrasted with an electrothermal process where, for a variety of reasons, alternating current is normally preferred.

[1] Tennessee Valley Authority, Knoxville, Tennessee.

In an electrothermal process, the heat derived from the electrical energy consumed is utilized to meet several requirements. In a phosphate smelting furnace, for example, heat distribution in a large furnace (say one drawing 12,500 kw) will be about as follows:

	% of total
Net heat requirements of the chemical reactions....	51
Sensible heat in the slag tapped from the furnace....	29
Heat losses from the surfaces of the furnace and electrodes..	9
Sensible heat in the furnace offgases...............	5
Sensible heat in the ferrophosphorus tapped from the furnace....................................	1
Heat not accounted for...........................	5
Total..	100

Obviously, the typical heat distribution given above will vary with several factors, particularly with the grade of rock phosphate used, and, of course, each electrothermal process will show a different heat distribution.

In processes that are here classified as electrolytic, there is likewise a wide variation in the proportion of electrical energy used to meet the several requirements of the particular processes. For example, in a chlorine-caustic cell, only a small proportion of the electrical energy is used other than in the electrochemical reaction. On the other hand, in the process used for the electrodeposition of aluminum, a considerable proportion of the total energy supplied is used to maintain the pot and pot contents at the necessary temperature. A typical distribution of the electric energy supplied to an aluminum-producing cell would be about as follows:

	%
Heat in aluminum removed...........................	5.9
Heat in waste gases.................................	7.7
Other heat losses..................................	46.4
Energy used in chemical reactions, mostly electrolytic..	40.0
Total..	100.0

In a survey of the electroprocess industries of a region, such as will be attempted in the present article, it is necessary to make some arbitrary decisions as to what operations are to be listed as electroprocesses. Plants producing elemental phosphorus, calcium carbide, aluminum, chlorine-caustic, and electrolytic manganese are clearly electroprocess plants. Another group may also be classed as electroprocess plants because the high temperatures used are not readily obtained except in electric furnaces. In this group fall plants producing ferrosilicon, ferrochrome, and other ferroalloys. However, in a third group of plants the use of electrothermal operations is convenient and economical, but is not essential. These plants use a great variety of electrically heated ovens, muffles, and crucibles primarily for convenience and ease of temperature control. This group of plants includes those making enamelware stove parts, vacuum bottles, gas heaters, clothes

Electrochemical Plants

	Year plant established*	Employees 1952*	Million kwhr used in fiscal year ending June 30, 1953†
Aluminum			
Aluminum Company of America	1913	8000	3,148
Reynolds Metals Company	1940	—	940 (smelting)
Chlorine-caustic			
U.S. Government, Wilson Dam, Alabama	1952	—	—
U.S. Industrial Chemicals Company	1942	—	59
Pennsylvania Salt Manufacturing Company	1949	114	Started in fiscal 1950. Now at rate of about 80
Velsicol Corporation	1946	100	34
Hydrogen-Oxygen			
Wilson and Company	1916	125	9.4
Electroplating			
Southern Electroplating Company (two plants)	1945	40	0.7
Manganese			
Electro Manganese Corporation	1939	126	37

Electrothermal Plants

	Year plant established*	Employees 1952*	Million kwhr used in fiscal year ending June 30, 1953†
Phosphorus			
TVA at Wilson Dam	1933	—	550
Monsanto Chemical Company	1936	500	895
Victor Chemical Works	1938	475	393
Shea Chemical Corporation	1952	175	Started in fiscal 1953. Now at rate of about 250
Carbide			
U.S. Government at Wilson Dam	1918	—	Plant idle
National Carbide Company	1952	205	Started in fiscal 1953. Now at rate of 500
Ferroalloys			
Tennessee Products and Chemical Corporation (two plants)	1917	690	246
Electro Metallurgical Company	1940	500	464
Pittsburgh Metallurgical Company	1949	264	284
Montana Ferroalloys, Inc.	1952	—	Estimated 92
Foundries			
Ross-Meehan Foundries	1889	450	18
Knoxville Iron Company	1868	500	13
Electrodes			
National Carbon Company	1937	300	141
Miscellaneous (using 2–24 million kwhr annually)			
Aladdin Industries, Nashville	1949	350	
American Lava Corporation, Chattanooga	1902	—	
Cleveland, Tennessee Enamel Company	1928	300	
Crane Company, Chattanooga	1921	1200	
Ferro Corporation, Nashville	1946	120	71
Florence Stove Company, Lewisburg, Tenn.	1869	500	
Gray and Dudley, Nashville	1862	250	
Murray Mfg. Company, Murray, Ky.	—	613	
Polynesian Arts, Inc., Mayfield, Ky.	—	182	
Temco, Inc., Nashville	1921	350	

* Nearly all of these data are from the 1952 edition of the *Directory of Tennessee Industries*. The number of employees shown presumably is for whole plants and does not indicate the number engaged in electroprocess operations only. Also it should be noted that the data for employees refer to the calendar year 1952 whereas the energy consumption is for the fiscal year ending June 30, 1953.

† All figures are for whole plants unless otherwise indicated.

dryers, etc., and those using electrically heated furnaces in melting scrap iron. The group is large and makes many products. In the present survey, some of the larger of these plants will be listed and discussed very briefly, although it is not logical to classify them as electroprocess plants. Some of them use relatively large amounts of electric energy, however.

The accompanying classification of plants in the TVA power service area is admittedly arbitrary and purposely omits the hundreds of plants that use electric energy only for such purposes as lighting, space heating, operation of motors, and other electromechanical devices, and also omits

mention of scores of little plants that use electroprocess operations incidentally or on a very small scale.

Relative Importance of Electroprocess Industries in the TVA Power Service Area

It is pertinent to the present review to indicate, if possible, the amount of electric energy consumed by electroprocess industries in the region as compared with the electrical energy used by other consumers. The quantities of energy used by the larger electroprocess plants have been shown in the table above, but it is not possible to give an accurate picture of the

whole situation. In the first place, there is a very large group of small plants in which electrothermal or electrolytic operations are incidental; and the energy thus consumed is a small part of the energy used in the plant as a whole. Data as to energy consumption in each plant of this large group could be assembled, but it would be a difficult and time-consuming task to separate the relatively small fractions of the total energy consumption that was used in electrothermal or electrolytic operations. A still larger distorting factor is the fact that the Atomic Energy Commission plants and a few other defense plants in the region use a very large amount of energy, some of which is undoubtedly applied in operations that would be classed as electrothermal or electrolytic. It is not permissible to discuss these defense plants but only to note in passing that they no doubt add considerably to the electroprocess energy consumption in the region.

The total quantity of electrical energy entering the TVA power net in fiscal 1953[2] was 27,348 million kwhr. This came from the TVA hydroelectric and steam-electric plants, from the Alcoa hydroelectric plants operated as a part of the TVA system, from the federally owned hydroelectric plants on the Cumberland River, and from privately owned companies under power purchase and exchange contracts. This energy was distributed as follows:

	Million kwhr	%
To distributors of TVA power	10,986	40.2
To directly served large industries	6,787	24.8
To Federal agencies	6,967	25.4
TVA interdivisional	619	2.3
Returned to neighboring power systems	654	2.4
System losses	1,335	4.9
Total	27,348	100.0

The total energy consumption by industries was about 18,150 million kwhr, of which 6967 million was by Federal agencies other than the TVA. As pointed out above, it is not known what part of the 6967 million kwhr of energy taken by Federal agencies other than the TVA should be classified as electroprocess. Nor is it known what part of the use by the industries served by TVA power distributors or directly by the TVA should be classified as electrochemical. Obviously, then, no accurate statement can be made as to the total electroprocess energy consumption in the region. However, the partial picture for the industries listed in the table is about as follows:

	Million kwhr annually	%
Aluminum	3750	44.41
Chlorine-caustic	253	3.00
Hydrogen-oxygen } Electroplating	10	0.12
Manganese	37	0.44
Phosphorus	2063	24.44
Carbide	1000	11.85
Ferroalloys	1086	12.86
Foundries	31	0.37
Electrodes	141	1.67
Miscellaneous	71	0.84
Approximately	8442	100.00

Aluminum-Producing Plants

There are two aluminum-producing plants in the region, that of the Aluminum Company of America, first established

[2] Throughout this article the fiscal year refers to the year ending June 30.

some forty years ago at Alcoa near Maryville, Tennessee, and the relatively recently built plant of the Reynolds Metals Company near Sheffield, Alabama.

Aluminum Company of America, Alcoa, Tennessee

The Aluminum Company of America began construction of its works at Alcoa, Tennessee, near Maryville, in 1913 and first poured aluminum in March 1914. The story of this operation has been one of frequent expansions over the past forty years until today it is a very large installation, the company's largest.

The initial smelting plant included only two "pot rooms" as they were called in those years. Power was purchased from the Tennessee Electric Power Company. The company's plans were, however, to produce its own hydroelectric power and for this purpose power plant sites had been purchased on the Little Tennessee River and its tributaries. Power from the company's Cheoah Dam was produced in 1919, followed by power from the Santeetlah Dam in 1928, the Calderwood Dam in 1930, the Thorpe (Glenville) Dam in 1941, and the Nantahala Dam in 1942. The name plate capacity of the generators installed at these five dams was about 360,000 kva. Some additional capacity was added later and the company has lately built or is now building some relatively small dams. The present capacity of the company's hydroelectric installations is about 415,000 kva.

Up to 1937 expansion of the company's power production facilities kept pace with the expansion of the Alcoa works, but when it then appeared that there would be a great need for aluminum, the company nearly doubled the capacity of the smelting plant, using power from the TVA net. In 1940–41 the world's largest aluminum rolling mill was added. At present the Alcoa works produces ingot, plate, sheet, foil, and pigment.

The smelting installation, which is the electroprocess part of the plant, is the largest aluminum reduction plant owned by the company. The floor space occupied is some 42 acres. The cells in the pot lines are of various sizes, some using Söderberg self-baking electrodes and some using prebaked carbon electrodes. The prebaked electrodes and carbon paste for the Söderberg electrodes are manufactured in the company's local electrode plant. About 0.75 lb of carbon electrode is required per pound of aluminum produced.

Initially, the bauxite ore from which the alumina used at Alcoa was produced was mined in Arkansas and refined in East St. Louis, Illinois. Later on, about 1917, the company opened bauxite mines in British Guiana, and some five years later began shipment of bauxite from this source. Later on, larger mining operations were begun in Dutch Guiana, and the ore was shipped to East St. Louis for refining. In 1937, when the Alcoa smelting plant was greatly expanded, the company built a bauxite-refining plant at Mobile, Alabama, whence most of the oxide for cell feed now comes. The company has, however, continued bauxite production in Arkansas on a relatively small scale and in 1952 built a plant to handle low grade Arkansas bauxite. Cryolite for the cells was originally imported from Greenland, but at present synthetic cryolite is used almost exclusively.

In 1941 the Aluminum Company of America and the TVA signed an agreement under which the company's dams and hydroelectric power installations are now operated as a part of the TVA power system, and the TVA supplies the company's total power requirements. In fiscal 1953 the Alcoa smelting plant produced about 140,600 tons of primary aluminum.

Reynolds Metals Company, Sheffield, Alabama

Construction of the Reynolds Metals Company's Listerhill reduction plant near Sheffield, Alabama, was begun in 1940 and the first aluminum poured in May 1941. The company had long pioneered in the fabrication of aluminum foil and its use in many forms. It had also produced aluminum powder and by 1940 was fabricating aluminum sheet, rod, bar, and structural forms.

Prior to 1941, Alcoa was the only producer of primary aluminum in the United States. The Listerhill plant was the Reynolds concern's first venture in the field of primary aluminum production.

The Reynolds Mining Corporation began the mining of bauxite in Arkansas in 1940, and in 1952 the Reynolds Jamaica Mines, Ltd., began shipment of Jamaican bauxite to the several refining plants now owned by Reynolds. The company also has large holdings of bauxite in Haiti and is now beginning production from these deposits.

The Listerhill plant has been expanded from time to time since 1940, and the company has also leased part of the buildings and grounds of U. S. Nitrate Plant No. 1 several miles from the Listerhill plant. In addition to primary aluminum, the company's plants near Sheffield now manufacture aluminum sheet, rod, bar, building materials, foil, and steel-reinforced aluminum cable.

The capacity of the Listerhill reduction plant is stated to be nominally 50,000 tons of aluminum per year. At 20,000 kwhr per ton of aluminum produced, the energy consumption of the plant at capacity would be about a billion kwhr per year. In fiscal 1953 the energy consumption of the reduction plant was actually 940 million kwhr with an average monthly load factor of 99%.

Chlorine-Caustic Plants

There are four chlorine-caustic plants in the region, namely, the U. S. Government plant near Sheffield, Alabama, built by the Monsanto Chemical Company for the Chemical Corps during the Korean trouble but never operated except in a trial run; Government-owned installations at Huntsville, Alabama, consisting of two chlorine-caustic plants, a part of the Redstone Arsenal, built during World War II and at present leased and operated by the U. S. Industrial Chemicals Company; the Pennsylvania Salt Manufacturing Company plant at Calvert City, Kentucky; and the Velsicol Corporation plant at Memphis, Tennessee.

U. S. Government Plant, Muscle Shoals, Alabama

This plant was built by the Monsanto Chemical Company for the U. S. Army. It was the first large plant in the United States in which DeNora cells were installed.

The DeNora cell is in the form of a long and narrow steel trough lined with a suitable material. Anodes are cylinders of graphite that pass through seal rings in the hard rubber cover of the trough. A thin stream of mercury flows along the floor of the cell and dissolves the sodium as it is formed. The mercury-sodium amalgam leaving the cells is pumped to the top of a steel tower packed with lump graphite. As the amalgam flows down over the packing it is brought into contact with water. The resultant caustic solution and mercury are withdrawn from the foot of the tower and the hydrogen from the top of the tower. The hydrogen may be used as fuel or for other purposes; the mercury is recirculated through the cells. The caustic solution is available as feed for a caustic concentrating evaporator, or for other purposes.

Brine used in the cells is also circulated. Spent brine is treated to remove the dissolved chlorine, fortified with fresh salt, filtered, and returned to the cells.

Each DeNora cell uses about 1.7 tons of salt and 3100 kwhr of energy per day and produces about a ton of chlorine, a ton and a half of caustic soda, and 10,000 ft³ of hydrogen.

The plant was completed in 1952 and given a brief trial run. It has remained idle to date, but the Government has now invited bids for sale or lease of the plant. Plant capacity is about 225 tons of chlorine per day.

U. S. Industrial Chemicals Company, Huntsville, Alabama

This company is a division of the National Distillers Products Company and at present leases the Government-owned chlorine-caustic plants at the Redstone Arsenal, Huntsville, Alabama. There are two of these plants located about three miles apart in the arsenal area. The plants were originally built for the Chemical Corps during World War II. After the war the plants were leased, first to the Solvay Process Company and then to the Algonquin Chemical Corporation whose assets were purchased by the National Distillers Products Company in 1952.

Each of the plants is equipped with 200 Hooker "S" chlorine cells having an annual production capacity of 18,250 tons of chlorine and 20,500 tons of caustic soda. Salt from Louisiana is purified at the plant and used to make the brine fed to the cells. The chlorine is dried, liquified, and shipped in tank cars. Caustic soda is concentrated to a 50% solution and likewise shipped. By-product hydrogen is wasted at present.

Consumption of energy and materials per ton of chlorine is 3000 kwhr, 1.75 tons salt, and 50 lb of sulfuric acid. It requires about 5.5 tons of steam for the concentration of a ton of caustic soda.

In fiscal 1953 the company had a peak power demand of 15,000 kw and used some 59 million kwhr at an average monthly load factor of 83%.

Pennsylvania Salt Manufacturing Company, Calvert City, Kentucky

In 1948 this company began the construction of a small chemical plant at Calvert City, Kentucky. In the next few years a number of other companies, notably, the Pittsburgh Metallurgical Company, the B. F. Goodrich Rubber Company, and the National Carbide Company (Airco) built nearby plants; Calvert City is fast becoming a notable chemical manufacturing center.

The Pennsalt chlorine-caustic plant was added to the company's initial installations and got into production in the spring of 1953. The present production capacity is some 50 tons of chlorine and 55 tons of rayon-grade caustic per day, along with about half a million cubic feet of hydrogen. It is one of the four plants in the United States now using DeNora cells.

The DeNora cell has been described in detail in many technical articles (1), as has also the Mathieson mercury-sodium amalgam cell (2). At the Pennsalt plant the cell is 40 ft long and is lined with cyanite granite imported from Italy. Chlorine lines are of Haveg and hydrogen lines of rubber. Part of the hydrogen is used in the production of hydrogen chloride supplied to the nearby Goodrich plant.

Expansion now under way will soon enable the plant to use power at the rate of 160 million kwhr per year.

Velsicol Corporation, Memphis, Tennessee

The Velsicol Corporation of Chicago, a division of the Avery Corporation, operates a chlorine-caustic plant at Memphis and uses the chlorine to produce insecticides.

The plant was expanded in 1953 to a capacity reported to be 44 tons of chlorine and 55 tons of caustic per day. By-product hydrogen will be piped to a neighboring plant for the hydrogenation of fats. The Velsicol plant has a power demand of 7500 kw and in fiscal 1953 used some 34 million kwhr of energy.

Electroplating Plants

Electroplating equipment is in use in a number of plants in the region but is a minor part of a large plant. A typical example of this sort is the electroplating equipment in the Rockwell Manufacturing Company plant at Tupelo, Mississippi, where certain machine parts are chromium plated.

Southern Electroplating Company, Memphis, Tennessee

The only large electroplating operation in the region is carried on by the above-named concern. The company has two plants in Memphis. Its Madison Street plant uses six 1500-amp rectifiers and includes a manually operated plating line for zinc plating. The plant also includes a job shop for the plating of copper, nickel, chrome, gold, and silver.

The main installation in the company's Kentucky Street plant is a Udylite full automatic plating machine for volume zinc plating, a Udylite six station rotary full automatic anodizing machine, and two Udylite zinc barrel plating machines. Also installed in the plant is an electrically heated copper brazing furnace in which a temperature of 2150°F can be maintained in a controlled atmosphere in an oven 3 ft wide and 13 ft long.

At present, one of the plants uses about 22,000 kwhr per month and the other 60,000 kwhr per month. In fiscal 1953 the two plants used 701,000 kwhr of electric energy.

Hydrogen-Oxygen Plants

Hydrogen is, of course, produced as a by-product in all the chlorine-caustic plants in the region and in some instances this hydrogen is being used for the hydrogenation of liquid fats.

There are two hydrogenation plants in Chattanooga that do not use by-product hydrogen. One of these generates hydrogen by the steam-ferrosilicon process. The other, Wilson and Company, uses electrolytic hydrogen produced at the company's plant under an arrangement with the National Cylinder Gas Company. The latter concern supplies Wilson and Company with hydrogen and markets the co-product oxygen. The connected load of the electrolytic equipment is about 1000 kw.

Electromanganese Plants

Electro Manganese Corporation, Knoxville, Tennessee

Electro Manganese Corporation operates two commercial electrolytic manganese plants, the only ones in the region. A small plant was first placed in operation in 1939 and by January 1941 electromanganese was being delivered in commercial quantities. The plant was expanded on three occasions, and by January 1951 it was producing slightly over ten short tons of pure manganese per day.

Demand for electromanganese was accelerated when Government restrictions were placed on civilian consumption of nickel. Stainless steel producers found that they could substitute electromanganese for nickel in certain types of stainless steel, and late in 1953 a new 10-ton per day plant was placed in operation by the Electro Manganese Corporation to meet increased demand.

Both plants operate on imported high grade oxide ores

brought in through the ports of New Orleans, Mobile, Norfolk, and Baltimore. Principal sources of ore are Africa, South America, and Cuba. At one time or another, manganese ores from every major producing country in the world have been used.

Both plants use the sulfate electrolyte process. Oxide ores are reduced to manganous oxide in electrically heated rotary kiln-type furnaces. Raw electrolyte is prepared by leaching the reduced ores with spent electrolyte returned from the cells. Iron is precipitated with the gangue in the leach tanks, after which the slurry is pumped to Dorr thickeners for clarification. Dorr underflow is filtered and combined with overflow. After pH adjustment, ammonium sulfide is added to remove nickel, copper, and other heavy metals which would interfere with manganese deposition. After further filtration and clarification steps, sulfur dioxide is added and solution is ready to be pumped to the cells. Manganese is deposited on stainless steel cathodes in diaphragm cells. Both rectifiers and motor-generator sets are used to supply direct current to the cell rooms. Total power consumption is about 5 kwhr/lb of metal produced. At periodic intervals, cathodes are removed from the cells, washed thoroughly, and dried. Manganese is stripped from the cathodes by flexing them in a jig. The product flakes off the cathodes in the form of chips about $\frac{1}{16}$ in. thick. It is packed in steel drums for shipment.

Almost fifty million pounds of electromanganese have been produced and sold since the company started operations. From 60–75% of the product goes into stainless and alloy steel production. The balance is consumed by nonferrous alloy producers and by the chemical industry.

In fiscal 1953 the plants used some 37 million kwhr. This was before the new 10-ton per day plant came on the line.

Phosphorus-Producing Plants

The presence of natural rock phosphate deposits in Middle Tennessee and the availability of relatively cheap power from the TVA power net led to the installation of phosphorus-producing plants in the region, beginning in 1934. At present there are four such plants, listed below in the order of their initial operation.

Plant	Initial operation	Approx. annual capacity as of 1953 (tons)
TVA at Wilson Dam, Alabama............	1934	30,000
Monsanto Chemical Company.............	1936	75,000
Victor Chemical Works....................	1938	34,000
Shea Chemical Corporation................	1953	20,000

TVA Plant at Wilson Dam, Alabama

The TVA has built and operated two large-scale furnaces of circular horizontal cross section and six of approximately rectangular horizontal cross section. Most of the six rectangular have been remodeled extensively from time to time. General features and dimensions of the largest (nominally 12,500 kw) of the rectangular furnaces were given in an article appearing in this JOURNAL (3). The second of the circular furnaces, installed in 1950, incorporated a novel feature in phosphate-smelting furnaces in that the crucible of the furnace was rotated slowly. This furnace and its performance have been described in two published articles (4, 5). A lengthy report covering TVA experience with phosphate-smelting furnaces is to be found in TVA's Chemical Engineering Report No. 3, and an article dealing with the design of such furnaces has been published by Curtis (6).

The six furnaces currently in use at the TVA plant are

usually operated at the following power loads: furnaces 1–4 in range 7000–7700 kw, average about 7380 kw; furnace 5 about 10,300 kw; and furnace 6 about 11,200 kw, or a total of some 51,000 kw. Based on the assumption that it requires about 11,750 kwhr per ton of elemental phosphorus recovered as such, the theoretical output of the plant, if operated continuously 365 days per year, would be some 38,000 tons of phosphorus annually. Actually, of course, no such operation is possible in a phosphate-smelting plant. Shutdown periods must be scheduled for major repairs and for periods of power shortage; and minor interruption will occur during scheduled operating periods due to an occasional broken electrode, minor repairs, or to interruptions in the gas-handling equipment serving the furnaces. In fiscal 1953 the six TVA furnaces operated 95.2% of the scheduled time and about 80% of the calendar time of the year. The practical capacity of the plant may therefore be stated as about 30,400 tons of phosphorus per year. In the event of a war and a great need for phosphorus, the plant could probably produce more than 38,000 tons by using overtime on repairs and by overloading the furnaces.

Monsanto Chemical Company's Phosphorus Plant Near Columbia, Tennessee

The Monsanto Chemical Company acquired a controlling interest in the Swan Corporation in 1933 and in 1935 absorbed this concern and its subsidiary, the Federal Phosphorus Company. The furnaces that the Swan concern had acquired at Anniston, Alabama, were originally built to produce ferromanganese during World War I. They were changed to ferrophosphorus production units by Swan, at first with little or no attempt to recover the elemental phosphorus that escaped conversion to ferrophosphorus. This created an intolerable air pollution problem. As a result of the installation of phosphorus recovery equipment, phosphoric acid eventually became the main product of the plant and ferrophosphorus a by-product. The proportion of the total phosphorus that went into ferrophosphorus could be varied from the minimum unavoidably formed from the iron present in the raw phosphate to any desired proportion by the expedient of adding iron filings, turnings, or scrap to the furnace charge.

At the time Monsanto took over the plant it was equipped with four 3000-kw furnaces. The Monsanto concern immediately began acquiring phosphate properties in Middle Tennessee and in 1936 put into operation a three-furnace phosphate-smelting plant in Maury County near Columbia, Tennessee.

The three furnaces initially installed had a nominal rating of 8000 kw each. Later it proved feasible to operate these furnaces at considerably higher loads.

The three electrodes per furnace were spaced at the corners of a triangle. The furnace shell was hexagonal in horizontal cross section, with three long and three short sides, but the shell was lined so as to form, in horizontal cross section, a triangle with rounded corners. Carbon electrodes 35 in. in diameter were used at first.

The peak load of the Monsanto plant did not exceed 37,000 kw in the period 1936–39, and, since some power was used in the plant elsewhere than on the furnace, presumably the three original furnaces were operated near their nominal capacities. In fiscal 1940 the peak power demand increased to about 50,000 kw when a fourth furnace, considerably larger than the three original ones, was added. A fifth furnace was added during fiscal 1949, increasing the peak demand to 75,000 kw. In fiscal 1951 the peak power demand again

jumped, this time to 120,000 kw, because of the addition of a sixth furnace and presumably because it had been found possible to operate some of the earlier-installed furnaces at a higher load than the nominal furnace rating. In fiscal 1953 the peak demand was 120,000 kw and the energy used was 895 million kwhr, with an average monthly load factor of 96%. If one guesses that 90% of this energy went into the furnaces and again guesses that the Monsanto furnaces require 12,000 kwhr per ton of phosphorus recovered (according to data published in 1950 by a Monsanto employee, the energy consumption was then 13,000 to 14,000 kwhr per ton of phosphorus) it appears that Monsanto's phosphorus production capacity at the Tennessee plant is about 75,700 tons and the actual production in fiscal 1953 was about 67,125 tons. In the August 2, 1952 issue of *Chemical Week*, the annual production capacity of Monsanto's six furnaces in Tennessee is given as 65,000 tons. Monsanto has also a phosphate-smelting plant at Soda Springs, Idaho, where 25,000-kw furnaces have been installed, and the company is now the largest phosphorus producer in the world.

The phosphate used in the plant comes from both Florida and Tennessee. The Tennessee matrix is mined by the company from its properties near the plant, beneficiated by hydrometallurgical methods, and prepared for furnace use by sintering in a standard sintering machine.

Shea Chemical Corporation Plant Near Columbia, Tennessee

This plant was put into operation in fiscal 1953. It is a single-train plant consisting of a phosphate drier, a nodulizing kiln, a drier for coke and silica, a phosphate-smelting furnace of 26,000-kw nominal capacity, a phosphoric acid plant, and a dicalcium phosphate plant.

The electric furnace is modeled after TVA Furnace No. 6 but expanded to about twice the capacity of the TVA unit. Graphite electrodes 35 in. in diameter are used. The present power load of the plant is 33,000 kw and the furnace is stated to have an annual production capacity of 20,000 tons of elemental phosphorus. The practical annual capacity is probably somewhat less than this.

Furnace offgases are cleaned in an electrostatic precipitator. The acid plant consists of a graphite combustion chamber, a cooler, a hydrator, and a stainless steel Venturi-type fume scrubber wherein phosphoric acid of 70–80% concentration is used to recover the acid mist from the waste gases.

The dicalcium phosphate plant includes a funnel-type continuous mixer in which the ground limestone is introduced at the top of the funnel in which the acid is entrained in a stream of air and blown tangentially into the throat of the funnel. The mixture then passes through a paddle-type mixer and is conveyed to storage. The dicalcium phosphate recovered from the storage pile is dried, ground, and sized for shipment. The dicalcium phosphate plant has a production capacity of 250 tons per day.

Victor Chemical Works Plant Near Mt. Pleasant, Tennessee

The Victor Chemical Works began producing phosphorus in an experimental blast furnace unit at the company's Chicago plant in 1924. In 1929 the company constructed a small commercial plant of this kind near Nashville, Tennessee. This plant is of some historical interest not only because of the blast furnace method used, but also because, for the time, lower grades of rock phosphate than normally prepared for fertilizer manufacture were used. The furnace charge was briquetted. Since the phosphorus content of furnace offgases was low, and the gases carried a relatively large burden of dust, the gas-cleaning equipment necessary to secure ele-

mental phosphorus of chemical grade was large, elaborate, and costly.

After electric power became available at low rates in the Tennessee Valley the company turned to the electric furnace method and built a phosphate-smelting plant near Mt. Pleasant, Tennessee, in 1937 and put the first furnace into operation in 1938. The initial furnaces in this plant were modeled on the TVA furnaces then in operation at Wilson Dam, Alabama. The second furnace at the plant went on the line late in 1939, a third early in 1940, and a fourth late in 1940, the last in anticipation of a military demand for phosphorus. At first a part of the output of the fourth furnace was sold to the TVA for fertilizer production, but the whole output was diverted to military use in 1942.

The company's Mt. Pleasant plant has been operated at a high load factor since 1940. The nominal capacity of the four furnaces as originally designed was 7500 kw each, but through improvements over the years the four-furnace load has been built up. In fiscal 1953 the peak load of the Mt. Pleasant plant was 52,000 kw, with an average monthly load factor of 98%. Actual energy consumption for the year was 393 million kwhr. Assuming that 90% of the plant energy consumption went to the furnaces and that it required 12,000 kwhr per ton of phosphorus recovered, production was in the neighborhood of 29,000 tons. Plant capacity is presumably somewhat greater than this, perhaps near 34,000 tons.

Initially the phosphate for the furnace charge was nodules prepared by one of the neighboring fertilizer companies, using the techniques developed by the TVA at Wilson Dam, Alabama, but late in 1939 the company put the first of its own three nodulizing kilns into operation. The company pioneered in the development of equipment to scrub the fluorine-carrying offgases from its nodulizing kiln and put the first such scrubber into operation in 1941. There is no attempt to recover fluorine compounds in marketable form. Water is used as the absorbent in the towers. The resultant acid solution is neutralized with lime, and the solids then separated in Dorr thickeners and discarded.

Phosphorus produced at the Mt. Pleasant plant is shipped to other of the company's plants for conversion to phosphorus compounds.

In 1947 the Victor Chemical Works put a phosphate-smelting furnace into operation in Florida and in 1950 began construction of a phosphate-smelting plant in Montana that is equipped with two 25,000-kw furnaces.

Calcium Carbide Plants

There are two plants in the region equipped to produce calcium carbide, but one of them, constituting a part of the old U. S. Nitrate Plant No. 2 at Wilson Dam (now the TVA Chemical Plant), has not been operated since World War II.

TVA Carbide Furnaces at Wilson Dam, Alabama

U. S. Nitrate Plant No. 2, built during World War I, was a cyanamide plant and included twelve carbide furnaces rated at 6000 kw each. Only a few of the furnaces were operated in a trial run of the plant in 1919.

After the TVA took over the plant, six of the carbide furnaces were removed to make room for phosphate-smelting furnaces. The other six carbide furnaces remained intact. During World War II, when acetylene was needed for synthetic rubber production, the TVA placed the six furnaces in operation in 1943 and during the war period produced 242,521 tons of carbide. The furnaces were thereafter shut down and have remained idle. During the fiscal year 1944 some 107,000 tons of carbide were produced and this pre-

sumably represents about the reserve available capacity in the Wilson Dam plant.

National Carbide Company, Calvert City, Kentucky

(A Division of Air Reduction Company, Inc.)

The Calvert City plant of this company built the second of the large electroprocess plants in this fast-growing industrial center. Construction was begun in 1951 and initial production of carbide attained early in 1953. The cost of the original two-furnace carbide and acetylene plant is said to be ten million dollars. The initial furnaces each have a capacity of 75,000 tons of carbide per year and by March 1954 the company expects to bring in two other furnaces of like capacity in connection with an eight million dollar expansion of the plant, bringing the total carbide capacity to 300,000 tons per year. After the expansion is completed it can use power at the rate of about one billion kwhr per year.

The two 30,000-kw furnaces, the first carbide furnaces of this type to be built in the United States and the largest carbide furnaces in the world today, are of the rotating crucible type developed by the Norwegian Elektrokemisk concern. Söderberg electrodes are used and the furnaces are tapped continuously into ingot molds carried on a slowly moving conveyor. Furnaces are of the closed type, rotated at some 50 to 100 hr/revolution; the by-product carbon monoxide is currently wasted by burning it.

Acetylene is piped from the acetylene generators to the nearby plant of the B. F. Goodrich Chemical Company.

The National Carbide Company acquired a 1500-acre tract of land around its Calvert City plant and has subdivided it into 15 plant sites, one of which is now occupied by the Goodrich plant.

Ferroalloy Plants

There are four plants in the region producing ferroalloys in addition to the iron foundries where alloys other than steel are made.

Southern Ferro Alloys Division, Tennessee Products and Chemical Corporation, Chattanooga, Tennessee

The Southern Ferro Alloys Company was organized in 1917 as a successor to the Chattanooga Electro Metals Company, and produced various grades of ferrosilicon. Over the years the plant was expanded and by 1944 it included five furnaces ranging in capacity from 1800–5000 kw. In addition to these, the Government had installed two 5000-kw furnaces in the plant. These were later purchased by the company. In 1947 the Southern Ferro Alloys Company was purchased by the Tennessee Products and Chemical Corporation and became a division of this corporation. The Tennessee Products and Chemical Corporation owns another plant in Chattanooga, known as its Alton Park plant, originally a coal carbonization unit, but later expanded to include the production of chemicals. Two 3500-kw ferrosilicon furnaces were also added to the Alton Park plant, and lately two 5000-kw ferromanganese furnaces were put into operation there. It is said that the company plans to consolidate all of its operations at this plant. It is estimated that when the electric furnace operations are consolidated the connected furnace load will be between 40,000 and 45,000 kw. In fiscal 1953 the two plants used 246 million kwhr at high monthly load factor. The new ferromanganese furnace will, of course, considerably increase the energy consumption above the fiscal 1953 figure.

Electro Metallurgical Company, Sheffield, Alabama

The Alabama works of this company, which is a division of the Union Carbide and Carbon Corporation, started operations in April 1940. Production capacity of the plant has been tripled since that date and the output is now (November 1953) some 8000 tons per month. Energy consumption for the smelting of raw ores currently amounts to about a million kwhr per day, and the consumption for the whole plant amounted to 464 million kwhr in fiscal 1953, with an average monthly load factor of 94%.

The company employs about 500 people at the Alabama plant and produces various grades of ferrosilicon, ferromanganese, silicomanganese, and zirconium alloy.

Pittsburgh Metallurgical Company, Calvert City, Kentucky

The Calvert City plant of this company went into operation in 1949, producing ferrochromium, ferrosilicon, and ferrochrome-silicon alloys, alloy pig iron, and similar products. In 1953 the power demand reached 63,000 kw and in fiscal 1953 the energy consumption was 284 million kwhr.

Montana Ferroalloys, Inc., Memphis, Tennessee

This company is a subsidiary of the Chromium Mining and Smelting Corporation of Chicago.

The Memphis plant went into operation early in 1952. It is equipped with three 7000-kw furnaces for the production of chromium and silicon ferroalloys. Normally only two of the furnaces are operated, producing some 12,000 tons of alloys per year. If the two furnaces were operated at full load continuously, the annual energy consumption would be 122.6 million kwhr. Actual energy consumption is probably in the neighborhood of 75% of the theoretical, i.e., some 92 million kwhr annually.

The alloys are shipped to steel mills or to the parent company's plant in Chicago which produces and markets "Chrom-X," "Sil-X," and "Chrom-Sil-X."

Electrodes

National Carbon Company, Columbia, Tennessee

The National Carbon Company, Inc., a division of the Union Carbide and Carbon Corporation, established a plant near Columbia, Tennessee, in 1937 for the manufacture of furnace electrodes. This plant was greatly expanded recently and is now the world's largest electrode manufacturing plant. Both carbon and graphite electrodes are produced. The company used some 141 million kwhr in fiscal 1953, most of this energy going into the resistor-type furnaces in which graphite electrodes are made.

Foundries

There are at least two foundries in the region that make enough use of electric furnace melting to be classed as electroprocess operations, and, in one of these, every operation uses electric energy as a source of heat.

Ross-Meehan Foundries, Chattanooga, Tennessee

This foundry is probably unique in the United States in that all its ovens, furnaces, etc., are electrically heated. These include melting furnaces, core ovens, and heat-treating and annealing furnaces. In the two melting furnaces both carbon steel and several alloy steels are produced, including steel for armor plate. Seven heat-treating furnaces are used for normalizing carbon steels and for homogenizing armor steels, the latter operating at temperatures up to 2150°F. The company also produces Meehanite alloy castings which

are heat-treated for normalization and relief of stresses. Electric energy consumption in fiscal 1953 was 18 million kwhr.

Knoxville Iron Company, Knoxville, Tennessee

This is an old company in Knoxville, claiming 1868 as the date of establishment. Of course, it used no electric energy at that date nor until long after. At present the company uses electric furnaces for melting scrap and for alloying. It uses gas heat for some of its operations. Electric energy consumption in fiscal 1953 was some 13 million kwhr.

Miscellaneous Plants Using Electric Furnaces Incident to Manufacturing

Only plants using more than two million kwhr annually for all purposes are listed. The largest energy consumer in the group uses about 24 million kwhr annually.

Aladdin Radio Industries, Inc., Nashville, Tennessee.—This company is a subsidiary of Aladdin Industries, Inc., also located at Nashville. Electrically heated ovens are used in processing powdered metals in the manufacture of electronic circuit parts.

American Lava Corporation, Chattanooga, Tennessee.—This concern, a subsidiary of the Minnesota Mining and Manufacturing Company, manufactures ceramic articles for use in electrical and other industrial equipment. Silicon carbide resistor furnaces are operated at about 1400°C for firing titanate ceramics. Nichrome resistor furnaces are used in metallizing ceramics, and dielectric heaters are used in drying ceramics.

Cleveland-Tennessee Enamel Company, Cleveland, Tennessee.—Electrically heated enamel driers and baking ovens are in use, with a total demand load of some 2000 kw. The company's chief product is porcelain enamel stove parts.

Crane Company, Chattanooga, Tennessee.—Crane manufactures enamel ware of various sorts, using electrically heated ovens and muffles.

Ferro Corporation, Nashville, Tennessee.—This company manufactures ceramic articles, frit, fiberglass, etc., using electrically heated equipment.

Florence Stove Company, Lewisburg, Tennessee.—Two electrically heated enameling ovens are in use at this plant, one of 1000 kva and the other of 1368 kva capacity.

Gray & Dudley Company, Nashville, Tennessee.—Products manufactured in the company's Nashville plant include gas and electric ranges, electric water heaters, gas furnaces, coal stoves, etc. A number of small (88-kw) enamel driers are used along with three 275-kw flat bed enamel baking furnaces. Paint enamel is baked in a 17.6-kw oven.

The Murray Manufacturing Company, Murray, Kentucky.—This company is a producer of gas and electric ranges. An electric furnace is used in fusing porcelain enamel for stove parts.

Polynesian Arts, Inc., Mayfield, Kentucky.—An electrically heated tunnel kiln is used in firing of decorated pottery.

Temco, Inc., Nashville, Tennessee.—Temco uses both gas-fired and electrically heated enameling furnaces in producing gas heaters and stove parts. The company also uses small induction-heated furnaces for heating tubing preliminary to forging.

New Electroprocess Plants in the Region

A number of new plants using electroprocess operations are now under construction in the region. These are:

Cramet, Inc.—This company is a subsidiary of the Crane Company. It is building a plant at Chattanooga for the

production of titanium under a U. S. Government loan, certificate of necessity, and contract for purchase of at least a part of the output. Presumably the Kroll process will be used. In this process titanium tetrachloride is first prepared and then reduced by magnesium in a fused-salt bath. The resulting magnesium chloride is separated from the sponge titanium by distillation in a vacuum.

The process makes use of electrical heating to such an extent as to be classified as a partially electrothermal operation.

Judging by the announced power consumption contemplated in the initial operation of the plant, the necessary chlorine and magnesium will be purchased. It is likely that any large plant using the Kroll process will eventually find it economical to install magnesium-chlorine electrolytic cells to permit recycling of the magnesium and chlorine in the process. Such an addition to the Cramet plant would greatly increase the energy required locally per pound of titanium produced.

Oldbury Electro-Chemical Company.—This concern is building a plant near Columbus, Mississippi, for the production of sodium chlorate and other chemicals. Initial operation is scheduled for 1954. The plant is said to cost $3,500,000 and to have an annual production capacity of 12,500 tons of chlorate.

E. I. du Pont de Nemours and Company.—A second titanium plant, financed by the Government, is to be built by du Pont near Waverly, Tennessee, adjacent to the TVA's New Johnsonville steam-electric power plant.

Power Supply in the Tennessee Valley Region

As of June 30, 1953 the installed capacity serving the TVA power system was 5,102,985 kw and net generation in fiscal 1953 was 23,744,919,465 kwhr. The system also handled an additional 3,602,771,802 kwhr received from neighboring power systems, making a total of 27,347,691,267 kwhr. Deducting system losses, power returned to neighboring power systems, power furnished Alcoa under contract involving Alcoa power plants, and TVA incidental uses, the net power sales in fiscal 1953 amounted to 23,678,681,109 kwhr.

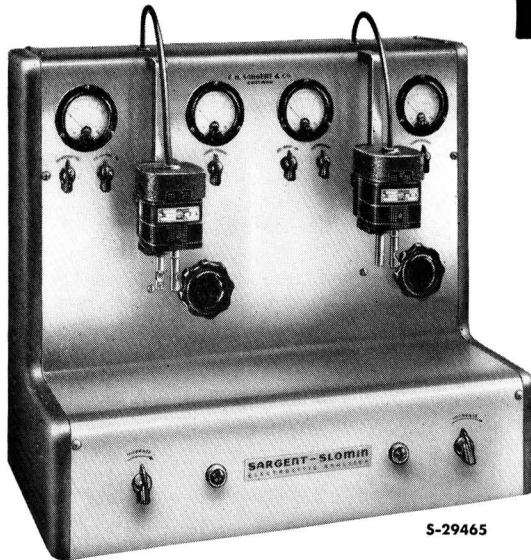Of the net generation cited above for fiscal 1953, hydro installations furnished 58.7%, coal-burning power plants 39.8%, and plants using gas or oil 1.5%. This situation is changing rapidly as the very large steam-electric plants that TVA is building come into production. As these plants are completed and the few hydroelectric units now under construction come on the line, the generating capacity will increase to some 6.1 million kw by the end of fiscal 1954, to 8.8 million kw at the end of fiscal 1955, to 9.9 million kw at the end of fiscal 1956, and when all units now under construction are on the line in fiscal 1957 the system will reach a capacity of about 10 million kw. By 1957, the AEC and other directly served Government plants will probably use about one-half of the total energy.

It is obvious from the above statement that power consumption in the region is growing rapidly. Increased demand comes from all segments of the power consuming group, i.e., Government plants, industrial plants, commercial establishments, and domestic consumers. The TVA estimates that some 750,000 kw capacity must be added to the system annually to meet these demands without any allowances for increases in the requirements of the Government plants. This means that a large new steam-electric plant must be added annually to meet the needs for the years immediately following 1957. Since it requires about three years from time of authorization to complete a large steam-electric plant, construction beyond that already in progress must be begun in the near future if industrial development in the region is to continue. There will probably be a few more small hydroelectric plants built on the tributaries of the Tennessee but the main reliance will rest on steam-electric plants. The environment for such new industrial plants is favorable in the region, and given adequate power there is no reason to doubt that the industrial growth will continue.
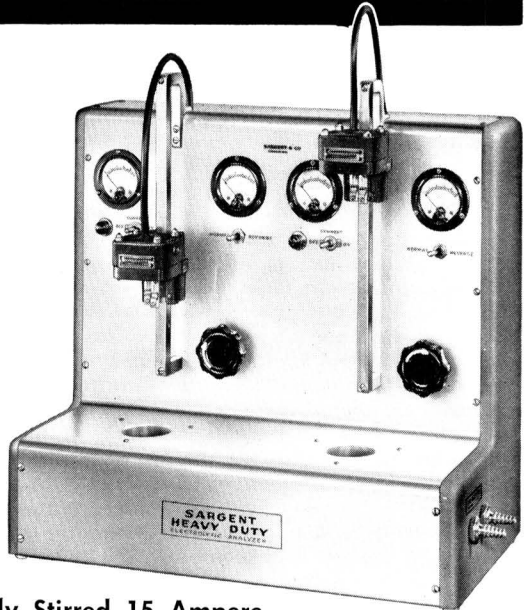
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Kinetics of the Reaction of Hydrogen with Zirconium[1]

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ABSTRACT

The rate of reaction of hydrogen with high purity zirconium was determined for the temperature range of 250° to 425°C at 1 atm pressure. The reaction was found to follow a parabolic law, and the parabolic rate constant in $(ml/cm^2)^2$ per second was calculated to be $k = 2.3 \times 10^5 e^{-17,200/RT}$ where $17,200 \pm 200$ cal/mole is the activation energy for the reaction.

INTRODUCTION

Kinetics of surface reactions of zirconium with nitrogen and oxygen have been discussed in previous papers from this laboratory (1, 2). The present paper concerns the kinetics of the zirconium-hydrogen reaction. Very little on this subject was found in the literature. Gulbransen and Andrew (3) investigated the reaction in the temperature range 235° to 300°C at pressures from 0.6 to 2.6 cm, using thin zirconium foil, 0.005 in. thick. Their conclusions can be summarized as follows: (a) a surface film is not formed as a product of the reaction; (b) the rate of the reaction deviates from a linear law; and (c) the rate of the reaction is directly proportional to the square root of the pressure.

The present study was made in the temperature range 250° to 425°C at a hydrogen pressure of 1 atm, using low-hafnium zirconium (0.01 weight % hafnium) in the form of solid cylinders.

EXPERIMENTAL

Method.—The method for measuring the rate of the reaction between zirconium and hydrogen was essentially that previously described for other zirconium-gas reactions (1, 2). A schematic diagram of the apparatus used is shown in Fig. 1. Vacuum-ground stopcocks greased with Apiezon N grease were used throughout except for the air inlets to the McLeod gauge and to the mechanical pumps. The system was evacuated by a 2-stage glass mercury-diffusion pump backed by a mechanical pump. The cold trap between the diffusion pump and the reaction system was cooled with liquid nitrogen. It was found necessary to place an additional trap, cooled with dry ice-acetone, adjacent to the reaction tube to remove contaminating grease and mercury vapors.

A modified White gas buret (4) was used to store the hydrogen and to measure the rate of con-

sumption of gas. The buret consisted of 10 bulbs, each of approximately 25 ml, and of a connected open-end full-length manometer, one arm of which was a graduated 25-ml buret. The entire assembly was maintained at constant temperature (± 0.5°C) with running water.

The Vycor reaction tube was sealed to the system with Apiezon W wax, and its dead volume was decreased by a bundle of fused Vycor rods. The reaction tube was heated by a resistance-wound furnace which was controlled by a Brown Pyro-Vane controller with a V20 Variac in the input line. Temperature was controlled to ± 5°C.

Prior to specimen preparation, machined zirconium cylinders about 2 cm long and 0.6 cm in diameter were degassed to about 1 to 2 ppm hydrogen by heating in vacuum at 900°C for 24 hr. Specimens were abraded with kerosene-soaked 240-, 400-, and 600-grit silicon carbide papers and washed in successive baths of naphtha, ether, and acetone. Care was taken to keep specimens under acetone until they were placed in the reaction tube.

The reaction tube was sealed to the system which, then, was evacuated to about 10^{-5} mm Hg as measured by the ion gauge. The specimen was annealed under vacuum for 1 hr at 800°C, after which the furnace was removed and its temperature adjusted to that of the rate run. The furnace was again placed around the reaction tube. The temperature was permitted to stabilize while hydrogen was being generated and stored.

With the specimen at the desired temperature, hydrogen was admitted from the buret and maintained at atmospheric pressure in the reaction tube by manual manipulations of the buret leveling bulb, except when the gas was expanded into the buret from storage bulbs. Short-time pressure fluctuations did not affect reaction rates. Readings, taken as the buret manometer arms were precisely leveled, were made as often as possible for rapid reaction rates and every 2 to 10 min for slower rates. The quantity of gas consumed by the specimen was the volume
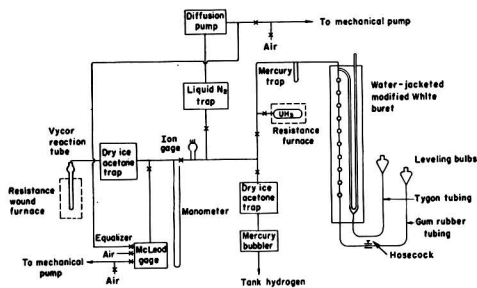
FIG. 1. Schematic diagram of modified hydrogen Sieverts apparatus.

added from the buret minus that remaining in the gas phase in the calibrated dead space. Geometric dimensions of specimens were used in calculating the quantity of hydrogen reacted per unit area.

Materials.—The pure zirconium used in these experiments was iodide crystal bar produced by the de Boer process, arc-melted, forged to $1\frac{1}{8}$ in.^{2} at 1450°F, hot rolled at 1450°F, and cold drawn to $\frac{3}{8}$-in. diameter rod. Test specimens were machined from this rod. Impurities in zirconium were determined by spectrographic, chemical, and vacuum-fusion analyses. Weight percentages of principal impurities detected were: silicon, 0.03; iron, 0.02; hafnium, 0.01; oxygen, 0.04; nitrogen, 0.002; and hydrogen, 0.003 (before degassing).

Pure hydrogen was obtained from the thermal decomposition of uranium hydride. The hydride was prepared by reacting tank hydrogen, dried in a dry ice-acetone cold trap, with degreased high purity uranium chips.

RESULTS AND DISCUSSION

Initial deviations are often observed for gas-metal reactions which follow the parabolic law, $w^2 = kt$. Gulbransen (5) has enumerated a number of complex factors which contribute to the breakdown of the law during early stages of the reaction. In addition to these phenomena, there may be interface effects. As was discussed by Jost (6) and Kubaschewski and Hopkins (7), these interface reactions may become rate-determining in initial stages of the reaction. The empirical equation which combines both reaction at an interface and diffusion through the film can be written in the form, $w^2 + \frac{k_p}{k_1} w = k_p t$. Here, k_1 represents the contribution of any linear interface reaction and k_p is the parabolic rate constant determined by diffusion through the growing film. If w is plotted as a function of t/w, the slope of the straight line is the parabolic rate constant, k_p. Such a plot is often more convenient to use than the quadratic plot, particularly for
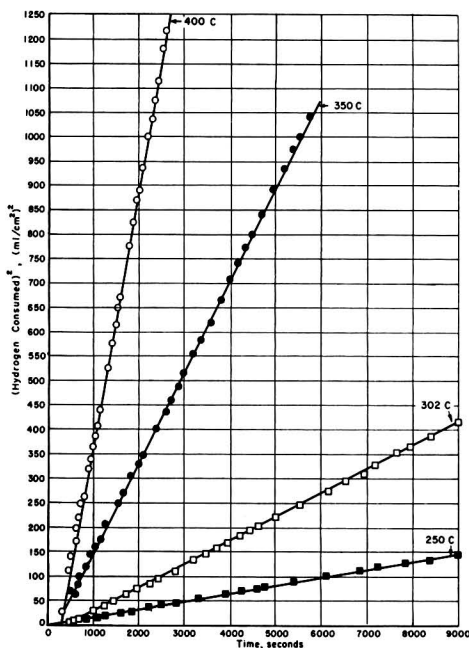
FIG. 2. Reaction of zirconium with hydrogen (ml H_2, STP, consumed per cm^2 metal surface)^2 vs. time.

those reactions where an induction period is present or initial stages of the reaction are uncertain.

The rate of the surface reaction of zirconium with hydrogen was measured in the range 250° to 425°C at 1 atm pressure. Results of several measurements are shown in Fig. 2 and 3. In Fig. 2, the square of the quantity (ml STP) of hydrogen consumed per unit surface area of the metal is plotted against time for four temperatures. Fig. 3 is a plot of w vs. t/w for two temperatures. It was found that, in all cases, the reaction conformed to the parabolic rate law with initial deviations in the direction of a slower initial rate. The duration of the induction period was usually less than five minutes and was independent of the annealing time, provided the system was evacuated to about 10^{-4} to 10^{-5} mm Hg.

In addition to the short induction period, there were also some deviations from the parabolic law after considerable hydrogen had been reacted. (The film thickness produced by the parabolic reaction ranged from 150μ at 300°C to 300μ at 425°C.) Deviations, which were always in the direction of a faster rate, did not occur below 300°C, and were not always present above that temperature. It is suspected that this breakdown of the parabolic nature of the reaction may be due to cracking of the film. It is not known why this effect was not reproducible.

FIG. 3. Reaction of zirconium with hydrogen

TABLE I. *Parabolic rate constants for the reaction of zirconium with hydrogen*

Temp., C ± 5°	Rate constant, k_p, (ml/cm²)²/sec	Slope of log-log plot
249	0.015	0.47
250	0.017	0.50
276	0.032	0.47
277	0.035	0.49
302	0.056	0.56
304	0.074	0.52
323	0.12	0.53
323	0.11	0.50
350	0.20	0.57
351	0.19	0.57
353	0.22	0.49
373	0.33	0.57
378	0.38	0.49
397	0.61	0.61
400	0.70	0.64
421	0.88	0.47
424	0.88	0.57
424	1.05	0.58
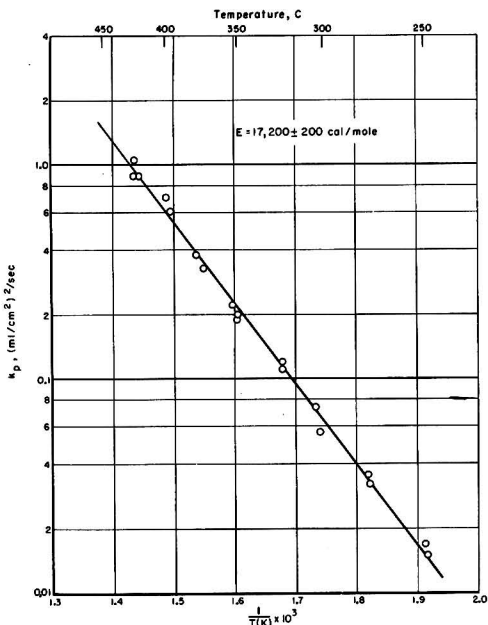
FIG. 5. Zirconium-hydrogen reaction, variation of reaction-rate constant with temperature.

FIG. 4. Hydrogen reacted with iodide zirconium at 302°C for 2½ hr at 743 mm Hg absolute pressure. 250×

A reaction product was formed on the surface of all specimens, in contrast with the findings of Gulbransen and Andrew (3) who reported the absence of a surface film. Metallographic examination of the surface film indicated it to be an apparently single-phase layer, as can be seen from the photomicrograph shown in Fig. 4. On the other hand, x-ray diffraction examination of the surfaces of several specimens revealed the presence of three phases: (a) an outer layer of tetragonal ZrH_2; (b) an intermediate layer of Hägg's (8) ZrH; and (c) an inner layer of a second tetragonal hydride phase. When the outer ZrH_2 was removed by light abrasion of the surface, the pattern of ZrH was obtained. Upon further abrasion, another hydride phase

appeared, adjacent to the metal. As discussed by Schwartz and Mallett (9), this latter hydride phase may be similar to the tetragonal phase of lowest hydrogen content reported for the hafnium-hydrogen system by Sidhu and McGuire (10). What effect these multiple hydride phases have on the kinetics of the zirconium-hydrogen reaction is not known.

If the parabolic law is obeyed, a plot of the logarithm of the amount of hydrogen consumed per unit surface area vs. the logarithm of time should give a straight line with a slope equal to 0.5. This was observed, as can be seen from Table I, where the parabolic rate constants, k_p's, calculated from the w vs. t/w plots are also given.

Fig. 5 is a plot of log k_p vs. $1/T$. The equation of the best straight line through the points from 250° to 425°C was determined by the method of least squares. The experimental energy of activation and the frequency factor were calculated from the Arrhenius-type equation, $k = Ae^{-Q/RT}$. Energy of activation was calculated to be $17,200 \pm 200$ cal/mole. The parabolic rate constant in $(ml/cm^2)^2/sec$ is $k = 2.3 \times 10^5 \, e^{-17,200/RT}$.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1954 issue of the JOURNAL.

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Potentials of Iron, 18-8, and Titanium in Passivating Solutions[1]

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ABSTRACT

Potentials of iron in chromates show a linear relation for $C/\Delta E$ vs. C, where C is concentration and ΔE is change of potential, suggesting that they follow the Langmuir adsorption isotherm. Maximum potential change corresponding to an adsorbed monolayer of chromate ions occurs at 0.0025 molar K_2CrO_4, which approximates the minimum concentration for passivity reported by Robertson. The evidence agrees with a primary mechanism of passivity based on adsorption rather than on oxide film formation. For example, potentials of iron exposed to several organic inhibitors, where the mechanism is undoubtedly one of adsorption, also follow the adsorption isotherm as shown by Hackerman and coworkers. Passivity of 18-8 stainless steel and titanium in sulfuric acid containing cupric or ferric salts appears similarly to be accompanied by adsorption of Cu^{++} or Fe^{+++}. The irreversible nature of the potentials is in accord with the view that the adsorbate, in part, is chemisorbed.

Hydroxyl ions in 4% NaCl produce more active potentials in passive 18-8 or titanium presumably by displacing adsorbed oxygen. Potentials of 18-8 in alkaline NaCl as a function of partial pressure of oxygen follow the adsorption isotherm, which adds confirming evidence that an adsorbed oxygen film is responsible for passivity. The decreased potentials between active and passive areas plus precipitation of passivity-destroying metal chlorides as hydrous oxides at incipient anodes accounts for inhibition of pitting in chloride solutions by alkalies.

Calculated Langmuir isotherm constants, taking into account competitive chemisorption processes, agree qualitatively with expected relative values based on chemical properties of metals and adsorbates.

Introduction

Chromates are in the class of inhibitors called passivators because the potential of iron immersed in a chromate solution is several tenths volt more noble than in water, and iron no longer corrodes visibly. Two points of view have been proposed regarding the mechanism of passivation by these and similar compounds. Hoar and Evans (1) proposed that chromates react with soluble ferrous salts throwing down a protective film of hydrated ferric and chromic oxides. Accordingly, a film of ferric oxide on air-exposed iron will, if introduced into chromates, be made more protective because the chromate "repairs" the film discontinuities. Since then, this view has been restated by several investigators (2–4). Mayne and Pryor (3) modified the picture somewhat, based on their electron diffraction studies, proposing initial adsorption of chromates followed by direct reaction with iron to form an unhydrated γ Fe_2O_3 film which they suggested was a better diffusion barrier layer than a film of hydrated oxides.

A second view attributes passivity to adsorption of chromate ions on the metal surface (5–8). Formation of an oxide film is considered unnecessary, although such a film may form eventually and aid in the over-all protection. The primary protection, however, is considered to result from satisfaction of valence forces of the surface metal atoms by chemical bonding with chromate ions, and without the metal atoms leaving their respective lattices. A similar mechanism has been proposed for specific organic inhibitors (9).

Passivators, in accord with this view, are substances having high affinity for the metal and accompanying high activation energy for any reaction which results in a new lattice belonging to a surface stoichiometric compound. These are the essential conditions for chemisorption. Consequently, an iron-chromium oxide or iron oxide, whichever forms ultimately when iron is exposed to chromate solutions, accumulates only slowly. Chlorine, for example, is not a passivator because, despite high affinity for the metal, its activation energy for reaction is low, resulting in rapid production of iron chlorides rather than a chemisorbed film of chlorine atoms. Oxygen, by way of contrast, readily

chemisorbs on many metals and is a good passivator. Halide ions break down passivity by competing with oxygen or other passivators for a place on the metal surface; but once they succeed, metal corrodes at such areas until additional passivator adsorbs.

Evans (10) and others (1, 3, 11) isolated oxide films on iron exposed to chromates and supposed these to be the primary source of protection. Circumstantial evidence of this kind is not conclusive, however, in view of the primary process of adsorption which, if it occurs at all, always precedes the formation of oxides or other compounds, and continues in effect even after the usually permeable, although relatively thick, oxide films are formed. In specific instances, some chemical reagents used for stripping of surface films may actually produce an oxide reaction product (12, 13). When this is the case, the stripping reagent may hasten reaction of adsorbed films, if not of other substances, with the metal, resulting in a surface compound where none existed before.

McKinney and Warner (14) in discussing a paper by Evans expressed doubt that chromates could act merely by precipitation of ferric-chromic oxides on the metal surface, in view of the fact that chromic salts are relatively poor inhibitors compared with chromates. Evans (15) replied that, when chromic salts precipitate a film of hydrated chromic oxide on cathodic areas, attack is not hindered; whereas with chromates, mixed hydroxides are precipitated locally at places where anodic attack would otherwise set in and prevents it from developing. This explanation, however, is less convincing in light of Robertson's (8) subsequent data which showed that molybdates and tungstates, analogous to chromates structurally, and inhibiting at the same minimum concentration, fail to oxidize ferrous salts [or do so extremely slowly (4)] and, hence, are quite unlike chromates in their capacity to precipitate a supposed protective anodic coating.[2]

[2] Criticism of Robertson's conclusions has been made on the basis that the otherwise weak oxidizing capacity of molybdate and tungstate in acid solution might be greater in neutral solutions (16) corresponding to actual conditions of pH at the surface of iron. However, the oxidizing tendency of these salts is *less* in neutral or alkaline media as compared with acid solutions (as can be demonstrated thermodynamically). This, in fact, was demonstrated for molybdates and tungstates by Pryor and Cohen by titrations in neutral media. They found only 11% of $0.0072N$ ferrous sulfate to be oxidized by $0.1N$ sodium tungstate after as long a period as three days, although they interpret this slow rate as sufficient to form the supposed protective film. Actually, molybdates and tungstates are less effective oxidizers than is dissolved oxygen.

This is not to say that iron does not reduce molybdates and tungstates in solution and become oxidized in the process. However, the minimum concentration of these substances for passivity or inhibition, identical with the

Rozenfel'd and Akimov leaned to the possibility that anodic polarization of iron by chromates was due to adsorption of the chromate ion (17). Indelli (18) also interpreted potential behavior of iron and 18-8 in chromates in terms of adsorption of the inhibiting ion.

Simnad (19), using radioactive chromium, concluded that the view of Hoar and Evans was corroborated by the almost similar pickup of radioactive chromium whether iron was immersed in chromic chloride or in chromates, and by the spotty deposition of radio-chromium salts on an iron surface exposed to chromates, presumably revealing anode areas. However, his conclusions do not take into account reaction of chromic chloride with iron to form hydrated oxides which adhere to the metal surface in the same manner as hydrous FeO, but which are not protective in the same sense as chromates. Similarly, chromates may be reduced at preferential metal areas, particularly if chlorides or sulfates are present in solution which accelerate consumption of the passivator (20). Impurities in the metal may also accelerate reduction of chromates.

Brasher and Stove (21) report that the amount of radioactive chromium picked up by abraded mild steel after three days' immersion as a function of chromate concentration follows the form of a typical adsorption isotherm. They find a maximum of 5.5×10^{15} chromium atoms/cm² geometric surface. Considering a probable value of the roughness factor for an abraded surface equal to 3 (22), and a diameter of CrO_4^{--} equal to 5.4 Å (23), their value corresponds to the equivalent of 4.5 layers of close-packed chromate ions. The number of layers would be less if correction were made for any chromate adsorbed on the air-formed surface oxide or reduced to chromic oxide during the three days' exposure.

Powers and Hackerman (24), also using abraded steel, found, in agreement with Brasher and Stove, that after two days' immersion in $10^{-3}M$ radiochromate at pH 7.5 there were 5.2×10^{15} chromium atoms remaining per cm² of surface, uniformly distributed.

Potential measurements of iron exposed to chromate solutions add to the pertinent evidence concerning the mechanism of passivation. Data of this kind are presented herewith, together with parallel data for 18-8 stainless steel and titanium in other passivating electrolytes.

PROCEDURE

Potentials were measured using a precision potentiometer and vacuum-tube galvanometer in conjunction with a silver chloride reference electrode

minimum concentration of chromates, despite differing oxidizing tendencies, suggests that the mechanism of protection does not depend on an oxidation-reduction reaction.

in 0.1*N* KCl. The potential of the latter on the hydrogen scale omitting liquid junction potentials is 0.288 volt at 25°C. All measurements were conducted in an air thermostat maintained within 0.2° of 25°C. Final values are for steady state where the net change within 12 hr was less than 5 mv. This often required successive measurements over several days. The maximum change, however, within a few centivolts was obtained usually during the first 24 hr.

Iron electrodes were prepared from high purity 0.030-in. diameter wire obtained by courtesy of the National Bureau of Standards (C < 0.001%, total impurities about 0.008%). Six-inch lengths were mounted in glass tubing and sealed, using polystyrene cement with about 1 cm of wire projecting. The surface was prepared by pickling in 10% H_2SO_4, followed by washing and immediate transfer to the test solution.

Electrodes of 18-8 were prepared from Type 304 0.028-in. diameter wire. The wire was first annealed by heating electrically to 1000°C and quenching in air, then was pickled in 15 vol % HNO_3, 2 vol % HF at 70°–80°C, and washed. It was immersed directly into the electrolyte to a depth of about 1 cm.

Titanium electrodes were made by cutting thin strips of Bureau of Mines cold rolled titanium, followed by pickling in HNO_3-HF at 70°–80°C. No heat treatment was employed.

Ferric ion concentration in sulfuric acid was determined by reduction first with stannous chloride, the excess of which was eliminated by adding $HgCl_2$, followed by titration with permanganate. Cupric ion concentration was determined by titration using thiocyanate. Dichromate or chromate solutions were made up by weighing out the required amount of salt. Low carbonate NaOH was prepared by cooling hot saturated NaOH and decanting into wax-lined bottles.

The cell used for potential determinations consisted of a 4-oz bottle fitted with a rubber stopper. A salt bridge containing the same solution as the electrolyte made contact with 0.1*N* KCl in which the silver chloride electrode was immersed. The latter electrode was mounted in a glass tube, the bottom of which was constricted to provide a liquid junction by means of a sealed-in asbestos fiber.

Air, first bubbled through caustic soda and water, was used to aerate and stir most of the solutions. When nitrogen was used, it was purified by passing over 4 ft of copper turnings maintained at 400°C.

In tests for reversibility,[3] the same metal electrode

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[3] Reversibility not in the thermodynamic sense, but referring to reproducibility of potentials as approached from either more concentrated or more dilute solutions.

was used throughout, but for measurements of potentials as a function of concentration, different electrodes in separate cells were set up. In view of the considerable time to reach steady state, the latter arrangement was the only practical procedure. This produced a greater scatter of the data, but also made the observed correlation of potential with concentration more convincing.

POTENTIAL DATA

Iron in Chromates

Iron in contact with distilled water attains noble values of potential as K_2CrO_4 is added. At a concentration of 0.0025 molar, the potential change is about 0.5 volt (Fig. 1). Further change at higher concentrations is not pronounced. The maximum potential change agrees with data presented by Burns (25) for iron in 0.01*N* $K_2Cr_2O_7$ solution.
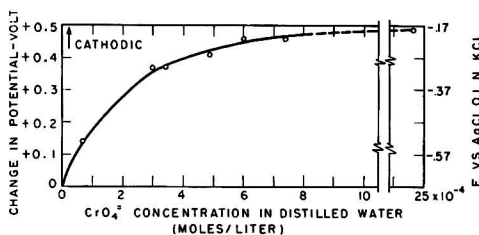
Fig. 1. Effect of $CrO_4^=$ additions on the electrode potential of electrolytic iron in distilled water; (25.0 ± 0.2°C); aerated solutions.

On first immersing the electrodes in a dilute solution of chromate, potentials are relatively active, changing to more noble values within about 2 to 4 hr. The time required is less as the concentration of chromate increases. Steady-state values in all cases were reached in less than 24 hr.

When the electrodes at steady state in 0.0025*M* chromate are transferred to progressively more dilute solutions, it is found that a maximum of half the ennobling effect of the chromate is lost. This is true even after exposure to distilled water for 41 hr.

18-8 Stainless Steel and Titanium

18-8 stainless steel corrodes in dilute sulfuric acid, but corrosion is effectively inhibited (26) on addition of small amounts of ferric or cupric salts. Similar inhibition is observed to hold for titanium (27, 28), but with the difference that the beneficial effects extend to hydrochloric acid, unlike the situation for 18-8. It is of interest, therefore, to determine the parallel potential behavior of 18-8 and titanium in sulfuric acid as these inhibitors are added. Potentials in 0.2*N* H_2SO_4 containing up to 0.191*M* ferric sulfate are summarized in Fig. 2, and for similar additions of cupric sulfate up to 0.70*M*
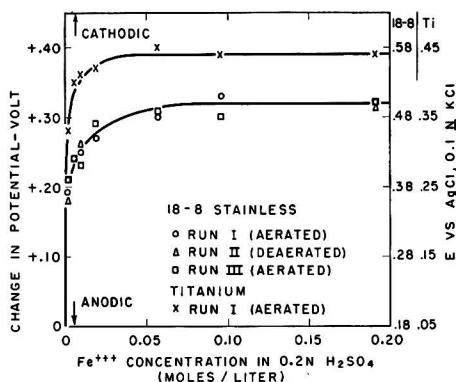
FIG. 2. Effect of Fe^{+++} additions on the electrode potentials of 18-8 stainless steel and titanium in $0.2N$ H_2SO_4; $(25.0 \pm 0.2°C)$.
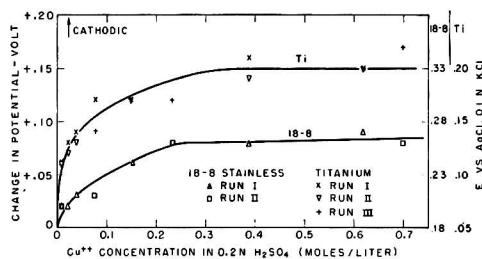
FIG. 3. Effect of Cu^{++} on the electrode potentials of 18-8 stainless steel and titanium in $0.2N$ H_2SO_4; $(25.0 \pm 0.2°C)$; aerated solutions.

in Fig. 3. Potentials of 18-8 in ferric sulfate solution, followed for several days, are found to become more noble by a maximum of 0.32 volt, whereas titanium similarly is ennobled to a maximum of 0.39 volt. Since 18-8 is initially more noble than titanium by 0.13 volt, final potentials are not far different. The general reproducibility of measurements can be gauged by a comparison of two separate runs for 18-8 in aerated solutions. In addition, one run in nitrogen-saturated solution showed that oxygen exerts no effect on the potential behavior.

Potentials of 18-8 and titanium are not reversible, as shown by data of Table I. On immersing 18-8, previously at steady state in $0.19M$ Fe^{+++}, into $0.002M$ Fe^{+++} (referring to $0.2N$ H_2SO_4), the second steady-state potential remained more noble by 0.07 volt after 27 hr of exposure than the original steady-state value of 0.18 volt. However, on re-immersing the electrode into $0.19M$ Fe^{+++}, the potential of 0.35 volt at the end of 20 hr was only 0.04 volt more noble than the original value.

With cupric sulfate additions, potential changes are less than for ferric sulfate, even though the final concentration of cupric ion is higher. Maximum ΔE averaged 0.08 volt for 18-8 and 0.15 volt for titanium.

TABLE I. *Test of reversibility*

Electrolyte	Initial ΔE (volt)	Change of concentration in moles/liter	Final ΔE (volt)
18-8			
$0.19M$ Fe^{+++} in $0.2N$ H_2SO_4	0.31		
	0.26	Decrease to 0.010	0.27 (4 hr)
	0.18	Decrease to 0.002	0.25 (27 hr)
	0.31	Increase to 0.191	0.35 (20 hr)
Titanium			
$0.70M$ Cu^{++} in $0.2N$ H_2SO_4	0.17		
	0.12	Decrease to 0.23	0.16 (1 hr)
	0.09	Decrease to 0.078	0.14 (1 hr)
	0.00	Decrease to 0.0	0.12 (1 hr)
	0.09	Increase to 0.078	0.13 (1 hr)
	0.12	Increase to 0.23	0.17 (1 hr)
	0.17	Increase to 0.70	0.19 (1 hr)
Iron			
$2.5 \times 10^{-3}M$ K_2CrO_4	0.49	Decrease to 0.0	0.25 (41 hr)
$0.35M$ NaOH in 4% NaCl	0.45		
	0.18	Decrease to 0.04	0.20 (1 hr)
	0.15	Decrease to 0.025	0.17 (1 hr)
	0.00	Decrease to 0.0	0.10 (1 hr)
	0.15	Increase to 0.025	0.17 (1 hr)
	0.18	Increase to 0.04	0.18 (1 hr)
	0.45	Increase to 0.35	0.35 (1 hr)
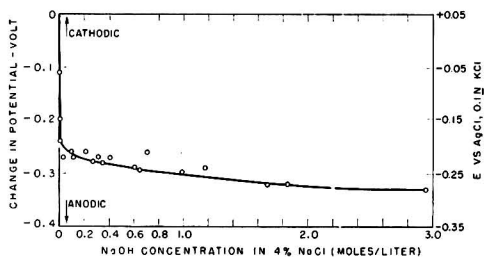
FIG. 4. Effect of NaOH additions on the electrode potential of 18-8 stainless steel in aerated 4% NaCl; $(25.0 \pm 0.2°C)$.

In aerated NaCl, 18-8 stainless steels in time corrode by pitting. Addition of alkali inhibits this type of attack (29). Titanium, on the other hand, is relatively resistant to pitting in chloride solutions without alkali additions, including sea water. The potential behavior of 18-8 in 4 % NaCl upon addition of NaOH up to 2.9 molar is shown in Fig. 4, and similarly in Fig. 5 for titanium with addition of NaOH up to 0.2 molar. Potentials were followed for a total period of about 120 hr. The remarkable difference in behavior of the metals in this electrolyte compared with previous electrolytes is that NaOH additions produce more *active* potentials, or decrease passivity as measured by potential. Effects are most pronounced with first additions of NaOH below
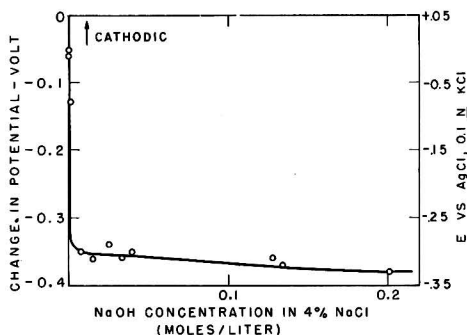
FIG. 5. Effect of NaOH additions on the electrode potential of titanium in aerated 4% NaCl; (25.0 ± 0.2°C).
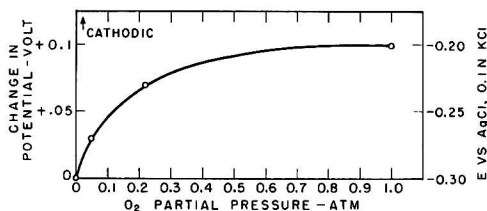
FIG. 6. Effect of varying O₂ partial pressure on the electrode potential of 18-8 stainless steel in 4% NaCl; 0.3M NaOH; (25.0 ± 0.2°C).

FIG. 7. Effect of NaOH additions on the electrode potential of electrolytic iron in 4% NaCl; (25.0 ± 0.2°C); aerated solutions.

about 0.01 molar, subsequent additions producing only slight change. The maximum change of potential for 18-8 was −0.33 volt and for titanium −0.38 volt, indicating again similar behavior of both metals.

It was also of interest to learn the effect of oxygen on the potentials of 18-8 in this system, because of the importance oxygen has with respect to passivity of stainless steels exposed to the atmosphere. Potential measurements were carried out in 4% NaCl containing 0.3M NaOH through which nitrogen, oxygen, or air was bubbled. Also, one gas mixture was prepared, containing 0.05 atm partial pressure oxygen, by compressing air and nitrogen to appropriate pressures in a single gas cylinder and using this mixture to aerate and stir the electrolyte. Results are given in Fig. 6 showing that oxygen, as expected, ennobles the potential of 18-8 as the partial pressure increases.

Potentials were also determined for iron in 4% NaCl as a function of NaOH additions. Here the potential becomes *more noble*, opposite to the trend for 18-8 or titanium (Fig. 7). About 24 hr or less were required for steady state. The values, on immersing the electrodes in several more dilute NaOH solutions after reaching steady state in 0.35M NaOH, were the same as previously determined within 0.02 volt (after one hour) and on returning the electrode to 0.35M NaOH, the potential was less noble by 0.1 volt (Table I). It is especially

significant that the potential of iron, initially active in 4% NaCl, and the potential of 18-8 initially noble, approach the same value on additions of NaOH. This suggests that the final surface states of iron and 18-8 (which contains 74% iron) in alkaline NaCl are comparable, despite large initial differences in neutral NaCl. Perhaps it is not surprising, therefore, that corrosion rates in alkaline NaCl are comparably low for both metals, but are quite different in neutral or near neutral NaCl solutions.

DISCUSSION

For each metal studied, the potential behavior as a function of passivator or inhibitor concentration resembles a typical adsorption isotherm. This relation is expected if inhibitors function by adsorbing on the metal surface, but would not be predicted, presumably, by any mechanism involving diffusion-barrier oxide or other type reaction-product films. Interpretation of the data, therefore, in terms of an adsorption process appears worthwhile.

Adsorption Isotherm and Potentials

The adsorption isotherm proposed by Langmuir (30) is expressed as follows:

$$x = \frac{abp}{1 + ap}$$

where x is the amount of gas adsorbed per unit area at pressure p, and a and b are constants. The constant b is equal to maximum adsorbate x_m at high values of p, and a is related to heat of adsorption (31). Assuming that Henry's law applies, this can be converted to a similar expression for adsorption from liquids where concentration of solute C substitutes for gas pressure p.

Furthermore, if the ions adsorbing on a metal surface form dipoles each of electric moment μ, electrostatic theory leads to the expression $4\pi n\mu$ for the total change of potential ΔE produced by n
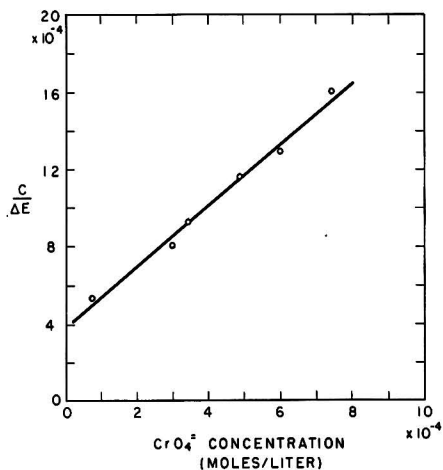
FIG. 8. Langmuir adsorption plot for electrolytic iron in distilled water containing $CrO_4^=$ inhibitor.

dipoles adsorbing per unit area of metal surface.[4] Therefore, ΔE is proportional to x, and maximum ΔE_m is similarly proportional to x_m.

Therefore, $$\frac{C}{\Delta E} = \frac{C}{\Delta E_m} + \frac{1}{a'\Delta E_m}$$

If the Langmuir isotherm applies, therefore, a linear relation should exist between $C/\Delta E$ plotted with C, the slope of which is equal to $1/\Delta E_m$, and the intercept is equal to $1/a'\Delta E_m$ at $C = 0$. Data for various inhibitor concentrations satisfactorily conform to this relation as shown by Fig. 8 to 13. Potentials for 18-8 and titanium in $0.2N$ H_2SO_4 containing Cu^{++} show a degree of scattering, caused probably by the small measured potential differences in these solutions compared with experimental variations, the maximum ΔE being only 0.08 to 0.15 volt. $C/\Delta E$ vs. C was not reproduced for Ti and 18-8 in 4% NaCl $+$ NaOH, even though linearity is obtained for all but the lowest NaOH concentrations. The test of linearity, however, loses significance when values of ΔE are essentially

[4] If one considers a supplementary diffuse double layer in accord with Gouy and Chapman, the additional potential change equals $4\pi\sigma/D\kappa$ (32) where σ is the total electric charge per unit area, D is the dielectric constant, and κ is equal to $(4\pi e^2/DkT [\Sigma n_i z_i^2])^{\frac{1}{2}}$ having the same significance as in the Debye-Hückel theory of electrolytes. Since κ has the dimensions of reciprocal length and may be identified with the effective separation of charges in the dipole layer, this expression, if $D = 1$, achieves the same form as the expression for a fixed dipole layer.

Adsorption of ions can be looked upon as forming new cathodic areas, the extent of which reaches a maximum at completion of a monolayer. Anodic areas are simultaneously restricted to a minimum corresponding to maximum anodic polarization by corrosion currents and a shift of potential to more noble values.
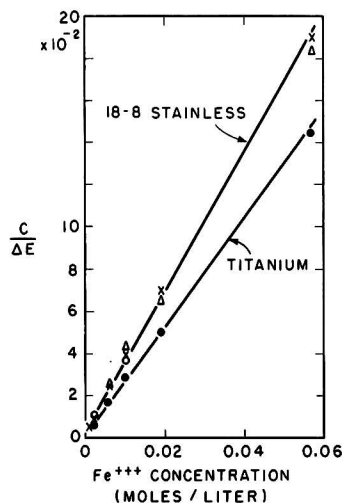
FIG. 9. Langmuir adsorption plot for 18-8 stainless steel and titanium in $0.2N$ H_2SO_4 containing Fe^{+++} inhibitor.
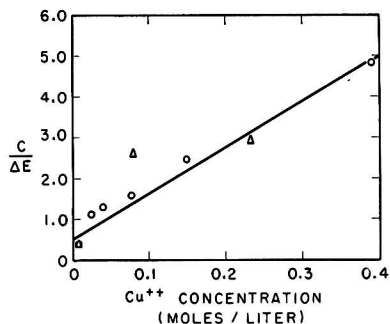
FIG. 10. Langmuir adsorption plot for 18-8 stainless steel in $0.2N$ H_2SO_4 containing Cu^{++} inhibitor.
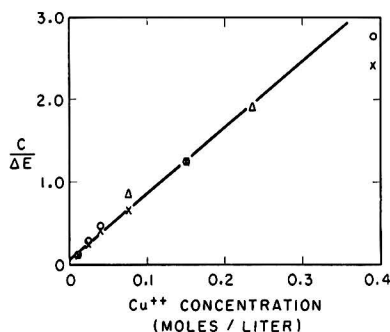
FIG. 11. Langmuir adsorption plot for titanium in $0.2N$ H_2SO_4 containing Cu^{++} inhibitor.

constant with change of inhibitor concentration, as is true in this instance.

Correspondence, by and large, of potential data to the Langmuir type isotherm points strongly to
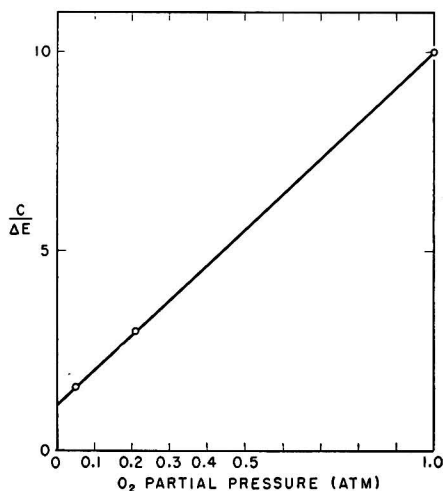
FIG. 12. Langmuir adsorption plot for 18-8 stainless steel in 4% NaCl with 0.3M NaOH, varying O₂ partial pressure.

FIG. 13. Langmuir adsorption plot for electrolytic iron in aerated 4% NaCl with NaOH additions.

the view that the inhibitors considered at present function by adsorbing on the metal surface. Furthermore, the observed correspondence suggests adsorption of the monolayer type, as was pointed out by Langmuir in the derivation of his isotherm equation. These conclusions are strengthened by measurements of Hackerman and Sudbury (33), showing that potentials of steel in contact with organic amine inhibitors also follow the Langmuir adsorption isotherm. The linearity of $C/\Delta E$ vs. C reported by them is especially significant, since it is generally conceded that organic inhibitors function by adsorbing on the metal surface (34, 35).

Maximum potential change, in accord with present considerations, occurs with formation of a complete monolayer of chemisorbed ions, any additional adsorption being accompanied by relatively small potential changes and lesser effects on the corrosion rate. It is important to note, therefore, that maximum change of ΔE in Fig. 1 for iron in chromates occurring at 2.5×10^{-3} molar, corresponds approximately to the minimum concentration of chromates (1×10^{-3} molar) found necessary by Robertson (8) for inhibition and passivity. It is probably reasonable to conclude, therefore, that optimum passivity is associated with a monolayer film of adsorbed chromate ions.

Part of the adsorbed chromate is chemisorbed and part is reversibly adsorbed, as is pointed out by the time necessary to achieve steady-state potentials, indicative of the usually longer times required for chemisorption, and by the partially irreversible nature of the potentials. Even after thorough washing in distilled water, iron passivated in radio-

active chromates shows residual radioactivity (19, 21, 24), and the potential is more noble than initially. The final irreversible or chemisorbed portion exerts about half the total effect on the potential. This result is in agreement with a similar observation of Gatos (36) who found that, on first immersing iron in chromate solutions, the amount of metal reacting initially when iron is made passive in concentrated nitric acid is less than in absence of chromate exposure, and that half this effect of chromate, but no more, could be removed by washing in water.

Powers and Hackerman (24) suggested adsorption of chromate ions on a surface oxide rather than on the metal. Although such adsorption presumably may occur, any mechanism of corrosion protection accompanying a film of this kind is not yet clear. An air-formed film, at least, is not necessary to adsorption. Preliminary measurements in this laboratory using radiochromate showed that the usual radioactivity is picked up by oxide-free Armco iron sheet (0.024 % C). Iron specimens were heated in dried pure H₂ at 1000°C, cooled in this gas, transferred to deaerated $10^{-3}M$ Cr⁵¹O₄, pH 1.9, out of contact with air, and after 2 to 17.5 hr, washed successively in three 200-ml portions of distilled water. Somewhat greater residual chromium (3×10^{16} atoms/cm²) was found than that reported by Brasher and Stove and by Hackerman and Powers for abraded iron. No residual radioactivity was found on similar specimens immersed directly into deaerated radioactive chromic perchlorate of pH 1.9.

Adsorption of Oxygen and Ferric, Cupric, and Hydroxyl Ions

Presumably, ferric and cupric ions also adsorb on 18-8 and titanium, producing passivity as gauged by reduced corrosion rates or noble potentials. Ions have a certain electron affinity and when adsorbed receive a certain amount of negative charge from the metal. The net effect, including the effect of negative ions in solution, is an over-all negatively charged ion layer near the surface and an equal positive image charge in the metal, similar to the situation for chromates. This accounts for increasingly noble potentials as more ferric and cupric ions adsorb, trivalent ferric ion being more effective in this respect than divalent cupric ion, corresponding also to the order of inhibition in dilute sulfuric acid (27).

The more active potentials of titanium and 18-8 in sodium chloride solution on addition of sodium hydroxide can be interpreted as competition between hydroxyl ion and oxygen for a place on the metal surface, the adsorbed hydroxyl ion producing a lower order dipole moment than adsorbed oxygen. Chemisorbed oxygen, according to one viewpoint, is primarily responsible for passivity (5, 37, 38) in these metals. If the partial pressure of oxygen is increased, the potential becomes more noble (Fig. 6) in agreement with this view. The potential change from 0 to 1 atmosphere oxygen amounts to only 0.1 volt, suggesting that the fundamental passive layer of chemisorbed oxygen in alkaline NaCl is only slightly disturbed by hydroxyl ions. This concurs with the observation that apparent equilibrium in this instance is effected between dissolved gas and molecularly adsorbed oxygen and not atomically adsorbed oxygen, as shown by the linearity of $p/\Delta E$ plotted with p but lack of linearity plotting $\sqrt{p}/\Delta E$ vs. $\sqrt{p}$, where p refers to partial pressure of oxygen. Previous quantitative adsorption data obtained for oxygen on 18-8 (39) provided evidence, in fact, that the alloy exposed two days to aerated water is covered by a close packed atomic oxygen layer over which a molecular oxygen layer is adsorbed. Were the chemisorbed atomic oxygen on 18-8 entirely displaced by OH^-, the potential change would be in the order of 0.5 volt, corresponding to complete breakdown of passivity, but a potential change of 0.4 volt occurs only in concentrated alkalies, e.g., 20% NaOH (40).

When iron, on the other hand, is immersed in alkaline NaCl, competition includes not only adsorbed OH^- and oxygen, but also adsorbed H. Iron exposed to an aqueous solution has a definite tendency to react, liberating hydrogen and hydrous ferrous oxide, the free energy for the reaction being negative (41) and independent of pH, so long as

these corrosion products form and no other. Hydrogen so produced adsorbs on the iron surface and, in neutral or alkaline solutions, escapes reluctantly as H_2 impeding corrosion reaction. With presence of dissolved oxygen, adsorbed hydrogen reacts to form water as rapidly as oxygen reaches the metal surface. If, however, rate of consumption falls below the diffusion rate to the surface, excess oxygen, in turn, can adsorb on the metal. This adsorption, when it occurs, is accompanied by a lowered corrosion rate and a more noble potential (passivity). Therefore, as hydroxyl ions are added to the solution, adsorbed H is increasingly displaced by OH^- and reaction of the former with dissolved oxygen slows down. Consequently, oxygen is in excess at the surface, and conditions are favored for its adsorption. Support of this state of affairs is provided by the observation that, in absence of oxygen, the potential of iron in water is more active when alkalies (42, 43) are added, as is expected from the reduced solubility of $Fe(OH)_2$ under these conditions. Only in presence of oxygen does the potential become more noble, the measured potential being a compromise between the iron and oxygen electrode values. In acid media, on the other hand, the iron electrode covered with adsorbed hydrogen behaves approximately as a reversible hydrogen electrode (44, 45). Since iron and 18-8 have about the same potential in aerated alkaline NaCl, the inference is that if oxygen is chemisorbed on 18-8, it is also, under these conditions, chemisorbed on iron and is responsible for observed passivity in both metals. The energy of bonding of oxygen to the metal need not be the same in both cases, however, and, therefore, the degree of passivity may differ.

Powers and Hackerman showed that competitive adsorption of CrO_4^{--} and OH^- takes place on Cr (46) and iron (24) surfaces, similar to competitive adsorption of H, O_2, and OH^- described above.

Pitting Tendencies of 18-8 and Titanium

Inhibition of pitting in 18-8 by hydroxyl ion can be accounted for by the reduced difference of potential between active and passive areas in the galvanic cells that account for pitting (47), since the passive areas are no longer so noble as before. In addition, metal chlorides at incipient pits react with hydroxyl ions which migrate rapidly to anodic areas to form metal hydroxides. Hydroxides, unlike soluble chlorides, do not continuously destroy passivity or, what is the same, do not maintain activity at the site of chemical disturbance; hence, the pit never gets started. With titanium, pitting tendency is decreased by the pronounced tendency of titanium chloride to hydrolyze to hydroxide or hydrous oxide even in absence of hydroxyl ions.

Hence, titanium, better than 18-8, resists pitting in sea water, and potential data indicate that in alkaline salt solutions, the tendency would be still less.

Separation of Charge in Dipole Layer

Values of ΔE in combination with the equation $\Delta E = 4\pi n \mu$ make it possible to calculate the average separation of negative charge in the adsorbed chromate layer from the iron surface. Assuming a diameter of chromate ion equal to 5.4 Å, there will be 4.0×10^{14} ions/cm² adsorbed in a close packed monolayer. A layer based on true surface rather than apparent area would still be equivalent in projected dipole moment to this number of ions. Since the change of potential produced by a monolayer is 0.5 volt (Fig. 1), the calculated value of d, where μ is equal to de (d = separation of negative and positive charge, and e = electronic charge), is $0.5/(300 \times 4\pi \times 4 \times 10^{14} \times 4.8 \times 10^{-10})$ or 0.07×10^{-8} cm. Hence, the excess electrons, according to this calculation, are, on the average, only 0.035×10^{-8} cm from the metal surface, since the positive image charge within the metal is at a similar distance from the surface. In other words, a relatively slight asymmetry of electron density at the metal surface suffices to explain the observed adsorption potentials.

Values of Langmuir Constants

Values of the Langmuir constants ΔE_m and a' are summarized in Table II. In general, ΔE_m calculated from the slope of $C/\Delta E$ vs. C agrees reasonably well with the observed maximum ΔE_m. For iron in alkaline NaCl, the difference in values suggests that potential relations are more complex than the simple adsorption of oxygen alone, in accord with the discussion of iron potentials above.

Values of a' are equal to the reciprocal of the concentration at which half the maximum potential shift is obtained. According to the Langmuir derivation, these values are larger as the heat of adsorption increases. Hence, O_2 on 18-8 and chromates on iron show appreciable affinity of adsorbate for metal. Similarly, ferric ions have greater affinity for 18-8 and titanium than cupric ions. The low value of a' for iron in alkaline NaCl supports the point of view that competitive chemisorption takes place between several species, e.g., H, OH^-, and O_2, heats of adsorption for one species tending to cancel out heats of desorption for the species it displaces. Competition between possible adsorbates very likely accounts for the partial reversibility of potentials involving chemisorbed films. In general, it should be emphasized that values of a' reflect a resultant heat effect of one or more

TABLE II. *Values for constants of Langmuir adsorption isotherm*

Electrode	Electrolyte	E vs. AgCl, 0.0N inhib., volt	ΔE_m (volt)		Intercept a'^{-1} ΔE_m^{-1}	a' (liters/mole)
			(calc)	(obs)		
18-8	Fe^{+++} in 0.2N H_2SO_4	0.18	0.30	0.33	0.001	3300
	Cu^{++} in 0.2N H_2SO_4	0.18	0.09	0.08	0.5	22
	O_2 in 0.3N NaOH in 4% NaCl	−0.30	0.11	0.1	0.0011	8400
Ti	Fe^{+++} in 0.2N H_2SO_4	0.05	0.37	0.38	0.001	2700
	Cu^{++} in 0.2N H_2SO_4	0.05	0.13	0.15	0.15	50
Fe	OH^- in aerated 4% $NaClCrO_4^{--}$ in H_2O	−0.78	0.26	0.46	0.065	59
		−0.67	0.63	0.5	0.00039	4000

competitive adsorption processes, even if the substance displaced is nothing more than physically adsorbed H_2O. The primary process, of course, has the largest effect. By and large, relative values of a' are in accord with the expected trend based on chemical properties of the metals and adsorbates.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1954 issue of the JOURNAL.

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Contribution to the Theory of Electropolishing[1]

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ABSTRACT

An ideal electropolishing process is characterized by a plateau of the current density-potential curve corresponding to the maximum diffusion rate of an acceptor for metal ions toward the anode. Such a process is amenable to a quantitative theoretical analysis. Formulas are derived for decrease of surface roughness as a function of the recess of the average surface, amount of metal dissolved per unit surface area, and product of current density and time.

INTRODUCTION

Jacquet (1) and others have shown that a plot of current density J vs. cell voltage or anode potential E gives a horizontal plateau for many solutions used in electropolishing processes. Such a curve is found whenever the diffusion of one reactant consumed by an electrode process is the controlling factor, i.e., the concentration of the reactant at the surface of the electrode is much less than its bulk concentration, and the effective thickness of the hydrodynamic boundary layer has a definite value determined by forced or natural convection. In particular, a limiting current density is observed for the electrodeposition of metals at a cathode. Kolthoff and Miller (2) have also observed a limiting current density for the anodic dissolution of mercury if the diffusion of complexing ions such as $S_2O_3^{--}$, SO_3^{--}, CN^-, and SCN^- is the limiting factor.

Elmore (3) has interpreted the occurrence of a limiting current density for the anodic dissolution of a metal by assuming that the solution at the surface of the anode is saturated with respect to a salt of the dissolving metal, and the current density is determined by the diffusion rate of metal ions from the surface of the electrode into the bulk solution. This interpretation, however, is contradictory to the fact that the potential of the anode can be varied within rather wide limits, e.g., between 0.25 and 1.5 volt for copper in 86% H_3PO_4 according to Walton (4), whereas a constant concentration of metal ions at the anode and a constant current density are compatible only with a constant electrode potential.

According to Edwards (5, 6), the plateau of the current density-potential curve is due to diffusion of an "acceptor" for metal ions toward the anode. When silver is electropolished in a cyanide bath (7), cyanide ions are the acceptor forming $Ag(CN)_2^-$. In highly concentrated phosphoric or perchloric

acid, the acceptor may be water whose significance has been discussed particularly by Darmois, Epelboin, and Amine (8). Water is needed for the formation of hydrated cations such as $Cu(OH_2)_4^{++}$. A limiting value of the current density corresponds to a maximum concentration gradient when practically all the acceptor approaching the anode readily reacts with metal ions, and thus the acceptor concentration at the anode is much lower than the bulk concentration. This interpretation of the plateau of the current density-potential curve implies that either the standard free energy of nonhydrated cations is much higher than that of hydrated cations, or the activation energy for the formation of nonhydrated cations is considerably greater than the activation energy for the formation of hydrated cations. A process satisfying these conditions will be called an "ideal electropolishing process."

MATHEMATICAL ANALYSIS OF AN IDEAL ELECTROPOLISHING PROCESS

Consider a sine-wave profile surface shown in Fig. 1 with a wave length, a, and an amplitude, b. At the surface of the electrode the concentration, c, of the acceptor determining the dissolution rate is supposed to vanish. Thus

$$c = 0 \text{ at } y = b \sin (2\pi x/a) \qquad \text{(I)}$$

where y is the distance from the "average surface plane" of the anode indicated by the dotted line in Fig. 1, and x is the coordinate parallel to the average surface plane.

If the dimensions a and b are much smaller than the effective thickness of the hydrodynamic boundary layer, only the innermost part of the boundary layer has to be considered, and thus flow of the liquid in the x or y direction may be neglected, since the velocity components at the surface of the electrode vanish. Then Fick's second law applies.
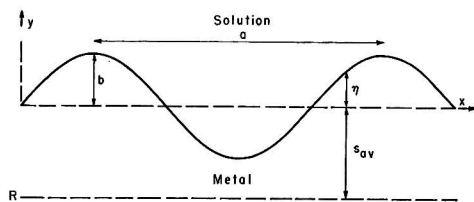
FIG. 1. Sine-wave profile electrode

FIG. 2. Schematic graph of acceptor concentration as a function of distance from the electrode.

For steady-state conditions it follows that

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}\right) = 0 \qquad \text{(II)}$$

where D is the diffusion coefficient of the acceptor.

Edwards (5, 6) has already obtained solutions of equation (II) by determining experimentally the distribution of the electrical potential in a trough, involving a large scale model of the electrode, filled with tap water, and using the similarity between differential equations and boundary conditions for the concentration and the potential field. To arrive at general conclusions, it seems profitable to consider an analytical solution of equation (II). A particular solution reads

$$c(x, y) = B[y - b \exp(-2\pi y/a) \sin(2\pi x/a)] \quad \text{(III)}$$

where B is a constant. If $b \ll a$, equation (III) virtually satisfies the boundary condition in equation (I) as is verified by substituting $y = b \sin(2\pi x/a)$ in equation (III) and letting the exponential function be unity as a close approximation since the exponent tends to zero for $b/a \to 0$.

Differentiation of equation (III) with respect to y yields

$$\partial c/\partial y = B[1 + (2\pi b/a) \exp(-2\pi y/a) \\ \sin(2\pi x/a)]. \qquad \text{(IV)}$$

From equation (IV) it follows that the concentration gradient becomes virtually independent of x and y at some distance from the electrode, i.e., if $y \gg a$. Furthermore, the constant B is found to be equal to the average value of the concentration gradient at the anode, $(\partial c/\partial y)_{\text{avg}}$. A linear dependence of concentration on distance y will be found only in the innermost part of the boundary layer where flow of liquid can be neglected. A schematic concentration distribution for the entire boundary layer is shown schematically in Fig. 2. The effective thickness of the boundary layer, δ, may be defined as the distance of the intersection of the tangent line on the c vs. y curve at $y = 0$, $x = 0$ and the extrapolated plateau of the bulk concentration c_o. Since equations (III) and (IV) presuppose a virtually constant concentration gradient at $y \gg a$, e.g., $y > 4a$, and thus the region $y < 4a$ must belong to the innermost
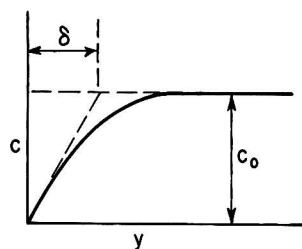
boundary layer, the effective thickness must be much greater than the wave length of the electrode profile. This is a necessary condition for the validity of equation (III) and subsequent equations derived therefrom.

Upon substituting $y = b \sin(2\pi x/a)$, expanding the exponential function, and neglecting terms involving higher powers of (b/a) except for the first power, the concentration gradient at the surface in the y direction is found to be

$$\left(\frac{\partial c}{\partial y}\right)_{y=b \sin(2\pi x/a)} \cong \left(\frac{\partial c}{\partial y}\right)_{\text{avg}} \left[1 + \frac{2\pi b}{a} \sin(2\pi x/a)\right] \text{ (V)}$$

$$\text{if } b \ll a, \qquad a \ll \delta$$

In view of the condition $b \ll a$, we may disregard the difference between the concentration gradient normal to the average surface plane and that normal to the local surface, e.g., at $x = 0$ and $x = \frac{1}{2}a$.

Next, consider the change in the shape of the surface profile as a function of time, t. Let η be the distance of a point at the surface from the average surface plane, and s_{avg} the distance of the average surface plane from the reference plane, R, inside the electrode (see Fig. 1). Then the distance of a point at the surface of the electrode from the reference plane, R, equals

$$s = s_{\text{avg}} + \eta \qquad \text{(VI)}$$

where

$$\eta = b \sin(2\pi x/a). \qquad \text{(VII)}$$

Decrease of distances s and s_{avg} per unit time is proportional to the local and to the average dissolution rate, i.e., proportional to the local and the average concentration gradient of the acceptor, respectively. Thus, in view of equation (V)

$$-ds/dt = C[1 + (2\pi b/a) \sin(2\pi x/a)] \qquad \text{(VIII)}$$

$$-ds_{\text{avg}}/dt = C \qquad \text{(IX)}$$

where C is a constant, which is equal to the product of the average concentration gradient, the diffusion

coefficient, and the volume of the metal reacting with one mole of the acceptor. Upon substituting equation (VI) in equation (VIII) and subtracting corresponding sides of equations (VIII) and (IX), it follows that

$$-d\eta/dt = C(2\pi b/a) \sin (2\pi x/a). \qquad \text{(X)}$$

Decrease of the distance s_{avg} of the average surface plane from the reference plane, R, is equal to the displacement, u, of the average surface plane with respect to its position at time $t = 0$. Thus

$$-ds_{\text{avg}} = du. \qquad \text{(XI)}$$

Dividing corresponding sides of equations (X) and (IX) and substituting equations (VII) and (XI), one obtains

$$-db/du = 2\pi b/a. \qquad \text{(XII)}$$

Upon integration, it follows that

$$b = b_0 e^{-2\pi u/a} \quad \text{if} \quad b \ll a,\, a \ll \delta \qquad \text{(XIII)}$$

where b_0 is the amplitude of the sine-wave surface profile at zero time and b is the amplitude at time, t, corresponding to the displacement, u, of the average surface plane.

From equation (XIII) we readily recognize that percentagewise the amplitude of short sine waves will decrease far more rapidly than the amplitude of long sine waves. In other words, "microroughness" will disappear more rapidly than "macroroughness" in accordance with many observations.

A triangular wave profile or any other periodic profile may be represented by a superposition of sine waves of different wave lengths and amplitudes as a Fourier series. During electropolishing the contributions of the shorter waves disappear more rapidly, and thus the profile approaches a sine wave profile involving the greatest wave length of the original pattern. This is in accord with results reported by Edwards (5, 6).

From equation (XIII) it follows that the displacement, u, for a decrease of the amplitude from b_0 to b is

$$u = a[\ln(b_0/b)]/2\pi. \qquad \text{(XIV)}$$

The corresponding loss of metal per unit area, $\Delta m/A$, is found to be

$$\Delta m/A = u\rho = a\rho[\ln(b_0/b)]/2\pi \qquad \text{(XV)}$$

where ρ is the density of the metal.

From a copper electrode having a sine-wave profile with a wave length of 0.0134 cm, which was investigated by Edwards (5, 6), one has therefore to remove 0.013 gram/cm² in order to obtain a decrease of the amplitude to half the initial value. This value is in accord with results reported by Edwards for the later stages of experiments when his samples had a nearly sine-wave profile.

The corresponding number of coulombs per unit area, equal to the product of current density, J, and time, t, is found to be

$$J(\text{amp/cm}^2)t(\text{sec})$$
$$= \frac{96{,}500}{EqW} \frac{a(\text{cm})\rho(\text{g/cm}^3)}{2\pi} \ln \frac{b_0}{b} \qquad \text{(XVI)}$$

where 96,500 is the numerical value of the Faraday constant in coulomb/equivalent and EqW is the equivalent weight of the metal. For copper, e.g., 96 coulombs are required in order to decrease the amplitude by a factor of 10 if the wave length is 0.01 cm.

The foregoing analysis is that of an ideal electropolishing process. The following complications may occur.

1. If the amplitude, b, is not much smaller than the wave length, a, equation (III) does not satisfy equation (I). Qualitatively, the foregoing conclusions remain valid, but a rigorous mathematical analysis would require the replacement of the one-term expression in equation (III) by a Fourier series.

2. If the wave length, a, is not much smaller than the thickness of the boundary layer, the decrease in amplitude will be less than calculated from equation (XIII). This can be readily recognized from a consideration of the extreme case that the thickness of the wave length of the profile is much greater than the effective thickness of the boundary layer. In this case no differences in the local diffusion rate of the acceptor can be expected. Since according to equation (XIII) electropolishing removes microroughness more rapidly than macroroughness if $a \ll \delta$, the case $a \gtrsim \delta$ is not of great interest, especially when the viscosity of the solution is rather high and, therefore, δ is fairly large, e.g., 0.1 cm.

3. In solutions consisting mainly of perchloric or phosphoric acid, enrichment of salt and depletion of water increase viscosity. Accordingly, the diffusion coefficient may not be constant. Under these conditions, equation (II) has to be replaced by a more involved expression and the foregoing analysis has only qualitative significance.

4. Further complications may be caused by the evolution of gas bubbles and, eventually, local variations of the reactivity of the dissolving metal, especially in the case of heterogeneous alloys so that equation (I) is not satisfied at all points of the surface of the electrode.

INTERPRETATION OF ETCHING

For a comparison, consider the behavior of an anode at which polarization is supposed to be negligible. Then the electrical potential φ along the surface is constant and may be set equal to zero as the reference potential. Using the notation introduced in Fig. 1 and equation (I), we have for a sine-wave profile anode

$$\varphi = 0 \text{ at } y = b \sin (2\pi x/a). \qquad \text{(XVII)}$$

Inside the electrolyte, the Laplace equation

$$\partial^2\varphi/\partial x^2 + \partial^2\varphi/\partial y^2 = 0 \qquad \text{(XVIII)}$$

holds. Consequently, we obtain the potential gradient at the surface of the anode in a form analogous to that for the concentration gradient indicated in equation (V),

$$\left(\frac{\partial\varphi}{\partial y}\right)_{y=b\sin(2\pi x/a)}$$
$$\cong \left(\frac{\partial\varphi}{\partial y}\right)_{\text{avg}} \left[1 + \frac{2\pi b}{a} \sin (2\pi x/a)\right] \qquad \text{(XIX)}$$
$$\text{if } b \ll a, \qquad a \ll \delta.$$

The local current density, J, is proportional to the local potential gradient according to Ohm's law. In view of the similarity between equations (V) and (XIX), equations (XIII) to (XVI) will hold if polarization is negligible. Consequently, the amplitude of a given roughness will decrease in the same manner as in the case of diffusion of an acceptor as the factor determining the local dissolution rate. Actually, however, polarization is not negligible. If the wave length a is small in comparison to the parameter k defined as the product of electrical conductivity and the absolute slope of the potential-current density curve, the current density

is far more uniform than according to equation (XVIII) for vanishing polarization (9).

For $a < 0.01$ cm and a current density J lower than the plateau of the J vs. E curve, we have $a \ll k$ and thus we have to expect a practically uniform current density if k is uniform, i.e., the slope of the current density-potential curve is the same at all points of the anode. At different crystallographic faces, however, the magnitude of activation polarization for the anodic dissolution of a metal is different, as is known from investigations involving single crystals (10). This corresponds to local variations of the slope of the current density-potential curve and the parameter k. Thus, different crystallographic faces dissolve at different rates, i.e., we observe electrolytic etching.

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Potentiometric Titration of Simple Salts with Potassium in Liquid Ammonia[1,2]

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ABSTRACT

By means of potentiometric titration of solutions of salts with solutions of potassium in liquid ammonia at $-38°$, it has been shown that bismuth(III) iodide is reduced to Bi^0, K_3Bi_3, and K_3Bi_5 without intermediation of either the $+2$ or $+1$ oxidation state of bismuth. Reduction of iron(II) bromide is very complex and apparently does not involve the intermediate formation of Fe^{+1}. Reduction of potassium nitrate involves only reduction of nitrate ion to nitrite ion, followed by precipitation of potassium hydronitrite. Data relative to reduction of cobalt(II) nitrate have permitted a choice between two possible reduction mechanisms previously proposed. Data presented in this paper clearly demonstrate the usefulness of the potentiometric titration technique in the study of the mechanism of inorganic reduction reactions in ammonia.

INTRODUCTION

In an earlier report (1), equipment and procedures useful in carrying out potentiometric titrations involving solutions of metals in liquid ammonia were described. Subsequently, these techniques have been applied to detection of intermediate oxidation states of Group III nontransitional elements with particular emphasis on aluminum (2–4).

Experiments described in this paper were carried out for the purpose of determining whether the potentiometric titration method might be useful in elucidating the mechanism of reduction of simple inorganic salts with solutions of metals in ammonia. For this purpose, halides and nitrates of two transitional and two nontransitional elements were employed, and the specific cases selected were deliberately ones studied previously by less exacting methods.

EXPERIMENTAL

Materials.—With the exceptions noted below, all materials employed in this work were reagent grade chemicals that were used without further treatment.

Bismuth(III) iodide was prepared in 72% yield by a method described elsewhere (5). Analysis calculated for BiI_3: Bi, 35.4. Found: Bi, 35.4. X-ray diffraction data for this product are listed in Table I.

Iron(II) bromide (as the 6-ammonate) was prepared as described by Watt and Jenkins (7).

Reagent grade potassium nitrate was recrystallized from water and dried to constant weight at 110°C.

Ammonated cobalt(II) nitrate was prepared by displacement of water of hydration with ammonia by recrystallization from liquid ammonia as follows. Cobalt(II) nitrate 6-hydrate was converted to the corresponding 2-hydrate by drying *in vacuo* over concentrated sulfuric acid. A 1-gram sample of the very finely divided 2-hydrate was placed on the fritted glass disk of a filter tube[5] and that end of the tube was sealed about 3 in. from the disk. The tube was cooled, inverted, air in the tube was displaced with ammonia gas, the end of the tube containing the salt was immersed in a dry ice-isopropanol bath at $-70°C$, and 3 to 4 ml of ammonia was condensed on the salt. The open end of the tube was then sealed, also about 3 in. from the filter disk. The tube was removed from the bath and allowed to warm to and remain at room temperature for three days. The saturated solution was then transferred by inverting the tube and immersing the empty end in a refrigerant bath at $-70°C$. When the temperature of this solution was allowed to return to *ca.* 25°, a small crop of well-defined pink crystals separated. In this manner, transfer of the solution and removal of crystals was repeated until a major portion of the salt had been crystallized from the ammonia solution. In the final transfer, the ammonated salt was retained on the filter disk and the solution was contained in the end containing the original sample. The tube was opened, the ammonia was allowed to

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[5] Ace Glass Company filter tube, porosity B, 10 mm ID.

TABLE I. *X-ray diffraction data for bismuth (III) iodide*

This work*		Literature†	
d, A	I/I₁	d, A	I/I₁
7.03	<0.1	3.25	0.7
5.97	<0.1	3.00	1.0
5.17	0.1	2.53	0.7
3.85	0.2	2.27	0.7
3.32	1.0	2.15	1.0
2.57	0.3	2.07	0.9
2.19	0.4	1.96	0.9
1.98	0.1	1.87	1.0
1.83	0.1	1.81	1.0
1.66	<0.1	1.29	0.7
1.40	0.1	1.25	0.7
1.36	0.1	1.10	0.7
1.32	0.1	1.09	0.7
1.07	<0.1	1.03	0.7
		1.02	0.7‡

* Data obtained using Cu K_α radiation, Ni filter, 30-kv tube voltage, 15-ma filament current, and 4-hr exposure.

† These data are taken from the ASTM Index of X-ray Diffraction Patterns and are attributed to Caglioti (6). Lack of agreement between our data and those of Caglioti is obvious and it is concluded that his data are in error since both interplanar spacing and relative intensity data for several different samples prepared in connection with the present work were in excellent agreement. More recently, in entirely independent experiments, these data have been confirmed by Phillip S. Gentile of this laboratory.

‡ Spacings corresponding to relative intensities <0.7 are not included.

evaporate, residual ammonia was displaced with dry, oxygen-free nitrogen, and the tube was transferred to a dry box wherein all subsequent sampling of the ammonated salt was done in an atmosphere of nitrogen. Analysis: calculated for $Co(NO_3)_2 \cdot 6NH_3$: Co, 20.6; NH_3, 35.8; calculated for $Co(NO_3)_2 \cdot 5NH_3$: Co, 22.0; NH_3, 31.7. Found: Co, 20.0; NH_3, 33.0. The composition indicated by these data is $Co(NO_3)_2 \cdot 5.7NH_3$.

Experimental methods.—With but one exception, equipment and methods used in this work were substantially the same as those described earlier (1). In a typical case, the solution to be titrated consisted of the salt in question dissolved in anhydrous liquid ammonia. Into this solution was immersed a platinum reference electrode and a differential electrode comprising a platinum wire immersed in a solution having the same composition as the solution to be titrated, and connected to the main body of this solution by means of a capillary tube. The differential electrode was connected to the positive terminal of the potentiometer.

The exception referred to above was concerned with titrations involving nitrate solutions. For these, a reference electrode comprising the half-cell: Cu; $Cu(NO_3)_2 0.1N$, KNO_3 (satd.), of the type used by Pleskov and Monossohn (8) was employed. This

change was incorporated when use of the usual platinum reference electrode gave anomalous results that are currently being further investigated.

The alkali metal used was potassium in all cases, and the titrations were carried out at $-38 \pm 1°C$. *Bismuth(III) iodide.*—In a typical experiment, a solution of 0.2298 gram of bismuth(III) iodide in 40 ml of liquid ammonia was titrated with a $0.0975N$ potassium solution. A black precipitate formed upon the first addition of potassium solution, and the reaction mixture assumed a purple color after addition of 17 ml of potassium solution. Total time required for this particular titration was 12 hr; data are shown in Fig. 1. In other titrations that differed only with respect to concentrations of reactants used, somewhat different results were obtained. For example, titration of 0.3485 gram of bismuth(III) iodide in 46 ml of ammonia with $0.0773N$ potassium solution over a period of 7 hr gave the data shown in Fig. 2. Results of the type shown in Fig. 1 and 2 were confirmed both with and without the use of potassium iodide as a supporting electrolyte.

In a related case, 0.0410 gram of potassium dissolved in 50 ml of liquid ammonia was titrated with a saturated solution of bismuth(III) iodide in liquid ammonia (0.2574 gram BiI_3 in 51.0 ml NH_3). Use of these conditions was dictated by limitations imposed by the capacity of available equipment and by solubility relationships; as a consequence, results
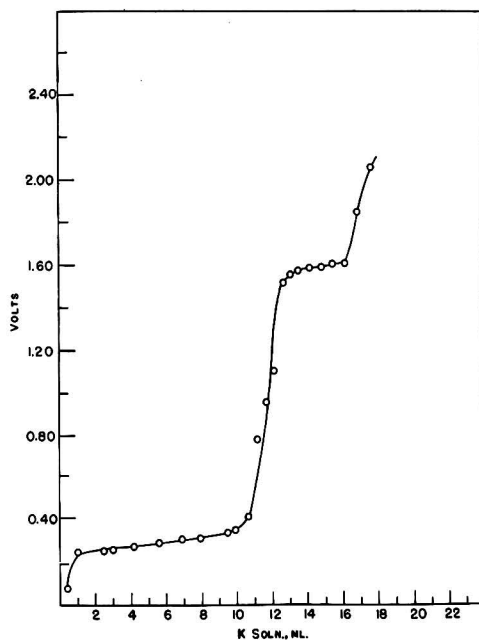
Fig. 1. Potentiometric titration: bismuth(III) iodide with potassium.
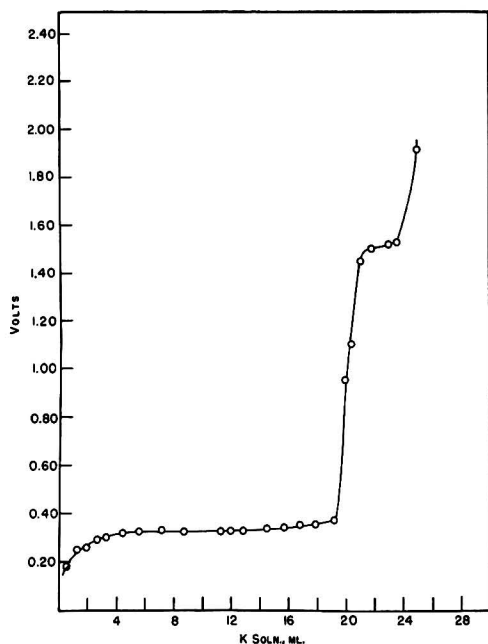
FIG. 2. Potentiometric titration: bismuth(III) iodide with potassium.
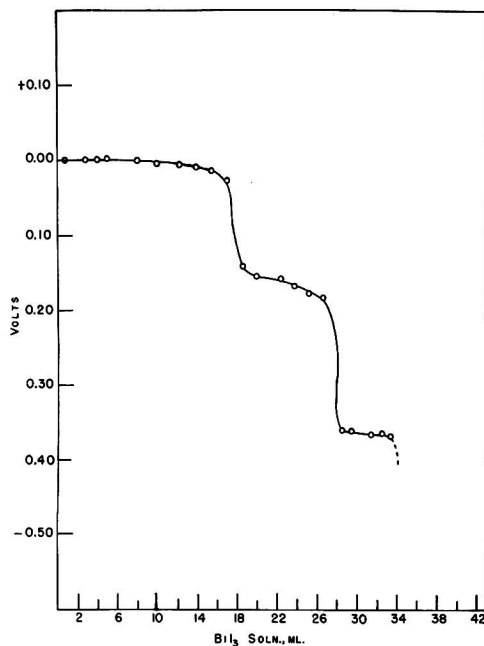
FIG. 3. Potentiometric titration: potassium with bismuth(III) iodide.

FIG. 4. Potentiometric titration: potassium nitrate with potassium.

must be interpreted on the basis of internal agreement rather than on an absolute basis. Complete titration required 7 hr; data are given in Fig. 3. The characteristic blue color of potassium solution was replaced by a distinct purple color after addition of 18.3 ml of saturated bismuth(III) iodide solution. After 33 ml had been added, the purple color decreased in intensity and the presence of a black precipitate was observed.

Iron(II) bromide.—Iron(II) bromide 6-ammonate (0.0917 gram) in 50 ml of liquid ammonia was titrated with 0.0449N potassium solution over a period of 6 hr. Early stages of the titration were characterized by erratic emf values; after 8.3 ml of potassium solution had been added, a progressive, but at no time abrupt, increase in potential began and amounted to a total change of 700 mv by the time 15.9 ml of potassium solution had been added. The characteristic blue color of potassium solution was not observed, even though an excess of almost two gram-atoms of potassium/mole of bromide was added.

Potassium nitrate.—A solution of 0.0332 gram of potassium nitrate in 45 ml of liquid ammonia was titrated with 0.0969N potassium solution. As titration proceeded over a period of 29 hr, the solution became yellowish-green in color, then intensely green, and finally a yellow precipitate formed. The titration curve is shown in Fig. 4.

FIG. 5. Potentiometric titration: cobalt(II) nitrate with potassium.

Cobalt(II) nitrate.—An ammonate (0.0602 gram) corresponding to the composition $Co(NO_3)_2 \cdot 5.4NH_3$ dissolved in 46 ml of liquid ammonia was titrated with $0.0868N$ potassium solution. The initially pink solution became green in color and a black precipitate formed concurrently. A total of 21 ml of potassium solution was added over a period of 13 hr; the final reaction mixture consisted of a black precipitate and a greenish-yellow supernatant solution. Data are given in Fig. 5.

DISCUSSION

Titrations involving bismuth(III) iodide and potassium were carried out for the twofold purpose of attempting to detect the formation of Bi^{2+} and/or Bi^+ and to clear up uncertainties in the results reported by Zintl and coworkers (9). In the reaction corresponding to Fig. 1, changes in potential occurred only upon addition of 12.0 and 16.5 ml of potassium solution; these values are to be compared with 12.0 and 16.0 ml calculated on the assumption of formation of Bi^0 and K_3Bi_3, respectively. Thus, the first reaction observed is the three-electron change resulting in precipitation of elemental bismuth, and there is no indication of intermediation of the +2 and +1 oxidation states of bismuth. Fig. 1 shows clearly the formation of the polybismuthide K_3Bi_3, but not the intermediate species K_3Bi_5. In

contrast, data of Fig. 2 show formation of Bi^0 and K_3Bi_5 upon addition of 20.4 and 24.6 ml of potassium solution. The corresponding calculated values are 20.4 and 24.5 ml. Zintl and coworkers (9) titrated bismuth(III) iodide with sodium solutions at $-60°$ and reported evidence for the formation of Na_3Bi, Na_3Bi_3, and Na_3Bi_5, although their evidence for the latter was admittedly inconclusive. While results of the present study are in reasonable agreement with those of Zintl and coworkers, it has been demonstrated that K_3Bi_3 may be formed without intermediation of K_3Bi_5 which exhibits an intense brown color in liquid ammonia solution; this color was 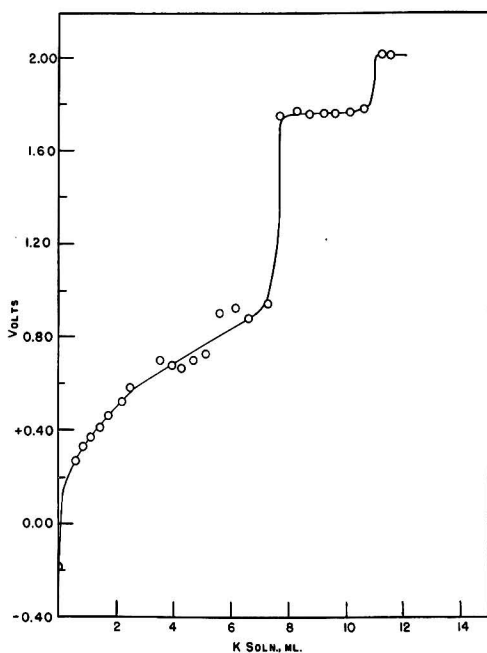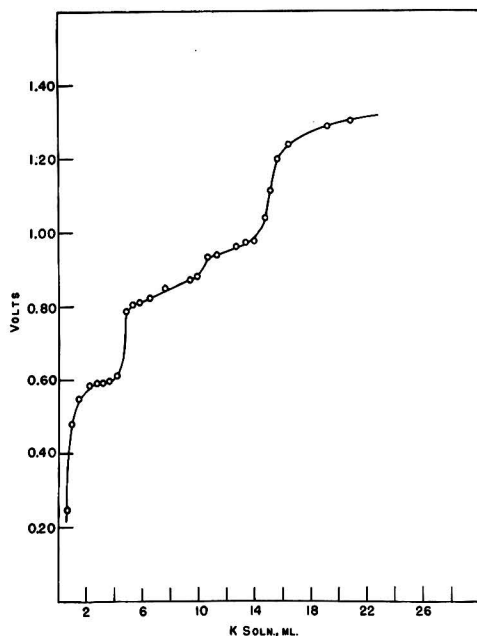not observed during the course of titration represented by Fig. 1. While the present work provides much more conclusive evidence for the existence of bismuthides of the type M_3Bi_5 (where M is an alkali metal), it is still not clear why these species are not formed in all cases. Zintl and coworkers suggested that the course of these reactions may be strongly dependent upon concentration, but the range of concentrations employed in the present work appears to rule out this explanation.

When potassium in liquid ammonia was titrated with saturated bismuth(III) iodide solution, the results obtained were in good agreement with comparable data for corresponding reactions with sodium (9). Marked changes in potential occurred after addition of 17.8, 28.2, and 34.0 ml of bismuth(III) iodide solution as compared with calculated values of 17.8, 26.7, and 35.6 ml corresponding to the formation of K_3Bi, K_3Bi_3, and Bi^0, respectively. For reasons indicated previously, the latter values were calculated on the basis of the volume of iodide solution required for formation of K_3Bi; this end point is visually detectable. Titrations of this type gave no evidence for the formation of K_3Bi_5.

Study of the reduction of iron(II) bromide was prompted by the desire to obtain evidence for the existence of Fe^+ in liquid ammonia solution. It has been shown previously (10) that principal products of this reaction are elemental iron and iron(I) nitride. The latter may arise from the following sequence of reactions.

$$FeBr_2 + K \rightarrow FeBr + KBr \qquad [1]$$

$$FeBr + K \rightarrow Fe + KBr \qquad [2]$$

$$FeBr + NH_3 \rightarrow FeNH_2 + NH_4Br \qquad [3a]$$

$$K + NH_3 \rightarrow KNH_2 + \tfrac{1}{2}H_2 \qquad [3b]$$

$$FeBr + KNH_2 \rightarrow FeNH_2 + KBr \qquad [3c]$$

$$3FeNH_2 \rightarrow Fe_3N + 2NH_3 \qquad [4]$$
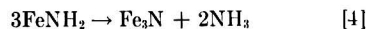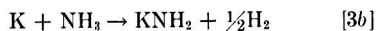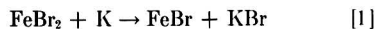
Iron(I) nitride most probably is formed by the de-ammonation of iron(I) amide which as indicated above may result from either ammonolysis of iron(I) bromide or from reaction between iron(I) bromide and potassium amide. In either case, the reduction of Fe^{+2} to Fe^{+1} must be postulated, and it was therefore considered worthwhile to attempt to obtain evidence for the existence of Fe^{+1} under these conditions.

In view of the immediate precipitation of elemental iron and the concurrent evolution of hydrogen (10), it follows that if iron(I) amide arises via reactions [1], [2], and [3a], competitive reactions with subsequently added potassium would involve reactions [1], [2], [3b], and the interaction of potassium with the ammonium bromide formed in [3a]. Of these, the latter and [3b] would probably proceed at the greatest rate. It is not surprising, therefore, that erratic potentials were observed in the early states of the titration. Although Fe^0 may, of course, result from the direct two-electron reaction with Fe^{+2}, there is an alternative mechanism that provides for both the precipitation of Fe^0 and at least the transitory existence of Fe^{+1}, i.e., reaction [1] followed by disproportionation,

$$2FeBr \rightarrow FeBr_2 + Fe^0 \qquad [5]$$
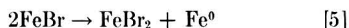
Thus, after formation of sufficient Fe^0 to catalyze [3b], the latter reaction would compete with the probably slow reaction [5].

Reduction of both alkali metal nitrates and nitrites to "hydronitrites" of the type M_2NO_2 has been observed previously (11–13) but only in terms of the identity of the initial and final substances. Formation of K_2NO_2 from KNO_3, for example, may follow the course,

$$KNO_3 + K \rightarrow K_2NO_3 \qquad [6]$$

$$K_2NO_3 + K + NH_3 \rightarrow KNO_2 + KOH + KNH_2 \qquad [7]$$

$$KNO_2 + K \rightarrow K_2NO_2 \qquad [7a]$$

or,

$$K_2NO_3 + 2K + NH_3 \rightarrow K_2NO_2 + KOH + KNH_2 \qquad [8]$$
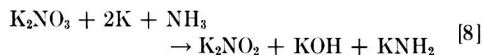
As shown in Fig. 4, however, changes in potential corresponding only to two- and three-electron changes were observed, i.e., upon addition of 7.4 and 10.9 ml of potassium solution, as compared with calculated values of 7.5 and 11.2 ml. Hence, it appears that the formation of K_2NO_3 as an intermediate does

not occur and that the only reactions that take place are,

$$KNO_3 + 2K + NH_3 \rightarrow KNO_2 + KNH_2 + KOH \qquad [9]$$

$$KNO_2 + K \rightarrow K_2NO_2 \qquad [10]$$
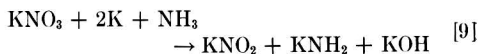
Watt and Keenan (14) suggested that reduction of cobalt(II) nitrate with potassium in ammonia may follow the course,

$$Co(NO_3)_2 + 2K \rightarrow Co(NO_2)(NO_3) + K_2O \qquad [11]$$

$$K_2O + NH_3 \rightarrow KOH + KNH_2 \qquad [12]$$

$$Co(NO_2)(NO_3) + KNH_2 \rightarrow Co(NO_2)(NH_2) + KNO_3 \qquad [13]$$

$$Co(NO_2)(NH_2) + KOH + NH_3 \rightarrow Co(NH_2)_2 + KNO_2 + H_2O \qquad [14]$$

$$KNO_3 + 2K \rightarrow KNO_2 + K_2O \qquad [15]$$
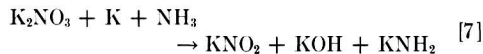
or alternatively,

$$Co(NO_3)_2 + 4K \rightarrow Co(NO_2)_2 + 2K_2O \qquad [16]$$

$$2K_2O + 2NH_3 \rightarrow 2KOH + 2KNH_2 \qquad [17]$$

$$Co(NO_2)_2 + 2KNH_2 \rightarrow Co(NH_2)_2 + 2KNO_2 \qquad [18]$$
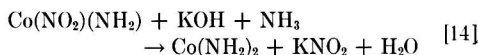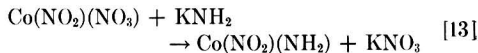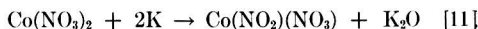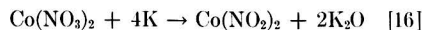
Both mechanisms were compatible with their experimental data, but the methods employed did not lead to data that would permit a choice between the two.

From the data of Fig. 5 it is evident that significant changes in potential occur after addition of volumes of potassium solution corresponding to 2, 4, and 6 gram-atoms of potassium/mole of cobalt(II) nitrate. That the reaction must follow the path suggested by equations [11] to [15] rather than [16] is strongly indicated by the occurrence of a marked change in potential after addition of two equivalents of potassium. Further evidence in favor of the first mechanism is found in the fact that the plateau at 0.8 volt (Fig. 5) is in agreement with that for the reduction of nitrate ion to nitrite ion found in the reduction of potassium nitrate (Fig. 4). The last of the three observed changes in potential [i.e., that which corresponds to 6 gram-atoms of potassium/ mole of cobalt(II) nitrate] is attributable to the previously observed (14) and relatively slow reduction of cobalt(II) amide to elemental cobalt.

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Potentiometric Titration of Ammines of Rhodium, Iridium, and Platinum with Solutions of Potassium and Potassium Amide in Liquid Ammonia[1,2]

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ABSTRACT

Potentiometric titration of tetrammineplatinum(II) bromide with potassium in liquid ammonia at −38°C shows that reduction of this salt to an ammine of platinum(0) is exactly a two-electron change and that the +1 oxidation state of platinum is not an intermediate. Similar reduction of bromopentammineiridium(III) bromide is apparently more complex and leads to observed changes in potential that do not correspond to any reasonable or probable reactions. Titration of this same iridium salt with potassium amide solution, however, provides evidence for stepwise replacement of bromine by amido groups followed by conversion of the resultant iridium(III) amide to (probably) a potassium amidoiridate(III). Bromopentamminerhodium(III) bromide and potassium amide react similarly, but only to and including the formation of rhodium(III) amide.

Introduction

In previous papers from this laboratory, development of a method for carrying out potentiometric titrations in liquid ammonia and use of this method in the study of unusual oxidation states and reduction reaction mechanisms have been described (1). This paper is concerned with similar studies involving reduction of ammines of certain transitional metal bromides with solutions of potassium in ammonia. In addition, two reactions in which liquid ammonia solutions of potassium amide were used as titrant are described; the course of reactions of this type has not previously been followed potentiometrically.

Experimental

Experimental details were in all respects analogous to those described earlier (1). In all cases reported in this paper, anhydrous liquid ammonia solutions that were titrated with either standard potassium or standard potassium amide solutions contained not only the ammine bromide of interest but also a suitable supporting electrolyte. The two electrodes consisted of a platinum reference electrode and a differential electrode of the type used previously (1, 5).

The differential electrode, which was connected to the positive terminal of the potentiometer, consisted of a platinum wire immersed in a solution having a composition the same as that of the solution to be titrated, and was connected to the main body of the latter solution via a fine capillary tube.

Appropriate ammine bromides of rhodium (2), iridium (3), and platinum (4) were prepared and characterized by methods described elsewhere.

Titration of tetrammineplatinum(II) bromide with potassium.—Preliminary experiments showed that adequately sensitive potentiometer readings could be obtained only through use of a supporting electrolyte. Accordingly, 0.1217 gram of $[Pt(NH_3)_4]Br_2$ and 0.10 gram of potassium bromide, both dissolved in 40 ml of liquid ammonia, were titrated with $0.0506N$ potassium solution over a period of 9 hr. The initially clear solution became progressively darker in color until near the end of titration, whereupon intensity of the color decreased relatively rapidly and the presence of a pale yellow precipitate was observed. Addition of a considerable excess of potassium failed to produce either the blue color characteristic of solutions of alkali metals in ammonia or the potential anticipated for an ammonia solution of potassium amide. The data are shown in Fig. 1.

Titration of trans-diammineplatinum(II) bromide with potassium.—Potentiometric titrations involving these two reactants gave results substantially identical with those in Fig. 1.

Titration of bromopentammineiridium(III) bromide with potassium.—In a typical case, 0.1114 gram of $[Ir(NH_3)_5Br]Br_2$ and 0.15 gram of potassium bromide in 70 ml of liquid ammonia was titrated with
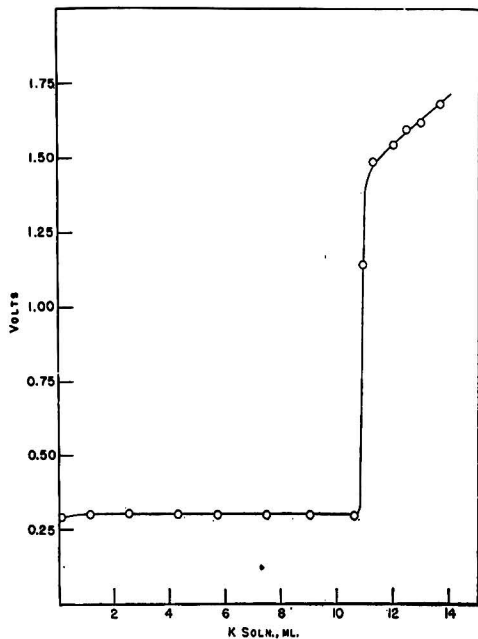
FIG. 1. Potentiometric titration: tetrammineplatinum (II) bromide with potassium.

FIG. 3. Potentiometric titration: bromopentammineirid ium(III) bromide with potassium amide.
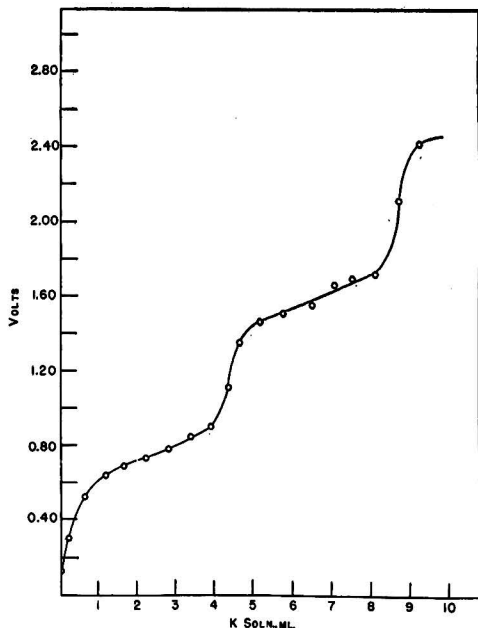
FIG. 2. Potentiometric titration: bromopentammineirid ium(III) bromide with potassium.

$0.0663N$ potassium solution (time, 14 hr). A precipi tate formed slowly, and the blue color of the potas sium solution was discharged rapidly during approxi mately the first half of the titration. Thereafter, rate
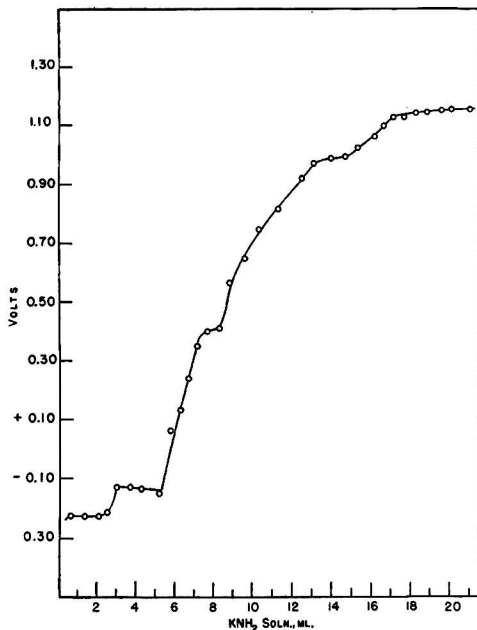
of reaction decreased markedly, the presence of a cream colored precipitate was observed, and equi librium was re-established relatively slowly after each addition of potassium solution. The blue color of the potassium solution persisted after addition of a total of 9.4 ml. The data are shown in Fig. 2.

Titration of bromopentammineiridium(III) bromide with potassium amide.—A solution of 0.125 gram of potassium bromide and 0.0931 gram of $[Ir(NH_3)_5Br]$-Br_2 in 50 ml of liquid ammonia was titrated with $0.0605N$ potassium amide solution over a period of 20 hr (Fig. 3). The amide solution was prepared by interaction of potassium and liquid ammonia in the presence of an iron wire catalyst in the vessel ordi narily used for preparation of standard alkali metal solutions (5). A white finely divided precipitate was observed after addition of 4.2 ml of potassium amide solution, and the following solution colors were ob served upon addition of the indicated volumes of titrant: 0, colorless; 7.0, yellow; 14, orange; 16.7, bronze.

Titration of bromopentamminerhodium(III) bromide with potassium amide.—In an experiment of the type described above, a solution of 0.91 gram of potassium bromide and 0.0433 gram of $[Rh(NH_3)_5Br]Br_2$ in 70 ml of liquid ammonia was titrated with $0.0266N$ potassium amide solution (time, 8 hr). Resulting data are given in Fig. 4. The intensity of color of the initially pale yellow solution decreased during addi tion of 6.5 ml of the amide solution, whereupon there appeared a turbidity that persisted until 10.0 ml had
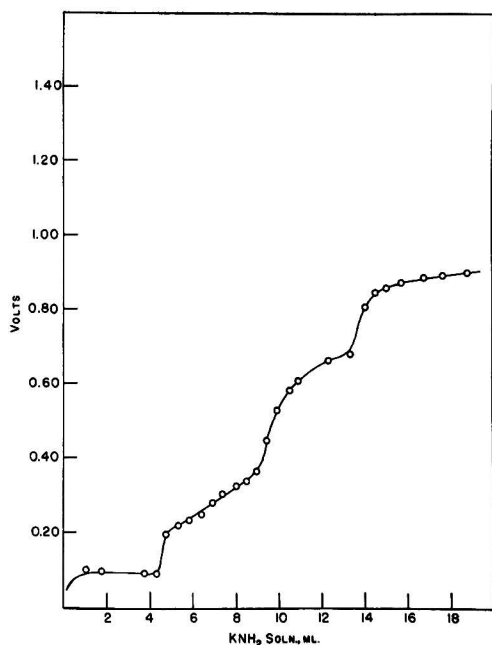
FIG. 4. Potentiometric titration: bromopentamminerhodium(III) bromide with potassium amide.

been added. Thereafter, the solution became progressively more intensely green in color until 14 ml had been added and the solution color began to change from green to yellow-green.

DISCUSSION

In studies leading to the conclusion that reduction of tetrammineplatinum(II) bromide with potassium in ammonia produces an ammine of platinum in the zero oxidation state (4), it became necessary to establish exactly the reaction ratio involved. Titrations of the type shown in Fig. 1 were carried out for this purpose and also with a view to determining whether this reaction proceeds via a single two-electron reaction or two consecutive one-electron 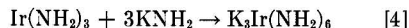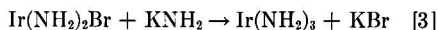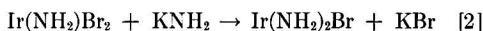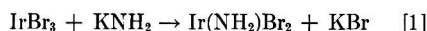changes. It is evident from Fig. 1 that intermediation of the +1 oxidation state is not involved and that reduction of one mole of the bromide requires exactly two gram-atoms of potassium. An increase in potential of the order of 1.3 volts occurred sharply upon addition of 11.0 ml of potassium solution; the volume calculated on the assumption of a two-electron change is 11.3 ml. That substantially identical results were obtained in titrations involving trans-diammineplatinum(II) bromide is consistent with the fact that the trans-isomer is slowly converted to the tetrammine in liquid ammonia at its boiling temperature (4).

In several titrations of bromopentammineiridium-

(III) bromide with potassium, changes in potential that apparently may not be correlated with any anticipated stoichiometry were observed. With reference to Fig. 2, for example, the increases in potential that occurred upon addition of 4.5 and 8.5 ml of potassium solution are to be compared with 6.5 and 9.7 ml calculated on the assumption of reduction of Ir^{+3} to Ir^{+1} and its subsequent reduction to Ir^0. Similarly, change in potential (and appearance of a permanent blue color) corresponding to complete reduction of Ir^{+3} to Ir^0 was also premature in all cases, and since different and authentic samples of the bromide were employed, these results cannot be attributed to impure starting materials. It is possible to postulate a mechanism in which it is assumed that Ir^{+3} is reduced to Ir^{+1} which in turn reduces Ir^{+3} to Ir^{+2} and the latter is reduced to Ir^0 upon further addition of potassium solution. If it is further assumed that (owing to competitive rates that may be involved) one-third of the Ir^{+1} is ammonolyzed to iridium(I) amide, then it may be shown that the observed changes in potential are almost exactly those to be anticipated under such conditions. This requires, however, that iridium(I) amide be stable in the presence of subsequently added potassium solution and that it constitute one of the final products. This is clearly incompatible with other data relative to the identification of pentammineiridium-(0) as the end product (3).

Changes in potential that are shown in Fig. 3 and that result from addition of 2.8, 5.8, 8.6, and 17.2 ml of potassium amide solution (calculated: 3.0, 6.0, 8.9, and 17.8 ml) apparently correspond to the reactions (coordinated ammonia omitted),

$$IrBr_3 + KNH_2 \rightarrow Ir(NH_2)Br_2 + KBr \quad [1]$$

$$Ir(NH_2)Br_2 + KNH_2 \rightarrow Ir(NH_2)_2Br + KBr \quad [2]$$

$$Ir(NH_2)_2Br + KNH_2 \rightarrow Ir(NH_2)_3 + KBr \quad [3]$$

$$Ir(NH_2)_3 + 3KNH_2 \rightarrow K_3Ir(NH_2)_6 \quad [4]$$

or,

$$Ir(NH_2)_3 + 3KNH_2 \rightarrow Ir(NHK)_3 + 3NH_3 \quad [4a]$$

This interpretation is further supported by the fact that iridium(III) amide has been isolated (in the form of the 1-ammonate) as the only ammonia-insoluble product of the interaction of the bromide and potassium amide in a $\frac{1}{3}$ mole ratio (3). Neither the present nor previous work (3) permits a choice between alternatives suggested by equations [4] and [4a].

From data shown in Fig. 4, it is apparent that reactions between bromopentamminerhodium(III) bromide and potassium amide are strictly analogous to those with the corresponding iridium compound,

i.e., equations [1] to [3], inclusive, except for the fact that rhodium(III) amide is not converted to a soluble species by action of excess potassium amide, i.e., rhodium(III) amide is less amphoteric than iridium(III) amide. Rhodium(III) amide has been independently isolated and characterized (2). Attention should be called to the fact that the volumes of potassium amide solution corresponding to the changes in potential shown in Fig. 4, i.e., 4.6, 9.5, and 14.0 ml, are higher than calculated volumes based on concentration of the potassium amide solution used, i.e., 3.8, 7.6, and 11.4 ml. However, if the final increase in potential is taken as evidence for the formation of rhodium(III) amide, which is reasonable in the light of other available evidence (2), then the two preceding changes in potential should occur upon addition of 4.7 and 9.3 ml.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1954 issue of the JOURNAL.

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Adherence of Electrodeposited Zinc to Aluminum Cathodes[1]

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ABSTRACT

An apparatus for measuring the adherence of zinc electrodeposited from acid zinc sulfate solutions on aluminum cathodes is described. Adherence was recognized as "sheet" or "spot" behavior. Chloride favored increase in sheet adherence and fluoride ion favored spot adherence. Mechanical, thermal, and electrolytic treatments of cathode surface as well as chemical composition of electrolyte were investigated. There was no correlation between surface roughness and adherence. Smaller aluminum crystals in the cathode surface favored stronger adherence.

The first stage of deposition was development of ovoid particles 8 x 5 microns, increasing in number until a complete sheet was obtained. Such particles preferred to develop at sharp points and crystal boundaries. Rupture of interface was observed microscopically in the aluminum surface. Zinc diffused into cathode with time, but aluminum on the surface of the zinc electrodeposit was attributed to fracture in aluminum during stripping. Mechanism of adherence was explained as an attachment at a varying number of active spots rather than by mechanical anchoring.

INTRODUCTION

In the commercial production of zinc by electrolysis, low adherence to an aluminum cathode is desirable. Separation of the zinc sheet from the cathode is effected manually, and the process of plating and stripping may be repeated up to 1000 times or more on a single cathode sheet before the aluminum is rejected from service, usually for reasons other than a damaged surface. Whereas electroplaters for ornamental or protective work require adherence values of probably 1000 or more kg/cm², production of electrolytic zinc commercially is best served if the adherence is between one and two kg/cm². In this paper, the measurement of adherence of zinc electrodeposits is described, and the mechanism of adherence is discussed by considering these results in relation to information obtained from the following investigations: (a) an examination of the microroughness of surfaces with "Talysurf" instrument (see later); (b) metallographic examination; (c) microscopic examination of first stages of electrodeposition; (d) examination of interface between cathode and electrodeposit; (e) chemical analysis of thin layers from the surface of metals at the interface after separation of the electrodeposit.

EXPERIMENTAL

Measurement of Adherence

The apparatus used for this purpose is illustrated in Fig. 1. It is a modification of the "Burgess" method described by Schlötter (1) giving results in absolute values, i.e., kg/cm². Schlötter soldered a metallic loop to the surface before pulling off the electrodeposit, but as this is undesirable for zinc electrodeposited on aluminum, a glue bond between the electrodeposit and the pulling bar was used.

For these measurements, cathodes 5 cm x 5 cm x 0.6 cm (thick) were cut from rolled aluminum sheet of a high grade of commercial purity. A single cathode was plated at a time in a beaker carrying electrolyte of the required composition. Anodes cut from pure lead sheet were used, one on each side of the cathode. Zinc was plated for three hours to a thickness of approximately 0.15 mm. These deposits were strong enough to be pulled off without breaking. A suitable area for the adherence test was 2.5 cm x 1.25 cm and this was outlined by grooving the face of the cathode sheet with a sharp pointed tool. The plated zinc sheet was cut along these lines with a very sharp knife and stripped from areas other than those required. For adherence values up to approximately 7 kg/cm² this proved satisfactory, but for greater adherence a smaller area of zinc was used.

Two test rectangles were marked on one face of the cathode sheet. One end of a steel bar 18 cm long and 2.5 cm x 1.25 cm cross section was glued to the back of one of the rectangles of zinc. The most satisfactory method for attaching the bar to the zinc sheet was to insert a piece of linen between the two metal surfaces and glue to each with a liquid glue, the whole being dried at 18°C for 15 hr.

A current density of 32 ma/cm² was used as a standard procedure in plating. The cell temperature was maintained at 35°C. The electrolyte was a solution of zinc sulfate (70 g/l zinc) in dilute

sulfuric acid (100 g/l of H_2SO_4). To this electrolyte was added one or more of the common impurities experienced in commercial zinc electrolysis. With only zinc sulfate-sulfuric acid solutions, no "addition" agent was necessary, but when additional ions were added, 24 mg/l of glue was used. When arsenic and/or antimony was present, then 10 mg/l of beta-napthol was also added. The addition agent was put in before electrolysis and the initial amount was sufficient for the three-hour plating period. Before each plate was deposited, the test cathode was immersed in the particular electrolyte for 16 hr at 18°C. Some exceptions to these standard procedures were also investigated.

Adherence values were difficult to reproduce with a high degree of accuracy, but it was possible to arrange results in groups according to certain ranges of adherence. The standard deviation of a determination from a single test area was ±50%. It was
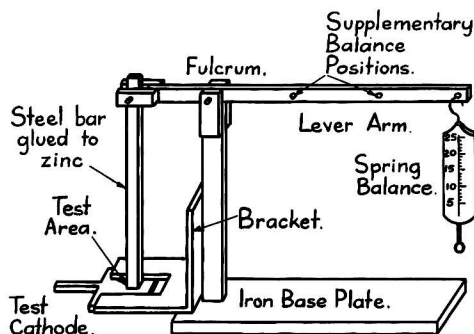

FIG. 1. Laboratory adherence tester

found that results from one side of the rolled aluminum sheet differed from those on the reverse side, so that for comparative purposes only one side of the sheet was used. The difference was related to crystal structure in the surface. Higher adherence was obtained on the surfaces with smaller crystals of aluminum.

Values for adherence from less than 0.1 to as high as 57 kg/cm² were observed. For this investigation, the important range of values was 1 to 2.5 kg/cm² and there was not much point in attempting to measure adherence in excess of 7 kg/cm². This was related to the requirements for manually stripping a zinc sheet from the aluminum cathode during the course of the commercial manufacture of electrolytic zinc. Sheets deposited under conditions giving adherence values in excess of this figure were far too difficult to remove.

In commercial plant practice it had been observed that on some occasions the electrodeposit adhered with reasonable uniformity over the whole cathode

surface, whereas, in other cases, adherence was experienced in smaller patches. Two types of adherence conditions were therefore specified and referred to descriptively as "sheet" adherence and "spot" adherence. In order to differentiate between these conditions in the test cathodes the following method was adopted for interpretation of results. A quantitative estimate of adherence was determined, using values from two adjacent test areas of the experimental cathodes. Spot adherence was identified from the ratio of the higher value to the lower value of adherence from two adjacent areas. On the other hand, the average value from adjacent test areas has been used as a measure of sheet adherence.

Values for spot adherence estimations varied over the range 1 to 13, whereas for sheet adherence values from 0.1 to 57 kg/cm² were recorded, as has already been indicated.

Tests giving spot adherence ratio values lower than 3 were considered satisfactory, whereas values in excess of 6 were considered to be high, and those in excess of 9 to be very high and unsatisfactory.

Tests were conducted under 53 sets of conditions and the most significant of these are given in Table I.

From these tests it was concluded that mechanical roughening of the aluminum surface did not necessarily result in increased adherence of the zinc deposit. Of the chemical factors tested in the electrolyte only chloride ion showed increase in sheet adherence of statistical significance. Spot

TABLE I

Test No.	Electrolyte composition (rolled surface of Al as cathode)	Adherence—kg/cm²		Ratio of adherence of adjacent areas
		Individual values	Average values	
1	Pure $ZnSO_4$ at 70 g/l Zn and 100 g/l H_2SO_4	1.1 & 1.3	1.2	1.2
2	Same as above, with addition of 16 g/l Mn as $MnSO_4$	1.9 & 1.8	1.85	1.1
3	Same as for test 2, plus 80 mg/l Cl as HCl	3.2 & 3.9	3.55	1.2
4	Same as for test 2, plus 200 mg/l Cl as HCl	6.0 & 5.3	5.65	1.1
5	Same as for test 2, plus 40 mg/l F as HF	0.85 & 0.85	0.85	1.0
6	Same as for test 2, plus 80 mg/l Cl as HCl and 100 mg/l F as HF	2.25 & 1.4	1.82	1.6
7	Same as for test 2, plus 80 mg/l Cl as HCl and 40 mg/l F as HF	2.25 & 2.55	2.4	1.1
8	Same as for test 7, but with 64-hr pickle	5.3 & 0.4	2.8	13.0
9	Same as for test 7, plus 0.5 mg/l Cu as $CuSO_4$	1.3 & 0.85	1.08	1.5
10	Same as for test 7, plus 10 mg/l Cu as $CuSO_4$	1.0 & 0.4	0.7	2.5

adherence was experienced when electrolysis was conducted in an electrolyte containing fluoride ion. This type of adherence was also experienced if the cathode had been pickled in acid electrolyte for a long period before electrodepositing. The effect after long pickling was the same, whether fluoride ion was present or not.

Surface Roughness Measurements

Through the services of the Defence Research Laboratories (one time Munitions Supply Laboratories), Maribyrnong, Victoria, Australia, measurements were obtained of the surface roughness of 31 specimens of aluminum and 6 of zinc using a "Talysurf" indicator-recorder. The description and use of this instrument has been published elsewhere by the D.R.L. (then called M.S.L.) (2).

Some of these results are given in Table II. No correlation was found between surface roughness so measured and the degree of adherence.

Metallographic Examination of Crystal Structure

Metallographic examination had limitations because the observation of crystal structure involved destruction of the surface used for electrodeposition.

For microscopic examination, specimens of aluminum were prepared by polishing selected areas of a cathode surface with fine abrasive cloth, followed by a buffing with alunite powder. The final finish was obtained by polishing with "Brasso,"[2] and using freshly prepared etchant of the following composition: 50% hydrochloric acid; 47% fuming nitric acid; and 3% pure hydrofluoric acid.

With a 30-sec etch, the orientation and size of crystals were clearly seen at a magnification of $900\times$. Surface scratches were widely enough spaced to enable clear fields to be observed at this magnification.

In all cases examined, the crystals were smaller in the specimens which had given higher values for the adherence of the electrodeposit (other factors remaining unchanged).

Microscopic Observation of Electrodeposition

Specimens of aluminum were examined microscopically after deposition of zinc had proceeded for periods such as 30, 60, 90, and 120 sec.

Zinc did not deposit as a uniform sheet but as small ovoid particles, each with its long axis normal to the plane of the aluminum surface. Size of these particles was remarkably uniform and with axis lengths of approximately 8 and 5μ. The number of particles rather than the size of individual particles

[2]"Brasso" is a product of Reckett and Colman Ltd., Hull, England, and is recommended for polishing soft metals.

TABLE II

Specimen examined	Talysurf meter readings		Adherence kg/cm²
	Max. & min.	Mean of six readings	
New aluminum, pickled 16 hr at 18°C; plated and stripped (electrolyte = pure zinc sulfate, 70 g/l Zn & 100 g/l H_2SO_4)	0.38–0.51	0.46	1.27
	0.38–0.51	0.43	1.15
	0.43–0.66	0.53	
	0.46–1.08	0.66	
Specimen as above, but electrolyte contained 16 g/l Mn and 200 mg/l Cl in addition	0.38–0.46	0.41	5.28
	0.43–0.81	0.53	6.05
Specimen as above, but electrolyte contained 16 g/l Mn and 4 mg/l F in addition to $ZnSO_4$ and H_2SO_4	0.41–0.53	0.51	0.84
	0.48–0.71	0.53	0.84
Specimen as above, but pickled 64 hr at 18°C in electrolyte with 40 mg/l F	0.81–1.02	0.91	7.75
	0.58–0.74	0.63	1.27
Specimen brushed by hand with steel wire brush. Pickled, plated, and stripped, electrolyte from commercial plant cells	1.78–2.59	2.16	1.69
	1.35–1.58	1.50	2.32
New aluminum, different sheet	0.28–0.30	0.28	—
	0.36–0.41	0.38	—
Same as above, but brushed by hand with steel wire brush	0.70–1.98	1.86	—
	1.60–2.29	2.03	—

increased as plating progressed. Also, by changing the surface treatment or electrolyte characteristics the rate at which these particles appeared could be varied. It would appear that these primary particles deposit at points where the aluminum oxide film is cracked or particularly thin. Where surface irregularities were conspicuous it was noted that particles developed preferentially at sharp peaks or ridges or at the lips of surface depressions. These, no doubt, were points of higher current density.

On a specimen prepared for examination of crystal structure, it was noted that particles preferred to form at crystal boundaries. This was in agreement with work reported by Kyropoulos (3) who studied the manner in which electrodeposits form on aluminum crystals.

Conditions which favored rapid development of primary zinc particles also favored strong adherence of the zinc electrodeposit, and vice versa. Conditions for strong adherence showed 20 to 30 times as many primary particles in 90 sec of plating as conditions for weak adherence.

It was found possible to obtain an estimate of the relative adherence of primary zinc particles by

manipulating a thin steel wire under the objective of the microscope when examining prepared specimens. Adherence of these particles was found to vary appreciably; those which were earliest to appear were generally more firmly attached than those appearing after a longer plating period.

Dependence of points of deposition on the oxide film was demonstrated by anodizing an aluminum cathode in a chromic acid bath. Using this as a cathode in acid zinc sulfate electrolyte, a continuous sheet of zinc was obtained, but it was attached to the cathode at only a very few points.

A film type of deposit was obtained following the technique of Bullough and Gardam (4), designed to remove the oxide film completely and limit its reappearance before deposition commences. The aluminum surface was prepared in a nitric-hydrofluoric acid bath, and then transferred to a sodium zincate bath, through water washes, without allowing the face to dry. A thin, but continuous, immersion deposit of zinc, very firmly adherent to the aluminum, was obtained in this manner. Attachment was virtually at an infinite number of points and adherence values of the order of the tensile strength of aluminum were recorded by Bullough and Gardam (4).

Film type deposits were also obtained in the current experiments when copper and lead were used as cathodes instead of aluminum.

Microscopic Examination of the Interface

Plated specimens, cut on the taper using the technique described by Nelson (5), were prepared but were not suitable for microscopic examination owing to the softness of the aluminum. A specimen cut normal to the plane of plating allowed zinc or aluminum to be etched individually, but at magnifications high enough to reveal the structure of the interface it was not possible to obtain both surfaces in focus simultaneously.

Specimens of smooth rolled aluminum which had been plated and stripped were examined microscopically. Small craters appeared in the surface after removal of the electrodeposit. In subsequent short periods of plating, primary particles of zinc preferred to form at the lips of these craters rather than in the depressions. These crater-like pits apparently had been foci of attachment for the original zinc deposit, and rupture had taken place in the aluminum surface. These craters were of the order of 1.5μ deep and several microns across; frequently several craters were joined to give trough-like indentations.

Bullough and Gardam (4) when examining the adherence of nickel deposits to aluminum and its alloys, using zinc as an intermediate layer, also observed fracturing in the aluminum.

A Brinell indenter was used to examine the hardness of specimens of aluminum and zinc. Nothing unusual was noted in specimens of aluminum for which values of the order of 40 were obtained. Values for the zinc were, however, appreciably higher. Over the surface of stripped zinc electrodeposited sheets, values varying between 150 and 225 were obtained, the average being approximately 200. On the other hand, with sections cut through the zinc sheet, normal to the face, values of the order of 70 were obtained. While all these values for zinc may have been unexpectedly high, nevertheless they are consistent with the microscopic observation of fracture in the aluminum surface, indicating greater softness of this metal.

Hanley and Clayton (6) investigated the adherence of zinc electrodeposits to aluminum cathodes. These authors explain the mechanism of adherence in terms of physical anchorage. Generally results obtained by the present author were in line with the findings of Hanley and Clayton, but it is not possible to agree on the mechanism of adherence. On the other hand, there are no results quoted by Hanley and Clayton which could not be explained by a theory of attachment at electrochemically active points.

ANALYSIS OF INTERFACIAL LAYERS

Some tests were made in which a thin layer of aluminum was scraped from the surface of a cathode after having been in service for some time in the commercial zinc plating plant. These scrapings were analyzed for copper and zinc. Of ten cathodes tested, five had been associated with a zinc electrodeposit which stripped easily, and five had been difficult to strip.

The thickness of the layer scraped averaged between 40 and 50μ. The analysis of the easily stripped cathodes averaged 0.071% copper and 3.44% zinc. Zinc content was remarkably uniform, but copper varied widely from sample to sample, from a maxi-

TABLE III

Depth of layer examined, microns	% Aluminum	Remarks
8.3	0.15	Commercial plant cathode, stripped easily
4.35	0.035	Commercial plant cathode, stripped with difficulty
4.2	0.015	Commercial plant cathode, stripped with difficulty
Not determined	0.0026	Pilot plant cathode, stripped easily

mum of 0.191 % to a minimum of 0.023 %. In the case of the cathodes which were difficult to strip, both copper and zinc concentrations were reasonably uniform, averaging 0.022 % and 2.43 %, respectively.

Hanley and Clayton (6) drew attention to the influence of copper in the electrolyte increasing the adherence of the electrodeposit, but this effect was not obtained in the present series of tests (see tests 9 and 10 in Table I). It is believed that the initial distribution of copper in the aluminum sheet exercises a controlling influence on the adherence, but the tests were not carried far enough to produce conclusive evidence on this point. The solid solubility of copper in aluminum is usually reported as 0.25–0.30 % at room temperature. Some workers, however, consider that the solubility is nearer 0.08–0.12 %. Copper concentration of the aluminum sheet used for cathodes covers this range, and presence of $CuAl_2$ as a solid phase may have some bearing on the problem.

The effect of pickling in spent electrolyte on the removal of zinc from the aluminum surface was examined. Large lumps of zinc left after stripping were removed quite effectively in this manner. Whether they fell off as the result of aluminum in the immediate vicinity being dissolved, or whether they dissolved preferentially in spite of the relative positions of zinc and aluminum in the electrochemical series was not examined critically. There was, however, obvious liberation of hydrogen from large lumps of zinc still attached to the cathode surface. The zinc of more particular interest for this investigation was that which had apparently diffused into the surface of the aluminum. It was observed that during the pickling process zinc was certainly not removed any faster than aluminum, but tests were not extended to determine whether the converse may have been the case, although such was not conspicuous.

Full sections of aluminum sheets were also analyzed for copper, and the following results were obtained from nine sheets of aluminum: 0.051, 0.27, 0.04, 0.05, 0.07, 0.153, 0.04, 0.04, and 0.006 % Cu. The heterogeneity with respect to copper was thus a property of the sheet as a whole, not confined to the surface, and not a result of electrolysis. The new aluminum sheet was free from zinc. There was no evidence that the zinc referred to in these analyses had been left in the aluminum as the result of fracturing of a bond during the stripping process, but it seemed quite logical to conclude that, with long periods of interfacial contact, diffusion could take place.

Four surfaces of zinc electrodeposit were scraped on the adhering side and analyzed for aluminum. Results are summarized in Table III.

While commercial plant cathodes appeared to leave more aluminum on the zinc face when stripping was relatively easy, this was not confirmed by pilot plant tests. It is believed that the presence of aluminum on the surface of the zinc can be attributed to the fracture of the bond in the aluminum sheet as observed in microscopic examinations reported above. It is unlikely that very much diffusion would have taken place during the plating period which was 72 hr in the case of sheets sampled for analysis of surface. More extensive sampling and analysis is required to provide a rational explanation on the basis of chemical analysis.

CONCLUSION

The mechanism of adherence of a zinc electrodeposit to an aluminum cathode is more plausibly explained in terms of attachment at a varying number of electrochemically active spots than by a concept of mechanical anchoring under ledges and crevices.

ACKNOWLEDGMENT

Any discussion of this paper will appear in a Discussion Section to be published in the December 1954 issue of the JOURNAL.

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Luminescence of the System β $Zn_3(PO_4)_2$-$Cd_3(PO_4)_2$:Mn[1]

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ABSTRACT

When zinc orthophosphate and cadmium orthophosphate mixtures are activated by manganese and fired at 850°C, phosphors are obtained whose luminescence is not a linear function of the mole proportions of the initial ingredients. The peak emission vs. composition curve shows several abrupt breaks which correspond to abrupt phase changes as determined by x-ray diffraction analysis.

INTRODUCTION

Luminescence of end members of the system β $Zn_3(PO_4)_2$-$Cd_3(PO_4)_2$ has been described by Smith (1), Andrews (2), and Kroeger (3). Color of the luminescence of zinc orthophosphate:manganese may vary from green to red, depending on manganese content and firing temperature (1). Cadmium orthophosphate:manganese was erroneously reported by Andrews (2) to have a red emission, but Kroeger (3) correctly described its emission as yellow. Although double activation of the cadmium salt by lead and manganese causes greater phosphorescence than that obtained by simple manganese activation, the yellow emission remains unaltered (4). McKeag (5) and McKeag and Randall (6) found that when halides in almost any form are added to cadmium orthophosphate, new compound formation occurs and structures of the type $Cd_3(PO_4)_2$:MX_2 result; halide fluxes cannot be used, therefore, without altering internal composition to some extent.

Andrews (2) prepared a zinc-cadmium orthophosphate containing equal weights of zinc and cadmium orthophosphates. If the possible use of hydrates is neglected, this mixture corresponds to approximately 40 mole % zinc orthophosphate. The mixture was fused "at full red heat for 15–20 min and poured onto a cold soapstone. The fluorescence under the iron spark is a light pink, and its phosphorescence is a deep red, resembling hot coals, and fairly persistent" (2).

PREPARATION

Zinc orthophosphate dihydrate was prepared as previously described (1). Cadmium orthophosphate

was prepared in a similar manner: disodium hydrogen phosphate was added to a cadmium sulfate solution; the precipitate was filtered, then dried at 160°C. The material thus obtained was a tetrahydrate, $Cd_3(PO_4)_2 \cdot 4H_2O$, the x-ray diffraction pattern of which agreed with the A.S.T.M. card index labeled "$Cd_3(PO_4)_2$" (7). Firing the hydrate at 650°C converts it to the anhydrous form, the x-ray diffraction pattern of which is given in Table I. A step-by-step dehydration occurs and some intermediate hydrate is formed; composition and stability range of this hydrate, however, were not determined.

In preparation of the phosphors, a water slurry of individual phosphates in proper molar ratio was ball-milled together with the requisite proportion of manganous sulfate for about 14 hr, then evaporated to dryness at 160°C. Equivalent results were obtained by coprecipitation of zinc-cadmium-manganese phosphates, but preparation of various zinc-to-cadmium ratios by ball-milling techniques was more convenient. After evaporation, samples were placed in quartz vessels and fired either at 650° or 875°C in air for two 1-hr periods. Samples were lightly ground between firings to promote homogeneity.

TESTING OF PHOSPHORS

X-ray diffraction analyses were made with nickel-filtered radiation from a copper target tube operated at 40 kv and 15 ma. Samples were rotated within a circular camera 14.32 cm in diameter.

Cathodoluminescent efficiencies and emission spectra were determined by use of a defocused electron beam having a current density of 1.5μa/cm² and an accelerating potential of 8000 volts. Peak efficiencies and spectral distributions of energy were measured by means of the spectroradiometer and the method described by Hardy (8).

TABLE I. *Diffraction data for anhydrous* Cd$_3$(PO$_4$)$_2$

Lattice spacing (d-) Å	Estimated relative intensity
4.3	0.80
4.0	0.40
3.8	0.40
3.42	1.00
3.35	0.80
3.29	1.00
3.15	0.30
3.06	0.35
2.95	1.00
2.89	0.20
2.82	0.30
2.65	0.90
2.59	0.70
2.50	0.30
2.43	0.90
2.30	0.10
2.15	0.20
2.10	0.20
2.02	0.20
1.97	0.35
1.92	0.35
1.87	0.20
1.84	0.20
1.77	0.20
1.70	0.25
1.65	0.15
1.59	0.25
1.57	0.15
1.54	0.10
1.51	0.20
1.47	0.10
1.435	0.30
1.402	0.10
1.390	0.20
1.360	0.20
1.265	0.20
1.235	0.20
1.220	0.20
1.210	0.20
1.140	0.30
0.990	0.30

RESULTS AND DISCUSSION

A number of binary phosphor systems are known in which the peak wave length of emission shifts in a regular manner with change in composition. Before this study was undertaken, it was assumed that the zinc-cadmium orthophosphate:manganese system would also exhibit a simple shift of color from the light red of zinc orthophosphate to the deep yellow of cadmium orthophosphate. Such a simple shift does not occur, however, as can be seen in Fig. 1, in which the peak wave length of emission is plotted vs. the mole per cent concentration of cadmium phosphate. Each rectangular box shown on the graph indicates relative variance obtained from a particular composition. Included within the rectangles are values obtained from manganese-concentration tests, firing-temperature studies, and
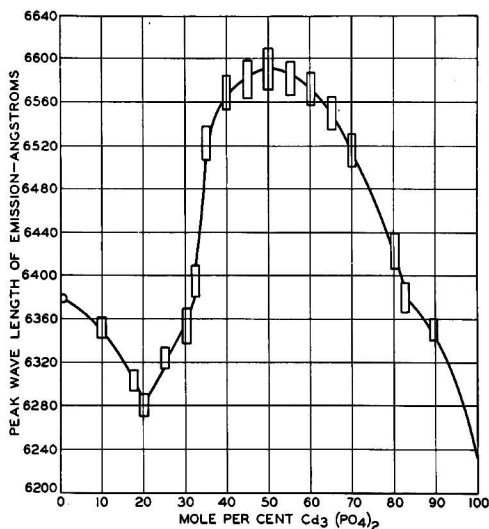
FIG. 1. Peak wave length, in Å, of emission as a function of composition in the system β Zn$_3$(PO$_4$)$_2$-Cd$_3$(PO$_4$)$_2$:Mn.

repetitive runs. Variances between repetitive runs were as great as those from processing variables, hence all values are grouped as a single unit.

Effect of manganese concentration.—As in zinc orthophosphate (1), concentrations of manganese between 2 and 5% did not change the position of the peak of emission. Since this investigation was concerned primarily with β Zn$_3$(PO$_4$)$_2$, concentrations below 2 mole % manganese were not tested systematically. This procedure was followed to insure the presence of only β Zn$_3$(PO$_4$)$_2$, for it has been established that lower manganese content gives rise to α Zn$_3$(PO$_4$)$_2$ (1). Only one spot check of 0.5 mole % manganese was made at the 50–50 composition. Although the efficiency of this sample was low, all other properties were similar to those of samples of higher manganese content. It was also found that x-ray diffraction patterns of pure cadmium orthophosphate containing as much as 5 mole % manganese were identical with those without added manganese. This result indicates that cadmium orthophosphate does not display a phase change upon addition of manganese as does the zinc analogue.

Effect of firing temperature.—Although the majority of tests were conducted at 875°C, several runs were made at 650°C to determine whether phase changes due to temperature would occur. Except in the 100 to 90 mole % zinc region, where the expected α to β shift occurred, no other phase change was found which was due solely to temperature. A possible trend toward shorter wave lengths was found at the 650° firing temperature and toward longer wave

lengths for the 875°C firing temperature, but it was quite indefinite. Efficiencies were about 20% better, however, at the 875° value, and it was for this reason that the majority of tests were made at that temperature.

Since results involving activator concentration and firing temperature showed no greater variances than did those between repetitive runs, they were included in the make-up of Fig. 1. The 650° values at high zinc concentrations were omitted, however, because it was obvious that the α form of zinc phosphate was present. Each series tended to give a slightly different curve, but the over-all shape of the curve and position of the breaks were substantially unchanged, the only difference being one of slight magnitude. The plot is a very sensitive one, so that small errors in measurement or preparation appear magnified.

Fig. 2 shows spectral energy distribution curves for β $Zn_3(PO_4)_2$:Mn, $Cd_3(PO_4)_2$:Mn, and a 50–50 mole ratio of the two substances. The curve of the 50–50 composition is symmetrical, without the hint of a double peak. This symmetry is evident in all other ratios as well. As the cadmium content is increased, the curve remains relatively narrow until a content of 20 mole % is reached. The curve broadens rather abruptly at about the same concentration at which emission starts to shift toward deep red, and remains relatively unchanged for all concentrations up to pure $Cd_3(PO_4)_2$. This fact is

FIG. 3. Schematic representation of typical x-ray diffraction patterns obtained for various compositions in the β $Zn_3(PO_4)_2$-$Cd_3(PO_4)_2$:Mn system.
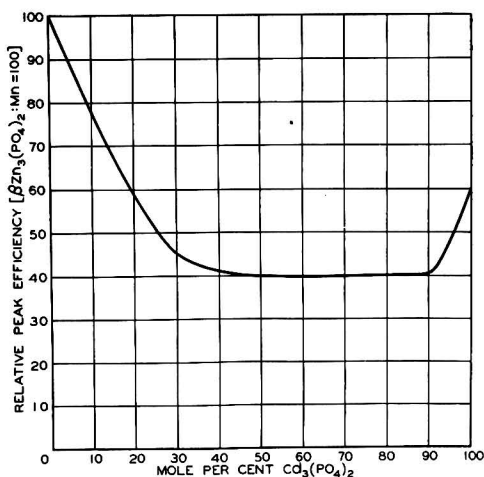
FIG. 4. Plot showing the variation in efficiency as a function of composition for the system β $Zn_3(PO_4)_2$-$Cd_3(PO_4)_2$:Mn fired at 875°C.

especially interesting because x-ray diffraction patterns indicate that pure phases are present at only a few points, all other points showing mixed phases (see Fig. 3). It might be assumed that each phase would have its own peak of emission and, with two phases present, either a double peak would be seen or the curve would be quite broad. Why this does not occur is not known.

Fig. 4 shows rather rapid decrease in peak efficiency as cadmium content is increased (preparation at 875°). At concentrations of about 40 or 50 mole % cadmium orthophosphate, the efficiency curve flattens to a value of about 40% of that of β $Zn_3(PO_4)_2$. The efficiency remains at that value until
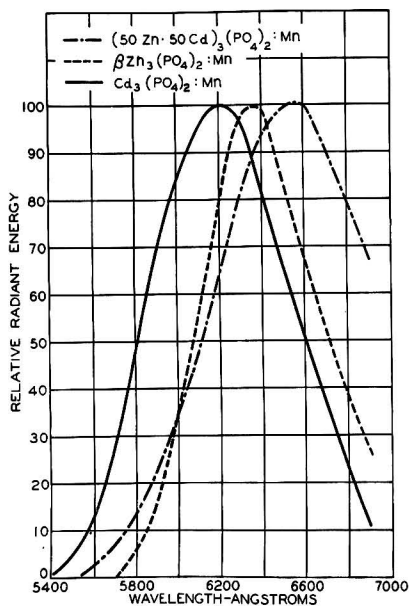
FIG. 2. Spectral energy distribution curves of the phosphors $[Zn_3(PO_4)_2$:$Cd_3(PO_4)_2]$:0.05 Mn, β $Zn_3(PO_4)_2$:Mn, and $Cd_3(PO_4)_2$:Mn.
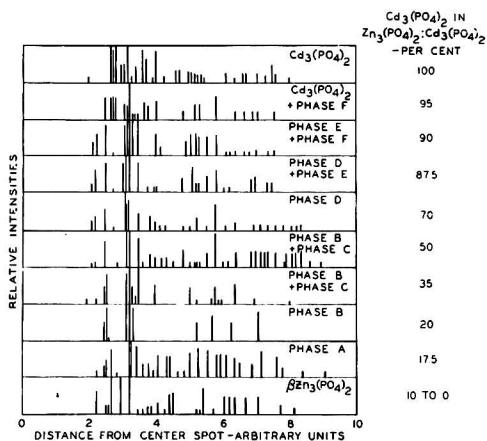
90% Cd$_3$(PO$_4$)$_2$ is reached, at which point it rises to 60% of Cd$_3$(PO$_4$)$_2$ itself.

From pure zinc orthophosphate to compositions with up to 17.5 mole % cadmium orthophosphate, the structure is essentially that of β Zn$_3$(PO$_4$)$_2$:Mn (see Fig. 3). At about the latter value a very abrupt phase change occurs which corresponds quite closely to the abrupt shift in peak of the emission curve (Fig. 1). The first phase, *A*, is of very narrow composition. At concentrations of 20 mole % cadmium orthophosphate another apparently pure phase, *B*, appears; this phase persists through concentrations having 50 mole % cadmium orthophosphate. Somewhere in the 50 mole % region a *C* phase is also found, but it could not be isolated. The *D* phase begins at concentrations of about 70 mole % cadmium orthophosphate and continues to concentrations of about 90 mole %; the *D* phase is contaminated in small portion by the *E* phase at concentrations of about 85 mole %. The *D* phase disappears at concentrations of 90 mole %, but another phase, *F*, is then found with the *E* phase. The *E* form could not be isolated; the appearance of the *E* form is coincident with another sharp break in the peak of the emission curve. At concentrations of 95 mole % cadmium orthophosphate, the *F* form is found together with normal cadium orthophosphate. No pure cadmium orthophosphate phase is present in the composition made with as much as 90 mole % cadmium phosphate.

Chloro-complexes of some of these phases are of interest. At and above 87.5 mole % cadmium composition, chloro-complexes were formed having emission and x-ray diffraction patterns essentially identical with those published by McKeag and Randall (6). At and below 20 mole % cadmium composition, emissions and patterns were distorted γ Zn$_3$(PO$_4$)$_2$ (1). Between these limits, however, no complexes were formed; the added chloride acted only as a "mineralizer" promoting crystal growth and did not affect emission or x-ray diffraction patterns.

CONCLUSIONS

When β zinc orthophosphate and cadmium orthophosphate mixtures are activated by manganese and fired at 875°C, phosphors are obtained whose luminescence is not a linear function of the mole proportions of the initial ingredients. The peak emission vs. composition curve shows several abrupt breaks, which correspond to abrupt phase changes as determined by x-ray diffraction analysis. There are probably six phases present in the β zinc orthophosphate-cadmium orthophosphate system, some of which are partially intersoluble. Three of these phases could be isolated, but the other three could not, even though only fractional percentage changes were made in regions where these compositions were thought to lie. Only two of the abrupt phase changes manifested themselves as abrupt changes in luminescence; the other variations showed only what would be expected from simple solid solutions. The unusual feature of these mixtures is that more abrupt changes in emission were not observed in the light of complex phase changes indicated by x-ray analyses. Lack of abrupt emission changes implies that the activator center was not altered radically by these phase changes, but rather was influenced in a very gradual manner.

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Sensitized Luminescence of CaF$_2$:(Ce + Mn)[1]

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ABSTRACT

Calcium fluoride activated by cerium and manganese is shown to be a sensitized phosphor of high quantum efficiency. Studies of its reflection and excitation spectrum reveal that both cerium singlets and aggregates of cerium ions serve as sensitizers for manganese. The range of interaction (K) over which energy may be transferred from sensitizer to activator was found to be from 30 to 80 lattice sites. Variation in K with increasing sensitizer and constant manganese concentration is interpreted as being due to the competition of two types of sensitizing centers rather than to an energy transfer between sensitizer ions.

INTRODUCTION

The sensitized luminescence of manganese-activated phosphors has been the subject of numerous investigations. While a number of sensitized systems of simple structure, principally alkali halides (1) and calcite (2), are known, the most recent investigations have been concerned with compounds of more complicated structure such as CaSiO$_3$:(Pb + Mn) (3), Sr$_3$(PO$_4$)$_2$:(Sn + Mn), Ca$_3$(PO$_4$)$_2$:(Ce + Mn) (4), and 3Ca$_3$(PO$_4$)2CaFCl: (Sb + Mn) (5). Although the interest in the more complicated systems originated largely in their practical application, it is from these phosphors that the most recent information concerning the mechanism of energy transfer and the range of sensitizer-activator interaction has been derived (6, 7, 8). Alkali halides and calcite, either for reasons of low activator or sensitizer solubility or because of poor luminescence efficiency, are not well adapted to the detailed investigation of the transfer mechanism and range.

Calcium fluoride is a compound of simple structure which has high solubility for both sensitizer and activator permitting preparation of efficient phosphor samples over a wide range of concentrations. It therefore appears to be ideally suited for the investigation of sensitized luminescence.

EXPERIMENTAL METHODS AND RESULTS

Preparation and Identification of Samples

No commercially available raw materials were found satisfactory for preparation of the phosphors studied. Although calcium and manganous fluorides sufficiently free of heavy metals were available, all samples of these materials were partially hydrolyzed, leading to oxidation of the manganese activator upon

firing. Some samples of calcium fluoride contained sufficient calcium hydroxide to produce a separate manganese-activated calcium oxide phase upon firing phosphor samples prepared from them.

A satisfactory calcium fluoride raw material can be prepared from calcium carbonate and hydrofluoric acid. When 25.0 grams of CaCO$_3$ are added to a solution of 25.0 ml of 48% HF in 250 ml of water, the calcium fluoride produced settles rapidly and may be washed by decantation. When dried at low temperature, preferably *in vacuo*, it suffers little or no hydrolysis, and samples will nearly completely disappear in a liquid of refractive index 1.434. The effect of using more concentrated acid is to produce finer particles of calcium fluoride which do not settle well, are more difficult to wash, and apparently are more susceptible to hydrolysis. Samples prepared from concentrated acid will not disappear in the refractive index medium mentioned above presumably because of the presence of an extra hydrolyzed phase. Of commercially available calcium fluoride, only optical quality crystals, either natural or synthetic, would meet the above described immersion test.

Cerous fluoride was prepared by a rather complicated procedure. Cerous nitrate solution was purified first with H$_2$S, then with ammonium sulfide in an alkaline solution of ammonium tartrate. Next, cerous oxalate was precipitated and washed. The oxalate was then dissolved in nitric acid; the solution was reduced with hydrogen peroxide, then the fluoride was precipitated with hydrofluoric acid. No attempt was made to separate other rare earths from cerium.

The most satisfactory source of manganese proved to be an ammonium manganous fluoride which is easily precipitated from manganous chloride solution with ammonium fluoride. The manganese content of this complex fluoride is somewhat variable; samples

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of it prepared in this laboratory averaged about 70.0 % MnF_2.

While luminescent preparations can be made simply by coprecipitation of the mixed fluorides and drying under an infrared lamp, the most efficient phosphors were prepared by dry mixing the component fluorides and firing at 1000°–1200°C in an inert atmosphere. Most of the samples prepared in this investigation were fired in platinum containers in helium or nitrogen at 1100°C. Inert gas was purified by passage over hot copper and calcium hydride. This firing technique produced samples with as much as 20 % Mn which were perfectly white by reflected light and free of any observable effects of manganese oxidation. No "skinning" of any sample was necessary.

Representative samples were examined by x-ray diffraction. All samples had the fluorite structure. Manganese produced a contraction, and cerium an expansion of the crystal lattice, as one would expect. Only in samples containing 20 % cerium was an extra unidentified line observed in the x-ray pattern. This line could not be correlated with any of the reported lines of any fluoride or oxide of calcium, cerium, or manganese.

Calcium Manganous Fluoride Phosphors

Many references to natural luminescent fluorite containing manganese have been made. Emission colors are variously reported as green to yellow. Synthetic manganese-activated fluorite was prepared by Wick (9), but no details of its emission spectrum were reported. Fig. 1 shows the cathode ray excited emission spectra of typical members of a series prepared in this laboratory and containing from 0.05 to 10.0 mole % Mn. Samples of from 0.05 % to 1.0 % Mn have an emission peak at 4900 Å.[2] With increasing manganese concentration, the emission peak shifts to longer wave lengths. At 5.0 % Mn the peak is at 5000 Å, while the peak of a 10.0 % Mn sample is at 5100 Å. A sample containing 20.0 % Mn was luminescent only at low temperature under cathode rays. None of the above described samples was appreciably excited by ultraviolet in the wave length range from 2200–4000, although a weak excitation band at 4000 Å exists in these phosphors as will be shown in a later section.

CaF₂(Ce) Phosphors

Kroger and Bakker (10) have briefly investigated calcium fluoride activated by cerium. They report

[2] In concurrent work, Dr. Arthur L. Smith, of Radio Corporation of America, located the emission peak of synthetic fluorite contining 1.0% Mn at 4950 Å. The reason for the minor discrepancy between his and the present work is not known, but may possibly be due to differences in either raw materials or preparation technique employed.
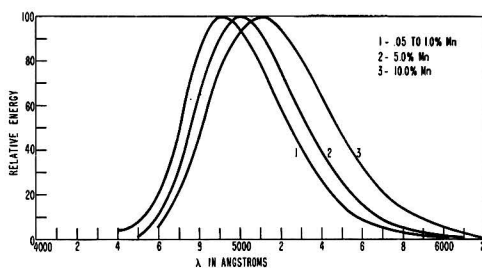
Fig. 1. Emission spectra of CaF₂:(Mn) under cathode ray excitation.
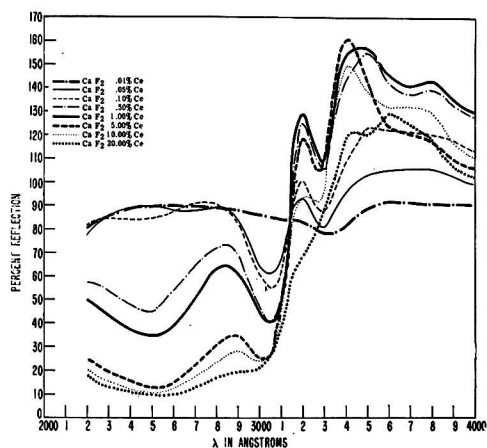
Fig. 2. Reflection spectra of CaF₂:(Ce)

an absorption edge at 3000 Å and an emission consisting of two peaks at 3100 Å and 3300 Å in a sample containing 1.0 % Ce. In a sample containing 10 % Ce, a third emission peak between 3500 Å and 4000 Å was observed.

In the present work, samples of from 0.01 to 20.0 mole % cerium were prepared. Absorption spectra of this series, as shown by the reflection curves of Fig. 2, are much more complicated than the simple edge described by Kroger and Bakker. At a concentration of only 0.01 % Ce, a single reflection minimum corresponding to an absorption band at 3300 Å is observed. With concentrations of from 0.05 % to 0.10 %, only one additional minimum at 3050 Å is obtained. With concentrations of 0.50 % Ce and higher, a band at about 2500 Å appears. While the absorption band at 3050 Å grows continuously with increasing cerium content, the band at 2500 Å grows much more rapidly at the higher cerium concentrations. At 1.0 % Ce the 2500 Å and 3050 Å reflection minima are about equal, while the 2500 Å minimum is predominant at all higher cerium concentrations.

Reflections of more than 100 % are obtained at
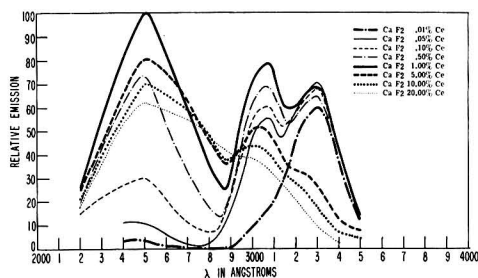
FIG. 3. Excitation spectra of CaF_2:(Ce) for 3850 Å emission band.

3200 Å and in two peaks between 3400 Å and 4000 Å. Apparent reflections of over 100%, due to luminescent emission, are obtained whenever the reflection spectrum of a phosphor is measured with the sample exposed to the total spectrum of the hydrogen lamp at the monochromator entrance slit, as was done in the present work.

Growth of the 3300 absorption band as a function of cerium concentration is obscured by the presence of the 3200 Å and 3400 Å emission peaks, while the growth of the 3050 Å absorption band is accentuated by its superposition upon the tail of the 2500 Å band. However, the presence of both the 3050 Å and 3300 Å bands in the sample containing only 0.05% Ce indicates that both of these bands are due to cerium singlets. The appearance of the 2500 Å band at only high concentrations of cerium and the rapid growth of this band relative to the singlet bands as a function of cerium concentration demonstrates that the shortest wave length absorption is due to cerium aggregates. For the present purpose, a cerium aggregate may be defined as consisting of at least two cerium ions whose proximity provides sufficient interaction to modify the absorption properties of the cerium center. The question of actual maximum separation of ions of an aggregate is left open.

Excitation spectra of CaF_2:(Ce) phosphors cannot be completely determined by the usual excitation measurement. The close proximity of the 3050 Å absorption and the 3200 Å emission bands as well as the proximity of the 3300 Å absorption to the emission at about 3400 Å prohibits the measurement of the excitation of the two short-wave emission bands by conventional methods. The technique of interposing filters between the phosphor sample and the phototube detector in order to separate the phosphor emission from light of the exciting wave length reflected from the sample surface could not be applied, since no filters could be found to effect the separation. The excitation spectrum for the 3800 Å emission was obtained in the usual manner by employing a Corning #5113 filter.

Fig. 3 represents the excitation spectra for the 3800 Å emission band. At the lowest cerium concentration a single sharp excitation peak at 3300 Å is obtained. As the cerium concentration is increased, a second excitation peak at about 3070 Å is observed. This latter peak grows relative to the 3300 Å peak with increasing cerium concentration. At a concentration of 0.10% Ce, an excitation peak at 2500 Å is well defined, and this peak is the most prominent at all higher concentrations. The latter excitation peak grows relative to the longer wave length excitation peaks with increasing cerium concentration, and its rapid growth at high cerium content is consistent with the interpretation that this peak is due to cerium aggregates. The growth of the 3070 Å peak relative to the 3300 Å peak is not obviously in agreement with the assumption that both these absorption bands are due to cerium singlets. However, it will be shown in the next section that the emission produced upon excitation in these two bands is not identical. Therefore, an identical behavior in the growth of the two excitation bands for only the 3800 Å emission should not necessarily be expected. It may be observed that the 2500 Å and 3070 Å excitation bands overlap considerably for all cerium concentrations except the lowest three, and that the amount of overlap increases with increasing cerium content.

Correction to equal energy of excitation was made only in the wave length range 2500–4000 Å; consequently, decrease in excitation shown at wave lengths shorter than 2500 Å is an exaggeration of the true decrease. However, since the excitation peak at 2500 Å coincides exactly with the absorption peak at this wave length, there can be little doubt that the peak is correctly located.

In the behavior of aggregate cerium ions as absorbers for 2500 Å radiation may lie the explanation why relatively high cerium concentrations are necessary for efficient excitation of other cerium-activated phosphors by 2537 Å radiation.

Since excitation spectra for all three emission bands could not be determined, information concerning the emission associated with the individual absorption bands was obtained by measuring the emission spectra of the phosphors with monochromatic exciting radiation in each of the three absorption bands. Exciting light was rendered monochromatic by passage through two quartz monochromators in series. Emission spectra were then recorded with a spectroradiometer in the conventional manner. For excitation in the 2500 Å band, 2537 Å radiation was employed, while for excitation in the 3070 Å band, the 2967 Å mercury line was used. The source of these mercury lines was an H-4 type mercury burner enclosed in a quartz envelope. For

FIG. 4. Emission spectra of CaF$_2$:(Ce)
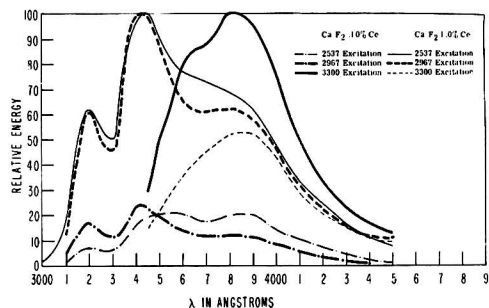
FIG. 5. Reflection spectra of CaF$_2$:(5.0% Mn, varying Ce).

3300 Å excitation, a band about 100 Å wide centered at the desired wave length was selected from the spectrum of either an AH-6 water-cooled mercury lamp or from a Xenon arc lamp. Emission spectra of all samples of the series were similar under any particular type of excitation. The emission of samples containing 0.10% Ce and 1.0% Ce are shown in Fig. 4. Under 3300 Å excitation, an emission consisting of a single peak at 3850 Å is obtained from the 1.0% Ce sample, while the emission of the 0.10% Ce sample shows resolution with a second peak at about 3650 Å. With both 2537 Å and 2967 Å excitation, emission peaks at 3200 Å and 3450 Å, as well as the 3850 Å peak, are observed. Minor variations in both peak positions and in their relative intensities were obtained as a function of cerium concentration, but emission spectra shown are typical for all members of the series. It can be observed with reference to Fig. 3 that excitation with 2967 Å radiation will result in absorption in both singlet and in aggregate cerium centers because of the overlap of the absorption bands of these centers at high cerium concentration. However, for cerium concentrations of 0.50% and lower, the overlap at 2967 Å is insignificant so that it can be stated with certainty that absorption in both the 3050 Å and 2500 Å bands produces all three emission peaks.

CaF$_2$:(Ce + Mn) *Phosphors*

While calcium fluoride activated separately by cerium and by manganese has been previously prepared, no sensitized combination of these two activators in fluorite seems to have been reported. In the present investigation, sensitized luminescence was observed in samples containing from 0.01% to 20.0% Ce and 0.05% to 20.0% Mn. Optimum concentration for 2537 Å excitation was found to be in the region of 1.0% to 10.0% of both cerium and manganese.

Reflection Spectra

Reflection spectra of sensitized phosphors are similar to those of phosphors containing only
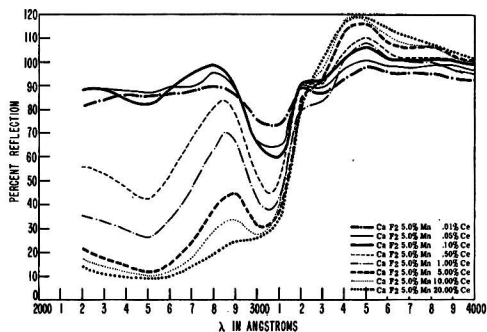
cerium. Fig. 5 shows the reflection spectra of a series of samples of 5.0% Mn and of varying cerium concentration. The three absorption bands found are located at the same wave lengths as in phosphors activated by cerium alone. The only distinguishing difference between the data of Fig. 5 and the reflection spectra of CaF$_2$:(Ce) phosphors is the smaller amount of ultraviolet emission obtained from phosphors containing manganese. Ultraviolet emission of these phosphors is depressed by transfer of energy to manganese, resulting in visible emission.

Reflection spectra of another series of phosphors of the same cerium contents but of 0.50% Mn were found to be identical with those of the 5.0% Mn phosphors except for the magnitude of the ultraviolet emission. The reflection spectra of two series of samples of constant cerium concentration but of varying manganese content from 0.05% to 20.0% were also determined. For samples of both 0.10% Ce and 1.0% Ce, reflection spectra were independent of manganese concentration, except in regard to the magnitude of the ultraviolet emission. It may, therefore, be concuded that no new absorption bands are introduceld by the presence of cerium + manganese pairs. In this respect, the sensitized calcium fluoride phosphor resembles most sensitized phosphors whose absorption spectra have been investigated. Notably, it differs from CaSiO$_3$:(Pb + Mn) in which Pb + Mn pairs appear to have a discrete absorption (7).

Excitation of Ce Emission

Excitation spectra for the 3850 Å-peaked ultraviolet emission of the CaF$_2$:5% Mn, Ce phosphors are shown in Fig. 6. Again, correction to equal energy of excitation was made only to 2500 Å. For all samples, the excitation peak in the region of 3300 Å is predominant. Poor sensitization of manganese should, therefore, be obtained at this wave length. The rapid growth of a 2500 Å excitation band due to cerium aggregates is not demon-
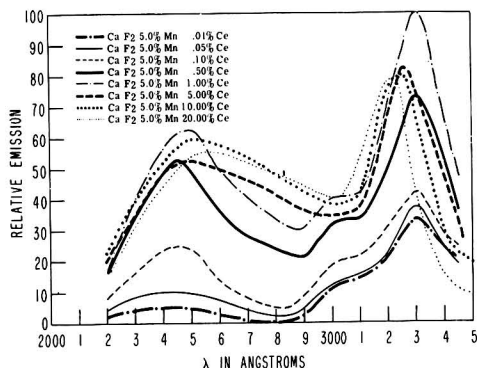
FIG. 6. Excitation spectra for 3850 Å emission band of CaF₂: (5.0% Mn, varying Ce).

strated in these curves. This growth should not be expected if good sensitization of manganese occurs in this band. In none of the samples is the 3050 Å excitation band well resolved, indicating that good sensitization should occur at this wave length.

Excitation spectra for ultraviolet emission obtained with other phosphor series were in agreement with the data for the series illustrated. A series containing constant 0.50% Mn and varying cerium concentrations showed the 2500 Å and 3050 Å bands in greater intensity relative to the 3000 Å band than was obtained with the 5.0% Mn series. Since at lower manganese concentration the opportunity for energy transfer and emission from manganese is lower than in the phosphors of 5.0% Mn, excitation spectra should more nearly resemble the data obtained for CaF₂: (Ce) phosphors. Measurements on phosphors of constant cerium but of varying manganese concentrations gave results also in agreement with data reported above. With 0.10% Ce and low manganese concentration, strong ultraviolet excitation peaks at 3050 Å and 3300 Å are obtained. As manganese is increased, the 3050 Å peak is suppressed. With 1.0% Ce present, excitation peaks at 2500 Å, 3050 Å, and 3300 Å are obtained with low manganese content. As the manganese concentration of this series is increased, the two short wave length peaks are reduced relative to the 3300 Å peak, indicating efficient sensitization of manganese in both the short wave length absorption bands.

Ultraviolet Emission Spectra

Ultraviolet emission spectra of Mn-activated CaF₂: Ce phosphors varied very little as a function of cerium concentration. As in the case of the phosphors activated with cerium alone, three emission peaks were obtained with either 2537 Å or 2967 Å excitation, but only a single peak at about 3800 Å was obtained with excitation at 3300 Å.
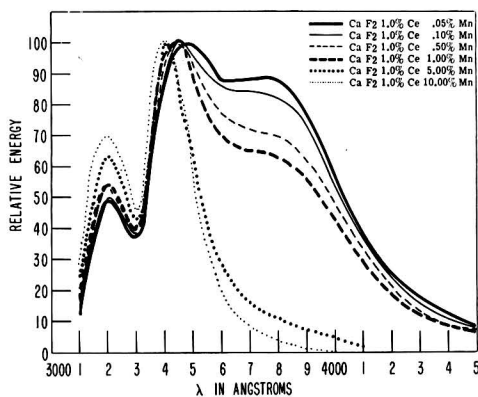
FIG. 7. Ultraviolet emission spectra of CaF₂: (1.0% Ce, varying Mn).

Minor differences occurred in the relative heights of the three emission bands of some samples, but no regular variation of peak intensities was found as a function of cerium concentration.

A more significant variation of ultraviolet emission spectra of phosphors of constant cerium but varying manganese concentration was obtained. As shown in Fig. 7 the 3800 Å emission of samples of 1.0% Ce is depressed relative to two short-wave emission bands with increasing manganese concentration. At a concentration of 5.0% Mn, the 3800 Å band is no longer distinguishable. Emission spectra shown were obtained with 2967 Å excitation. Results with 2537 Å excitation were similar.

Excitation Spectra of Manganese Emission

Excitation spectra of the manganese emission of a series of samples with 5.0% Mn are shown in Fig. 8. As expected, poor excitation occurs in the 3300 Å band. All samples have a strong excitation at 3050 Å. while the 2500 Å band grows relative to the 3050 Å band with increasing cerium content in agreement with the assumption that it is due to aggregated cerium ions. While aggregates of activators are recognized as luminescent centers in

FIG. 8. Excitation spectra for manganese emission of CaF₂: (5.0% Mn, varying Ce).

FIG. 9. Manganese emission spectra of CaF$_2$:(5.0% Mn, varying Ce) under monochromatic 2537 Å excitation.

many systems, no previous evidence for the behavior of aggregated ions as sensitizers for manganese appears to have been reported. The very slight rise in excitation at 4000 Å is real. From measurements on samples of varying manganese content it was found that this band peaks at about 4000 Å and is dependent on manganese, not upon cerium, concentration. It is apparently due to a weak manganese absorption band.

Manganese Emission Spectra

Manganese emission spectra under optical excitation were obtained with monochromatic excitation from the double monochromator arrangement mentioned earlier. Since the excitation energy available at 2537 Å is very low with this arrangement, a 1P21 photomultiplier tube was used as the detector in the spectroradiometer. Use of this tube prevented reliable calibration of the system at wave lengths longer than 6000 Å.

Emission spectra of a series of samples of 5.0% Mn and of varying Ce concentration obtained with 2537 Å excitation is shown in Fig. 9. Increasing cerium content shifts the emission to longer wave lengths. A shift from 5150 Å to 5550 Å in the emission peak is obtained upon a cerium concentration increase from 0.10% to 20.0%. Emission spectra of samples containing less than 0.10% Ce could not be obtained with 2537 Å excitation because of the low concentration of cerium aggregates in these samples.
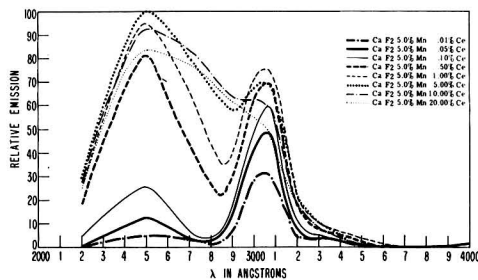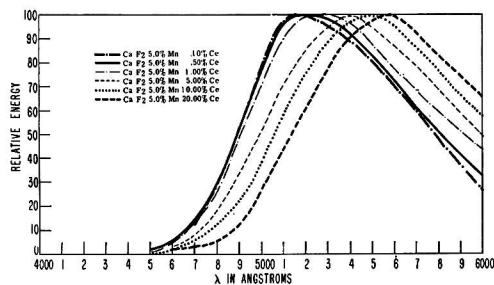
TABLE I. CaF$_2$:5.0% Mn—*2537 Å excitation*

1 % Ce	2 QE Ce	3 QE Mn	4 Total QE	5 $B = \dfrac{QEMn}{QECe}$	6 K
0.01	0.44	5.1	5.5	11.6	49.3
0.05	1.8	20.9	22.7	11.6	49.3
0.10	3.0	32.7	35.7	10.9	48.2
0.50	7.5	87.7	95.2	11.7	49.5
1.0	7.4	75.9	83.3	10.2	47.0
5.0	6.8	82.6	89.4	12.1	50.1
10.0	7.0	87.7	94.7	12.5	50.7
20.0	7.1	76.7	83.8	10.8	48.1

TABLE II. CaF$_2$:5.0% Mn—*2967 Å excitation*

1 % Ce	2 QE Ce	3 QE Mn	4 Total QE	5 $B = \dfrac{QEMn}{QECe}$	6 K
0.01	9.0	39.6	48.6	4.4	32.8
0.05	12.5	58.8	71.3	4.7	33.9
0.10	14.5	68.3	82.8	4.7	33.9
0.50	10.4	62.0	72.4	6.0	
1.0	9.2	60.7	69.9	6.6	
5.0	7.0	66.6	73.6	9.4	
10.0	7.1	72.8	79.9	10.2	
20.0	6.3	62.2	68.5	9.8	

Only manganese ions coupled to aggregated cerium absorbing centers are excited by 2537 Å. Different emission spectra were obtained upon excitation in the 3050 Å absorption band of cerium singlets and upon excitation with cathode rays. Further details of the emission spectra of these phosphors will be reported in a separate publication.

Quantum Efficiency

Quantum efficiencies of two series of phosphors were measured by a method similar to that described by Kroger (11). Separation of the cerium and manganese emissions was made with filters. Corning ≠5970 was employed for the ultraviolet measurement and Corning ≠3387 was used for the visible emission. Details of the method of measurement will be reported separately.

Quantum efficiencies of samples containing either 5.0% Mn or 0.50% Mn and 0.01% to 20.0% Ce are shown in columns 2, 3, and 4 of Tables I, II, III, and IV. Samples of lower manganese content could not be measured with any accuracy. Total quantum efficiencies as high as 95% were obtained with some samples of 5.0% Mn, while the maximum total quantum efficiency obtained with samples of 0.50% Mn was about 82%. The tables indicate that high transfer efficiency, evidenced by high quantum efficiency for manganese emission, is obtained when the 5.0% Mn phosphors are excited in either the absorption band of cerium singlets or in the aggregated cerium absorption band.

TABLE III. CaF$_2$:0.50% Mn—*2537 Å excitation*

1 % Ce	2 QE Ce	3 QE Mn	4 Total QE	5 $B = \dfrac{QEMn}{QECe}$	6 K
0.05	1.8	0.63	2.4	0.35	59.2
0.10	8.6	3.6	12.2	0.42	69.2
0.50	58.0	19.5	77.5	0.34	57.8
1.0	62.8	19.6	82.4	0.31	53.3
5.0	41.4	18.7	60.1	0.45	73.4
10.0	38.2	20.0	58.2	0.52	82.6
20.0	47.8	19.0	66.8	0.40	66.4

TABLE IV. CaF_2:0.50% Mn—2967 Å *excitation*

1 % Ce	2 QE Ce	3 QE Mn	4 Total QE	5 $B = \dfrac{QEMn}{QECe}$	6 K
0.05	40.2	6.8	47.0	0.17	31.0
0.10	59.5	11.9	71.4	0.20	36.0
0.50	61.7	15.8	77.5	0.26	
1.0	61.9	18.1	80.0	0.29	
5.0	38.2	18.2	56.4	0.48	
10.0	36.0	16.4	52.4	0.46	
20.0	41.8	15.0	56.8	0.36	

DISCUSSION

Several explanations of the phenomenon of sensitized luminescence have been proposed. These explanations have been reviewed by Botden (8). Since some of the mechanisms had been disproved on the basis of experimental evidence, Botden was concerned with the evaluation of three theories.

The first theory attributes transport of energy from sensitizer to activator to a so-called long wave exciton of the base lattice. The optical absorption of this exciton is assumed to be forbidden so that its existence is not normally recognized. This mechanism was suggested but not indorsed by Botden and Kroger (6).

A second theory proposed by Botden and Kroger ascribes excitation of the manganese activator to a direct transfer of energy between neighboring sensitizer and activator. Transfer between only nearest neighbor "pairs" of activators and sensitizers is assumed possible. To account for the high transfer efficiency existing in efficient phosphors, Botden and Kroger assumed that there is a preferential production of activator-sensitizer pairs in the phosphor synthesis. These authors also suggest that an excited sensitizer ion may transfer its energy to a neighboring sensitizer ion and hence to an activator, in order to account for the high transfer efficiency observed.

The third theory is that of Schulman (7) who proposed that energy is transferred from sensitizer to activator over distances greater than those separating only nearest neighbor pairs. From measurements of the absorption spectra of $CaSiO_3$:(Pb + Mn), Schulman concluded that transfer from an excited lead ion could take place to about the nearest 28 manganese ions.

Botden's critical evaluation of the three theories was based upon their predictions of the dependence of the ratio

$$B = \frac{\text{quantum efficiency of manganese emission}}{\text{quantum efficiency of sensitizer emission}}$$

upon the sensitizer concentration at constant manganese concentration. He demonstrated that

the first two theories predicted a decrease in B with increasing sensitizer concentration, whereas the third theory predicted no dependence of B upon sensitizer content. Botden found experimentally that in the systems $Ca_3(PO_4)_2$:(Ce + Mn), $Sr_3(PO_4)_2$:(Sn + Mn), $Ca_2P_2O_7$:(Sn + Mn), $Mg_2P_2O_7$:(Ce + Th + Mn) (12), and $3Ca_3(PO_4)_2 \cdot CaF_2$:(Sb + Mn) that B increased with increasing sensitizer concentration in disagreement with all three theories. Therefore, he concluded that all three were either incorrect or incomplete. He further demonstrated that an extension of Schulman's explanation which included the transfer of energy from sensitizer to activator via other sensitizer ions would account for the dependence of B upon sensitizer concentration. His calculation of K (the number of cation sites surrounding an excited sensitizer to any one of which energy may be transferred if it is occupied by an activator) gave values from 26 to 50 in agreement with the value obtained by Schulman.

Values of B, the ratio of manganese to cerium quantum efficiencies, for both 2537 Å and 2967 Å excitation are shown in column 5, Tables I, II, III, and IV. Under 2537 Å excitation, there is no increase of B with increasing cerium concentration. This is obviously apparent from data of the series of samples containing 5.0% Mn. While data of the samples containing 0.50% Mn show some scatter because of poorer precision in the measurement of these less efficient samples, nothing resembling a real increase in B with cerium content can be observed. With 2967 Å excitation, a constant B is obtained up to a concentration of 0.10% Ce in the 5.0% Mn phosphors. Less data at low cerium concentration are available for the 0.50% Mn concentration, but, for this manganese concentration as well, B can be interpreted as constant up to 0.10% Ce. At concentrations of 0.50% Ce and greater, B increases with increasing Ce concentration under 2967 Å in agreement with the results of Botden.

The behavior of CaF_2:(Ce + Mn) suggests an explanation of the dependence of B upon cerium concentration which does not involve transfer of energy between sensitizers.

A dependence of B upon sensitizer concentration in the absence of any sensitizer to sensitizer transfer can be expected in a system in which: (a) two species of sensitizers with different transfer ranges (K) exist; (b) the species of sensitizer with the greater transfer range is favored by an increase in sensitizer concentration; (c) the excitation energy is shared by the two sensitizer species. As the sensitizer concentration is increased, more of the excitation energy is absorbed by sensitizing centers with the greater transfer range. The increased transfer range of the system makes manganese emission more probable

with respect to sensitizer emission since the excited sensitizers have an opportunity to transfer energy to activator centers situated at greater distances from the sensitizer. Therefore, the ratio B will increase with increasing sensitizer content.

Sensitized System

In order to conclude that the foregoing mechanism takes place in a sensitized system it is necessary to demonstrate that:

1. Two species of sensitizer centers exist in the system with one type favored at higher sensitizer concentrations.

2. No sensitizer-to-sensitizer transfer takes place when each type of center is excited separately. Evidence for this must be no dependence of B upon sensitizer concentration when the centers are separately excited.

3. The sensitizer species favored at high sensitizer concentration must have a greater transfer range (K).

4. An increase of B is obtained with increasing sensitizer content when the excitation energy is shared by the two types of absorbing centers.

An examination of the data obtained from CaF$_2$:(Ce + Mn) reveals that this system meets all four specifications listed.

1. Both reflection and excitation data demonstrate that two types of sensitizer species exist with different absorption and excitation bands. The 3050 Å and 3300 Å bands appear at low cerium concentrations, while the 2500 Å band is created only at higher cerium contents and grows relative to the long wave length bands with increasing cerium concentration. The assignment of the long wave length bands to cerium singlets and the 2500 Å bands to aggregated cerium ions is an obvious designation.

2. No increase in B is observed from the data of Tables I and III under 2537 Å. This indicates that no sensitizer-to-sensitizer transfer occurs upon excitation in the aggregated cerium absorption band. B increases with cerium content under 2967 Å only in samples containing more than 0.10 % Ce. From the excitation spectra of Fig. 6 and 8 it may be seen that considerable overlap of the singlet and aggregate cerium excitation bands exists at 2967 A in samples with concentrations of cerium higher than 0.10 %. It is therefore only in the samples of 0.10 % and lower cerium concentration that 2967 Å radiation excites only singlet cerium absorbers. Within this concentration range no dependence of B upon cerium content is observed under 2967 Å as well. It can therefore be concluded that no evidence for a transfer of energy from sensitizer to sensitizer exists.

3. The transfer range of aggregated cerium ions is

greater than the range of cerium singlets. The transfer range K may be determined from the ratio B according to the relationship

$$B = \frac{1 - (1 - X\text{Mn})^K}{(1 - X\text{Mn})^K} \quad \text{(I)}$$

in which X Mn is the mole fraction of manganese. The formula represents the ratio of the number of sensitizers having at least one manganous ion within the nearest K cation sites to the number of sensitizers not having a manganous ion within this range of lattice positions. No specification to denote either the presence or absence of sensitizer aggregates is needed in the formula since this specification would appear in both the numerator and denominator of the expression. In this relationship, radiationless transitions are neglected. The derivation of this ratio was made by Schulman (7) who related it to the ratio of Pb + Mn pair absorption to Pb singlet absorption in CaSiO$_3$:(Pb + Mn). The relation of the same expression to B, the ratio of the quantum efficiencies of activator to sensitizer emission, was made by Botden (8), who concluded that its use is not justified for systems in which an energy transfer between sensitizers takes place. However, the demonstration that no sensitizer-to-sensitizer energy transfer takes place in calcium fluoride justifies the use of the formula with this system. Values of K calculated from the above formula are tabulated in column 6 of Tables I, II, III, and IV. The transfer range of singlet cerium sensitizers is found to be about 35, and good agreement is found in the data for both manganese concentrations. The value of K found for aggregate cerium sensitizers in the case of the 5.0 % Mn samples is about 50, whereas in the case of 0.50 % Mn the average value of K was found to be 66.

4. An increase of B as a function of cerium concentration is obtained when both the aggregate and singlet cerium sensitizers are simultaneously excited. It may be observed with reference to Fig. 6 and 8 that because of the overlap of the aggregate and singlet cerium excitation bands at 2967 Å, excitation energy of this wave length is shared by the two species of sensitizer ions. As the cerium concentration is increased, an increased number of sensitizer aggregates are formed, and the ratio of aggregates to singlets increases. Since aggregates have a greater transfer range than singlets, an increase in B is observed as a function of cerium concentration under 2967 Å excitation. From excitation data, it appears that significant overlap of excitation bands occurs only at concentration of 0.50 % Ce and greater. An increase in B as a function of cerium should be observed, therefore, only within this concentration range. The latter con-

clusion is corroborated by the data of Tables II and IV.

No variation in K as a function of either manganese or cerium content is predicted by the derivation of equation (I). No variation of K for singlet cerium sensitizers is obtained, nor is any variation of K for aggregate cerium sensitizers observed in the 5.0% Mn series. In the samples of 0.50% Mn, the value of K for cerium aggregates shows a spread from 53.3 to 82.6. Since this spread is simply a scatter, not a regular function of the cerium content, it must be within the limits of experimental error for these samples. Better precision in the determination of K at higher manganese concentrations is to be expected. Not only are samples of higher manganese concentration more easily reproducible since small errors in manganese content are less significant, but the value of K is a less sensitive function of B at the higher manganese content. At a value of $K = 50$, the slope of the curve of K vs. B has a value of about 150 for 0.50% Mn, whereas the slope of the curve for 5.0% Mn at the same value of K is only about 1.5. The values of the slope were calculated from

$$\frac{dK}{dB} = \frac{-(1 - X\mathrm{Mn})^K}{\ln(1 - X\mathrm{Mn})}$$

Therefore, although it appears more desirable to calculate K from data obtained at high manganese content in order to obtain better precision, it is necessary to demonstrate that no sensitizer-to-sensitizer transfer exists at low manganese contents as well, for at high manganese contents, sensitizer-to-sensitizer transfer should not be expected since the probability that at least one of the K sites around a sensitizer ion is occupied by an activator is so great that energy transfer between sensitizers is improbable. The probability that at least one of the K sites is occupied by an activator in a sample containing 5.0% Mn with $K = 50$ is 0.92. However, at a concentration of 0.50% Mn with the same values of K, the probability is only 0.22. Therefore, if sensitizer-to-sensitizer transfer existed in the calcium fluoride system, it would have appeared at the lower manganese concentration.

From the determination of K it may be concluded that the transfer range of aggregate cerium sensitizers is about 50% greater than that of cerium singlet centers. This is based on the value of K for cerium aggregates obtained at high manganese concentration, where the determination is made with better precision.

Interpretations of Difference in K

The simplest explanation of the higher value of K for cerium aggregates might be based on the geometry of the phosphor system. A cerium aggregate could be considered as consisting of a pair of singlet cerium sensitizers whose fields of possible transfer sites (K) overlap. Sensitization of a manganous ion situated at any lattice site included in the overlapping fields could occur following absorption in either of the cerium ions of the aggregate. Transfer from the more remote sensitizer to the activator could take place via the intermediate sensitizer. This process would involve a limited type of sensitizer-to-sensitizer transfer which is restricted to cerium ions constituting an aggregate. While this explanation cannot be completely excluded, it is not particularly attractive. In regarding a cerium aggregate as a pair of singlet sensitizers, absorption and excitation properties which distinguish the aggregate center from the singlet center are overlooked. Moreover, further evidence against this explanation may be derived from manganese emission spectra. Excitation of cerium singlets produces a manganese emission situated at shorter wave lengths than the manganese emission observed upon excitation of cerium aggregates. According to the intermediate transfer scheme, the manganese emission spectrum should be affected only by the cerium ion from which it receives the transferred energy directly. This would be particularly true if the separation between cerium ions constituting an aggregate is greater than the distance between nearest cation neighbors.

A second interpretation of the difference in K for singlet and aggregate sensitizers is more plausible. From the excitation data of Fig. 2 and 6, it may be observed that the 3050 Å and 3300 Å excitation bands overlap at all cerium concentrations. It has been demonstrated that poor excitation of manganese occurs upon excitation in the 3300 Å band while efficient excitation takes place upon irradiation at 3050 Å. Obviously at all cerium contents the excitation energy is shared by the two excited states of the cerium singlet ion upon excitation at 2967 Å, while it is only from the higher of these two states that efficient transfer can proceed. In the determination of B it is assumed that energy transfer is governed only by the consideration that a manganese ion is situated sufficiently near to a sensitizer ion. The probability that a sensitizer ion is in an excited state from which transfer can proceed is assumed to be unity. In the case of 2967 Å excitation, this probability is less than unity since the absorbed quantum can produce excitation of the sensitizer to either of two states. If an expression which incorporates this probability could be used to define B, a higher value of K than that reported here for cerium singlets would be necessary in order to account for the measured value of B. Since no way of approximating a value of this probability is at hand, the determination of K for cerium singlets cannot be further refined at the present time.

Although this interpretation invalidates the value of K obtained for cerium singlets, it does not affect the value determined for cerium aggregates. It does not concern the demonstration that no sensitizer-to-sensitizer transfer occurs in this system and that the observed variation in B under 2967 Å excitation at high sensitizer concentrations is due to the competition of two types of sensitizing centers.

Although the absence of sensitizer-to-sensitizer transfer has been shown in the CaF$_2$:(Ce + Mn) system, its existence in other systems as proposed by Botden may be quite correct. However, it should be pointed out that in the systems discussed by Botden the existence of two types of sensitizer species with different transfer ranges was not considered, although aggregates of sensitizers existed in the concentration range he studied. For none of these systems is sufficient absorption and excitation data available to determine whether aggregated sensitizers constitute a distinct species of sensitizer center.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1954 issue of the JOURNAL.

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Effect of Solvents and Electrolytes on Polarograms of Carbon Tetrachloride[1]

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ABSTRACT

Polarographic reduction of carbon tetrachloride has been studied in different mixtures of organic solvents with water, using a number of alkali halides and tetraalkylammonium halides as supporting electrolytes. On the positive side of the electrocapillary maximum of mercury, a marked effect of the nature of the anion of the supporting electrolyte on the half-wave potential was observed. On the negative side of the electrocapillary maximum, the cation effected a similar change. It was further observed that reduction became more difficult with increasing concentration of organic solvent. The last can be interpreted in terms of a change in activation energy of the electron transfer process. An equation has been derived which gives the effect of drop-time on the observed half-wave potential for irreversible reactions where the rate of the electron transfer process is the limiting factor. This has been verified experimentally with carbon tetrachloride. Finally, factors governing the occurrence of maxima on the polarographic wave in predominantly aqueous solutions have been investigated.

INTRODUCTION

During recent years a steadily increasing amount of work has been done on the polarographic reduction of organic halides (1–6). Von Stackelberg and Stracke (2) found that the half-wave potentials of halogenated hydrocarbons are independent of the pH of the medium, and that iodides are reduced more easily than bromides, and these, in turn, more easily than chlorides. By controlled-potential, large-scale electrolysis of some halogenated hydrocarbons showed that in most cases waves represented conversion of a carbon-halogen bond to a carbon-hydrogen bond according to the following all-over scheme:

$$RX + 2e + H_2O \rightarrow RH + X^- + OH^-$$
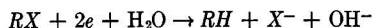
For halogenated organic acids, the polarographic wave is pH-dependent and is shifted to more negative values with increasing pH (3–5). Elving and coworkers (5), studying the polarographic wave of α-bromo-n-butyric acid, found that an increase in ionic strength in the alkaline region displaced the half-wave potential to more positive values, whereas the effect was opposite in the low pH region and much less pronounced. In some cases, they observed that the half-wave potential, at constant pH and ionic strength, depended on the kind of buffer used.

Shreve and Markham (7) reported on the effect of organic solvent on the polarographic reduction of p-nitroaniline. A marked shift of the half-wave

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potential to more negative values occurred with increasing ethanol concentration.

Only scattered remarks can be found in the literature about the effect of organic solvents on polarographic reduction of organic halogen compounds. It has been reported that half-wave potentials for halogenated acetones are shifted to more negative values by the addition of alcohol (8). Von Stackelberg and Stracke (2), working in a 90% butanol-water solution, found half-wave potentials up to 0.10 volt more negative than corresponding potentials in a 75% dioxane-water solution. Gergely and Iredale (6) mentioned, without data, that the half-wave potential for some aromatic iodo compounds was a function of the ionic strength, the alcohol content of the solution, and the nature of the cation of the supporting electrolyte. Rosenthal, Albright, and Elving (9) found that increasing ethanol concentration in the alkaline region shifted the half-wave potential of 2-bromo-n-alkanoic acids to more negative values, whereas, in the acid region, evidence of a shift was inconclusive.

A stepwise removal of the halogen atoms has been reported for carbon tetrachloride (2, 10). In 75% dioxane and $0.05M$ tetraethylammonium bromide, two waves were observed (2) with half-wave potentials of -0.78 volt and -1.71 volts. The latter corresponds well to the wave at -1.67 volts for the reduction of chloroform. In a (2:1) methanol-water mixture containing $0.10M$ tetramethylammonium bromide (10), waves for carbon tetrachloride were found at -0.75 volt and -1.70 volts and, for chloroform, at -1.70 volts. In this laboratory (11)

carbon tetrachloride gave a wave at -1.01 volts in 75% dioxane and $0.10M$ lithium chloride. It is obvious that the medium has a profound effect upon reduction, and that a more systematic investigation of the influence of the medium on the half-wave potential is needed. With more data on polarographic reduction of organic halogen compounds it should eventually be possible to formulate the reaction mechanism.

The present investigation deals with polarographic reduction of carbon tetrachloride in mixtures of methanol and water, *n*-propanol and water, acetone and water, and a (1:1) mixture of benzene and methanol, using various inorganic salts and tetra-alkylammonium halides as the supporting electrolyte. In a few instances, the effect of ionic strength on the half-wave potential and the influence of concentration of carbon tetrachloride on the wave-shape are also reported. Polarographic reduction of chloroform was investigated briefly in methanol-water mixtures to allow comparisons to be made with the second wave of carbon tetrachloride.

EXPERIMENTAL

Chemicals.—Mallinckrodt's "analytical reagent" grade of carbon tetrachloride, chloroform, methanol, acetone, and benzene was used without further purification. The *n*-propanol was Eastman white label. All the salts used were polarographically pure.

Apparatus.—Measurements of polarographic waves were made manually with a Sargent Model XII Polarograph. In some cases a Sargent Model XXI Recording Polarograph was used to study wave-shapes. Applied potentials were measured at each setting against a potentiometer. All potential measurements were made against an external saturated calomel electrode (S.C.E.) at 27°C. The S.C.E. was connected to the sample cell by means of an agar bridge. Potassium chloride was used as the salt in the bridge for runs with an inorganic salt as supporting electrolyte. When using a tetraalkylammonium halide as electrolyte, the last part of the bridge was made of tetraethylammonium bromide. Resistance of the circuit was measured with a Serfass Conductance Bridge, Model RC M 15. The capillary used had a value for *m* of 1.46 mg$^{2/3}$/sec$^{1/6}$ at open circuit in $0.1M$ potassium chloride.

Preparation of the solutions.—The supporting electrolyte was dissolved in 25 ml of a mixture of the organic solvent and water. Carbon tetrachloride was added in form of 0.50 ml of a 6.9×10^{-2} M solution in the pure organic solvent. Since this investigation was primarily concerned with the effect of the medium on the half-wave potential, no

measurements were taken to determine exact concentrations of organic halide in solutions.

Procedure.—Nitrogen was passed through a portion of the supporting electrolyte before going through the solution in the polarographic cell. Deaeration of 30 min for predominantly organic solutions and 15 min for predominantly aqueous solutions was found to be sufficient to remove oxygen. Then, 0.50 ml of the stock solution of the alkyl halide was added and the mixture flushed for an additional period. In the pure organic solvents one could flush for several minutes without a significant decrease of concentration of the alkyl halide, whereas in water only a few seconds of degassing was possible, owing to the high volatility of the alkyl halide in this medium.

All the data were corrected for residual current as obtained from a blank (prepared in a similar way by adding 0.50 ml of pure organic solvent) and for *IR*-drop. Unless otherwise stated, experiments were run at a head of mercury of 78 cm, and the solutions were $0.05M$ in supporting electrolyte.

RESULTS

Effect of Organic Solvents on Half-Wave Potentials of Carbon Tetrachloride

Table I gives the half-wave potential for the first wave of carbon tetrachloride in a series of methanol-water mixtures. With all salts studied, changing from water to 20% methanol had little or no effect on the half-wave potential. Beyond 20% the half-wave potential rapidly became more negative and then more or less leveled off, depending on the supporting electrolyte, at very high concentrations of organic solvent.

The second half-wave potential (Table II) was also shifted to more negative values by addition of methanol; the effect was, however, less pronounced. In all mixtures investigated, the second half-wave potential of carbon tetrachloride was practically

TABLE I. *Effect of the concentration of methanol and the nature of the $0.05M$ supporting electrolyte on half-wave potentials vs. S. C. E. of the first wave of carbon tetrachloride. Values are for $-E_{1/2}$*

Vol. ratio methanol/ water	LiNO₃	LiCl	LiBr	KI	(CH₃)₄ NBr	(C₂H₅)₄ NBr	(CH₃)₄ NI	(C₃H₇)₄ NI	(C₄H₉)₄ NI
Methanol	1.09	1.10	1.08	1.08	0.89	0.82	0.92ᵃ	0.87	0.88
5:1	0.95	0.95	0.95	0.95	0.82	0.74	0.81		0.74
2:1	0.78	0.80	0.78	0.79	0.70	0.62	0.70	0.65	0.64
1:1		0.59	0.60	0.64	0.58	0.50	0.61		0.59
2:3	0.46	0.47	0.48	0.59	0.46	0.44	0.57	0.57	0.57
1:4	0.35	0.35	0.40	0.54	0.40	0.37	0.53		0.53
Water	0.35	0.35	0.40	0.53	0.40	0.37	0.53		0.53

ᵃ A saturated solution, less than $0.05M$, was used.

TABLE II. *A comparison of half-wave potentials (vs. S.C.E.) for chloroform with that for the second-wave of carbon tetrachloride in methanol-water mixtures containing 0.05M electrolytes. Values are for* $-E_{1/2}$

Vol ratio CH₃OH/H₂O	(CH₃)₄NBr		(C₂H₅)₄NBr		(CH₃)₄NI		(C₃H₇)₄NI		(C₄H₉)₄NI		(CH₃)₄NCl CCl₄	LiCl CCl₄	KJ CCl₄
	CCl₄	CHCl₃	CCl₄	CHCl₃	CCl₄	CHCl₃	CCl₄	CHCl₃	CCl₄	CHCl₃			
CH₃OH	1.64	1.62	1.73	1.72	1.66ᵃ				1.90				
5:1	1.65	1.65	1.72	1.72	1.64	1.65			1.89	1.91			
2:1	1.64	1.64	1.68	1.68	1.63	1.63	1.75	1.76	1.84	1.84			
1:1	1.60	1.60	1.62	1.63	1.60	1.60			1.77				
2:3	1.57	1.57	1.59	1.59	1.57	1.58	1.65	1.66	1.73	1.72			
1:4	1.54	1.54	1.53	1.54	1.55	1.55			1.68	1.68	1.54	1.71	1.72
H₂O	1.53	1.54	1.50	1.51	1.53	1.53			1.65	1.65			

ᵃ A saturated solution, less than 0.05M, was used.
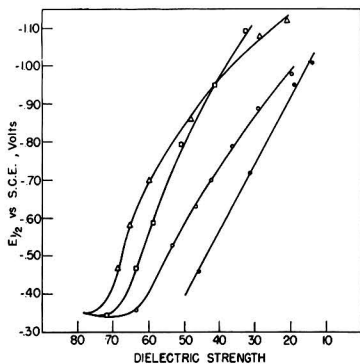
FIG. 1. Half-wave potential of the first wave of carbon tetrachloride as a function of the dielectric strength of mixtures of organic solvents with water. Electrolyte 0.05M lithium chloride. □—methanol-water; △—*n*-propanol-water; ○—acetone-water; ●—dioxane-water [data for dioxane solutions are taken from reference (11)].

identical with the first half-wave potential of chloroform, in agreement with previous observations (2, 10).

The very large shift with change in solvent for the first half-wave potential made it desirable to investigate the reduction in other media. Therefore, studies were made on *n*-propanol-water mixtures and on acetone-water mixtures; Fig. 1 shows the observed half-wave potential vs. the dielectric strength (12) of the solvents (without added electrolyte). As with methanol-water mixtures, reduction became more difficult at higher concentrations of organic solvent. One might have expected methanol and propanol solutions of the same dielectric strength to give the same half-wave potential,[3] but this was not the case. It is difficult to state what effect, if any, the capillary activity of the alcohols has on the half-wave potential.

The apparent numbers of electrons involved in the reaction, α, were calculated from the equation of the waves.

[3] Strictly speaking, solvents should only be compared at zero ionic strength, but the effect of ionic strength appears to be the same in both solutions.

$$E = E_{1/2} + \frac{0.06}{\alpha} \log \frac{i_d - i}{i}$$

In general, α-values of the first wave of carbon tetrachloride (Fig. 2) decreased markedly with increasing methanol concentration up to about 60% methanol, while at concentrations above 60% α increased slightly. Only with tetrabutylammonium iodide as electrolyte did α decrease throughout the region. Fig. 3 gives α of the second wave of carbon tetrachloride as a function of methanol concentration.
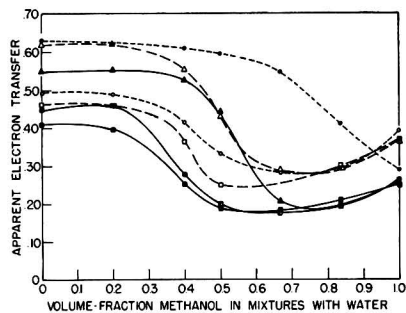
FIG. 2. α-values for the first wave of carbon tetrachloride as a function of methanol concentration and nature of the 0.05M electrolyte. ■—LiCl; ▨—LiBr; ▲—KI; □—(CH₃)₄NBr; △—(CH₃)₄NI; ○—(C₂H₅)₄NBr; ●—(C₄H₉)₄NI.
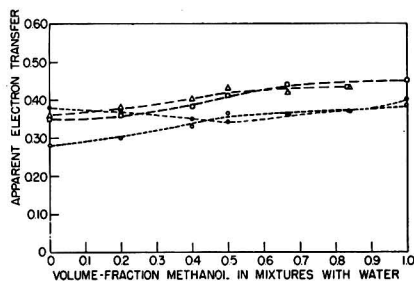
FIG. 3. α-values for the second wave of carbon tetrachloride as a function of methanol concentration and nature of the 0.05M electrolyte. □—(CH₃)₄NBr; △—(CH₃)₄NI; ○—(C₂H₅)₄NBr; ●—(C₄H₉)₄NI.

TABLE III. *Half-wave potentials vs. S.C.E. of the first wave of carbon tetrachloride in (1:4) methanol-water mixtures containing 0.05M electrolytes*

Electrolyte	$-E_{1/2}$	Electrolyte	$-E_{1/2}$
LiCl	0.35	LiBr	0.40
KCl	0.35	(CH₃)₄NBr	0.40
NH₄Cl	0.35	(C₂H₅)₄NBr	0.37
(CH₃)₄NCl	0.34	KSCN	0.44
HCl	0.34	KI	0.54
LiOH	0.35	(CH₃)₄NI	0.53
LiNO₃	0.35	(C₄H₉)₄NI	0.53

FIG. 4. Effect of ionic strength on the first half-wave potential of carbon tetrachloride. Curve 1—LiCl in a (1:4) methanol-water mixture; curve 2—KI in a (1:4) methanol-water mixture; curve 3—LiCl in a (2:1) methanol-water mixture; curve 4—LiCl in methanol.

Effect of Nature of Supporting Electrolyte and Ionic Strength on Half-Wave Potential

The most extensive investigation of the effect of supporting electrolyte on the half-wave potential of carbon tetrachloride was carried out in methanol-water mixtures where eight different electrolytes were studied. Data in Table I show clearly that in predominantly aqueous solutions the first half-wave potential is a function only of the anion of the supporting electrolyte. The same anion effect on the first half-wave potential in predominantly aqueous solutions was found with *n*-propanol-water mixtures and acetone-water mixtures. In high concentrations of methanol, the first half-wave potential of carbon tetrachloride does not depend upon which alkali salt is used as supporting electrolyte, but does depend upon the cation of the supporting alkyl-ammonium halide. On the other hand, only a cation effect was observed for the second half-wave potential throughout the whole range of solvent mixtures (Table II).

In order to get further insight into the observed anion effect on the first half-wave potential in predominantly aqueous solutions, six additional electrolytes were investigated in the (1:4) methanol-water mixture (Table III). The *pH* had little or no effect, as shown by the constancy of the half-wave potential in going from a lithium hydroxide to a hydrochloric acid solution. Different chlorides, nitrates, and hydroxides gave the same half-wave potential, −0.35 volt, while other anions shifted the potential to more negative values. Iodides shifted it more than thiocyanates,[4] and these, in turn, more than bromides. Wave shape was also affected by anions, steepness increasing upon going from chlorides to bromides to iodides (Fig. 2).

As shown in Fig. 4, increasing the ionic strength of an alkali halide shifted the first half-wave potential to more negative values in predominantly aqueous solutions, and to more positive values in predominantly organic solutions. Different tetraalkylammonium halides produced a similar shift.

[4] It was difficult to get maximum-free waves in the thiocyanate solutions.
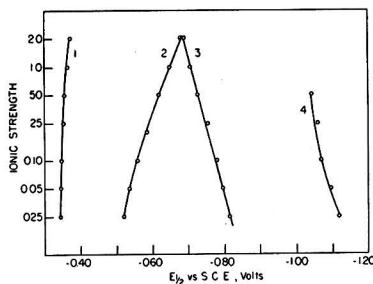
The large iodide effect in the (1:4) methanol-water mixture is obvious from these curves. In pure methanol, however, increasing concentrations of iodide and chloride produced the same shift. For the second half-wave potential a shift to more positive values throughout the whole region from water to methanol was found with increasing ionic strength of different tetraalkylammonium halides. •

Effect on Shape of Polarographic Wave of Concentration of Carbon Tetrachloride, Temperature, and Head of Mercury

Maxima often occurred on the first polarographic wave of carbon tetrachloride in predominantly aqueous solutions and thereby complicated the waves. Therefore, a series of experiments were carried out to get an idea of the factors governing occurrence of maxima. It was found that formation of maxima was favored at higher concentration of carbon tetrachloride, at longer drop times, and at higher temperatures.

Curves in Fig. 5 showing the effect of concentration of carbon tetrachloride and head of mercury, the latter used as a measure of the drop time, on the polarographic wave in a (1:4) methanol-water mixture, were obtained on the same sample. For one particular concentration of carbon tetrachloride, currents were measured at each potential setting with the mercury reservoir at different levels. After finishing one set of curves in this way, the solution was flushed for a few seconds to decrease the concentration of carbon tetrachloride, and a new set of curves obtained. Fig. 5 shows that in the region of the maxima, the current increased upon lowering the head of mercury, the reverse of the relationship for a diffusion-controlled process. When the concentration of carbon tetrachloride was very high, this rule was apparently not obeyed because curves for lower heads of mercury lay below curves for higher heads. However, polarograms obtained with a
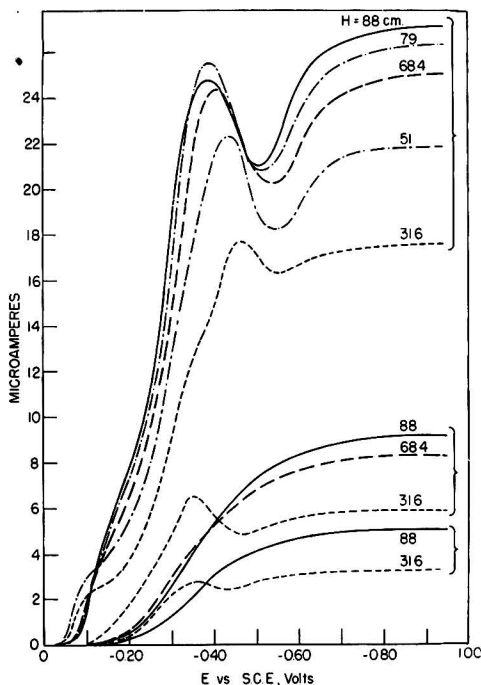
FIG. 5. Effect of concentration of carbon tetrachloride and the head of mercury on the polarographic wave in a (1:4) methanol-water mixture containing 0.05M lithium chloride. All curves within a given bracket were obtained at one particular concentration of carbon tetrachloride.

Sargent Model XXI Recording Polarograph on solutions of very high concentration of carbon tetrachloride showed that, in the region where the maxima occurred, the current-time curves for individual drops also had irregular shapes and went through one or two maxima. This "discharge," shown in Fig. 6, obviously prevented the current from attaining higher values.
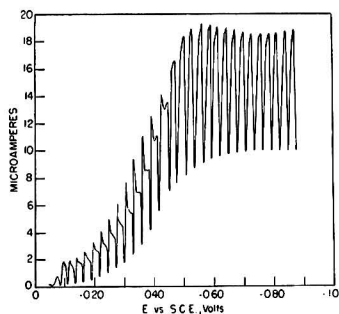
FIG. 6. First wave of carbon tetrachloride, at approximately five times the usual concentration, in a (1:4) methanol-water mixture containing 0.05M lithium chloride.
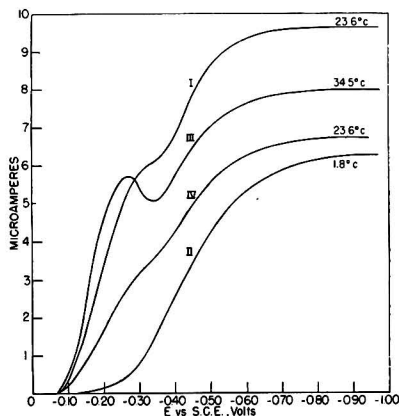
FIG. 7. Effect of temperature on the first wave of carbon tetrachloride in a (1:4) methanol-water mixture containing 0.05M lithium chloride. Numbers attached to the curves give the order in which the runs were made.

In an effort to determine whether or not an adsorption wave was involved, the temperature dependence of the maximum was investigated. A number of runs were carried out on the same sample in the order indicated by numbers attached to each curve in Fig. 7. In these runs, three times the usual concentration of carbon tetrachloride was used to accentuate changes in wave shape that accompany a change in temperature. Some carbon tetrachloride was lost when heating the sample for the high-temperature run as seen from a comparison of the values for the limiting current in the two runs at 23.6°C. In spite of this fact, it is clear that the size of the maximum increased with temperature. It is also interesting to note that no maximum occurred on the polarographic wave at 1.8°C. The possibility of suppressing the maximum with gelatin was also tried, but, in the usual concentration of 0.005% gelatin there was no effect.

In spite of these irregularities, the limiting current for the first wave showed normal diffusion-controlled behavior, i.e., limiting current was proportional to the square root of the height of the mercury reservoir, and had a temperature coefficient of 1.3% per degree.

Influence of Temperature and Head of Mercury on Half-Wave Potential

The temperature-coefficient of the first half-wave potential of carbon tetrachloride was unusually high. In a (2:1) methanol-water mixture, in a (2:1) acetone-water mixture, and in a (1:1) benzene-methanol mixture using potassium iodide, lithium chloride, and tetraalkylammonium halides as supporting electrolytes, the half-wave potential shifted about +3.7 mv/°C. In a (1:4) methanol-water

mixture with lithium chloride and potassium iodide as electrolyte the temperature-coefficient was 3.1 mv/°C. The slightly lower temperature-coefficient in aqueous solutions may indicate a lowering of the activation energy of the electrode process, but the difference is small and may not be significant.

Drop time was another factor of importance for the half-wave potential of carbon tetrachloride. A small shift of the half-wave potential with changing drop time has been predicted by Strehlow and von Stackelberg (13) from a consideration of a modified Ilkovic equation. The shift was predicted, and found to be slightly negative with increasing drop time for thallous and cadmium ions. For carbon tetrachloride, increasing the drop time from 5.5 sec to 16 sec shifted the half-wave potential +0.08 volt in a (2:1) methanol-water mixture which was 0.10M in tetramethylammonium bromide. This shift was opposite in sign and of larger magnitude than the shift predicted by Strehlow and von Stackelberg. This behavior of the half-wave potential may account for the discrepancy between the half-wave potential of the present study and that found by Kolthoff and coworkers (10) using the same solution.

An inspection of the waves revealed that the shift of half-wave potential with increasing drop time was due to the fact that the first part of the wave was nearly independent of the head of mercury, whereas the latter part was not (Fig. 8). It was necessary to determine whether this behavior was a general phenomenon, or whether it applied only in this case because the first part of the wave was located on the positive side of the electrocapillary maximum. A run was made with 0.10M potassium chloride in a (5:1) methanol-water mixture, where nearly the whole wave was located on the negative side of the electrocapillary maximum. The same relationship between the half-wave potential and the height of the mercury reservoir was found.

DISCUSSION

Effect of Added Electrolytes on Half-Wave Potential

A large anion effect on the first half-wave potential was observed in predominantly aqueous solutions and a cation effect in predominantly organic solutions. For the second wave only a cation effect was observed. This behavior leads one to suppose that the difference may be explained by the fact that the two waves in aqueous solutions are located on different sides of the electrocapillary maximum of mercury.

A study of Table III reveals that there exists a relationship between the effect of different anions on the half-wave potential and on the electrocapillary curve of mercury. Anions shifted the half-wave potential in the following order: Cl⁻ < Br⁻ < SCN⁻ < I⁻, which is in the same order as their capillary activity (14). The less capillary active anions OH⁻, NO₃⁻, and Cl⁻ gave the same half-wave potential. A relationship between half-wave potential and electrocapillary activity is further substantiated by observing the effect of different iodide concentrations on half-wave potential. Using the shift of the electrocapillary maximum as a measure of the capillary activity, Fig. 9 gives curves for the observed half-wave potential and of the potential of the electrocapillary maximum (14) as a function of the iodide concentration. The shift of the half-wave potential with increasing iodide concentration is of

FIG. 8. Effect of the head of mercury on the first wave of carbon tetrachloride in a (2:1) methanol-water mixture containing 0.1M tetramethylammonium bromide.

FIG. 9. Effect of iodide concentration on the first half-wave potential of carbon tetrachloride and on the electrocapillary curve of mercury. Curve 1—half-wave potential in (1:4) methanol-water mixtures containing potassium iodide; curve 2—electrocapillary maximum of mercury in (1:4) methanol-water mixtures containing potassium iodide; curve 3—electrocapillary maximum of mercury in water containing sodium iodide (14).

the same magnitude as the shift of the electrocapillary maximum.

This electrocapillary effect on the half-wave potential may be explained by the properties of the electrical double layer which exists between the solution and the mercury drop. Capillary active anions are strongly adsorbed to the mercury surface and form, at potentials more positive than that of the electrocapillary maximum, a sheath of negative ions very close to the mercury drop (the inner Helmholtz plane) (15). Consequently, the electrical potential is much more negative in the inner Helmholtz plane than at the mercury drop, and electrons need more energy to overcome this electrical potential barrier before effecting reduction of the carbon tetrachloride molecule in the inner Helmholtz plane or just outside it. Introduction of more strongly adsorbed anions or higher concentrations of a particular adsorbable anion produces a greater barrier, which in turn requires higher energy of electrons, i.e., a more negative potential to effect reduction. Thus, a change from chloride to iodide of the same concentration results in shifting a half-wave potential on the positive side of the electrocapillary maximum to more negative values.

The fact that waves in the predominantly aqueous solutions are steeper with iodides as electrolyte than with chlorides can be accounted for also. The adsorbed anions are more rapidly desorbed in the case of iodides for a given change toward a more negative potential (16). Thus, the more rapid decrease of this opposing potential in the iodide solutions should favor a steeper polarographic wave.

Similar reasoning can be used to explain the positive shift of the half-wave potential by capillary active cations on the negative side of the electrocapillary maximum. Here, a sheath of adsorbed positive ions produces a potential drop which facilitates reduction. Unfortunately, sufficient data are not available on the capillary activity of tetraalkylammonium salts to allow the effects to be compared. It is, therefore, difficult to say whether or not the shift of the half-wave potential can be explained completely by a capillary activity effect. It is interesting to note that a similar shift of the half-wave potential has been observed by Ashworth (17) in a study of the reduction of benzophenone and fluorenone.

Mechanism of Electrode Reaction

A high temperature coefficient of the half-wave potential is usually associated with an irreversible reaction. The temperature coefficient of the first half-wave potential of carbon tetrachloride, about $+3.4$ mv/°C, is one of the highest values observed for a polarographic reduction. For comparison, a

coefficient of 3 mv/°C was found in the reduction of hydrogen ions (18).

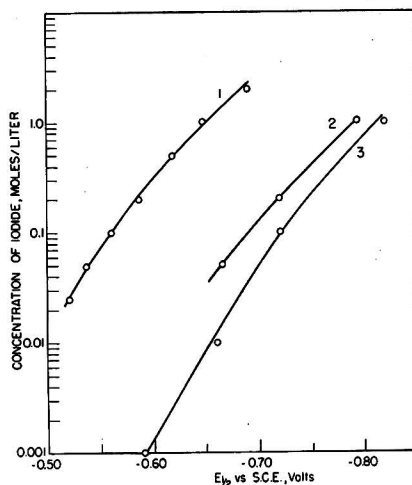Further indication of the irreversibility of a polarographic reduction can be found in the behavior of the polarographic wave with respect to the height of the mercury reservoir. If the electron-transfer reaction is very slow, the current in the beginning of the wave is limited not by diffusion, but by the drop time-independent electron-transfer reaction rate. This can be shown by making use of the following equation based on the absolute reaction-rate theory for electrode processes (19):

$$\frac{i}{nFA} = [Ox] \cdot k_1 \cdot e^{(-\alpha' EnF)/(RT)}$$
$$- [Red] \cdot k_2 \cdot e^{[(1-\alpha')EnF]/(RT)} \tag{I}$$

Where A is the area of the electrode; α' is the fraction of the applied potential acting in the direction of reduction; and k_1 and k_2 are the rate constants for the forward and backward electron-transfer reactions in the absence of applied potential. k_1 and k_2 depend on the free energy of activation, ΔF^*, and the standard reduction potential, E^0, of the reaction in the following way:

$$k_i = \frac{kT}{h} \cdot e^{(-\Delta F_i^*)/(RT)} \tag{II}$$

$$\frac{k_2}{k_1} = e^{-(nFE^0)/(RT)} \tag{III}$$

where k and h are the Boltzmann and Planck constants, respectively. Concentrations of oxidant and reductant at the interface are given by the Ilkovic equation:

$$i_d - i = \text{const.} \; nFD_{ox}^{1/2}m^{2/3}t^{1/6}[Ox] \tag{IV}$$

$$i = \text{const.} \; nFD_{Red}^{1/2}m^{2/3}t^{1/6}[Red] \tag{V}$$

Introducing these expressions into equation (I) and remembering that the area of the mercury drop is proportional to $m^{2/3} t^{2/3}$,

$$i = \cfrac{i_d}{1 + \cfrac{D_{ox}^{1/2}}{D_{Red}^{1/2}} \cdot e^{(E-E^0)nF/(RT)}} \\ + \text{const.} \; \cfrac{D_{ox}^{1/2}}{k_1 \cdot t^{1/2}} \cdot e^{(\alpha' EnF)/(RT)} \tag{VI}$$

For present purposes, this is considered as:

$$i = \frac{i_d}{1 + A + B} \tag{VII}$$

We shall now use this equation to consider the shape of the polarographic wave in three cases:

1. $A \gg B$. When the electron-transfer is rapid, the last exponential in the denominator of equation (VI) can be neglected and the equation becomes

the regular equation for "reversible" polarographic waves where the current is proportional to $m^{2/3} t^{1/6}$, and the half-wave potential is essentially independent of drop time.

2. $A \ll B$. This is a highly irreversible reduction, where the electron-transfer process is very slow and, hence, k_1 is small. The first exponential in the denominator of equation (VI) may be neglected so that the current is given by:

$$i = i_d \left[1 + \text{const.} \frac{D_{ox}^{1/2}}{k_1 \cdot t^{1/2}} \cdot e^{(\alpha' E n F)/(RT)} \right]^{-1} \quad \text{(VIII)}$$

At the beginning of the wave, the term 1 may be neglected and the current is independent of the height of the mercury reservoir. At more negative potentials (near the middle of the wave) the term with the exponential is of the same order of magnitude as 1, and the current depends on the drop time, though it is not proportional to $m^{2/3} t^{1/6}$. At still more negative values, where the exponential in equation (VIII) may be neglected, limiting current is proportional to $m^{2/3} t^{1/6}$ and shows the normal diffusion-controlled behavior.

In this case, the coefficient of the logarithmic term in the equation for the polarographic wave at 30°C is given by:

$$\frac{dE}{d\left(\log \dfrac{id - i}{i} \right)} = \frac{0.06}{\alpha' n} \quad \text{(IX)}$$

The half-wave potential, more negative than the reversible value in case 1, depends on the drop time in the following way:

$$\frac{dE_{1/2}}{d(\log t^{1/2})} = \frac{0.06}{\alpha' n} \quad \text{(X)}$$

That is, the half-wave potential should be shifted to more positive values with longer drop times, and the magnitude of the shift should be given by the coefficient of the logarithmic term. A plot of the half-wave potential vs. the logarithm of the square root of the drop time should yield a straight line.

3. $A \simeq B$. This case is for an intermediate degree of "irreversibility." The current near the beginning of the wave should be only slightly affected by drop time, whereas the limiting current should show normal diffusion-controlled behavior. The half-wave potential should be found in a region intermediate between the values found in cases 1 and 2, and should depend on the drop time in some complicated manner.

Data for carbon tetrachloride fall into case 2 since the limiting current showed normal diffusion-controlled behavior, whereas the current at the beginning of the wave was independent of drop time. Furthermore, the half-wave potential shifted
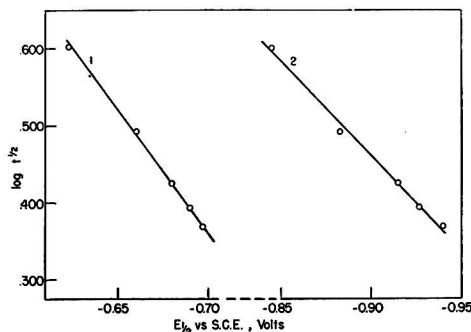
FIG. 10. Half-wave potential of carbon tetrachloride as a function of drop time. Curve 1—01.M $(CH_3)_4NBr$ in a (2:1) methanol-water mixture; curve 2—0.1M KCl in a (5:1) methanol-water mixture.

to positive values with increasing drop times. Curves in Fig. 10 show that there is a linear relationship between the half-wave potential and the logarithm of the square root of drop time which should be found if the reduction at the beginning of the wave is limited by the rate of the electron-transfer reaction. For a 0.10M potassium chloride—(5:1) methanol-water solution, equation (X) gave 0.15 for $\alpha' n$ and the slope of the polarographic wave gave 0.20. Agreement between the two is reasonably good and indicates that the rate of the electron-transfer reaction is the limiting factor at the beginning of the wave.

The different observed effects of solvents and electrolytes on the polarographic wave of carbon tetrachloride can be represented by the following reaction scheme:

$$CCl_4 + e \rightleftarrows [CCl_3\text{—}Cl]^- \rightleftarrows CCl_3 + Cl^- \quad \text{(XI)}$$

$$CCl_3 + e \rightarrow CCl_3^- \quad \text{(XII)}$$

$$CCl_3^- + H_2O \rightarrow CHCl_3 + OH^- \quad \text{(XIII)}$$
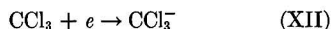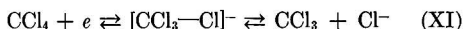
There is a slow addition of one electron to carbon tetrachloride to form an unstable transition state complex of the form $[CCl_3\text{—}Cl]^-$, which at once dissociates to a free radical and a chloride ion. At potentials necessary for this first reduction step, the free radical is immediately reduced further to a negative ion which, in turn, reacts with water to give chloroform. Any factor that contributes to stabilizing the transition state complex, and thereby lowers the activation energy of the first step (k_1 becomes higher), would displace the half-wave potential to more positive values. This is in accord with the observation that reduction is more easily accomplished in water than in organic solvents. Recalling the observed effect of capillary active electrolytes on the half-wave potential, it is obvious that an inactive salt should be used as the support-

ing electrolyte when comparing the effect of solvents on the wave.

Equation (XI), which gives the first step in the reduction of carbon tetrachloride, might indicate a specific chloride effect on the half-wave potential. This is not observed. The reason for this seemingly contradictory behavior is that the chloride effect enters equation (VI) only in the factor before the last exponential in the denominator. It has just been shown that when the polarographic reaction is highly irreversible owing to a slow electron-transfer process, this exponential may be neglected, i.e., equation (VIII) is operating.

Maxima on the Polarographic Wave

Behavior of the maximum for carbon tetrachloride is difficult to reconcile with currently accepted theories of maximum formation. The observation that current-time curves for individual drops in the region of maximum formation had irregular shapes and went through one or two maxima (Fig. 6) might indicate adsorption phenomena, where each maximum on the current-time curve corresponds to a different adsorption process. However, the effect of temperature makes an explanation based upon adsorption less likely. The electrokinetic theory set forth by Antweiler (20), where a difference in potential at different parts of the drop causes streaming of the solution around the drop, might help to explain the phenomena. One would expect capacity currents to be smaller than observed currents. It is possible that a new reaction mechanism favored by higher temperatures occurs in the predominantly aqueous solutions.[5]

ACKNOWLEDGMENT

Discussions with Mr. Hugh Keily as well as criticism of the manuscript by Professor David C.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1954 issue of the JOURNAL.

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[5] After the present manuscript had been submitted for publication, the authors found an abstract of the work of Frumkin and Florianovitch (21) in which the shift toward positive potentials of the reduction waves for nitrates, bromates, and iodates by the addition of cations was explained by a theory very similar to the one proposed here for carbon tetrachloride. Likewise, a paper by Kivalo, Oldham, and Laitinen (22) has just been published in which the hexaaquonickel (II) ion was employed to show experimentally dependence of half-wave potential on drop time and of the current on head of mercury in much the same way that carbon tetrachloride was used in the present study.

FTC Cites Evis Manufacturing Company on Advertising Claims

This item will be of particular interest to members of the Corrosion Division, as well as to the members of the Society in general.

Advertising claims that the Evis Water Conditioner "makes hard water feel, taste, and act softer," giving it a "silky-smooth quality" for hair, bath, dishes, laundry, and car wash, without the use of chemicals, are "false, misleading and deceptive" according to a Federal Trade Commission complaint.

The complaint cites Evis Manufacturing Company, San Francisco, together with Joseph T. Voorheis, as president, and Arthur N. Wells, as vice president.

According to the complaint, the product is a metal device which "has the appearance of an oversized pipe coupling with an interior cross post integrally cast in place." It is intended to be fitted into water systems for the purpose of beneficially treating and conditioning water.

The complaint lists as false and misleading the company's representations that the product:

Is made of a specially processed cast metal and has a catalytic effect on water passing through it which changes its physical behavior in many beneficial ways.

Solves hard water problems, causing "hard" water to become soft.

Removes and reduces unpleasant odors and flavors in water, making it taste better, and improves the taste of coffee and other foods.

Requires the use of less soap and reduces the cost of heating water.

Eliminates or reduces the harshness of water to the hands and causes dishes and glassware to dry without leaving water stains.

Removes grease from drains and prevents and removes scale from boilers, water heaters, pipes, shower nozzles, and other parts of a water system.

Prevents, reduces, and eliminates scum, rust stains, and corrosion and retards the pitting of metal.

Improves the action of chemicals used for water softening purposes

Leaches out alkali and salts in soil, improves the growth and production of various agricultural and orchard products and plants, and improves the texture and structure of soil.

Reduces the amount of water required for agricultural irrigation.

The respondents were granted 20 days to answer the complaint. Hearings in the case began April 8 in San Francisco. NOTE: Following the above complaint was a formal "Notice" to the Evis Manufacturing Company, from the Federal Trade Commission, notifying the Evis Company of the hearing set for April 8, 1954 at San Francisco, California.

The Evis Company was given until April 8 to "show cause why an order should not be entered requiring you to cease and desist from the violations of law charged in this complaint." This means, of course, that the Evis Company can either admit or deny the FTC charges.

Special Corrosion Program at M.I.T.

A special one-week summer program in Corrosion, to summarize the fundamental and recent advances in this field, will be given at the Massachusetts Institute of Technology June 21–25.

Dr. Herbert H. Uhlig, Professor of Metallurgy, will be in charge of the summer program. Special lecturers, in addition to Professor Uhlig, will include Milton Stern, Research Associate in Metallurgy at M.I.T.; W. Z. Friend and F. L. LaQue of the International Nickel Company, Inc.; L. P. Sudrabin of the Electro Rust-Proofing Corporation; R. M. Burns of the Bell Telephone Laboratories, Inc.; and Professor Norman Hackerman of the Department of Chemistry, University of Texas.

The program, according to Professor Uhlig, will include a presentation of fundamentals of corrosion reaction and control, followed by consideration and discussion of proper selection of corrosion resistant materials, chemical treatment of the environments, theory and practice of cathodic protection, selection of coatings and alloys economically feasible for reducing corrosion losses, and corrosion testing. Lecture table demonstrations will be shown and ample opportunity will be provided for questions and informal discussions.

In addition, registrants will visit the William F. Clapp Laboratories at Duxbury, Massachusetts, on Saturday, June 26, where Mr. A. P. Richards, president of the laboratories, will describe various research projects in marine fouling.

Tuition for the one-week special summer program in Corrosion will be $100. Further information and application blanks are available from the Summer Session Office, Room 7-103, M.I.T., Cambridge 39, Mass.

Programs in Instrumental Chemical Analysis

Two special summer programs in Instrumental Chemical Analysis, to enable chemists in industry and government laboratories to study the application of new instrumental techniques and methods in the field of applied

analytical chemistry, will be given during the 1954 Summer Session at the Massachusetts Institute of Technology.

The first program, from August 16–20, will be devoted to electrical methods of instrumental chemical analysis; the second, from August 23–27, will deal with optical methods of instrumental chemical analysis.

Both programs will be under the direction of Dr. David N. Hume and Dr. Lockhart B. Rogers, Associate Professors of Chemistry at M.I.T., who are in charge of the Institute's Instrumental Analysis Laboratory.

The two one-week summer programs are designed to provide, for both electrical and optical methods of instrumental analysis: 1. adequate background in the fundamental principles and theory involved; 2. understanding of representative practical applications; and 3. demonstrations of typical commercial instruments.

The program in electrical methods of instrumental chemical analysis will emphasize polarography, potentiometry, conductimetry (audio- and radio-frequency), amperometric titrations, automatic titration methods, and applications of thermistors and self-balancing recording potentiometers. A discussion of the principles of nonaqueous titrimetry is included.

The second program, in optical methods of instrumental chemical analysis, will cover spectrophotometry (visible and ultraviolet), colorimetry, fluorimetry, turbidimetry, nephelometry, photometric titrations, reflectance techniques, and flame photometry.

Tuition for each of the one-week programs will be $100. Further information and application blanks are available from the Summer Session Office, Room 7-103, M.I.T., Cambridge 39.

Westinghouse to Build Metals Development Plant

As a major step in an expanding metallurgical program, the Westinghouse Electric Corporation will build a new metals development plant at Blairsville, Pa. Scheduled for completion by late 1955, the new plant will be devoted to metallurgical development and pilot production of special alloys and special castings. Development activities at Blairsville will supplement but not duplicate specialized metallurgical effort now being carried on at the Company's aviation gas turbine, atomic power, and lamp divisions. A wrought alloy department will be completely equipped for melting, forging, hot and cold strip rolling, and heat treating.

E. B. Yeager Receives Cleveland Technical Societies Council Award

The annual award of the Cleveland Technical Societies Council for outstanding accomplishment by an engineer or scientist under 37 years of age, living in the Cleveland metropolitan area, was presented to Dr. Ernest B. Yeager on March 15, 1954. Dr. Yeager, who is 29 years old, is currently Associate Professor of Chemistry and Technical Director of the Ultrasonic Research Laboratory at Western Reserve University. He graduated from N. J. State Teachers College with an A.B. in mathematics (*Summa cum Laude*), and received his M.S. (1946) and Ph.D. (1948) in physical chemistry from Western Reserve University holding a Coffin Fellowship during this latter period.

E. B. YEAGER

He is serving The Electrochemical Society at present as Vice-Chairman of the Theoretical Division and is Vice-Chairman of the Cleveland Section. A member of many other scientific organizations, he is also Chairman of the Cleveland Section of the Spectrographic Society, and recently was chairman of several symposia sponsored by the Acoustical Society. Dr. Yeager has contributed numerous papers in the fields of electrochemistry (particularly electrode processes), ultrasonic waves, chemical and electrochemical reactions in ultrasonic fields, emission, and spectroscopy. He has appeared before many scientific and technical societies to discuss the research work being carried out by himself and his associates at Western Reserve University.

Flexible Leads

M. Eaton, coauthor with S. B. Thomas of the paper "Flexible Leads for Low-Frequency Electric Furnaces" which appeared in the February issue of the JOURNAL, informs us that since the paper was published he has learned that the original flexible leads of the type described were invented by Mr. Lund of La Societe des Electrodes de la Savoie. He has also been informed that Mr. Lund served with distinction in the Norwegian Resistance Movement during World War II and died as a prisoner of war in Germany.

N. J. Zinc to Take Over Cyanamid Co. Plant

In a joint statement by American Cyanamid Company and The New Jersey Zinc Company, it has been announced that the companies have entered into a contract under which the Zinc Company will purchase the Cyanamid Company's Gloucester City, N. J., titanium dioxide plant. The plant will be turned over to the Zinc Company after Cyanamid's new and larger titanium dioxide plant at Savannah, Ga., now under construction, has been completed and placed in operation. It is expected that this turnover will be made some time in the latter part of 1955.

Westinghouse Flotation Cells Installed

One of the largest flotation plant installations in the United States was recently completed when the last of 720 new flotation cells went into service at a large western copper concentrator. The plant is used for the recovery of copper and molybdenum.

The new cells, all powered by 15-hp 1750-rpm Westinghouse Electric Corporation Lifeline motors, replace 526 older-type cells driven by low-speed 10-hp motors. They are arranged in 45 rows, each containing 16 cells. Installation was made a few rows at a time, resulting in minimum disturbance to normal operations.

New Development by General Electric

The General Electric Company's top research official has disclosed the development of perfect crystals of pure iron, one-hundred times stronger than any known metallic crystal and inherently resistant to rust.

Explaining crystals as the building blocks that make up metals and alloys, Dr. C. G. Suits, vice president and director of research, said the perfect crystals represent for the first time metals that are as strong as theory predicts they should be and, as such, "provide a new and exciting dimension in metallurgy." He described the crystals as metallic whiskers about one thousandth of an inch thick and an inch or so in length. They were produced in the company's Research Laboratory in Schenectady, N. Y., by Dr. Robert L. Fullman and Arno Gatti. According to Dr. Suits, the first observations of metallic whiskers were made at the Bell Telephone Laboratories.

New Plant for Fisher Chemical Division

Work has been begun on a new plant of the Fisher Chemical Division in Fair Lawn Industrial Park, N. J. According to Aiken W. Fisher, president of Fisher Scientific Company, the new plant, to be completed in the fall of 1954, will be "the largest plant in the United States designed exclusively for reagent-grade chemicals." In addition to two buildings devoted to manufacturing, laboratory analysis, and packaging, a third building will house a research section for the development of new chemicals and new chemical sources.

SECTION NEWS

Cleveland Section

The March meeting of the Cleveland Section was held at the Cleveland Engineering Society on March 9, 1954. This was the occasion of the annual meeting of the Cleveland Section during which local electrochemists are given an opportunity to discuss original research before the Section.

Prior to the meeting, dinner was served, after which Dr. M. Merlub-Sobel, of Horizons Incorporated, spoke on "Natural Resources of Israel and their Utilization." Dr. Merlub-Sobel is currently on leave of absence from the position of Associate Professor of Chemical Engineering, Hebrew Institute of Technology, Haifa. Having personally participated in a number of projects aimed at utilization of the resources of Israel, he was able to give a good picture of progress made since founding of the nation of Israel.

Chairman Cahoon presided at the meeting and Vice-Chairman Yeager introduced the three local speakers. Dr. J. F. Yeager, of National Carbon, reported on his work at Western Reserve University on "Electrodeposition of Nickel." He discussed equipment and procedures used to make measurements of concentration polarization on nickel sulfate baths.

Anthony J. Kolk, of Horizons Incorporated, spoke on "Periodic Phenomena at the Platinum Electrode." He described the periodic voltage characteristics of the electrode and reported on investigations toward explanation of their behavior. This work was done at Case Institute of Technology.

Robert W. Penn, of Western Reserve University, then spoke on "Effects of Ultrasonic Waves on Concentration Gradients at Electrodes." He described his equipment, polarization curves obtained, and significance of the data, indicating that such high-frequency sound energy acts to depolarize an electrode to a limit.

MERLE E. SIBERT, *Secretary*

Midland Section

The program of the March 10 meeting of the Midland Section included dinner at the Country Club, followed by a Shell Oil Company movie, "Pipe Lines," and a talk by Dr. Howard T. Francis who is Director of Electrochemical Research, Armour Research Foundation.

Dr. Francis had a very interesting subject, "Corrosion Studies Using Rotogenerative Technique—Corroscope." He traced the development of the Corroscope from the measurement of the current flow in corrosion by means of auxiliary reference electrodes and a potentiometer, to the use of an oscillograph which measures the degree to which any point on a rotating cathode is an anode or cathode, to its present state of development in which the corroding specimen is scanned for possible anodic areas on a cathode ray tube.

Dr. Francis stated that, although the equipment was not entirely perfected, it had many uses, and that proposed corrosion inhibitors can be checked in a few minutes.

MARSHALL NEIPERT, *Secretary-Treasurer*

Pacific Northwest Section

The winter meeting of the Pacific Northwest Section was held on February 3, 1954, at Wright's Diner in Spokane, Washington. Approximately

40 members and guests attended a dinner and later heard an interesting lecture by Dr. H. H. Uhlig, Vice-President of the Society, and Professor of Metallurgy at Massachusetts Institute of Technology.

Dr. Uhlig, discussing "The Electrochemical Aspects of Corrosion," pointed out the five most common types of corrosion and illustrated these with lucid examples. He then reviewed electrochemical mechanisms involved and showed how an understanding of these mechanisms could be applied to the elimination of corrosion.

Dr. Uhlig noted the extreme youth of the science of corrosion and emphasized the need for the education of industrialists, designers, and the general public in recognizing the enormous losses due to corrosion. An application of the principles of corrosion can do much to reduce these losses.

The meeting was concluded with a spirited discussion following Dr. Uhlig's talk.   •

G. H. KISSIN, *Secretary-Treasurer*

Philadelphia Section

Robert J. McKay, President of The Electrochemical Society, was the speaker at the March 10 meeting of the Philadelphia Section. After about 40 members and guests had met and dined with the speaker at the Lenape Club, Mr. McKay spoke on the subject of oxygen concentration cells in corrosion.

Mr. McKay outlined briefly the early history of work pertaining to the role of oxygen in galvanic cells. The dearth of such work for some 120 years after the first observations in the early 1800's now seems remarkable in the light of the significance which is attached at present to such studies for a complete understanding of corrosion. He also pointed out that only about 30 years ago the electrolytic theory of corrosion was based entirely on the existence of dissimilar electrodes and that it has been only since that time that the importance of variation in concentration of surrounding electrolyte has become recognized.

Mr. McKay then described some experimental work which he has been conducting recently on oxygen concentration cells comprising steel electrodes immersed in salt water with oxygen supplied to one of the electrodes which then becomes cathodic while the other electrode dissolves. The quantitative data which he has obtained under a variety of conditions should lead to a

fuller understanding of many important problems of corrosion. The numerous questions raised at the close of Mr. McKay's address attested to the keen interest in this subject.

GEORGE BODAMER, *Secretary*

Washington-Baltimore Section

Mr. Sigmund Schuldiner, of the Naval Research Laboratory, discussed "Hydrogen Overvoltage on Bright Platinum" at the February 18 meeting of the Washington-Baltimore Section. Mr. Schuldiner defined hydrogen overvoltage and gave a description of the various components which comprise an overvoltage measurement. A thermodynamic-kinetic derivation of the Tafel equation was given, assuming the reversible discharge of hydronium ions followed by a rate-controlling combination reaction.

The experimental techniques used were described and results of hydrogen overvoltage measurements on bright platinum over the pH range 0.5–12.1 were given. Effects of added sodium and ammonium ions and pH were shown and relative rates of the over-all hydrogen producing reactions at low current densities were determined. A theoretical discussion of the mechanism of hydrogen overvoltage in these solutions followed, and the relationship between the pH effect on overvoltage and the buffer capacity of the solutions was shown.

FIELDING OGBURN, *Secretary*

MEETINGS OF OTHER ORGANIZATIONS

L'ALUMINIUM FRANCAIS and LA SOCIETE CHIMIQUE DE FRANCE, Scientific Congress and Exhibition, Paris, June 14–19, celebrating centenary of the first production of industrial aluminum in France by Henry Sainte-Claire Deville. Program and other relevant information available from the Secretary, L'Aluminium Francais, 23 Rue Balzac, Paris (8e), France.

INSTRUMENT SOCIETY OF AMERICA, third annual Analytical Instrument Clinic to be held in conjunction with the First International Instrument Congress and Exposition, Philadelphia, Sept. 13–15. Advance registration required. For registration forms and further information write Dr. Axel H. Peterson, Mellon Institute, 4400 Fifth Ave., Pittsburgh 13, Pa.

FIRST INTERNATIONAL · INSTRUMENT CONGRESS AND EXPOSITION, Philadelphia, Sept. 13–24.

THIRD SALON DE LA CHIMIE ET DES MATIÈRES PLASTIQUES, Paris, Dec. 3–12.

NEW MEMBERS

In March 1954 the following were elected to membership in The Electrochemical Society:

Active Members

CHARLES E. BATES, General Motors Corp., West Willard Street, Muncie, Indiana (Battery)

MICHAEL D. BENEDICT, The Gillette Co., Research Lab., Boston, Mass. (Corrosion)

PAUL F. BENTE, JR., E. I. du Pont de Nemours and Co., Niagara Falls, N. Y. (Electrodeposition)

BUSHNELL BEST, Great Lakes Carbon Corp., Niagara Falls, N. Y. (Industrial Electrolytic)

ROBERT COX, N. V. Koninklijke Nederlandsche Zoutindustrie, Boortorenweg 27, Hengelo (O), Netherlands (Battery, Corrosion, Electrodeposition, Electro-Organic, Electrothermic, Industrial Electrolytic, Theoretical Electrochemistry)

EUGENE D. GRYGLAS, Cinch Mfg. Corp., mail add: 2855 N. Linder Ave., Chicago, Ill. (Electrodeposition)

RICHARD J. HALSTED, Glidden Co. Chemical Pigments Div., mail add: 213 Dumbarton Road, Baltimore, Md. (Industrial Electrolytic) .

DONALD E. HASBROUCK, U. S. Rubber Co., 1230 Ave. of the Americas, New York, N. Y. (Battery, Electric Insulation)

RICHARD P. HUNNICUTT, General Motors Corp., mail add: 627 Woodlawn Ave., Royal Oak, Mich. (Electrodeposition)

WILLIAM M. KING, Clevite Brush Development Co., mail add: 1827 E. 291 St., Wickliffe, Ohio (Electrodeposition) Formerly Associate Member

ERIC A. OLLARD, British Non-Ferrous Metals Research Association, Euston Street, London N. W. 1, England (Electrodeposition, Theoretical Electrochemistry) Faraday Transfer

HAROLD DeBLOIS RICE, Gar Precision Parts Inc., 36 Ludlow St., Stamford, Conn. (Corrosion, Electrodeposition, Electronics, Industrial Electrolytic)

BILL F. ROTHSCHILD, Federal Mogul Corp., 2355 Stadium Blvd., Ann Arbor, Mich. (Corrosion, Electrodeposition)

CLEMENT G. STEIDL, Oxford Paper Co., mail add: 17 Porter Ave., Rumford, Maine (Industrial Electrolytic)

WILLIAM F. SWIGER, Lavino Chemical Co., mail add: 16 2nd St. N.E., Carrollton, Ohio (Electrodeposition, Industrial Electrolytic)

THOMAS ZWADZKI, Firestone Plastics Co., Pottstown, Pa. (Electric Insulation)

Active Reinstatement

FREDERICK H. PERFECT, Reading Chemicals, mail add: 1556 Penn Ave., Wyomissing, Pa. (Electrothermic)

Associate Members

ROGER J. LABRIE, National Bureau of Standards, Washington, D. C. (Electrodeposition)

WAYNE G. POLZIN, Diversey Corp., 1820 Roscoe St., Chicago, Ill. (Electrodeposition)

JOSTEIN J. VADLA, National Carbon Co., mail add: 228 4th St., Niagara Falls, N. Y. (Industrial Electrolytic)

Student Associate Member

HERMAN WISSENBERG, University of Michigan, mail add: 911 Hutchins St., Ann Arbor, Mich.

PERSONALS

H. W. SCHMIDT, Dow Chemical Company, Midland, Mich., and C. P. LARRABEE, U. S. Steel Corporation, Vandergrift, Pa., have been named members of the Technical Practices Committee of the National Association of Corrosion Engineers. This committee will be the policy making group for the association's technical activities.

CARLTON M. DEAN, Monsanto Chemical Company, St. Louis, Mo., has been made director of engineering sales of the company's newly created Research and Engineering Division, formed as part of an over-all move to provide more effectively for anticipated growth. Mr. Dean was manager of engineering sales in the Organic Chemical Division.

IDA M. PATTERSON, chemist at the Naval Research Laboratory, Washington, D. C., recently transferred from the Chemistry Division, Electrochemistry Branch, to the Metallurgy Division, Corrosion Branch.

WILLIAM M. RAYNOR has been assigned to assist the vice-president in charge of sales at Foote Mineral Company, Philadelphia, Pa. Mr. Raynor will continue as manager of Special Products Sales of the company in addition to his new responsibilities.

LESTER E. LIGHTON, vice-president in charge of engineering at the Electric Storage Battery Company, Philadelphia, Pa., was recently granted a patent by the U. S. Patent Office for an improvement in storage battery cells. Mr. Lighton now has six patents to his credit.

JOHN E. BARKLEY, one of the country's leading research managers in the physical chemical field, has become manager of physics and chemistry research for the Mechanical Division of General Mills, Inc., Minneapolis, Minn. He was formerly head of physical-chemistry research at Armour Research Foundation, Chicago, Ill.

HERBERT P. DENGLER has joined the staff of the Esso Engineering Department, Standard Oil Development Company, Linden, N. J.

ELMER A. THURBER, a pioneer member of the technical staff of Bell Telephone Laboratories, has recently been appointed a representative of the Chemical Physics Department at the Allentown, Pa., plant of Western Electric Company. In his new capacity he is responsible for chemical engineering services requisite to advanced development and pilot production of electronic devices.

BOOK REVIEWS

ELECTROCHEMICAL CONSTANTS, National Bureau of Standards Circular 524. For sale by Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C. 310 + iv pages, $2.00.

This monograph reports the proceedings of the National Bureau of Standards Semicentennial Symposium on Electrochemical Constants held at the NBS on September 19–21, 1951. Taking part in the symposium were a distinguished group of electrochemists, many being leaders in their respective fields. The title of this book is somewhat misleading since it contains many excellent reviews on modern electrochemical theory as well as discussions on the present status of electrochemical constants.

The standardization of specific electrochemical constants are considered in papers on: (*a*) the faraday constant, (*b*) conductance, (*c*) moving boundary measurements, (*d*) diffusion coefficients, (*e*) thermal diffusion, (*f*) the unit of emf, (*g*) the pH scale, (*h*) activity coefficients, (*i*) electrical double layers, and (*j*) polarographic constants. The problems of inclusions in the silver of the silver coulombmeter and with septa in standard voltage cells are the subject of two articles.

Included also are papers on electrochemical kinetics dealing with: reaction rates in dilute electrolyte solutions; the mechanism of overvoltage; parameters of electrode kinetics; and electrokinetics of capillary systems and colloidial solutions. Other topics are: absolute half-cell potentials; iodide-iodine solutions with the emf centrifuge; thermoelectric and thermomagnetic effects; and use of potential diagrams in interpreting inorganic chemistry. A few of the papers appear only in abstract form. The discussion which followed the presentation of each paper was recorded and is included in the monograph.

The book is well bound and nicely printed on a good grade of paper. It is a worthwhile addition to an electrochemist's library.

D. R. TURNER

THE COMPOSITION AND ASSAYING OF MINERALS by John S. Remington and Wilfrid Francis. Published by the Philosophical Library, Inc., New York, 1953. 127 pages, $5.50.

Students and workers in the mineralogical sciences will find this text book a convenient working reference to the techniques of identification and analysis of the common rock and ore forming minerals. Some 100 of the 127 pages of the text are given over to the descriptive mineralogy of ore minerals and the specific qualitative and quantitative techniques of identification. Detailed procedures and typical analyses are given for the assay of gold-silver, zinc, lead, and manganese ores. In the remaining text is made a brief presentation of the rapid and preliminary qualitative tests of physical and chemical mineralogy, and of the descriptive mineralogy of the more common rock forming silicates. (An error was noted on page 115. In the determination of SiO_2 by volatilization weight loss, HF should be substituted for HCl.) The text is concluded with a useful 9-page appendix of chemical and mathematical data.

Although it is not intended to be an exhaustive treatment, the book suffers from the lack of an index and reference citations. In particular, lack of reference to the rapid and accurate Bureau of Standards colorimetric methods of silicate rock analysis is a serious omission. The need for standardization between the English and the American mineralogical nomenclatures and formulations is also evident. The authors' expression of mineral compositions in terms of oxides and sulfides gives the undesired impression of a double salt. More conventional structural formulas are to be preferred.

As a supplementary working reference and handy guide, this book should prove useful to those working in the earth sciences and related fields.

STEWARD S. FLASCHEN

LETTER TO THE EDITOR

Journal Advertising

Dear Sir:

This letter carries my reasons for being disappointed on seeing advertising carried within the Technical Section of the March issue of the JOURNAL. Considering the fine job done by the present editorial staff and the increasingly higher standards achieved by papers currently published, it is painful to level criticism at a job otherwise magnificently done. But to let the present violation of the Technical Section pass by unnoticed, and thereby assent to it by silence, would be to fail my responsibility as a member of the Society and as a past member of the editorial staff.

High standing is achieved by a journal such as ours through the publication of high-quality scientific papers. There is at no time any suspicion of compromise between the allowable reported facts and the claims of the advertisers. The chips fall where they may, whether or not those who pay for or solicit ads are offended or pleased by the published papers. In other words, published papers obviously and invariably dominate the publication, and scientific considerations alone determine the policy governing papers accepted or rejected for publication. Advertisements, on this basis, are placed where they do not intrude into the main body of the publication, and, in order to remove even faint suspicions, advertisements are never al-

lowed to scramble the Technical Section any more than they are allowed as subject matter of a submitted paper.

The above is the policy I believe we should follow. Our journal deserves every reasonable chance of growing into an acceptable scientific publication, a trend to which many of our members are contributing much of their personal time and effort without compensation. This trend can only be maintained by keeping publication standards high, and relegating all advertising, without exception, to a secondary role in the JOURNAL makeup. Any other policy, I am convinced, marks a step backward.

Ideally, the JOURNAL should accept only dignified (not lurid, tabloid-type) advertising, each page of which is referred to the beginning or end of the JOURNAL. If the Society at any time is in need of income beyond revenues of this kind, we had better turn to increased sustaining memberships, or increased dues, or to a system of charging authors per page for papers published, rather than place on sale our standing in scientific circles. Only in this way do I believe

that we discharge our primary responsibility to the authors and readers of the technical and scientific papers we publish, and only in this way can the Society hope to achieve financial security based on an increasing membership and an expanding dependable support from industry.

H. H. UHLIG
Massachusetts Institute of Technology
Department of Metallurgy
Cambridge, Mass.

RECENT PATENTS

Selected by Fred. W. Dodson, Chairman of the Patent Committee, from the Official Gazette.

February 2, 1954

Gilbert, Jr., P. T. and Arthur, E. P., 2,668,143, Glass Electrode

Kröger, F. A., and Boomgaard, J. van den, 2,668,148, Thallium Activated Calcium Phosphate Phosphor Containing Aluminum

Foyn, K., 2,668,183, Electrode Suspension Mechanism and Method of Operation

Taylor, C. F., Briggs, W. E., and Weary, J. F., 2,668,184, Multiple Photocell Structure

Castlen, R. C., 2,668,185, Visible Liquid Level Indicating Nonspill Vent Mechanisms

Ouweltjes, J. L., 2,668,252, Electric Lamp

February 9, 1954

Wernlund, C. J., 2,668,795, White Brass Plating

Ekstein, C., 2,668,867, Photocell Construction

Nelson, C. G., 2,668,868, Flat Dry Cell Battery Pack

Bowden, J. J., Reissue 23,778, Method of Fluidizing Slag In the Manufacture of Steel by Open Hearth and Electric Furnace Processes

February 16, 1954

Larsen, E. I., Doty, A. S., and Williams, D. A., 2,669,512, Electric Contact Material and Method of Making the Same

Dooley, W. P., 2,669,542, Electrolysis of Sodium Sulfate

Larsen, B. M., 2,669,593, Aspirator Thermocouple Mounting for Measuring the Temperature of Hot Gases

André, H. G., 2,669,594, Electrical Accumulator

Gary, W. W., Jr., 2,669,595, Alkaline Battery

Nelson, F. H., 2,669,596, Reserve Battery Enclosure

Ruben, S., 2,669,597, Electric Current Producing Cell with Tin Anode

Marko, A., and Kordesch, K., 2,669,598, Process for Manufacturing Porous Carbon Electrodes

Clark, E., 2,669,599, Storage Battery Plate Separator

Geiselman, R. A., and Biggs, G. C., 2,669,673, Arc Furnace Control System

February 23, 1954

Hecht, B. P., and Koury, F., 2,669,767, Selenium Rectifier

Bungay, G. W., 2,670,326, Producing Curved Electrotypes

Rader, C. M., 2,670,327, Electrolytic Liquid Treating Device

West, O. A., 2,670,394, Shield Means for Pilot Burners and Thermocouple of Gaseous Fuel Burners

Audubert, R., and Calmar, C., 2,670,-395, Method for the Preparation of Depolarizers for Electric Cells

Field, B. R., 2,670,396, Venting and Pressure Release Arrangement of Electric Accumulators

LITERATURE FROM INDUSTRY

"ELECTROPLATING WITH RHODIUM." Illustrated booklet lists data and directions for electroplating with rhodium. Includes information on physical and electrical properties, corrosion resistance, and thickness specification of rhodium, and the cost of plating. General instructions given on preparation of work, electrocleaning, underplating, plating baths and their maintenance, stripping. Some practical hints for the plater are also discussed. Baker & Co., Inc.   P-202

D-C ELECTRICAL EQUIPMENT. A complete line of d-c electrical equipment for use in electroplating processes is pictured and described in a new 4-page, 2-color bulletin. The line includes d-c generators, rectifiers, PR controllers, tank rheostats, and special panels. An unusual feature of the bulletin is that both generators and rectifiers are covered, and their respective characteristics listed side by side. Information is given for the generators on standard voltage ratings, special construction of the brushes and holders, design of shunts, type of sleeve bearings, and construction of the generator ring. Photos are included for all equipment covered. Hanson-Van Winkle-Munning Co.   P-203

TWO ACCURATE WAYS TO MEASURE HIGH RESISTANCE are discussed in a recent issue of Keithley Engineering Notes. The first method, involving a Keithley vacuum tube electrometer and shunt, permits measurements to 124,-000,000 megohms full scale, at an absolute accuracy of within 5%. The second method employs an electrometer and low-leakage capacitor, and achieves similarly high sensitivity. Both methods permit the measurement of resistances far byond the reach of bridges, megohmmeters, and wall galvanometers. Keithley Instruments.   P-204

SODIUM SESQUISILICATE. Publication has been announced of a booklet which describes in detail the properties and uses of Metso 99, sodium sesquisilicate. It deals with the evaluations of sodium sesquisilicate with respect to the basic detergent properties of wetting, emulsification, dirt suspension, and prevention of redeposition. Also included is a demonstration of the product's ability to protect sensitive metals such as magnesium, copper, zinc, and brass when used alone or in conjunction with synthetics and polyphosphates. Popular detergent uses and general directions are tabulated by industry. A copy of the booklet will be sent to anyone requesting it on company stationery. Philadelphia Quartz Co.   P-205

LABORATORY OVENS. The subject of a new 8-page bulletin (FS-230) is the laboratory oven, an apparatus equally important to research, testing, quality control, clinical, and educational laboratories. Listed and described is the complete line of Fisher "isotemp" ovens. A summary is given of the basic studies in heat transfer that led Fisher engineers to turn the conventional "box"

heated by warmed air into a uniform-temperature apparatus heated by its own aluminum walls. Fisher Scientific Co.   P-206

PRINTED CIRCUIT SOCKETS. Currently off the press is a descriptive sheet on MYCALEX (Registered trade mark of the Mycalex Corporation of America) glass-bonded mica printed circuit sockets, giving specifications for various grades of MYCALEX. Mycalex Corp. of America.   P-207

NEW PRODUCTS

VOLTAGE DIVIDERS. Two new resistive voltage dividers, Models 2006 and 2007, have been announced. Have maximum inputs of 2000 and 20,000 volts, respectively, and input impedances of 10^{12} ohms. These voltage dividers make available a new type of high-impedance d-c kilovoltmeter. Features include unusual portability, polarity sensitivity, very short time constant, and wide selection of voltage ranges. Typical applica-

tions for the new equipment are in measuring voltages on cathode ray tubes, TV picture tubes, x-ray and radiation equipment, leakage of high-voltage insulators, and testing the voltage breakdown of cables. Keithley Instruments.   N-69

COLD CATHODE ELECTRONIC COUNTER. A precision, direct readout cold cathode electronic counter (Model RC) designed to operate at speeds up to 10,000 counts per minute and having a total counting capacity of 9,999,999 is now available. It operates at an accuracy precision of ±0 while maintaining a low power consumption. Features include longer life and accurate dependability, complete independence from line voltage variations and fluctuations, easy readability, efficient and instantaneous operation. Haledy Electronics Co.
                                    N-70

ELECTRONIC TEMPERATURE CONTROLLER. High sensitivity, long term stability, reliability, and low cost are featured in a new two-zone electronic temperature controller. The unit is designed for a wide range of industrial applications in all industry where accurate temperature control is required, including applications in petrochemical processing, the plastic molding and extruding field, and explosives manufacturing. Also suitable for use in laboratory work. Standard ranges are zero to 100, 300, or 500 degrees Fahrenheit and Centigrade. Sensitivity is 0.1°F on all ranges. Only two vacuum tubes are employed and the unit is encased in a strong cast aluminum housing. Robertshaw-Fulton Controls Co.   N-71

GLENNITE SUBMINIATURE RESISTORS. In response to the demand for very small, low power components, a unique line of Glennite subminiature resistors has been developed. Especially suitable for transistorized assemblies, the resistors can be used individually in multiples, in packaged R-C circuits, or incorporated into printed networks. Made of a special material deposited on a thin

ceramic base. Dimensions and electrode and lead arrangement are flexible enough to accommodate any special requirements. The Glenco Corp.   N-72

REDOX-O-TROL, a new apparatus, provides precise, automatic control of electrochemical reactions by controlling electrode potentials and has sufficient output for preparing selective reduction and oxidation products in substantial quantities. Controls electrode potentials within 100 mv. Has been used successfully in the preparation of pinacols of p-aminoacetophenone and p-aminopropiophenone. Useful also for electrolytic separation and determination of metals and for precise control of numerous chemical reactions. Outputs delivered range from 0.1 to 7 amperes at voltages from 1 to 27. American Instrument Co., Inc.   N-73

HIGH TEMPERATURE GERMANIUM DIODES. A "Red Dot" series of germanium diodes for high temperature applications is now being produced. Especially developed for equipment operating at a high ambient temperature, they have far superior forward and reverse characteristics than conventional diodes at high operating temperatures. May be identified by the special "Red Dot" marking on the glass housing. Each unit so well sealed that exposure to 95 plus % relative humidity for 500 hr at temperatures from 0°–85°C will not appreciably change back resistance or cause appearance of hysteresis. Designed for either clip-in or solder-in application. International Rectifier Corp.   N-74

INTEGRATING INSTRUMENTS. Two new integrating instruments, one current-integrating and the other current-squared integrating, have been announced. The instruments are designed for the solution of quality control problems encountered by the manufacturers of yarn, wire, strip metals, photo film, rope, plastics, and similar products in continuous moving processes. Permit rapid determination of the average thickness and standard deviation of tested samples; contain no control springs and have a special mechanism that provides a high degree of damping; afford unusually accurate readings. General Electric Co.   N-75

ULTRASONIC-POWER GENERATOR. The "Sonogen" Model 500 ultrasonic-power generator is designed primarily for ac-

celerating the cleaning and degreasing of small parts and metal objects such as strip, wire, and tubing, as well as complex components. It functions by activation of the cleaning solvent in which is immersed the low-voltage focused ceramic transducer. Radio-frequency output of the generator is 500 watts continuously at 450,000 cycles per second. In addition to cleaning, the Sonogen is an economical source of ultrasonic power for many other laboratory and production uses involving liquids, such as emulsification, dispersion, and the acceleration of chemical reactions. Branson Instruments, Inc.
                                    N-76

EMPLOYMENT SITUATION

Please address replies to box shown, % The Electrochemical Society, Inc., 216 W. 102nd St., New York 25, N. Y.

Position Wanted

ELECTROMETALLURGIST. B.S., M.S., and Ph.D. degrees in metallurgy. Permanent resident alien. Eight years in nonferrous and corrosion research. Knowledge of corrosion, hydro- and electrometallurgy, radiography, x-ray diffraction, spectro-analysis, and heat treatment. Desires position in research, production, or plant control with opportunity for experience and advancement. Location immaterial. *Reply to Box 355.*

To receive further information on any New Product or Literature from Industry listed above, send inquiry, with key number, to JOURNAL of The Electrochemical Society, 216 West 102nd Street, New York 25, N. Y.

Please print your name and address plainly.

The Electrochemical Society

INSTRUCTIONS TO AUTHORS OF PAPERS

FORM

Manuscripts submitted for publication should be in triplicate to expedite review. They should be typewritten, double-spaced, with $2\frac{1}{2}$–4 cm (1–$1\frac{1}{2}$ in.) margins.

Title should be brief, followed by the author's name and his business or university connection.

Abstract of about 100 words should state the scope of the paper and give a brief summary of results.

ILLUSTRATIONS

Drawings will be reduced to column width, 8 cm ($3\frac{1}{8}$ in.), and after reduction should have lettering at least 0.15 cm ($\frac{1}{16}$ in.) high. Original drawings in India ink on tracing cloth or white paper are preferred. Curves may be drawn on coordinate paper only if the paper is ruled in blue. All lettering must be of lettering-guide quality. See sample drawing on reverse page.

Photographs must be glossy prints and mounted flat.

Captions for all figures must be included on a separate sheet. Captions and figure numbers should not appear in the body of the figure.

General—Figures should be used only when necessary. Omit drawings or photographs of familiar equipment. Figures from other publications are to be used only when the publication is not readily available, and should always be accompanied with written permission for reprinting.

REFERENCES

Literature and patent references should be listed at the end of the paper on a separate sheet, in the order in which they are cited. They should be given in the style adopted by *Chemical Abstracts*. For example:

R. Freas, *Trans. Electrochem. Soc.*, **40**, 109 (1921).

H. T. S. Britton, "Hydrogen Ions," Vol. **1**, p. 309, D. Van Nostrand Co., New York (1943).

H. F. Weiss (To Wood Conversion Co.), U. S. Pat. 1,695,445, Dec. 18, 1928.

UNITS OF MEASUREMENT

Metric units should be used throughout but, where desirable, English units may be given in parentheses.

Corrosion rates in the metric system should preferably be expressed as milligrams per square decimeter per day (mdd), and in the English system as inches penetration per year (ipy).
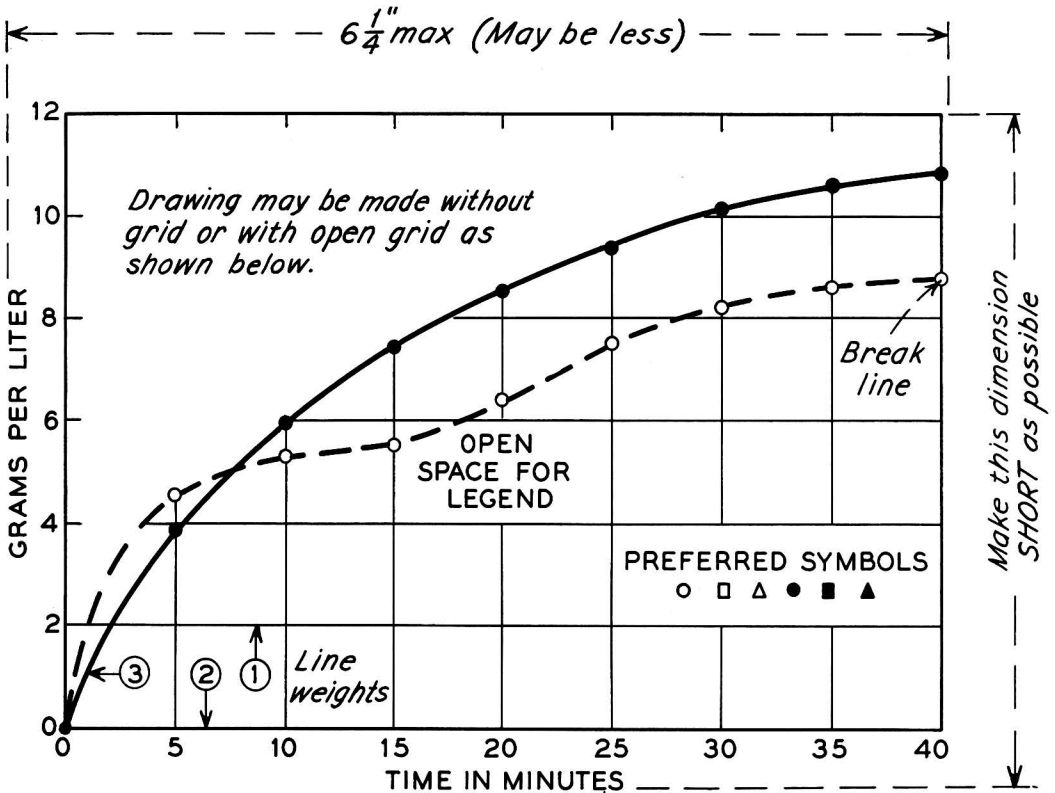
As regards algebraic signs of potentials, the standard electrode potential for $Zn \rightarrow Zn^{++} + 2e$ is negative; for $Cu \rightarrow Cu^{++} + 2e$, positive.

GENERAL

Authors should be as brief as is consistent with clarity, and must omit all material which can be regarded as familiar to specialists in the particular field.

The use of proprietary names, trade-marks, and trade names should be avoided if possible. If used, these should be capitalized so that the owner's legal rights are not jeopardized.

$6\frac{1}{4}"$ max (May be less)

Make this dimension SHORT as possible

Drawing may be made without grid or with open grid as shown below.

GRAMS PER LITER

Break line

OPEN SPACE FOR LEGEND

PREFERRED SYMBOLS
○ □ △ ● ■ ▲

③ ② ① Line weights

TIME IN MINUTES

Remarks: Line weight ② is used for borders and zero lines. When several curves are shown, each may be numbered and described in the caption. Lettering is approx. ⅛".

SAMPLE CURVE DRAWING FOR REDUCTION TO $\frac{1}{2}$ SIZE

Sustaining Members of The Electrochemical Society

Air Reduction Company, Inc., New York, N. Y.

Ajax Electro Metallurgical Corporation, Philadelphia, Pa.

Alloy Steel Products Company, Inc., Linden, N. J.

Aluminum Company of America, New Kensington, Pa.

Aluminum Company of Canada, Ltd., Montreal, Canada

American Machine & Foundry Co., Raleigh, N. C.

American Platinum Works, Newark, N. J. (2 memberships)

American Potash & Chemical Corp., Los Angeles, Calif.

American Zinc, Lead and Smelting Company, St. Louis, Mo.

Armour Research Foundation, Chicago, Ill.

Auto City Plating Company Foundation, Detroit, Mich.

Bell Telephone Laboratories, Inc., New York, N. Y.

Bethlehem Steel Company, Bethlehem, Pa. (2 memberships)

Buffalo Electro-Chemical Company, Buffalo, N. Y.

Burgess Battery Company, Freeport, Ill. (4 memberships)

Canadian Industries Limited, Montreal, Canada

Chrysler Corporation, Detroit, Mich.

Columbia-Southern Chemical Corporation, Pittsburgh, Pa.

Consolidated Mining and Smelting Company of Canada, Ltd., Trail, B. C. (2 memberships)

Corning Glass Works, Corning, N. Y.

Crane Company, Chicago, Ill.

Diamond Alkali Company, Pittsburgh, Pa. (2 memberships)

Dow Chemical Company, Midland, Mich.

Wilbur B. Driver Company, Newark, N. J.

E. I. du Pont de Nemours & Company, Inc., Wilmington, Del.

Eagle-Picher Company, Joplin, Mo.

Eaton Manufacturing Company, Stamping Div., Cleveland, Ohio

Electric Auto-Lite Company, Toledo, Ohio

Electric Storage Battery Company, Philadelphia, Pa.

The Eppley Laboratory, Newport, R. I.

Ford Motor Company, Dearborn, Mich.

General Chemical Division, Allied Chemical & Dye Corporation, New York, N. Y.

General Electric Company, Schenectady, N. Y.

General Motors Corporation, Research Laboratories Division, Detroit, Mich.

Gould-National Batteries, Inc., Depew, N. Y.

Graham, Crowley & Associates, Inc., Chicago, Ill.

Great Lakes Carbon Corporation, Niagara Falls, N. Y.

Hanson - Van Winkle - Munning Company, Matawan, N. J. (2 memberships)

Harshaw Chemical Company, Cleveland, Ohio (2 memberships)

Hooker Electrochemical Company, Niagara Falls, N. Y. (3 memberships)

Houdaille-Hershey Corporation, Detroit, Mich.

International Graphite & Electrode Div., Speer Carbon Company, St. Marys, Pa. (2 memberships)

International Minerals & Chemical Corporation, Chicago, Ill.

International Nickel Company, Inc., New York, N. Y. (3 memberships)

Kaiser Aluminum & Chemical Corporation, Division of Metallurgical Research, Spokane, Wash.

Mathieson Chemical Corporation, Niagara Falls, N. Y.

McGean Chemical Company, Cleveland, Ohio

Merck & Company, Inc., Rahway, N. J.

Metal & Thermit Corporation, New York, N. Y.

Monsanto Chemical Company, St. Louis, Mo.

National Carbon Division, Union Carbide and Carbon Corporation, New York, N. Y. (2 memberships)

National Cash Register Company, Dayton, Ohio

National Research Corporation, Cambridge, Mass.

Niagara Alkali Company, Niagara Falls, N. Y.

Norton Company, Worcester, Mass.

Pennsylvania Salt Manufacturing Company, Philadelphia, Pa. (2 memberships)

Philco Corporation, Lansdale, Pa.

Philips Laboratories, Inc., Irvington-on-Hudson, N. Y.

Potash Company of America, Carlsbad, N. Mex.

Promat Division, Poor & Company, Waukegan, Ill.

Ray-O-Vac Company, Madison, Wis.

Rockwell Spring and Axle Company, Coraopolis, Pa.

Solvay Process Division, Allied Chemical & Dye Corporation, Syracuse, N. Y. (3 memberships)

Stackpole Carbon Company, St. Marys, Pa.

Standard Steel Spring Division of the Rockwell Spring and Axle Company, Coraopolis, Pa.

Stauffer Chemical Company, San Francisco, Calif.

Sylvania Electric Products Inc., Bayside, N. Y. (2 memberships)

Sarkes Tarzian, Inc., Bloomington, Ind.

Tennessee Products & Chemical Corporation, Nashville, Tenn.

Udylite Corporation, Detroit, Mich. (2 memberships)

Union Carbide Company, Electrometallurgical Division, New York, N. Y.

United Chromium, Inc., New York, N. Y.

Vanadium Corporation of America, New York, N. Y.

Victor Chemical Works, Mt. Pleasant, Tenn.

Wagner Brothers, Inc., Detroit, Mich.

Western Electric Company, Inc., Chicago, Ill.

Western Electrochemical Company, Los Angeles, Calif.

Westinghouse Electric Corporation, E. Pittsburgh, Pa.

Willard Storage Battery Company, Cleveland, Ohio.

Yardney Electric Corporation, New York, N. Y.

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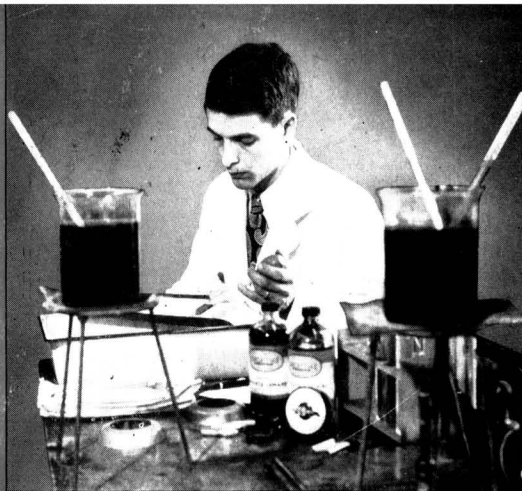
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