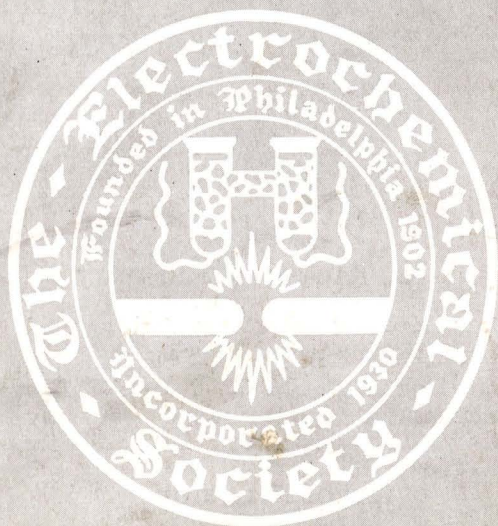


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January, 1954



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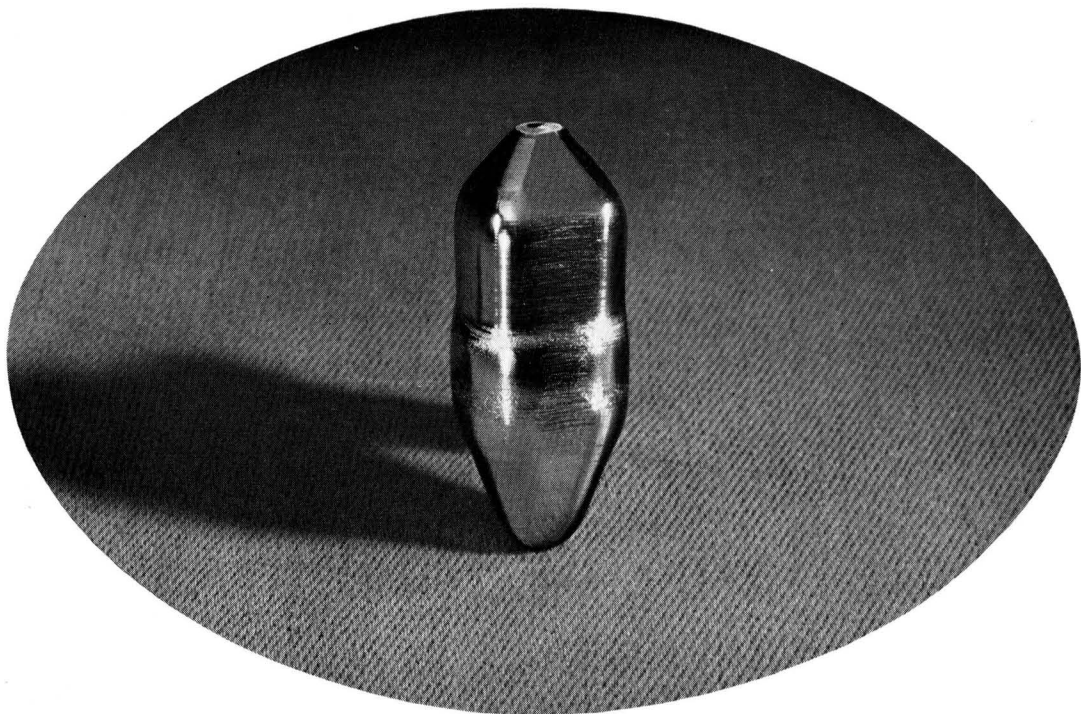
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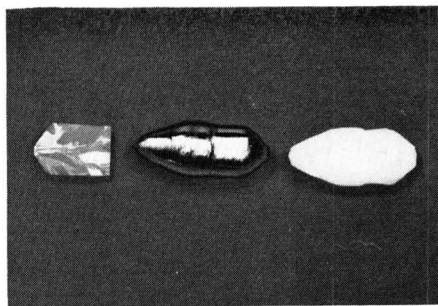
Germanium crystal grown at Bell Telephone Laboratories (life size). It is sliced into hundreds of minute pieces to make *Transistors*. Transistor action depends on the flow of positive current-carriers as well as electrons, which are negative. Arsenic—a few parts per 100,000,000—added to germanium produces prescribed excess of electrons. With gallium added, positive carriers predominate. Latest junction type *Transistor* uses both kinds of germanium in the form of a sandwich.

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Heart of a *Transistor*—Bell Telephone Laboratories' new pea-size amplifier—is a tiny piece of germanium. If *Transistors* are to do their many jobs well, this germanium must be of virtually perfect crystalline structure and uniform chemical composition. But it doesn't come that way in nature.

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This original technique is another example of the way Bell Laboratories makes basic discoveries—in this case the *Transistor* itself—and then follows up with practical ways to make them work for better telephone service.



Section of natural germanium, left, shows varying crystal structure. At right is sectioned single crystal grown at Bell Laboratories.

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“The Twentieth Century Is Canada’s”

THE second of the JOURNAL’s series of three articles on the electrochemical and electrometallurgical industries in Canada appears in this issue. Whereas the first dealt with these industries broadly across the whole Canadian scene, this one concentrates on the five easternmost of the ten provinces—Quebec, New Brunswick, Nova Scotia, Prince Edward Island, and Newfoundland.

In all the world, Quebec stands unique, among political entities, in the generation and consumption of electric power. It generates and uses more per capita than does any whole nation. And the average price per kilowatt hour paid for industrial power sets an example; it is less than half a cent.

There are sound economic reasons for that happy situation, which prevails despite the fact that the major part of generating capacity in Quebec is investor-owned, and therefore subject to full federal, provincial, and municipal levies.

Chief of those reasons is the very fact of the rich availability of water power; topography and dependable precipitation have combined so that its development is relatively inexpensive. Second, stemming from the first, is the extent to which advantage has been taken of that availability; very large proportions of the power produced are consumed in great blocks by immense industries, with a resultant decrease in cost of delivery.

Relevant, too, is the force of dependable man power at hand, to direct that electrical energy into its industrial functions.

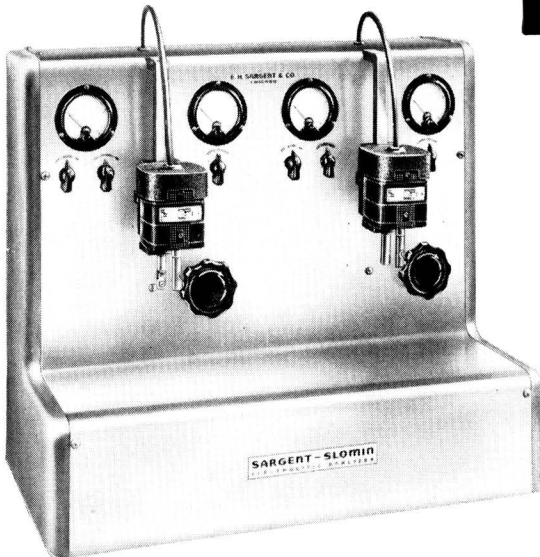
As well as Quebec, however, Canada’s sea-washed provinces on the east coast are rapidly developing their resources and new technology, and are ready to march forward at every opportunity. Except Newfoundland, they are not as rich relatively in undeveloped water power as is Quebec, but they have at their doorsteps great stores of coal for thermal generation of electricity.

Moreover, there is a great will on the part of each province to further its own industrial expansion, particularly through the utilization of its natural resources in the production of electricity. And situated as they all are on the ocean shipping routes, they have an advantageous position for the importation of raw materials and the export of processed goods.

Canada, conscious of her part in world economy and in the defence of the free world, is also sensible of her own domestic growth. She has been told, and believes, that to an important degree “the Twentieth Century is Canada’s.” She is working to make it so, and welcomes new ideas and new development.

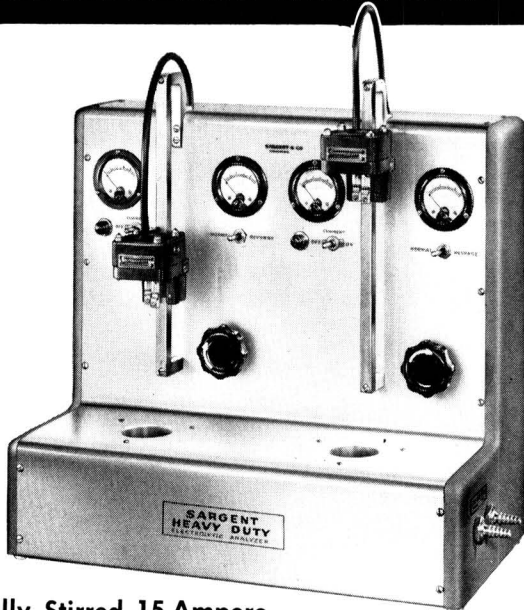
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ELECTROCHEMICAL AND ELECTROMETALLURGICAL INDUSTRIES OF CANADA

Part II. Quebec, The Maritime Provinces, and Newfoundland¹

A. C. Holm²

Introduction

In this second of a series of three articles dealing with the electroproducts industries of Canada and their inseparable partners, the hydroelectric power developments, attention will be given to those projects which are located in the five eastern provinces—Quebec, New Brunswick, Nova Scotia, Prince Edward Island, and Newfoundland. In the next article, further enterprises of this nature will be described which are located in Ontario and the western provinces, including the Yukon and Northwest Territories. There is no political or economic significance in this arbitrary division of the nation into two halves; it just happens that this provides about an equal division of the subject matter. Canada's major power-consuming industries are located, in numbers and in size, more or less in direct ratio to the amount of power available; as Quebec has about one-half the power, so it has almost one-half of the large electroproducts industries. Ontario, with 30% of the installed power, British Columbia, with 10%, and Manitoba, with 5%, account for most of the remaining half.

The Province of Quebec

It is perhaps fitting that this tour of Canada's electroproducts industries and major power developments should begin in the Province of Quebec. Here began Canada's chemical industry in 1674, when one Nicolas Follin was granted the exclusive right to make potash; here water power was first harnessed for commercial mechanical uses, at the Petit Pré mill near Quebec City in 1691; and at Les Forges, on the St. Maurice River near Trois-Rivières, iron ore was first smelted in 1736 in the earliest commercial metallurgical plant of North America. Here, also, Canada's first electrochemical plant went into operation at Masson, near the junction of the Lièvre and Ottawa rivers, in the early 1890's, to produce electrolytic potassium chlorate. Today, the Province of Quebec leads all of Canada in the variety and value of its electrometallurgical and electrochemical products, as well as in the output of hydroelectric power.

The Province of Quebec, with an area of almost 600,000 square miles, greater than that of France, Germany, and Spain combined, is Canada's largest province. Its population of 4,269,000, over 80% of French descent, is second in numbers to that of Ontario only, and represents 29% of Canada's total. Its manufacturing industries produce about one-third of Canada's goods, its forests account for nearly one-half of Canada's pulp and paper output, and its mines produce

about one-third of the nation's minerals in point of value. Quebec possesses nearly one-half of Canada's installed hydroelectric power and over one-third of the nation's remaining undeveloped potential. The undeveloped hydroelectric resources of Quebec, which are rated as being economically and technically exploitable, amount to about 19 million horsepower, greater than the hydro resources of any other Canadian province and equal to about 21% of the undeveloped hydroelectric resources of the whole United States.

Of the various factors that have operated to attract electrometallurgical and electrochemical industries to Quebec, the most important are the availability of raw materials, either indigenous or imported, excellent transportation facilities, and the huge resources of exceptionally low-cost, dependable, year-round electric power. The three geographical divisions of the province—the Appalachian Highlands in the southeast, the St. Lawrence Lowlands, and the famed Laurentian Shield north of the St. Lawrence River—all contribute a great variety of minerals, of which the most important economically have been gold, copper, zinc, and asbestos. The electroproducts industries have so far made use mainly of Quebec's copper ores, with gold, silver, selenium, and tellurium as by-products, and of brucite, ilmenite, limestone, and sand. However, the province has at times produced large quantities of concentrates of zinc and lead, molybdenite, chromite, apatite and pyrite for export, which under favorable circumstances might someday undergo treatment within the province by electrothermic or electrolytic means. Tremendous reserves of high grade iron ore have been discovered in the Ungava (northeastern) region of Quebec, and are about to be exploited; electrothermic iron and steel production is a future possibility. The Precambrian rocks of the Laurentian Shield, covering some 90% of the area of Quebec, are believed to be a veritable storehouse of minerals; of this area perhaps only 10% has received adequate geological exploration—the potentialities in mineral wealth are thus enormous. What Quebec lacks in the way of native raw materials she is able to import cheaply, thanks to her unrivalled geographic location astride the mighty St. Lawrence River, which provides a ship channel of a minimum of 32½-ft depth almost 1000 miles inland from the Atlantic Coast to Montreal. The St. Lawrence canal-lock system gives access to the Great Lakes, westward from Montreal through a 14-ft channel; this may be deepened to 27 ft if the St. Lawrence Seaway project is adopted. During the shipping season of approximately seven months, vessels bring in many thousands of tons of raw materials, such as coal, salt, bauxite, phosphate rock, ilmenite, and steel scrap, for Quebec's electroproducts industries, and carry away ferroalloys, abrasives, calcium carbide, aluminum, magnesium, copper, titanium slag, and other products. In addition

¹ This is the second in a series of three articles on Canada provided by A. C. Holm, Canadian Regional Editor.

² Shawinigan Chemicals Limited, Shawinigan Falls, Quebec, Canada.

tion, well-developed railway, highway, and air-line systems provide access to all inland points.

In the past, at least, imported Canadian or foreign raw materials have been equally as important to Quebec's electroproducts industries as her indigenous materials, and foreign markets, in the U. S. or overseas, have taken the major part of the production. As Quebec develops more of her own mineral deposits, and as the expanding Canadian economy provides more markets within Canada's boundaries, these relationships may change somewhat. Neverthe-

Newfoundland (including Labrador)—together account for only about 20% of the nation's total area, and about 40% of the population. But they produce about 53% of Canada's electrical power each year.

Table I shows, for each of these eastern provinces, by preliminary estimates up to the end of last year (1953), the installed hydroelectric capacity, the known water power resources remaining to be developed, and the production of electricity from all sources during 1953.

As was illustrated in the first article in this series, almost all of the electric power in these provinces is from hydro stations, rather than thermal, and from central stations contributing to the public supply.

One of those provinces, Quebec, alone supplies about half of the power of the whole country. About twice the area of Texas but with only about half of that state's population, and accounting for about a quarter of Canada's people, Quebec possesses some of the largest hydroelectric generating stations in the world, and is continuing steadily to add to them. But so far, she has harnessed only about 29% of her known hydroelectric resources, and has a rich store of

TABLE I. *Electric power by provinces, estimated to 12/31/53*

Province	Water resources (thousand hp)		Production 1953 (million kwhr)
	Developed	Undeveloped	
Quebec	7706	18,580	37,000
New Brunswick	162	251	1,135
Nova Scotia	171	32	1,120
Prince Edward Island	3	1	33
Newfoundland	304	3,056	1,200

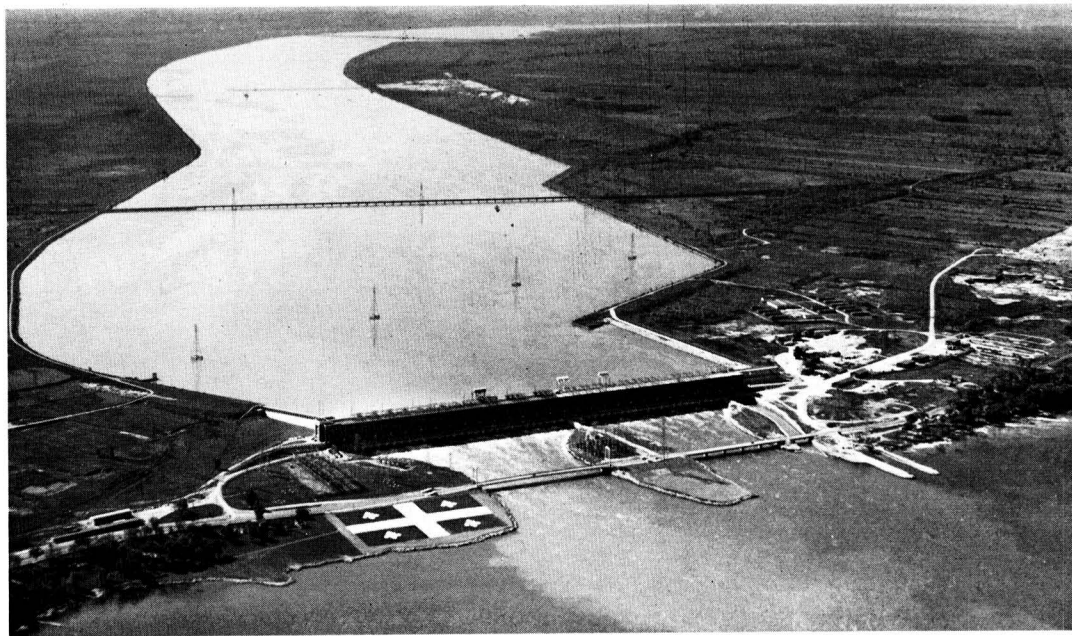


FIG. 1. Bird's eye view of sections 1 and 2 of the Beauharnois Generating Station which has now reached a total capacity of 1,400,000 hp. When No. 3 section is completed, the total capacity will exceed 2,000,000 hp.

less, with Canada's heaviest concentration of industries and markets spread out for 4000 miles in a band of some 200 miles in width along the U. S. border, good transportation will remain of prime importance to Quebec, irrespective of any foreign trade considerations. But however important the access to raw materials and markets may be, in almost all cases the governing factor in the location of electrometallurgical and electrochemical industries in Quebec has been the availability of enormous amounts of exceptionally low-cost, dependable year-round hydroelectric power.

Hydroelectric Power Developments in Quebec

The five most easterly of Canada's provinces—Quebec, New Brunswick, Nova Scotia, Prince Edward Island, and

water power remaining within economic transmission distance of established industrial areas.

Eighty-five hydroelectric generating stations, with individual capacities ranging from 2000 hp to 700 times that amount of energy, feed the immense amount of power into Quebec's industry, commerce, homes, and farms. That wealth of power, developed at relatively low cost, has been the principal factor in the conversion of Quebec's economy in just the past two or three decades, from one based principally on agriculture to one based largely on industry.

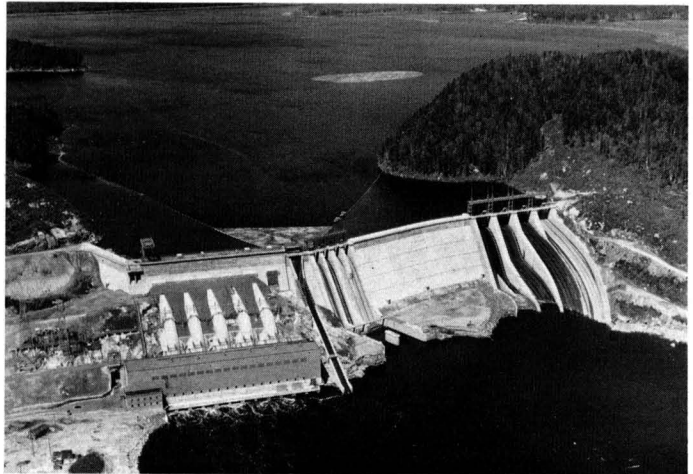
Thirty-five rivers, most of them flowing south and east from the Laurentian Divide toward the St. Lawrence, contribute the greater part of the power supply. The greatest of them, from the point of view of power production at pres-

ent, are the St. Lawrence, the St. Maurice, the Saguenay, the Ottawa, and the Gatineau. The generating capacities of the first three of these are linked together by a power-grid which covers virtually all of the industrial sections of the province, permitting interchange of power as needed. Soon that grid will be extended, to reach from the Bersimis in the northeast, beyond the Saguenay, to the Windsor area of Ontario, opposite Detroit, in the southwest—a distance of 1000 miles.

The mightiest power-house in Quebec now is that called Beauharnois, only 20 miles from the center of Montreal. Owned by the Quebec Hydro-Electric Commission, it takes a large part of the flow of the St. Lawrence diverted through a 20-mile canal, and with the completion of additions by the end of last year, will have a capacity just under 1,420,000 hp. Another section, to yield between 660,000 and 770,000 hp, is envisaged for the future, to give Beauharnois an ultimate capacity of something over 2,000,000 hp.

On the St. Maurice River, which flows into the St. Lawrence about 100 miles northeast of Montreal, is a chain of six developed power sites in a 135-mile stretch of river. Part

FIG. 2. Aerial photograph of the newest of The Shawinigan Water and Power Company's chain of hydroelectric generating stations on the St. Maurice River at Trenché. The first five generating units were completed in 1951, and a sixth is being added now to give the plant a total capacity of 390,000 hp.



© Photographic Surveys (Quebec) Limited, Montreal

of the Shawinigan Water and Power Company's generating system, and successively using water from great storage reservoirs, they develop a total of 1,532,000 hp, and additions now being built at three of them will increase that total to almost 1,700,000 hp. The Shawinigan Company also has plans prepared for the development of four more sites on the St. Maurice, to develop almost 700,000 additional hp in the future.

From north to south, and including the extra machines now being installed, the present St. Maurice River generating stations are:

Rapide Blanc	244,500 hp
Trenché	390,000 hp
La Tuque	272,000 hp
Grand'Mère	200,500 hp
Shawinigan Falls	416,500 hp
La Gabelle	172,000 hp

Together with Shawinigan's generating stations on other rivers, including those of the subsidiary Quebec Power Company, those plants supply not only the rich St. Maurice

Valley—with its chemical plants (including the subsidiary Shawinigan Chemicals Limited, which has calcium carbide, chemical, and stainless steel divisions, and a neighboring associate producing resins and plastics), aluminum plants, the world's greatest concentration of pulp and paper mills, and many other industries—but also 25,000 square miles of the rest of Quebec. The little city of Shawinigan Falls alone, with a population of about 30,000, uses about as much electric power as does the City of Toronto, Ontario, which has about 30 times as many people.

The St. Maurice Valley has been frequently compared with the Tennessee Valley, because of its repeated use of the same water to produce electric power and commodities. But the average selling price of that power is far less than that of the TVA, even though it yields heavy federal, provincial, and municipal taxes and other levies.

Near the head of the Saguenay River and on its satellite streams, in the Lake St. John area of northeastern Quebec, are the great power plants of the Aluminum Company of Canada and its power subsidiaries. Much of the power generated goes to Alcan's immense aluminum smelter at Arvida

(the largest in the world) and at Isle Maligne, but those generating stations contribute also to the public supply in the "Kingdom of the Saguenay."

Largest of the power plants is Shipshaw No. 2, with its 12 generating units of 100,000 hp each. It was built within a few months, early in World War II, to make possible the production of sorely-needed aluminum, and, like the other Alcan developments, it provides an outstanding example of raw materials being carried far to low-cost power; all of the materials of aluminum-making, except manpower and electric power, are imported hundreds or thousands of miles to the Saguenay—and profitably.

Closely tied with Shipshaw No. 2, and sharing its water supply, is Shipshaw No. 1, built earlier, with a capacity of 300,000 hp. Farther upstream, near the Lake St. John discharge, is the Isle Maligne plant, of 540,000-hp capacity; part of its power is sent under contract to the Shawinigan Company's system. And on the Peribonka, which flows into Lake St. John, are two new Alcan plants—The Chute du Diable and Chute à la Savane, each of 270,000 hp.

A number of other generating stations, of smaller size,

serve the area with its pulp and paper mills and other industries, its cities, towns, and farms.

East of the Saguenay is the Bersimis, which flows from the Laurentian Divide to the St. Lawrence. There, about 90 miles above its mouth, the Quebec Hydro-Electric Commission is now building a development which is to have a capacity of 1,000,000 hp, the first production being scheduled for 1956. A lake, the Cassé, is to be raised by 165 ft, flooding 200 square miles of bush-country, and a tunnel from its lower end will run $7\frac{1}{2}$ miles to a subterranean power-house, where a townsite named Labrieville is now being built for the staff.

Part of the station's output is destined for the Gaspé Peninsula; to carry it there, transmission lines are being built 84 miles to Manicouagan; then four separate submarine conductors, 4000 feet apart, will cross the $31\frac{1}{2}$ miles of the St. Lawrence at a maximum depth of 1200 ft, to Les Boules; and from there another transmission line will run 158 miles to Murdochville.

Some of the power, it is expected, will be transmitted 450 miles southwest, as far as Montreal, and some to the now-

new hydroelectric capacity was scheduled for completion, and as much more within the following two years. Still in the future are such proposed developments as the Lachine Rapids plant, within the City of Montreal—an integral part of the St. Lawrence seaway plan, and with a potential 1,250,000 hp of hydroelectric capacity—and the Carillon, a few miles away on the Ottawa, with an estimated capacity of about half a million hp.

Thermal stations, in the Province of Quebec, already infinitesimal in importance of production, reached near-extinction, unable to compete with the phenomenally inexpensive operation of hydroelectric plants.

Electroproducts of Quebec

Aluminum

Canada's output of primary aluminum, representing nearly 25% of the world's production, is centered entirely in the Province of Quebec at present, in four smelters owned and operated by the Aluminum Company of Canada, Limited; a fifth smelter of this company is now under con-

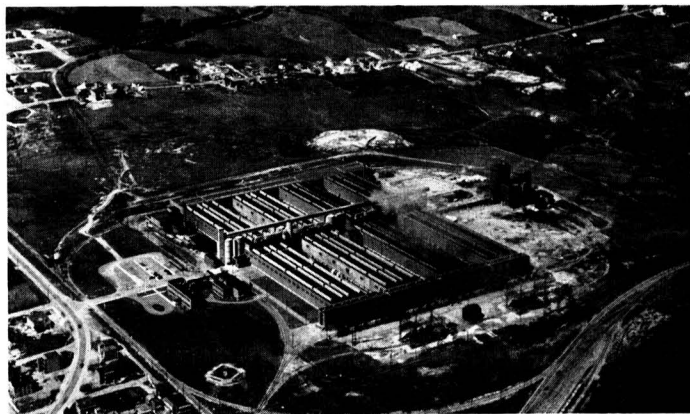


FIG. 3. Smelter of the Aluminum Company of Canada, Limited, at Shawinigan Falls, Quebec. It has a capacity of 60,000 metric tons of aluminum ingot annually, and uses about 180,000 hp of electrical energy.

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developing mining region of Chibougamau, about 200 miles to the west of Labrieville.

Forty miles downstream on the Bersimis, another development, of 500,000 hp, remains for the future.

On other tributaries flowing into the St. Lawrence over its 500-mile course from the area where Ontario, New York, and Quebec all join, down to the Gulf of the St. Lawrence, there are various hydroelectric developments, in a wide range of capacities. And on the Quebec-controlled sections of the 685-mile Ottawa, which joins the St. Lawrence at the Island of Montreal, are nine of them, with more scheduled for the future. (There are ten others on the Ottawa under Ontario's control.) Those Ottawa River plants on the Quebec side range in capacity from 112,000 hp at Chats Falls to just 2800 on the Winneyway inflow at the upper reaches. They total about 440,000 hp.

On the fifth of Quebec's present main power rivers, the Gatineau, which flows into the Ottawa River opposite the city of Ottawa, are six hydroelectric developments owned by the Gatineau Power Company, and totalling 616,000-hp capacity. A considerable part of their power is sent across the provincial boundary to Ontario. The largest of those plants is the Paugan, of 238,000 hp.

Within Quebec during 1953, almost half a million hp of

struction at Kitimat, British Columbia. The four Quebec smelters operating at capacity produce about 500,000 tons of primary aluminum per year. The amounts of power and raw materials consumed by these operations are truly staggering, and illustrate clearly why aluminum smelters must be located near sources of abundant cheap power and near shipping lanes. One ton of aluminum requires some 20,000 kwhr and nearly 7 tons of raw materials, including 4 tons of bauxite, for its production. The four Quebec smelters, now running at capacity, have a power load of some 1,600,000 hp and a raw material consumption equivalent to some 200 box car loads daily. Furthermore, over 80% of the product, i.e., some 1100 tons a day, is exported out of the country.

Bauxite is brought from British Guiana, 3000 miles away, and French Guiana, to Port Alfred on the Saguenay River within 20 miles of Arvida, the site of Alcan's ore-treating plant and its largest smelter. At Arvida, the bauxite is refined by the Bayer process to anhydrous alumina which is distributed to the various smelters. This process consumes soda ash, lime hydrate, and caustic soda, the latter from Alcan's caustic-chlorine plant at Arvida. Petroleum coke (shipped in from Texas and Gulf ports), pitch, tar, and metallurgical coke are used to prepare Soderberg anodes and pot linings. Fluorspar from Alcan's mines in Newfoundland

is beneficiated and treated with sulfuric acid to produce hydrogen fluoride, which, in turn, is reacted with calcined alumina to prepare aluminum fluoride. Hydrogen fluoride is also reacted with sodium aluminate to prepare synthetic cryolite, which supplements the natural cryolite imported from Greenland. Cryolite and aluminum fluoride are essential ingredients of the cell electrolyte, to which the refined alumina is added to be electrolyzed to metal. Alcan produces its own sulfuric acid (for HF) at Arvida, starting with the fluosolids-roasting of zinc concentrates from northwestern Quebec mines.

The approximate annual production rates and connected power loads of Alcan's four Quebec smelters at the present time are as follows:

	<i>metric tons</i>	<i>hp</i>
Beauharnois	32,000	100,000
Shawinigan Falls	60,000	180,000
Isle Maligne	80,000	250,000
Arvida	320,000	1,070,000*
Totals	492,000	1,600,000

* Includes caustic-chlorine and magnesium plants.

The first aluminum smelter in Canada was built in 1901 at Shawinigan Falls, Quebec, at the same time that the Shawinigan Water and Power Company began its development of the St. Maurice River at that site. This original plant, with additions, operated until 1945 when the pot-lines were dismantled and the plant converted entirely to the production of aluminum wire and cable. The Arvida smelter, on the Saguenay River some 40 miles below Lake St. John, was started in 1925, to get a site closer to deep-water shipping and to hydro resources which could be reserved almost exclusively for the great expansion of the aluminum industry which was then expected. This smelter was gradually enlarged involving also the construction of powerhouses, deep-water wharves, railways, and a townsite. During World War II, when Canadian aluminum production was stepped up from 75,000 tons in 1939 to 450,000 tons in 1943, the Arvida Works grew at a tremendous rate to become the largest aluminum smelter in the world. Today it covers an area 1½ miles long by ¼ mile wide; it has been reported to have 25 pot-lines with a total of 2500 pots.

During World War II a smelter was built at Isle Maligne (to which further capacity was added in 1952); an additional smelter at Shawinigan Falls, which is the one now operating there; a smelter at La Tuque on the upper St. Maurice River, since dismantled; and the fourth, presently operating smelter at Beauharnois on the St. Lawrence River southwest of Montreal.

With its existing smelters in Quebec operating at capacity, the Aluminum Company of Canada is planning ahead for eventual possible doubling of its output when its new smelter site in British Columbia will have reached its ultimate development.

Magnesium

Quebec lays claim to the first production in North America of magnesium metal in commercial quantities, in 1915 by the Shawinigan Electro Metals Company, a now defunct subsidiary of the Shawinigan Water and Power Company. Today, one of Canada's two magnesium producers is located in Quebec, at the Arvida plant of the Aluminum Company of Canada. Alcan started pilot-plant production by the electrolytic process from magnesium chloride in 1943, expanded output to about 1000 tons per year in 1945, and in 1952

stepped up its capacity to about 4000 tons annually. Part of this output is under contract to the United Kingdom Ministry of Materials; part is used by Alcan for alloying purposes, and the remainder is sold.

The raw material for Alcan's magnesium is brucitic limestone from its mine at Wakefield, Quebec, northwest of Ottawa, which is treated to yield a concentrate with about 90% MgO. At Arvida this is processed to magnesium chloride, using some of Alcan's chlorine supplied from its caustic-chlorine plant at that location.

Copper

Electrolytically refined copper is produced by Canadian Copper Refiners Limited at Montreal East. This company is about 92% owned by Noranda Mines Limited and receives crude copper from Noranda's huge smelter at Noranda, Quebec, as well as from the smelter of the Hudson Bay Mining and Smelting Company, at Flin Flon, Manitoba. Approximately 70,000 tons of Noranda anode copper and 40,000 tons of Flin Flon blister copper are processed annually at the Montreal East refinery. This plant will also receive in a couple of years crude copper from the new smelter of Gaspé Copper Mines, a Noranda subsidiary, now being built in Holland township in the Gaspé region not far from the St. Lawrence Gulf port of Mont-Louis. Besides the conventional electrolytic cell installations, Canadian Copper Refiners also has an electric arc furnace for copper melting. Power is supplied by "Hydro-Quebec" (Quebec Hydro-Electric Commission).

While Quebec has a number of active copper mines, there is only one copper smelter and one electrolytic refinery in the province at present. Canadian Copper Refiners has been in operation since 1931.

Selenium and Tellurium

These two metals are recovered as by-products of the electrolytic refining of copper by the Canadian Copper Refiners Limited at Montreal East. They collect in the copper anode slimes, are separated chemically, and refined electrolytically. Production of selenium runs about 100-150 tons annually and of tellurium 20-30 tons. The Montreal East refinery, with a rated annual capacity of 450,000 lb of selenium, is said to be the largest selenium plant in the world.

Cerium (Mischmetal)

Since 1940 Shawinigan Chemicals Limited at Shawinigan Falls, Quebec, has produced commercial cerium metal by a fused salt electrolysis method. The product is a mixture of rare earth metals containing about 50% cerium, used in various alloys and principally as a pyrophoric alloy with iron in lighter-flints. The raw material is imported rare earth chloride salt made from Brazilian monazite. Capacity of the plant at Shawinigan Falls is about 60,000 lb per year.

Chlorine and Caustic Soda

Three producers of electrolytic chlorine and caustic soda are located in Quebec—Canadian Industries Limited at Shawinigan Falls, Dominion Alkali and Chemicals Limited at Beauharnois, and the Aluminum Company of Canada Limited at Arvida. Salt is brought in to Quebec from other parts of Canada or from the U. S. The chlorine and caustic soda output is to a large extent consumed by Quebec's pulp and paper industry.

The Canadian Industries Limited plant at Shawinigan Falls went into operation in 1939. It employs mercury cells,

Shawinigan power, and some 215 employees. Besides direct sales of caustic soda, chlorine, and hydrogen gas, this plant provides chlorine for HCl gas and various organic chemicals produced at this site.

The Dominion Alkali plant at Beauharnois, owned by Dominion Tar & Chemical Company Limited, produces liquid chlorine and 50% liquid caustic soda; it employs Krebs' mercury cells and power from Hydro-Quebec. Operation began in 1949, and press reports at that time placed the rated annual capacity at about 18,000 tons of chlorine and 22,000 tons of caustic soda.

The Arvida plant of the Aluminum Company of Canada was the first commercial plant to utilize the improved Mathieson horizontal stationary mercury cell; operation began in late 1947. Production is now at a rate of about 20,000 tons chlorine and 25,000 tons caustic soda annually. Alcan uses the caustic soda in its Bayer alumina process, and a small part of its chlorine for magnesium chloride; the remainder of the chlorine is liquefied and sold.

Hydrogen Peroxide

The only production of electrolytic hydrogen peroxide in Canada is carried on at Shawinigan Falls, Quebec, by Canadian Industries Limited. Output of "100-volume" hydrogen peroxide began in 1935; a 50% expansion of production was undertaken in 1952. The process is reported to be based on the electrolysis of ammonium bisulfate solution.

Electrolytic Hydrogen and Oxygen

At the Shawinigan Falls plant of Canadian Resins and Chemicals Limited, a leading producer of synthetic vinyl resin and plastic compound (Vinylite), a stand-by electrolyzer is installed to furnish pure hydrogen, which is required for this firm's production of vinyl resin (Vinylite) plasticizers and intermediates. This unit employs mechanical rectification of alternating current for its d-c supply, and, at the time of its installation in 1949, was one of the first applications on this continent of this type of rectifier.

Electrolytic Chlorates

The first commercial electrochemical plant in Canada was set up in the early 1890's at Masson, Quebec, by A. MacLaren, S. P. Franchot, and W. T. Gibbs to produce potassium chlorate by an electrolytic process. When this plant was destroyed by fire, the enterprise was directed to other electro products, and in 1897 the Electric Reduction Company Limited was formed with British capital to produce phosphorus at nearby Buckingham. During World War I, production of potassium and sodium chlorates was resumed by this company. In 1935, the firm was reorganized as the Electric Reduction Company of Canada Limited, its present style. During World War II, production of chlorates was extended to include perchlorates of potassium and ammonia by use of sodium perchlorate from a platinum-copper electrolysis of sodium chlorate solution. In 1950-1951 production facilities for sodium and potassium chlorates were expanded to handle some 20,000 tons per year; some of this was destined for export markets, while some was ear-marked for the domestic pulp and paper industry to supply chlorine dioxide bleach.

Electric Furnace Phosphorus

The Electric Reduction Company of Canada Limited has carried on the production of phosphorus at Buckingham, Quebec, since 1897, and is thus the oldest operating electro-

chemical company in Canada. It is also one of the few-remaining English-controlled firms in Canadian chemistry, being held by Albright and Wilson of Oldbury, England, who also control Oldbury Electrochemical Company, producers of phosphorus products, in the United States.

Production of phosphorus at Buckingham was originally based on phosphate deposits in the locality. At that time, Quebec led the world in the production of phosphate rock; mining operations ceased, however, with the development of more cheaply-produced Florida phosphates. Present production of phosphorus at Buckingham utilizes imported phosphate, and is on a scale of some 8000 tons per year. Besides yellow phosphorus, "Erco" now produces at Buckingham phosphoric acid and a large number of phosphates and pyrophosphates, as well as phosphorus sesquisulfide. By-products of phosphorus furnace operations are ferro-phosphorus and rock wool. Erco also generates some of its own hydroelectric power on the Lièvre River.

At Varennes, Quebec, on the south shore of the St. Lawrence River below Montreal, the Electric Reduction Company of Canada is bringing into production a new electric furnace phosphorus plant. The first units, consisting of two 15,000-kw furnaces, will increase Erco's phosphorus output by about 14,000 tons per year. Electric power is being supplied by the Shawinigan Water and Power Company.

Calcium Carbide

The sole producer of calcium carbide in the Province of Quebec is Shawinigan Chemicals Limited, whose plant at Shawinigan Falls is the largest of its kind in the British Commonwealth. This company traces its origin to the Shawinigan Carbide Company, which went into operation at Shawinigan Falls in 1904 as one of the first customers of the Shawinigan Water and Power Company, utilizing electric power generated in Shawinigan's first hydroelectric power development on the St. Maurice River at this site.

With T. L. ("Carbide") Willson, the Canadian-born inventor of the commercial carbide process, as its vice-president, the Shawinigan Carbide Company in its early years set up 12 ingot-type furnaces with a combined capacity of 2000 tons of carbide per annum. Later, this enterprise took the name of Canada Carbide Company and came under the control of the Shawinigan Water and Power Company. Today, its descendant, Shawinigan Chemicals Limited, a wholly-owned subsidiary of the Shawinigan Water and Power Company, operates five furnaces at Shawinigan Falls with an installed capacity of over 200,000 tons carbide per annum, for which it employs over 100,000 hp.

Shawinigan Chemicals Limited quarries its own limestone, burns it to lime in eight large rotary kilns, produces some of its own coke by an unique process, and charges lime and coke to the continuously operating carbide furnaces, of which the largest is operated at 22,000 kw. The furnaces are equipped with Soderberg electrodes, Shawinigan being the first carbide producer on this continent to install this type of electrode. Anthracite coal for the preparation of these electrodes is calcined in continuous, vertical electrical retorts with the coal acting as resistor. Only approximately 20% of Shawinigan's output of calcium carbide is now sold as such, the remainder being used to generate acetylene gas on which a gigantic organic chemical enterprise has been built up at Shawinigan Falls. Chief organic products are acetic acid and acetic anhydride, vinyl acetate, ethyl acetate and other solvent esters of acetic acid, butanol and vinyl acetate synthetic resins.

At Shawinigan Falls this Company produces also alloy steels in electric furnaces, cerium metal, and acetylene black. Shawinigan Chemicals Limited operates the world's largest plant and the only one on this continent for the production, by thermal decomposition of acetylene, of acetylene black, which is an important constituent of dry cells because of its high electrical conductivity and absorptive capacity for electrolyte. Products of Shawinigan Chemicals Limited are sold around the world, with the U. S. being the largest consumer of its exports.

Shawinigan Chemicals Limited together with its parent, the Shawinigan Water and Power Company, has long been prominent in electrochemical and electrometallurgical development work. Besides developing their carbide furnaces from the early single-phase, batch, ingot type to the present three-phase, continuous, tapping furnaces, the Shawinigan companies at various times have carried on research and development work on electrically powered units such as a gas producer, coal calcining retort, coking retort, lime burner, and electric steam boilers; on production of electrolytic

Beauharnois generating station of the Quebec Hydro Electric Commission. Among its products are ferrosilicon, silicon metal, silicocalcium, and zirconium alloys.

Electro-Reagents (Quebec) Limited, also located at Beauharnois, came into operation in 1953. This plant produces high-silicon ferrosilicon, at present mainly for its parent company, Dominion Magnesium Limited, of which it is a wholly owned subsidiary. This ferrosilicon is required for the production of magnesium by the Pidgeon process, operated by Dominion Magnesium at Haley, Ontario. This new \$1 million plant is managed by Atlantic Metallurgical Corporation, a Quebec subsidiary of the Chromium Mining and Smelting Corporation Limited.

Electric Reduction Company of Canada Limited produces ferrophosphorus as a by-product of phosphorus production at Buckingham, and similar output will result from its new plant at Varennes, Quebec.

Shawinigan Chemicals Limited recovers a 20% silicon ferrosilicon as a by-product from its carbide furnaces at Shawinigan Falls.



FIG. 4. The calcium carbide division of Shawinigan Chemicals Limited at Shawinigan Falls, Quebec, the largest producer of carbide in the British Commonwealth. It uses about 100,000 hp of electrical energy. Beside it, to the right, is the stainless steel and alloys division of the company.

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magnesium, manganese and cerium metals, and electrolytic manganese dioxide; on electric furnace smelting of ilmenite ore, and on electric furnace production of ferrosilicon, mineral wool, and fused phosphate fertilizer, as well as on other projects in which electrical energy played a prominent role. Some of these developments have attained commercial applications, notably electric steam boilers, calcining retorts for anthracite coal, magnesium and cerium metals, and electric smelting of ilmenite ore. But for the past 50 years, the name 'Shawinigan' is perhaps best known to electrochemists in connection with the production of calcium carbide, of which over 3,000,000 tons have been produced in the last 30 years alone at Shawinigan Falls.

Ferroalloys

In Canada production of ferroalloys is all carried on in electric furnaces. In the Province of Quebec are located two plants devoted to ferroalloy production, while at three other plants a ferroalloy is produced as a by-product of other operations.

St. Lawrence Alloys and Metals Limited is located at Beauharnois, Quebec, and obtains power from the nearby

Simonds Canada Abrasive Company Limited has a by-product 12% silicon ferrosilicon from its aluminous abrasive furnaces at Arvida, Quebec.

Mineral Wool

The Electric Reduction Company of Canada Limited has produced mineral wool using as a raw material electric furnace slag from its phosphorus production at Buckingham.

Artificial Abrasives and Refractories

The Canadian Carborundum Company Limited produces crude silicon carbide at Shawinigan Falls. Started in 1917, this plant was, and may still be, the largest plant in the world producing crude carborundum.

Electro-Refractories and Abrasives Canada Limited produces crude silicon carbide at Cap-de-la-Madeleine, Quebec (on the St. Maurice River near Trois-Rivieres). A 50% expansion of plant capacity was completed in 1951. Production capacity is about 5000 tons per year, with a power load of about 6000 hp.

Norton Company also operates a plant at Cap-de-la-Madeleine, to manufacture silicon carbide abrasive ("Crys-

tolon"). First operated in early 1951, this plant doubled Norton's Canadian output of "Crystolon."

The above three plants are located in the St. Maurice Valley and draw their power from the Shawinigan Water and Power Company.

Simonds Canada Abrasive Company Limited operates a plant at Arvida to produce fused aluminum oxide abrasive. This company, a division of Simonds Saw and Steel Company, has an installation of eight 550 kw, Higgins-type aluminous abrasive furnaces. At capacity, the power load is about 6800 hp. Production includes regular, semifrangible, and heavy duty types of abrasive; ferrosilicon is a by-product.

Titanium Slag and Iron

Discovery of a tremendous ore body in Quebec of ilmenite containing some 88% of combined titanium and iron oxides, and the development of an electric smelting process to treat this ore, led to the formation of the Quebec Iron and Titanium Corporation in 1948 and the subsequent construction of an electric smelting plant at Sorel, Quebec, which is the only one of its kind in the world. The process is essentially a selective reduction of iron oxide from the ore, forming as one product a slag containing some 70% TiO_2 and little iron oxide, and a fairly pure iron, containing chiefly carbon and sulfur as impurities, as the second product. Because of the high melting point of the slag, the operation is carried out in an electric furnace. The need for large amounts of relatively low-cost power and access to deep-water shipping governed the selection of the site at Sorel, where a large block of power was made available by the Shawinigan Water and Power Company.

Ore is mined in the Allard Lake region and shipped over a 27-mile company-owned railway line to Havre St. Pierre on the north shore of the St. Lawrence, whence it is carried by vessel to Sorel. The Sorel smelter has been designed to treat some 1500 tons of ore daily at full capacity, the plans calling for five electric arc smelting furnaces and two electric arc iron refining furnaces. Molten slag from the smelting furnaces is cooled, crushed, and shipped out by vessel or by rail, while molten iron tapped from the smelters is charged to the refining furnaces for a desulfurizing operation, after which it is cast. The slag is sold for the production of titanium pigments, while the iron is sold as a good-grade melting stock for steel production. Experimental operation of the first smelting furnace began in late 1950.

The Quebec Iron and Titanium Corp. is jointly owned by the Kennecott Copper Corporation and the New Jersey Zinc Company.

Iron Powder

At Cap-de-la-Madeleine, near Trois-Rivières, Quebec, another new enterprise has started up fairly recently to produce iron powder for powder metallurgy applications. At the plant of Ferrum, Limited (incorporated in 1947) an electric furnace is used to melt down steel scrap with graphite, the metal being then cast in water into pellets which are subsequently ball-milled. The resulting product, an iron powder with less than 0.1% carbon, is sold for use in powder metallurgy.

Electric Furnace Steel

The availability of low-cost hydroelectric power on a 24-hr basis has given rise to a flourishing business in the electric furnace melting of steel for castings and ingots in the Province of Quebec. About one-quarter of Canada's electric

steel furnaces are to be found in this province. Operations and equipment are of a conventional nature; the products cover a wide range of applications in carbon and alloy steels. The following are all located within the Province of Quebec: Canadian Tube & Steel Products Limited, Montreal; Canadian Car and Foundry Company Limited, Montreal; Sorel Industries Limited, Sorel; Sorel Steel Foundries Limited, Sorel; Griffin Steel Foundries Limited, St-Hyacinthe; Lynn MacLeod Metallurgy Limited, Theford Mines; Manganese Steel Castings Limited, Sherbrooke; Canadian Unitcast Steel, Limited, Sherbrooke; Dominion Brake Shoe Company Limited, Joliette; and Shawinigan Chemicals Limited (Stainless Steel & Alloys Division), Shawinigan Falls.

The foregoing list of 17 products of the electrochemical and electrometallurgical industries of Quebec is believed to cover all of the direct electroproducts and to enumerate their various producers within the province. This survey is confined to the *direct* electrochemical and electrometallurgical products; no attempt is made to include the many derivatives made from these products. Nor has any attention been given to the large consumers of power for mechanical purposes or for electric steam boilers—in both of which applications Quebec's huge pulp and paper industry leads the field.

The Province of New Brunswick

Moving eastward from Quebec on our tour of Canada's electroproducts industries, we find in the Province of New Brunswick a good potential for such industries in the future, but no establishment of this nature at the present time. The lack of electrochemical and electrometallurgical industries in New Brunswick may be attributed mainly to lack of cheap power in quantity and lack of suitable mineral production. However, recent power surveys and mineral explorations indicate the possibility of a vast improvement in this situation.

The Province of New Brunswick has an area of nearly 28,000 square miles and a population of about 536,000, i.e., about 3.7% of Canada's population. It produces about 2% of Canada's manufactures, about 0.8% of its minerals, and about 1.5% of its electric power. Products of its forests have been of prime importance (pulp and paper and lumber); other manufactures, agriculture, fisheries, and mining add to its income. In St. John it has one of Canada's main Atlantic ports, open the year round.

New Brunswick has an installed hydroelectric capacity of about 162,000 hp, including the newly-completed station at the Tobique Narrows. All told, there are eight hydroelectric plants of more than 2000 hp each. Central stations, as opposed to industry-owned plants producing power for their own use alone, generate about two-thirds of the total electrical energy annually; about one-third of that central station production is thermally generated. While the undeveloped hydroelectric potential at various sites has been estimated at 251,000 hp, further studies may reveal that a much larger output may be feasible. The St. John River, if given extensive regulating and storage facilities, has been estimated to have a potential of 700,000 hp alone. The cost of its development has been estimated at over \$220 millions, however, and agreement would have to be reached with the neighboring State of Maine and the Province of Quebec on the use of its waters. Still more remote are the proposals for harnessing the giant tides of the Bay of Fundy, the world's highest tides, on New Brunswick's southeastern coast. At the head of the Bay of Fundy (in Chignecto Bay) one scheme envisages the development of 2.3 million hp, at a cost of

\$400 millions. Others have advocated a location at Cape Split, Nova Scotia, at the entrance to Minas Basin, while still others have argued the merits of a tidal-power development on Passamaquoddy Bay, near the Maine coastal border, which would yield an estimated 1 million hp at an initial cost of \$100 millions. The size and cost of such projects makes their realization under present conditions quite improbable; however, few would be so rash as to assert that such large amounts of power would never be needed in this area and that the cost would always be prohibitive. Tidal power, if developed at the head of the Bay of Fundy, would appear to be within economic transmitting distance of any point in the Provinces of New Brunswick, Prince Edward Island, and Nova Scotia.

Mineral production in the Province of New Brunswick has consisted mainly of coal, gypsum, cement-making materials, peat moss, a little petroleum and natural gas, with sporadic mining of iron and manganese ores. But in the past two years an unprecedented amount of base-metal exploration has taken place in the northern part of the province, resulting in many promising finds of lead, zinc, copper, pyrite, and manganese. In the vicinity of Bathurst it is reported that a tremendous ore body has been discovered, containing chiefly sulfides of lead and zinc together with copper and silver, which has created speculation on the prospects of a fully-integrated smelter for this area.

These possibilities of the availability of indigenous ores and of moderate or even tremendous amounts of electric energy, existing coal supplies, and the province's favorable location with regard to shipping and foreign markets, all combine to give promise of some type of electroproduct output in New Brunswick in the future.

The Province of Nova Scotia

What has just been said about New Brunswick's prospects of electrometallurgical or electrochemical production, may, with slight alteration, also be applied to the Province of Nova Scotia. Except for a limited production of electric furnace steel, Nova Scotia lacks any electroproducts output today. But she possesses ample reserves of coal, salt, limestone, gypsum, and barytes as raw materials, a location which would permit her to import and export large tonnages cheaply, and the possibility of almost unlimited generation of electric power based on indigenous coal or on the harnessing of the mighty tides of the Bay of Fundy. Any or all of these factors may be expected to lead to eventual expansion of her electroproducts output.

The Province of Nova Scotia, with an area of about 21,400 square miles and a population of 663,000 stands second only to tiny Prince Edward Island in density of population. With about 4.5% of Canada's population, she produces about 2.5% of its manufactures, 4.8% of its minerals, and about 1.5% of its electrical energy. She produces over 30% of the nation's coal, 84% of its gypsum, and 99% of its barite.

Nova Scotia's internal hydroelectric resources have been almost fully developed. The developed power stands at about 171,000 hp, the undeveloped power at about 32,000 hp. Steam power derived from coal is in the ascendancy, the thermal installations now being about 154,000 hp, with more scheduled. With her coal mining now becoming more mechanized, Nova Scotia is hoping to keep power costs low. However, perhaps her best prospect for low-cost power in quantity would lie in the much-debated possibility of harnessing the tides in the Bay of Fundy, which wash a large part of her western coastline.

While bituminous coal of excellent quality accounts for over 80% of Nova Scotia's mineral production, she also turns out important quantities of salt, gypsum, and barytes, and has large deposits of limestone in reserve. There is a small output of base-metal (lead-zinc) ore, and showings of copper and tungsten ore. But her greatest industry, iron and steel, is built up on iron ore imported from Newfoundland. With her excellent ice-free harbors, Nova Scotia is in a good position to import other raw materials for processing, but has done little of this as yet. Fisheries, agriculture, forest products, and miscellaneous manufacturing all contribute to the province's wealth.

Electric steel melting furnaces are to be found at the following locations:

Dominion Iron and Steel Limited, Sydney, N. S.—This is a subsidiary of the giant Dominion Steel and Coal Corporation, Limited, which mines coal in Nova Scotia and iron ore in Newfoundland, and on these has built up a fully integrated iron and steel industry in Nova Scotia. Besides open-hearths, it operates at Sydney one 10-ton electric furnace, of the top-charging type with 4000 kw transformer capacity. This produces special quality forging steels, low alloy and low carbon steels.

Maritime Steel Foundries Limited, New Glasgow, N. S.—This company operates an electric steel melting furnace of 4-ton size for the production of castings.

The Province of Prince Edward Island

This is the smallest of Canada's Provinces, with an area of 2184 square miles and a population of 106,000. The land is extremely fertile and about 85% of it is cultivated. Agriculture and fisheries provide the main income, with manufacturing being confined to the preparation of dairy products. Lacking in forests, minerals, and sizeable streams, there is no lumbering or mining carried on, and water power sites are almost nonexistent. There is about 2300 hp of hydro power installed and about 21,700 hp of thermal power. Needless to say, there are no electroproducts industries on "The Island."

The Province of Newfoundland

The island of Newfoundland with its mainland dependency, Labrador, comprises Canada's newest province, having entered into Confederation in 1949. As a good deal of Newfoundland and the major part of Labrador has not yet been adequately surveyed with regard to water power and mineral resources, it is impossible to predict what the chances are of establishing electroproducts industries, at present nonexistent, on the island or on the mainland. From early indications, however, there would appear to be no lack of either minerals or water power for development, and it will probably be the hard economic facts of production costs, shipping charges, and market possibilities that will determine whether or not electroproducts industries could thrive in this somewhat remote area.

The island of Newfoundland has an area of about 42,700 square miles while Labrador comprises 112,000 square miles; all but some 8000 of the combined population of 383,000 are residents of the island. Mineral production, to date all from the island, accounts for some 2.6% of Canada's total, and consists mainly of ores containing zinc, iron, lead, fluorspar, copper, silver, and gold, in decreasing order of value. Hematite has been mined for 50 to 60 years from the Wabana deposit on Bell Island, and although over 40 million tons have been extracted for export to Canada, the U. S., and to Europe, the known submarine reserves are estimated to be

sufficient for several centuries at present rates. The complex lead-zinc-copper ore at Buchans has been mined heavily since 1928, and concentrates are shipped to the U. S. and Europe. Newfoundland supplies over 90% of Canada's fluorspar. Limestone is another important product. A tremendous amount of mineral exploration work has been proceeding in Newfoundland and Labrador since confederation, and reports of widespread mineral occurrences are common. In Labrador, a huge deposit of high-grade hematite has been discovered in the now-famous Labrador Trough along the Quebec border. Copper, titanium, nickel, lead, zinc, asbestos gypsum, and other minerals all appear to be future possibilities.

Fishing, pulp and paper and lumbering, and water power also contribute heavily to Newfoundland's development, and these, together with mining, are all being vigorously pushed today by Newfoundland's government and by several large corporations who have obtained extensive exploration and development concessions on the island and on the mainland.

The development of water power in the province is favored both by topography and climate. Of Canada's five easternmost provinces, Newfoundland ranks second to Quebec in developed and potential hydroelectric power resources. Some 304,000 hp have already been developed, and the undeveloped potential has been estimated at over 3 million hp. Surveys of water power resources are still incomplete and little definite information has been published hereon as yet. On the south-central coast of the island it is

estimated that some 400,000 hp could be developed from several sites; there are other possibilities elsewhere. In Labrador, one of the largest single undeveloped power sites in the world is found on the Hamilton River at Grand Falls, some 315 ft high. This river, with several others in Labrador's interior, promises a potential of several million horsepower if their regulation and development prove feasible.

Newfoundland has a rather tenuous narrow-gauge railway line some 700 miles long running between the two main ports of St. John's on the east and Port aux Basques on the west. It serves, amongst others, the paper mills at Cornerbrook and Grand Falls, the Buchans mine, and the international civil airport at Gander. The main shipping ports are Bell Island (for iron ore), Botwood (pulp, paper, and Buchans concentrates), Cornerbrook (pulp and paper), St. John's and Port aux Basques. The latter two are usually free of ice all winter.

Newfoundland will have many problems to solve in the exploration, development, and marketing of her many resources. But if the vigor and enthusiasm of present activity is an indication, these problems will be solved in time, and Canada's newest province should enjoy a wide-spread industrialization and sound prosperity—some of it possibly based on electroproducts.

NOTE:—In the third and final article of this series it is proposed to deal with the individual electroproducts industries and power developments in the Provinces of Ontario, Manitoba, Saskatchewan, Alberta, and British Columbia, and in the Yukon Territory and the Northwest Territories.

The Reaction of Nitrogen with, and the Diffusion of Nitrogen in, Beta Zirconium¹

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ABSTRACT

The rate of reaction of nitrogen with high-purity zirconium was determined for the temperature range of 975° to 1640°C at 1 atm pressure. The reaction followed a parabolic law and the parabolic rate constant in (ml/cm²)²/sec was calculated to be

$$k = 5.0 \times 10^3 e^{-48,000/RT}$$

where 48,000 ± 1500 cal/mole is the activation energy for the reaction. The rate of diffusion of nitrogen in beta zirconium was obtained for the temperature range of 920° to 1640°C at 1 atm pressure. Diffusion-rate calculations based on a solution of the usual diffusion equation gave a diffusion coefficient,

$$D = 1.5 \times 10^{-2} e^{-30,700/RT} \text{ cm}^2/\text{sec.}$$

The energy of activation of diffusion, 30,700 cal/mole, has a probable error of 1000 cal/mole. The calculated entropy of activation for diffusion is 3.5 cal/mole degree. The limiting solubilities of nitrogen in beta zirconium were determined from the diffusion data. The heat of solution of nitrogen in beta zirconium is 12,900 ± 500 cal/mole.

INTRODUCTION

Kinetic studies of gas-metal reactions have gained great impetus since Pilling and Bedworth (1) published their classic paper on the oxidation of metals at high temperatures. The various laws of film growth have been adequately treated in the literature (2-11) and will, therefore, not be discussed here. The purpose of the present investigation was twofold: (a) to study the over-all kinetics of the zirconium-nitrogen reaction, and (b) to study the interstitial diffusion of nitrogen in zirconium.

The reaction of nitrogen with zirconium has been described by Gulbransen and Andrew (12) in the temperature range 400° to 825°C, and by Dravnieks (13) at 860° to 1050°C. Both investigations showed that the zirconium-nitrogen reaction follows the parabolic law. Rates of diffusion of nitrogen in beta zirconium with a high hafnium content (1.8-2.2%) were reported in a paper from this laboratory (14). When the purer zirconium (0.015% hafnium) became available, it was decided to repeat the diffusion studies in conjunction with kinetic studies of the zirconium-nitrogen reaction at high temperatures.

EXPERIMENTAL

Method

To determine the rate of reaction between zirconium and nitrogen, the rate of consumption of

nitrogen by a specimen of metal at high temperature was measured. The apparatus used was a modified Sieverts type, consisting of a Vycor reaction tube, sealed by means of a greased, ground-glass ball joint to a glass manometer system, which was connected through stopcocks to a vacuum system and a gas buret. The system was evacuated by a 2-stage glass mercury-diffusion pump backed by a mechanical pump. A cold trap, cooled with a dry ice-acetone mixture, was placed between the diffusion pump and the reaction system. The sample was heated by high-frequency induction, using a 2-kw Lepel converter. The temperature was controlled to ± 5°C by adjustment of a V20 Variac in the converter input line and by use of an external variable resistance connected across the power leads in parallel with the work coil.

The zirconium specimens were machined cylinders about 4 cm long by 0.7 cm in diameter. A hole was drilled through the sample about 1/8 in. from one end, using a No. 46 drill. A graphite tube, which extended about 1/16 in. on either side of the sample, was inserted in the drilled hole. The tube served to prevent interaction between the zirconium sample and the thermocouple. A platinum-platinum + 10% rhodium thermocouple was threaded through the graphite tubing, and the butt-welded bead was located at the center of the sample diameter. The thermocouple ends were soft soldered to similar leads which were permanently sealed in the reaction-tube cap. The thermocouple was used both to measure the sample temperature and to suspend the sample in the reaction tube.

It was found necessary to correct the thermo-

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couple temperature readings because, in using induction heating with the specimen suspended by the thermocouple, the thermocouple wires conducted heat from the hot junction, causing the readings to be low. This correction was made for work in an atmosphere of nitrogen in the temperature range 975° to 1640°C. The thermocouple was calibrated against a Pyro optical pyrometer² sighted on a hohlraum in the sample through a Pyrex window. The differences in temperatures between the thermocouple and the calibrated pyrometer readings were considerable. At 975°C, the thermocouple reading was 75 degrees low, and at 1650°C, the thermocouple reading was 140 degrees low.

The 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 the specimens under acetone until they were placed in the reaction tube.

With the specimen at the desired temperature, purified nitrogen was admitted from a gas buret. Further nitrogen additions were made, as needed, to keep the pressure at 500 to 760 mm. Pressure measurements were made every 2 min at the start of each run and at longer time intervals as the reaction rate decreased. Nitrogen, present in the apparatus as a gas phase, was determined from pressure measurements on a full-length open-end mercury manometer and the calculated dead space of the system. The difference between the amount of nitrogen added and that remaining in the gas phase was the amount absorbed by the specimen.

To convert total quantity reacted to quantity per unit area, the geometric dimensions of the specimen were used. Upon completion of a run in which nitrogen was reacted with zirconium for a predetermined time, the system was evacuated, and the specimen cooled rapidly. Rapid cooling was necessary because of the diffusion studies. This was easily accomplished since the heating was done by induction. When the high-frequency converter was shut off, the temperature fell from 1000° to about 400°C in 2 min.

After a reaction-rate run was completed, lengths equal to the radius of the cylindrical sample were cut from the ends of the specimen and discarded. The rest of the sample was machined radially into several layers of equal weight which were then analyzed for nitrogen content by a modified Kjeldahl method. The concentration in the surface layer, including the alpha and gamma layers, was

² The pyrometer was calibrated for reading through the Pyrex window over a range of temperature up to 1800°C against a ribbon-filament tungsten lamp standardized at 100-degree intervals by the National Bureau of Standards.

not used in the calculations. The remaining layers contained only nitrogen which had diffused as solute through the beta zirconium core. Diffusion coefficients were determined by the graphical method (14), using the average nitrogen concentrations of each layer, the average radius of the layers, and the time of diffusion.

Materials

The pure zirconium used in these experiments was iodide crystal bar produced by the de Boer process, double arc melted, and cold rolled into a $\frac{3}{8}$ -in. diameter rod. Test specimens were machined from this rod. Impurities in the zirconium were determined by spectrographic, chemical, and vacuum-diffusion analyses. The weight percentages of the principal impurities detected were: iron, 0.025; hafnium, 0.015; silicon, 0.01; tin, 0.01; oxygen, 0.005; nitrogen, 0.001; and hydrogen, 0.0005.

The nitrogen used was prepared by passing purified tank nitrogen (The Matheson Company) over zirconium turnings, heated at 850°C. The gas was then dried by passing through a dry ice-acetone cold trap. Mass spectrographic analysis showed that the only measurable impurity was 0.2% argon.

SURFACE REACTION

The rate of the surface reaction of zirconium with nitrogen was measured in the range 975° to 1640°C at 1 atm pressure. Adherent golden-yellow films of ZrN were observed throughout the temperature range in agreement with the observation of Dravnieks (13). Results of the measurements for several runs are shown in Fig. 1 and 2. The square of the amounts (ml STP) of nitrogen consumed per unit surface area of the metal are plotted against time. It was found that, in all cases, the reaction conformed to the parabolic rate law, $w^2 = kt$, with occasional deviations in the direction of a slower initial rate. This initial slower rate was attributed to a contaminating layer of oxide. This effect was less evident at higher temperatures because of the solution of the oxide film in the metal. The induction period varied from 0 to 20 min at temperatures 975° to 1305°C and from 0 to 5 min at temperatures 1305° to 1640°C. Also, the slight thermal fluctuations of the dead space, both in the reaction zone and the room-temperature parts of the apparatus, may result in slight deviations in measurements of the amount of nitrogen absorbed. Again, such deviations tend to have a more marked effect when the volumes of gas absorbed are relatively small, as is the case in experiments carried out below 1100°C.

A plot of the logarithm of the amount of nitrogen consumed per unit surface area vs. the logarithm of

time should give a straight line with a slope equal to 0.5 if the parabolic law is obeyed. As can be seen from Table I, such behavior was observed.

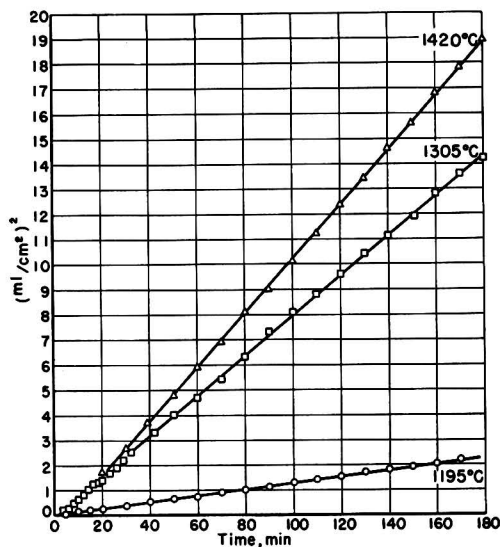


FIG. 1. Reaction of zirconium with nitrogen (ml N_2 consumed per cm^2 metal surface) 2 vs. time.

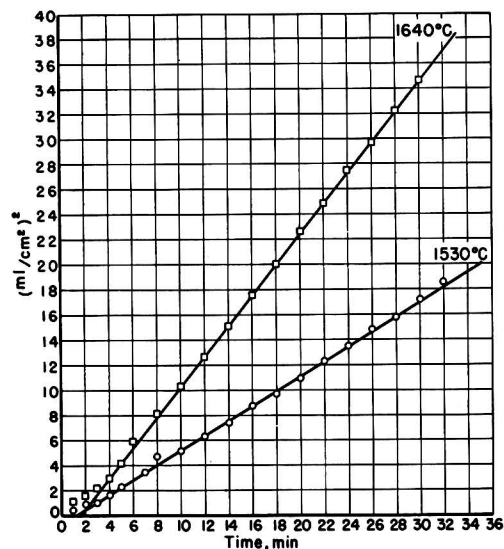


FIG. 2. Reaction of zirconium with nitrogen (ml N_2 consumed per cm^2 metal surface) 2 vs. time.

The rate constants (k) calculated from the various plots and the slopes of the log-log plots are given in Table I, together with the temperature and the length of each run. The reproducibility of the measurements is evident. In most cases, there

was a variation of about 25% in the constants. The variation between runs at constant temperature

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

Temp., $^{\circ}\text{C} \pm 5^{\circ}$	Length of run, min	Rate constant (k), (ml/cm^2) 2 /sec	Slope of log-log plot
975	300	2.0×10^{-5}	0.47
1030	300	5.4×10^{-5}	0.55
1085	180	1.7×10^{-4}	0.54
1085	180	5.9×10^{-5}	0.61
1085	300	1.1×10^{-4}	0.60
1140	240	1.2×10^{-4}	0.62
1195	170	2.1×10^{-4}	0.51
1195	180	3.2×10^{-4}	0.56
1195	180	7.0×10^{-4}	0.55
1305	180	1.3×10^{-3}	0.52
1305	120	7.5×10^{-4}	0.57
1420	180	1.8×10^{-3}	0.53
1420	180	3.2×10^{-3}	0.48
1420	60	1.7×10^{-3}	0.54
1475	60	7.2×10^{-3}	0.54
1530	180	7.1×10^{-3}	0.48
1530	60	1.1×10^{-2}	0.51
1530	32	9.7×10^{-3}	0.54
1640	30	2.0×10^{-2}	0.55

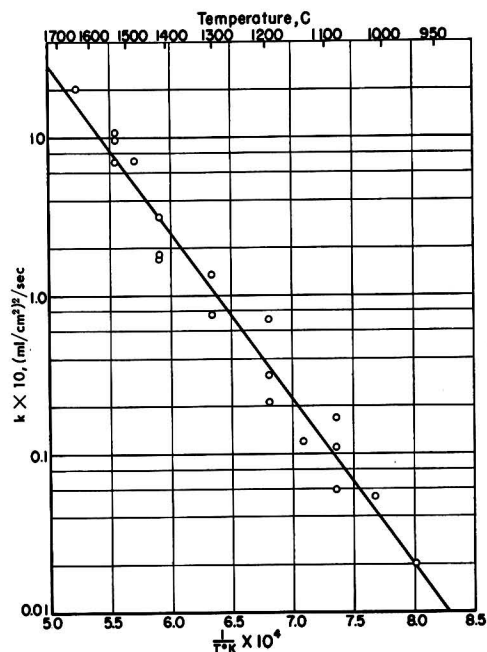


FIG. 3. The zirconium-nitrogen reaction—variation of reaction rate constant with temperature.

may be due, in part, to differences in the surface roughness from one sample to another.

Fig. 3 is a plot of $\log k$ vs. $1/T$. The equation of the best straight line through the points from 975 $^{\circ}$

to 1640°C was determined by the method of least squares; and the experimental energy of activation and the frequency factor were calculated by the Arrhenius-type equation, $k = Ae^{-Q/RT}$. The energy of activation for the low-hafnium pure zirconium is $48,000 \pm 1500$ cal/mole, as compared with the value of 52,000 cal/mole obtained by Dravnieks (13) for the high-hafnium zirconium. The rate constant in $(\text{ml}/\text{cm}^2)^2/\text{sec}$ is $k = 5.0 \times 10^8 e^{-48,000/RT}$.

DIFFUSION WITHIN THE METAL

As defined previously (14), c_0 is the constant concentration maintained at the surface and a is the radius of the cylinder. The values Dt/a^2 and c_0 , and the diffusion coefficients obtained from them graphically (14), are listed in Table II. The temperature variation of the diffusion coefficient can be evaluated

TABLE II. Diffusion coefficients of nitrogen in zirconium

Time, min	Temp, °C ± 5°	c_0 , wt %	Dt/a^2	$D \times 10^7$, cm^2/sec
600	920	0.13	0.013	0.55
300	975	0.12	0.008	0.72
300	1030	0.21	0.015	1.3
180	1085	0.22	0.01	1.5
300	1085	0.28	0.015	1.3
240	1140	0.21	0.017	1.9
170	1195	0.27	0.024	3.4
180	1195	0.30	0.02	3.1
180	1195	0.34	0.042	6.3
127	1305	0.41	0.042	7.7
180	1305	0.47	0.09	11.0
120	1305	0.44	0.028	6.3
60	1420	0.47	0.035	14.0
180	1420	0.56	0.15	17.0
60	1475	0.72	0.055	25.0
60	1530	0.82	0.10	35.0
32	1530	0.70	0.055	39.0
30	1640	0.92	0.055	51.0

by the equation, $D_\beta = D_0 e^{-Q/RT}$. Fig. 4 is a plot of $\log D_\beta$ vs. $1/T$ for the low-hafnium zirconium. The equation of the best straight line through the points from 920° to 1640°C was determined by the method of least squares. The experimental energy of activation is $30,700 \pm 1000$ cal/mole, and the diffusion coefficient in cm^2/sec is $1.5 \times 10^{-2} e^{-30,700/RT}$. This is in fair agreement with the earlier value reported, $3 \times 10^{-2} e^{-33,600/RT}$, from this laboratory (14) on high-hafnium zirconium.

The entropy of activation for diffusion can be estimated from the experimental value of D_0 and the approximation suggested by Wert and Zener (15). Nitrogen diffusion through beta zirconium is assumed to be interstitial. Furthermore, the assumption is made that as the solute atom moves from one interstitial position to an adjacent interstitial position its potential energy varies in a simple sinusoidal manner. Then, from Wert and

Zener (15), the vibration frequency γ is given by the approximation

$$\gamma = \left(\frac{E}{2m\lambda^2} \right)^{1/2},$$

where E is assumed approximately equal to the energy of activation, m is the mass of the solute atom, and λ is the distance between the interstitial positions. From the expression for *bcc* lattices, $D_0 = \frac{1}{6} a_0^2 \nu \exp(\Delta S/R)$ (a_0 , the lattice constant = 3.62 Å for beta zirconium), ΔS can be evaluated. λ is assumed to be $a_0/2$ (15) and ΔS was calculated to be 3.5 cal/mole deg in agreement with Zener's prediction that a low positive value for the entropy

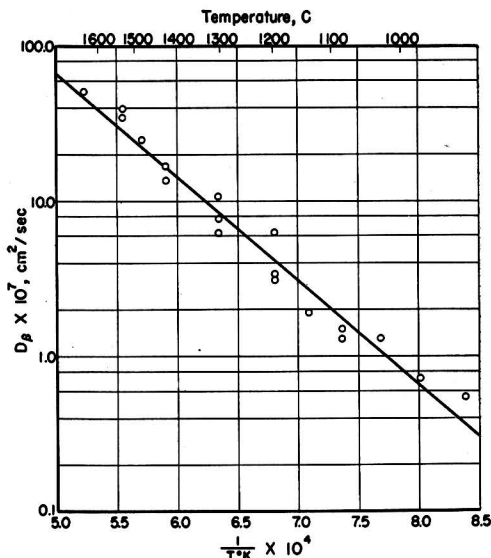


FIG. 4. Diffusion of nitrogen in zirconium—variation of diffusion coefficient with temperature.

of activation suggests that diffusion occurs through the lattice and not through grain boundaries or other short-circuiting paths. A similar calculation was made for the diffusion of nitrogen in beta titanium. Using the results of Wasilewski (17), $D_\beta = 3.5 \times 10^{-2} e^{-33,800/RT}$, the entropy of activation for diffusion was calculated to be 5.3 cal/mole deg. However, for the diffusion of nitrogen in thorium, data from this laboratory (18) indicate that a negative entropy of activation for diffusion is also possible. From $D = 2.1 \times 10^{-3} e^{-22,500/RT}$, ΔS was calculated to be -4.4 cal/mole deg.

SOLUBILITY OF NITROGEN IN BETA ZIRCONIUM

As pointed out previously (14), the solubility limit of nitrogen in beta zirconium is the concentra-

tion just inside the interface between the beta and alpha phases. The calculated c_0 is, then, the approximate limiting solubility of nitrogen in beta zirconium at the given temperature. The calculated c_0 's are listed in Table II and a plot of the c_0 values is given

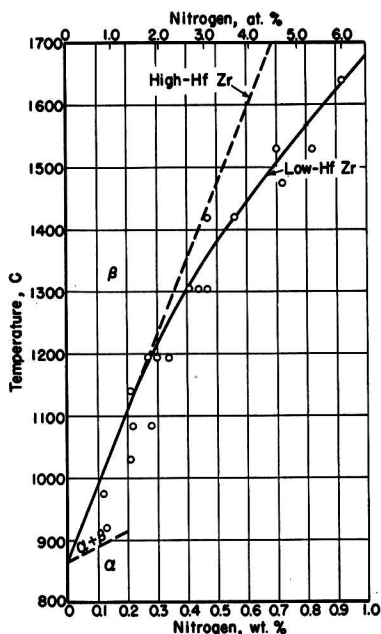


FIG. 5. Solubility limits (c_0 's) of nitrogen in beta zirconium

in Fig. 5. A smooth curve, which is considered the approximate boundary between the beta and alpha-plus-beta phases, was drawn through these points. The solubility limit previously (14) determined for high-hafnium zirconium is also shown. The dashed

line is suggested to indicate the possible boundary between the alpha and alpha-plus-beta phases.

The solubility in weight per cent nitrogen in zirconium over the temperature range 920° to 1640°C can be expressed as

$$\log c_0 \text{ (in wt \%)} = -\frac{2810}{T} + 1.42.$$

The heat of solution for nitrogen in zirconium obtained from this equation is $\Delta H = 12,900 \pm 500$ cal/mole.

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

REFERENCES

1. N. B. PILLING AND R. E. BEDWORTH, *J. Inst. Metals*, **29**, 529 (1923).
2. C. WAGNER, *Z. physik. Chem.*, **B21**, 25 (1933).
3. T. P. HOAR AND L. E. PRICE, *Trans. Faraday Soc.*, **34**, 867 (1938).
4. J. BARDEEN, W. H. BRATTAIN, AND W. SHOCKLEY, *J. Chem. Phys.*, **14**, 714 (1946).
5. D. CUBICCIOTTI, *J. Am. Chem. Soc.*, **72**, 2084 (1950).
6. E. A. GULBRANSEN, *Trans. Electrochem. Soc.*, **81**, 327 (1942).
7. E. A. GULBRANSEN AND K. F. ANDREW, *This Journal*, **96**, 364 (1949).
8. H. A. MILEY, *Trans. Electrochem. Soc.*, **81**, 391 (1942).
9. N. F. MOTT, *Trans. Faraday Soc.*, **36**, 472 (1940).
10. N. F. MOTT, *Trans. Faraday Soc.*, **43**, 429 (1947).
11. J. T. WABER, *J. Chem. Phys.*, **20**, 734 (1952).
12. E. A. GULBRANSEN AND K. F. ANDREW, *J. Metals*, **1**, 515 (1949).
13. A. DRAVNIKS, *J. Am. Chem. Soc.*, **72**, 3568 (1950).
14. M. W. MALLETT, E. M. BAROODY, H. R. NELSON, AND C. A. PAPP, *This Journal*, **100**, 103 (1953).
15. C. WERT AND C. ZENER, *Phys. Rev.*, **76**, 1169 (1949).
16. C. ZENER, *J. Applied Phys.*, **22**, 372 (1951).
17. R. J. WASILEWSKI, Private communication.
18. A. GERDS AND M. W. MALLETT, To be published.

The Reaction of Silver Alloys with Sulfur in Mineral Oil

II. Examination of Reaction Films and Mechanism of Reaction¹

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ABSTRACT

Reaction product films grown on silver alloys by reaction with sulfur in mineral oil were examined by spectroscopic, X-ray, and electron-diffraction techniques. Interpretation of the results leads to a mechanism of reaction in which the rate-determining step during the steady phase is diffusion through a strained interfacial zone of constant thickness, comprised of the sulfide of the alloying element dissolved in β -silver sulfide, altering the number of normal lattice defects. The sulfide of thallium, which, unlike all the other alloying elements, yields a sulfide with a cation/anion ratio similar to silver sulfide, is exceptional.

INTRODUCTION

A study of the kinetics of the reaction between many silver alloys and sulfur dissolved in mineral oil demonstrates that the solution of an alloying element in silver causes a retardation in the steady-state reaction rate (1). Generally speaking, the whole reaction may be broken down into two phases: the initial reaction similar to that with silver alone; the later reaction differs from that of silver (except for silver-thallium alloys) and follows a linear weight gain-time pattern. The linear relationship which describes this later steady state seems not to be particularly dependent on the chemical nature of the alloying element dissolved in silver.

To explain this unusual behavior, an understanding of how the composition and structure of the reaction films formed on silver alloys differ from that of "normal silver sulfide," is required. Of particular concern is the final disposition of the alloying element.

The purpose of this paper is to report the analyses of these tarnish films, and to formulate a mechanism of reaction.

EXPERIMENTAL

Spectrographic examination of films.—Samples of stripped sulfide films were diluted with nine parts of a buffer composed of equal parts of barium nitrate and ammonium sulfate and analyzed with a Zeiss Medium Quartz Spectrograph. Quantitative estimations of the amounts of alloying elements in the films were made by comparison with standards prepared with silver nitrate and salts of the alloying elements (usually the nitrate). The thicknesses of the stripped films varied from 10,000–50,000 Å. These are described as "thick" films in the discussion below.

¹ Manuscript received February 27, 1953. This paper was prepared for delivery before the Wrightsville Beach Meeting, September 13 to 16, 1953.

X-ray diffraction examination.—"Thick" films were stripped, powdered, and analyzed by the powder method with a General Electric XRD-1 instrument employing a cylindrical camera and copper or cobalt radiations.

Electron diffraction examination.—The electron diffraction analyses were made with a General Electric electron diffraction instrument. Both "thin" films (1000–4000 Å) and "thick" films were examined on the alloy panels by a reflection technique. "Very thin" films (less than 1000 Å) were also stripped and examined by transmission.

Film stripping technique.—A strip of a silver alloy which had reacted with sulfur was made the anode in a solution of 0.8*N* nitric acid solution at room temperature and electrolyzed for 5 min with a current density of 4 amp/dm². The strip was transferred to warm dilute nitric acid solution, rinsed, and then transferred to water. In water, the film was shaken loose, rinsed with water, then acetone, and finally dried.

A separate sample of the same silver alloy was given the same electrolytic treatment to determine whether objectionable anodic films were formed by this treatment.

RESULTS

Spectrographic examination.—The results from the spectrographic analyses of the reaction films are summarized in Table I. The sulfide films grown on the silver alloys of aluminum, magnesium, and manganese contain only a trace of the alloying element. However, an appreciable amount of the alloying element was found in the films grown on alloys of antimony, cadmium, indium, thallium, and zinc. It is significant that in every case the alloying element was evident. It was not possible to get reproducible values from a single sample of the film grown on the cadmium alloy. Deviations of $\pm 40\%$

from the 7.0% value were observed. This non-uniformity indicates that there were local concentrations of cadmium in the film, some regions being richer in cadmium than others. The precision of the results reported for the other films is better, being of the order of $\pm 10\%$, with $\pm 20\%$ for the zinc and $\pm 25\%$ for the indium alloy.

X-ray diffraction examination.—The x-ray examination of the films from silver and silver alloys gave only the pattern for β -silver sulfide, which has been assigned a monoclinic (pseudo-orthorhombic) structure by Ramsdell (2). The pattern for the film from the 9.6% Zn alloy was an exception in that extra lines were observed which were not identifiable, e.g., not ZnS or ZnO. None of the other patterns gave any indication of the presence of alloying element, the sulfide of the alloying element, or any compound of the alloying element in these films.

Electron diffraction examination.—Both thin and thick films were examined by electron diffraction

TABLE I. Spectrographic examination of films

Alloy from which film was stripped	Emission line (or lines) used	Estimated amount of alloying element present in film
%		%
Pure Ag	2721.8	0
4.0 Al-Ag	2568.0	0.015
1.8 Sb-Ag	2877.9	0.45
30.0 Cd-Ag	2265.0	7.0
11.8 In-Ag	2710.3	0.4
0.4 Mg-Ag	2776.7, 2779.8	0.04
4.3 Mn-Ag	2605.7	0.01
2.9 Tl-Ag	2918.3, 3229.8	0.9, 0.6
5.9 Tl-Ag	2918.3, 3229.8	0.95, 0.7
9.6 Zn	3302.9, 3345.0	0.5

using the reflection technique. Only patterns for β -silver sulfide were observed. However, the interplanar spaces in the patterns obtained from some of the films deviated from the X-ray spacings for pure β -silver sulfide. These deviations are believed to be indicative of distortions in the silver sulfide lattice. To make a quantitative estimation of this distortion, a "deviation" was calculated by subtracting the X-ray spacing from the electron diffraction spacing for each line. The deviations for all the lines in a given pattern were then averaged and this "average deviation" is given in Table II.

It is apparent that the distortion is, in general, not only greater for the thin films, but decreases or disappears as the film grows outward. The maximum error involved in the measurement of the deviation is less than 0.01 Å per line, so the deviation for the thin films is considerably more than that possible by an accumulation of experimental errors. On the other hand, most of the deviations observed in the

thick films could be accounted for by experimental error.

Films on several high alloys gave greater distortions. The deviation observed with the sulfide film from pure silver was quite small and of the order of experimental error in the measurement.

Further measurements on films of the order of thickness of 500 Å which had been stripped from the basis metal were made by a transmission

TABLE II. Film distortions from deflection measurements

Basis alloy composition	Average deviation (Å $\times 10^3$)
Thin films	
%	
24.4 Zn-Ag	+3.86
15.3 In-Ag	+3.75
0.8 Mg-Ag	+2.67
1.2 Pb-Ag	+2.58
1.6 Al-Ag	+2.40
19.8 Cd-Ag	+2.17
Ag	+0.75, +0.91
3.2 In-Ag	+0.71
2.9 Tl-Ag	+0.60
5.1 Zn-Ag	+0.08
5.9 Tl-Ag	0.00
9.4 In-Ag	-0.41
Thick films	
12.6 Zn-Ag	+1.79
1.2 Pb-Ag	+1.00
Ag	+0.47
0.8 Mg-Ag	+0.40
2.1 Sn-Ag	+0.33
5.1 Zn-Ag	+0.16
1.6 Al-Ag	-0.13
15.3 In-Ag	-0.42
3.2 In-Ag	-0.47

TABLE III. Film distortions from transmission measurements

Basis alloy composition	Average deviation (Å $\times 10^3$)
%	
Ag	-0.06
3.2 In-Ag	-0.09
30.0 Cd-Ag	-0.92
12.6 Zn-Ag	-1.60

technique. Only the pattern for silver sulfide was recorded. The measured distortion is reported in Table III, and it is significant that the distortion present in the film when the film was attached to the alloy disappeared, or the deviation shifted in a negative direction.

DISCUSSION

The spectroscopic examination of the films showed that sulfide films grown on silver alloys of

cadmium, antimony, indium, thallium, and zinc contained an appreciable quantity of the alloying element. The films grown on aluminum, magnesium, and manganese alloys contained only a trace of the alloying element. Nevertheless, the X-ray diffraction analysis in all cases indicated only the pattern for β -silver sulfide. This was confirmed by electron diffraction examination both with a reflection technique and a transmission technique. Therefore, the conclusion was drawn that when alloying elements are present in the film they exist in the form of their sulfides dissolved in β -silver sulfide.

This conclusion is limited by the fact that all but the reflection electron diffraction measurements were made on stripped films, i.e., the system studied had been disturbed before the actual measurements. An examination of the surface (metallic) of the alloy after reaction would contribute greatly to our knowledge of the system. We would be able to determine whether or not there was a concentration of the alloying element on the surface of the alloy hindering reaction through the formation of a diffusion barrier. But, here again, to examine the reacted surface the sulfide film must be stripped. In so doing we would alter completely the system we would study. Another limitation imposed is that of the lack of sensitivity of diffraction measurements to minor constituents in mixtures. The electron diffraction apparatus is probably the best instrument now available for the study of surface reactions. However, various experimenters claim that a concentration of less than 5% would remain undetected in a mixture. The system here under investigation, by virtue of the well-formed silver sulfide crystals, is particularly suited for examination by diffraction techniques.

The electron diffraction analyses show that usually the film just formed is distorted. As the film grows the extent of distortion decreases and largely disappears as the thick film is attained. If the film is stripped from the silver alloy, the distortion is relieved or the positive deviation is shifted to a negative value.

The thick films appear similar in structure to that of "normal" silver sulfide which would suggest that the cause of the observed steady-state rate is located at the metal-film interface.

Mechanism of Reaction

A postulated mechanism of reaction of the silver alloys with sulfur must account, first, for the rapid reaction during the early stage of the reaction life, and, second, for the decreased rate exhibited during the steady-state phase which constitutes the greater part of the reaction. The behavior of the

silver-thallium alloys, which differ from the main body of alloys, must also be explained.

The analyses of the reaction films indicate that the sulfide of the alloying element exists in the films in solution in the silver sulfide lattice. There is a concentration of the sulfide of the alloying element near the interface. This is the interpretation placed on the distortion observed in the sulfide lattice in the very thin film, but not in the thick film. This distortion is also associated with the attachment of the sulfide film to the alloy surface as shown by the relief of the distortion when the very thin films are removed from their metallic support.

More weight is given to the results obtained from the electron diffraction examination because, in this case, we dealt with an undisturbed system.

Thus, during the first rapid stage of the reaction, an interfacial layer comprised of the alloying element sulfide dissolved in β -silver sulfide is developed, giving a strained lattice. The rate-determining step during this stage is the diffusion of dissolved sulfur to the alloy strip surface. This distorted zone achieves a given thickness for a specific alloy. From then on the growth is slow, with the rate-determining step being diffusion through this interfacial zone.

The process by which silver sulfide grows has been demonstrated to be one of diffusion of silver cations and electrons through a film which contains cation vacancies, the gradient of which vacancies governs the diffusion (3). Solution of the sulfide of the alloying element in the silver sulfide lattice changes the number of lattice defects. All of the sulfides of lower cation/anion ratio than Ag_2S decrease the rate of reaction after about 100 hr. These are Al_2S_3 , Sb_2S_3 , PbS , CdS , In_2S_3 , MgS , PdS , MnS , SnS , and ZnS . Films grown on silver-thallium alloys behave much like those grown on unalloyed silver. The thallium sulfide, Tl_2S , with the same cation/anion ratio as Ag_2S , enters into the Ag_2S lattice without disturbing it and also without affecting the steady-state rate.

The distortion observed in the majority of the films is more than that to be expected from the growth of a sulfide lattice with certain lattice spacings on an alloy with different lattice spacings, since such distortion was not observed in thin films grown on thallium alloys.

The rate-determining steps for the two phases of the reaction are: (a) the diffusion of sulfur in solution to the metallic strip; and (b) the diffusion of silver cations and electrons through an interfacial zone of constant thickness. The interfacial zone is comprised of an alloying element dissolved in silver sulfide.

The reaction rates are of an order accountable for by hindered diffusion through silver sulfide. However, experimental work reported here does not discount the formation of a barrier zone of alloying element at the interface between the metallic strip and the film. As suggested above, the presence of this zone would be difficult to prove experimentally. The possibility of the alloying element remaining in solution in silver and diffusing backward as a significant step in the mechanism is unlikely.

The expected rate of diffusion of many of these alloying elements in silver may be approximated with data collected by Jost (4). The observed rate of reaction is 10^3 - 10^6 times that expected by this process.

On the other hand, the extrapolated diffusion rates for silver in lead and aluminum are sufficiently rapid to account for the rates of reaction with sulfur.

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

REFERENCES

1. R. T. FOLEY, M. J. BOLTON, AND W. MORRILL, *J. Electrochem. Soc.*, **100**, 538 (1953).
2. L. S. RAMSDELL, *Am. Mineralogist*, **28**, 401 (1943).
3. C. WAGNER, *Z. physik. Chem.*, **21B**, 25 (1933); in "Atom Movements," p. 153, American Society for Metals, Cleveland, Ohio (1951).
4. W. JOST, "Diffusion, In Solids, Liquids, Gases," Academic Press Inc., New York (1952).

The Rate of Dissolution and the Passivation of Titanium in Acids with Ammonium Fluoride Added¹

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ABSTRACT

Although Ti is very resistant to the action of all acids, except HCl, H₂SO₄, and especially HF, its resistance breaks down if soluble fluorides are added to the acidic solutions. It was found that the HF liberated by acids partially dissolves the protective film that is always present on the surface of Ti. Hydrogen ions then are discharged at the local cathodes, which are now exposed to the acids through the pores of the film. In agreement with this concept, the rate of dissolution of Ti increases only slightly with increased concentration of a strong acid (HCl, H₂SO₄), at a constant concentration of NH₄F, but it increases greatly with increased concentration of NH₄F (at a constant concentration of the strong acid).

If the concentration of NH₄F is increased still further, the Ti becomes passive, and simultaneously its potential decreases to -0.94 volt (hydrogen scale). This passivation could be explained by formation of a partial salt film on the surface of the dissolving Ti, and by increase of hydrogen overvoltage on local cathodes, because of the NH₄F present.

INTRODUCTION

Titanium dissolves readily in pure hydrofluoric acid, slowly in hydrochloric acid, and more slowly in sulfuric acid (1, 2). In all other acids titanium is nearly insoluble, but it reacts with many of these acids if some water-soluble fluoride is added to the acid. In the presence of such a fluoride, titanium is attacked by strong acids such as nitric, hydrobromic, hydroiodic, and perchloric; acids of medium strength (phosphoric); and even by weak dilute acids such as formic and acetic acids. Trifluoroacetic acid also reacts violently with titanium if the acid is diluted with water.

The intention of this investigation was to collect data concerning the proceedings and the rate of dissolution processes in the presence of soluble fluorides, in order to get some insight into the mechanism of this kind of dissolution.

The experiments were made with Remington Arms 1.6 mm thick rolled titanium sheet of a purity of ~ 97.6% (1). Squares of 1 cm² surface area were cut, imbedded in Bakelite, and without any heat treatment, only 1 cm² of the titanium plates was exposed to the action of the acid. The rate of dissolution was computed from the volume of hydrogen evolved. Purest NH₄F was added to the solutions. The experimental arrangement was the same

as described previously (1), and duplicate sets of experiments were made in each instance.

RATE OF DISSOLUTION OF TITANIUM AT A CONSTANT CONCENTRATION OF AMMONIUM FLUORIDE

In Fig. 1, the rate of dissolution of Remington Arms titanium in hydrochloric and sulfuric acids of increasing concentrations at a constant concentration of ammonium fluoride (0.05*M*) is shown.

The lowest curve shows the rate of dissolution of Ti in purest sulfuric acid. The rate of dissolution increases if ammonium fluoride is added, but increases only slightly, in all cases, with the concentration of the acid, even though 10*N* hydrochloric acid is already a nearly concentrated acid. Each experimental point is the mean value of two experiments, and represents the maximum rates of dissolution. The dissolution usually began with a short period (or no period) of induction, then came a flat maximum, and finally the rate decreased slowly. The duration of each run was from 4-10 hr. As compared with the rate of dissolution in purest sulfuric acid, the rate is greatly increased by the presence of ammonium fluoride, and it is still higher with the dissolution in hydrochloric acid. However, the increase of the rate with the concentration of the acids is nearly the same in both cases. This is proved by the slopes of the straight portions of the curves, which are very nearly equal.

Some of the experiments were continued in the acids over a period of from 50-70 hr, in order to find out whether or not the rate of dissolution de-

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depends on the absolute amount of hydrofluoric acid liberated by the displacement reaction, assuming that the reaction goes to



completion. It was found that the dissolution continues at a considerable rate after a time, when, according to reaction (I), all the HF available was used up. This fact clearly shows that hydrochloric

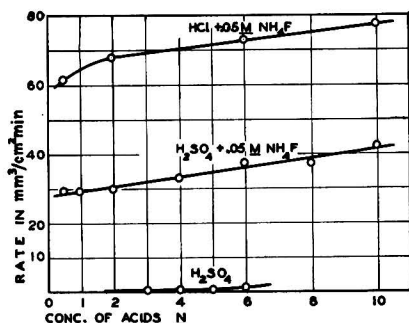


Fig. 1. Rate of dissolution of Ti in pure sulfuric acid, and in hydrochloric and sulfuric acids, at a constant concentration of NH_4F (0.05M), 1 mm² of hydrogen corresponds to 0.001424 mg Ti.

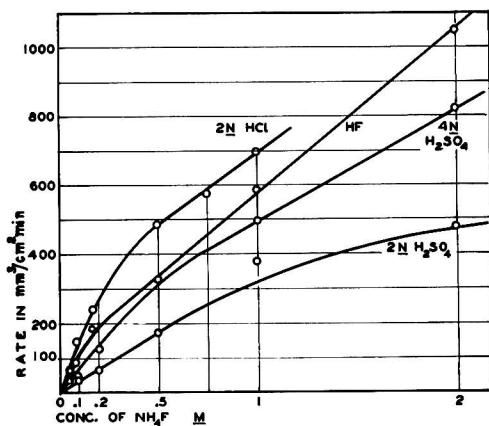


Fig. 2. Dissolution rates of Ti in constant concentration of HCl and H_2SO_4 , plus increasing amounts of NH_4F ; 1 mm² of hydrogen corresponds to 0.001424 mg Ti.

and sulfuric acids attack titanium at a much faster rate in the presence of F^- than when F^- is not present.

RATE OF DISSOLUTION OF TI IN ACIDS AT AN INCREASING CONCENTRATION OF NH_4F

The rates of dissolution of titanium in 2N hydrochloric acid, in 2N and in 4N sulfuric acid, in the presence of increasing amounts of NH_4F are

shown in Fig. 2. For comparison, the rates obtained in pure hydrofluoric acid are shown in the same diagram. The rates of the previous diagram, at 2N acid with 0.05M ammonium fluoride, are represented by the first points on this graph. There is a considerable increase in the rates with increasing concentration of NH_4F , from 0.05 to 2 molar, while in the previous diagram the rate in hydrochloric acid increased only from 62 to 77 mm³/cm² min, while changing the concentration of the acid from 0.5 to 10N. This behavior again shows the great influence of NH_4F , or of F^- , on the acceleration of the process of dissolution. The fact that the rate in the mixtures of 2N hydrochloric acid and ammonium fluoride was found to be greater than in hydrofluoric acid alone, again testifies to the increased reactivity of hydrochloric in the presence of fluoride ions.

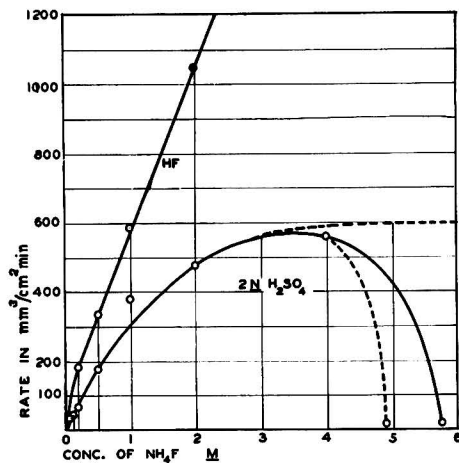


Fig. 3. Rates of dissolution of Remington Arms Ti in 2N H_2SO_4 , with increasing amounts of NH_4F added. The HF curve is drawn for comparison.

It was of interest to know how a further increase in ammonium fluoride concentration would influence the rate of dissolution. The effect of increasing additions of ammonium fluoride to the 2N sulfuric acid is shown in Fig. 3. We would expect that the rate of dissolution should increase and approach some constant value, as shown by the horizontal dashed curve. Instead of this, the rate dropped quickly as soon as the concentration of ammonium fluoride in the solution exceeded 4M (two experiments are represented by the descending portion of the solid curve, and by the dashed curve). The drop in the rate was so severe that it is justifiable to speak of passivation of the titanium. The same phenomenon also occurred in hydrofluoric and in other acids, with the rate sometimes dropping down to 0, and then increasing slightly. Table I shows the degree

of passivation of titanium by ammonium fluoride. The final rate of dissolution in the presence of large amounts of ammonium fluoride was only $\frac{1}{35}$, or less, of the maximum rate.

POTENTIAL MEASUREMENTS

In order to find out the reasons for the passivation observed, potential measurements of titanium in the presence of large amounts of ammonium fluoride were made in air and in nitrogen. Table I shows the normality of the acid and the molarity of the ammonium fluoride. There were 30 grams of the salt in a total volume of 158–160 cm³ of the acid.

In every case, when the investigation was being made in air, after the aforementioned quantity of ammonium fluoride was added to the acid being used, whether sulfuric or hydrofluoric, the potential of the titanium electrode dropped to very negative values (down to -0.94 volt) within 20–60 min. Simultaneously, the titanium electrode turned dark, and the rate of hydrogen development fell off to

TABLE I. Passivation of Ti by NH₄F; N₂ atmosphere

Acid	[NH ₄ F] M	Rate in mm ² /cm ² min	Final rate/maxi- mum rate
2N H ₂ SO ₄	0	0.0	—
2N H ₂ SO ₄	3.5	580	—
2N H ₂ SO ₄	5.8	84 → 17	1/34
2N H ₂ SO ₄	4.9	34 → 0 → 17	1/34
1N HF	0	590	—
1N HF	5.9	26 → 0 → 17	1/35
1N HF	4.9	34 → 17	1/35
1N HF	4.9	25 → 17	1/35

nearly a complete stop. Then, within the next 60 min, the potential rose, and after some time dropped again more slowly, finally reaching a potential of approximately -0.78 volt, which is roughly the potential of a titanium electrode in pure hydrofluoric acid. Nevertheless, the rate of dissolution was still very low, although it did rise slightly from its lowest reading (Table I). All of these potential fluctuations were probably related to the formation and breakdown of some kind of films on the titanium surface. This conclusion followed from the fact that in every case in air the acid mixture first turned greenish-yellow until the maximum negative potential was reached, indicating the formation of the complex ion [TiFe₆]³⁻; then at the constant potential reading the solution became colorless, which indicates the formation of the colorless complex ion [TiF₆]²⁻, because of the presence of oxygen (oxidation of the trivalent titanium ion of the complex to tetra-

valent).² Each salt present might be in equilibrium with a separate kind of film on the titanium.

This view was supported by the behavior of titanium in the same mixtures, but in a nitrogen atmosphere. The drop of the potential was as severe as in the first case, but then the potential stayed fairly constant after some initial fluctuations (Fig. 4). However, the potential was far below that reached in pure hydrofluoric acid. The rate of dissolution was very low (Table I). The color of the solution was greenish-yellow throughout the whole experiment. The electrodes were bright and shiny when removed from the flask after the runs and did not display any discoloring surface film, although the presence of a thin salt film was not excluded. The surface of the titanium soon turned dark, especially when it was washed with water. The behavior of the electrical potential of this

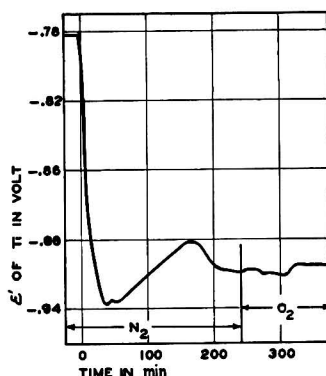


Fig. 4. Potential of Ti in HF in the presence of large amounts of NH₄F (Table I).

oxidized electrode, in the ammonium fluoride-acid mixture in air, was very similar to that already described. Strangely enough, if the nitrogen were replaced by air, as shown in Fig. 4, the potential did not change appreciably.

There is a fundamental difference in the passivation phenomenon just described, and the passivation of many other metals. While, in the latter case, the potential of the metal becomes more positive during passivation, the potential of titanium and of a few other metals (8) becomes less positive, accompanied by a decrease in the rate of dissolution. Under respective conditions, titanium also shows the usual anodic passivation (9).

Attempts were made to prove the increase of resistance of the titanium electrode during passivation. For this purpose the internal resistance of a

² The difficultly soluble, dark violet crystals of (NH₄)₂[TiF₆] were not obtained (7).

Ti|HF, NH₄F|Pt cell, just after switching off the current, produced by the cell itself, was measured. In the case of the presence of a salt film, a greatly increased internal resistance should be expected. However, the measurements revealed that the resistance on the titanium surface increased only slightly when the ammonium fluoride concentration exceeded 4*M*. This increase in resistance was not sufficient to explain the whole drop in the rates of dissolution (Table I), and revealed the porosity of such a salt film if it was present on the dissolving surface.

OVERPOTENTIAL IN PRESENCE OF AMMONIUM FLUORIDE

In order to get some further clue to the passivation observed and, as the dissolution of titanium in hydrofluoric acid is an electrochemical process (1), it was of importance to know the behavior of the

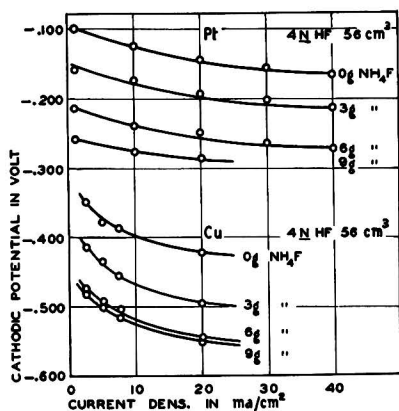


Fig. 5. Overpotentials on a platinized Pt and Cu electrode (covered with finely divided Cu) in 4*N* HF, in the presence of NH₄F.

local cathodes on the titanium in the presence of large amounts of ammonium fluoride.

For the measurement of hydrogen overvoltage, the cell Ti|HF, NH₄F|Pt (or with a copper cathode) was again chosen. The necessary current density was produced by the cell itself, in order to avoid complications which might be caused by anodically developed oxygen, using an external current. The cathodic potential was measured during the flow of the current by a 1*N* calomel reference electrode, whose capillary was touching the cathode. Thus, the overvoltage measurements were performed by the direct method (3), and the current density was adjusted by manipulating an exterior resistance (resistance box).

The cathodic potential curves were obtained at different current densities in 4*N* hydrofluoric acid

(56 cm³), to which, subsequently, amounts of ammonium fluoride in 3-gram increments were added. The results obtained are shown in Fig. 5.

All the measurements made show definitely that the hydrogen overvoltage of the metals, platinum and copper, increases with the increasing concentration of ammonium fluoride in the electrolyte. As all the curves in Fig. 5 follow Tafel's equation, the increase in overvoltage can be characterized by the increase of the constant, *a*, of Tafel's equation (4-6). This equation, as applied to the calculation of the negative cathodic potential, η (or overvoltage in volt), is as follows:

$$\eta = -(a + b \log i)$$

Here *a* and *b* are constants and *i* is the current density in milliamper/cm². Table II shows that the

TABLE II. Cathodic potential of platinized platinum in 4*N* HF, with NH₄F added; volume of the HF: 56 cm³

<i>i</i> in m amp/cm ²	NH ₄ F in mole/l	<i>a</i>	<i>b</i>	η in volt calc.	η in volt obser.	Δ
10	0	0.089	0.0523	-0.141	-0.127	-0.014
20	0	0.089	0.0523	-0.157	-0.161	+0.004
30	0	0.089	0.0523	-0.166	-0.175	+0.009
40	0	0.089	0.0523	-0.173	-0.191	+0.018
10	1.4	0.156	0.0270	-0.183	-0.174	-0.009
20	1.4	0.156	0.0270	-0.191	-0.189	-0.002
30	1.4	0.156	0.0270	-0.196	-0.200	+0.004
40	1.4	0.156	0.0270	-0.199	-0.213	+0.014
10	2.7	0.213	0.0301	-0.243	-0.235	-0.008
20	2.7	0.213	0.0301	-0.252	-0.245	-0.007
30	2.7	0.213	0.0301	-0.257	-0.263	+0.006
40	2.7	0.213	0.0301	-0.261	-0.271	+0.010
10	3.9	0.255	0.0219	-0.277	-0.275	-0.002
15	3.9	0.255	0.0219	-0.281	-0.283	+0.002

potential calculated from the equation is in good agreement with those obtained experimentally, and that the constant, *a*, increases from 0.089 up to 0.255, with increasing ammonium fluoride additions.

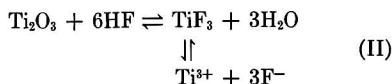
In the case of copper, there was still better agreement between the calculated values of the cathodic potential and those actually obtained experimentally. The constant, *a*, increased from 0.335 to 0.455, while the concentration of ammonium fluoride (in the hydrofluoric acid) increased from 1.4 to 3.9*M*. The increase of the constant, *a*, with the concentration of the ammonium fluoride, was linear in both cases. The constant, *b*, of the copper overvoltage curves, fluctuated between 0.064 and 0.084, indicating a steeper slope of the straight lines than for those of platinum. The influence of sodium fluoride additions upon the overvoltage had a similar, if not stronger, effect. The behavior of agar-

agar solutions added to the acid in separate experiments was analogous, although not so strong. It is also very possible that other metals would exhibit a similar cathodic behavior in the presence of ammonium fluoride.

DISCUSSION

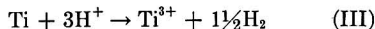
There is some difficulty in trying to explain the phenomena observed, but on the basis of the experiments performed, the following conclusions were developed concerning the mechanism of the dissolution of titanium in acids, in the presence of soluble fluorides.

It cannot simply be assumed that the rate of dissolution of titanium is proportional to the concentration of the hydrofluoric acid liberated according to reaction (I) because the dissolution of titanium continues with a considerable rate after the hydrofluoric acid has been used up. However, the increased action of hydrochloric, sulfuric, and many other strong and weak acids can be explained as follows. It was previously shown that the phenomena observed in the dissolution of titanium in acids can only be explained by the presence of a protective film on the titanium surface, this film being soluble in hydrofluoric acid, but nearly or completely insoluble in other acids (1). The film, which frequently is even clearly observable on the surface of the metal, probably consists of lower oxides of titanium (Ti_2O_3 ?), or of some basic salts. Only free hydrofluoric acid is capable of partially dissolving the film on titanium, and so the film is always in equilibrium with the hydrofluoric acid displaced according to equation (I), by the acid HR:



As hydrofluoric acid is a weak acid, reaction (I) becomes possible with very many acids, even weak acids, according to the law of mass action.

The film becomes thinner, with increasing concentration of the hydrofluoric acid, the pores increase, and the metal subsequently goes into solution at a greater rate, according to:



The dissolution of the metal in the pores proceeds because of the action of local elements. The formation of basic salts or of an oxide film, which otherwise would occur during the dissolution process, is prevented by the hydrofluoric acid present. Thus, the thickness of the protective film is determined by the concentration of the hydrofluoric acid.

In agreement with this concept is the slow increase in the rate with increasing concentrations of

HR, at a constant concentration of ammonium fluoride (Fig. 1), for, according to the law of mass action, the concentration of hydrofluoric acid increases only slowly with appreciable increase of [HR]. Therefore, the thickness of the film is reduced slightly, which in turn accounts for only a small increase in the rate of dissolution. Hydrochloric acid is more active than sulfuric acid because of the higher hydrogen ion concentration.

The gradual tapering off of the dissolution reaction (although the hydrogen ion concentration of the acid solution is still high) is explained by the possibility of the binding of F^- by Ti^{3+} :



as the $[Ti^{3+}]$ increases steadily during the dissolution process, and the $[F^-]$ decreases. With decreasing HF concentration, the film becomes thicker, the pores narrow, and the rate of dissolution decreases.

If the $[NH_4R]$ is now increased, with a constant [HR], then, of course, the [HF] increases strongly (Fig. 2), as can be shown by applying the mass action law. The thickness of the film decreases, and the rate of dissolution of titanium increases appreciably with increasing $[NH_4F]$.

Increasing the concentration of ammonium fluoride still more should have made the rate independent of $[NH_4F]$. Instead, the rate decreased sharply as soon as the 4*N* concentration was exceeded.

The explanation, according to the theory of local currents, is as follows. The rate of dissolution, V , as calculated from the increase of hydrogen volume, Δv (developed on the surface area, A) during the time Δt is given by equation (V), which was derived by one of the authors in 1930 (10). This equation is slightly modified here to obtain the correct (positive) sign for the rate of dissolution:

$$V = \frac{\Delta v}{\Delta t A} = kz^1 \frac{\eta - \epsilon^1}{r} \quad (V)$$

k being a constant, ϵ^1 the dissolution potential, η the overvoltage (potential) of the local cathodes, r the average resistance of each local cell, and z^1 the number of local cathodes per surface unit (1). Equation (V) was used in 1933 to discuss the possibilities of protection of metals from corrosion, and especially the case of increased hydrogen overvoltage was emphasized (11). A similar equation for the same purpose was used by Mears (12) and Mears and Brown (13) in 1949 and 1950.

At passivation, the rate V drops to low values, and usually can be explained by the shift of ϵ^1 toward positive potentials. The difference $\eta - \epsilon^1$ then becomes small, and the corrosion current drops to nearly zero. However, for passivity in the case of

titanium, the other three variables (z^1 , η , and r) are responsible, because of the very strange potential behavior of the passivated titanium (Fig. 4), the potential becoming more negative. Consequently, this passivation is different than with most of the other metals, and cannot be explained by the change in potential.

A noteworthy reason for the passivity of titanium is the formation of the thin salt layer, as already mentioned. However, because of the low electrical resistance of this layer, it must have large pores, so that the dissolution can proceed in these pores at a rather high rate. Therefore, the salt layer, by shielding and blocking a part of the number of active cathodes (z^1), decreases the rate of dissolution, but only partially explains the reason for passivation.

The real reason for passivation of the titanium lies in the increase of the hydrogen overvoltage on the local cathodes (or decrease of the cathodic potential) because of the presence of the ammonium fluoride, as is clearly demonstrated by Fig. 5. The emf of the local elements in the pores drops, and a very low current density results. This condition is contrary to the behavior of metals where the passivity is the result of a high current density in the pores of the protective film present on the surface of the passivated metal. In this case, the current density is very low, and is the reason, probably together with the extremely low $[Ti^{3+}]$, for the very negative potential of Ti. The $[Ti^{3+}]$ is low because of a complex ion formation with the ammonium fluoride which has been added.

The conclusion is that the passivation of titanium by ammonium fluoride is caused by the decrease in the number of active local cathodes

(covered by the salt film), and by the increase of overvoltage (polarization) on the free cathodes. Evidently these two effects overbalance the increase in the rate of dissolution, expected from the lowering in the anodic potential and the decrease in the resistance of the electrolyte, and as a result the rate of dissolution of Ti drops sharply.

Thus this case of passivation is in agreement with the theory developed by one of the authors (10, 11), and recently by Mears (12).

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

REFERENCES

1. M. E. STRAUMANIS AND P. C. CHEN, *This Journal*, **98**, 234 (1951).
2. M. E. STRAUMANIS AND P. C. CHEN, *Corrosion*, **7**, 229 (1951); *Metall*, **7**, 85 (1953).
3. C. F. PRUTTON AND S. R. MARON, "Fundamental Principles of Physical Chemistry," p. 586, Macmillan Co., New York (1947).
4. J. TAFEL, *Z. phys. Chem.*, **50**, 645 (1905).
5. G. KORTUM AND J. O. M. BOCKRIS, "Textbook of Electrochemistry," Vol. II, pp. 420, 426, Elsevier Publishing Co., New York (1951).
6. M. E. STRAUMANIS, in G. M. Schwab's, "Handbuch der Katalyse," Vol. VI, 166 (1943).
7. A. PICCINI, *Atti Linc.*, **1**, 47 (1885); *Gazz. chim. ital.*, **16**, 106 (1886).
8. R. B. MEARS, *This Journal*, **95**, 1 (1949).
9. C. D. HALL, JR., AND N. HACKERMAN, *J. Phys. Chem.*, **57**, 262 (1953).
10. M. STRAUMANIS, *Z. physik. Chem.*, **A148**, 349 (1930); *Korrosion u. Metallschutz*, **9**, 1 (1933).
11. M. STRAUMANIS, *Korrosion u. Metallschutz*, **9**, 229 (1933); *ibid.*, **11**, 49 (1934).
12. R. B. MEARS, *This Journal*, **95**, 1 (1949).
13. R. B. MEARS AND R. H. BROWN, *This Journal*, **97**, 75 (1950).

The Electrolytic Preparation of Molybdenum from Fused Salts

I. Electrolytic Studies¹

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ABSTRACT

Potassium hexachloromolybdate (III), K_3MoCl_6 , dissolved in molten alkali halides may be electrolyzed to deposit pure molybdenum at the cathode. The effect of the operating variables on the nature of the deposit is discussed.

INTRODUCTION

In recent years, interest in the refractory metals has been stimulated by the need for materials for use at exceptionally high temperatures. Much attention has been given to molybdenum because of its availability in this country (1) and its favorable mechanical and physical properties at elevated temperatures (2).

In view of this interest, a research program was initiated to determine the feasibility of an electrolytic method for its production. Not only was the production of pure molybdenum powders of interest, but, further, the possibility of producing coherent molybdenum electrodeposits was explored. This latter is of particular interest since it would provide a means of by-passing the rather complicated powder-metallurgy techniques now used for producing molybdenum objects. When only surface properties are important, a coating of molybdenum may be applied to an object, thus conserving much of this critical metal and further enabling one to take advantage of the structural properties of the basis metal. In addition, electroforming with molybdenum would result in elimination of not only powder metallurgy but also many difficult and expensive fabrication steps.

Historical

The present commercial method of producing the metal consists of reducing pure molybdic oxide with hydrogen to form a fine powder which is then worked by powder metallurgy methods. Recently, a method of producing ingots by vacuum arc-melting has been brought to a stage of pilot-plant operation (3). A method for producing molybdenum deposits on objects has recently been described (4) which

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involves the reduction of molybdenum pentachloride vapor by hydrogen in a sealed vessel at about 20 mm Hg total pressure and at 800° to 1100°C. Another method for producing molybdenum deposits (5) employs the thermal decomposition of molybdenum carbonyl at about 600°C below 0.1 mm Hg.

A thorough analysis of the literature and many attempts to duplicate published claims lead to the conclusion that pure molybdenum has not heretofore been electrodeposited from aqueous solutions, organic solvents, or from molten salts.

Deposits containing as much as 50% Mo alloyed with iron, nickel, or cobalt, as the second element, may be obtained by electrolysis of acidic or slightly alkaline citrate solutions (6), and deposits of somewhat lower Mo content alloyed with iron or cobalt can be obtained from concentrated alkali solutions (7); but examination of the properties of these deposits, when built up to a thickness of 0.001 in. to 0.002 in., shows that, when the molybdenum content exceeds about 25–30%, the deposits have a high oxide content, are very weak, and usually crumble on stripping of the basis metal. Further, the phase diagrams for the binary systems of molybdenum with nickel (8), iron (9), and cobalt (10) indicate that alloys containing less than about 90% molybdenum would not have satisfactory properties at elevated temperatures.

Much work has been done in attempts to obtain pure molybdenum from organic and other low-temperature nonaqueous systems, but little has been published because of the lack of positive results (11–13).

The work of Ksycki and Yntema (14) is the most recent paper on electrodeposition of molybdenum from aqueous systems. Deposits from their bath [Reference (14) p. 55] whose thicknesses were 0.1 and 0.4 microns were analyzed² and found to

² Microanalysis performed by R. A. Paulson of this Bureau.

contain 74 and 80% molybdenum, respectively. MoO_2 contains 75% molybdenum. Electron diffraction studies³ indicated the possible presence of small amounts of free molybdenum in the deposits.

The literature on the electrolysis of aqueous solutions of molybdenum compounds contains a large amount of conflicting information. After a thorough analysis of the literature and many attempts to duplicate claims (14-20), it can be stated with certainty that no electrodeposit whose major constituent is molybdenum metal has been obtained by the electrolysis of aqueous or organic electrolytes, with the possible exception of deposits which grow to only a few microns in thickness and then cease forming. The properties and composition of deposits as thin as these are extremely difficult to determine. This opinion is in agreement with Childs and coworkers (4) and Lander and Germer (5).

An interesting process is described in Gmelin (21) with references to two review articles (22), one of which is clearly a translation of the other, and neither of which gives reference to the original publication. In this process, molybdenum pentachloride, silica, and sodium chloride are heated, and the effluent vapors passed through molten sodium chloride, which is electrolyzed. Molybdenum is said to deposit at the cathode, which may be either copper or molten lead. This process may be that originally described by Gin (23).

Another process recommended a mixture of calcium molybdate and molybdenum carbide dissolved in bauxite (24), while still another recommended the electrolysis of molten calcium molybdate (25). Kratky and Bruckner (26) electrolyzed a melt of barium or calcium chloride and, after the electrolysis had begun, a water-free molybdenum salt was added. The calcium or barium metal already present in the bath from the initial electrolysis is said to reduce the molybdenum salt to molybdenum metal. Forland recommended a mixture of equimolar proportions of molybdenum pentachloride, sodium chloride, and aluminum chloride which melts below 200°C (27). He claims that the low melting point of the mixture permits electrolysis at 200°C without appreciable volatilization of the molybdenum pentachloride. This electrolysis was performed here, using a U tube as described by the inventor. Copious evolution of fumes both of the molybdenum pentachloride and the aluminum chloride occurred. The cathodic deposit was a very fine spongy black powder which reacted with water with the evolution of gas.

Andrieux reported the cathodic deposition of

³ Electron diffraction studies performed by M. Swerdlow of this Bureau.

molybdenum from a molten bath consisting of borax, sodium fluoride, zinc oxide, and molybdic acid at about 1000°C (28). In the same paper, rather similar solutions and conditions with other metals are said to produce borides rather than the free metal.

As a result of work which appears later in this study, it seems highly improbable that pure molybdenum metal can be deposited from an oxygen-containing melt, and that reports indicating this has been accomplished should be carefully checked.

EXPERIMENTAL PROCEDURES AND APPARATUS

Scope.—In determining the scope of this study it seemed, from an examination of the literature, and from some experience with the electrolysis of molten titanium compounds (29), that the most promising solvent would be mixtures of alkali chlorides. Therefore, practically all of the work was done in this medium. The molybdenum compounds chosen for investigation were those of greatest stability in each oxidation state of molybdenum. Of the hexavalent compounds, the molybdates are undoubtedly extremely stable, so sodium molybdate was the compound chosen. No hexachloride is known to exist, and the hexafluoride boils at 35°C.

The most stable of the quinquivalent compounds is the pentachloride, which boils at 268°C. However, it has an appreciable vapor pressure above 150°C. In addition, it is rapidly hydrolyzed by atmospheric moisture at room temperature. Since a fair amount of work with this compound in molten salts has already been done, no further study of it, other than the check of the Forland patent described above, was undertaken.

Of the tetravalent molybdenum compounds, the complex octacyanide is probably the most stable. It was prepared here and its properties were checked. The tetrahalide decomposes before melting and is decomposed by air, light, etc. Of the trivalent molybdenum compounds, the complex hexachloride is the most stable, and proved to be particularly suited to accomplish the purpose of this study. Most of this paper deals with the electrolysis of solutions of this compound. The divalent chloride is the most stable of the simple molybdenum halides and was chosen as the divalent compound for study in this work.

The electrolytic studies presented in this paper are concerned mainly with the reactions at the cathode. Insoluble anodes, diaphragms, etc., for electrowinning are now under study.

Equipment.—Since it was decided, on the basis of previous work—with titanium, to do all electrolyses in an inert atmosphere, it was necessary to design equipment for that purpose. The requirements which were set for the equipment included: (a) upper

temperature limit of 1000°C; (b) automatic temperature control; (c) manipulable electrodes in a closed system; (d) visibility of electrodes and electrolyte during operation; (e) cathode agitation; and (f) sufficiently leak-proof apparatus to maintain an internal pressure of 1 mm and to maintain an adequate protective atmosphere under a reasonably small flow of argon.

It became apparent that the design of such equipment could be greatly simplified if induction heating were used. A photograph of the equipment as finally assembled is shown in Fig. 1, and a schematic detail drawing in Fig. 2. A Pyrex glass cylinder, (A), 2 $\frac{3}{4}$ in. in diameter and 18 in. high, closed at the bottom, was placed in the furnace coil, (B), which was about 6 in. high and mounted on a transite platform. Inside the Pyrex tube was placed a ceramic cylinder, (C), made from "Alfrax" body

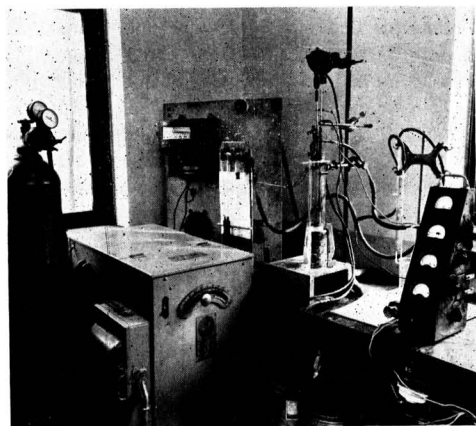


FIG. 1. Apparatus for electrolysis of fused salts

and a small amount of binder, the purpose of which was mainly that of thermal insulation. Inside the ceramic cylinder was placed the machined graphite crucible, (D), made of AGR⁴ graphite. The crucible was 6 in. high, 2 in. O.D., and had a $\frac{1}{4}$ -in. wall thickness. A thin sheet of mica was used between the Pyrex envelope and the furnace coil since it was found that this reduced the tendency to arc through the glass and crack it. A rubber bung, (E), was used to close the top of the Pyrex cylinder. One central and five peripheral holes were drilled through the bung, 5-in. lengths of tightly fitting glass tubing were inserted in four of the holes, and short lengths of rubber tubing were fitted to the tops of the glass tubes. A rod, $\frac{1}{4}$ in. in diameter and 2 ft long, (F), was inserted through the center hole and served as a cathode. It was connected at the top to a variable

⁴ National Carbon Company, Cleveland, Ohio.

speed stirring motor, (G), by a tightly fitting rubber coupling. Through the holes around the periphery of the bung were inserted a McDaniel refractory thermocouple protection tube (glazed), (H), long enough to reach the bottom of the crucible, and a $\frac{1}{4}$ -in. diameter tungsten rod which served to hold the rod or sheet anode, (I), by means of a molybdenum connector, (J). A third peripheral outlet was used as an escape chimney, (K), and was fitted with a screw clamp, while in the fourth (which had no glass tube) was inserted a stainless steel tube, (L), extending to within 2 or 3 in. of the top of the crucible. It served as a gas inlet or

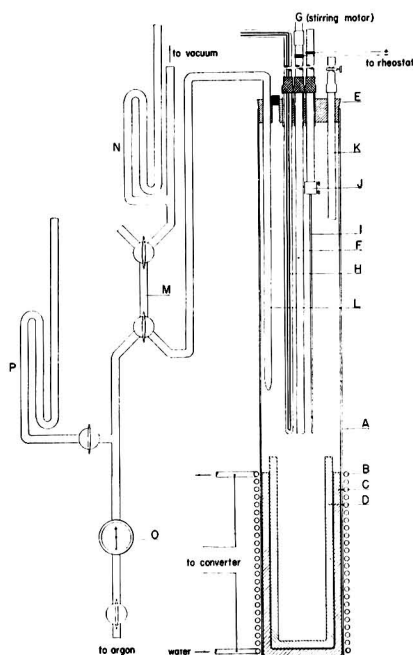


FIG. 2. Schematic diagram of electrolysis cell and auxiliary equipment.

evacuation port. The fifth hole was closed with a rubber stopper and was used only for potential and polarization studies. The furnace was supplied with power by an Ajax-Northrup 3KVA mercury spark-gap converter, which was controlled by a chromel-alumel thermocouple and a Brown controlling pyrometer, placed in the input circuit of the converter. The heating rate was rapid, the melt reaching a temperature of 900°C in about ten minutes. An air-cooling coil was placed around the top of the Pyrex cylinder near the rubber bung; thus the area around the bung was always kept cool to the touch. With the water cooling in the furnace coil around the glass and the ceramic crucible separating the glass

from the heated crucible, the thermal gradient was sufficiently large to permit long periods of operation with the charge at 900°C without softening the glass.

General procedure.—The procedure is as follows.

Electrolysis.—The electrolytes consisted of a mixture of alkali chlorides and a salt of molybdenum. The alkali chloride mixture henceforth is called the "halide solvent." A typical electrolysis run was performed in a manner designed to exclude, insofar as was possible, traces of moisture or contamination by air. The procedure began with the purification of the "halide solvent" by fusing it at a temperature a few hundred degrees above its melting point in the crucible in which the electrolysis would be done. It was then allowed to cool in an argon atmosphere. The Pyrex vessel was then opened and the previously dried molybdenum compound quickly added on top of the solid halide solvent. (The method of drying the molybdenum compound was determined by the properties of the compound itself.) The bung and attached equipment were then set in place, with the anode and cathode withdrawn above the crucible. The system was evacuated, filled with argon to 3 or 4 cm above atmospheric pressure, and the argon flow continued. After flushing the system, the heating was started, and, as soon as the salts melted, the thermowell was inserted into the melt. At the desired operating temperature, the anode and cathode were inserted into the melt, the cathode connected to the stirring motor, the electrical leads connected, and the electrolysis begun. The flow rate of the argon was set at any value between 200 and 3000 cc/min as desired during the run, but the outlet chimney was always adjusted to maintain a pressure above atmospheric inside the system throughout the run.

When very hygroscopic material, such as lithium chloride, was present, the following additional pretreatment before electrolysis was required in order to expel all moisture and oxycompounds. The bath was heated to 900°C at the same time that the argon flow was increased to about 3000 cc/min. This rapidly drove out any released moisture and volatile oxycompounds, and reduced their opportunity to attack the solution. After 15–30 min at this temperature, the solution was cooled to the operating temperature, the argon flow reduced to the usual value of about 300 cc/min, and the solution electrolyzed at low current density until the deposits showed no oxide present.

At the end of a run, the cathode, anode, and thermocouple were withdrawn from the melt and allowed to cool in the inert atmosphere, while the electrolyte itself cooled and froze. The system was not opened until the temperature inside was below

100°C. After removing the bung with the anode and cathode, an auxiliary bung was quickly replaced, the system evacuated and filled with argon, and the electrolyte stored in an inert atmosphere for later runs. The rubber sleeves through which the electrodes and thermocouple well were passed were lubricated with silicone stopcock grease and all stationary joints were sealed with Unichrome⁵ stop-off lacquer No. 323, as was the joint between the Pyrex envelope and the large rubber bung.

The cathode deposit was separated by first soaking the cathode in boiling 10% hydrochloric acid. Contrary to some statements in the literature this does not appreciably attack molybdenum. After the adhering salts from the electrolyte were dissolved, the deposit, if powder, was removed by scraping, hammering, chiseling, or whatever procedure was required by the nature of the deposit. This was then lightly ground in a mortar and washed with distilled water. Fines and any impurities lighter than molybdenum remained suspended while the molybdenum settled out. The liquid was decanted, and this was repeated until the supernatant liquid was practically clear. The molybdenum was then filtered, washed with acetone, and dried.

Except where otherwise indicated, the cathode was a ¼-in. diameter tungsten rod immersed to a depth of about 3 in., giving a cathode area of 0.15 dm² (2.3 in.²). It was rotated at 300 rpm. The anode was a pure commercial molybdenum⁶ sheet, 0.5 in. x 0.030 in., immersed to the same depth.

The molybdenum anode was used mainly to simplify the investigation of the cathode reactions. It was found early in the work that molybdenum dissolves with 100% current efficiency in the molten chloride electrolyte. As a result, there were no complications introduced by anodic products, oxidation of the electrolyte, or any other factors usually associated with an insoluble anode. In electrowinning, a divided cell with an insoluble anode and some convenient anolyte may be required.

Analysis.—Many analyses for molybdenum were performed using the volumetric Jones reductor method (30) and a few using the gravimetric method of precipitation in acid solution with α -benzoin oxime (31).

Metallography.—The microstructure of the molybdenum deposits was investigated by mounting specimens in Bakelite or Lucite and polishing by standard methods.⁷ The samples were etched with Murakami's reagent, which consists of 10 grams of

⁵ United Chromium, Inc., New York, N. Y.

⁶ Fansteel Metallurgical Corporation, North Chicago, Ill.

⁷ The metallographic specimens were prepared by F. P. Brodell of this Bureau.

potassium ferricyanide and 6 grams of sodium hydroxide dissolved in 200 ml of water.

ELECTRODEPOSITION

General Considerations

Potassium hexachloromolybdate (III), K_2MoCl_6 , (for preparation see Part II of this series), was the most satisfactory electrolyte for electrodepositing molybdenum from fused baths. The salt was used in two types of halide solvents: (a) 1:1 mixture (by weight) of sodium chloride and potassium chloride, and (b) the eutectic mixture⁸ of lithium chloride and potassium chloride. Preliminary tests, with baths containing different concentrations of the molybdenum salt, indicated that the best deposits were obtained with baths nearly saturated with the molybdenum salt at the temperature of deposition.

longed electrolysis, a quantity of current equivalent to about 1 amp-hr/gram of bath was passed through a small batch of bath (B). This was enough current to replace the initial quantity of molybdenum in the bath about 20 times. The bath was still in operating condition after this experiment, and no evidence of deterioration was observed.

The deposits from bath (A) usually consisted of rather coarse powders, with an average diameter of about 0.01 in. In many instances, however, a layer of the deposit immediately next to the cathode, about 0.001 in. in thickness, was adherent to the cathode and appeared quite dense. A typical deposit from bath (A) is shown in Fig. 3, and a cross section of the adherent molybdenum layer next to the cathode is shown in Fig. 4. It was about one crystallographic grain thick.

TABLE I.—Deposits from K_2MoCl_6 —KCl—NaCl Solution

No.	Conc. mole %	K_2MoCl_6 wt %	Current density (amp/dm ²)	Plating time (hr)	Wt of deposit collected (g)	Type of deposit
1	2.0	12	30	1.0	0.25	Nonmetallic black powder
2	2.0	12	100	0.5	—	Nonmetallic black powder
3	3.3	18	3	1.5	—	Nodular superficially coherent Mo deposit overlying thin coherent layer
4	3.3	18	100	0.5	6.7	Dendritic Mo powder overlying adherent layer (see Fig. 12)
5	4.9	25	3	1.5	0.86	Superficially coherent nodular deposit overlying adherent layer
6	4.9	25	30	1.0	2.8	Powder agglomerates consisting of trees and large multifaceted crystals of molybdenum over an adherent layer
7	4.9	25	100	0.5	8.5	Granular metallic powder over adherent layer (see Fig. 3 and 4 and col. 3, Table IV)
8	4.9	25	Periodic reverse 30 direct 60 reverse	1.0	3.2	Powder consisting of small platelets over about 0.002 in. of adherent plate

All deposits were prepared at 900°C.

The deposition was carried out over a range of current densities from 3 to 100 amp/dm² and over a range of temperatures from 600° to 900°C. The lithium chloride-potassium chloride melt had an advantage over the sodium chloride-potassium chloride melt in that it could be operated at a lower temperature, and coherent deposits, as well as powders, could be obtained from it. It had the disadvantage of being very hygroscopic, and required somewhat more care. The compositions, in weight per cent, of the two baths used for most work were: (A) NaCl 37.5%; KCl 37.5%; K_2MoCl_6 25%, at 900°C; (B) LiCl 34%; KCl 41%; K_2MoCl_6 25%, at 600°–900°C. The composition of other baths tried is given in Table I.

To demonstrate the life of the bath under pro-

⁸ The composition by weight of this mixture is 45.5% lithium chloride, 54.5% potassium chloride.

The deposits obtained from bath (B) at 900°C (Fig. 5 and 6) were similar to those from bath (A), except that the grain-size of the deposit was somewhat finer and the coherent layer of molybdenum under the powder was thicker than with bath (A).

At 600°C and 3 amp/dm² coherent deposits (Fig. 7 and 8) were produced which could not be obtained from either bath at 900°C. Fig. 9 shows a coherent tubular deposit of molybdenum from which the cathode has been dissolved. It was about 2 in. long, 0.25 in. in diameter, with a wall thickness of 0.02 in. The tube was hard and brittle, but mechanically sound. Its external surface was quite rough. The density was 9.6 g/cm³ or about 94% of the theoretical density of molybdenum. In comparison, powdered molybdenum, which has been pressed and sintered, has a maximum density of about 92% of the theoretical density (32). The

tube was deposited on a tubular steel cathode coated with 0.001 in. of silver, and closed at the end. Neither iron nor copper cathodes could be used as they were attacked by the solution, ap-

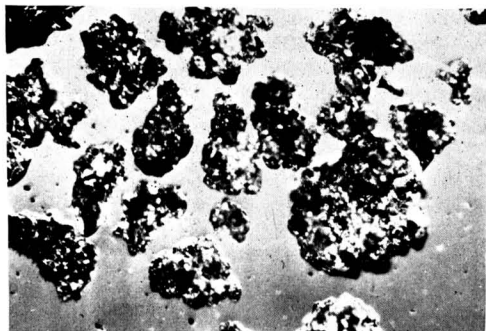


FIG. 3. Deposit of molybdenum powder—bath A. 50×



FIG. 4. Cross section of adherent molybdenum layer after removal of overlying powder—bath A. 500×

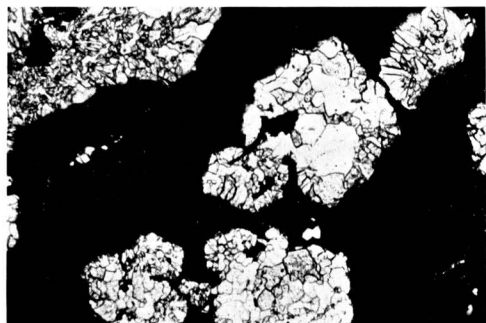


FIG. 5. Granules of Mo powder etched to show grain structure—bath B. 100×

parently chemically displacing molybdenum from the melt. At 600°C and 100 amp/dm², the fine grain powder deposits shown in Fig. 10 and 11 were produced.

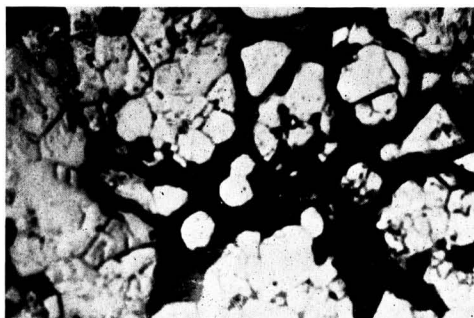


FIG. 6. Cross section of molybdenum deposit adjacent to cathode after removal of loose powder—bath B, 900°C. 500×

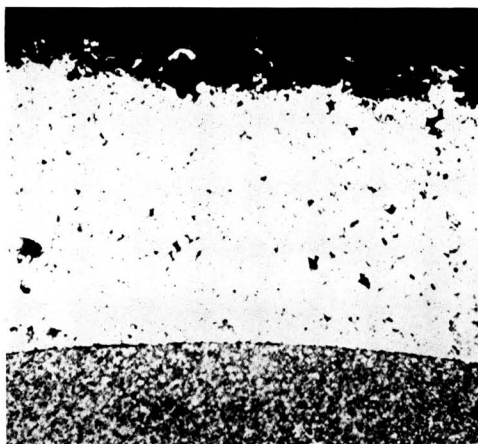


FIG. 7. Cross section of coherent molybdenum deposit from bath B, 600°C. 100×

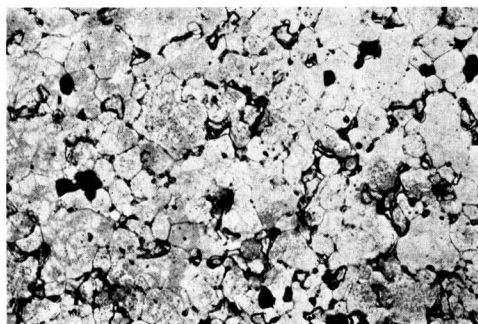


FIG. 8. Same as Fig. 7, etched to show grain structure. 500×

The purity of the molybdenum deposits was established by chemical and spectrochemical analyses as discussed below.

Variables Involved in the Deposition of Molybdenum

The study of the variables involved in the deposition of molybdenum was made for the purpose of determining how they affected the purity and the physical nature of the deposit. The most important factor in obtaining pure deposits of molybdenum was the purity of the reagents and the atmosphere above the electrolytic cell.

Oxygen and moisture.—The exclusion of air and moisture from the salts composing the melt and the



FIG. 9. Electroformed molybdenum tube and cup



FIG. 10. Molybdenum powder from 100-gram batch produced at 600°C from bath *B*. 50X.

atmosphere above the cell was of extreme importance for producing pure molybdenum deposits. Before this was recognized, impure deposits were obtained which contained oxide. Such deposits usually consisted of a layer of black powdery material adjacent to the cathode with a layer of molybdenum crystals over it. A black powder was also formed in the melt. X-ray diffraction analyses⁹ established

⁹ Analyses performed by F. A. Mauer and H. E. Swanson of this Bureau.

that these black powders were largely Mo_2O_3 mixed with a small proportion of metallic molybdenum.

During runs with contaminated melts or atmospheres, volatile blue and white products condensed on the upper walls of the glass envelope. These were probably oxymolybdenum compounds of valence 4 or 5 formed by oxidation of the K_3MoCl_6 . Bath (*B*), containing the hygroscopic lithium chloride, was particularly prone to give such results until the procedure previously described for pretreating the melt before electrolysis was worked out.

The importance of maintaining an oxygen-free melt was demonstrated by two additional experiments: (a) a bath which was operating satisfactorily

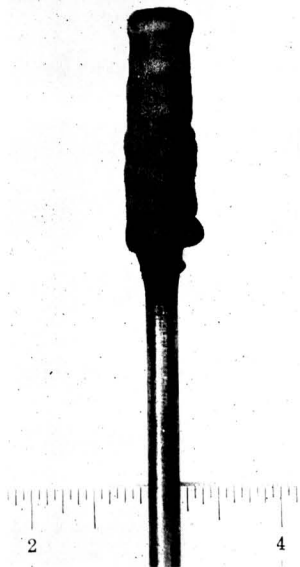


FIG. 11. Molybdenum powder deposit on cathode, as it appears after immersion in dilute HCl to dissolve adhering electrolyte.

was opened briefly to the air; the resulting deposit and melt contained black oxide; and (b) the introduction of about 0.1% by weight of sodium molybdate into a melt completely stopped the deposition of molybdenum. The changes of cathode potential occurring during the experiments will be discussed in Part III of this series.

Composition of melts.—The main difference between the two baths, (*A*) and (*B*), is that the latter may be operated at a lower temperature. More coherent deposits were obtained from bath (*B*) at 600°C than from bath (*A*) at 900°C. Apparently temperature is the most important variable in this case, as the deposits obtained from bath (*B*) at 900°C, although somewhat more coherent than those from bath (*A*), were nevertheless powdery in

nature. However, a careful comparison of a number of deposits from the two baths at 900°C indicates that the presence of the lithium salt does have a beneficial effect on coherence and reduction of grain size apart from the temperature effect. This is not necessarily a specific effect of the lithium ion itself, but may be because of the presence of a trace of moisture which could not be removed from this very hygroscopic material. Moisture, although harmful in large quantities, might be beneficial in trace amounts. Both baths operated at about 100%

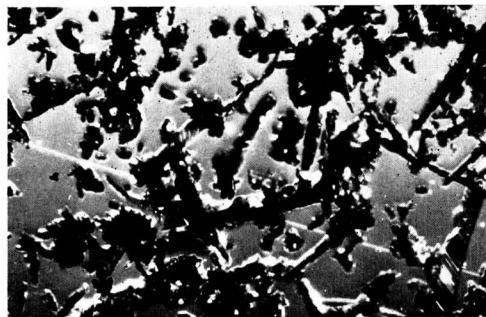


Fig. 12. Dendritic molybdenum powder—bath A. 50X

point than (B), two halide melts containing aluminum chloride were tried, but as the solubility of K_2MoCl_6 was not very high in these melts below 600°C, no further work was done with them. A comparison of these halide melts with bath (B) is given in Table II.

Current density.—The current densities used varied from 3 amp/dm² to 100 amp/dm². Adherent and coherent deposits were obtained only from bath (B) at 3 amp/dm². At higher current densities the deposits from both bath (A) and bath (B) were noncoherent, consisting of either dendrites or granular powder. The effect of current density on the deposits from baths (A) and (B) is shown in Tables I and III.

Periodic reversal of current was used with bath (A) in an attempt to obtain smooth coherent deposits. No improvement was noted, although a wide range of direct and reverse cycles was tried. The forward cycles ranged from 20–60 sec duration with current densities from 30 to 100 amp/dm². The reverse cycles ranged from 6–15 sec duration with current densities from 60 to 200 amp/dm². No smoothing was obtained on periodically reversing current when depositing coherent molybdenum from bath (B) at 600°C and 3 amp/dm².

TABLE II. Solubility of K_2MoCl_6 in low melting halide solvents

No.	Bath composition*				Temp. °C			
	AlCl ₃	KCl	LiCl	K ₂ MoCl ₆	300	400	500	600
1†	—	2.7	2.3	1.7	Solid	Solid	Dark red liquid mixed with small solid phase	Uniform dark red liquid
2	4.3	1.2	—	1.1	No solubility of Mo compound. Clear melt above red salt	Melt above solid Mo compound very slightly colored	Reddish brown solution with some solid phase	Same as at 500°C with only small solid phase remaining
3	4.0	—	0.8	1.1	Same as 2	Clear melt above Mo compound	Similar to 2 but more solid present	Similar to 2 but solid phase larger

* The concentration of K_2MoCl_6 in the three mixtures is in the range of 4 to 5 mole %.

† Composition No. 1 corresponds to bath (B).

cathode current efficiency over a wide range of current density.

Only a few variations in bath compositions were studied. A few tests were made with the KCl-NaCl halide solvent with lower concentrations of molybdenum than in bath (A). The data are given in Table I, No. 1–4. The dendritic deposit of No. 4 (Fig. 12) consisted of needles 0.5 to 1.5 mm long and was characteristic of the solution of intermediate concentration of molybdenum. The needles were practically monocrystalline except for small crystals growing at edges, points, or other irregularities on the needles. To find a bath with a lower melting

Anode.—In all of the electrolyses, a molybdenum anode was used. The anodes corroded cleanly with 100% efficiency. This is an advantage if this process is used for electroplating or electrorefining, but electrowinning would require either a soluble anode other than molybdenum, or more likely an insoluble anode. Insoluble anodes would require a divided cell since the molybdenum compound is very easily oxidized anodically. This was shown by an experiment in which the molybdenum anode touched the carbon crucible, thus making it anodic. The current efficiency of the anodic solution of molybdenum was considerably reduced, and the content

of molybdenum in the melt dropped considerably. The experiment indicated that anodic oxidation of the K_3MoCl_6 to volatile molybdenum compounds at a graphite electrode occurred about as readily as anodic solution of the molybdenum anode.

Voltage.—The voltage required for deposition of molybdenum was very low when using molybdenum anodes. It varied from about 0.045 volt at a current density of 3 amp/dm² to about 1.5 volt at 100 amp/dm². This indicates that the electrolytic deposition and solution of molybdenum occurs with

TABLE III. Deposits from K_3MoCl_6 -KCl-LiCl solution

Temp, °C	Current density (amp/dm ²)	Plating time (hr)	Wt deposit collected (g)	Type of deposit
600	3	5	2.9	Coherent rough plate, 0.02 in. thick (see Fig. 7, 8, 9)
900	3	5	—	Superficially coherent powder covering about 0.01 in. of badly cracked and porous plate (see Fig. 6)
600	6	4	—	Powder composed of microscopic dendrites over coherent plate
600	30	1	5.7	Fine-grained powder (5.3 g) over approximately 0.0015 plate (0.43 g)
600	100	1.75	29.0	Very fine-grain powder (see Fig. 10 and 11 and col. 1, Table IV)
900	100	1	17.9	Malleable nodular powder deposit (see Fig. 5 and col. 2, Table IV)

The composition of all solutions is that of bath (B).

very little polarization. The cathode polarization is discussed more fully in Part III of this series.

Characteristics of Deposits

Purity of the deposits.—The purity of molybdenum is an important matter, since the ductility of molybdenum, particularly at low temperatures, is believed to depend upon the absence of certain impurities such as oxygen and nitrogen. The molybdenum content of the electrolytic powders was over 99% as determined chemically. Spectrochemical analyses of three specimens of electrolytic powders (No. 1, 2, and 3, Table IV) are compared with three specimens of commercial molybdenum, one of which is a spectrochemical standard, and with a sample of specially purified molybdenic oxide. The electrolytic powders compare favorably in purity with the standard specimens and commercial products.

The oxygen content of the electrolytic powders was determined by heating in dry hydrogen at 1060°C and noting the loss in weight.¹⁰ The specimens prepared under the best conditions had an oxygen content of about 0.026%. With further improvement in the atmosphere of the electrolytic cell and in the purity of the compounds, this should be capable of being reduced further. A qualitative test showed that the chloride content of the powders was negligible. Powders of columns 2 and 3, Table IV, are at least 99.9% Mo.

Properties of the deposits.—The appearance of the deposits has already been described. The electroformed tube previously mentioned was brittle, but some nodular powders obtained by electrolysis at 900°C (see Fig. 5) were somewhat malleable, as they could be slightly flattened with a hammer. The hardness of the powders ranged from 245 to 285 Vickers hardness number. Some of the powder was compacted in a mold under a pressure of 30 ton/in.² The compact, a cross section of which is shown in Fig. 13, was strong and had a density of 8.36 g/cm³. Further work will be done to determine the properties of the molybdenum after being subjected to sintering and rolling.

Electrolysis of Other Molybdenum Compounds

Molybdenum dichloride.—The interest in molybdenum dichloride stems from the fact that it is the most stable of the molybdenum halides. It is inert in moist air at room temperature and may be heated at 600°C in an inert atmosphere without decomposition. It is only slowly attacked even by nitric acid or aqua regia. Its great stability is attributed to its existence as the trimer, Mo_3Cl_6 , or hexamer, Mo_6Cl_{12} .

Twelve grams of molybdenum dichloride (for preparation, see Part II of this series) was dissolved in 100 grams of the lithium chloride-potassium chloride eutectic mixture to make a 4 mole-% solution of $MoCl_2$. This was electrolyzed in an inert atmosphere as described previously.

The conditions of electrolysis were the same as those used with K_3MoCl_6 in the KCl-LiCl solvent, i.e., 600°C, 100 amp/dm² for 30 min. The results of the run were inconclusive and the experiment may need to be repeated. A rough treed deposit of molybdenum was obtained with a cathode current efficiency of only 37% based on Mo^{2+} and 55% based on Mo^{3+} . The solidified melt remaining after the run appeared similar to those obtained with K_3MoCl_6 , and analyses showed that all the molybdenum present was in the trivalent state. These

¹⁰ The method used was kindly communicated to the authors by H. E. Hostetter, Climax Molybdenum Company, Detroit, Michigan.

TABLE IV. Spectrochemical analysis of electrolytic and commercial molybdenum powders†

Impurity	Sample No.						
	1	2	3	4	5	6	7
Aluminum	W	VW	VW	VW	VW	—	W
Barium	—	—	—	—	VW	—	—
Calcium	VW	—	T	T	T	T	—
Cobalt	VW	—	VW	VW	VW	—	VW
Chromium	T	—	—	VW	T	—	—
Copper	VW	T	T	VW	VW	VW	T
Iron	W	VW	VW	W	VW	VW	W
Magnesium	VW	T	T	VW	VW	T	T
Manganese	VW	—	—	W	VW	W	VW
Nickel	VW	—	—	VW	VW	—	VW
Lead	VW	T	T	T	T	—	T
Silicon	W	VW	VW	W	VW	W	W
Silver	T	—	—	—	—	—	—
Tungsten	—	—	—	—	—	W	—
Oxygen*	0.257%	0.026%	0.068%	0.268%			

Col. 1—part of 110-g batch from LiCl-KCl solution.

Col. 2—sample from LiCl-KCl solution produced with specially purified melt.

Col. 3—sample from NaCl-KCl solution.

Col. 4—Commercial molybdenum powder (Westinghouse Corp.).

Col. 5—Commercial molybdenum sheet used as anodes (Fansteel Corp.).

Col. 6—Specially purified MoO₃ used as spectroscopic standard.

Col. 7—Molybdenum powder (Hardy) used as spectroscopic standard.

W, weak = 0.01–0.1%.

VW, very weak = 0.001–0.01%.

T, trace = 0.0001–0.001%.

* Not determined spectroscopically.

† Spectrochemical analysis performed by E. M. Krumrine of this Bureau.

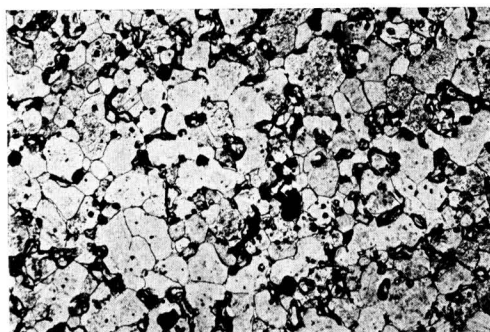


FIG. 13. Cross section of compacted and presintered molybdenum bar prepared from electrolytic molybdenum powder. 100 \times .

results indicate: (a) that Mo²⁺ in the melt is anodically oxidized to Mo³⁺ quite readily; and (b) that Mo²⁺ is not reduced to metal at the cathode readily, if at all. To confirm these indications a molybdenum dichloride melt would have to be

electrolyzed with separate anode and cathode compartments.

Sodium molybdate.—In previously published attempts to electrodeposit molybdenum from fused electrolytes, the alkali molybdates have been favored salts because they melt readily without decomposition. Mention was made above that small quantities of molybdates in a K₂MoCl₆ bath inhibited the deposition of pure molybdenum. Therefore, the production of pure molybdenum from fused molybdates is not to be expected.

Two molybdate melts were electrolyzed at 900°C and 100 amp/dm² with a molybdenum anode as was done with the K₂MoCl₆ in the KCl-NaCl solvent. They were: (a) pure anhydrous sodium molybdate, and (b) sodium molybdate, 13 grams dissolved in 100 grams of a melt consisting of equal parts by weight of sodium and potassium chloride. The results with both melts were similar. The bulk of the reaction product was found dispersed throughout the melt as a black, water-insoluble powder containing about 77% molybdenum, corresponding

to MoO₂ (75% Mo). Only a very thin, somewhat metallic looking film, covered by a black powder, remained on the cathode. An x-ray diffraction examination of the material on the cathode indicated that it contained molybdenum metal, Mo₂O₃, and Mo₂C. The latter must have been deposited from a secondary product resulting from the reaction of a molybdenum compound with the carbon crucible. The black cathode product was estimated to contain about 50% free Mo. Electrolysis of the sodium molybdate melt at 3 amp/dm² produced no deposit at all at the cathode.

Potassium octacyanomolybdate (IV).—Preliminary experiments with potassium octacyanomolybdate, K₈Mo(CN)₈, indicated that it was not sufficiently stable at elevated temperatures to permit it to be electrolyzed. The compound was prepared by the method of Bucknall and Wardlaw (33) and dehydrated without decomposition at 110°C. The pure salt, when heated in a sealed tube at 625°C, did not melt, but decomposed into gases and a black residue. Analysis by x-ray diffraction showed that the residue contained, among other substances, KCN and gamma-Mo₂N in about equal proportions. Since it may be expected that the cyanide complex would be more compatible with a molten cyanide solvent than with a molten chloride, a melt was made with about equal parts of KCN, NaCN, and the octacyanide, and heated in a sealed tube to 625°C. This mixture also did not melt, although KCN-NaCN alone has a melting point slightly above 500°C. The change in color, mainly to black, indicated that the molybdenum compound had decomposed.

SUMMARY AND CONCLUSIONS

This study of the electrolysis of molybdenum compounds in fused salts has shown that a solution of potassium hexachloromolybdate (III) dissolved in a mixture of alkali halides can be electrolyzed in an inert atmosphere to produce deposits of pure molybdenum at the cathode.

The recommended compositions and operating conditions for the deposition of pure molybdenum are:

	grams		grams
(A) KCl	50	(B) KCl	54.5
NaCl	50	LiCl	45.5
K ₂ MoCl ₆	33	K ₂ MoCl ₆	33
900°C		600°-900°C	

The solutions may be operated at any current density up to 100 amp/dm² with a cathode current efficiency of 100% to produce deposits of 99.9+ % molybdenum. No information at higher current densities has been obtained. At high current densities, powders are obtained from both baths, but

with solution (B) operated at 600°C and 3 amp/dm², coherent dense deposits of molybdenum up to 0.02 in. thick have been produced. It is believed that this is the first reported instance of the production of coherent massive electrodeposits of molybdenum.

ACKNOWLEDGMENTS

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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.

REFERENCES

1. H. W. DAVIS, "Molybdenum," from "Minerals Yearbook," U. S. Bureau of Mines, p. 785 (1949).
2. R. M. PARKE, *Metal Progress*, **60**, 81 (1951); J. J. HARWOOD, *Product Eng.*, **23** (1), 121 (1952).
3. R. M. PARKE AND J. L. HAM, *Trans. Am. Inst. Mining & Met. Engrs.*, **171**, 416 (1947).
4. W. J. CHILDS, J. E. CLINE, W. M. KISNER, AND J. WULFE, *Trans. Am. Soc. Metals*, **43**, 105 (1951).
5. J. J. LANDER AND L. H. GERMER, *Trans. Am. Inst. Mining & Met. Engrs.*, **175**, 648 (1948).
6. H. J. SEIM AND M. L. HOLT, *Trans. Electrochem. Soc.*, **96**, 205 (1949).
7. L. F. YNTEMA, U. S. Pat. 2,428,404 (1947).
8. R. M. PARKE, in "Metals Handbook," p. 1230, American Society for Metals, Cleveland, Ohio (1948).
9. W. P. SYKES, *ibid.*, 1210.
10. M. HANSEN, "Der Aufbau der Zweistofflegierungen," J. Springer, Berlin (1936).
11. K. WOLF, Dissert. Aachen Tech. Hochschule (1917); Gmelin's "Handbuch der Anorg. Chem.," 8th ed., Syst. 53, Molybden, p. 155 (1935).
12. WOLFRAM-LAMPEN, A. G., German Pat. 237,014 (1910).
13. H. S. BOOTH AND M. MERLUB-SOBOLOV, *J. Phys. Chem.*, **35**, 3319 (1931).
14. M. J. KSYCKI AND L. F. YNTEMA, *Trans. Electrochem. Soc.*, **96**, 48 (1949).
15. A. CHILESOTTI, *Z. Elektrochem.*, **12**, 146, 173, 197 (1906).
16. C. G. FINK AND C. H. ELDRIDGE, Canadian Pat. 274,429 (1927).
17. L. F. YNTEMA, *J. Am. Chem. Soc.*, **54**, 3775 (1932).
18. E. POKORNY AND K. SCHEIDER, German Pat. 582,528 (1934).
19. W. P. PRICE AND O. W. BROWN, *Trans. Electrochem. Soc.*, **70**, 423 (1936).
20. K. A. PAUL, Russian Pat. 53,756 (1938); *C.A.*, **35**, 1326 (1941); A. S. MININ, Russian Pat. 59,863 (1941); *C.A.*, **39**, 873 (1945).
21. GMELIN'S "Handbuch," *op. cit.*, p. 35.
22. H. ALTHERTUM, *Z. angew. Chem.*, **42**, 4 (1929); G. M. DYSON, *Chem. Age, London*, (Monthly Metallurgical Section) **18**, 33 (1928).
23. G. GIN, *L'Electricien*, **32**, 107 (1906).
24. *Metallborse*, **18**, 1155 (1928).

25. J. W. BECKMANN, U. S. Pat. 973,336 (1910).
26. A. KRATKEY AND W. BRUCKNER, German Pat. 263,301 (1911).
27. T. R. FORLAND, U. S. Pat. 1,305,350 (1919).
28. J. L. ANDRIEUX, *Ann. chim.*, [10] **12**, 499 (1929).
29. A. BRENNER AND S. SENDEROFF, *This Journal*, **99**, 223C (1952).
30. SCOTT'S "Standard Methods of Chemical Analysis," (N. H. Furnam, Editor) 5th ed., Vol. 1, p. 594, D. Van Nostrand Co., Inc., New York (1939).
31. *Ibid.*, p. 591.
32. C. G. GOETZEL, "Treatise on Powder Metallurgy," Vol. 1, p. 668, Interscience Publishers, Inc., New York (1949).
33. W. R. BUCKNALL AND W. WARDLAW, *J. Chem. Soc.*, **1927**, 2983.

The Electrolytic Preparation of Molybdenum from Fused Salts

II. The Preparation of Reduced Molybdenum Halides¹

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ABSTRACT

An improved method for the preparation of potassium hexachloromolybdate (III), K_2MoCl_6 , is described. Potassium molybdate is dissolved in hydrochloric acid and the solution electrolyzed in a divided cell. Hydrogen chloride gas is then added to the catholyte to precipitate K_2MoCl_6 .

A new method for preparing molybdenum dichloride, $(MoCl_2)_x$, is described. Molybdenum pentachloride is reduced with molybdenum powder to the trichloride. This is then heated to produce the molybdenum dichloride by thermal dissociation.

INTRODUCTION

The methods in the literature for preparing potassium hexachloromolybdate (III), K_2MoCl_6 , and for molybdenum dichloride, $(MoCl_2)_x$, were found to be unsatisfactory for the preparation of large quantities of material, and so new procedures were developed which are described herein.

POTASSIUM HEXACHLOROMOLYBDATE (III)

Potassium hexachloromolybdate (III), K_2MoCl_6 , was first prepared by Chilesotti (1) and later by Bucknall and coworkers (2). The latter's procedure is based on an electrolytic reduction of a solution of molybdic acid in strong hydrochloric acid, followed by addition of potassium chloride. The method yielded a pure anhydrous product, but since it involved very dilute solutions and evaporations under reduced pressure, it was inconvenient for the preparation of large amounts of the salt. Modifications were introduced which eliminated these defects and gave a very interesting insight into the chemistry of the formation of this compound.

The procedure used in this laboratory for preparation of potassium hexachloromolybdate (III), K_2MoCl_6 , is as follows. Potassium molybdate, 480 g, was dissolved in 1050 ml of water, and this solution was added to 1050 ml of 12*N* hydrochloric acid in a 3-liter beaker. (Note: If the acid is added to the molybdate solution, molybdic acid precipitates and is very difficult to redissolve.) The beaker was loosely covered with a plastic disk into which had

been drilled one large central hole, two smaller holes near the outer edge at both ends of a diameter, and a third smaller hole near the outer edge. A porous aluminum cylinder, closed on the bottom, was filled with 200 ml of 12*N* hydrochloric acid and inserted through the central hole of the cover. This cylinder served as a diaphragm between the anolyte it contained and the catholyte around it. Two sheets of platinum, used as cathodes, were held by platinum wires through corks placed in the two opposite holes in the cover, and a glass tube connected to a nitrogen tank was inserted through a cork in the third outer hole of the cover. A 1/2-in. diameter graphite rod, serving as anode, was inserted into the anolyte and the level of the anolyte was adjusted to the same height as that of the catholyte.

The solution was electrolyzed with a current of 20 amp (cathodic current density, about 7 amp/dm²) for 8 hr.

The course of the electrolysis was followed by taking samples of the catholyte, adding them to excess ferric alum solution, and titrating with potassium permanganate. When the reducing power of the catholyte became constant, the electrolysis was stopped. The catholyte was agitated during the electrolysis by a stream of nitrogen, and the anolyte received periodic additions of concentrated hydrochloric acid to replace that lost by electrolysis and as spray. The temperature of the catholyte rose during the electrolysis to 65°C, and the solution became dark red. The catholyte was removed, heated to 95°C, and saturated with hydrogen chloride gas. As the solution cooled, more hydrogen chloride gas was added and crystals of K_2MoCl_6 separated. These were filtered, washed with 1600 ml of 12*N* hydrochloric acid, 1600 ml of 1:1 12*N* HCl-alcohol mixture, and 1600 ml of methanol. The red crystals

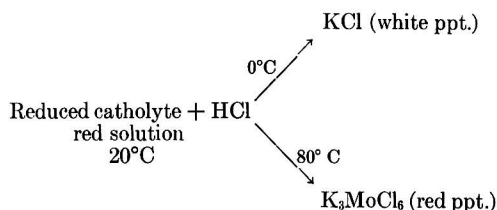
¹ Manuscript received April 7, 1953. This paper was prepared for delivery before the Philadelphia Meeting, May 4 to 8, 1952. Based on a thesis submitted by Seymour Senderoff to the Faculty of the Graduate School of the University of Maryland in partial fulfillment of the requirements for the Ph.D. degree.

were dried by heating under reduced pressure, and analyzed.

The analysis gave Mo, 22.6% and Cl, 50.2% (theoretical—Mo, 22.5% and Cl, 49.9%). A yield of 400 grams or about 70% of calculated was obtained.

Properties

During the development of this method a series of reactions were observed which demonstrate that the $[\text{MoCl}_6]^{-3}$ ion is extremely stable in acid solution and not subject to rapid reversible dissociation and formation at room temperature. If the catholyte is reduced and saturated with hydrogen chloride gas without permitting its temperature to rise, and then cooled to near 0°C , potassium chloride precipitates. If instead of cooling after saturation with hydrogen chloride, the solution is heated at this point to above 80°C , K_3MoCl_6 precipitates, i.e.,



This conclusively demonstrates that the reduced catholyte, before heating, contains potassium ions, cations containing trivalent molybdenum, and chloride ions, and little, if any, complex molybdenum anions.

On cooling, the potassium chloride crystallizes because of its insolubility in concentrated hydrochloric acid. On heating, however, the reaction $\text{Mo}^{3+} + 6\text{Cl}^- \rightarrow [\text{MoCl}_6]^{-3}$ occurs and K_3MoCl_6 precipitates. On cooling the mother liquor from this precipitation, more K_3MoCl_6 separates but no KCl, because most of the K^+ has been removed in the precipitation of the complex salt. Were $[\text{MoCl}_6]^{-3}$ in equilibrium with Mo^{3+} and Cl^- , as is the case with complexes such as $[\text{Ag}(\text{CN})_2]^-$ or $[\text{Ag}(\text{NH}_3)_2]^+$, the K_3MoCl_6 would have precipitated immediately on saturating the reduced catholyte with hydrogen chloride. Probably the major function of the evaporations used by previous investigators to prepare this salt was the formation of the complex ion by heating, rather than merely concentrating the salts.

The salt, K_3MoCl_6 , is a brick-red stable salt. It precipitates without any water of crystallization, but, if insufficient hydrogen chloride is added before precipitation, an aquo complex, possibly $\text{K}_2[\text{MoCl}_5\text{H}_2\text{O}]$ (2), may precipitate. The water cannot be removed from this compound by heating without decomposing the compound. The K_3MoCl_6

may be heated in air at 110°C without any decomposition. In the dry state it is stable to light and not hygroscopic. It may be heated in vacuo to at least 600°C for 20 hr without observable decomposition or melting. This is particularly significant when one remembers that MoCl_5 is unstable above 340°C (4) and that at 650°C it is completely decomposed to MoCl_2 and Mo metal. This further demonstrates that the K_3MoCl_6 is not a double salt which may be represented by the formula $3\text{KCl} \cdot \text{MoCl}_6$, but that it is a salt of the highly stable complex anion, $[\text{MoCl}_6]^{-3}$. When very hot its color darkens slightly, but it lightens again on cooling. It is rapidly decomposed at 600°C , however, if in contact with air or moisture. The standard procedure finally adopted for removing the last traces of adsorbed water from the compound before using it in a molten electrolyte was to heat it in vacuo at 250°C for two to three hours and then to store it in a desiccator.

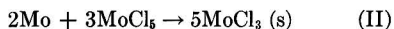
MOLYBDENUM DICHLORIDE

Molybdenum dichloride, $(\text{MoCl}_2)_x$, where the x has been shown by various investigators to be 3 or 6 (3), was first prepared by Blomstrand (5) by the thermal decomposition of molybdenum trichloride which he obtained by the hydrogen reduction of molybdenum pentachloride. The difficulties in this procedure were noted by Liechti and Kempe (6) and others who suggested various precautions and modifications. The hydrogen reduction of molybdenum pentachloride is particularly difficult and attempts here to accomplish this resulted in impure products with poor yields. Lindner and co-workers (7) describe what is alleged to be a superior method in which molybdenum powder is chlorinated by reaction with phosgene at 610°C .

This reaction was attempted both as directed and with a number of modifications but was unsatisfactory for the preparation of appreciable amounts of pure material. After consulting the thermodynamic data on the molybdenum halides collected by Quill (4), a method was devised which proved quite successful. According to Quill, the reaction:

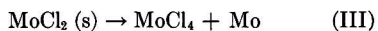


at 340°C at 1 atm total pressure reaches equilibrium with MoCl_4 at a partial pressure of 0.7 atm and MoCl_5 at a partial pressure of 0.3 atm. Further, at 330°C the reaction:



goes practically to completion with the MoCl_5 at 1 atm pressure.

Lastly, the reaction:



does not begin until 530°C is reached and at 600°C the equilibrium pressure of MoCl_4 is only 1 atm.

By heating molybdenum powder with an excess of molybdenum pentachloride in a sealed tube at 350°C, reaction (II) may be accomplished while reaction (I) is suppressed. When the molybdenum powder is all used up, the excess molybdenum pentachloride may be removed and the molybdenum trichloride heated at some temperature below 600°C to form MoCl_2 , without reaction (III) occurring to a large extent.

An attempt to reduce molybdenum pentachloride to molybdenum dichloride by reduction with molybdenum at high temperature in one step did not give a pure product. This was probably due to the molybdenum powder being coated over with MoCl_2 which prevented further reaction of the molybdenum metal. The two-step procedure, however, was quite successful, although it was necessary to perform the final step at 650°C, resulting in slight contamination of the MoCl_2 by molybdenum powder. Below this temperature the disproportionation of the trichloride proceeded somewhat slowly.

The following was the procedure used: 7.6 g of Mo powder was mixed with 36.6 g of MoCl_5 (4.6 g MoCl_5 excess) and charged into a Pyrex gauge glass tube 1.5 cm diameter and 30 cm long. The tube was evacuated, sealed, and placed in a steel pipe closed at both ends. The entire assembly was allowed to stand in a furnace at 350°C for 48 hours. The tube was tilted during this heating so that most of the product would be at one end. After cooling, the other end was opened and a "condensing angle" was sealed onto the open end. The "condensing angle" was a 12-in. length of the same gauge glass, bent in the middle to an angle of about 120°. The tube was again evacuated and sealed and set in the furnace with the 6-in. length beyond the bend protruding out of the furnace. The temperature was brought up slowly and the excess molybdenum pentachloride collected in the cold end.

When most of the pentachloride had distilled over (at about 300°C) the temperature was raised to 650°C and held there for 24 hours to effect the disproportionation and further purification. Although the hot end softened and flattened considerably, the glass did not collapse or break, and the bright yellow dichloride, $(\text{MoCl}_2)_x$, remained in the hot portion of the tube. Fourteen grams of relatively pure material were obtained for a yield of 65% based on the molybdenum powder used. Analysis showed it to contain 58.3% Mo and 43.7% Cl. Theoretical composition for MoCl_2 is 57.4% Mo and 42.6% Cl. A slight excess of molybdenum may be present in the product and is probably due to free molybdenum metal formed by decomposition of the MoCl_2 . This could have been avoided by

heating for a much longer time at about 600°C instead of 650°C, but since a small amount of free molybdenum metal would not be harmful in an electrolysis test, it was not considered necessary to do this.

Properties

The material must be used in the condition in which it is produced. Attempts to remove the free metal with dilute nitric acid resulted in the formation of a hydrate, $x\text{MoCl}_2 \cdot y\text{H}_2\text{O}$ from which the water could not be removed without decomposing the salt. The $(\text{MoCl}_2)_x$ is slightly soluble in alcohol, but an alcoholate is formed, and attempts to drive off the alcohol also resulted in decomposition.

A sample of MoCl_2 was mixed with a portion of a eutectic mixture of lithium chloride and potassium chloride which had been previously fused and ground. The mixture had the following composition in weight per cent: MoCl_2 , 12.3%; LiCl , 40.3%; KCl , 47.4%; and was a 4.4 mole per cent MoCl_2 solution. On heating this mixture in an evacuated sealed tube to 600°C, the charge became completely fluid and, on freezing, it was observed to have become a uniform bright red. A complex halide had evidently formed.

SUMMARY

A simplified method for the preparation of potassium hexachloromolybdate (III) and a new method for the preparation of molybdenum dichloride has been described.

ACKNOWLEDGMENTS

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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.

REFERENCES

1. A. CHILESOTTI, *Atti reale accad. Lincei*, [5] **12** II, 67 (1903); *Gazz. chim. ital.*, **33** II, 354 (1903).
2. W. R. BUCKNALL, S. R. CARTER, AND W. WARDLAW, *J. Chem. Soc.*, **1927**, 513.
3. N. V. SIDGWICK, "Chemical Elements and Their Compounds," Vol. II, p. 1061, Oxford (1950).
4. L. L. QUILL, "The Chemistry and Metallurgy of Miscellaneous Materials," paper 8, p. 276 ff, McGraw Hill Book Company, New York (1950).
5. C. W. BLOMSTRAND, *J. prakt. Chem.*, **77**, 97 (1859).
6. L. P. LIECHT AND B. KEMPE, *Liebigs Ann. Chem.*, **169**, 354 (1873).
7. K. LINDNER, E. HALLER, AND H. HELWIG, *Z. anorg. v. allgem. Chem.*, **130**, 209 (1923).

The Electrolytic Preparation of Molybdenum from Fused Salts

III. Studies of Electrode Potentials¹

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ABSTRACT

Polarization and equilibrium potential studies in molten halide solutions are described. A new reference half-cell, i.e., Ag, AgCl, was used. It was found that molybdenum is rather noble (between copper and silver) in the emf series in this system, but that oxides are preferentially deposited if oxycompounds are present. Evidence for ionic association and complex formation in molten halides at 600°C is discussed.

INTRODUCTION

In order to obtain some insight into the electrochemistry of the fused salt systems (1), measurements of cathode potentials were made on some of them, and the static potentials of a number of metal-metal salt systems in the same halide were measured.

EXPERIMENTAL

Reference Electrode

To measure electrode potentials, a reference electrode, which is constant, reproducible, and reversible, is required. Yntema and his students (2) described a reference electrode for use in molten salts between 100° and 200°C which consisted of an aluminum rod in a ternary mixture of AlCl_3 - NaCl - KCl . This was not suitable in the range of interest, i.e., 600°-900°C, mainly because of the volatility of AlCl_3 . An ideal molten electrolyte for this range of temperature is silver chloride, which melts at 455°C, boils at 1550°C, and is easily prepared with high purity. No other stable valence states of silver exist to provide ambiguity of composition, and, in the absence of light, the chloride undergoes no visible decomposition when heated for long periods of time. Oxide contamination, which is a serious problem in most molten systems, does not occur in silver chloride because silver oxide decomposes at about 300°C, and, if formed during filling of a cell, would be destroyed when the cell is brought up to temperature.

That the Ag, AgCl(l) cell is reversible and

practically nonpolarizable was shown by Aten, den Hertog, and Westenberg (3) who reported that silver dissolved anodically and deposited cathodically from molten silver chloride at 475°C, and that the polarization voltage was only 0.5 mv at a current density of 1 amp/dm². This was confirmed in tests described below.

In the design of a cell, one serious disadvantage of the Ag, AgCl(l) electrode had to be considered. Since silver is quite noble, its presence in an electrolyte in which the potential of a base-metal electrode was being measured would cause a serious error. On the other hand, the presence of a foreign electrolyte, containing a base-metal ion, in the molten AgCl would have a minor effect on the potential of the reference electrode as its effect would be dependent only on the slight decrease in the concentration of AgCl in the cell. The cell was designed, therefore, to minimize diffusion and convection, and to cause the direction of flow of molten liquid, if any, to be toward the molten silver chloride rather than toward the electrolyte, and to have a large amount of silver chloride present so that small impurities of base-metal electrolyte entering it would cause negligible changes in its potential.

The reference electrode cell is shown in Fig. 1. It is made of fused silica and consists of two tubes (A, D) of 9-mm bore connected by a heavy walled capillary (B) of 1.5-mm bore. Another capillary tube (C) is fitted as shown, onto one of the larger tubes. The end of this capillary is bevelled to an angle of about 60°, and is the equivalent of the Luggin capillary used as a probe for measuring potentials in aqueous solution. At the point where capillary (B) enters tube (D), there is a constriction which is tightly packed with asbestos. Molten silver chloride is poured into tube (A) and suction is

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applied to tube (D) [while stopping up the opening of (C)] until a tiny bead of silver chloride is drawn through the asbestos plug. A clean $\frac{1}{8}$ -in. rod of silver is inserted into the molten chloride to within one inch of the bottom of tube (A) and held in that position by a silver disk fitting over the top of the tube. A silver wire is silver-soldered to the top of the silver rod. The entire cell was anchored at the top in an aluminum fixture in which it was rigidly held by spring-loaded set screws. This fixture also held the cathode in contact with the end of capillary (C). A strip of molybdenum sheet serving as anode was bent to a half-cylinder and placed over the outside of tube (A). It was held by a clamp, to

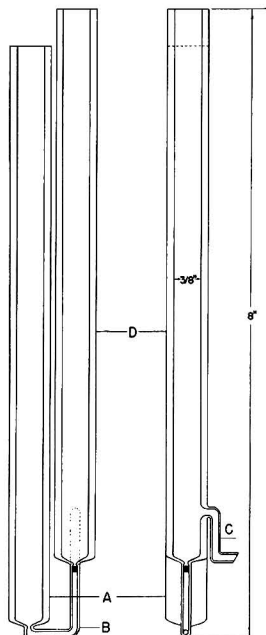


Fig. 1. Detail of reference electrode half-cell

which a heavy plastic-insulated wire was attached. This wire was wound as a helix and served as an anode lead.

The entire assembly was suspended by the cathode from the electrode connector, (J),² the anode lead wire and the wire from the silver reference electrode were drawn through holes in the rubber stopper in the bung, (E),² and the system closed. After the procedure described earlier (1) for establishment of an inert atmosphere was followed, the electrolyte in the crucible was melted and the electrode assembly lowered into the crucible. The electrolyte then entered tube (D), through capillary (C), and formed a liquid junction with the silver chloride at the

² See Fig. 2, Reference (1).

asbestos plug. The levels of the solutions were adjusted so that the level of the electrolyte in (D) was slightly higher than that of the silver chloride in (A). The asbestos plug was tight enough to prevent flow of solution through it except under applied vacuum, as when filling the cell, but the levels were adjusted in this manner so that if flow did occur it would be toward the silver chloride rather than toward the electrolyte. Current was passed through the cell (cathode area = 0.1 dm^2) as for plating. The current was set and held at each value for about one minute while the potential between the cathode and reference electrode was measured using a potentiometer and high-sensitivity galvanometer. Zero current values were taken before and after each run, and they usually agreed fairly well.

When measuring equilibrium potentials, the anode was not used, and the cathode hung above capillary (C) rather than in contact with it. The same procedure for maintaining an inert atmosphere was followed. Potentials were read at half-hour intervals, and when the potential remained constant within 1 mv for 3 hr, that value was taken as the equilibrium potential.

The reproducibility and reversibility of the reference electrode was confirmed in the following manner. Silver chloride was poured into both sides of the quartz cell, capillary (C) was sealed, and silver rods inserted in both legs of the cell. The entire unit was immersed in molten potassium chloride-lithium chloride eutectic mixture which was maintained at 600°C . The immersed area of the electrodes was 0.025 dm^2 . The initial potential difference of 3.0 mv fell in 1 hr to 0.4 mv, at which point the potential difference became constant. This potential difference is probably due to some small asymmetry in the two electrodes, contact potentials, etc. The cell was then polarized by passing current through it for 5-min periods. The circuit was then opened and the potential read.

After passing 1 ma through the cell, the 0.4-mv potential was re-established in less than 30 sec after opening the circuit. With 2.5 ma, 1 min was required, and with 5 ma (equivalent to 0.2 amp/dm^2) the cell was permanently polarized, its potential being 1 mv 30 min after opening the circuit. Since full-scale deflection of the galvanometer used during the measurements corresponded to a current of $0.6 \mu\text{amp}$, the possibility of polarizing the cell while balancing the potentiometer was negligible. That the cell is reversible is demonstrated by the fact that one of the silver rods was anode, and the other cathode during polarization, and, up to 2.5 ma, the cell reverted rapidly to normal on stopping the polarizing current. The reversibility of the molybdenum electrode in the K_2MoCl_6 -alkali halide melt

was demonstrated by the electrodeposition and anodic solution of the metal at low current densities and low polarization.

Cathode Potential Measurements

A solution of K_2MoCl_6 in LiCl-KCl eutectic mixture of a standardized composition (4.1 mole % K_2MoCl_6) was prepared and purified by thermal and electrolytic means (1). The reference electrode cell, with molybdenum anode and cathode, was inserted into the melt and allowed to stand until the static potential became fairly constant. Readings were then taken at 20 points in the current density

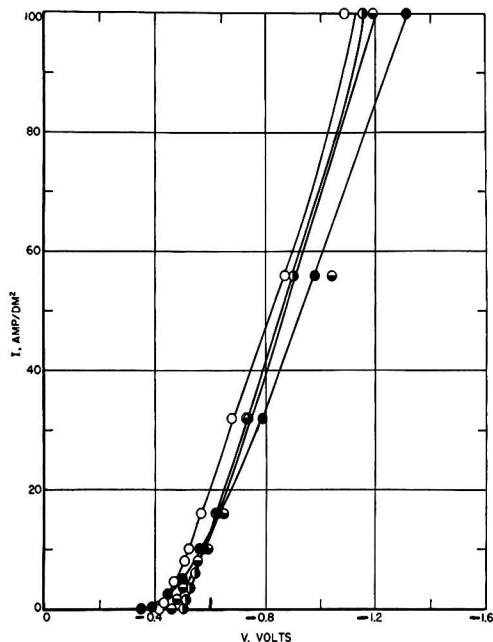


Fig. 2. Cathode potential curves for solution of K_2MoCl_6 in LiCl-KCl (0-100 amp/dm²) measured against silver-silver chloride electrode. ●—600°C; ○—700°C; ◐—800°C; ◑—900°C.

range from 0-100 amp/dm². Fewer points were taken in the upper than in the lower part of the range because, at high current density, the nature of the cathode surface changes very rapidly and makes the values obtained less reliable. Current density-potential curves were determined at 600°, 700°, 800°, and 900°C. Duplicate runs were made for each temperature, no two runs at the same temperature being done consecutively. In addition, the runs at different temperatures were done in random sequence, so that the effects of time or systematic variation in the solution would not be confused with a temperature effect. The average value of the two

determinations of cathode potential for each current density and temperature was used in plotting the isothermal cathode potential curves. Fig. 2 shows these over the entire range of 0-100 amp/dm². Fig. 3 shows the 0-10 amp/dm² range on an expanded scale. On the whole, the values are reproducible to about ± 10 mv.

The static or equilibrium potentials range from 0.349 volt to 0.501 volt between 600° and 900°C with a temperature coefficient of $+5 \times 10^{-4}$ volts/deg. The silver reference electrode is the positive (noble) pole.

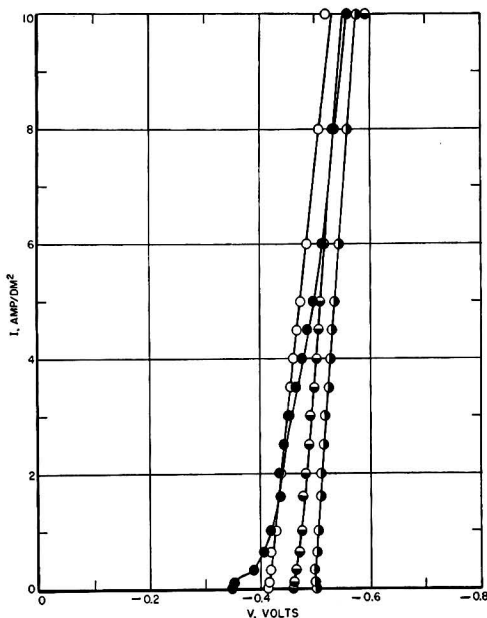


Fig. 3. Low current density portion of curves of Fig. 2 (0-10 amp/dm²) measured against silver-silver chloride reference electrode. ●—600°C; ○—700°C; ◐—800°C; ◑—900°C.

When the same solutions were contaminated by exposure to air, the current density-potential curves shown in Fig. 4A were obtained. The equilibrium potentials ranged from 0.071-0.034 volt between 600° and 800°C with a temperature coefficient of -2×10^{-4} voltage. Heating to 900°C and/or electrolysis restored the solution to its original condition.

These results show conclusively that air contamination ennobles the potential of a molybdenum electrode in the solution by about 0.3-0.4 volt.

In order to study the cathode potentials in a system containing potassium molybdate, a solution consisting of 45.5 grams of LiCl, 54.5 grams of KCl, and 18.5 grams of K_2MoO_4 (4.1 mole % K_2MoO_4) was prepared and current density-voltage curves run

under inert atmosphere, with usual precautions for drying the salts. The initial values of equilibrium potentials varied from 0.75–1.25 volts, with no reproducibility between the zero current potential at the beginning and end of the run. The silver electrode was still the positive pole. In any event, this unstable potential showed the electrode to be much less noble than in the trivalent molybdenum solution. The solution was then electrolyzed, after which stable equilibrium potentials were obtained. The values were 0.029 volt at 600°C and 0.052 volt at 900°C, or about the same as in a melt con-

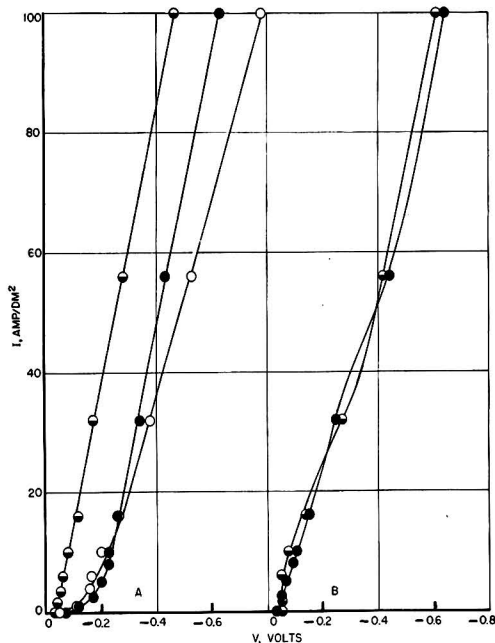


FIG. 4A. Cathode potential curves for air-contaminated K_2MoCl_6 solution. ●—600°C; ○—700°C; ●—800°C.

FIG. 4B. Cathode potential curves of solution of K_2MoO_4 in $LiCl-KCl$. ●—600°C; ●—900°C. (Both measured against silver-silver chloride reference electrode.)

taminated with air. The temperature coefficient was $+8 \times 10^{-5}$ volts/deg in this range. These values remained in this range despite heating, electrolysis, or other treatment. The cathode potential curves for this solution are shown in Fig. 4B. The potential values obtained in this solution are not as reproducible as in the uncontaminated trivalent molybdenum solution.

Equilibrium Potentials of Other Metals in Molten Lithium Chloride-Potassium Chloride

To obtain some information about the emf series in molten halide melts at 600°C, and particularly

the position of molybdenum in this series, equilibrium potential data were obtained for zinc, ferrous iron, cuprous copper, and silver, each in 4.1 mole per cent solutions of their chlorides in the $KCl-LiCl$ eutectic mixture in the absence of air. The anhydrous salts were prepared in the following manner. Commercial anhydrous C.P. zinc chloride and ferrous chloride, $FeCl_2 \cdot 4H_2O$, were dried in a current of dry hydrogen chloride at 400°C for two hours. Cuprous chloride was washed free of cupric compounds with water and dried at 450°C in a stream of dry hydrogen chloride. Since zinc was molten at the temperature of the experiments, the zinc electrode consisted of a pool of zinc in the bottom of the vessel. Electrical contact was established with a tungsten rod sealed in glass. Measurements were made as described earlier.

Table I gives the equilibrium potentials found for these systems.

Also included in the table is the equilibrium potential found for molybdenum under conditions similar to those used for the other metals. This

TABLE I. Potential, E , of M electrode in 4.1 mole % M chloride dissolved in $KCl-LiCl$ (eutectic composition) against the $Ag, AgCl$ (pure) reference electrode at 600°C

M	E (volt)
Zinc	-1.277
Iron (divalent)	-1.033
Copper (monovalent)	-0.626
Molybdenum (trivalent)	-0.349
Silver	-0.312

table represents the emf series for these elements at 600°C at a concentration of 4.1 mole per cent in $LiCl-KCl$ eutectic mixture as solvent.

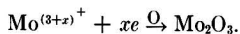
DISCUSSION OF RESULTS

Current Density-Potential Curves

One of the most important facts demonstrated previously (1) was the inability to obtain a pure molybdenum deposit from solutions containing oxygenated salts or even from solutions of non-oxygenated salts which have been slightly contaminated with air or moisture. Whenever oxygenated compounds were present, the current efficiency for molybdenum deposition was reduced and molybdenum oxides were formed in the deposit, as shown by x-ray diffraction. A consideration of the potential measurements with the pure trivalent molybdenum, air-contaminated trivalent molybdenum, and molybdate solutions clearly demonstrates the cause of this behavior. In addition, it gives some insight into the electrochemistry of these systems. The equilibrium potential of a molybdenum electrode in

an air-contaminated trivalent molybdenum solution is about 0.4 volt lower (more noble) than in a pure trivalent molybdenum solution. A difference of this magnitude indicates that the electrode reactions occurring in the two systems must be entirely different. Not only is this shown by the magnitude of the difference in potential but by the fact that the temperature coefficient of the potentials differs in magnitude and sign.

Consider the manner in which oxides deposit on the cathode from contaminated solutions. Since the trivalent molybdenum salt is easily oxidized by air at these temperatures, one of the effects of the contamination must be to produce oxygenated compounds of molybdenum in which the molybdenum has a valence higher than three. The potential measurements showed that the reduction of these intermediate valence molybdenum compounds to the trivalent oxide proceeds at a more noble potential than does the reduction of trivalent molybdenum to molybdenum metal. That is, the higher, more negative potential is characteristic of the electrode reaction, $\text{Mo}^{3+} + 3e \rightarrow \text{Mo}$; and the more noble potential is characteristic of a reaction which may be written:



It is apparent that oxygen must be absent from the system in order to obtain pure molybdenum. Therefore, from a contaminated bath at low current density one would expect no molybdenum deposit at all, only oxides, and at high current density, when the cathode has become sufficiently polarized to reach the deposition potential for molybdenum metal, both processes should occur. At 600°C, the cathode in a contaminated bath does not reach the potential at which molybdenum can codeposit with the oxide until a current density of 30–40 amp/dm² is attained, and, at 900°C, it barely reaches it at 100 amp/dm².

In the initial potential measurements on the potassium molybdate solution no equilibrium potential at all was obtained with a molybdenum electrode. The unstable potential observed was more than 0.5 volt less noble than that for reducing trivalent molybdenum to metal. This suggests that a molybdate solution is actually not in equilibrium with a molybdenum electrode, that is, the reaction $\text{MoO}_4^- + 6e \rightarrow \text{Mo} + 4\text{O}^-$ either does not occur or never reaches equilibrium. The very high initial potential observed is of no consequence with regard to electrode reactions since, after electrolysis for a short while, it changes to a stable potential of about the same value as that obtained with an air-contaminated trivalent solution.

The molybdate solutions and the contaminated

trivalent molybdenum solutions turn blue during electrolysis, which confirms the presence of molybdenum compounds with a valence of 4 or 5, and it is these, rather than the hexavalent molybdenum, which are in equilibrium with the electrode. Breaks in the curve occur in the vicinity of 0.3 volt at about 30 amp/dm², and these probably represent the beginning of the reduction of trivalent molybdenum to metal. Since the potentials measured in the electrolyzed molybdate solution and in the air-contaminated trivalent molybdenum solution are about the same, the same reaction may be occurring. This is confirmed by x-ray diffraction which identified Mo_2O_3 in the deposit from the molybdate and in the deposit from the trivalent molybdenum solution.

The potentials of a molybdenum electrode in dilute solutions of K_2MoO_4 and K_3MoCl_6 in AlCl_3 - NaCl - KCl mixture at about 200°C were reported (4) to be about the same. They are the same because those experiments were all run with the solutions exposed to air and all of the solutions were purified by electrolysis. Therefore, this compared electrolyzed molybdate solution with an air-contaminated trivalent molybdenum solution, solutions which were shown here to give very similar cathode potential curves. Neither of these solutions, however, gives pure molybdenum deposits, so the deposition potentials which were reported cannot be ascribed to any definite electrode reaction.

Relation Between Cathode Potential Curves and the Nature of the Deposit

The cathode potential curves for deposition of molybdenum at the various temperatures were examined to determine whether they correlated with the physical form of the deposit. The molybdenum deposits obtained from the fused baths were powdery or dendritic, with the exception of the deposits obtained from the 600°C bath below a current density of 3 amp/dm²; it is of interest to inquire whether this is related to the observed cathode potential curves. In deposition from aqueous solution, the production of fine-grained smooth deposits is often associated with a higher polarization than that attending the deposition of the coarsely crystalline or spongy deposits from solutions of simple salts. The smoother deposits may not necessarily be caused by the higher polarization, but apparently the same conditions that yield the smoother deposits also cause the higher polarization.

The cathode potential curve for molybdenum deposition at 600°C (Fig. 3) has a slight change in curvature at about 3.5 amp/dm², which corresponds approximately to the change of deposit from the coherent to the powdery form. However, this break

is so slight that it is barely beyond the precision of measurement, and may be considered as the effect of the change in surface area of the deposit on the cathode potential, rather than a change in the nature of the electrode reaction. The slope of the curve for 600°C is somewhat flatter than the curves obtained for the higher temperatures over the whole range of current density from 0–100 amp/dm² thus indicating a higher polarization. It is only from the 600°C bath that smooth coherent deposits are obtained at low current density. They became powdery above 3 amp/dm², but this is probably the usual "burning" which is observed with all plating solution at high current densities.

The main difference between the current density-potential curve for deposition at 600°C and at the higher temperatures appears to be the presence of a break in the 600°C curve at about 0.25 amp/dm². This break indicates that a change in the electrode reaction occurs at this point and that it may be the source of the polarization observed in this bath. It is suggested that this represents the current density at which the slow dissociation of the (MoCl₆)³⁻ becomes the rate-controlling step of the reaction. Below this point, the deposition of molybdenum may occur by discharge of the Mo³⁺ ion, but above this point the concentration of the simple molybdenum ion in the cathode film is essentially zero, and deposition proceeds by discharge of the complex anion.

At 900°C, the rate of dissociation of the complex anion is sufficiently great to permit deposition to occur from the simple cation over the full range investigated and so the deposits are powdery at all current densities. When operating at 600°C, as the current density is decreased from high values to 3 amp/dm², the deposit changes from powdery to coherent. On lowering the current density still further, the deposit changes back to powdery at a current density corresponding to the observed break in the curve at 0.25 amp/dm². This hypothesis is in accord with observations on the thermal stability of the salt K₃MoCl₆, which is quite stable at 600°C (in vacuo), but at 900°C produces a slight sublimate. This is indicative of a slight dissociation of the complex into MoCl₃, which, in turn, is not stable at that temperature. Other evidence for the slow dissociation of (MoCl₆)³⁻ are its reactions in water solution (5) and its magnetic susceptibility which indicates that it exists as the very stable octahedral structure with a *d²sp³* bond type. Further evidence for the view that the molybdenum is present as a stable complex in the fused salt bath comes from observations of the potentials of other metals in fused electrolytes, as described in the following section.

Static Potentials of Molybdenum and Other Metals in Fused Electrolytes

The equilibrium potentials of molybdenum and four other metals in a fused KCl-LiCl melt containing each metal in a concentration of 4.1 mole per cent are given in Table I. The point of most interest is that molybdenum is relatively noble, being very close to silver in potential. Thus, it is not surprising that iron and copper displace molybdenum from a molten plating bath. The noble position of molybdenum in this series also suggests that these baths might be very well suited for electrowinning. This prediction requires caution with respect to particular metallic impurities, since the various metals might not take the same positions in this series as they do in the aqueous system. It appears that nickel may be more noble than copper in this fused halide system.

Metal salts appear to form complexes in fused baths just as they do in aqueous solutions. A comparison of the emf series in three types of fused baths and in water solution is shown in Table II.

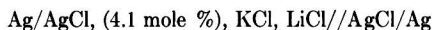
All the potentials have been calculated with reference to a silver electrode immersed in a solution of a silver salt at the same concentration as the other metals in the series. For example, column 4 is obtained from Table I by taking the potential of silver in a 4.1 mole per cent solution (potential 0.312 volt) as the reference electrode instead of silver in pure molten silver chloride. Column 1 is calculated from the data of Verdieck and Yntema (6) for one mole per cent solutions of salts of the indicated element in AlCl₃-KCl-NaCl solvent at 200°C. Column 2 was calculated from the measured values of the potentials of Daniell cells consisting of: M/pure molten chloride of M//pure molten chloride of N/N, where M and N are metals, at 600°C given by Lorenz [(7) Vol. III]. (The value for tin is at 350° but the author states that the temperature coefficient of the potential is very small in this case.) Column 3 is the familiar emf series for electrolytes of unit activity in aqueous systems, taking the silver instead of the hydrogen electrode as zero.

The potentials in columns 1 and 2, for the aluminum chloride type solvent and the pure fused halides, respectively, are quite close. The potentials in the fused KCl-LiCl bath in column 4 are between those in an aqueous media in column 3 and those in columns 1 and 2. A significant difference between the pure molten salt system, column 2, and the aqueous system, column 3, is the absence of solvation in the former, since there is no solvent; and the existence of extensive solvation of the ions by water in the latter. If this is the cause of the differences in the two series, then the salts dissolved in the aluminum chloride mixture (column 1) are in a

condition very similar to the pure molten state, while the salts dissolved in the KCl-LiCl mixture (column 4) are to some extent solvated.

The calculation of the activity of metal ions in fused salt baths of the type in column 4 lends support to the view that salts therein are solvated. The voltage, E , of the following cell was calculated from data of Lorenz (7) and from the data given here: Zn/ZnCl₂ (4.1 mole %) KCl, LiCl//ZnCl₂ (pure)/Zn; $E = 0.850$ volt at 600°C. Substituting this value of emf in Nernst's equation gives the activity³ of zinc in the 4.1 mole per cent solution as 10⁻⁸ mole per cent. This shows that zinc is rather tightly complexed in the alkali halide melt. Lorenz has demonstrated the existence of a complex chloroplumbate anion in the molten mixture of KCl-NaCl-PbCl₂ and in KCl-PbCl₂ by transference measurements [(7) Vol. II]. However, all metal salts apparently do not form complexes in molten alkali halides.

A similar calculation for silver dissolved in a KCl-LiCl melt shows that silver, in contrast to zinc and lead, does not form complexes to any extent. From the data of Table I, the voltage of the following cell:



is 0.312 volt. Calculation of the activity of silver in the alkali halide melt yields 1.6 mole per cent as compared to the actual concentration of 4.1 mole per cent, thus indicating very slight complexing. A calculation on a similar silver chloride concentration cell was made with data taken from Suchy (8) who, however, did not give complete data on the mole per cent silver in his alkali halide melt. The results of this calculation confirmed the above, which shows that silver chloride does not appreciably form complexes in the alkali halide melt. In all of these calculations, liquid junction potentials have been neglected.

The comparison between the potentials in the aluminum chloride-alkali halide melt and the pure metallic halide melts indicated that complexing of metal compounds did not occur in the aluminum chloride melt. The explanation of the difference between the aluminum chloride type melt (column 1, Table II) and the alkali halide melts (column 4, Table II) is that all of the potassium chloride and sodium chloride in the former melt has been complexed by the aluminum chloride which is present in excess to form stable ions of the form, (AlCl₄)⁻, so that no alkali halide remained for the complexing of the other metals. From these results it seems that

solvents for molten salts may be compared as to their relative tendency to accept or donate anions just as solvents in acid-base phenomena are compared as to their tendency to accept or donate protons.

Studies of complex formation in molten salts may be of considerable interest in problems of electrodeposition of metals from these systems, since it is known that in aqueous systems many metals are better deposited from complex ions than from simple ions.

SUMMARY AND CONCLUSIONS

Potential and polarization studies have shown that the inability to obtain pure molybdenum deposits from systems containing oxygenated salts stems from the fact that the deposition of oxides occurs at a potential of about 0.3 or 0.4 volt more noble than the reduction to metal. As a result, even slight contamination of the electrolyte by air, moisture, or oxycompound results in gross con-

TABLE II. EMF series in various media
 E (volt)

Type of electrolyte	1. Fused AlCl ₃ -KCl-NaCl	2. Fused pure salt	3. Aqueous	4. Fused KCl-LiCl
Element				
Zinc.....	0.42	0.43	1.6	0.97
Lead (ous).....	0.30	0.32	0.92	—
Iron (ous).....	0.19	—	1.2	0.72
Tin (ous).....	0.17	0.07	0.93	—
Copper (ores).....	0.04	—	0.28	0.31
Molybdenum.....	—	—	—	0.04
Silver.....	0	0	0	0

tamination of the deposit with oxides, even when operating at high current densities.

Polarization studies have shown that the cathode polarization is small at the higher temperatures, but somewhat greater at 600°C. There is also some evidence that the reaction mechanism differs at 600°C from the mechanism at higher temperatures. It is believed that the production of coherent deposits results from the higher polarization involved in plating from a stable complex anion of molybdenum and from the fact that the operating temperature is well below the recrystallization temperature of molybdenum.

The relative position of zinc, iron, copper, molybdenum, and silver in the emf series in molten lithium chloride-potassium chloride eutectic mixture as solvent at 600°C has been established. Molybdenum has been shown to be more noble than all but silver. The values for the potentials obtained indicate that these metals tend to form complexes in this solvent and are present mainly as the chloro-metal anion.

³ The standard state of unit activity is taken to be that of the metal ion in the pure salt.

The use of potential measurements such as these in determining solvation or complex-formation in molten electrolyte solvents has been explored.

A new reference electrode for measuring potentials in molten salts has been described. It consists of silver in pure molten silver chloride contained in a suitable cell to reduce contamination of the electrolytes due to diffusion and convection. The reference electrode has been shown to be stable, constant, and reversible. It is easy to prepare and may be used over a wide range of temperature.

ACKNOWLEDGMENTS

The authors express their sincere appreciation to Dr. W. Blum, National Bureau of Standards, and to Dr. W. J. Svirbely, Professor of Chemistry, University of Maryland, for their advice and guidance during the course of this investigation and to the

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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.

REFERENCES

1. S. SENDEROFF AND A. BRENNER, *This Journal*, **101**, 16 (1954).
2. R. G. VERDIECK AND L. F. YNTEMA, *J. Phys. Chem.*, **46**, 344 (1942).
3. A. H. W. ATEN, H. J. DEN HERTOG, AND L. WESTENBERG, *Trans. Electrochem. Soc.*, **47**, 265 (1925).
4. E. E. MARSHALL AND L. F. YNTEMA, *J. Phys. Chem.*, **46**, 353 (1942).
5. S. SENDEROFF AND A. BRENNER, *This Journal*, **101**, 28 (1954).
6. R. G. VERDIECK AND L. F. YNTEMA, *J. Phys. Chem.*, **48**, 268 (1944).
7. R. LORENZ, "Die Electrolyse Geschmolzener Salze," Vols. 1 and 2 (1905) and Vol. 3 (1906), W. Knapp, Halle A. S.
8. R. SUCHY, *Z. anorg. Chem.*, **27**, 165, 193 (1901).

The Acid Dissociation of the Aquaoscandium Ions

II. Effect of Temperature and of Ionic Strength¹

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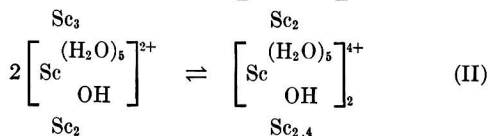
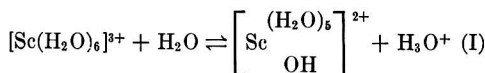
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ABSTRACT

The first dissociation constant of hexaquaoscandium ion and the dimerization constant for the hydroxylpentaquaoscandium ion have been determined over the temperature range 10°–40°C in aqueous solutions, whose ionic strengths were adjusted with sodium perchlorate. From these data, approximate values of ΔH and ΔS have been calculated. The effect of electrolyte concentration on the above equilibrium constants is also reported.

INTRODUCTION

In an earlier publication (1), it was shown that the acidity of the aquaoscandium ion in perchlorate systems may be explained by assuming the following equilibria to be of major importance:

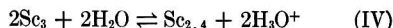


It was found convenient to define the hydroxyl number:

$$n \equiv (3 - a) + \frac{C_{\text{NaOH}} - C_{\text{HClO}_4}}{C} \quad (\text{III})$$

where a is the ratio of perchlorates to scandium atoms in the solid scandium perchlorate hydrate employed to prepare the buffer solutions studied; C , C_{HClO_4} , and C_{NaOH} are stoichiometric molar concentrations of total scandium salt, perchloric acid, and sodium hydroxide, respectively; and n represents the stoichiometric number of hydroxyl groups per scandium atom in the systems studied.

Representing the equilibrium constants for equations (I) and (II) by K_1 and K_d , respectively, and defining the constant for the over-all process:



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as K_0 , it follows that:

$$K_0 = C_{\text{H}}^2 C_{2,4} / C_3^2 = K_1^2 K_d \quad (\text{V})$$

where C_{H} , C_3 , C_2 , $C_{2,4}$ are the equilibrium concentrations of H_3O^+ , Sc_3 , Sc_2 , and $\text{Sc}_{2,4}$, respectively.

On substituting data obtained by study of buffer systems at 25°C and an ionic strength of 1.00₀, principally NaClO_4 , in the equation:

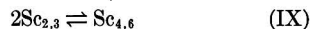
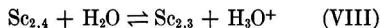
$$\frac{C_{\text{H}}(Cn + C_{\text{H}})}{C(1 - n) - C_{\text{H}}} = K_1 + \frac{2[C(1 - n) - C_{\text{H}}]}{C_{\text{H}}} K_0 \quad (\text{VI})$$

the constants given in Table IV for 25°C and $\mu = 1.00_0$ were obtained. When these constants are, in turn, substituted in the equation:

$$\begin{aligned} C_{\text{H}}^3 + C_{\text{H}}^2(Cn + K_1 - 2K_0) \\ + C_{\text{H}}[C(1 - n)(4K_0 - K_1)] \\ - 2K_0[C(1 - n)]^2 = 0 \quad (\text{VII}) \end{aligned}$$

values of C_{H} are obtained which may be compared with experimental values. At $n < 0.5$, agreement between experimental and calculated values of $-\log C_{\text{H}}$ was found to be excellent.

Since at higher values of n the agreement became progressively poorer, it was suggested that further polymerization by steps such as:



becomes increasingly important at higher values of n . Similar equilibria are proposed by Pedersen (2), Graner and Sillén (3), and Ahrlund (4) in explaining the acidity of $\text{Cu}(\text{NO}_3)_2$, $\text{Bi}(\text{ClO}_4)_3$ and $\text{UO}_2(\text{ClO}_4)_2$ systems, respectively.

It is the purpose of the paper which follows to present experimental data obtained under other experimental conditions, to discuss the effect of ionic strength and of temperature on the equilibria, and

to develop the thermodynamic constants for the system.

Experimental Method

Details of the experimental method, purification of reagents, and methods of calculation have been described previously (1). The data which follow are comparable in every respect with those presented for 25°C and $\mu = 1.00_0$.

EXPERIMENTAL DATA

The experimental data obtained are summarized in Tables I through III. Values of $-\log C_H$ as a function of n for scandium buffers at $C = 1.00 \times 10^{-2}M$, $\mu = 1.00_0$, and $t = 10.0$ and 40°C are presented in Table I. Table II summarizes similar data for buffers with $C = 1.25 \times 10^{-3}M$, while Table III includes all data obtained at $t = 25^\circ C$ and $\mu \approx 1.00_0$. The effect of temperature is also illustrated by Fig. 1 which is based on data from Table I. The effect of ionic strength is illustrated in Fig. 2, taken from data in Table III.

The method employed to evaluate equilibrium constants for the several sets of experimental conditions studied was essentially that described in the earlier publication. However, it was necessary to modify the method slightly because of the considerably smaller number of buffers studied under conditions other than $t = 25^\circ C$ and $\mu = 1.00_0$.

In calculating constants from the data on the effect of ionic strength, two equations of the form of equation (VI) were evaluated at each ionic strength, employing experimental data for buffers at $C = 1.25_0 \times 10^{-3}$ and $n = -0.013$ and $+0.187$. The resulting pairs of equations when solved simultaneously led to the sets of constants presented in Table IV.

Since considerably more data are available at $\mu = 1.00_0$ and $t = 10^\circ C$ or $40^\circ C$, five equations were employed for the evaluation of each set of constants. The resulting equilibrium constants are also given in Table IV.

It was pointed out previously that values of the constants depended markedly on the n values chosen as a source of data in setting up equation (VI). In addition, there is a much less marked dependence on C . Therefore, if values of the constants for different experimental conditions are to be compared, they must be derived from data obtained at comparable values of n and C .

In order that this comparison have the greatest possible validity, we have therefore recalculated the constants for $t = 25^\circ C$ and $\mu = 1.00_0$ from two additional groups of data. In one case, the data group was chosen to be comparable with data employed in

calculating constants at varying ionic strength; in the other case, to be parallel with constants at varying temperatures. These constants are also given in Table IV.

When the several sets of constants are employed to calculate values of $-\log C_H$ for the buffer systems examined, the values given in the "calculated" columns of Tables I to III are obtained. The differences

TABLE I. $-\log C_H$ for Sc Buffers at $C = 1.00 \times 10^{-2}M$, $\mu = 1.00_0$

n	$-\log C_H$ at $t = 10^\circ C$			$-\log C_H$ at $t = 40^\circ C$		
	exp.	calc.	diff.	exp.	calc.	diff.
-0.213	2.622	2.672	-0.050	2.588	2.622	-0.034
-0.0130	3.235	3.322	-0.087	2.986	2.996	-0.010
+0.187	3.865	3.867	-0.002	3.332	3.329	+0.003
0.387	4.148	4.151	-0.003	3.594	3.585	+0.009
0.527	—	—	—	3.739	3.762	-0.023
0.587	4.365	4.416	-0.051	3.807	3.842	-0.035
0.787	4.578	4.771	-0.193	4.025	4.194	-0.169
0.933	4.719	5.412	-0.693	4.174	4.733	-0.559
1.033	4.820	5.689	-0.869	4.253	5.064	-0.881
1.181	4.959	4.978	-0.019	4.373	4.397	-0.024

TABLE II. $-\log C_H$ for Sc buffers at $C = 1.25 \times 10^{-3}M$, $\mu = 1.00_0$

n	$-\log C_H$ at $t = 10^\circ C$			$-\log C_H$ at $t = 40^\circ C$		
	exp.	calc.	diff.	exp.	calc.	diff.
-0.117	3.822	3.684	+0.138	3.505	3.476	+0.029
-0.067	3.868	3.785	+0.083	3.536	3.527	+0.009
-0.0170	3.963	3.893	+0.070	3.583	3.580	-0.003
+0.103	4.188	4.131	+0.057	—	—	—
0.209	—	—	—	3.821	3.811	+0.010
0.260	4.445	4.378	+0.067	3.887	3.876	+0.011
0.327	4.508	4.470	+0.033	—	—	—
0.419	—	—	—	4.044	4.054	-0.010
0.527	4.734	4.734	0.000	4.167	4.184	-0.017
0.577	—	—	—	4.202	4.250	-0.048
0.696	4.922	4.993	-0.071	—	—	—
0.780	—	—	—	4.423	4.595	-0.172
0.827	5.023	5.280	-0.257	—	—	—
0.933	5.131	5.721	-0.590	4.524	5.151	-0.627
0.949	—	—	—	4.579	5.273	-0.694
1.033	5.167	6.183	-1.016	4.591	5.482	-0.891
1.181	5.244	5.470	-0.266	4.638	4.777	-0.139

between experimental and calculated values are of the same magnitude as was observed for the much larger number of buffers studied previously, and exactly the same trends in the differences are noted at all temperatures and ionic strengths studied.

Effect of Ionic Strength on the Equilibrium Constants

While it would be most desirable to obtain thermodynamic values of the dissociation constants at infinite dilution from the values of the constants given

TABLE III. Effect of ionic strength on C_H in Sc Buffers at 25°C

Ionic strength M	Conc Sc 10^4 °C		-log C_H at $\mu =$					
			-0.0130	+0.187	0.387	0.587	0.787	0.987
0.500	5.016	exp.	3.318	3.728	3.990	4.214	4.424	4.613
		calc.	3.341	3.724	3.998	4.265	4.622	5.890
		diff.	-0.023	+0.004	-0.008	-0.051	-0.198	-1.277
	2.508	exp.	3.526	3.864	4.097	4.350	4.556	4.736
		calc.	3.530	3.860	4.128	4.395	4.752	6.021
		diff.	-0.004	+0.004	+0.031	-0.045	-0.196	-1.288
	1.254	exp.	3.740	4.003	4.237	4.452	4.674	4.837
		calc.	3.717	3.996	4.253	4.519	4.876	6.147
		diff.	+0.023	+0.007	+0.016	-0.067	-0.202	-1.310
0.100 ₀	2.50 ₀	exp.	3.470	3.776	4.047	4.279	4.497	4.693
		calc.	3.525	3.772	4.028	4.291	4.646	5.914
		diff.	-0.055	+0.004	+0.019	-0.012	-0.149	-1.221
	1.25 ₀	exp.	3.673	3.909	4.139	4.384	4.620	4.806
		calc.	3.664	3.918	4.159	4.418	4.772	6.042
		diff.	+0.009	-0.009	-0.020	-0.034	-0.152	-1.236
0.0100 ₀	1.25 ₀	exp.	3.594	3.799	4.014	4.216	4.441	4.627
		calc.	3.594	3.799	4.009	4.247	4.590	5.320
		diff.	0.000	0.000	+0.005	-0.031	-0.149	-0.693

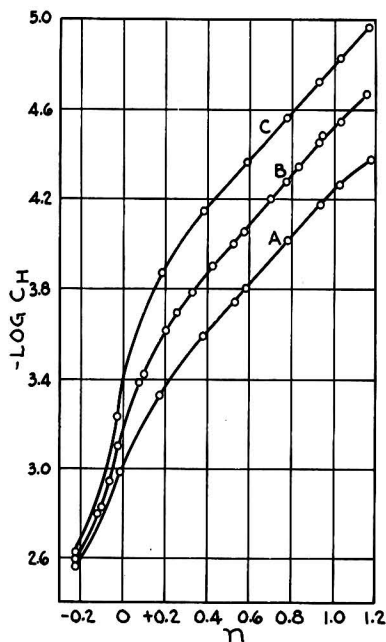


FIG. 1. Effect of temperature on the acidity of scandium perchlorate solutions at $C = 1.00_0 \times 10^{-2}M$; $\mu = 1.00_0$; and $t =$ curve A—40°C, curve B—25°C, curve C—10°C.

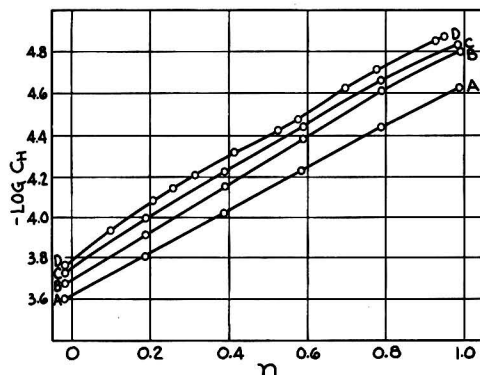


FIG. 2. Effect of ionic strength on the acidity of scandium perchlorate solutions at $t = 25^\circ C$, $C = 1.25_0 \times 10^{-2}M$; $\mu =$ curve A—0.0100, curve B—0.100, curve C—0.500, and curve D—1.00.

Hückel equation are not valid at ionic strengths above 0.1 unless specific salt effects can be evaluated. For a trivalent ion, such as that involved in this study, it is highly questionable whether an extrapolation from $\mu > 10^{-3}$ is valid. Consequently, only the empirical relationships between μ and the constants, which can be inferred from the tabulated data, can be presented.

Effect of Temperature on the Equilibrium Constants

in Table IV, the data available are not suitable for this purpose. Even for a univalent ion, extrapolations based on various modifications of the Debye-

Of the "many empirical equations which have been employed for representing the ionization con-

stants of weak electrolytes as a function of T , and for computing the thermochemical functions. . . .” (5) the authors have chosen to employ the relationships due to Harned and Robinson (6). On substituting data from Table IV into their equation:

$$-\log K = A/T + B + CT \quad (\text{XI})$$

the following relationships are obtained for $\mu = 1.00_0$ mostly in NaClO_4 :

$$-\log K_1 = -4408.3T^{-1} + 41.163 - 0.0724T \quad (\text{XII})$$

$$-\log K_0 = +4937.3T^{-1} - 15.593 + 0.0170T. \quad (\text{XIII})$$

The related equations below, given by Bates and Pinching (7), were then employed in calculating values of the thermochemical properties of the system.

$$\Delta F = 2.3026R(A + BT + CT^2) \quad (\text{XIV})$$

$$\Delta H = 2.3026R(A - CT^2) \quad (\text{XV})$$

$$\Delta S = 2.3026R(-B - 2CT) \quad (\text{XVI})$$

$$\Delta C_p = 2.3026R(-2CT) \quad (\text{XVII})$$

However, since the equilibrium constants derived here are not the thermodynamic values at $\mu = 0$, the parameters A , B , and C of equations (XII) and (XIII) will not lead to true thermodynamic properties of the system. Furthermore, since no valid method of evaluating the activity coefficients of the species involved in the equilibrium constants is apparent, it is not possible to calculate the thermodynamic dissociation constants.

Nevertheless, the standard state for the systems could be defined as the state in which the solutions are essentially one molar in NaClO_4 ; the thermochemical properties calculated could then be considered to be referred to a standard state. The calculation is, therefore, based on this definition, instead of infinite dilution as the standard state. The superscript zero in equations (XIV) to (XVII) has been omitted in order to avoid confusion of the symbols with those defined in the more customary manner.

Employing for R the Birge value of $1.9869 \text{ cal mole}^{-1} \text{ deg}^{-1}$, the values of the above properties have been calculated. They are presented in Table V, along with related properties for the dimerization reaction calculated as follows. Values of ΔF and ΔH were obtained by appropriate addition of equations and energy terms; ΔS for the dimerization was then calculated from ΔF and ΔH values by substitution in the fundamental equation:

$$\Delta F = \Delta H - T\Delta S \quad (\text{XVIII})$$

While the values are given to two significant figures in Table V it must be emphasized that these figures are somewhat questionable. When the entire calculation is repeated, employing different but parallel groups of data to calculate the constants, one obtains equilibrium constants and thermochemical properties which differ from those presented in the table. However, the signs, orders of magnitude, and trends exhibited in the recalculated values are similar in every respect to those presented in Table V.

TABLE IV. *Equilibrium constants for the acidic dissociation of the aquoscandium ion at various experimental conditions*

Temp, °C	Ionic strength, μ	Equilibrium constants		
		$10^3 K_1$	$10^3 K_0$	$10^{-3} K_d$
25	1.00 ₀	1.17 ₂	1.01 ₆	7.38
10	1.00 ₀	0.808	0.221 ₄	3.39 ₃
25	1.00 ₀	1.62 ₃ *	0.927*	3.51 ₃ *
40	1.00 ₀	3.87 ₃	3.20 ₁	2.13 ₄
25	0.0100 ₀	2.45 ₃	4.47	7.43
25	0.100 ₀	1.81 ₀	2.15 ₄	6.58
25	0.500	1.25 ₃	1.26 ₅	7.99
25	1.00 ₀	1.18 ₅ †	0.889†	6.35†

* Employed only in determining effect of temperature on the equilibria.

† Employed only in determining effect of ionic strength on the equilibria.

TABLE V. *Thermochemical properties of the aquoscandium ion acid system in 1M NaClO₄*

Reaction	Temp °C	ΔF kcal mole ⁻¹	ΔH kcal mole ⁻¹	ΔS Cal mole ⁻¹ deg ⁻¹	ΔC_p Cal mole ⁻¹ deg ⁻¹
First acid Dissociation K_1	10	+6.6	+6.4	-0.7	+190
	25	6.5	9.3	+9.	200
	40	6.3	12.	19.	210
Over-all K_0	10	8.6	16.	27.	-44
	25	8.2	15.	25.	-46
	40	7.9	15.	22.	-49
Dimerization K_d	10	-4.6	3.6	28.	—
	25	-4.8	-2.9	6.	—
	40	-4.8	-9.7	-15.	—

For example, on carrying out three independent calculations, leading to three independent sets of thermochemical properties, the signs of ΔS exhibit the same reversal of sign for the first acid dissociation and dimerization steps as indicated above, although the magnitudes of ΔS may vary considerably.

In the previous paper (1) it was pointed out that dependence of the constants on n and C undoubtedly reflected contributions from higher dissociation and polymerization steps. These contributions are, in turn, probably responsible for the variations in equilibrium constants discussed above. However, if one

employs parallel data at the several temperatures in evaluating the constants, one may assume as a first approximation that the contributions of higher steps are essentially equal and, therefore, are cancelled out on evaluation of the temperature coefficients.

To the extent that these assumptions are correct, and since no comparable data have yet been presented for an aquometal ion, the authors feel that these data may be of considerable interest to workers in the field.

Note added in proof. The neglect of the equilibria for the higher polymers $\text{Sc}_{3,5}$; $\text{Sc}_{4,6}$; $\text{Sc}_{5,7}$; $\text{Sc}_{6,8}$, etc., may well explain the dependence of ΔH and ΔS on the C and n values used, and may also explain the trends in the thermodynamic quantities. Sillén, at the Symposium on Co-ordination Chemistry held in Copenhagen, August 9 to 13, 1953, presented a method for calculating the equilibrium constants involved in polynuclear complexes, and preliminary

calculations for scandium, on the assumption of repeated reaction, show reasonable agreement with the experimental data.

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

REFERENCES

1. M. KILPATRICK AND L. POKRAS, *J. Electrochem. Soc.*, **100**, 85 (1953).
2. K. J. PEDERSEN, *Kgl. Danske Videnskab. Selskab. Mat.-fys. Medd.*, **20** (7), 27 (1943).
3. F. GRANER AND L. G. SILLÉN, *Acta Chem. Scand.*, **1**, 631 (1947); *Nature*, **160**, 715 (1947).
4. J. AHRLAND, *Acta Chem. Scand.*, **3**, 374 (1949).
5. H. S. HARNED AND B. B. OWEN, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., p. 509, Reinhold Publishing Company, New York (1950).
6. H. S. HARNED AND R. A. ROBINSON, *Trans. Faraday Soc.*, **36**, 973 (1940).
7. R. G. BATES AND G. D. PINCHING, *J. Am. Chem. Soc.*, **71**, 1274 (1949).

Equivalent-Circuit Model of the Transference Cell¹

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ABSTRACT

An equivalent-circuit model characterized by remarkable pictorial simplicity is proposed for a cell with reversible electrodes in contact with a solution of a suitable binary electrolyte, nonuniform in concentration. The capacitance part of the circuit is related to the free energy change of the dilution process, while the resistance parts are related to the cation and anion transports. On the basis of the model, correct equations are derived for (a) the conductance of the solution, (b) the diffusion of the electrolyte (Nernst equation), and (c) the concentration cell with transference. In addition, equations, which have not been subjected to experimental test, are derived for (d) capacitance of the condenser, (e) current as a function of applied potential difference, and (f) concentration difference as a function of applied potential difference. Mixtures of electrolytes are considered briefly. On the basis of the model, a method is proposed for the determination of thermodynamic properties of electrolytes by transference cell measurements which does not involve a measurement of the transference number. The range of applicability of the model to various aspects of electrochemistry is discussed, and the concept of diffusion potential is critically re-examined.

INTRODUCTION

Electrode and ion-transport processes are both essential elements of every electrochemical cell. It is sometimes possible to study one of these processes with negligible interference from the other. For example, in electrical conductance and moving-boundary experiments, the ion-transport processes of interest are isolated from electrode phenomena by appropriate experimental technique. Conversely, in electromotive force measurements, carried out for the purpose of deriving thermodynamic properties, careful experimental design can sometimes reduce ion-transport processes to a position of negligible significance. Generally speaking, the interpretation of data is facilitated when the reversible and irreversible processes are not intermingled.

The great bulk of electrolytic processes occur, however, with just such intermingling. A simple classical illustration of this is the concentration cell with transference, where the diffusion of ions is unavoidably present during emf measurements. Also in this category is the inverse of the concentration cell with transference, i.e., a concentration gradient is generated by electrode and ion transport processes upon application of an external voltage.

The same arrangement results when convection is eliminated from the electrogravitational process described by Murphy (1) by operating with horizontal electrodes. It is discussed by Murphy and Batzer (2) as an example of a type *H* (for horizontal) cell. Many other examples of cells in which electrode and ion-transport processes must be treated together can be found throughout the field of electrochemistry.

We propose herein an equivalent-circuit model of a cell which involves integrated electrode and ion-transport processes, including the specific types mentioned above. This model emphasizes the importance of time-independent or steady states in cells where current is flowing and concentration gradients are present. From the model, long-established equations for conductance, for the diffusion of ions, and for the concentration cell with transference are derived, as well as some others which have not been subjected to experimental test. It thus serves as a quantitative basis of reference for a number of experimental facts, and it is so simple that it possesses considerable pedagogical appeal. The model is heuristic in nature, suggesting, for example, a new approach to the determination of the thermodynamic properties of electrolytes.

The term "transference cell" refers to a system with two identical reversible electrodes in contact with an electrolytic solution, one or more ions of which participate in the electrode reaction. By "reversible" it is meant that the clearly specifiable reaction at one electrode occurs in exactly the reverse manner at the other, and that there is no activation or resistance overpotential at the elec-

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trodes. The applied or measured potential is always less than that required for decomposition of the solution, i.e., concentration gradients, but no changes in composition are established in the cell as a result of passage of current. The familiar "concentration cell with transference" is a special case of the transference cell when there is a concentration gradient, but no external current.

Throughout the article, the silver-silver chloride electrode, chloride ion system is adopted for illustration. Complete dissociation of the electrolyte, e.g., KCl, is assumed. Three aspects of this cell are shown in Fig. 1. In section (a) the system is in

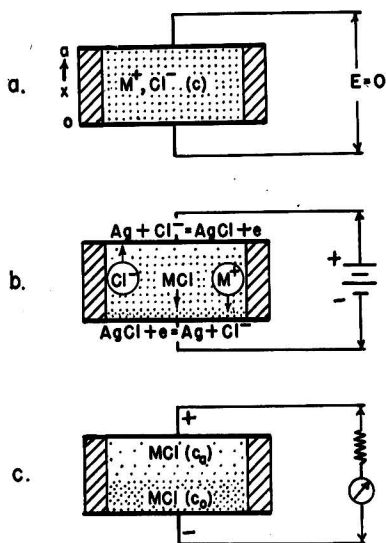


Fig. 1. Cross sections of the transference cell. Heavy horizontal bounding lines represent silver-silver chloride electrodes; cross-hatching, insulating spacer; density of dots, concentration of electrolyte. (a) Cell in equilibrium, concentration uniform; (b) cell with external applied voltage, representing "charging" of the cell; and (c) concentration cell with transference, emf being measured with high resistance voltmeter.

equilibrium, with a uniform concentration and no external voltage. In section (b) an external voltage has been applied, but changes in concentration have occurred near the electrodes only. This corresponds to a Hittorf transference experiment. Because of the density differences which arise, the cathode is situated at the bottom to avoid convection currents. In section (c) the concentration difference between the top and bottom electrodes leads to an external emf; this is a concentration cell with transference. The external battery of (b) has been replaced by a high-resistance voltmeter. In (b) a substantial current in the external circuit

passes, while in (c), for a measuring instrument of infinite sensitivity, there is no external current at all.

It is evident that continued passage of current in (b), followed by removal of the external current source, leads to a concentration cell with transference (c). It has been shown (3, 4) that the steady-state concentration distribution reached after prolonged current passage is linear for the ideal case.

EQUIVALENT CIRCUIT

The application of equivalent-circuit models to electrochemical problems is not new. Electrical double-layer phenomena at mercury-solution interfaces in particular have been interpreted by this means. Grahame (5, 6), in his capacitance studies, noted the presence at certain polarizing potentials of a very large capacity effect due to oxidation-reduction phenomena at the electrodes. He called this a "pseudocapacity" to distinguish it from true double-layer capacity. Breyer and Gutman (7) referred to this as a "dynamic capacitance."

The condenser and other elements of our equivalent circuit are similar to those utilized by Grahame and by Breyer and Gutman in that they involve oxidation-reduction at the electrodes, but differ in that they also involve concentration gradients throughout the solution. Moreover, we have restricted ourselves to the simplest types of electrode processes and are primarily concerned with the time-independent or steady state achieved by steady application of a d-c voltage. These states would have no chance of attainment with the a-c methods employed by Grahame and other investigators, who were primarily interested in double-layer phenomena. The "steady states" in a-c work are time averages over a number of cycles, but the variables are changing during periods of the order of one cycle.

Equivalent-circuit models are also important in the interpretation of the dielectric properties of crystals. According to MacDonald's model (8), charge carriers within the crystal may be responsible for a large part of the capacitive reactance.

The postulated equivalent circuit of the transference cell is given by Fig. 2a and 2a'. The latter circuit diagram, which contains two condensers in one arm, illustrates the complete blocking action to the external circuit of charges passing through R_+ , which is analogous to the blocking action of positive ions by the electrodes in the transference cell. On the other hand, the mathematical treatment is simplified if a single condenser is retained in the left arm; the capacitance of the condenser in Fig. 2a is obtained by series addition of the capacitances of the two condensers in Fig. 2a'.

Qualitative considerations which lead to the model are as follows:

<i>Cell</i>	<i>Equivalent Circuit</i>
Current is carried by parallel movement of two charge carriers, M^+ and Cl^- ions, with different ionic conductances l_+ and l_- .	There are two parallel arms in the circuit with different resistances R_+ and R_- , where $R_+/R_- = l_-/l_+$.
The electrodes are "permeable" to Cl^- ions. (The electrode reaction consumes or liberates Cl^- ions.)	Negative charge passes directly from the external source through R_- .
The electrodes are blocking to M^+ ions. (The electrode reaction does not involve M^+ ions.)	Charges passing through R_+ are blocked from the external circuit by condensers (Fig. 2a').
A concentration gradient generates an external voltage.	A charged condenser leads to an external voltage.
A concentration gradient is self-equalizing by diffusion in the absence of an applied voltage.	In the absence of an applied voltage, a charged condenser will automatically discharge through R_+ and R_- .

Further details of correspondence between the cell and circuit are restricted to the steady state:

<i>Cell</i>	<i>Equivalent Circuit</i>
The chemical potential of the electrolyte varies with position in the cell, but is invariant with respect to time. Cl^- ions are flowing continuously through the cell, while M^+ ions are stationary.	The electrical potential varies with position, but is invariant with respect to time. Negative charges are flowing continuously through R_- , but no charge flows through R_+ .

A virtual transfer of dQ/F equivalents of M^+ (and hence of MCl) from the anode, contacting solution of activity a_a , to the cathode, contacting solution of activity a_c , leads to an increase in free energy of the system of $dG = 2(dQ/F)RT \ln(a_c/a_a)$ (G is the free energy of the system and F is the faraday constant.)

If the circuit is indeed electrically equivalent to the cell, it follows from elementary thermodynamic considerations that

$$E_c = 2(RT/F) \ln(a_c/a_a). \quad (I)$$

It is to be noted that E_c is the potential difference at the electrodes with steady-state current flowing in the external circuit; but during internal discharge of the cell (Fig. 2c) with no current flowing in

the external circuit, the measured potential difference will be less than E_c .

Referring to Fig. 2b, it is stressed that dQ is the charge passed through the left-hand side of the circuit only. Concurrently with this process, an additional charge dQ' passes through the right-hand side in a purely dissipative manner; therefore, this feature of the circuit is consistent with the lack of reversibility in the cell as a whole. The model clearly specifies that all reversible phenomena of the cell are to be associated with the condenser, and all irreversible phenomena with the resistances.

Each of the three circuit elements of Fig. 2a is nonlinear; that is, the currents through the resistance are not proportional to the potential drops, and the charge on the condenser is not proportional to the voltage across its plates. For steady-state operation and ideal behavior of the cell, suitable

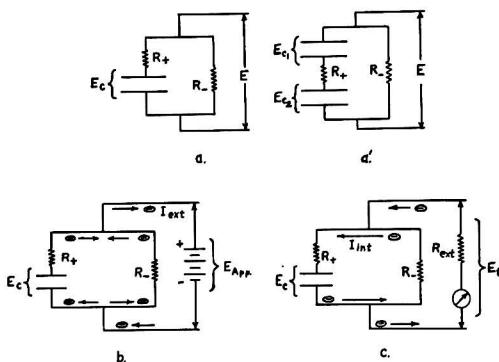


FIG. 2. Equivalent circuit corresponding to cells of Fig. 1. (a) Basic circuit; (a') alternate basic circuit with dual condensers; (b) charging with external source; and (c) internal discharge (free diffusion).

mathematical relations between emf, current, and concentration are readily found.

In Fig. 2b, the current corresponding to Fig. 1b is analyzed. The flow of negative charge through the right-hand side is electrically equivalent to a positive charge flowing in the opposite direction. The current in the external circuit is the sum of these two.

The current during internal discharge of the cell is shown in Fig. 2c. The internal current is equivalent to free diffusion of the salt, with the flux of positive ion equal to the flux of negative ion, as required by the electroneutrality condition. From the electrical circuit standpoint, this means that the current through the left must be equal to that through the right. Only an infinitesimal current flows through the external circuit to actuate the potentiometer. The internal current is fictitious in the sense that it cannot be measured as an electric

current, but it is by no means a new concept. As early as 1888 Nernst (8) postulated that the diffusion of the ions of an electrolyte constituted an internal electric current, and he was led thereby to the concept of "diffusion potential," which arises because of the different mobilities of ions. Although the diffusion potential has had many applications since Nernst's time, it is an objectionable concept from the operational viewpoint, since it cannot be measured directly. We propose in this treatment to express the physical behavior of the system in terms of the external potential applied to, or generated by, the cell.

Discharge of the cell of Fig. 2c could also occur by short-circuiting the voltage measuring device. This can be referred to as "external discharge," in contrast to the "internal discharge" of free diffusion, which occurs irreversibly whether an external circuit is present or not.

MATHEMATICAL TREATMENT

The Cell Resistance

In order to demonstrate electrical equivalence of cell and circuit in quantitative fashion, the further assumptions are made that activities may be replaced by concentrations and that conductances are linear functions of the concentration. These assumptions, together with those made earlier, characterize what will be referred to as an ideal transference cell. In this case the mathematical conditions for equivalence of cell and circuit are:

$$E_c = (2RT/F) \ln C_o/C_a \quad (\text{II})$$

$$R_+ = (l_+/Al_+) \int_0^a (1/C) dx \quad (\text{IIIa})$$

$$R_- = (l_-/Al_-) \int_0^a (1/C) dx \quad (\text{IIIb})$$

where a is the distance between the parallel electrodes of area A , C is the local concentration in equivalents per cc, and l_+ and l_- are the mobilities (equivalent ionic conductances). In the case of the linear concentration distribution which is attained in the steady state,

$$R_+ = \{a/Al_+(C_o - C_a)\} \ln (C_o/C_a) \quad (\text{IVa})$$

$$R_- = \{a/Al_-(C_o - C_a)\} \ln (C_o/C_a) \quad (\text{IVb})$$

When the ratio C_o/C_a is close to unity, these equations reduce to

$$R_+ = a/Al_+C_o; R_- = a/Al_-C_o. \quad (\text{Va, b})$$

The true cell resistance, as seen by the external circuit, is evidently obtained by parallel combination of these elements:

$$\begin{aligned} R_{\text{cell}} &= R_+R_-/(R_+ + R_-) \\ &= \{a/A\Lambda(C_o - C_a)\} \ln (C_o/C_a) \quad (\text{VI}) \end{aligned}$$

where $\Lambda = l_+ + l_-$ is the equivalent conductance of the salt. In the limit as $C_o \rightarrow C_a$,

$$R_{\text{cell}} = a/A\Lambda C_o, \quad (\text{VII})$$

which is just the cell resistance that would be measured with a uniform electrolyte by an a-c method. On the other hand, examination of Fig. 2 shows that the apparent resistance in the steady state is

$$R'_{\text{cell}} = a/Al_-C_o, \quad (\text{VIII})$$

since no net current flows through the left-hand side.

Self-Discharge of the Cell—Verification of Nernst's Diffusion Equation

During the self-discharge of the cell (free diffusion, Fig. 2c), the internal current density, I_{int} , produces a difference of potential $AI_{\text{int}}(R_+ + R_-)$ across the series combination of resistances, which is equal in magnitude, but opposed in sign, to E_c . Combining this relation with equations (II) and (IV),

$$I_{\text{int}} = (2RT/F)\{(C_o - C_a)/a\} \cdot \{l_+l_-/(l_+ + l_-)\} \quad (\text{IX})$$

However, I_{int} is also equal in magnitude, but opposed in sign, to the product FJ of the faraday constant and the diffusion flux J , for which Fick's law of diffusion

$$J = I_{\text{int}}/F = D(C_o - C_a)/a \quad (\text{X})$$

is valid, where D is the diffusion coefficient. It follows from equations (IX) and (X) that

$$D = (2RT/F^2)l_+l_-/(l_+ + l_-) \quad (\text{XI})$$

which is Nernst's equation (8). Ample experimental verification for this equation has been provided in cases where ideal conditions are approached.

The measured emf of the self-discharging cell is just E_t , that of a concentration cell with transference. In terms of the potential drops across the resistors, E_- and E_+ ,

$$E_t = E_- = E_c - E_+ = E_c - \frac{l_-}{l_+} E_-,$$

whence

$$E_t = \frac{l_+}{l_+ + l_-} E_c = t_+ E_c. \quad (\text{XII})$$

This is a verification of another long-established equation. Equations (VII), (XI), and (XII) are a concise summary of the known properties of the ideal transference cell. The accuracy of the equivalent circuit model has, therefore, been

established by the derivation of these equations on the basis of it.³

Capacitance of the Condenser

On charging the condenser, the potential difference across its plates increases, corresponding to an increasing concentration gradient in the transference cell. By equation (II), the minimum work done in transferring the infinitesimal quantity of electrolyte $dy = dQ/F$ is

$$FE_c dy = 2RT \ln \frac{C_o}{C_a} dy. \quad (\text{XIII})$$

The energy dissipated in the right-hand resistor is not included in this calculation; furthermore, the transfer may be imagined to occur infinitesimally slowly, so that there is no energy dissipation in the left-hand resistor. Under these conditions, the system is always in a steady state, with a linear concentration gradient. The concentration at the mid-point between the electrodes remains constant, and the electrolyte transfer takes place across this dividing line.

The concentration at any point and the number of moles transferred are connected by the relation

$$CV = 4y \left(\frac{2x}{a} - 1 \right) + n_0, \quad (\text{XIV})$$

where V is the volume of the cell and n_0 the number of moles of electrolyte. Since C cannot be less than zero at the anode, y is limited to values between zero and $n_0/4$ for the linear concentration distribution.

Equation (XIII) may be integrated after substituting (XIV):

$$\begin{aligned} \text{work} &= 2RT \int_0^y \ln \frac{C_o}{C_a} dy \\ &= 2RT \int_0^y \ln \frac{n_0 + 4y}{n_0 - 4y} dy \\ &= \frac{RT}{2} \left\{ (n_0 + 4y) \ln \left(1 + \frac{4y}{n_0} \right) \right. \\ &\quad \left. + (n_0 - 4y) \ln \left(1 - \frac{4y}{n_0} \right) \right\} \end{aligned} \quad (\text{XV})$$

When $n_0 \gg 4y$, corresponding to a low emf, this equation reduces to⁴

$$\text{work} = \frac{8RTy^2}{n_0}. \quad (\text{XVI})$$

³ The derivation of equation (VII) started with the assumption that the ionic conductances are independent of one another; since this assumption leads to the correct result for the concentration dependence of cell resistance [equation (VII)], the law of independent ionic migrations is verified.

⁴ The first two terms in the series expansion of $\log(1 + 4y/n_0)$ and $\log(1 - 4y/n_0)$ are retained.

In transporting y equivalents, Fy coulombs are passed through the left-hand side of the circuit. Thus, the work done in charging the condenser, in the region where equation (XVI) is valid, is proportional to the square of the charge transferred, a characteristic of a normal condenser. The capacitance of the condenser is evidently $n_0 F^2 / 16RT$. Unlike a normal condenser, the capacitance is directly proportional to the number of moles of electrolyte, but independent of the electrode separation or area.

The capacitance for a typical case is enormous by any ordinary standard. Suppose, for example, that $n_0 = 10^{-4}$ equivalent, a quantity which would be contained in a decinormal solution filling a 1 cm³ cell. At room temperature, the capacitance is

$$\frac{10^{-4} \times (9.65)^2 \times 10^8}{16 \times 8.316 \times 298.1} = 21.2 \text{ farad}$$

This exceeds by many powers of ten the capacitance of any radio condenser of comparable size.

Current as a Function of Applied Voltage

Since all of the components in the equivalent circuit model are nonlinear, the cell as a whole will not be expected to follow Ohm's law. For any point within the cell, equation (II) becomes

$$dE/dx = (2RT/F) d \ln C/dx \quad (\text{XVII})$$

in the steady state. Since $I = t_{-} C A dE/dx$ [compare equation (VIII)], it follows that

$$I = (2RT/F) t_{-} A dC/dx \quad (\text{XVIII})$$

While dC/dx is constant throughout the cell, dE/dx is obviously not so, being greater at the points of lower concentration. The E of this equation is the total potential difference measured by Ag-AgCl electrodes, but, as indicated previously, it is also the potential difference across the condenser plates under steady-state operation.

Upon integrating equation (XVIII), and noting that when $x = a/2$, $C = C_{or}$, the original uniform concentration of electrolyte, there results the equation

$$C = \frac{IF}{2t_{-} RT} \left(x - \frac{a}{2} \right) + C_{or} \quad (\text{XIX})$$

Substituting (XVII) into (XVIII), integrating over x , and solving for I , one obtains

$$I = \frac{4C_{or} t_{-} \Lambda RT}{aF} \tanh EF/4RT \quad (\text{XX})$$

The E in this equation is the total applied potential. By expanding the hyperbolic tangent and retaining only the first term, we obtain an equation valid for small applied potentials:

$$I = C_{or} t_{-} \Lambda E/a \quad (\text{XXI})$$

Ohm's law is, therefore, satisfied under this con-

dition; however, the conductance measured under steady-state operation is t_- times the value measured under uniform concentration conditions.

When $EF/4RT$ becomes very large, the hyperbolic tangent approaches unity, equation (XX) becomes

$$I = 4C_{or} t_- \Delta RT/aF, \quad (\text{XXII})$$

and the current density is independent of applied potential.⁵

Equation (XX) has also been obtained in a mathematical analysis by Piguet, Kuhn, and Kuhn (10). The assumptions inherent in their derivation lead, however, to an incorrect result for the emf of a concentration cell with transference.

Concentration as a Function of Applied Voltage

The concentration difference between the electrodes may be expressed in terms of the current density by application of equation (XIX):

$$C_o - C_a = \frac{IFa}{2l_- \Delta RT} \quad (\text{XXIII})$$

Substituting (XX) into (XXI), we have

$$C_o - C_a = 2C_{or} \tanh \frac{EF}{4RT} \quad (\text{XXIV})$$

This equation has also been obtained by Piguet, Kuhn, and Kuhn (10). According to equation (XXIV), the ratio $\frac{C_a - C_o}{C_{or}}$ is dependent only on the applied potential for the system under study, but independent of transference number and conductance. The elimination of terms characteristic of irreversible processes from the concentration-potential relation is relevant to our discussion below.

For small values of E , equation (XXIV) becomes

$$\frac{C_a - C_o}{C_{or}} = \frac{EF}{2RT} \quad (\text{XXV})$$

For practical purposes this is equivalent to equation (XIV). For large values of E , equation (XXIV) leads to the result

$$C_o - C_a = 2C_{or} \quad (\text{XXVI})$$

Since the total number of moles is conserved, this equation shows that the limiting condition at high applied potential is reached when the concentration at $x = 0$ has doubled, while that at $x = a$ has fallen to zero.

Extension of Theory to Mixtures

While the foregoing mathematical treatment has been applied to only the simplest case, a 1-1 elec-

⁵ A potential difference between the electrodes of 0.6 volt, corresponding to a $\tanh(EF/4RT)$ of 0.9999, is regarded as large. Above this voltage, decomposition of the solution with cathodic evolution of hydrogen may occur. Equation (XIX) is no longer valid at such voltage.

trolyte in an ideal transference cell, a single electrolyte of any other valence type could be handled easily. The treatment of mixtures is more complex, requiring the introduction of additional elements into the electrical circuit model, and additional parameters in the equations. The detailed treatment will be deferred to a later paper, but it is worthwhile here to outline the procedure for a relatively simple case: electrodes again reversible to the chloride ion, electrolyte a mixture of two chlorides, e.g., NaCl and KCl. The equivalent circuit of this

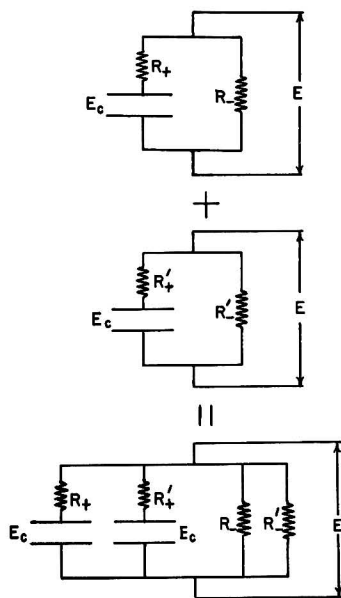


FIG. 3. Diagrams illustrating parallel additivity of circuit elements for two single electrolytes to obtain equivalent circuit for mixture.

cell is obtained by parallel combination of circuits for each salt, as if the other were absent (Fig. 3).

It is assumed in this treatment, as before, that the system is thermodynamically ideal, and that Kohlrausch's law of independent ionic mobilities is obeyed. Since these conditions will not be met in a practical case, the equations based on this model are intended merely as illustrative of the approach.

Application of a polarization potential will produce, in the steady state, a solution with a concentration ratio C_o/C_a which is the same for each constituent. When this potential is released, the emf of the resulting concentration cell with transference is given by

$$E_t = [(t_+)_{1} + (t_+)_{2}]E_o, \quad (\text{XXVII})$$

$$(t_+)_{1} = (C_+)_{1}(t_+)_{1}/[(C_+)_{1}\Delta_1 + (C_+)_{2}\Delta_2]$$

$$(t_+)_{2} = (C_+)_{2}(t_+)_{2}/[(C_+)_{1}\Delta_1 + (C_+)_{2}\Delta_2]$$

In general, when an indefinite number of cations are present in the system with the common chloride ion:

$$E_i = E_c \sum_i (t_+)_i; \quad (\text{XXVIII})$$

$$(t_+)_i = (C_+)_i (l_+)_i / \sum_j (C_+)_j \Lambda_j$$

$(C_+)_i$ = concentration of the i th cation species

$(l_+)_i$ = mobility of the i th cation species

Λ_i = equivalent conductance of the chloride salt of the i th cation species.

It is evident that the nonsteady states prevailing in the general classical problem of junction potentials will involve much greater mathematical complexity. Nevertheless, the pictorial simplicity of the equivalent circuit model should be of assistance in setting up equations for a particular junction potential problem. Diffusion problems in multi-electrolyte systems are also accessible to the model.

DISCUSSION

What is Diffusion Potential?⁶

The equivalent circuit model of Fig. 2 contains three elements, each characterized by its own potential difference when the solute is diffusing freely from an initial steady-state concentration distribution; moreover, each is directly measurable in principle by appropriate experimental technique, if electrodes reversible to the desired ion can be found. Thus, the potential across R_- is obtained directly from the circuit of Fig. 2. If the electrolyte were HCl, the potential across R_+ would be directly measurable through reversible hydrogen electrodes (Fig. 4). None of these potentials is equivalent to Nernst's diffusion potential, which is postulated to arise in a solution because of different rates of migration of ions across a concentration gradient. This potential difference is not directly measurable in principle, but must be calculated on the basis of assumptions in the Nernst theory from measurements on the emf of the cell as a whole. For non-ideal solutions, these assumptions are inexact; furthermore, cell emf's in the case of mixtures are strongly dependent on the structure of the junction, and it must be emphasized that all such measurements involve the use of electrodes with characteristic properties on which the magnitude of the measurement depends. Diffusion potential, however, is postulated to be a property only of a solution containing a diffusing electrolyte.

This problem, and the equivalent one of single ion activities, has been dealt with at length by Guggen-

⁶ The terms "junction potential" and "diffusion potential" are used interchangeably.

heim (11), who sums up the situation as follows: "The electric potential difference between two points in different media can never be measured, and has not yet been defined in terms of physical realities; it is therefore a conception which has no physical significance."

Taylor (12) arrives at a similar conclusion, pointing out that single ion activities or free energies, and the potential at a liquid junction, are not thermodynamically defined, but are "purely mathematical devices, which may indeed be employed safely with considerable freedom."

MacInnes and Longworth (13) discuss several types of liquid junctions, and, in agreement with Guggenheim and Taylor, take the position that only the observed cell emf has real thermodynamic significance. Nevertheless, these writers follow the general practice of ascribing a definite numerical value to the junction potential in the simpler cases, where the assumptions involved in their mathematical treatment are reasonably secure.

The concept of diffusion potential in simple

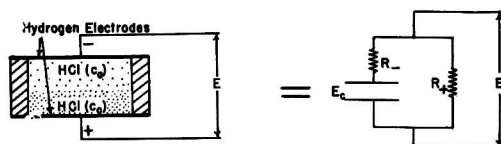


FIG. 4. Transference cell with electrodes reversible to cation and its equivalent circuit.

systems, when properly interpreted, does lead to correct results. On the other hand, the extensive body of literature which has accumulated around this interpretation suggests that it is not wholly satisfactory, even as a mathematical device. Classical electrochemical problems now interpreted in terms of diffusion potential seem to call for a new approach which involves only operational concepts. The equivalent circuit model of this paper might serve as a starting point. It will have to be shown, of course, that the model can be extended to non-ideal systems; this point is considered in the next section.

Non-ideal Systems

The successful results obtained in the case of the ideal transference cell are a strong temptation to take the general premises of the model as valid for non-ideal systems as well. Equation (II) would be replaced in this case by

$$E_c = \frac{2RT}{F} \ln \frac{(a_{\pm})_o}{(a_{\pm})_a} \quad (\text{XXIX})$$

where a_{\pm} is the mean activity of the electrolyte. The conductance would no longer be proportional to concentration, but this is unimportant to our

discussion; in the steady state, the applied potential difference is the same as E_c , the significant quantity from the thermodynamic standpoint, irrespective of the dependence of conductance on concentration. Clearly, we have a new means for determining activities of electrolytes. The technique of MacInnes and coworkers (14) for determining activity coefficients through transference cell measurements make use of equation (XII), but this requires, in addition, a different kind of experiment to determine the transference number. The method suggested here seems to offer a real advantage in economy of experimental effort. However, it has to be admitted that at the present time the validity of our model cannot be guaranteed by theoretical arguments for the non-ideal case, and no data by which a decisive experimental test can be made appear to have been recorded in the literature.

In designing a critical experiment, it would be unsafe to take the potential applied to the working electrodes as a measure of the cell emf. Any irreversible electrode effects due to slow kinetics of the electrode reaction, or resistance of the silver chloride film, would yield a value too high, if these factors are not negligible. Such effects are representable as an unknown series resistance added to the circuit of Fig. 2a. The difficulty could be circumvented by the use of probe electrodes at appropriate points in the cell, which would carry only the infinitesimal current required for potentiometric measurements.

A different cell design from that illustrated in Fig. 1 would be necessary. Figure 5a shows a suitable basic design, which differs from the previous one in having perforated or mesh electrodes close together and surrounded by electrolyte solution. Electrolyte is then free to pass through the electrode system. In the steady state, the concentration gradient is between the electrodes, while above and below the electrodes are solutions of uniform concentration, into which the probe electrodes may be inserted. The positioning of the latter is not critical. Both the working and the probe electrodes are silver-silver chloride. The former are visualized as being large with a copious supply of silver chloride on the cathode. The probe electrodes can be very small.

The equivalent circuit of this cell is shown in Fig. 5b, and is to be compared with that of Fig. 2a', which has dual condensers. The heavy lines represent the working circuit, and the light lines within the dotted areas, A and B, the additional circuit elements required for correspondence with the solution above and below the working electrodes, in which the probe electrodes are situated.

This equivalent circuit is evidently more complex than that of Fig. 2a', but the steady-state behavior is the same. If it is assumed that the measuring instrument requires only a vanishing current, in the steady state the two circuits A and B contribute nothing to the measured voltage. Irreversible over-voltage effects are representable as unknown resistance R_1 , R_2 , R_3 , and R_4 . In the measuring circuit, the voltage drops across R_3 and R_4 will be small, but in the working circuit the voltage drops across R_1 and R_2 could be large.

The optical methods of analysis now extensively employed in electrophoresis, diffusion, and ultracentrifuge investigations would be suitable for concentration determinations in such an experiment, or the solutions could be drained from their compartments and subjected to chemical analysis. It is well to bear in mind that attainment of the steady state

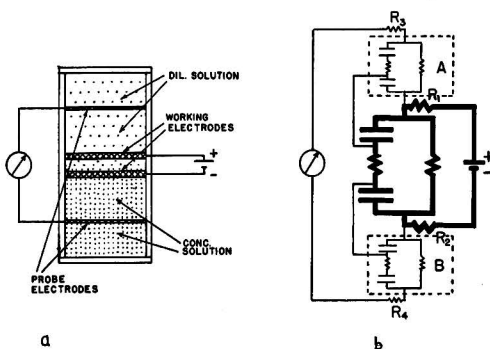


FIG. 5. Basic cell design (a) and equivalent circuit (b) for the determination of thermodynamic properties of the electrolyte MCl.

from a uniform solution would be a matter of hours or days; this time could be shortened by commencing the experiment with all conditions approaching those of the steady state as closely as possible.

It may be argued that the introduction of another irreversible process—steady current flow—on top of diffusion would introduce more uncertainty into the interpretation of emf measurements than is encountered where diffusion alone is present (concentration cell with transference). The equivalent circuit model suggests, however, that when two concurrent irreversible processes are properly balanced (coupled), interpretation of the reversible part of the system is facilitated. This point is to be considered further in a later paper, where the transference cell is treated by the methods of thermodynamics of the steady state.

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

REFERENCES

1. G. W. MURPHY, *This Journal*, **97**, 105 (1950).
2. G. W. MURPHY AND D. BATZER, *This Journal*, **99**, 520 (1952).
3. H. J. S. SAND, *Phil. Mag.*, (6), **1**, 45 (1901).
4. T. R. ROSEBRUGH AND W. L. MILLER, *J. Phys. Chem.*, **14**, 816 (1910).
5. D. C. GRAHAME, *J. Am. Chem. Soc.*, **63**, 1207 (1941).
6. D. C. GRAHAME, *This Journal*, **99**, 370C (1952).
7. B. BREYER AND F. GUTMAN, *Trans. Faraday Soc.*, **43**, 785 (1947).
8. J. R. MACDONALD, *Bull. Am. Phys. Soc.*, Cambridge, Mass., Meeting, 1953. Details to be published.
9. W. NERNST, *Z. physik. Chem.*, **2**, 613 (1888).
10. J. PIGUET, W. KUHN, AND H. KUHN, *Helv. Chim. Acta*, **34**, 1183 (1951).
11. E. A. GUGGENHEIM, *J. Phys. Chem.*, **33**, 842 (1929).
12. P. B. TAYLOR, *J. Phys. Chem.*, **31**, 1478 (1927).
13. D. A. MACINNES AND L. G. LONGSWORTH, *Cold Spring Harbor Symposia Quant. Biol.*, **4**, 18 (1936).
14. A. S. BROWN AND D. A. MACINNES, *J. Am. Chem. Soc.*, **57**, 1356 (1935).

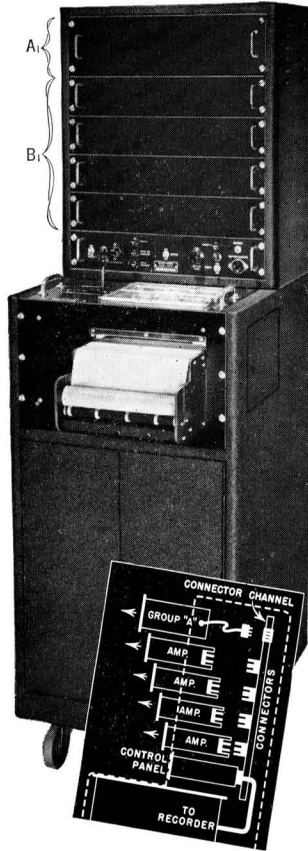
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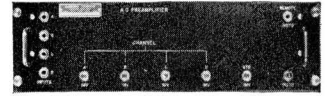
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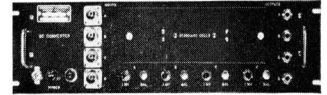
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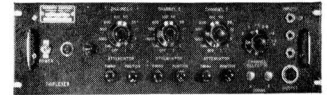
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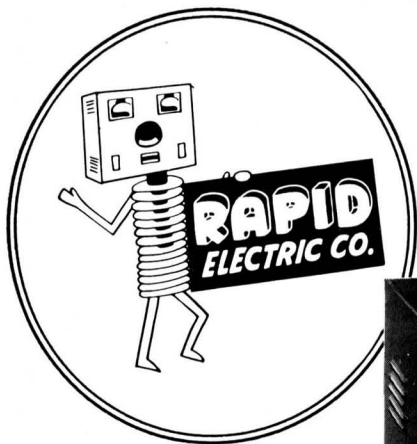
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Coulometry—Related Phenomena of Electrolysis and Current-Sweep Polarography¹

N. Howell Furman²

Introduction

For several recent years, a number of new or modified aspects of electroanalytical methods have been studied in our laboratories. Recently, emphasis has shifted to the determination of substances in the milligram range and lower, down even to the submicrogram range. Our first war-time research in 1942 evolved a procedure that consisted in the electrolysis of traces of metals such as copper, lead, cobalt, cadmium, iron, nickel, zinc, etc., into a small mercury cathode, followed by removal of the mercury by distillation and polarographic or spectrophotometric examination of the residue (1). During war-time, it was not possible to explore other techniques for estimating the metals that were present in the mercury cathode. It was recognized that, without exceedingly careful technique and proper admission of air (oxygen) during the distillation, the more volatile metals such as cadmium might be lost. Subsequently, Cooper (2) investigated the determination of other metals amalgamated with mercury by making the amalgam the anode in a capillary dropping assembly and taking polarograms. This technique gave good qualitative information and semiquantitative results, even on five-component mixtures. The results with simpler amalgams appear to be of interest in connection with the determination of the diffusion coefficients of metals in mercury as solvent medium (3).

Recently, Rogers and coworkers (4) and Cooke (5) have had good success in using coulometric or polarographic techniques of combined methods in estimating submicrogram amounts of metals electrolyzed into mercury.

Schmidt (6) has found that controlled potential electrolysis of a dilute amalgam as anode permits one to electrolyze out and determine elements such as copper, lead, cadmium, and zinc, whereas the passive metals, cobalt and nickel, in presence of excess of iron do not electrolyze out. He has demonstrated that amounts of the first four metals ranging from a few micrograms up to several milligrams may be removed from the mercury and then estimated polarographically. Presumably the passive metals may then be recovered by distillation of the mercury and estimated by polarographic, spectrophotometric, or other methods.

The developments thus far mentioned have been concerned primarily with electrolysis and polarography. The present paper is concerned primarily with coulometry.

Coulometry

Coulometric methods have been open for development since the publication by Faraday of his fundamental laws of electrolysis. For a great many years, the classical coulometric method with cells in series has been studied in courses in physical chemistry, or for fundamental standardization purposes (7).

The technique has been advocated for the precise determination of equivalent weights (8). Recently there has been a very decided increase in interest in various coulometric methods for analytical and other purposes.

Controlled potential electrolysis in conjunction with series oxyhydrogen coulometers has been developed by Hickling (9) and by Lingane (10).

A fundamental idea that is essential to a number of modern developments in coulometry for analytical purposes is that of the addition of a substance to a solution for the purpose of generating therefrom at 100% current efficiency a reagent to carry out a definite chemical reaction, thus dispensing with the necessity of preparing and storing standard solutions. This mode of approach seems to be due to Szebelledy and Somogyi (11) who studied brominations and neutralizations in this fashion. They did not appear to realize the full advantages and simplicity of the approach since they used indicators to detect end points and a series silver coulometer for current integration. They achieved a high degree of precision.

It is of interest that some of the present popularity of the coulometric method is due, in part at least, to early studies on surface coatings and corrosion films. Among the earliest of modern studies along this line is one by Grower (12) on the thickness of tin coatings on copper wires. His apparatus is represented schematically in Fig. 1. He was able to differentiate between the pure tin layer and the underlying layer, and also visually when the intermediate layer of copper-tin alloy was dissolved and the pure copper color appeared. Gas coulometers were used for the quantitative measurements.

A very significant development is contained in a study by Campbell and Thomas (13) on the thickness of experimental corrosion or tarnish films of oxide of sulfide or mixtures of oxide and sulfide on pure copper or silver foils. This paper clearly demonstrates the principle of electrolysis at constant current with simple measurement of time to a potentiometric end point or a succession of such points. This type of study has recently been repeated by Allen (14) who found that purest copper, after cleaning by electrolytic polishing and transfer to a system that could be evacuated, developed a film of cuprous oxide of average thickness of 6.5 Å, whereas exposure to air from 0.5 hr typically developed a 15 Å film, whereas after several hours in dry air the films grew to 20–25 Å thickness. The effect of different techniques of washing after polishing could be clearly examined.

The anodic stripping of electrolytic coatings by a constant current to a potentiometric cutoff point was developed by Francis (15) as a convenient method for estimating the thicknesses of electrodeposited coatings of one metal on another.

The evolution of the modern application of the coulometric method to general classes of reactions in solution received its major recent advance from the extensive series of researches by Swift and his associates (16) who have given the name "coulometric titration" to the process of development of a

¹ Palladium Medal Address delivered at the Wrightsville Beach Meeting, September 15, 1953.

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determination, whereas in many inorganic estimations small samples can be added to the solution and titrated without adding a fresh generating solution. Hydroquinone has been titrated successfully with errors averaging 0.5% in the range 100–300 micrograms of hydroquinone, 2% in the 12–90 microgram range, and 3% in the 1–3 microgram range (27).

Determinations with photometric indication in the ultraviolet range have been made by J. W. Handleman (unpublished) for the bromination process. The coulometric generator electrodes were inserted in the solution that was contained in the special cell described by Bricker and Sweetser (28). The bottom of this cell was of dimensions to fit the 1-cm compartment of the Beckman DU spectrophotometer. Brominations of 60–80 micrograms of resorcinol gave an average error of 0.4%. These studies make it apparent that one might combine all the advantages of photometric estimations with the coulometric determination principle, such as generation of successive known amounts of reagent beyond the end point.

Current-Sweep or Potentiometric Polarography

Polarization curves on background medium and medium plus reagent are useful in coulometry as well as in various electrochemical methods. It was found profitable to build a number of resistor decades of such characteristics that current could be increased by definite increments. Current voltage curves were then taken by reading emf between reference electrode and generator electrode positioned to avoid or minimize IR drop (29). Later, a continuously variable current was applied more conveniently with the aid of a triode, the grid of which was varied in voltage to give an essentially linear current in the plate circuit. The actual electrode and cell to be used in a coulometric process could be thus used to determine current efficiency for the generation of a reagent. This procedure gives a conservative estimate of the permissible conditions for generation with substantially 100% efficiency. A comprehensive discussion and analysis of the utilization of polarization curves in analytical electrochemistry has recently appeared from the Ecole Supérieure laboratory in Paris (30).

In sweeping the current it was observed that polarograms could be constructed manually at rotating platinum electrodes with less tendency to form time maxima or rounded humps at the usual point where maxima are apt to occur when the voltage is increased point by point. Later experiments (unpublished) with automatic current-sweep were disappointing with solid electrodes, but preliminary observations indicate that there may be desirable features in the current-sweep idea as applied to the dropping capillary mercury electrode. These possibilities are being explored further by R. N. Adams.

Other Coulometric Techniques

The coulometric titration technique may obviously be utilized with any valid type of end-point indication. Various potentiometric, amperometric, and photometric procedures have been tested and there are many other possibilities which have already been used or will lend themselves to give automatic end points, actuate control devices, etc. Carson has developed automatic devices (31) and has used the derivative polarographic idea (32) in good advantage for indication when the solution must be heated during coulometric titration.

Automatic methods.—Analysis and probably control of gas or liquid streams is possible by mixing sample and reagent in a fixed ratio by a proper pump or other mixing device. The current that is needed to keep the mixture continually titrated to a definite index point may be calibrated in terms

of concentration of the substance titrated. The general form of apparatus is indicated schematically in Fig. 3. This type of coulometric application was first described by Shaffer and coworkers (33).

Automatic titration to an end point is possible in batch operations, and a suitable analytical system has been described by Carson (34).

Coulometric generation of standard solutions.—It is possible to generate certain solutions coulometrically at constant current in a portion of the apparatus that is external to the solution to be titrated. DeFord and associates (35) have demonstrated the desirability of this procedure by generating alkali from sodium sulfate, the cathode and anode process being separated by a diaphragm of glass wool in an inverted U-tube with inlet tube at the bottom of the U. This mode of procedure obviously is capable of extension through many branches of volumetric analysis. The resultant change in volume of the solution titrated is a possible unfavorable factor for micro applications.

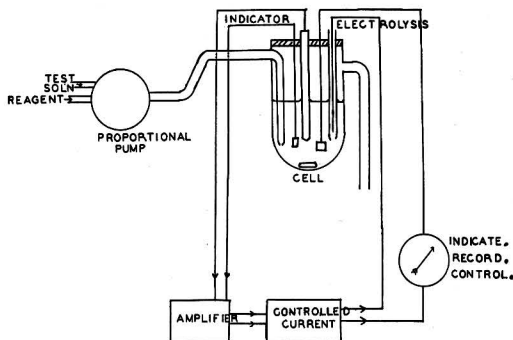


Fig. 3. Coulometric indication in testing flow systems. The indicator circuit activates the current control so that the mixture of reagent and test solution or gas is titrated constantly to maintain a predetermined value of the indicating system.

The constant current-time principle has been used from time to time to generate hydrogen or oxygen to be added as a known component of a gaseous mixture, to prepare dilute standard solutions of various sorts, and probably for other uses.

This review has not been designed to be all-inclusive but rather to describe some recent developments that have made coulometry of increasing analytical usefulness. The majority of papers that have not been mentioned here can be readily located through the papers cited or through a review paper that appeared recently (36).

Acknowledgment

This award of the Palladium Medal is obviously in recognition of a long-continued group effort involving colleagues and students. It is a pleasure to acknowledge the writer's thorough training in research in analytical electrodeposition under the guidance of the late Professor L. W. McCay, and the excellent instruction in electrochemistry, especially potentiometry, conductometry, and classical coulometry that was given by Professor Emeritus G. A. Hulett in his graduate laboratory course. This instruction led to association with Dr. I. M. Kolthoff in the authorship of "Potentiometric Titrations." With few exceptions, the doctoral theses of the writer's graduate students have been in the field of electrochemical studies as applied in chemical analysis. A number of

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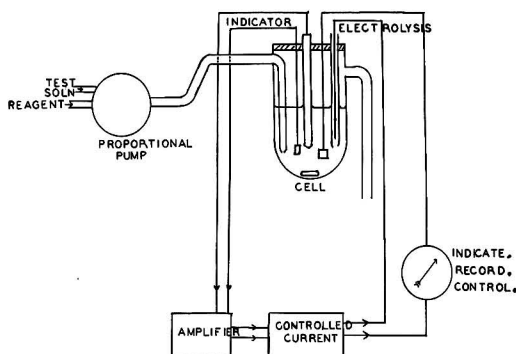


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undergraduate researches of supervisees have also been in this field, and a number of these have been published. These various efforts have served as the basis for the award.

REFERENCES

1. N. H. FURMAN, C. E. BRICKER, AND B. MCDUFFIE, *J. Wash. Acad. Sci.*, **38**, 159 (1948).
2. N. H. FURMAN AND W. C. COOPER, *J. Am. Chem. Soc.*, **72**, 5667 (1950).
3. W. C. COOPER AND N. H. FURMAN, *ibid.*, **74**, 6183 (1952).
4. S. S. LORD, JR., R. C. O'NEILL, AND L. B. ROGERS, *Anal. Chem.*, **24**, 209 (1952).
5. W. D. COOKE, *ibid.*, **25**, 512 (1953).
6. W. E. SCHMIDT, Dissertation, Princeton University, Princeton, N. J. (1953).
7. E. B. ROSA AND G. W. VINAL, *Bull. Bur. Standards*, **13**, 479 (1916); *Proc. Nat. Acad. Sci. U. S.*, **3**, 59 (1917).
8. E. L. QUINN AND G. A. HULETT, *J. Phys. Chem.*, **17**, 770 (1914); an illustration of this type of research is given in this work.
9. A. HICKLING, *Trans. Faraday Soc.*, **38**, 27 (1942).
10. J. J. LINGANE, *J. Am. Chem. Soc.*, **67**, 1916 (1945).
11. S. SZEDELLEDY AND Z. SOMOGYI, *Z. anal. Chem.*, **112**, 313, 323, 332, 385, 391, 395, 400 (1938).
12. G. G. GROWER, *Am. Soc. Testing Materials, Proc.*, **II**, **17**, 129 (1917).
13. W. E. CAMPBELL AND U. B. THOMAS, *Trans. Electrochem. Soc.*, **76**, 303 (1939).
14. J. A. ALLEN, *Trans. Faraday Soc.*, **48**, 273 (1952).
15. H. T. FRANCIS, *This Journal*, **93**, 79 (1948), C. T. KUNZE AND A. R. WILEY, *ibid.*, **99**, 354 (1952).
16. S. W. SEASE, C. NIEMANN, AND E. H. SWIFT, *Anal. Chem.*, **19**, 197 (1947).
R. J. MYERS AND E. H. SWIFT, *J. Am. Chem. Soc.*, **70**, 1047 (1948).
D. J. MEIER, R. J. MYERS, AND E. H. SWIFT, *ibid.*, **71**, 2341 (1949).
R. A. BROWN AND E. H. SWIFT, *ibid.*, **71**, 2717 (1949).
W. S. WOOSTER, P. S. FARRINGTON, AND E. H. SWIFT, *Anal. Chem.*, **21**, 1457 (1949).
W. J. RAMSAY, P. S. FARRINGTON, AND E. H. SWIFT, *ibid.*, **22**, 332 (1950).
P. S. FARRINGTON AND E. H. SWIFT, *ibid.*, **22**, 889 (1950).
17. R. P. BUCK, P. S. FARRINGTON, AND E. H. SWIFT, *ibid.*, **24**, 1195 (1952).
18. P. S. FARRINGTON, D. J. MEIER, AND E. H. SWIFT, *ibid.*, **25**, 591 (1953).
19. F. I. TRISHIN, *Zhur. Anal. Khim.*, **3**, 21 (1948).
20. J. EPSTEIN, H. A. SOBER, AND S. D. SILVER, *Anal. Chem.*, **19**, 675 (1947).
21. C. N. REILLEY, W. D. COOKE, AND N. H. FURMAN, *ibid.*, **23**, 1030 (1951); *ibid.*, **24**, 1044 (1952).
22. W. D. COOKE AND N. H. FURMAN, *ibid.*, **22**, 896 (1950).
23. N. H. FURMAN, W. D. COOKE, AND C. N. REILLEY, *ibid.*, **23**, 945 (1951).
24. W. D. COOKE, C. N. REILLEY, AND N. H. FURMAN, *ibid.*, **23**, 1662 (1951).
25. N. H. FURMAN, C. N. REILLEY, AND W. D. COOKE, *ibid.*, **23**, 1665 (1951).
26. N. H. FURMAN, C. E. BRICKER, AND R. V. DILTS, *ibid.*, **25**, 482 (1953).
27. W. D. COOKE, C. N. REILLEY, AND N. H. FURMAN, *ibid.*, **24**, 205 (1952).
28. E. MÜLLER, "Elektrometrische (potentiometrische) Massanalyse," 6th ed., p. 52, Steinkopf (1942); lithoprinted by Edwards Bros., Ann Arbor, Mich. (1945).
29. R. N. ADAMS AND N. H. FURMAN, *Anal. Chem.*, **25**, 1564 (1953).
30. C. E. BRICKER AND P. B. SWEETSER, *Anal. Chem.*, **24**, 409 (1952).
31. R. N. ADAMS, C. N. REILLEY, AND N. H. FURMAN, *ibid.*, **25**, 1160 (1953).
32. R. GAUGUIN, *Anal. Chim. Acta*, **7**, 172 (1952).
R. GAUGUIN, *ibid.*, **7**, 360 (1952).
R. GAUGUIN AND G. CHARLOT, *ibid.*, **7**, 408 (1952).
R. GAUGUIN AND G. CHARLOT, *ibid.*, **8**, 65 (1953).
J. BADOZ-LAMBING, *ibid.*, **7**, 585 (1952).
33. W. N. CARSON, JR., *Anal. Chem.*, **25**, 466 (1953).
34. C. N. REILLEY, W. D. COOKE, AND N. H. FURMAN, *ibid.*, **23**, 1223 (1951).
35. P. A. SHAFFER, JR., A. BRIGLIO, AND J. A. BROCKMAN, JR., *ibid.*, **20**, 1008 (1948).
36. W. N. CARSON, JR., *ibid.*, **25**, 226 (1953).
37. D. D. DEFORD, J. N. PITTS, AND C. J. JOHNS, *ibid.*, **23**, 938 (1951); *ibid.*, **23**, 941 (1951).
38. P. S. TUTUNDZIC, *Anal. Chim. Acta*, **8**, 168 (1953); *ibid.*, **8**, 182, 184 (1953).

Nathaniel Howell Furman—The Man and His Work

R. M. Burns¹

I can think of no more agreeable way to end a vacation in Maine than to fly down here today to tell you what I know about the 1953 Palladium Medalist. I first met Howell Furman in 1919 upon my return to Princeton from the war. He too was out of uniform and had joined the Princeton faculty as assistant professor after having taught at Stanford University. A native of New Jersey, his trip to California had impressed him with the wild and Gargantuan qualities of the West. He has been satisfied ever since to live in the East.

Our medalist's choice of New Jersey as a state in which to be born may be considered as very early evidence of prophetic vision, for New Jersey with its billion dollar chemical industry leads the nation in chemical manufacture and in number of chemists. The village of Lawrenceville, near Princeton, has the distinction of claiming him as a native son. Here as a

boy, he worked summers in his father's old fashioned general store, the town's headquarters, which also housed the post office. An additional source of income was the sale of lost golf balls which, in spare moments, he hunted on the Lawrenceville School golf course across the street from his home. No doubt it was this early acquaintance with golf balls that led to his later addiction to the game. Not that he has ever let golf seriously interfere with chemistry. Indeed he originated the saying that: "He who shoots 100 has no business playing golf; he who shoots 80 has no business." I am not sure where this leaves President Eisenhower.

To go back to Lawrenceville, it was natural that he should go to the well-known boy's school there and on to Princeton. At the latter, he impressed both teachers and members of the class of 1913, and was thought likely to succeed.

Another important vital statistic concerns Lawrenceville, for there lived in that town the attractive Hannah Henderickson, sister to Furman's close companion at Lawrenceville

¹ Bell Telephone Laboratories, Inc., Murray Hill, New Jersey.

and Princeton. Now, the results of a joint research, carried out in Duluth by investigators from the universities of Maryland and Minnesota, show that 42% of the marriages in Duluth were of couples living within 20 blocks of each other. Those familiar with the size of Lawrenceville will understand that on this basis alone the marriage of Miss Henderickson and our medalist was inevitable. This took place in 1919, and now, 34 years later, I merely observe that both must be complimented for good judgment. There is a son, Richard Howell, and a daughter-chemist, Carol, who married and as Mrs. Samuel Kirkwood, wife of a biochemist, has provided three grandchildren. The principal attraction of Vermont where the Furmans spend the summer is the visit with these youngsters and their parents. Of course, there are golf courses in the Green Mountains and Lake Champlain has offered sailboat-racing. As far as I can discover, Howell Furman has not walked the 260 miles of the Long Trail—Vermont's greatest asset; he prefers the automobile as a means of locomotion. He indulged in his first Chevrolet in 1924 and, since that time, has proved himself General Motors' best customer by wearing out eight more Chevies.

This stick-to-it-iveness is characteristic of our medalist. It finds expression in his loyalty to friends, to Princeton, and to his profession, in the diligence and care with which he prepares his lectures, and the persistence with which he pursues his researches. Studious, reserved, but friendly, Furman is well known for his dry humor and his apt and entertaining stories. He is so conscientious and dependable that he finds himself all too often appointed to some committee, the members of which usually permit him to do all of the work.

When he entered the Princeton Graduate School, Furman came under the influence of Professor Leroy McCay who had been a student of Bunsen. A teacher of great enthusiasm and energy, insatiable curiosity, and strong optimism, McCay inspired his student with these qualities and Furman, in turn, has transmitted the spirit of research and the urge to teach to present-day students. Commenting on graduate training, Furman has stated:

"The spirit of research is, I believe, essential to the best of advanced university training, provided one always keeps in mind the fact that our primary purpose is to assist in the education of our students."

The importance of experimentation and knowledge of the scientific literature has always been stressed at Princeton. Furman's remote predecessor, John MacLean, who became professor of chemistry in 1795 and was thus the first to hold this post in an American college, offered the following advice to the president of Yale College: "Be as obliging as to inform Dr. Dwight that I am of the opinion that it is impossible for me to acquire even a slight knowledge of chemistry without either making experiments or seeing them performed and that to become proficient in the science will require extensive reading . . . the most valuable part of chemical writings is to be found in the publications of the different learned societies in Europe. . . ."

As chairman of the Department, Professor Furman has added administrative work to his teaching and research by merely adding more working hours to the day. He has devoted fruitful effort to long range planning as well as to the more immediate administrative affairs. With his usual conscientiousness, he has given much thought to the problems that confront academic institutions and their young scholars—scientists and teachers these days. However, in spite of many duties and responsibilities, he continues to find time for personalized teaching and never misses spending an after-

noon a week in the laboratory instruction of undergraduate students.

Early in his career, Furman recognized the need for improved textbooks for teaching analytical chemistry and so he translated for American use Kolthoff's books on indicators and volumetric analysis. A little later, he wrote with H. H. Willard "Elementary Quantitative Analysis, Theory and Practice," the leading college text on the subject (shortly to come out in its 4th edition). It has been translated into German and Spanish. Finally, Professor Furman is Editor-in-Chief and contributor of several chapters of Scott's "Standard Methods of Chemical Analysis," that essential reference work for all analytical laboratories.

Our medalist's scientific work has found publication in more than 80 papers. He has applied and extended the use of electrochemical principles to the purposes of analytical chemistry with great imagination and skill. He is distinguished for his pioneer work in the field of potentiometric titrations. Pointing out the value of electrochemistry in the teaching of chemical analysis, he has proceeded to illustrate the thesis by originating new and more sensitive electrometric methods based on potentiometry, amperometry, coulometry, and polarography. A large part of Dr. Furman's research has been associated in one way or another with oxidation-reduction reactions. Early potentiometric studies utilizing ceric sulfate as an oxidant are described in more than a dozen papers which show the advantages of this now widely used reagent. From this potentiometric basis, it was natural that he should undertake projects in the related fields of electrodeposition, polarography, and coulometric titrations.

Dr. Furman and his students have developed techniques along these lines that are of great value in trace metal analysis. One scheme involves the electrodeposition of trace metals in a mercury cathode, distillation of the mercury, and polarographic analysis of the residue. Another method consists in coulometric titration with electrolytically generated ceric ions in a ferric sulfate medium. In this case, quantities of uranium as small as 5 micrograms can be determined with good accuracy and precision by the oxidation of quadrivalent uranium, using a cadmium amalgam reductor for the prior reduction of the uranium from the hexavalent to the quadrivalent state and employing a sensitive amperometric end point.

Professor Furman contributed significantly to the Manhattan—or atomic bomb—project. Faced with the problem of detecting uranium and transuranic elements in the presence of almost every other element and of determining many of the common elements in the presence of uranium, the group under his leadership successfully devised the necessary procedures. Among the several techniques that have been declassified and summarized in a National Nuclear Energy monograph is that of extracting trace elements as cupferrate complexes with organic solvents. It is not exaggeration to say that Professor Furman's efforts in the field of extraction were instrumental in the development of the large-scale production of vital ingredients for the atomic bomb. That this work involved long hours and required communication of reports and ideas as well as experimentation and administrative duties is evident from the fact that the night girl at Western Union used to say: "As soon as I get the call from N. H. Furman, I know it is time to close up the office."

Our medalist has received many honors and has engaged in many extracurricular activities. Phi Beta Kappa and Proctor fellow at Princeton, Robert Stuart Brokos fellow for study abroad; at various times associate editor of *Chemical*

Reviews and Analytical Edition of Industrial and Engineering Chemistry and advisor to its successor *Analytical Chemistry*. He was the first recipient of the Fisher Award for achievement in analytical chemistry. A member of many technical societies, he joined The Electrochemical Society in 1920 and has published several papers in its *TRANSACTIONS*. He was president of the American Chemical Society during its Diamond Jubilee year, and thus, in connection with the International Congress of Pure and Applied Chemistry, represented American chemistry in its largest world-wide interaction. The following excerpts from his presidential address indicate his broad vision of the responsibilities of chemists in modern society:

"It is certain that future efforts of chemists and chemical engineers will, if properly utilized, be a most powerful constructive force for the future welfare of mankind. . . . Let us resolve to use our skills and talents together with whatever persuasive powers we may possess toward every constructive activity for the future benefit of mankind."

A distinguished Princeton classmate of Professor Furman adds the following touch to the portrait I have tried to sketch:

"To my mind, Howell's outstanding trait is his unselfishness. However, his unselfishness is of a rare type, so unobtrusive that one may have to know him for years before becoming aware of it. He is extremely helpful to other people, but he gives his help so casually that he is likely to go unthanked. He talks very little about doing the right thing, but simply does it as a matter of course, demanding nothing for himself in return.

"Of all the incidents in life which have built up my faith in human nature, the outstanding one was the action of the American Chemical Society in selecting as its President a man who had asked for himself as little as Howell Furman."

Over the fireplace in the Frick Chemical Library at Princeton is an inscription attributed to the mathematician Ptolemy which may be translated "He is not dead who hath given new life to Knowledge." In this light, our medalist radiates great vitality.

So Ladies and Gentlemen, I give you Nathaniel Howell Furman, Educator, Scientist, Gentleman, and leader in American analytical chemistry.

MANUSCRIPTS AND ABSTRACTS FOR SPRING MEETING

Manuscripts are now being received for the Spring Meeting of the Society, to be held at the La Salle Hotel in Chicago, May 2, 3, 4, 5, and 6, 1954. Subjects to be covered at the technical sessions will be Electric Insulation, Electronics, Electro-Organic Chemistry, Industrial Electrolytics, and Theoretical Electrochemistry.

To be considered for this meeting, triplicate copies of manuscripts or abstracts (not to exceed 75 words in length) must be received at Society headquarters, 216 West 102nd Street, New York 25, N. Y., *not later than January 15, 1954.*



Bureau of Standards Vindicated in AD-X2 Dispute

A special committee of the National Academy of Sciences has confirmed the much-disputed finding of the Bureau of Standards that a battery additive, AD-X2, is worthless but harmless, and has found the Bureau's battery work is "excellent."

The report released by Secretary of Commerce, Sinclair Weeks, on November 13 was unequivocal in praising the work of the Bureau of Standards and in confirming the Bureau's finding that AD-X2 is without merit. The report states, "We conclude from our studies and investigations that the quality of the work of the National Bureau of Standards in the field of lead acid battery testing is excellent. This statement is made without reservations. Our opinion is that the quality of the work of the Bureau in this field is better now than at any time in the past. This is partly because of the closer cooperation of the Bureau's Statistical Engineering Laboratory with the Electrochemical Section in the design and interpretation of battery tests."

Summary of Finding on AD-X2

Following is the Committee's finding on AD-X2: "We find no data obtained from any well-designed scientific experiment which is inconsistent with the hypothesis that AD-X2 behaves like a corresponding mixture of sodium and magnesium sulfates, and is substantially neutral in its effect upon a lead acid storage battery. These experiments included a total of over 400 cells, a substantial number of which were selected or approved for tests by Pioneers." Conclusion on AD-X2: "We conclude that the relevant data now available to us regarding the effects of AD-X2 are adequate to support the position of the National Bureau of Standards that the material is without merit." The committee recommended that no further tests be undertaken by the committee or under its supervision.

This culminates one of the most bizarre episodes in the history of the

Bureau. Last March the Secretary of Commerce, Sinclair Weeks, brought down on his head a storm of protest when he dismissed Allen V. Astin from his post as Director of the National Bureau of Standards, giving as one of his reasons his feeling that the Bureau had been unfair in its testing of the battery additive. Astin defended the Bureau's work. The widespread publicity attending the dispute raised considerable question in the press as to the integrity and objectivity of the personnel at N. B. S.

ECS Protest

The Electrochemical Society, as well as the majority of the nation's other scientific societies, promptly protested and asked a review of the facts by a competent scientific body. Secretary Weeks temporarily reinstated Dr. Astin and asked Dr. Detlev W. Bronk, President of the National Academy of Sciences, to appoint a committee to review the work of the Bureau in the field of battery additives and to make such additional tests as might be needed to settle the question as to the merits of AD-X2. Since that time Craig Shaeffer, formerly Assistant Secretary of Commerce, who had investigated the problem for Mr. Weeks and had recommended Astin's dismissal, has resigned his post and Dr. Astin has been permanently reinstated. Secretary Weeks has expressed himself as gratified at the vindication of the Bureau and at Dr. Astin's willingness to remain as Director.

In 1948, Pioneers, Inc., manufacturers of AD-X2, protested the fact that the Bureau of Standards would not make a specific exception in the case of their product from its general finding that no battery additive had been proved to have substantial merit. Since there was no indication that AD-X2 was different in any important way from many other similar mixtures of sodium and magnesium sulfates which were known to be worthless, the Bureau

was unable to change its position. After the Post Office Department started proceedings to issue a fraud order against Pioneers, Mr. Jess Ritchie, president of the company, appealed to the Select Committee on Small Business of the U. S. Senate to investigate alleged discrimination against his product. Further tests of AD-X2 were made by N. B. S. during the summer of 1952 which, the Bureau concluded, confirmed their earlier findings. Pioneers charged that these tests had been improperly conducted and refused to accept the report. The Senate Committee then arranged for independent tests to be made at the Massachusetts Institute of Technology. A report of this work, issued by the Senate Committee on December 18, 1952, was accompanied by a press release and a commentary by Dr. Keith J. Laidler, consultant to that committee and a former consultant to Pioneers. Dr. Laidler stated that the M.I.T. tests "demonstrate beyond a reasonable doubt that this material is in fact valuable and give complete support to the claims of the manufacturer." He then went on to criticize severely the tests made by the Bureau of Standards and other government agencies and to question the objectivity of the investigators. These charges made headline news in the nation's papers and after the change of administration in January, the new Secretary of Commerce asked his assistant Mr. Shaeffer to look into the Bureau's handling of the case, with the result that in March Dr. Astin was asked to resign.

On May 4, Secretary Weeks asked Dr. Bronk to appoint a committee of scientists to review the entire problem. In July, the committee, headed by Zay Jeffries, retired Vice-President of the General Electric Company, Chemical Division, was commissioned to review the work of the Bureau of Standards relating to Battery AD-X2. They were instructed to proceed as they thought best, to appraise the Bureau's work and procedures, and to perform such addi-

tional tests as seemed necessary and desirable. The ten-man committee, made up of scientists from seven universities, the Rockefeller Institute, and two industrial concerns, found itself faced with thousands of pages of testimonials, statements, reports, and experimental data. After careful and detailed study of the available material, the Jeffries Committee decided that the differences between treated and untreated cells, if any, were too small to be detected in any except the most carefully controlled tests. The M.I.T. report, so highly regarded by Dr. Laidler and so frequently quoted as evidence of the Bureau's errors, was found by the Committee to be too limited in scope to determine the merits of the additive. It was noted that the report does not even purport to evaluate AD-X2 and that the tests were only exploratory in nature and "appear not to have been designed for the purpose of evaluating AD-X2."

Only 4 Well-Controlled Tests Made

The Jeffries Committee based its findings on four sets of well-controlled tests, the general design of which was proposed by Mr. Ritchie. Three of these tests were done for Pioneers, Inc. The remaining data were those obtained by the Bureau of Standards since 1951. In reports which came to light after the close of the Senate Small Business hearings in June, Professor T. P. Dirkse, of Calvin College, Grand Rapids, Michigan, and Dr. R. S. Dean of the Chicago Development Company of Riverdale, Maryland, had each concluded that their respective tests had shown no significant difference between cells treated with AD-X2 and untreated controls. The United States Testing Company of Hoboken, New Jersey, reported some effects which might have indicated some merit for the additive. Careful study of the supporting data convinced the Jeffries Committee that one of the differences reported probably resulted from poor control of experimental conditions and that the other effect, while statistically significant, is of no practical importance and, as shown by the Bureau's studies, is one which disappears with subsequent charging.

The Committee found no effects of the additive large enough to be of practical value and such effects as were observed corresponded to well-known laws of physical chemistry. In no case was the behavior of AD-X2 different from that of a corresponding simple

mixture of sodium and magnesium sulfates.

The membership of the Committee was as follows: Zay Jeffries, Chairman, Vice-President (Retired), General Electric Company, Chemical Division; Elmer K. Bolton, Director of Chemical Department (Retired), E. I. du Pont de Nemours and Company; William G. Cochran, Professor of Biostatistics, Johns Hopkins University; J. P. Fugassy, Professor of Physical Chemistry, Carnegie Institute of Technology; John G. Kirkwood, Professor of Chem-

istry, Yale University; Victor K. LaMer, Professor of Chemistry, Columbia University; Lewis G. Longworth, Member, Rockefeller Institute for Medical Research; Joseph E. Mayer, Professor of Physical Chemistry, University of Chicago; Fred E. Terman, Dean, School of Engineering, Stanford University; Samuel S. Wilks, Professor of Mathematical Statistics, Princeton University. Charles I. Campbell of the National Academy of Sciences staff served as Secretary.—UBT

New "Modern Electroplating" Now Available

"Modern Electroplating" is now available from the publisher, and with its publication John Wiley & Sons launches a definitive series of books developed and sponsored by The Electrochemical Society. Allen G. Gray, technical editor of *Steel*, edited the new volume.

An integrated book containing the latest theory and practical aspects, "Modern Electroplating" originated as the published papers and discussions of the 1941 symposium of the Society. These and additional studies, completely revised and rewritten by 39 specialists, form the present work.

As a result of this combined effort, all the common metals and alloys and their accepted plating methods are covered. Uncommon metals and their potentials are also reviewed, and the specialized problem of plating on aluminum and magnesium considered. Each chapter is organized according to this pattern: principle; function of constituents of bath; operating conditions; maintenance and control; preparation of basis metals; and finishing of deposits.

Professor M. L. Holt of the Chemistry Department, University of Wisconsin, is assistant editor of the volume. The Editorial Advisory Board consists of William Blum, Charles L. Faust, A. Kenneth Graham, Henry B. Linford, Frederick A. Lowenheim, Harold J. Read, Ralph A. Schaefer, and Richard M. Wick. The new volume, containing 563 pages, is priced at \$8.50, and can be obtained from John Wiley & Sons, Inc., 440 Fourth Ave., New York 16, N. Y.

Members of The Electrochemical Society should send their orders for the volume direct to Society headquarters, 216 West 102nd Street, New York 25, N. Y., in order to obtain the 33 $\frac{1}{3}$ % discount given members. If a remittance of \$5.67, payable to John Wiley & Sons, is included with the order sent to Society

headquarters, members will not be billed for postage. However, members living in New York City must also include an additional 17¢ for city sales tax.

"The Corrosion Handbook," edited by H. H. Uhlig and published by John Wiley & Sons in 1948, was also sponsored by the Society and has therefore been included under the new official heading, The Electrochemical Society Series. Forthcoming volumes are planned which will be of interest to those already in the electroplating industry and also to industries that contemplate using electroplating processes to advantage.

Chemical Profession in Cleveland Makes Awards

The Fifth Annual Dinner of The Chemical Profession in Cleveland (sponsored by a joint committee representing The American Chemical Society, Alpha Chi Sigma, American Institute of Chemical Engineers, The Electrochemical Society, and American Institute of Chemists), was held on November 11, 1953 at the Hollenden Hotel, with more than 400 chemists and guests in attendance.

The feature address was given by Nobel Laureate, Professor Harold C. Urey, of The Institute of Nuclear Studies, University of Chicago, on the subject "Cosmic Chemical Engineering." Dr. Urey demonstrated the application of the disciplines and techniques of chemistry and chemical engineering in the study of the theories of the earth's origin, and emphasized the need of the chemists' cooperation with other sciences in determining the ultimate solution of this and other cosmological problems.

Four chemists were honored by their colleagues with The Cleveland Award for distinguished service to the chemical profession. The award recognized not only their personal scientific achieve-

ments, but especially their unselfish and persevering effort in promoting the effectiveness of the one or more professional societies which they have served. Dr. A. G. Bowers (President, The Gerson-Stewart Corporation) presented the certificates of merit to:

Gordon M. Juredine: Research chemist with The Harshaw Chemical Company; past chairman of The Cleveland Section, American Chemical Society; active member of The American Institute of Chemists; former editor of *Isotopics* (A.C.S. publication, Cleveland Section); served on the National Council of both A.C.S. and A.I.C.; and has been a leader in the fight for legal and professional recognition of chemists.

George W. Heise: National Carbon Company, retired in 1953; one of the founders of The Cleveland Section and also National President (1947) of The Electrochemical Society; a lifetime of active service to The Electrochemical Society, American Chemical Society, Alpha Chi Sigma, Sigma Xi, Faraday Society, and Phi Lambda Upsilon. Distinguished for his scientific achievements in industrial electrochemistry, and an elder statesman who encouraged and educated a great number of younger chemists to active service in the various chemical societies.

Raymond W. Erwin: National Carbon Company, retired in 1946; active leadership of numerous program committees to promote effectiveness of local sections of American Chemical Society, Electrochemical Society, Alpha Chi Sigma, and other Cleveland technical organizations. His 36 years' service, particularly in promoting the cooperation of chemical societies in civic activities, have done much to establish the prestige of the chemical profession in Cleveland.

Curry E. Ford: National Carbon Company; member of the ASTM, The Electrochemical Society, and American Institute of Chemical Engineers (past chairman, Cleveland Section, 1947). Particularly distinguished for active leadership in the latter organization, and in committee work in promotion of the technical and civic responsibilities of chemical engineers.

The fact that the nominations for the first Cleveland Award singled out three men from the same organization implicitly honors the policy of more than 30 years' duration of The National Carbon Company in encouraging the extracurricular activities and professional growth of chemists through their societies.

DIVISION NEWS

Theoretical Electrochemistry Symposium Scheduled for Chicago

The Theoretical Division of The Electrochemical Society is planning a symposium on "Special Methods in Electrochemistry" for the spring meeting of the Society in Chicago, May 2-6, 1954. The symposium will consist of both invited and contributed papers on such special phases as a-c electrolysis, amperometric techniques, oscillographic studies, tracer techniques, and the use of ultrasonics in electrochemistry.

Authors having material appropriate for this symposium should send five copies of a 75-word abstract to Society headquarters, 216 West 102nd Street, New York 25, N. Y., and a single copy of the abstract to Ernest Yeager, Vice-Chairman, Theoretical Electrochemistry Division, Department of Chemistry, Western Reserve University, Cleveland 6, Ohio, as soon as possible and certainly no later than January 15, 1954. Those desiring publication of their papers in the *JOURNAL* should submit three copies of the manuscript to Society headquarters.

SECTION NEWS

Chicago Section

The speakers for the October 2 meeting of the Chicago Section were three university students. The speakers and their subjects were:

1. E. P. Marbach, one of Professor H. J. McDonald's students in the Graduate School and Stritch School of Medicine of Loyola University of Chicago, "Some Clinical Chemical Applications of Electromigration in Stabilized Electrolytes."

2. R. E. Meeker, an Abbott Research Assistant to Professor Ralph Pearson of the Chemistry Department of Northwestern University, "Electrochemical Study of Fast Ionic Reactions."

3. M. E. Melnichak, working under Professor Warren Johnson of the Chemistry Department of the University of Chicago, "Detection and Determination of Chromium Ion Intermediates in Chromate Reductions."

At the November 6 meeting of the Chicago Section the advantages of a fast nuclear breeder reactor, as well as

other interesting phases of atomic energy, were discussed by Dr. Frank G. Foote, Director of the Metallurgy Division of the Argonne National Laboratory.

Dr. Foote described the nature and type of metallurgical problems faced in the construction of nuclear reactors,



FRANK G. FOOTE

and presented some of the techniques used in solving these problems. Methods used in handling less known metals, such as zirconium, beryllium, and uranium, were discussed.

The corrosion problems faced in high temperature water systems were compared with those encountered in liquid sodium or sodium-potassium systems operating at high temperatures. It was pointed out by the speaker that although water is usually considered a relatively stable, noncorrosive substance when compared to such materials as the alkali metals, its use in high temperature stainless steel systems posed the more difficult corrosion problems. It was also pointed out that the eutectic mixture of sodium-potassium had the added advantage of a lower freezing point than water.

The meeting was followed by a discussion period. The questions asked indicated active interest on the part of the audience.

Officers of the Chicago Section for the 1953-1954 year are:

Chairman—H. T. Francis
Vice-Chairman—B. F. Freeberg
Treasurer—E. L. Koehler
Secretary—A. H. Roebuck, Argonne National Laboratory, Chicago

A. H. ROEBUCK, *Secretary*

India Section

The Second Technical Meeting of the Section for 1953 was held on September 28, 1953, at the Indian Institute of Science, Bangalore, with Professor

Brahm Prakash, Head of the Department of Metallurgy, Indian Institute of Science, in the chair in the unavoidable absence of Professor M. S. Thacker, Chairman of the Section. Dr. J. C. Ghosh, Director, Indian Institute of Technology, Government of India, Kharagpur, delivered a lecture on the electrolytic oxidation of organic compounds using porous carbon anodes. The speaker congratulated the India Section for its activities in spite of the limited membership, and expressed the hope that organizations of this type would function effectively as a liaison between research and industry in India. He then gave an account of the research work carried out in the Indian Institute of Science on the electrochemical preparation of some organic compounds; *p*-benzoquinone and chlorobenzene from benzene, ethylene chlorohydrin and ethylene glycol from ethylene, chloral from alcohol [Ghosh, *et al.*, *J. Sci. Ind. Research (India)*, **11B**, 356 (1952)]. The advantages of using thick-walled porous carbon anodes are: low cost; chemical inertia; catalysts can be deposited easily in the pores; the wicking action of the anodes offers attractive possibilities in electrolytic reactions in which compounds insoluble in aqueous electrolytes are to be used as cathodic or anodic depolarizers. The experimental details, operating conditions, use of catalysts, and the important results were described and illustrated. With a vote of thanks to the speaker, the meeting came to a close.

J. BALACHANDRA, *Secretary-Treasurer*

New York Metropolitan Section

The Section met at dinner on November 18, and had as guest speaker Dr. L. G. Longworth of the Rockefeller Institute for Medical Research. His topic was "Diffusion in Liquids and the Stokes-Einstein Relation."

Dr. Longworth told of the long search for a method of measuring diffusion coefficients with a precision of 0.1% instead of the usual 1%. The method finally chosen was that of free diffusion in a modified Tiselius cell. An ingenious method was devised to obtain an initially sharp boundary between solution and solvent, and to correct for the small discrepancy from ideal sharpness. With a suitable optical system, spreading of the boundary could be followed by an analysis of Rayleigh interference fringes. Measurements were presented for a number of sugars, amino acids, and peptides in aqueous solution.

Dr. Longworth showed how small variations in diffusion coefficients with concentration, even for these near non-electrolytes, could be detected by non-Gaussian distribution in the diffusing boundary; how empirical relations can be set up with molecular weight or molecular volume; and to what extent the Stokes-Einstein relation, strictly valid only for large, spherical, non-polar molecules in dilute solution, can be applied to the substances chosen for study.

CECIL V. KING,

Member of the Executive Committee

Niagara Falls Section

The November 12th meeting of the Niagara Falls Section was a joint meeting with the National Association of Corrosion Engineers and was held at the Red Coach Inn at Niagara Falls.



J. C. SEARER

Dr. J. C. Searer, Director of Resins Applications Research at Durez Plastics and Chemicals Incorporated, gave an interesting talk on "Modern Trends in Plastics."

Dr. Searer reviewed the increased use of synthetic resins and plastics during the past 25 years and presented comparative production figures for the common metallic materials. The effect of the tremendous increase in the amount and numbers of plastic materials on the chemical industries supplying the raw materials was discussed. Dr. Searer described and presented samples of the many various types of plastics, including plastics "alloyed" with other materials to give desirable properties.

JOHN E. CURREY, *Secretary*

Philadelphia Section

The Philadelphia Section was fortunate to have as its first speaker of the 1953-1954 season Dr. J. O'M. Bockris. Dr. Bockris, who comes from the

Imperial College of Science and Technology, London, is currently Visiting Professor in Electrochemistry at the University of Pennsylvania. His talk, entitled "Research Vistas in Electrochemistry," was given on November 4 at the Harrison Laboratory of the University and was preceded by an enjoyable social hour and dinner at the Lenape Club. Some 50 members and guests attended the dinner and about 75 persons were present at the talk.

In introducing his subject, Dr. Bockris mildly scolded the industrialists (and academicians as well) for their lack of support of research and instruction in fundamental electrochemistry; but he attributed this attitude to an understandable disappointment in the application of existing theories to most electrochemical problems. These "two most unfortunate historical coincidences in electrochemical history" were, namely: (a) the early exploitation of Nernst's thermodynamic treatment which led to attempted applications far outside its validity even though it was unable to cope with real electrode processes; and (b) the introduction by Debye of the statistical ionic theory which was essentially a limiting theory and proved to be intrinsically inapplicable to even moderately concentrated solutions. Consequently, it has been felt that a comprehensive theory of solutions of practical strength was doomed to failure.

Since the beginning of the last war, however, Dr. Bockris pointed out that there has been a considerable rebirth of interest in the field, largely as a result of many important new applications, e.g., ion exchange, polarography, electrophoretic separation of biologically important substances, etc., together with certain fundamental theoretical investigations, for example, those relating to rate processes as applied to electrode potentials. A review of the literature during this period has shown a distinct trend toward a molecular-kinetic interpretation of electrode processes and a decline of the thermodynamic viewpoint.

In stressing the growth and importance of the kinetic method Dr. Bockris described its success in furthering our understanding of two seemingly unrelated problems in electrochemistry: (a) the mechanism of hydrogen evolution and (b) the structure of silicate melts. In the former it has aided in distinguishing between various likely mechanisms by permitting evaluation of significant numerical criteria. In the

latter it has rendered meaningful the observed equivalent conductivity if parameters of rate equations connected with it are evaluated and related to composition and structure. In brief,



J. O'M. BOCKRIS

the findings point toward the formation of anionic complexes for metals of small radius and high valency; this, together with the constancy of the energy of activation for viscous flow over more than one-half the range of composition for systems of the type $M_xO_y \cdot SiO_2$, must lead us to reorganize our views regarding such systems, since these results are entirely incompatible with the classical theory of liquid silicates in which there are presumed to be infinite chains and sheets of Si-O-Si units.

In closing, Dr. Bockris listed four subjects he felt to be of especial immediate interest in electrochemical research: (a) the application of recent theoretical developments in electrode kinetics, (b) adsorption on solid surfaces from solution; (c) theoretical evolution of absolute galvanic potential differences; and (d) the mechanism of current transport through nerve fibers.

GEORGE W. BODAMER, *Secretary*

NEW MEMBERS

In November 1953 the following were elected to membership in The Electrochemical Society:

Active Members

JOHN M. FINN, JR., Horizons Incorporated, mailing add: 2734 Southington Ave., Shaker Heights, Ohio (Electronics and Theoretical Electrochemistry)

ALEXANDER HANNAH, Research and Development Division, Wyandotte Chemical Corporation, Wyandotte, Mich. (Corrosion, Electrodeposition, and Theoretical Electrochemistry)

BERTRAM C. RAYNES, Horizons In-

corporated, mailing add: 21950 So. Lake Shore Blvd., Euclid, Ohio (Electronics and Industrial Electrolytic)

RAYMOND H. SEVIN, Miniere & Metallurgiques, mailing add: 86 Rue Cardinet, Paris, France (Electrothermic and Industrial Electrolytic)

WILLIAM P. SHUMAN, JR., Lehigh University, mailing add: 1609 Primrose Lane, Bethlehem, Pa. (Battery and Theoretical Electrochemistry).

WALTER G. ZELLEY, Aluminum Research Laboratories, mailing add: 168 Jefferson Ave., New Kensington, Pa. (Electrodeposition)

GASTON F. DUBOIS

Gaston F. DuBois, prominent consulting engineer, and former officer and director of Monsanto Chemical Company, died at Barnes Hospital in St. Louis, Missouri, on November 1.

Born at LeLocle, Switzerland, August 9, 1880, Mr. DuBois was educated at the Federal Polytechnic Institute at Zurich, Switzerland, from which he received a degree in chemical engineering in 1903. This was followed by a post-graduate course in electrochemistry at the Technische Hochschule, Dresden, Germany.

Recognized as one of the foremost figures in the development of the American chemical industry, Mr. DuBois was the recipient of many awards, culminating in 1943 in the Perkin Medal, the chemical industry's highest honor.

Among his numerous achievements was the first successful commercial production in this country of caffeine, glycerophosphates, and bismuth metal; he was active in the research of many basic compounds such as rubber chemicals, plasticizers, resins, and pharmaceuticals. He was also one of the few men instrumental in making the United States independent of foreign supplies of critically needed dyes and drugs during World War I, generally recognized as the real beginning of the chemical industry here.

Mr. DuBois had been associated with the Monsanto Chemical Company since 1904 as production manager, vice-president, technical director, president, and vice-president in charge of research and development, respectively. In 1939, he became a member of the company's executive committee. He retired in 1945, but remained as a member of the Board of Directors until 1949.

Mr. DuBois joined The Electrochemical Society in 1929.

LETTER TO THE EDITOR

What! No Flashlight?

Dear Sir:

Through the kindness of O. W. Storey, I have before me the startling definition of the dry cell as it appears in The Van Nostrand Chemists Dictionary, D. Van Nostrand Company, Inc., New York, 1953:

DRY CELL. A small electric battery widely used to supply small electric currents at low voltages, for radio sets, bell circuits, and various alarm systems and control devices. It consists of a central carbon anode, and of a zinc cup acting as cathode, and container for the cell. The electrolyte is a wet paste of ammonium chloride, with some zinc chloride, and manganese dioxide (depolarizer).

Which brings to mind a quotation from John Masefield (Sonnets. 14) culled by M. R. Hatfield some years ago:

"... A thing of watery salt
Held in cohesion by unresting cells
Which work they know not why..."

Further comment seems superfluous. I had a hard time deciding whether to send this to you or to the Van Nostrand editors. You lost.

G. W. H.

BOOK REVIEWS

ELEKTROCHEMIE — THEORETISCHE GRUNDLAGEN UND ANWENDUNGEN by G. Milazzo; revised and translated into German from the first Italian edition. Springer, Vienna, 1952; XIII + 419 pages, \$8.60.

The original Italian edition of this book appears to have had a successful career as a text for university courses. Professor Milazzo is himself in charge of the teaching of electrochemistry at the University of Rome and his course, as represented by the book, establishes a rational balance between electrochemical principles (including thermodynamic foundations, properties of electrolytic solutions, galvanic cells, electrode potentials, etc.) and the various applications to analytical chemistry, electrometallurgy, industrial electrochemistry, etc. There are separate chapters on experimental methods, the electrolysis of molten salts, primary and secondary cells, the electrochem-

istry of colloids and electrokinetics, and the electrochemistry of gases. The great abundance of tables of numerical data is a particularly welcome feature.

Besides a warm introduction by Professor Bonino of Bologna, the German edition is presented by Professor Wolfgang Pauli Sr. of Zurich at whose suggestion Dr. Schwabl of Vienna undertook the translation. Professor Pauli felt that this book was unique in its covering of the whole of electrochemistry in a manner conveniently accessible to workers in other fields. At the same time it offers a compact, reasonably accurate, and up-to-date account of electrochemistry even for the specialist. That these functions are well fulfilled by Professor Milazzo's book seems to be demonstrated by its favorable reception in several foreign countries. In the U. S. the theoretical portion of the book may be regarded by some as differing somewhat from our set ways of presenting electrochemistry, but the availability under one cover of electrochemical theory, practice, and applications should make this treatise a desirable addition to any scientific library.

The book is attractively presented and beautifully printed on excellent paper.

PIERRE VAN RYSELBERGHE

ELEMENTS OF HEAT TREATMENT by George M. Enos and William E. Fontaine. Published by John Wiley & Sons, Inc., New York, and Chapman & Hall, Limited, London, 1953. 286 pages, \$5.00.

This well illustrated book is a practical introduction to the heat treatment of metals—primarily steels. It is not a book for the metallurgical specialist or the metal physicist. It is written in simple language and is well suited to the needs of beginners, design and mechanical engineers, and all those who want a clear deliberately uncomplicated review of basic metal treating techniques.

The content of the book is as follows:

1. The first one-sixth of the book presents a very brief introduction to the ideas of crystal form, of microstructure and phase diagrams, and a complete but equally brief account of the mechanical testing of metals. These short sections seem just about adequate to their purpose.

2. The middle two-thirds or more of the book is devoted to steel and its heat treatment. Here the coverage is very thorough indeed. Concepts and techniques ranging from classification of steels, through hardenability, to sur-

face hardening are well described, usually without reference to mechanisms.

3. The last two chapters are devoted to rather short discussions of heat treatment of nonferrous alloys and of equipment and methods used in practice.

It is believed that the attempt of the authors, as stated by them in their preface, to set down the fundamental theory involved in the heat treatment of metals has been substantially achieved.

E. E. SCHUMACHER

RECENT PATENTS

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

September 22, 1953

Willard, A. R., 2,652,617, Machine for Manufacturing Battery Plates

Brennan, J. B., 2,653,119, Plates Adapted for Use in Electrolytic Devices

Greig, H. G., 2,653,126, Method of Marking

Brenner, A., and Burkhead, P., 2,653,-

127, Methods of and Baths for Electrodepositing Cobalt or Cobalt-Molybdenum Alloys

Brenner, A., Burkhead, P. S., and Sentel, C. A., 2,653,128, Method of and Bath for Electrodepositing Tungsten Alloys

Ruffe, W. H., 2,653,178, Thermocouple Device

Baldwin, J. H., 2,653,179, Primary Battery and Method of Making the Same

Hignett, H. W. G., and Hersch, P., 2,653,180, Alkaline Storage Battery and Process for Preventing its Self-Discharge

Ballard, R. J., 2,653,266, Vapor Electric Device

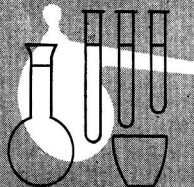
Vokac, C. W., Rothenberger, G. M., and Morey, W. A., 2,653,269, Hydraulic-Electrical Apparatus for Automatically Regulating the Position of Direct Arc Electric Furnace Electrodes

Huge, H. M., 2,653,293, Battery Charger

September 29, 1953

Gregory, E. D., Lillendahl, W. C., and Wroughton, D. M., 2,653,869, Manufacture of Ductile Vanadium

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METSO DETERGENTS

PHILADELPHIA QUARTZ CO. 1156 Public Ledger Bldg., Phila., Pa.

- Sejersted, J., and Bockman, O. C., 2,653,878, Process for the Production of Electrodes
- Aannerud, S. A., 2,653,905, Process for Total Treatment of Copper-Containing Iron Pyrites
- Bitzer, G., 2,653,906, Anticorrosion Needle Mounting
- Best, S. G., 2,653,983, Thermocouple Unit
- Godeas, M. S., 2,653,984, Electric Storage Battery
- Philipps, T. E., 2,653,985, Battery Plate Separator
- Philipps, T. E., 2,653,986, Battery Plate Separator
- Baty, J. A., 2,653,987, Porous Material Useful in Battery Separators
- Rupp, J. L., 2,653,988, Storage Battery and Mounting and Connection Means Therefore
- Wright, D. A., 2,654,045, Thermionic Cathode for Electric Discharge Devices

October 6, 1953

- Thierfelder, C. W., 2,654,675, Luminescent Screen Composition
- Calderon, E. R., and Slomin, G. W., 2,654,701, Plating Aluminum
- De Long, H. K., 2,654,702, Electrodeposition of Metal From Alkaline Cyanide Bath
- Brown, H., 2,654,703, Electrodeposition of Bright Nickel, Cobalt, and Alloys Thereof
- Brown, H., and High, L. R. B., 2,654,704, Electroplating of Nickel
- Case, B. C., 2,654,705, Nickel Plating
- Gaylor, P. J., 2,654,706, Electrolytic Regeneration of Spent Caustic
- Saffel, D. E., 2,654,707, Anodizing Rack
- Zaugg, S., 2,654,794, Sealed Storage Cell and Battery and Method of Manufacturing the Same
- Brill, O. H., and Solomon, F., 2,654,795, Electrode for Electric Batteries and Method of Making Same
- Goodrich, R. R., 2,654,852, Photoconductive Target for Cathode-Ray Devices
- Weimer, P. K., 2,654,853, Photoelectric Apparatus
- Petersen, C. C., 2,654,862, Cell for Electrical Measurement of Liquid Dielectrics

October 13, 1953

- Donath, G. A., 2,654,939, Storage Battery Grid Plate Casting and Trimming Machine
- Gullett, W. W., 2,655,456, Manganese Dioxide for Primary Cells
- Chester, A. E., 2,655,471, Chromium Electroplating

- Hilliard, R. V., and Baroch, C. T., 2,655,472, Process of Extracting and Recovering Metals by Leaching and Electrolysis
- Lowenheim, F. A., 2,655,473, Electrolytic Detinning
- Schutze, H. G., and Cier, H. E., 2,655,474, Photochemical Production of Olefinic Hydrocarbons
- Zvanut, C. M., 2,655,550, Melting Furnace with Thermocouple Reception Means
- Ellis, G. B., 2,655,551, Magnesium-Cuprous Chloride Reserve Battery
- Fuller, L., and Szper, J. A., 2,655,552, Separator for Electric Secondary Batteries
- Cepon, R. J., 2,655,626, Selenium Rectifier

October 20, 1953

- Miller, L. A., Dunn, J. H., and Neher, C. M., 2,656,313, Photochemical Production of Benzene Hexachloride
- Osterheld, C. M., 2,656,314, Corrosion Preventing Means
- Nagy, R., and Wollentin, R. W., 2,656,320, Zinc Silicate Phosphor
- Hindall, A. L., and Carson, W. D., 2,656,399, Method and Apparatus for Curing Positive Storage Battery Plates
- Carson, W. D., and Hindall, A. L., 2,656,400, Manufacture of Negative Plates
- Everett, F. L., 2,656,401, Breaker Mechanism for Deferred Action Batteries
- Fischbach, A., and Hochberg, F., 2,656,402, Electrode for Primary Batteries
- Coulter, W. H., 2,656,508, Means for Counting Particles Suspended in a Fluid
- MacKay, J. R., 2,656,526, Chlorine Concentration Sensitive Apparatus

October 27, 1953

- Stern, G., Sindeband, S. J., and Scanlan, J. P., 2,656,595, Chromium-Alloyed Corrosion-Resistant Metal Powders and Related Products
- Conant, L. A., and Gillies, D. M., 2,656,596, Tungsten-Chromium-Alumina Metal Ceramics
- Sindeband, S. J., Stern, G., and Scanlan, J. P., 2,657,127, Production of Chromium-Alloyed Corrosion-Resistant Metal Powders and Related Products
- Stern, G., Sindeband, S. J., and Scanlan, J. P., 2,657,128, Silicon-Alloyed Corrosion-Resistant Metal Powders and Related Products and Processes
- Stern, G., Sindeband, S. J., and Scan-

- lan, J. P., 2,657,129, Aluminum-Alloyed Corrosion-Resistant Metal Powders and Related Products and Processes
- Jennings, P. A., 2,657,130, High-Temperature Steel and Articles
- Mengali, O. J., and Middleton, A. E., 2,657,152, Process of Producing an Electro-Photographic Plate
- Berman, H., and Katz, S., 2,657,176, Electrodeposition of Copper and Copper Alloys Upon Zinc and Zinc Alloys
- Rendel, G. H., 2,657,177, Plating Thickness Regulator
- Bretschneider, O., 2,657,247, High-Temperature Electric Furnace and Process of Operation
- Kurth, F. F., 2,657,249, Storage Battery
- Homer, H. H., and Lowry, E. F., 2,657,325, Electrode for Electric Discharge Lamps
- Payne, W. H., 2,657,327, Adjusting System for Furnace Controls
- Hill, R. A., 2,657,346, Dry Contact Rectifier

LITERATURE FROM INDUSTRY

GFB-LGL OZONATOR. Preliminary information bulletin gives data on the GFB-LGL Ozonator for tests of rubber and rubberlike materials. This ozonator generates, maintains, and measures a continuous flow of ozone, under controlled conditions of temperature and flow rate, through a specimen exposure chamber. G. F. Bush Associates. P-177

SYNTHETIC ORGANIC CHEMICALS. 1954 edition of the booklet "Physical Properties of Synthetic Organic Chemicals" presents data on more than 330 products and features 36 new chemicals. For easy reference, the chemicals are arranged by family groups. Condensed data on applications are presented, and physical properties are given in tabular form. Carbide and Carbon Chemicals Co. P-178

G-E TIME SWITCH CATALOG. Illustrated 24-page bulletin (GEA-5965) contains selection and application information, as well as descriptions of the various types and models available. Features, specifications, operating data, and pricing information are also included. General Electric Co. P-179

PLANE GRATING SPECTROGRAPH. Brochure entitled "Jaco Ebert 3.4 Meter

Plane Grating Spectrograph" is available to those interested in analytical instrumentation and related problems. Describes the first commercially available spectrograph to be equipped with a plane grating. Jarrell-Ash Co. P-180

NORTON HEATING ELEMENTS. New "Hot Rod" CRYSTOLON Heating Elements are fully described in a booklet just published. The manual covers such subjects as expected service life, operating temperatures, mounting methods, power consumption and electrical data, specifications, operating suggestions, and accessories. Norton Co. P-181

STORAGE BATTERY SERVICE MANUAL. Newly revised 44-page publication covers in nontechnical language how a battery is constructed, how it works, how to maintain battery stock, how to install and service automotive batteries, and how to make certain battery repairs. A section is devoted to car generator systems. Definition of often-used electrical terms and a complete index are also included. The Association of American Battery Manufacturers. P-182

FILTER PUMPS. 8-page bulletin describes filter pumps and equipment. The booklet goes into the design and application of corrosion resistant filter pumps, and discusses solutions that can be filtered. Photographs show the pump in action; a chart with various filter pump models, motor types, and price is also included. Setheo Mfg. Co. P-183

NEW PRODUCTS

VOLTAGE REGULATED POWER SUPPLY. The new Kepco Model #2400 power supply, of interest to all users of electrical and electronic equipment, features two regulated B supplies completely isolated from each other, one regulated C supply, and two unregulated filament supplies isolated from each other. Excellent regulation, low ripple content, and low output impedance distinguish these B and C supplies. Kepco Laboratories. N-39

"NOBRUSH" FREQUENCY CONVERTER. A convenient and compact motor-generator unit to convert 60 cycles to 400 cycles has been developed. By the use of the "Nobrush" construction, unusual efficiency, compactness, long life, durability, and reduced maintenance are achieved. Outputs of 150 volt-

ampere to 25 kva, single- or three-phase, are available with motor drive for any standard frequency or voltage. Georator Corp. N-40

NEW STANDARDIZED INSULATORS. A new E-I series of hermetically-sealed, lug-type, lead-thru insulators is now available; specially designed for use on condensers, transformers, and general applications. Electrical and mechanical features are: ratings from 2000-4000 volts (rms), compression sealed, practically indestructible, mount from inside or outside of can, and lead-thru wires up to 0.060. Electrical Industries. N-41

RCA CAMERA TUBE. Smallest TV camera tube ever developed for broadcast use—the Vidicon-type which weighs only two ounces—promises greater efficiency and economy. Only a fraction of the size of an iconoscope tube normally used for film pickup, it is up to three times more sensitive and has a spectral-response characteristic approaching that of the human eye. Its photoconductive surface provides a precise picture reproduction which is unaffected by electron redistribution, edging effects, or flare. Suitable for reproduction of color films on a monochrome system. RCA Victor Division, Radio Corporation of America. N-42

PHOSPHOR BRONZE. Phosphor bronze strip, precision-rolled to very close tolerances and to thin gauges and foils, for use in the chemical, food processing, and bottling industries is now available. Possesses high tensile and yield strength, good ductility, resiliency, high fatigue strength, wear resistance, and good bearing qualities. Typical uses include: bellows and diaphragms; high strength springs and wire brushes; switches, socket and plug contacts; fuse clips; printed circuits, etc. American Silver Company, Inc. N-43

DIAPHRAGM MOTOR CONTROL VALVE. An improved valve, designated "Series 800," has been introduced for use with wide-band, proportional control instruments. Features a completely redesigned diaphragm motor with pressed steel case plates. In addition, it offers a sturdy, attractive yoke with mounting bosses on both sides for auxiliary equipment; a unique locking arrangement for securing the body stem to the spring stem; and either bolted or screwed stuffing boxes. Minneapolis-Honeywell Regulator Co. N-44

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SWR AMPLIFIER. A new instrument (Model TAA-16B) has been announced for the purpose of determining standing wave ratios or the comparison of any two demodulated signals. The amplifier features dual input channels with gain sufficient for full scale meter deflection with less than 2 microvolts input. May be used broadband from 500-5000 cycles or may be sharply tuned over this range by means of panel controls. A crystal protective circuit is incorporated to minimize possibility of burnout due to accidental application of bolometer voltage. Browning Laboratories, Inc. N-45

To receive further information on any New Product or Literature from Industry listed here, send inquiry, with key number, to JOURNAL OF THE Electrochemical Society, 216 West 102nd Street, New York, N. Y.

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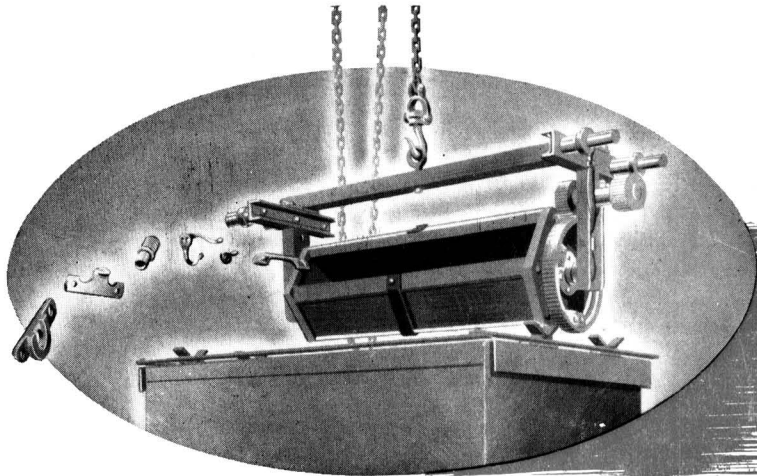
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- Wilbur B. Driver Co., Newark, N. J.
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- E. I. du Pont de Nemours & Company, Screen Division, Towanda, Pa.
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- Electric Auto-Lite Company, Toledo, Ohio
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- General Motors Corp., 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 Co., St. Marys, Pa. (2 memberships)
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- Kaiser Aluminum & Chemical Corp., 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.
- Philco Corporation Co., Lansdale, Pa.
- Phillips 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.
- Sarkes Tarzian, Inc., Bloomington, Ind.
- Solvay Process Division, Allied Chemical & Dye Corporation, Syracuse, N. Y. (3 memberships)
- Stackpole Carbon Company, St. Marys, Pa.
- Standard Steel Spring Company, Coraopolis, Pa.
- Stauffer Chemical Company, San Francisco, Calif.
- Sylvania Electric Products Inc., Bayside, N. Y. (2 memberships)
- 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.
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