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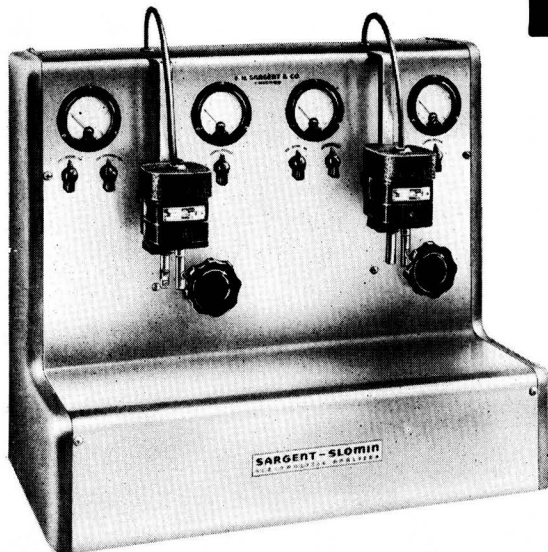
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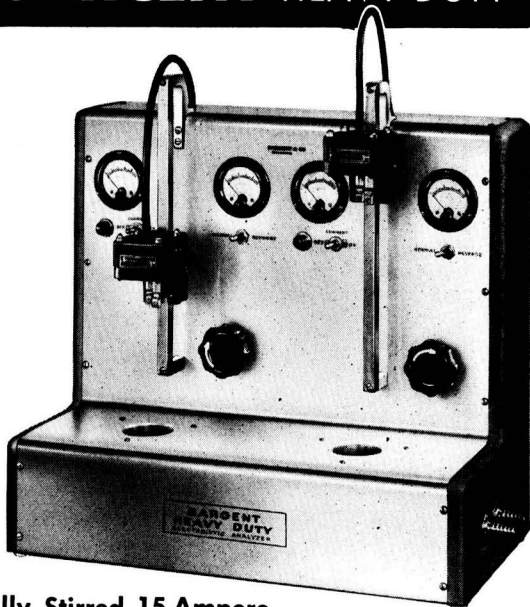
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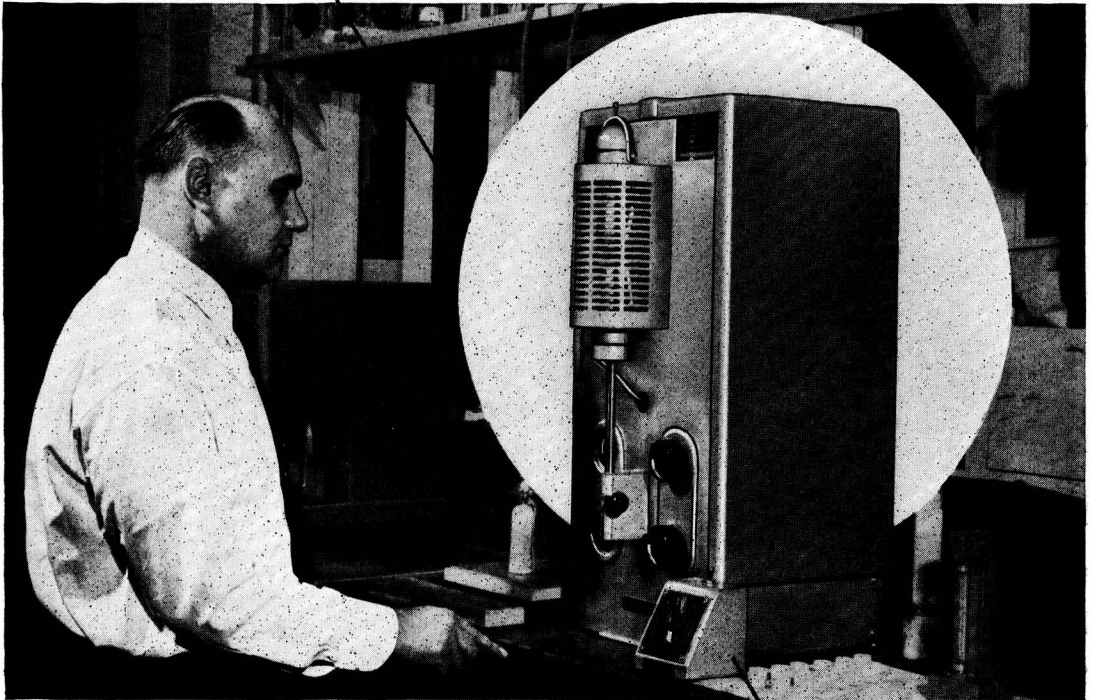
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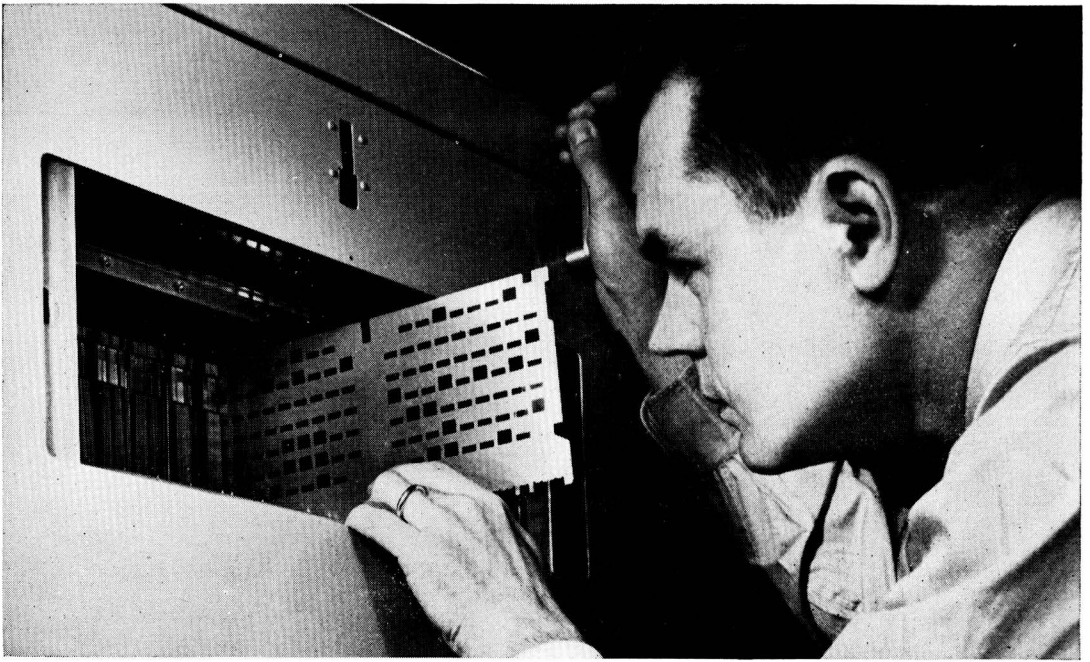
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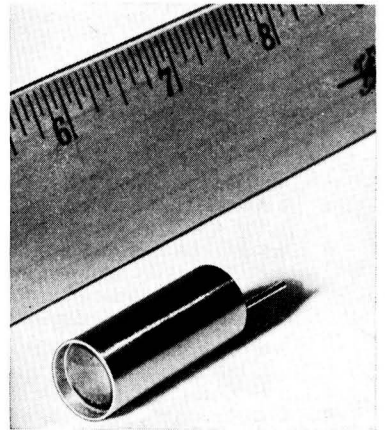
## CARDS FOR CONVERSATION

To find out how to route Long Distance calls a dial system needs lots of information—fast. To provide it Bell Laboratories engineers developed a new kind of card file—one that dial systems can read.

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The “card file” will have its widest use in speeding Long Distance calls that are now dialed by a telephone operator and may one day be dialed by you personally. It is another example of how Bell Telephone Laboratories helps telephony to grow, as costs are kept down.

Checking perforated metal card in Bell's new “card file” which uses Phototransistors to help route Long Distance telephone calls along the best routes. If the first voice-way is in use, a “detour” is swiftly found. The equipment is known in telephony as a “card translator.”



New Phototransistor unit. Light entering the cylinder is focused by the lens on a piece of germanium that responds by generating current. Like the Transistor, the Phototransistor was invented in Bell Telephone Laboratories.



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## Electrochemical Industry of Canada

*In* this issue of the JOURNAL is the first of three articles concerning the electrochemical and electrometallurgical industries in Canada, and the virile electrical generation network on which they depend.

Electrochemistry and electrometallurgy have already made gigantic strides in Canada. Their continued advance is assured, for the electric industry in Canada is marching ahead year after year.

Last year it generated 69 billion kwhr, next after only the United States and presumably the Soviet Union. In straight terms of energy, on the formula that a kilowatt is equal to the strength of 13 men, and assuming a human work-year of 2,400 hours, that electrical energy gave Canada the equivalent of a working force of 368,000,000 men. Or, because just two-thirds of Canada's electrical power is devoted to industry, say it's equal to only 240,000,000 men.

Fanciful? Yes, but the nation north of the border, about one-tenth the population of the United States, is nevertheless recording some astonishing achievements.

She is sixth among all nations in production of goods. She is third in world trade. She is vital to the United States not only as a continual good neighbor and because of her strategic position, but also as a supplier of things the United States needs and as a market for American goods.

Canada has an immense wealth of natural resources, and one of the greatest of them all is her abundance of water-power which permits relatively inexpensive development. Of the 20 greatest hydroelectric generating stations on this continent, half are in Canada—and more are being built all the time. Recently the rate has approached a million horsepower annually.

This first article, by V. G. Bartram, of Montreal, president of Shawinigan Chemicals Limited and several associated companies, treats of electrochemistry, electrometallurgy, and electric generation throughout the length and breadth of Canada generally. The second article in the series will go into detail of those three phases of the subject in Canada's five eastern provinces—Quebec, New Brunswick, Nova Scotia, Prince Edward Island, and Newfoundland. The last article will treat of the other five provinces—Ontario, Manitoba, Saskatchewan, Alberta, and British Columbia—and also the Yukon and Northwest Territories.

There is no part of Canada that does not hold some interest for the American industrialist today. The nation of the north is growing steadily, and opening new stores of treasure. She is always willing to share them.

—A. F. G. CADENHEAD

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**+ No loss of efficiency due to overheating —**

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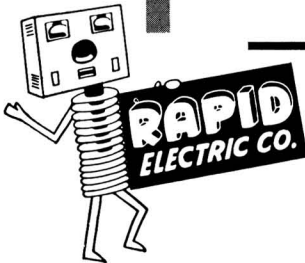
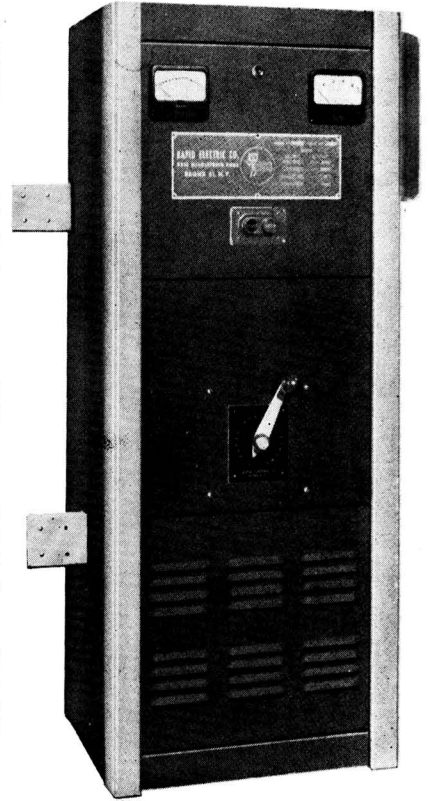
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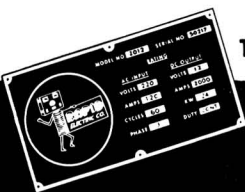
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## THE ELECTROCHEMICAL AND ELECTRO-METALLURGICAL INDUSTRIES OF CANADA<sup>1</sup>

V. G. Bartram<sup>2</sup>

The twentieth century belongs to Canada! This slogan, first hopefully phrased in the early 1900's by Sir Wilfrid Laurier, then Canada's Premier, is often heard these days as writers in Canada and in other countries point to the great strides Canada has made in the past fifteen years in her industrialization and in the development of her natural resources. Many excellent articles have appeared in recent months extolling Canada's remarkable progress, and it is not the intention to present here yet another such review. Rather it is the purpose of this series of three articles to examine briefly Canada's electrochemical and electrometallurgical industries, as well as the great hydroelectric developments which have brought them into being, as part of her rapidly growing economy.

### General Industrial Expansion

Canada's industrial growth within the span of the past two decades has been one of the economic marvels of this century. With a population even today of less than 15 millions, Canada has grown to be the sixth ranking industrial power and the third greatest trading nation of the world. In value of Gross National Product per capita, Canada stands second only to the U. S.; in trade per capita, it is exceeded only by New Zealand. For a decade it has been the world's leading exporter of nonferrous metals. In 1951, for example, Canada exported nickel, zinc, aluminum, copper, and lead to a value of \$478,000,000, a record never approached by any other country. Canada now leads the free world in production of nickel, platinum and platinum metals, titania slag, newsprint, and asbestos; it stands second in production of aluminum, gold, and cadmium metal; is third in output of zinc, silver, and cobalt, and fourth in copper and lead. Developments now underway promise to place Canada among the front ranks of the world's producers of petroleum, natural gas, and ores of iron, tungsten, and uranium. But not only as a primary producer is Canada's record outstanding; manufacturing has also advanced on a broad front and Canada has become a leading exporter of a number of manufactured articles. Gross value of manufacturing production in 1951 was over \$16 billion, more than four times the 1939 value. Further evidence of Canada's remarkable record of growth is presented in Table I.

Canada's extractive and manufacturing industries received a great impetus during World War II, when the nation's productive capacity was strained to the utmost to supply materials sorely needed by the Allied countries. Thus Canada in these years produced nickel, copper, lead, and zinc to a total value of about one billion dollars, for a time supplied close to

40 per cent of the Allied requirements of aluminum, as well as much desperately needed calcium carbide and ferroalloys—to mention only a few products. Yet, while undoubtedly strongly stimulated by wartime exigencies, Canada's burgeoning economy has proven to have sound foundations in the years of relative peace that have followed. In many respects, Canada's industrial growth has been even more spectacular since the end of the war than during it. Ample proof of this may be found in the statistics of Table I. Since 1948, the combined physical output of nickel, copper, lead, and zinc has increased some 28 per cent, gold 25 per cent and silver 51 per cent, and iron ore 289 per cent. From 1946-52, petroleum refining capacity almost doubled; use of crude oil of Canadian origin increased over eightfold; and in 1952 new discoveries of gas and oil occurred in Canada at the rate of one every two days. The value of metallic minerals produced in 1952 was about \$727,916,000, just 2½ times the 1946 value.

TABLE I

	Gross national product at market prices	Physical volume of production 1935-1939 = 100		
		Million dollars	Index of all industrial production	Index of manufactures
1939	5,707	109.3	107.8	112.7
1946	12,026	171.9	189.9	237.7
1948	15,613	196.3	215.5	243.2
1949	16,462	199.6	217.0	239.9
1950	18,122	211.5	228.1	253.7
1951	21,241	226.5	242.1	267.8
1952	22,984	232.9	246.2	272.4
1953 (May)	—	257.4	272.7	—

In the chemical and allied products group, which includes many electropducts, output at \$806,200,000 was over five times the 1939 value and more than double the 1944 wartime peak (not corrected for inflated prices). Capital expenditures in this group of industries from 1946-53, inclusive will total about \$630 millions, of which some \$370 millions appear in the last three years.

During the period under review, the population of Canada has increased at a far slower rate than industrial production, being 14,692,000 on March 1, 1953, as against 12,292,000 in 1946, and 11,267,000 in 1939.

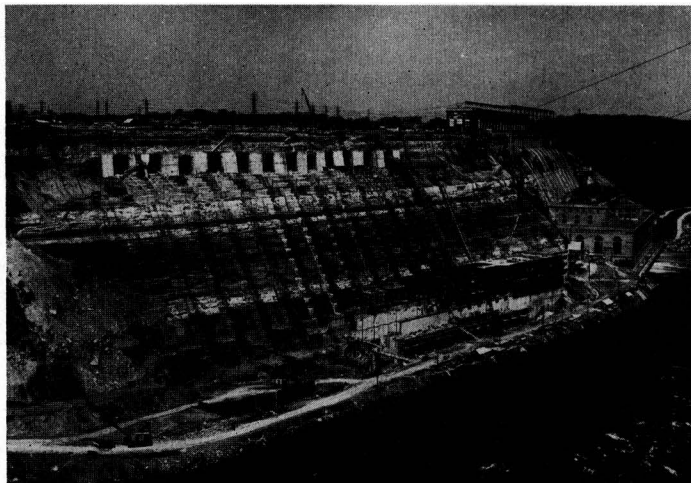
Thus, measured by almost any yardstick, the record of rapid industrialization that has occurred in Canada over this period is truly impressive.

### Importance of Electropducts in Canada's Economy

It is generally acknowledged that Canada's electrochemical and electrometallurgical industries have contributed in great measure to her extraordinary industrial growth. The example

<sup>1</sup> This article, and two succeeding articles on Canada, have been provided for the JOURNAL by A. C. Holm, Canadian Regional Editor.

<sup>2</sup> President, Shawinigan Chemicals Limited, Montreal, Quebec.



Superstructure of the ultramodern powerhouse at Ontario Hydro's 1,200,000-horsepower development takes shape at the base of the 300-foot cliff on the lower Niagara Gorge. The new development, the Sir Adam Beck-Niagara G.S. No. 2, is scheduled for initial service in 1954 with six units in operation. Five more units will be placed in service in 1955 and the remaining one in 1956. The structure at the right is the 525,000-horsepower Sir Adam Beck-Niagara G.S. No. 1 which was placed in operation in 1922.

TABLE II. Production of typical electroproducts in Canada  
1,000's of net tons

Year	Silicon carbide (crude)	Fused alumina (crude)	Ferroalloys	Chlorine	Aluminum ingot	Refined zinc	Refined copper	Refined lead
1935	18.5	51.2	63.4	—	23.2	149.5	173.3	163.8
1939	17.2	51.1	85.5	—	82.8	175.6	231.7	190.6
1940	24.6	85.3	149.4	—	109.1	185.7	261.9	220.1
1945	45.4	133.2	171.6	—	215.7	183.3	228.9	163.1
1946	50.0	119.2	139.4	—	194.1	185.7	167.2	165.7
1947	51.7	146.4	227.1	—	299.1	178.3	202.4	162.0
1948	52.9	144.8	232.7	—	367.1	196.6	221.3	160.0
1949	46.4	113.2	202.1	96.0	369.5	206.0	226.1	146.1
1950	44.8	126.9	180.5	131.0	396.9	204.4	238.2	170.0
1951	70.3	195.4	250.9	155.0	447.1	218.6	245.5	162.0
1952	—	—	232.0	169.5	499.8	223.1	197.0	177.4

Other Products—(Approximate and unconfirmed):

Magnesium	} 1952	2307 tons total
Calcium metal		
Cobalt	(1951)	475 tons
Tin	(1951)	173 tons
Calcium carbide	(1950)	400,000 tons

of aluminum is of itself almost sufficiently spectacular to win such recognition for the whole electroproducts industry. But when one attempts to present statistical evidence for the electroproducts industry as a whole in support of such an assertion, the difficulty arises that production figures for many of these products are not available for publication. However, some idea of the growth of these industries may be gleaned from the examples listed in Table II. Practically without exception, all of the electroproducts of Canada, a list of which is given in Table III, have undergone a substantial expansion of production during or since World War II, or are about to undergo expansion.

For a few nonferrous metals and ferroalloys, production figures are available or can be estimated from published data. In Table IV an attempt is made to summarize production data for six products which are definitely known to result from electrowinning, electrorefining, or electrothermic operations. In some cases the production figures have had to be estimated, and their accuracy cannot be guaranteed; however, they are sufficiently accurate for our purpose. It will be seen that in the

TABLE III. Electrochemical and electrometallurgical products  
(Commercial-scale operations—Canada, 1953)

(A) ELECTROCHEMICAL PRODUCTS

Chlorine, Caustic Soda, Hydrogen.  
Oxygen, Hydrogen.  
Hydrogen Peroxide.  
Chlorates of Sodium, Potassium, Bromium.

(B) ELECTRIC FURNACE PRODUCTS

Calcium Carbide (for acetylene-based chemicals).  
Calcium Carbide, Cyanamide, Dicyandiamide, Cyanide.  
Ferroalloys (ferrosilicon, ferromanganese, ferrochrome, silicomanganese, ferrozirconium, ferro-phosphorus. Exothermic silicon—and chrome alloys).  
Yellow phosphorus.  
Titanium slag and steel.  
Rock wool.  
Artificial graphite.  
Silicon carbide; other artificial abrasives, and refractories.  
Fused alumina.  
Tungsten carbide.  
Steel melting (for castings, ingots, etc. Carbon steel, alloy steels, heat resisting steels, stainless steels. Iron powder for powder metallurgy).  
Sodium silicate.

(C) METALS

1. ELECTROLYTIC

Aluminum	Indium
Zinc	Cerium (Mischmetall)
Copper	Bismuth (byproduct)
Lead	Selenium (byproduct)
Nickel	Tellurium (byproduct)
Magnesium	Silver, Gold (byproduct)
Cadmium	Platinum and Platinum Metals*

2. THERMAL

Magnesium  
Calcium  
Cobalt  
Tin  
Titanium (semicommercial)

\* Anode slimes containing these are exported for refining; the pure metals are not produced in Canada.

past two years these six items alone have accounted for a production of some 1,400,000 tons annually and a value at the works estimated to be about \$550,000,000 per annum. For

all of the forty-odd electroproducts listed in Table III a very rough estimate of the total value of production might then be in the order of \$750,000,000. This would rank the electroproducts industry third or fourth among the major manufacturing industries of Canada, being preceded only by the pulp and paper, slaughtering and meat-packing, and possibly also by the motor vehicles industries.

Another measure of the stature of the Canadian electroproducts' industry is the place taken by these products in the nation's exports. Here again statistics for many of these products are not available for publication. However, it would ap-

TABLE IV. Six leading electroproducts—  
production and exports

Commodity—year	Production		Exports		Exports		
	Net tons	Value* \$ millions	Net tons	Value \$ millions	As % of total produc- tion	% to U. S.	% to U. K.
<b>1. Aluminum (Primary)</b>							
1950	396,882	113.9	335,726	96.4	85	48	41
1951	447,095	141.2	354,414	112.0	79	30	54
1952	499,810	172.7	412,590	142.7	83	28	62
<b>2. Copper (Electrolytically refined only)</b>							
1950	238,204	111.0	134,244	59.7	55	38	48
1951	245,466	135.6	101,832	59.0	41	28	51
1952	196,985	112.9	113,675	71.4	58	46	37
<b>3. Nickel (Electrolytically refined only)</b>							
1950	68,000*	61.8	66,894	57.6	98	73	18
1951	75,000*	82.3	72,357	75.6	94	67	24
1952	78,200*	83.0	77,058	79.7	99	67	22
<b>4. Zinc (Electrolytically refined only)</b>							
1950	204,367	63.9	146,880	40.6	72	74	24
1951	218,578	87.1	146,132	55.4	67	58	38
1952	223,139	77.9	166,864	61.3	75	43	52
<b>5. Lead (Electrolytically refined only)</b>							
1950	170,023	49.2	116,963	32.5	69	91	7
1951	162,001	59.6	107,157	38.5	66	57	33
1952	177,389	57.3	134,953	42.8	76	78	21
<b>6. Ferroalloys (Electric furnace)</b>							
1950	180,500	25.2	122,479	17.1	68		
1951	250,900	41.2	190,454	31.3	76		
1952	232,000	39.5	179,000*	30.4	77		
<b>Totals</b>							
1950	1,257,976*	452.0*	923,186	303.9	73		
1951	1,399,040*	547.0*	972,346	371.8	70		
1952	1,407,523*	542.3*	1,084,140*	428.3	77		

\* Estimated Figures.

pear that of the 40-odd commodities listed in Table III probably less than half a dozen are not exported in part from Canada; this does not take into account the dozens of derivatives of these main products, many of which are also exported. Referring again to Table IV, the six electroproducts listed represent an export tonnage of about 1,000,000 tons annually, with a declared value of about \$372 million in 1951 and about \$428 million in 1952. Making a very rough guess as to the export values of all the other Canadian electroproducts listed in Table III, a conservative estimate of the total export value of all electroproducts would be in the order of \$500-\$600 million. Accordingly, the electroproducts group would easily

take third place among the various classes of commodities exported from Canada. This is shown in Table V, wherein are named the commodity groups as listed under Foreign Trade in the Canada Year Book, with a new group, "Six Leading Electroproducts," inserted which comprises only the six electroproducts listed in Table IV. Products of forest and farm lead by a wide margin, accounting for some two-thirds of Canada's exports; this is not surprising in view of the country's tremendous output of newsprint, woodpulp, lumber, wheat, and the like. But of all remaining exports (not of forest or farm origin) the electroproducts group (as a whole) would appear to account for almost one-half of the value.

TABLE V. Summary of all domestic exports from Canada—  
1950-52 (\$ Millions—Declared values)

Commodity group	1950	1951	1952
1. Wood Products and Paper...	1,112.9	1,399.1	1,366.8
2. Agricultural, Animal, and Fishery Products.....	990.5	1,213.2	1,421.4
3. Six leading Electroproducts..	303.9	371.8	428.3
4. Iron and Steel and their products.....	256.2	319.0	376.6
5. Nonferrous Metals and their products.....	170.5	229.4	308.8
6. Nonmetallic Minerals and products.....	103.7	131.5	143.5
7. Chemicals and Fertilizers....	100.5	131.7	124.6
8. Miscellaneous items.....	50.7	81.9	103.4
9. Fibers and Textiles.....	29.6	36.9	27.7
Total value of all domestic exports.....	3,118.5	3,914.5	4,301.1

#### Notes

Group 3. Comprises: Primary Al; Electrolytic Cu, Ni, Zn, Pb; Ferroalloys.

Group 4. Except Ferroalloys. Steel melted in electric furnaces is included here.

Group 5. Except 5 electrometals included in Group 3. Other electrometals are included here.

Group 6. Includes artificial abrasives and possibly other electroproducts.

Group 7. This group includes calcium carbide and derivatives and other electroproducts.

It should perhaps be again emphasized that the figures shown for electroproducts in Tables IV and V refer to only six out of the 40-odd electrochemical and electrometallurgical products made in Canada. Also, in the case of the five non-ferrous metals listed, the production and export figures given apply only to that portion of the total production of these metals which is electrolytically refined or produced.

Further strong evidence of the important role played by electroproducts in the Canadian economy are the following facts. Among her electroproducts industries Canada numbers:

1. The world's largest aluminum smelter, at Arvida, Quebec. A second smelter, which may well outgrow Arvida eventually, is now under construction at Kitimat, British Columbia (Aluminum Company of Canada).

2. The world's largest electrolytic zinc refinery, at Trail, B. C. (Consolidated Mining and Smelting Company).

3. The world's leading electrolytic nickel producer (International Nickel Company).

4. The world's first electric smelter for titanium slag and steel, at Sorel, Quebec (Quebec Iron and Titanium Corporation).

5. The world's largest cyanamide-ex-carbide plant, and the only one of its kind in North America (North American Cyanamid Company at Niagara Falls, Ontario).

6. The world's largest crude silicon-carbide plant, at Shawinigan Falls, Quebec (Canadian Carborundum Company).

7. Artificial abrasives plants which produce 85 per cent of North American supplies of crude abrasives (6 major producers in Ontario and Quebec).

8. The largest calcium carbide-acetylene products plant in the British Commonwealth, at Shawinigan Falls, Quebec (Shawinigan Chemicals Limited).

9. The world's largest producer of selenium and tellurium metals (Canadian Copper Refiners, Montreal East, Quebec).

Finally, indirect evidence of the magnitude of the electro-products industry in Canada is the fact that Canadian industry consumes per capita more electrical energy than any country in the world except Norway. In the Province of Que-

bec, which leads all other Canadian Provinces in electrochemical and electrometallurgical output, the consumption of kilowatt hours per capita is larger than in any other area of the world. This subject will be discussed more fully in the following section.

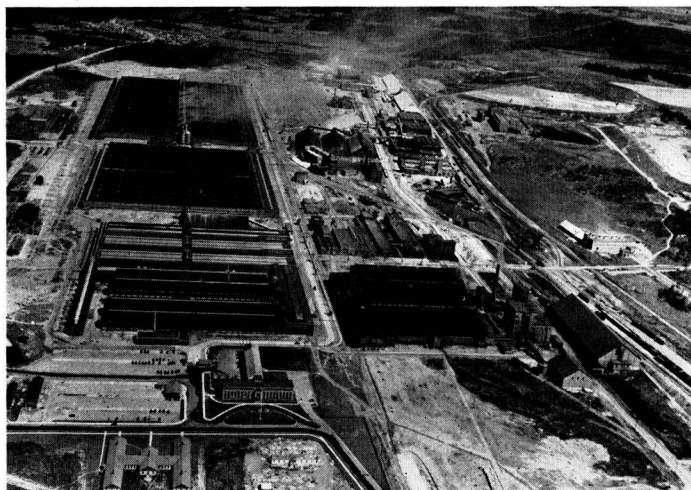
Since the war, the installations added have approached 1,000,000 horsepower each year. In hydroelectric stations alone, the additions are expected to exceed 880,000 horsepower in 1953, at least 895,000 in 1954, another 900,000 in 1955, and still another 615,000 in 1956. Those figures cover only the projects which are at present actually under construction or definitely planned; they do not include such proposed immense developments as the St. Lawrence seaway power plan, or the diversion of headwaters of the Yukon.

Table VI lists, by provinces, the total commercial potential of water-power resources, the installed hydroelectric capacity as at the beginning of 1953, the hydro additions then underway, and the installed thermal-plant capacity.

Table VII shows Canadian production as in 1951, in total and per capita, compared with other nations in the generation of electricity.

Table VIII illustrates the electrical production which Canada draws from her installed capacity, equal to more than one horsepower per capita, and the low cost of that production as reflected in selling prices per horsepower and per kwhr.

The federal bureau of statistics, remarking in an official bulletin that the nation enjoys about the lowest average electrical costs in the world, says that in 1951 the average domestic consumer paid 1.6 cents per kwhr in Canada, as against 2.8 cents in the United States, while the average rate to com-



Aerial view of Arvida Works of Aluminum Company of Canada, Limited.

bec, which leads all other Canadian Provinces in electrochemical and electrometallurgical output, the consumption of kilowatt hours per capita is larger than in any other area of the world. This subject will be discussed more fully in the following section.

#### Power in Abundance

In 1952, Canada generated about 69 billion kilowatt-hours of electric power. That was about the same as the United Kingdom, which has three times the population. Only the United States, with its more than 400 billion kilowatt-hours, and the Soviet Union, which is believed to have produced about 100 billion, had greater supplies.

More than 95 per cent of that electricity in Canada was generated from water power. Nearly 90 per cent, too, was produced by central electric stations contributing to the public supply, rather than by industries for their own use. More than half of the total was generated by investor-owned utilities rather than by government-owned systems—which are almost entirely provincial or municipal, since the federal government's ownership of water power is confined almost wholly to the Yukon and Northwest Territories.

At the beginning of this year, with an installed capacity of 14,770,000 horsepower, Canada had developed just a little more than 20 per cent of her known water-power resources—a total of 65,400,000 horsepower commercial potential—and

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mercial and industrial customers was 0.6 cents in Canada and 1.4 cents in the United States.

Three principal factors make possible this inexpensive electricity, despite Canada's relatively scattered population and consequent distribution costs. Those factors are the very high proportion of low-cost hydroelectric power rather than thermal; the favorable natural conditions of topography and precipitation which make construction and operation rela-

TABLE VI. *Electric Power in Canada—1/1/53* (In thousands of horsepower)

Province	Hydro			Thermal installed
	Total potential	Installed	Under constr.	
Newfoundland.....	3,360	286.7	24	4.2
Prince Edward Is.....	4	2.3	—	21.7
Nova Scotia.....	203	162.4	9	153.5
New Brunswick.....	433	135.5	27	90.5
Quebec.....	26,285	7,250.4	931	2.5
Ontario.....	9,440	4,400.5	1,238	605
Manitoba.....	7,230	735.9	80	22.1
Saskatchewan.....	1,455	111.8	—	276
Alberta.....	1,630	207.8	53	223
British Columbia.....	14,300	1,444.8	817	29.9
Yukon & NWT.....	1,060	31.5	1	1.4
Canada.....	65,400	14,769.6	3,180	1,429.8

TABLE VII. *Production of electricity—1951*

	Millions of kwhr	Kwhr per capita
Canada.....	62,500	4,470
Quebec.....	30,620	7,500
Ontario.....	18,930	4,100
British Columbia.....	4,700	3,900
Prairie Provinces.....	4,570	1,760
Maritime Provinces.....	2,180	1,680
United States.....	432,320	2,800
Soviet Union (estimated).....	100,000	500
United Kingdom.....	60,000	1,185
West Germany.....	51,300	1,070
Japan.....	41,200	480
France.....	36,000	850
Italy.....	29,400	635
Sweden.....	19,200	2,750
Norway.....	17,360	5,250
Union of South Africa.....	11,680	920
Australia.....	10,500	1,200
Switzerland.....	10,250	2,160
Poland.....	9,950	400
Belgium.....	9,450	1,100
Spain.....	7,200	257
Netherlands.....	5,800	570
Austria.....	5,650	820

tively economical even for hydro plants; and the fact that large proportions of the electricity produced go in large blocs to industrial consumers. Almost one-fifth of the total output goes to the pulp and paper industry, and one-sixth to smelting and refining of metals.

In all, about two-thirds of Canada's gross production of electric power goes to industry. Table IX gives, as of a while ago, the approximate division of that proportion between the leading divisions of manufactures, and the all-Canada estimated average cost in each, in cents per kwhr.

Here, in order of consumption, are the general requirements, in kilowatt-hours, for the production of various electrochemical and electrometallurgical products:

Aluminum, 24,000; Magnesium, 20,000; Nitrogen (Cyanamid process), 15,000; Silicon Carbide, 9,000; Ferroalloys, 4,000-8,000; Graphitized products, 3,000-8,000; Zinc (Electrolytic), 4,000; Caustic Soda and Chlorine, 3,400; Alumina (Fused), 3,200; Calcium Carbide, 3,000; Cadmium, 2,500; Steel Furnaces, 600; Copper Refining, 400.

All of these processes are used, most of them extensively, in Canada now. Other processes which will require vast quantities of power are nearing full development—and low-cost hydroelectric power awaits them in Canada.

TABLE VIII

Province	Production, 1952 (million kwhr)		Average price (centrals) 1951	
	Industrial	Central	\$ per hp year	¢ per kwhr
Newfoundland.....	1,000	171	37.68	1.6
Prince Edward Island.....	—	28	56.29	3.7
Nova Scotia.....	160	955	45.31	1.6
New Brunswick.....	360	741	54.29	1.3
Quebec.....	900	32,142	20.42	0.4
Ontario.....	2,200	18,169	29.53	0.7
Manitoba.....	8	2,696	32.48	0.6
Saskatchewan.....	3	1,073	37.31	1.4
Alberta.....	12	1,146	50.74	1.8
British Columbia.....	2,600*	4,667*	42.86	1.3
Canada.....	7,243	61,788	29.31	0.6

\* Including Yukon and Northwest Territories.

TABLE IX

Manufacturing industry	% Utilization	Kwhr per \$ of gross products	Avg. cents per kwhr
Nonferrous Metals.....	34.4	7.29	0.3
Wood and Pulp.....	33.8	4.90	0.4
Iron and Steel.....	10.4	1.26	0.6
Chemicals.....	8.2	5.21	0.4
Nonmetallic Minerals.....	6.3	2.24	0.4
Vegetable.....	2.7	0.38	1.0
Textile.....	2.4	0.56	0.9
Animal.....	1.2	0.19	1.3

The second and third articles in this series will treat, in some detail, of the major hydroelectric developments in each area of Canada, both actual and future.

#### Location and Development of Electroproducts Industries

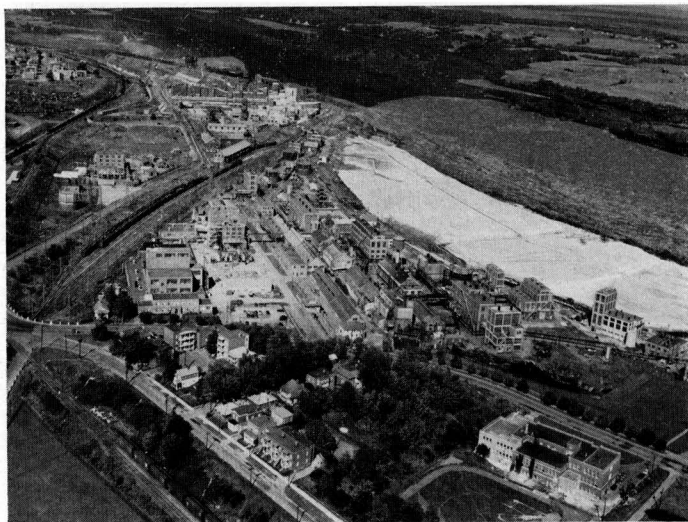
The establishment of Canada's electrochemical and electrometallurgical industries has proceeded according to three general patterns. The normal procedure has been for an electroproducts industry to move into an area, usually already well populated, where excess hydroelectric power was available at low rates, from existing power developments. The second type of development has been initiated by the discovery of huge ore bodies, usually quite remote from settlements or from fuel supplies, which sooner or later necessitated the harnessing of large water powers in the vicinity for the purpose of electrowinning or electrorefining the metal content of the ore. And, finally, the third, more recent type of establishment has seen the electrometallurgical project preceded

by a deliberate seeking out and developing of new hydroelectric power resources, usually in remote, undeveloped areas, for the express purpose of providing enormous amounts of power at low cost for this one particular project. All three types of development are proceeding in Canada at the present time.

The earliest electrochemical developments in Canada belong in the first category, the result of efforts to exploit local cheap hydroelectric power. This type of development has been responsible for the creation of some of Canada's largest electroproducts centers. The first example of this type was an electrolytic potassium chlorate plant built in the early 1890's near Buckingham, Quebec. This was superseded in 1896 by an electric furnace phosphorus plant, to which was added in 1898 the production of ferrochrome from Quebec ores. Today, the Electric Reduction Company of Canada Limited is carrying on the production of electric furnace phosphorus, ferrophosphorus and mineral wool, as well as electrolytic chlorates, at Buckingham, Quebec.

electroproducts center has grown up around the more recent, huge Beauharnois hydroelectric station on the St. Lawrence River near Montreal. Here there are located two plants producing ferroalloys, an aluminum smelter, and a chlorine-caustic soda plant.

Besides the four major electroproducts centers named above producing more than one type of product, there are a large number of other localities where a single type of operation is carried on, which may be grouped in our first category, i.e., of projects set up to utilize existing low-cost power. Here may be mentioned Sault Ste-Marie, Ontario, where the Chromium Mining and Smelting Corporation Limited produces ferrochromium, ferrosilicon and various exothermic silicon, and chrome alloys. At Windsor, Ontario, Canadian Industries Limited produces caustic soda, chlorine, and hydrogen, and operates another plant at Cornwall, Ontario, for these same products. At Montreal East, in Quebec, Canadian Copper Refiners Limited produce electrolytic copper with selenium and tellurium as byproducts. At



Some of the 80-odd buildings in the plants of Shawinigan Chemicals Limited at Shawinigan Falls, Quebec. Starting with limestone from its own quarries, coal and coke, and hydroelectric power, these plants produce carbide, acetylene, and a long list of organic chemicals, as well as acetylene black, resins, and stainless steel.

In the decade beginning 1900, large-scale electrochemical and electrometallurgical developments took place in Canada, mainly due to the availability of lost-cost hydro power generated at Niagara Falls, Ontario, and at Shawinigan Falls, Quebec. In this period there were built large plants for the production of calcium carbide, cyanamide, ferroalloys, artificial abrasives, and chlorine in the Niagara area, and aluminum and calcium carbide at Shawinigan Falls. Today the Niagara district produces such electroproducts as carbide, cyanamide, cyanide, sodium silicate, ferroalloys, artificial abrasives and refractories, artificial graphite, electrolytic nickel, rock wool, and electric steel. At Shawinigan Falls, on the St. Maurice River in Quebec, Canada's first aluminum smelter started operations in 1901, coincident with the first hydroelectric development of the Shawinigan Water and Power Company at this site. In the same year the Shawinigan Carbide Company was formed, which has since become Shawinigan Chemicals Limited. Besides aluminum and calcium carbide, Shawinigan Falls now produces also silicon carbide, chlorine, caustic soda and hydrogen, hydrogen peroxide, cerium (mischmetal), and electric steel, as direct electroproducts, besides many derivatives. Another large

Varenes, Quebec, on the south shore of the St. Lawrence River east of Montreal, a new plant of the Electric Reduction Company of Canada is about to go into operation to produce electric furnace phosphorus. A few miles further east at Sorel, Quebec, the Quebec Iron and Titanium Corporation has brought a new electric smelting plant into operation to produce titanium slag and steel from ilmenite ore. At Cap-de-la-Madeleine, at the confluence of the St. Maurice and St. Lawrence rivers, new production facilities have sprung up in recent years for artificial abrasives (Electro Refractories and Abrasives Canada Limited, and Norton Company) and for iron powder (Ferrum Limited). These latter plants, east of Montreal, receive their power from the six hydroelectric developments on the St. Maurice River of the Shawinigan Water and Power Company.

In this first group of industries we should perhaps also include chlorine plants operated by paper mills for their own purposes, i.e., bleaching of pulp. Such plants are to be found at Marathon, Temiskaming, Espanola, and Cornwall, all in Ontario. Dow Chemical of Canada operates a chlorine plant at Sarnia, Ontario, and the Aluminum Company of Canada one plant at Arvida, Quebec. Four other chlorine

plants were mentioned earlier, viz., Windsor and Cornwall in Ontario and Beauharnois and Shawinigan Falls in Quebec. The eleventh and latest chlorine plant in Canada is being built at Duvernay, Alberta.

And finally, an important member of this first category of electroproducts industries set up to utilize available low-cost power is the electric steel melting furnace. In 1952 about 18 per cent of Canada's steel for ingots and castings was melted in electric furnaces. There are some 83 electric steel furnaces operated by 36 different firms scattered across Canada; of these furnaces about 42 are located in Ontario, 23 in Quebec, and 11 in British Columbia.

The foregoing examples show clearly how the availability of low-cost hydroelectric power has been responsible for the establishment of a great many electroproducts industries in Canada. In many cases these industries are turning out products far in excess of Canada's requirements; a few are using imported raw materials. It is highly probable that many of these projects would never have been set up in Canada

nickel ore deposits in the Sudbury area of Ontario. This company in 1952 supplied over 75 per cent of the nickel used by the free world. "Inco's" electrolytic nickel refinery is located at Port Colborne, Ontario, while the electrolytic refining of blister copper and the major smelting operations are carried on at Copper Cliff, Ontario.

To this second group of electrometallurgical developments belongs also the electrolytic zinc plant of the Hudson Bay Mining and Smelting Company Limited at Flin Flon, Manitoba. Located only slightly south of the 55th parallel near the Saskatchewan-Manitoba border, it is the most northerly of Canada's electrometals industries. Blister copper from the Flin Flon smelter goes to Montreal East in Quebec for electrolytic refining. A hydroelectric development on the Churchill River makes possible the production of electrolytic zinc at Flin Flon, which has been carried on since 1930.

Two other electrometallurgical projects based primarily on local mineral deposits rather than on existing power supplies may be mentioned: that of Dominion Magnesium Lim-

Smelters and other plants of the Consolidated Mining and Smelting Company at Trail, B. C.



at all had not large quantities of dependable, inexpensive electric power been available from existing developments.

Turning now to the second group of electroproducts developments, those initiated primarily by the exploitation of ore deposits rather than of hydroelectric power resources, the earliest and most outstanding example is that of the Consolidated Mining and Smelting Company at Trail, British Columbia. Availability of tremendous supplies of lead-zinc ore in the area, nearby hydroelectric power resources, and access to coke have made Trail one of the leading chemical-metallurgical centers of the world. This company now produces zinc, lead, cadmium, bismuth, gold, silver, and indium by electrolytic separations or refining, and tin by an electrothermal process. At Trail "Cominco" also operates a large plant for electrolytic hydrogen and oxygen. Low-cost hydroelectric power for these processes has been obtained from a series of developments on the Kootenay River.

Another striking example of the use of electrometallurgy in exploiting ore-bodies is provided by the International Nickel Company of Canada, Limited, which produces electrolytically refined nickel, copper, silver and gold, and partially refined mixtures of the platinum metals from its huge copper-

ited at Haley, Ontario, and the recently completed plant of Kennametal of Canada Limited in British Columbia. The former utilizes local dolomite deposits to produce high purity magnesium by the Pidgeon process in high-vacuum retorts heated in electric resistor furnaces. Dominion Magnesium Limited also produces high-purity calcium metal in the same plant, and has produced other metals experimentally, notably titanium. In British Columbia, where important tungsten ore bodies are being developed, Kennametal of Canada Limited has begun electric furnace smelting of tungsten ore to produce tungsten carbide; this plant is located at Port Coquitlam, British Columbia.

Attention has recently been given to the possibility of producing electric furnace pig iron from iron ores in British Columbia and from the huge deposits of the Iron Ore Company of Canada and of Fenimore Iron in the Ungava region of Quebec. The latter area offers a large potential of hydroelectric power. However, little is known as yet of the economic feasibility of such possible developments, which are under study by various interests.

In the third category of electrometallurgical establishments in which the characteristic feature is the development of

huge hydroelectric power facilities for the exclusive use of the new project, the outstanding and, as yet, only example in Canada today is that of the Aluminum Company of Canada Limited. It has previously been mentioned that the first smelter of this company was set up at Shawinigan Falls, Quebec, in 1901 to take advantage of a power site developed there by the Shawinigan Water and Power Company. During World War II another smelter was established at Beauharnois, Quebec, an additional smelter at Shawinigan Falls, and a third at La Tuque on the St. Maurice River to use power available at those sites; the La Tuque smelter has since been dismantled. In the early 1920's it became apparent that the growing demand for power on the St. Maurice River on the part of other consumers would limit the amount available for aluminum. The Aluminum Company, therefore, began in 1925 a new development of its own in the Saguenay Valley of Quebec, where a large power potential existed. This area, at that time devoted mainly to farming and forestry, has since become the largest aluminum producer in the world, with smelters at Arvida and Isle Maligne, near the outlet of Lake St. John. The combined capacity of the company's present four smelters in Quebec accounts for nearly 25 per cent of the world's production of primary aluminum. Arvida now also produces caustic soda and chlorine and magnesium metal by electrolytic methods as further operations of the Aluminum Company, and fused alumina in a plant of the Simonds Canada Abrasive Company Limited, making this one of the large electroproducts centers of Canada.

But so tremendous is the world's demand for aluminum and so vital the supply of huge amounts of low-cost power for its production, that the Aluminum Company of Canada has now embarked on another combined power and smelter project, this time some 400 miles north of Vancouver, British Columbia, at Kemano and Kitimat in entirely undeveloped country to harness the approximate 2,000,000 hp obtainable there.

While the Aluminum Company of Canada presents the only existing examples of such large-scale moves into the northern wilderness in search of cheap power, there is evidence that other firms are thinking along the same lines. The Ventures-Frobisher Limited interests are reported to be investigating an area along the Yukon-British Columbia border of the Upper Yukon River where some 4-5 million hp are believed to be obtainable from relatively low-cost, successive hydro developments not too far removed from ice-free tide-water. Speculation is rife that such developments may give rise to a chain of smelters capable of treating ores from the Yukon, Alaska, and coastal British Columbia areas as well as imported foreign ores, to yield such products as iron and steel, ferroalloys, and cobalt. It has been reported that a 25,000 hp "pioneer" plant is to be installed by late 1955; however, no fixed plans have been announced as yet.

#### Future Opportunities

What the future may hold in store for Canada's electroproducts industries cannot be forecast, but there would appear to be no known obstacles in the way of a continuing development for the remainder of this century that will match

or surpass the achievements since 1900. All the prerequisites seem to be met: abundant raw materials, alert technology, a growing demand for the products, good transportation facilities, and, above all, abundant, inexpensive power. It is estimated that only about one-half of Canada's land area has received adequate mineral exploration; recent discoveries of tremendous reserves of petroleum, natural gas, iron ore and ilmenite ore, and important widespread indications of base-metals, plus tungsten and uranium, point to the potentialities. Accumulated "know-how" is extensive and sound; many important technological "firsts" have been achieved in Canada, e.g., world's first commercial electrolytic lead, North America's first cyanamide and magnesium plants. The world's need for high-purity metals as well as other electroproducts is constantly growing as known mineral deposits become depleted and electric power shortages develop in countries other than Canada. This is especially true of Canada's closest neighbor and best customer, the United States. The Paley Report has clearly underlined the growing dependence of the United States on other countries for many minerals. Table IV in this article shows that of six leading electroproducts of Canada from 40-99 per cent of total production is being exported, of which 30-90 per cent is going to the United States. Canada possesses well-developed railway and steamship facilities for the movement of raw materials and products, and the expected imminent deepening of the St. Lawrence Seaway should improve shipping possibilities. As for electric power, notwithstanding the very active development of hydro resources in the past, over 75 per cent of Canada's commercially economic hydroelectric resources lie undeveloped, in all about 50,000,000 hp. Some of this can be made available to the present heavily industrialized areas at relatively low rates, while other more remote resources may be used near their sites by developments such as we have seen at Flin Flon and Kitimat. And thermal power may play a larger role in the future, with the development of Western Canada's huge oil and natural gas reserves and their long distance transmission by pipelines, which is just beginning, and the extensive mechanization of coal mining on Canada's eastern seaboard. In such long-range forecasting, the possibilities of atomic power and even of tidal power in some locations, while today seemingly remote, should not be overlooked.

Two minor flaws mar this almost perfect picture of future possibilities—high tariffs on some products entering the United States, and import restrictions in many overseas nations. Yet Canada is confident that its enormous reserves of raw materials and electric power available at relatively low cost, and the pressing needs of other nations, will obliterate these barriers to trade.

In electroproducts, Canada indeed can claim a substantial share of the twentieth century!

*NOTE: In the second article of this series, it is proposed to deal in some detail with individual electroproducts industries and power developments in Quebec, the Maritime Provinces, and Newfoundland, while the third article will discuss such developments in Ontario and the Western Provinces, including the Yukon and the Northwest Territories.*



# The Rate of Dissolution of Zinc and Cadmium in Chromic Chloride Solutions<sup>1</sup>

CECIL V. KING AND NATALIE MAYER

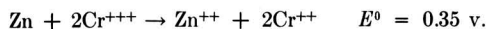
*Department of Chemistry, New York University, New York, New York*

## ABSTRACT

The relative potentials of the zinc-zinc ion, chromous-chromic ion systems might lead one to expect smooth progress of the reaction  $\text{Zn} + 2\text{Cr}^{+++} \rightarrow \text{Zn}^{++} + 2\text{Cr}^{++}$ . However, various other reactions are possible, and the dissolution or corrosion process is complicated; it is electrochemical in nature, and, in some solutions, rapid enough to permit transport control of the rates. The dissolution rate is highly dependent on the form of chromic ion present, on pretreatment of the metal surface, in some solutions on the acidity, and, under some conditions, the main reaction is hydrogen evolution with little reduction of chromic ion.

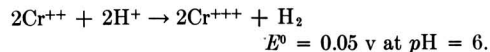
## INTRODUCTION

The dissolution of zinc in chromic chloride solutions was chosen for study for a number of reasons. The reduction of chromic ion to chromous does not require conversion of hydrogen ion to water as is usual with "depolarizers." The normal potentials of oxidizing and reducing couples are not dependent on hydrogen ion concentration; they are not widely different, but will allow essentially complete reaction:



It was desired to compare the reaction kinetically with reactions of similar type, for example, the oxidation of copper and silver by ferric and ceric ions (1-3). Finally, it was hoped to compare the reaction of zinc with that of iron and cadmium, where the driving potentials are smaller; this aim has been only partly realized.

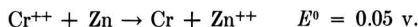
Several reactions can and do complicate the dissolution-reduction process. Chromic chloride solutions are acidic through hydrolysis, and, while pure zinc scarcely reacts with pure acid of such pH, catalytic hydrogen evolution becomes important in some solutions. Chromous salts are metastable in even slightly acid solutions:



Nevertheless, stable solutions of chromous salts can be prepared for analytical use by quantitative reduction of acidified chromic salts (or dichromate) by amalgamated zinc (4). Platinum and other substances

catalyze the reaction with hydrogen ion, and the reversible  $\text{Cr}^{++}-\text{Cr}^{+++}$  potential cannot be established on a platinum electrode (5). Oxygen reacts rather rapidly and, eventually, completely with chromous ion, but even traces of oxygen make the reversible potential measurements difficult (5).

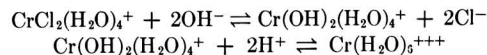
It is possible for zinc to carry the reduction to metallic chromium



There is no direct proof in the present research that this reaction takes place, since chromium was not identified as a product. However, hydrogen evolution with zinc and its absence with cadmium seems probably due to the formation of zinc-chromium couples.

The rate of dissolution is highly dependent on the form of chromic ion present. Aqueous chromic chloride solutions contain (6) the green dichlorotetraquo ion  $\text{CrCl}_2(\text{H}_2\text{O})_4^+$  and the purplish-blue (violet when very dilute) hexaquo ion  $\text{Cr}(\text{H}_2\text{O})_6^{+++}$ . At equilibrium, all of the ion is in the purple form in solutions up to 0.6M, while more concentrated solutions contain increasing amounts of the green form (42% at 8M). Solutions freshly prepared from the green hydrated salt contain the green ion, which changes to the purple ion or the equilibrium mixture slowly, requiring 18 hours or more at 25°C. Acidity favors the purple form, but inhibits the attainment of equilibrium; if acid is added to a freshly prepared dilute green solution, it remains green indefinitely.

This rather complicated behavior is explained as follows (7): conversion of green ion to violet occurs in two stages, and requires the presence of hydroxyl ions



<sup>1</sup> Manuscript received January 20, 1953. This paper was prepared for delivery before the Wrightsville Beach Meeting, September 13 to 16, 1953. From a Ph.D. thesis submitted by Natalie Heyman Mayer to the Graduate School of New York University, February 1953. Work done under Contract AT (30-1)-816 of the U. S. Atomic Energy Commission with New York University.

The first reaction takes place slowly in dilute acid, not at all in more concentrated acid. The intermediate ion is green. If a small amount of base (not enough to precipitate the hydroxide) is added to a dilute green solution, displacement of chloride takes place rapidly; acidification after a few minutes gives the purple form at once.

The two forms have different hydrolysis constants (8):  $K$  (green) =  $1.9 \times 10^{-6}$ ;  $K$  (purple) =  $1.6 \times 10^{-4}$  at 25°C. (These are for the first stage of hydrolysis, and the values vary considerably with ionic strength of the solution.) Formation of purple ion from green automatically slows down the conversion, since it increases the acidity.

#### EXPERIMENTAL

Cylinders of Special Purity zinc,<sup>2</sup> about 2.5 cm long and 2.0 to 1.6 cm in diameter (decreasing with use), were rotated in the solutions as in previous work (1-3). A few experiments with analytical grade zinc showed no significant difference except in hydrochloric acid alone. Some experiments were done with cadmium cylinders of similar dimensions; the metal was of best commercial grade.

All solutions were deaerated, and the experiments were carried out under nitrogen. The purple solutions were prepared by boiling, then cooling and storing under nitrogen until equilibrated (all solutions are green at the boiling point). Green solutions were prepared by dissolving the salt in, and diluting with, deaerated distilled water, with nitrogen continuously bubbling through.

Since the hydrated chromic chloride is hygroscopic, solutions were made at the approximate concentration desired, and analyzed. Stock solutions were made when possible, but many of the green solutions had to be used immediately. For analysis, the chromic ion was oxidized to chromate with sodium peroxide, excess being decomposed by boiling; then phosphoric acid and excess standard ferrous sulfate were added, and the remaining ferrous ion titrated with standard dichromate, using diphenylamine sulfonic acid as indicator. Mean concentrations are given below, and the actual concentrations were seldom more than 3 per cent different.

In some of the runs, a 600-ml beaker was used, and it was equipped with a plastic refrigerator bowl cover with close-fitting holes to admit the motor shaft, nitrogen inlet tube, etc. When it was desired to use small samples to be discarded after a few minutes, run, 65 to 100 ml of solution was placed in a small square bottle with neck slightly larger than the cylinder and Bakelite sleeve which covered the extended motor shaft. Nitrogen was admitted through a tube fitted into a hole in the side of the bottle. In

both methods, air was largely, though not rigorously, excluded.

At first, the temperature was maintained at  $30^\circ \pm 0.1^\circ\text{C}$ , but when the temperature coefficient was found to be low and the reproducibility of rates poor, most of the experiments were done at room temperature, between 25° and 30°C.

All rates were measured by weighing the cylinders, which were initially abraded and finally polished with No. 600 silicon carbide paper, or were etched after such polishing, as described below. Average weight losses per minute in short runs are plotted in the graphs. These may be taken as approximately "instantaneous" rates, except where the rate is obviously changing rapidly with time.

In the polarization experiments, current was supplied by dry cells and measured with calibrated meters. Electrical connection was made through mer-

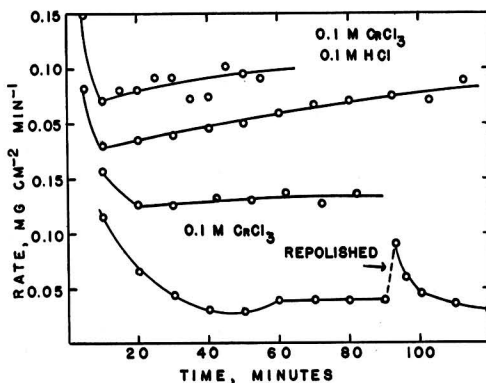


Fig. 1. Zinc cylinder (1.9 cm diameter) rotated in 500 ml purple chromic chloride solution at 2160 rpm, 30°C.

cury in a steel cup mounted on the motor shaft; a steel spring, fitted in a slot in the motor shaft extension, helped to make good contact with the metal cylinders. A platinum sheet 8 x 12 cm served as a second electrode.

#### Experiments with Purple Solutions

The cylinders were rotated for periods of 2 to 15 min, at 2160 rpm (~12000 cm/min peripheral speed), in 500 ml of solution at 30°C. During this time, 6 to 20 mg zinc ordinarily dissolved; after weighing, the cylinder was reimmersed in the same solution. The metal was polished at the start of each series of runs; the surface soon became dull and, in time, developed a gray-black film. The rates behaved as shown in Fig. 1 and 2. Results in identical solutions were similar, but varied widely in successive runs, either with the same or with different cylinders. Different methods of polishing, including

<sup>2</sup> New Jersey Zinc Sales Company, New York, N. Y.

bringing the zinc surface to a bright mirror finish in chromic acid etching baths, gave similar results.

Hydrogen evolution always accompanied the dissolution, and, even in runs of several hours duration, there was no evidence of reduction of chromic to chromous ion in the bulk of the solution. Low concentrations of added hydrochloric acid had little effect; larger amounts increased the rate appreciably, and diminished the amount of black film formation. In long runs, the cylinders developed a few deep pits. If not removed completely by abrading the cylinders, these developed further in subsequent runs; eventually a few new pits would appear.

Analysis of the gray-black film proved difficult. Enough was scraped from a cylinder to subject to x-ray analysis, but it showed no crystalline structure. The film was allowed to develop in several 3- to 5-hour runs, and removed each time in the same

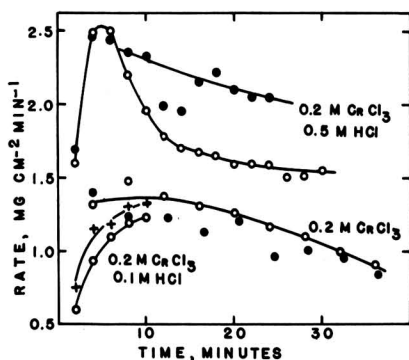


FIG. 2. Zinc cylinder (1.9 cm diameter) rotated in 500 ml purple chromic chloride solution at 2160 rpm, 30°C.

sample of dilute nitric acid. The solution was colorless and gave no test for any chromium salt.

When rotated, the metal acquires and maintains only a very thin film. When left stationary in the solution for 24 hours, a thicker film is formed. This is not removed by dilute nitric acid, but turns green in concentrated nitric acid. It can then be removed in boiling, dilute hydrochloric acid, and gives a green solution containing chromic chloride.

This seems to identify the initial black film as chromous oxide  $\text{CrO}$ , which does not dissolve in dilute acids, but is oxidized to  $\text{Cr}_2\text{O}_3$  by concentrated nitric acid. Evidently hydrogen evolution at the zinc surface causes the  $\text{pH}$  to rise, and all chromous ion formed is precipitated as  $\text{CrO}$ . It is possible that chromic hydroxide or oxide is also formed, but this could not be proved.

A sample of 0.15M purple chromic chloride (50 ml) was run slowly through a Jones reductor column filled with dry, 20-30 mesh (unamalgamated) zinc;

the  $\text{pH}$  of the solution increased from 2.3 to 3.9, but there was no apparent reduction. After thorough washing, dilute sulfuric acid was run through, and the emerging solution was intensely green in color. Evidently chromic hydroxide or a basic salt had been retained on the zinc. If either a chromous compound or metallic chromium was formed, it was not evident.

Initial rates (i.e., with the zinc repolished for each point) were now run, with a wide range of added hydrochloric acid; the results are shown in Fig. 3. The more acid solutions were green, since they were deaerated by boiling, and it was not known at the time that the presence of acid would prevent equilibration on cooling. Hydrogen evolution was copious, and the green solutions changed to purple in longer runs. This is due to the pronounced increase in  $\text{pH}$  at the zinc surface, which allows exchange of

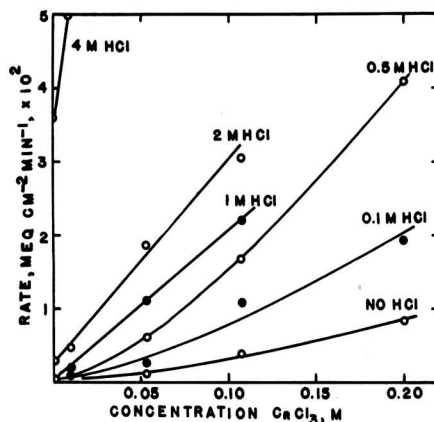
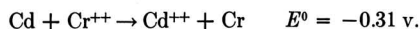


FIG. 3. Effect of HCl on dissolution rate of zinc cylinder at 2160 rpm, 25°-30°C, 65 ml chromic chloride solution.

hydroxyl for chloride in the green ion, with subsequent conversion to purple ion in the bulk of the solution.

In these runs the zinc surface always became gray, but definite films were not evident in the more acid solutions. Even in long runs the solutions did not change to the characteristic blue of chromous chloride, nor could chromous hydroxide be identified on the addition of base. There was no way of testing for metallic chromium on the zinc surface, although it was suspected that this was responsible for the hydrogen evolution.

For comparison, similar experiments were carried out with cadmium cylinders of similar dimensions. While cadmium can reduce chromic ion to chromous with the concentrations used here, it cannot carry the reduction to metallic chromium:



The rates obtained are plotted in Fig. 4 and 5. Rates for both zinc (Fig. 3) and cadmium are given in milliequivalents to facilitate comparison.

Cadmium dissolves about half as fast as zinc under these conditions; no visible films are formed on the surface, no hydrogen is evolved, and, in longer runs (45 min or more), much of the chromic ion is reduced. The more acid green solutions change, not to purple, but to the characteristic blue of chromous chloride. Addition of sodium hydroxide precipitates

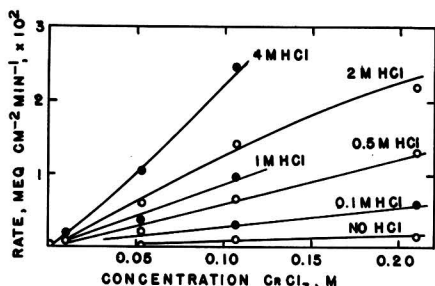


Fig. 4. Effect of HCl on dissolution rate of cadmium cylinder at 2160 rpm, 25°-30°C, 65 ml chromic chloride solution.

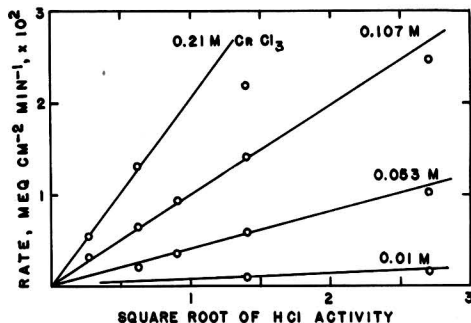


Fig. 5. The rates of Fig. 4 vs. square root of HCl activity

yellow-brown  $\text{Cr}(\text{OH})_2$ , which slowly changes to blue-green  $\text{Cr}(\text{OH})_3$  in the air.

None of these rates are additive for acid and chromic ion. The difference in reactivity of zinc and cadmium in deaerated hydrochloric acid alone is very evident. Cadmium dissolves at a scarcely appreciable rate even in 4M HCl on the scale of Fig. 4; zinc dissolution increases exponentially with acid concentration.

#### Experiments with Green Solutions

The cylinders were rotated in 65-ml samples of solution for periods of  $\frac{1}{2}$  to 5 min, during which time 20 to 50 mg of zinc ordinarily dissolved. The rates increase as the zinc becomes etched, as shown in

Fig. 6, levelling off in 15 to 40 min, depending on the concentration. The rates were more reproducible with etched zinc, but, if not used for a day or more, a cylinder had to be re-etched for some time to repeat the maximum rate.

The experiments described below were done with etched cylinders. The zinc surface became dull, but no corrosion film was apparent. Each cylinder consisted of only a few single crystals which were clearly visible. The surface remained smooth to the eye and touch, but under the microscope appeared very rough, each crystal looking somewhat like the surface of a corroded file. There was no pitting; in the course of the experiments some crystal faces dissolved more

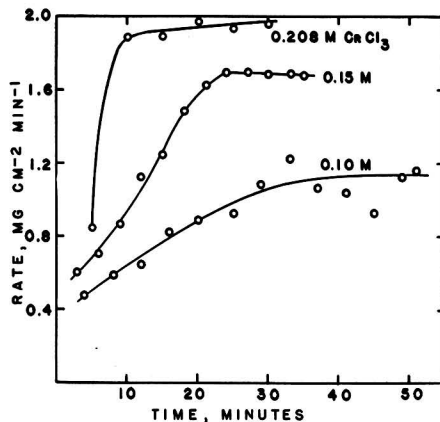


Fig. 6. Zinc cylinder (1.8 cm diameter) rotated in 65 ml green chromic chloride solution at 2160 rpm, 23°-25°C, fresh solution for each point. Another run in 0.15M  $\text{CrCl}_3$  rose more slowly to 1.63 after 65 min.

than others, resulting in flattened spots on the cylinders.

Hydrogen evolution was visible in somewhat less than half these experiments, and began suddenly after a few minutes of rotation in the solution. It appeared to be a chance occurrence and showed no correlation with conditions or concentration. When hydrogen was evolved, the rates were less reproducible, but not distinctly low or high. In longer runs, the solutions changed to purple when hydrogen was produced, and there was no test for chromous ion; if no hydrogen was evolved, in 45 min or more the solution became blue and  $\text{Cr}(\text{OH})_2$  could be precipitated.

Fig. 7 shows the effect of rotational speed of the cylinder on the rate, and Fig. 8 gives more details of the dependence of rate on concentration. It will be shown below that most of these rates are in the range of diffusion (or transport) control, but it is obvious that this is not true for all concentrations and ro-

tational speeds, since, if it were, the rates would be linear with both variables.

*Temperature Coefficients*

Rates were measured in two green chromic chloride solutions at two rotational speeds, at temperatures between 10° and 70°C, and the results are shown in

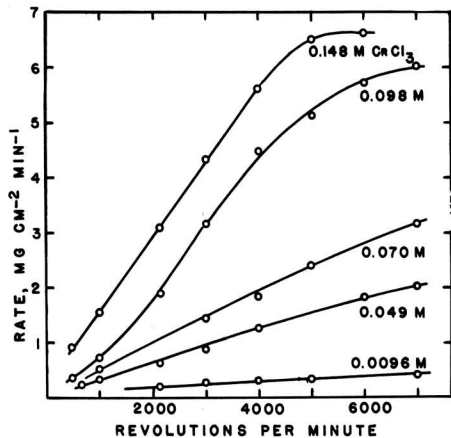


FIG. 7. Etched zinc cylinders rotated in 400 ml green chromic chloride at 27°C.

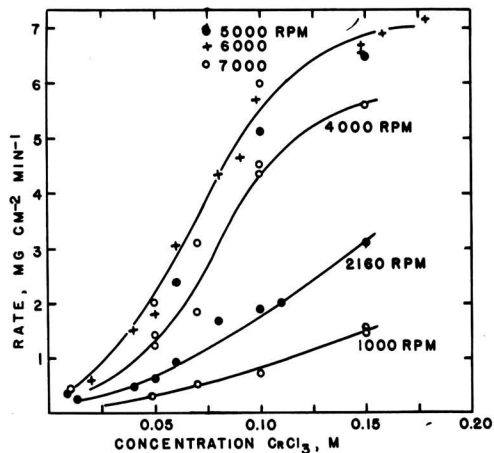


FIG. 8. Etched zinc cylinders rotated in 400 ml green chromic chloride at 27°C.

Fig. 9. The solutions used are permanently green at the boiling point, but change fairly rapidly to purple between 50° and 70°C. Consequently, a 400-ml sample was heated rapidly to the appropriate temperature and the rotating cylinder immediately immersed for a 30- or 60-sec period. The highest weight loss was 83 mg in 30 sec. Because of the method, the accuracy is not high.

The change in slope of the curves for 6000 rpm above 50°C indicates a change in mechanism rather than conversion to the purple ion, since it does not occur at 2160 rpm. The lower-temperature slopes give activation energies lying between 4000 and 6000 cal/equivalent, which is in the range of diffusion activation.

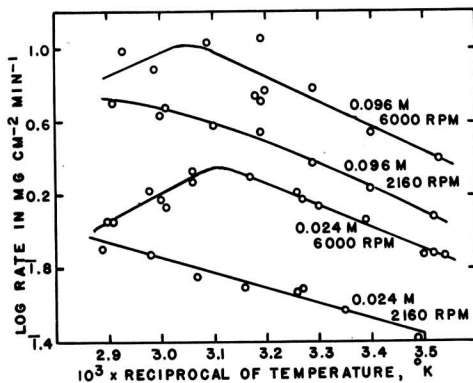


FIG. 9. Temperature coefficient in green chromic chloride solutions; zinc cylinders 1.8 cm diameter.

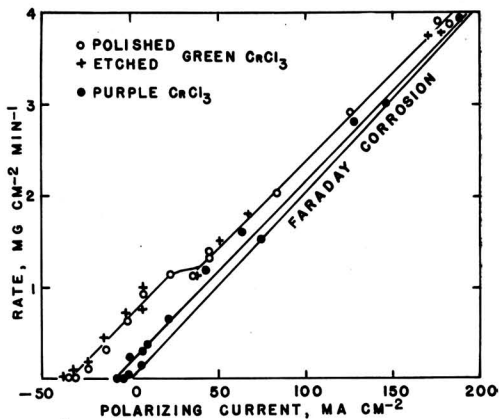


FIG. 10. Cathodic and anodic polarization of zinc cylinders 1.7 cm diameter, 2160 rpm, 27°C.

*Polarization of the Zinc*

Zinc cylinders rotating at 2160 rpm in 400 ml of solution were subjected to cathodic and anodic polarization (at ~27°C) in both purple and green solutions, using an auxiliary platinum electrode. The results are shown in Fig. 10. The metal is readily protected from corrosion by a cathodic current, about 8 ma/cm<sup>2</sup> being necessary in purple solutions, 30 to 40 ma/cm<sup>2</sup> in green solutions. The time of immersion was 5 min in purple, 3 min in green solutions for each measurement, and it is rather surprising that

polished and etched zinc dissolves at nearly the same rate in the latter solutions when polarized. In view of the variability of rate measurements sometimes found, it is not certain whether the polarization curve should be drawn as shown in Fig. 10, or whether a straight line should be drawn through all the points for green solutions. In any case, there is probably some reduction in free corrosion on anodic polarization.

## DISCUSSION

### Purple Solutions

It may be concluded from the observations with purple chromic chloride solutions that the rate of zinc dissolution is never controlled by transport of chromic ion to the surface. The main reaction is hydrogen evolution and is electrochemical in nature in that permanent, separate anodic and cathodic areas are established. There is some reduction to chromous, and, at low acidities, CrO is formed and partially blocks the surface, accounting for the low rates.

Free hydrogen evolution requires either the formation of metallic couples or catalytic reduction of hydrogen ion by the chromous ion formed. Lack of hydrogen evolution with cadmium, although reduction takes place, suggests that deposition of metallic chromium on the zinc is responsible for the cathodic areas. The formation of couples and the entire rate control seems to be determined "accidentally" (which may mean the exact condition of the zinc surface), hence the rates vary widely from run to run, change with time, etc. The behavior resembles that of zinc in acidified solutions of methylene blue (9), which is slowly reduced with "catalytic" evolution of 30 to 40 times as many equivalents of hydrogen, and pitting of the zinc. Possibly metal impurities in the dye deposit on the zinc and form couples, as is assumed here for chromium.

The enormous effect of added hydrochloric acid suggests that chromic ion is not reduced directly by either zinc or cadmium, but rather by atomic hydrogen on the metal surface. The dissolution of zinc is complicated, but reaction with cadmium proceeds smoothly, probably with quantitative reduction of chromic ion. In the latter case, the rates, as shown in Fig. 4 and 5, can be approximately represented by the equation:

$$dn/dt = kC_{Cr^{+++}}a_{HCl}^{1/2}$$

where  $a_{HCl}$  is the hydrochloric acid activity (10).

It is important in such a case to estimate the maximum rate at which chromic ion could reach the cadmium surface by convective-diffusive transport if the surface process were very rapid. One way to do this is by means of an equation developed by Wagner (11)

for the rotating cylinder-turbulent flow experimental system:

$$dn/dt = 0.010 cv(D/\nu)^{0.83} \quad (I)$$

This equation is based on the method of dimensionless group analysis (12) to correlate previous experimental work (13); the values 0.010 and 0.83 are constants,  $v$  is the peripheral speed of the cylinder,  $D$  the diffusion coefficient of the reagent, and  $\nu$  the kinematic viscosity of the solution.

Substituting in equation (I) the values:  $c = 0.107M$  ( $107 \times 10^{-6}$  moles  $cm^{-3}$ ),  $v = 12000$   $cm \text{ min}^{-1}$ ,  $\nu = 0.0090$   $cm^2 \text{ sec}^{-1}$  for dilute aqueous solutions,  $D = 7.4 \times 10^{-6}$   $cm^2 \text{ sec}^{-1}$ , estimated from the value for ferric ion at 15°C (14), the calculated maximum rate becomes  $dn/dt = 3.5 \times 10^{-2}$   $meq \text{ cm}^{-2} \text{ min}^{-1}$ . This is less than twice the highest experimental value for this concentration (Fig. 5). It is concluded that the lower rates in Fig. 5 are controlled mainly by the surface process, and that the highest points fall below the straight lines because a partial concentration gradient is set up (mixed rate control).

### Green Solutions

The over-all picture for zinc dissolving in green chromic chloride solutions is that the rate process hovers between chemical (or electrochemical) and diffusion control. With polished cylinders, the former is slower and rate-controlling; as the surface becomes etched its real area becomes greater, the chemical rate increases, and transport to the surface becomes the slowest process.

At the lowest concentrations of Fig. 8, the rates are not at maximum values, since they increase with concentration faster than the latter. Above 6000 rpm, there is little if any increase in rate, and, at 4000 rpm and above, the rates approach maximum values at 0.15M CrCl<sub>3</sub>. At intermediate values one can expect transport-controlled rates.

An alternative method of testing observed rates is to calculate the "effective diffusion layer thickness" by means of the Nernst equation:

$$\delta = \frac{DAc}{dn/dt} \quad (II)$$

and compare the values found with those for known transport-controlled reactions. Table I gives values of  $\delta$  calculated from the rates of Fig. 7 for 5000 rpm. These may be compared with values ranging from  $4.0 \times 10^{-4}$  to  $4.4 \times 10^{-4}$   $cm$  found previously for acetic and hydrochloric acids with similar cylinders rotating at 5000 rpm (15).

Values of  $\delta$  vary somewhat with  $D$ , as can be seen by combining equations (I) and (II), but this is unimportant. The two low values of Table I, corresponding to higher rates than expected, are perhaps

due to greater roughness of the surface at the higher concentrations. A "roughness factor" can be inserted in equation (I) and is necessary, if increased turbulence is caused at the metal interface (11). It is also possible that these high rates were caused by dissolution with hydrogen evolution in addition to chromic reduction.

It would be of interest to study rates in the green solutions with added acid. If there were no hydrogen evolution, all rates of chromic reduction should be transport-controlled, since the chemical rates would no doubt be increased. If hydrogen evolution started (as by "accidental" deposition of chromium), the rates should be higher and dependent on the acidity,

TABLE I. *Effective diffusion layer thickness*  
 $D = 7.4 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ , 5000 rpm, cylinder  
 diameter 1.9 cm

$C_{\text{CrCl}_2}, M$	Rate, $\text{meq cm}^{-2} \text{ min}^{-1}$	$\delta$ , cm, $\times 10^4$
0.0096	0.010	4.2
0.049	0.047	4.6
0.070	0.072	4.3
0.098	0.156	3.5
0.148	0.198	3.3

but extremely variable from one experiment to another.

#### CONCLUSIONS

In this work with zinc and cadmium dissolution in chromic chloride solutions, three rate-controlling processes have been found operative under suitable conditions.

1. Transport of chromic ion, by convection and diffusion, to the metal surface. This process is rate-controlling with zinc in the green solutions, provided the chemical rate is sufficiently high, as with an etched surface and probably with enough hydrogen ion present (although this factor was not tested). Also, accidental hydrogen evolution may vitiate the transport control.

2. Simple chemical control, as with cadmium in

the purple solutions with added acid. The dissolution of zinc in the same solutions is probably partly under the same type of chemical control, but the process is complicated by simultaneous hydrogen evolution, and the over-all rates are considerably greater.

3. An electrochemical process in which chromium is probably deposited on the zinc, forming couples; hydrogen evolution is then the main reaction, and the rates vary in accidental fashion. Since hydrogen ion is used up, the pH rises at the zinc surface and varying amounts of chromous oxide, perhaps chromic oxide or hydroxide, are formed. Precipitation of these solids, with indefinite amounts of chromium, leads to great variation in the dissolution rates.

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

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# Some Properties of Tin-II Sulfate Solutions and Their Role in Electrodeposition of Tin

## II. Solutions with Tin-II Sulfate and Sulfuric Acid Present<sup>1</sup>

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### ABSTRACT

Density, refractive index, surface tension, viscosity, freezing point depression, conductivity, transference number, and the electrode potential to pure tin and hydrogen, respectively, have been measured for a range of tin-II sulfate-sulfuric acid solutions. The effects of the sulfuric acid on these properties are noted. Relationships between concentration and the magnitude of these properties and various derived properties are determined. Possible structural species existing in the solutions are suggested.

### INTRODUCTION

Some physical properties of aqueous tin-II sulfate solutions have been reported in a previous paper (1). In the present paper the same properties are studied for the aqueous system, tin-II sulfate-sulfuric acid. Using the information given in the two papers as a basis for comparison, a study of physical properties of similar solutions containing addition agents should enable one to determine which of these physical properties, if any, vary in the presence of effective addition agents. The work on addition agents will be reported in the next paper of this series.

### EXPERIMENTAL

The procedures and equipment have been previously reported (1). It was necessary to substitute a low-temperature thermometer, graduated in 0.1°C divisions, for the differential thermometer in the freezing point work.

Since the properties studied are a function of both the molar concentration of the tin-II sulfate present and its mole fraction,<sup>2</sup> it was thought best to confine the major part of the experimental work to a series of concentrations at the same mole fraction. The mole fraction selected was 0.32. However, additional baths, sufficient in number to indicate the effect of varying mole fraction, were run.

### RESULTS

Molar concentrations are given in Table I, together with experimental values of the physical properties measured. Experimental values for the electrical properties measured are given in Table II.

<sup>1</sup> Manuscript received December 15, 1952. This paper was prepared for delivery before the Montreal Meeting, October 26 to 30, 1952.

<sup>2</sup> Mole fraction, as used in this paper, is defined as the number of moles of tin-II sulfate divided by the total number of moles of tin-II sulfate and sulfuric acid.

Refractive index measurements are plotted vs. the molar concentration of tin-II ion in Fig. 1. The effect of mole fraction variation is shown by the

TABLE I. Some physical properties of SnSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> solutions

Concentrations		Density (g/ml)	Refractive index	Viscosity (poise)	Surface tension (dynes/cm)	Freezing point (°C)
Moles tin-II sulfate/liter	Moles sulfuric acid/liter					
0.028	0.065	1.006	1.3343	0.0090	72.7	-0.18
0.060	0.131	1.017	1.3363	0.0092	72.5	-0.58
0.112	0.234	1.032	1.3390	0.0095	—	-0.99
0.172	0.373	1.052	1.3426	0.0099	73.2	-1.65
0.225	0.506	1.070	1.3460	—	73.7	-2.38
0.262	0.529	1.079	1.3471	0.0105	—	-2.47
0.340	0.769	1.109	1.3530	0.0115	73.3	-3.91
0.405	1.029	1.134	1.3566	0.0120	73.9	-5.19
0.462	1.039	1.146	1.3590	0.0124	74.7	-5.57
0.519	1.180	1.167	1.3623	0.0137	74.7	-6.57

TABLE II. Some electrical properties of SnSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> solutions

Moles tin-II sulfate/liter	Specific conductivity (mhos)	E <sub>Sn, Sn<sup>++</sup></sub> (volts)	E <sub>H<sub>2</sub>, H<sup>+</sup></sub> (volts)	Transference No. Sn <sup>++</sup> H <sup>+</sup>	
0.028	0.0325	0.2266	0.0655	0.07	0.65
0.060	0.0652	0.2263	0.0520	0.05	0.79
0.112	0.1088	0.2243	0.0384	0.06	—
0.172	0.1797	0.2240	0.0284	0.00	0.72
0.225	0.2342	0.2240	0.0284	-0.12	0.82
0.262	0.2429	0.2270	0.0301	-0.09	0.66
0.340	0.2246	0.2269	0.0125	-0.05	0.26
0.405	0.2809	0.2252	0.0165	-0.04	0.21
0.462	0.3357	0.2224	0.0138	+0.07	0.58
0.519	0.4435	0.2276	0.0193	-0.03	0.66

family of curves. While the 0.32 mole fraction series is the only one studied in detail, it is apparent that refractive indices for other mole fractions arrange



themselves in the order of mole fraction. In regard to the 0.32 series curve, it is to be noted that there is a break at about 0.27 moles per liter. For comparison purposes the curve for pure tin-II sulfate ( $n = 1.00$ ) solutions has been included (1). While the plot is not presented, the molar refraction curve shows a gradual increase in the magnitude of molar refraction up to 0.3M tin-II sulfate. Above 0.3M, this curve levels off at a value of about 24.

A graph of the density data is not presented because the curves resemble those for refractive index. There is a marked inflection in the 0.32 mole fraction curve at approximately the same concentration of tin-II ion as in the corresponding refractive index plot.

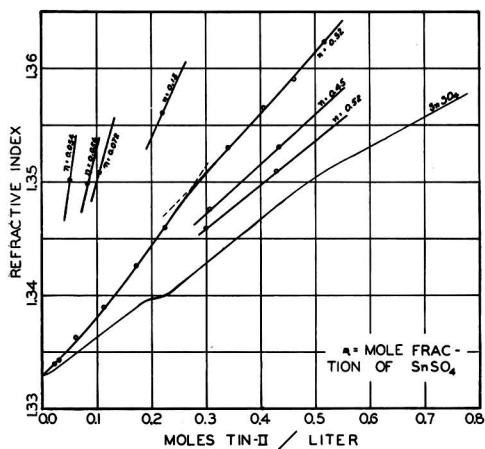


FIG. 1. Variation of refractive index of SnSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> solutions with molar concentration of SnSO<sub>4</sub> for various mole fractions of SnSO<sub>4</sub>.

The surface tension measurements are given in Table I, but are not presented in graphic form. However, the following points may be significant. For all solutions studied the surface tension is greater than that of pure water (71.8 dynes/cm). This indicates that the molecular species present in the solutions are, at least partially, in the ionic form. Macleod's constant (2) was calculated at each concentration; the plot obtained is similar to that shown in Fig. 1.

Absolute viscosity data are plotted in Fig. 2. The curves for sulfuric acid (3) and tin-II sulfate solutions are included for comparison. The points for mole fractions other than 0.32 mole fraction are omitted in this and the following plots since in all cases they arrange themselves in the order of mole fraction as shown in Fig. 1. The dotted line represents the theoretical viscosity of tin-II sulfate-sulfuric acid solutions. It was obtained by summation of the con-

tributions of tin-II sulfate and sulfuric acid, respectively, no interaction between these substances being assumed. Relative viscosity and specific viscosity were calculated for each concentration of

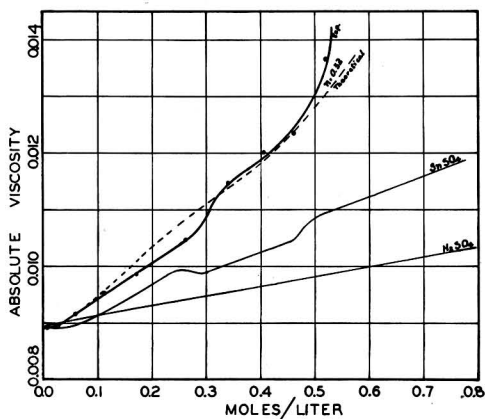


FIG. 2. Variation of absolute viscosity (poises) with concentration of SnSO<sub>4</sub> for the 0.34 mole fraction SnSO<sub>4</sub> series. The curves for pure SnSO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> solutions are shown for comparison. The theoretical viscosity, assuming additivity of viscosity of the constituents, is shown as a broken line.

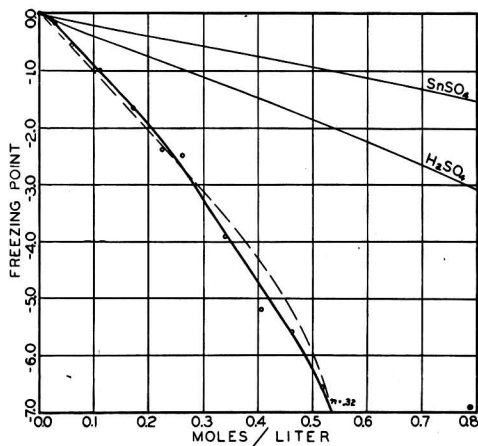


FIG. 3. Variation of the freezing points (°C) of the 0.34 mole fraction series of solutions with concentration of SnSO<sub>4</sub>. The SnSO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, and theoretical 0.34 mole fraction series curve are shown for comparison.

tin-II ion. These two plots are not shown since they duplicate the general features shown in Fig. 2.

Freezing point data are presented in Fig. 3. It is noteworthy that for the 0.32 mole fraction series the theoretical curve, obtained by summing contributions of tin-II sulfate and sulfuric acid, closely parallels the experimental curve to about 0.2 M tin-II sulfate.

At higher concentrations the experimental depressions are greater than theoretical. The values for van't Hoff's  $i$  increase steadily with increasing concentration in the 0.32 mole fraction series.

Specific conductivity and equivalent conductivity data are plotted vs. concentration of tin-II in Fig. 4 and Fig. 5, respectively. Conductivity variation with

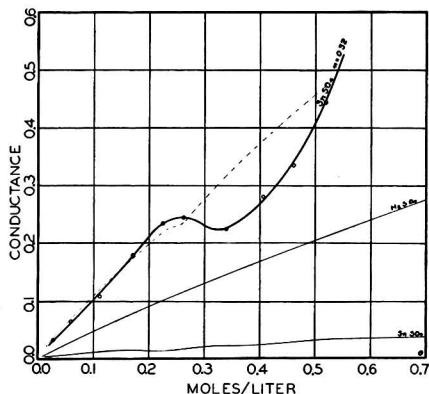


Fig. 4. Variation of the specific conductance of the 0.34 mole fraction series of solutions with concentration of  $\text{SnSO}_4$ . The  $\text{SnSO}_4$ ,  $\text{H}_2\text{SO}_4$ , and theoretical 0.34 mole fraction series curve are shown for comparison.

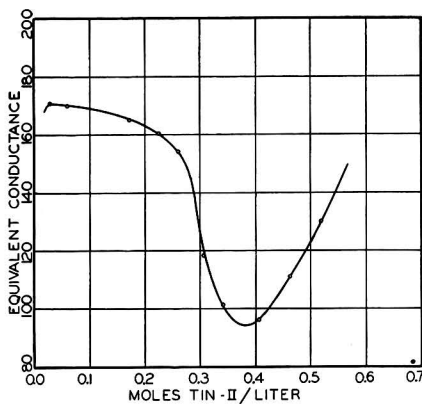


Fig. 5. Variation of equivalent conductance (0.34 series) with  $\text{SnSO}_4$  concentration.

change in concentration of sulfuric acid and vs. total sulfate was also studied. The plots obtained indicate that conductivity follows tin-II concentration more closely than acid or total sulfate concentration, especially at higher total concentrations. Using Onsager's equation, the equivalent conductance at infinite dilution was calculated for each concentration of tin-II ion, and the values plotted. Two straight lines result, one ranging from 0.03M to 0.3M, and the other from 0.3M to 0.6M tin-II ion.

Transference data are presented in Fig. 6. The transference number for tin-II is small and positive until nearly 0.2M tin-II. At higher concentrations it is negative, reaching a minimum value at about 0.23M and increasing slightly thereafter. The curve for transference number for hydrogen ion practically duplicates that for equivalent conductance. This is expected since hydrogen ion is the predominant

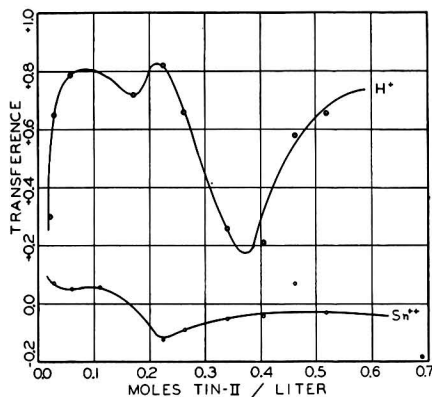


Fig. 6. Variation of transference by tin-II and hydrogen ions, respectively, with  $\text{SnSO}_4$  concentration.

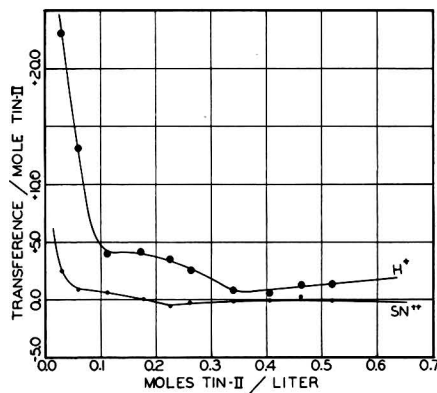


Fig. 7. Variation of the ratio of transference number to the molar concentration of tin-II with  $\text{SnSO}_4$  concentration.

carrier of the current in these solutions. As found with conductivity, the transference by hydrogen ion seems to vary as a function of the tin-II concentration, rather than the concentration of sulfuric acid or total sulfate. In Fig. 7 the ratio of the transference of each of the ions to molar concentration of tin-II is plotted vs. molar concentration of tin-II.

Electrode potentials are plotted vs. tin-II concentration in Fig. 8. Activity coefficients, based on these measurements, are shown in Fig. 9. The plots for activity are not shown, but the curve obtained for

hydrogen ion is similar to that for specific conductivity.

The plating behavior as expected is unsatisfactory. In general, increasing the acid ratio increases the brightness of the crystals, while increasing the tin-II ratio increases the grayness of the deposits. At lower current densities, especially in the still bath, there is a tendency to give gray powdery deposits, the clumps

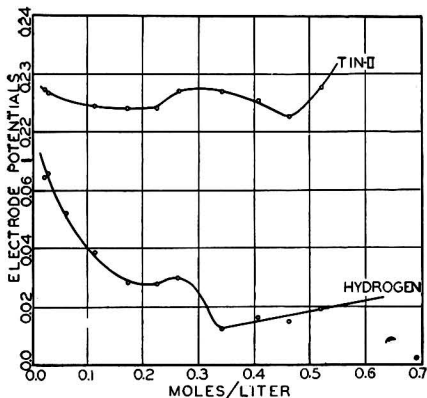


Fig. 8. Variation of single electrode potentials (volts) with concentration of  $\text{SnSO}_4$ .

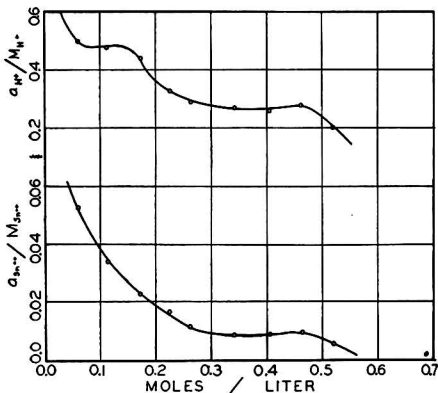


Fig. 9. Variation of activity coefficients of hydrogen and tin-II, respectively, with  $\text{SnSO}_4$  concentration.

of powdery crystals becoming tighter with increasing electrolyte concentration. Increasing current density and concentration result in increasingly longer branched needles, the branching becoming progressively less with increasing concentration. There is, as expected, severe gassing at high current densities and low tin-II concentrations.

#### DISCUSSION

This discussion must be concerned primarily with the 0.32 mole fraction tin-II sulfate series of solu-

tions, since this series is the only one in which a reasonably complete range of concentrations was studied. A study of the plots presented indicates two general concentration ranges of consistent behavior: the first, 0.0–0.2M tin-II sulfate and, the second, from approximately 0.3–0.6M tin-II sulfate. For concentrations between these ranges, that is, 0.2–0.3M, the curves obtained by plotting property vs. molar concentration show a break or pronounced change in slope. It may also be noted that when the theoretical curves obtained by summation of the effects of pure tin-II sulfate and pure sulfuric acid are plotted, the deviation from the experimental value changes sign between 0.20–0.30M. The conclusion drawn is that there are two areas of behavior for solutions of 0.32 mole fraction tin-II sulfate-sulfuric acid. Consequently the molecular species present must be different in each, with a transition between species falling between 0.2–0.3M.

*Concentration range 0.0–0.2M.*—In this range the contributions of tin-II sulfate and sulfuric acid to a given property are very nearly additive. This indicates that, for the most part, the two components are acting independently of one another. This range represents those concentrations of sulfate ion in which the tin-II exists either as simple ions, molecules, or the complex  $\text{Sn}[\text{Sn}(\text{SO}_4)_2]$  depending upon concentration as presented in the previous paper (1).

As shown in Fig. 6, the transference number of tin-II is positive in this concentration range. It decreases steadily with increasing concentration, becomes zero at about 0.18M tin-II; it is negative at higher concentrations. This is indicative of the presence of free tin-II ion, the number of free tin-II ions decreasing with concentration. The gradual decrease in concentration of free tin-II ion is also indicated by the activity coefficient of tin-II. The numerical value of this latter property decreases with increased concentration in the concentration range under study.

Freezing point data also give some light as to the nature of the molecular species present in solutions within the 0–0.2M tin-II range. With reference to Fig. 3 it is seen that the theoretical curve obtained by summing contributions of tin-II sulfate and sulfuric acid, if one assumes no appreciable interreaction, closely parallels the curve obtained from the experimental data. This indicates that tin-II exists in ultimate particles similar to those in pure tin-II sulfate solutions of corresponding concentration. That is, the tin-II sulfate exists in low concentrations as tin-II ions, sulfate ions, and tin-II sulfate molecules, with the relative amounts of each changing in favor of the molecular form with increasing concentration.

Theoretical freezing points may also be calculated

by use of concentration data in Table I and activity data derived from the electrode potentials given in Table II. Using the concentration of free ions, as given by the activity, and the concentration of molecules, as given by the difference between molar concentration and activity, the following freezing points may be calculated for the respective solutions in this concentration range:  $-0.31^\circ$ ,  $-0.61^\circ$ ,  $-1.05^\circ$ ,  $-1.63^\circ\text{C}$ . The calculated value for the  $0.225M$  solution is  $-1.98^\circ\text{C}$ . The corresponding experimental freezing points are  $-0.18^\circ$ ,  $-0.58^\circ$ ,  $-0.99^\circ$ ,  $-1.65^\circ\text{C}$ ;  $-2.38^\circ\text{C}$  for the  $0.225M$  solution. This correspondence between calculated and experimental values further supports the view that within this concentration range the tin-II exists in varying ratios of simple tin-II ions and tin-II sulfate molecules, the actual ratio being a function of the concentration of the solution. Above  $0.2M$  the theoretical freezing points agree with the experimentally determined values only on the assumption of the existence of the tin-II in complex negative ions.

Molar refraction does not vary linearly with concentration in this region. This also lends support to the supposition that a change in ratio of the various particles is taking place.

On the basis of the evidence presented it seems probable that simple molecules and ions of tin-II sulfate and sulfuric acid exist in the lower part of the concentration range. As concentration increases the molecular tin-II sulfate increases at the expense of the simple tin-II ions, possibly followed by the appearance of some  $[\text{Sn}(\text{SO}_4)_2]^-$  complex ion.

*Concentration range 0.3–0.6M.*—In this range the existence of the tin-II in complex ions is indicated. Transference by tin-II is negative (Fig. 6). The activity coefficient levels off at very low values (Fig. 9). Theoretical values for specific conductance obtained by summing contributions by each component are much larger than the experimental, indicating heavy complex ions (Fig. 4).

The existence of one fundamental species of particle in solutions in this concentration range is indicated by the nearly constant values for the ratios of a given property to the concentration of tin-II ions, that is the contribution per mole of tin-II ion to a given property becomes constant or nearly so. This is ordinarily possible only if the ultimate particle of the substance in solution remains constant. The slight slope of some of the lines obtained on plotting these molar quantities vs. tin-II concentration may be explained by slight changes in ionization of the complex acids present. Plots of this type are shown for transference and activity in Fig. 7 and 9, re-

spectively. Molar refraction becomes practically constant at a value of 24 in this concentration range. The ratio of specific viscosity to tin-II concentration is also practically constant. Equivalent conductance (infinite dilution) as calculated using Onsager's equation, gives a straight line in this concentration range.

Two sulfatostannite ions may be postulated,  $[\text{Sn}(\text{SO}_4)_2]^-$  and  $[\text{Sn}(\text{SO}_4)_3]^{2-}$ . Calculation of freezing points, assuming the former, yields theoretical values much below experimental. Only by using  $\text{H}_4[\text{Sn}(\text{SO}_4)_3]$  and  $\text{H}_2\text{Sn}[\text{Sn}(\text{SO}_4)_3]$ , and assuming a high degree of ionization of these sulfatostannous acids, can the experimentally determined freezing points be accounted for. The high degree of ionization of sulfatostannous acid assumed in such calculations is inconsistent with the experimentally determined values of hydrogen ion activity. Apparently the measurement as made cannot be a true measure of the activity of hydrogen ion in these relatively concentrated solutions. That a high degree of ionization is present is verified by the high values of surface tension in this concentration range.

Miyamoto (4) made conductivity measurements on  $\text{SnSO}_4\text{--H}_2\text{SO}_4$  systems. He postulated the  $\text{H}_2\text{Sn}(\text{SO}_4)_2$  and  $\text{H}_2\text{Sn}_2(\text{SO}_4)_3$  systems as most probable.

*Mole fractions other than 0.32.*—No thoroughgoing study of other mole fractions has been undertaken. However, a range of samples to give mole fraction values of 0.034, 0.056, 0.072, 0.129, 0.40, 0.44, and 0.52 was prepared. As shown by Fig. 1, families of curves result. These curves arrange themselves in the order of mole fraction of tin-II sulfate. For the high acid electrolytes there is better agreement in many properties, e.g., transference by hydrogen ion, if the property is plotted vs. total sulfate concentration rather than tin-II concentration.

#### ACKNOWLEDGMENT

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

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# Electroplating on Titanium<sup>1</sup>

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## ABSTRACT

A method for obtaining adherent electrodeposits on titanium is described. It consists in subjecting titanium to an anodic etch prior to plating, under controlled conditions. Bath composition and operating variables are discussed, and photomicrographs showing the mechanical nature of the bond are given. Conditions for electropolishing titanium are also reported.

## INTRODUCTION

Titanium has recently emerged from the class of rare metals, and is in the process of becoming an important structural material. Its outstanding properties are a high strength-to-weight ratio and excellent corrosion resistance to a great number of chemicals at room temperature.

The need for electroplating on titanium may arise for several reasons, such as decorative plating, improved resistance to high-temperature gases, improved mechanical properties of the surface, or joining of titanium parts.

Titanium is an extremely active metal. Its high corrosion resistance is due to the fact that the metal becomes covered with an impervious and tightly adherent oxide film. This film, however, makes it very difficult to obtain adherent electrodeposits on the metal. Conditions required to remove the oxide are usually so drastic that the metal reacts violently once the surface film is dissolved; under such conditions it becomes very hard to apply a sound electrodeplate, or even a strike, to the titanium.

A survey of the literature cast little light on the problem. Some mention was made by Couch and Brenner (1) of obtaining adherent deposits on titanium using a dry lithium hydride, ethyl ether, etc. However, this technique was considered impractical insofar as the present problem is concerned. Conventional methods for plating on common metals were tried on titanium; these met with no success. Such methods include straight pickling in HF, "nickel pickle" (simultaneous cathodic pickling and nickel deposition), or immersion plates (which yield adherent electrodeposits on aluminum or magnesium).

It was apparent that the activity of the titanium surface was so great in aqueous solutions that an oxide-free surface could not be maintained. In order

to reduce the reactivity of the titanium metal, yet maintain it oxide-free, nonaqueous solutions were investigated.

Some plate adherence was achieved by subjecting the metal, prior to plating, to a cathodic treatment in a bath whose main constituent was ethylene glycol, and which also contained a zinc salt, HF, and a small amount of water. This will be discussed below.

The most successful approach to the problem of obtaining adherent electrodeposits on titanium was to subject the metal to an anodic etch prior to plating. This procedure is described in detail below.

## EXPERIMENTAL

*Raw material.*—The bulk of the experiments were carried out with commercially pure titanium sheet.<sup>3</sup> Several lots of RC-55 (Rem-Cru) and Ti75-A (Titanium Metals Corporation), 0.025–0.065 in. thick, were used. A few tests were performed with RC-130 B (Rem-Cru) alloy.<sup>3</sup>

*Preparation before plating.*—Titanium sheet specimens 2.5 in. x 1 in. were used. They were cathodically cleaned (when required) in a solution of 20 g/l of sodium orthosilicate at 70°C, and rinsed. This was followed by pickling in a solution containing 185 cc/l of 48 per cent HF and 8.6 cc/l of 70 per cent HNO<sub>3</sub> until the specimen looked clean, and drying. The metal was next subjected to the anodic etching treatment.

*Plating.*—After anodic etching, specimens were rinsed and then given a copper strike at room temperature, without stirring, in the following solution: CuCN, 23 g/l; NaCN, 34 g/l; Na<sub>2</sub>CO<sub>3</sub>, 15 g/l. The current was first brought up to 50 amp/ft<sup>2</sup> (5.4 amp/dm<sup>2</sup>), then brought back to about 15 amp/ft<sup>2</sup> (1.62 amp/dm<sup>2</sup>) after a few seconds. Plating was continued for 3 to 5 minutes.

The copper strike, after another rinse, was followed

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<sup>3</sup> RC-55: C—0.05–0.2%; O, N, Fe—few hundredths to a few tenths % each; other elements—trace.

Ti75-A (nominal): Fe—0.1%; N—0.02%; O—trace; C—<0.04%; W—<0.08%.

RC-130B (nominal): Mn—4%; Al—4%; O, N, Fe—same as RC-55.

by a copper plate at room temperature, with stirring, from the following bath: 448 g/l  $\text{Cu}(\text{BH}_4)_2$  [sp gr 1.36];  $\text{HBF}_4$  to pH 0.6. Plating was carried on at 50 amp/ft<sup>2</sup> (5.4 amp/dm<sup>2</sup>) for about 10 minutes in most cases (about 0.0005 in.). For heavy plates (about 0.005 in.), plating time was 40 minutes at 100 amp/ft<sup>2</sup> (10.8 amp/dm<sup>2</sup>).

*Testing.*—The mechanical properties of electroplates were tested by scraping them with a knife. If no detachment could be observed, the specimen was clamped in a vise and bent by hammering through a 180° angle. The adherence of the plate in the bent areas was then examined.

In the later stages of the work, a more severe test was substituted for the bend test. One end of the specimen was again clamped in a vise, and then subjected to repeated flexing, using both a bending and a twisting motion. Again, the plate was examined for detachment. The bend and flex tests were naturally most severe when performed on heavy electroplates.

The final test of adherence was the solderability test (which was most severe on thin electroplates). This test consisted of soldering a copper strip onto the electrodeposit, then pulling off the strip. If the joint broke wholly in the solder, the specimen passed the test. In other cases, portions of the copper plate would be pulled off; the size of these areas was a measure of the quality of the plate.

#### THE ANODIC ETCH

Under proper conditions, anodic etching prior to plating yielded fully adherent copper electroplates (0.0005–0.005 in. thick), which passed the bending, flexing, and solderability tests. Good results were obtained with commercially pure titanium as well as RC-130 B alloy. Etching was carried out in an essentially nonaqueous bath.

#### Mechanism

The anodic etch, under the right conditions, leads to a rough surface that provides mechanical keying of the electrodeposits. Fig. 1 to 3 clearly show the pockets and reentrant angles created by anodic etching. The surface roughness of these specimens may be as high as 50 microinches root mean square. Plating on this rough surface takes place with good throwing power, and the pockets appear to be completely filled with the plated metal. At the same time, the electroplate surface becomes increasingly smooth as plating proceeds, until it is almost comparable to that of a metal electrodeposited on a smooth base. Even with 0.0005 in. of copper, a fairly smooth plate surface is obtainable.

The mechanical nature of the bond is best illustrated in Fig. 1 to 3. It is supported by the fact that

no substance other than titanium metal was found on the surface of anodically etched specimens by spectrographic and electron diffraction techniques,

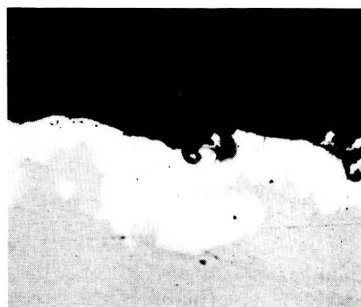


FIG. 1. Anodically etched titanium.  $\times 500$ . Unetched. (In the photomicrographs illustrating this paper, the titanium base metal is the phase in the lower portions. The specimens shown in Fig. 1, 2, and 4 were plated with nickel for metallographic polishing purposes.)

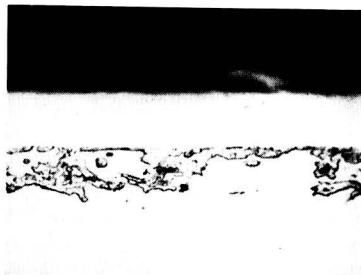


FIG. 2. 0.5-mil copper plate on anodically etched titanium.  $\times 500$ .  $\text{H}_2\text{O} + \text{H}_2\text{O}_2 + \text{NH}_4\text{OH}$ .

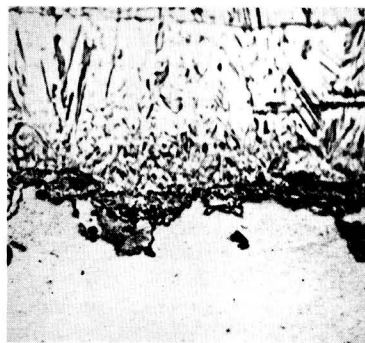


FIG. 3. 5-mil copper plate on anodically etched titanium.  $\times 500$ .  $\text{H}_2\text{O} + \text{H}_2\text{O}_2 + \text{NH}_4\text{OH}$ .

which means that no special chemical compound is formed by this etching. Furthermore, the degree of roughness of the surface bears a definite relationship to the adherence of electrodeposits. Under proper conditions, many etching baths can be operated so

as to yield a very smooth, electropolished surface on titanium (Fig. 4); plates on such a smooth surface have never been adherent. With improper current distribution, etching can take place in low current density areas and polishing in high current density areas on the same specimen; subsequent electroplating yields adherent deposits in the etched areas only.

#### Anodizing Conditions

When titanium is made anode in a bath in which it is reactive (e.g., a bath containing HF), several possible reactions may take place:

1. The current may be insufficient to prevent local (chemical) action, with the evolution of hydrogen. In extremely active baths, it may be altogether impossible to stop this local action at any reasonable current density. The type of surface obtained under such conditions varies from an even, clean, uniformly etched metal to a fairly smooth

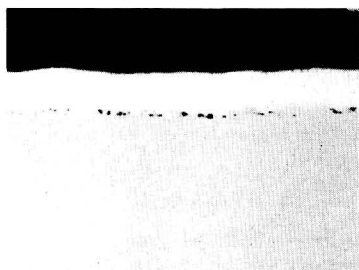


FIG. 4. Electropolished titanium.  $\times 500$ . Unetched

grayish or blackish film. Such surfaces do not lead to adherent plates.

2. In low activity baths, an anodic treatment may lead to the formation of an impervious oxide film, which is usually colored, the color depending upon the applied voltage. This is comparable to the anodizing of aluminum. The passivated anode offers a high resistance to the passage of current, which drops to a low value. Again, the adherence of electrodeposits on such a base is very poor.

3. It is in baths of intermediate activity that the anodizing of titanium yields the type of etched surface desired for electroplating. In such a bath, if increasing current is applied (starting from zero), several effects may be observed. At first, the main result is a decrease in the local chemical action (which takes place with displacement of hydrogen). Until local action has stopped completely, the weight of metal dissolved from the anode per unit time decreases, even though an increasing amount of anodic current is applied. When a certain value of current density has been reached, which varies with

bath composition, temperature, etc., the local action is eliminated, and the anodic dissolution of titanium continues without gassing (see Fig. 5). Under such conditions, it is possible to obtain the type of etched surface desirable for electrode deposition, or, by varying operation conditions, an electropolished surface (Fig. 4). The volume of the experimental baths was about 300 cc. During the course of experiments, the composition of the bath was altered slightly by evaporation and hydrogen evolution. As evidenced by the data in Fig. 5, the weight loss per unit time in the range of local action was highly sensitive to the changes in composition. Since the reproducibility in the range of local action was poor the curves

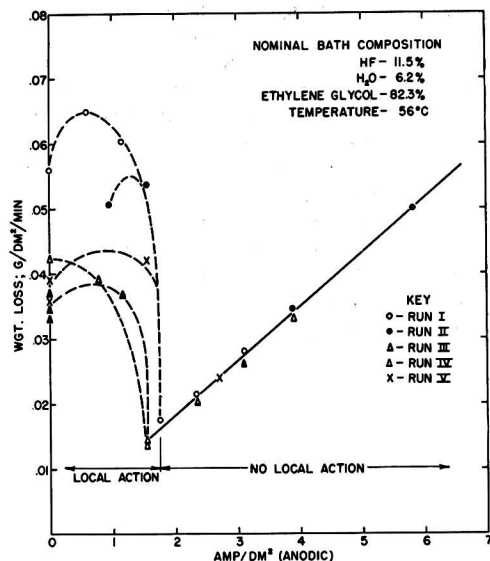


FIG. 5. Weight loss of titanium during anodic treatment vs. current density.

connecting the points in that range are merely conjecture, and are drawn with broken lines. In general, with increasing use of the bath, the weight loss in the range of local action decreases. The only effect in the range of no local action with prolonged use of the bath is to decrease the severity of the etch. The apparent valence change of titanium during anodic dissolution was determined from weight loss measurement, on the assumption that the metal dissolves at 100 per cent current efficiency (in the range of no local action). The values found were somewhat in excess of 3, and were slightly higher for electropolishing than for etching. Such determinations are complicated by possible side reactions at the anode, such as the oxidation of Ti<sup>++</sup> and Ti<sup>+++</sup> compounds or of hydrogen bubbles.

### Operating Variables

A number of solutions with low water content were investigated. Best results were obtained with baths based on ethylene glycol and HF. A typical composition would be the following: 15 per cent by weight HF; 6 per cent H<sub>2</sub>O; 79 per cent ethylene glycol. Such a bath should be operated at 55°–60°C, at 50 amp/ft<sup>2</sup> (5.4 amp/dm<sup>2</sup>), or slightly less. The required etching time is 15 to 30 minutes. When applying current, it is recommended that it be brought up above the desired value (to help stop local action), then brought back to the operating level. Agitation or circulation of the solution is helpful, if not essential. Cathodes may be graphite, copper, nickel, or any other material which is not reactive in the bath. It is preferable to remove the specimen from the bath with the current on, to prevent local action; certainly the work should be withdrawn from the etching solution very rapidly after the current is turned off.

As a general rule, etching conditions are favored by higher temperatures, higher HF content, and lower current densities. Each bath has a useful etching range of temperature and current density. The upper limit of the temperatures would be set by excessive local action, the lower limit by the transition from etching to electropolishing. The lower limit of current density is again determined by the onset of local action (Fig. 5), and the upper limit by electropolishing.

As mentioned before, electrodeposits do not adhere to electropolished surfaces. It is readily seen that the control of current distribution is very important; if the current density is excessive on certain areas, they may become electropolished. Also, if the current density falls below a critical value at certain spots, they are no longer protected against local action, and the adherence of plates is poor at these points.

The useful range of etching current densities is greater at higher temperatures, as well as at higher HF concentrations, as long as local action is prevented.

Bath composition may influence not only the etching range, but also the severeness of the etch. Thus, at increasing water content, the etch may become deeper, but the etching range is reduced in favor of local action, making control more difficult.

It was found that these baths did not deteriorate on standing; however, some loss in activity was noted with use. Partial rejuvenation was obtained by small additions of HF. Extensive study of these factors was not undertaken.

Fairly good results have been obtained from a wholly inorganic bath based on phosphoric acid:

53.9 per cent by weight H<sub>3</sub>PO<sub>4</sub>; 12.5 per cent HF; 15.5 per cent NH<sub>4</sub>HF<sub>2</sub>; 18.1 per cent H<sub>2</sub>O. This bath is more active than the one based on ethylene glycol, but more difficult to control. Its useful etching range was 35°–45°C, with current densities of 30–50 amp/ft<sup>2</sup> (3.23–5.4 amp/dm<sup>2</sup>). This shows that it may be possible to use a number of different solutions for the anodic etching of titanium and its alloys before plating.

### Electropolishing

Electropolishing of titanium was a side product of the research on anodic etching for plating.

A solution based on HF and ethylene glycol, but slightly lower in HF than the etching solution, may be recommended for electropolishing, e.g., 6 per cent by weight HF; 6 per cent H<sub>2</sub>O; 88 per cent ethylene glycol. This bath should be operated at room temperature or slightly above (up to 40°C), at current densities in excess of 50 amp/ft<sup>2</sup> (5.4 amp/dm<sup>2</sup>), and preferably around 75–100 amp/ft<sup>2</sup> (8.1–10.8 amp/dm<sup>2</sup>). Better electropolishing solutions than the above can probably be compounded, and the above composition is given mainly as a guide. However, even from the above bath, very smooth finishes (as low as 2.5 microinches rms) were obtained.

### Zinc Strike

Cathodic treatment of titanium in a bath consisting of ethylene glycol, HF, a small amount of water, and a zinc salt showed that, on application of current, zinc deposited on the cathode at first, but soon redissolved even though no interruption of current occurred. If the specimen was removed before the redissolution of the zinc, the deposit could easily be scraped off. During and after dissolution of the zinc, a black film formed on the titanium surface. Deposition of copper on this black film gave adherent coatings. The electrodeposits adhered to the extent of passing the bend test when the deposits were 0.5 mil in thickness. These deposits did not pass the solderability test and heavier deposits, 3.0 mils to 5.0 mils in thickness, would not pass the bend test. The conditions required for formation of the black film differed greatly between the lots of commercially pure grades of titanium and titanium alloys used. Because of the difficulty of control and the inability to obtain satisfactory adherence, this approach was discarded.

### SUMMARY AND CONCLUSIONS

Conventional methods used to obtain adherent electrodeposits on other metal fail in the case of titanium.



However, fully adherent copper electroplates (up to 0.005 in. thick) on titanium are obtained when the material is anodically etched, prior to plating, in a solution based on HF and ethylene glycol, under controlled conditions of temperature and current density. Metallographic examination indicates that the bond between plate and basis metal is a mechanical one, due to interlocking between the etched surface of the titanium and the plated metal which appears to "throw" well into the cavities created by the etch.

Under different operating conditions, an anodic treatment of titanium will yield an electropolished surface, which is not good for adherent plating.

#### ACKNOWLEDGMENT

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

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# An X-Ray Study of the Effect of Organic Compounds on the Crystal Growth of Nickel during Electrodeposition<sup>1</sup>

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## ABSTRACT

X-ray diffraction analyses were made of nickel electrodeposits prepared in the presence of organic compounds. The compounds varied in their ability to alter the grain size and the degree and/or type of preferred orientation. Compounds most effective in increasing the cathode potential during deposition both decreased the grain size and changed the type of preferred orientation to a type other than (100) or to a random distribution of the crystals. Compounds of lesser effectiveness in increasing the cathode potential reduced the grain size, but had no effect on the preferred orientation. Brittle deposits were characterized by an orientation other than (100), and the ductile deposits were characterized by a (100) preferred orientation. The results of this study and the work of other authors indicate that a major fraction of mirror-bright nickel electroplates exhibit no preferred orientation.

## INTRODUCTION

A comprehensive study of the interaction of organic compounds with a nickel surface during electrodeposition is being carried out. As part of this study, x-ray diffraction analyses have been made of deposits prepared in the presence of 29 different organic compounds in order to determine the effects of these compounds on crystal growth.

## EXPERIMENTAL

All plating experiments were carried out in a bath, commonly referred to as the Watts bath, with the following composition:  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  240 g/l,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  45 g/l, and  $\text{H}_3\text{BO}_3$  30 g/l. A large stock solution was prepared and was purified in the conventional manner by treatment with  $\text{NiCO}_3$ ,  $\text{H}_2\text{O}_2$ , and activated carbon. The pH was adjusted in all experiments to 4.0 with HCl. The exact plating conditions used in the individual experiments will be described later.

The cathode consisted of a polycrystalline sphere of copper,  $\frac{5}{8}$  in. in diameter, with a small shaft for handling. The cathode was used in the spherical form because of the ability to secure uniform current density distribution over the surface, and because of the ease in making x-ray analysis. The cathode was electrolytically polished in 42.5 per cent by volume phosphoric acid before insertion in the plating bath. The anode consisted of a cylindrical nickel sheet resting on the periphery of a 400-ml beaker used as the plating cell. X-ray analysis indicated that the polycrystalline copper cathodes themselves exhibited no preferred orientation. Thus, any preferred orienta-

tion observed in the nickel electroplate resulted solely from the deposition, and not from a continuation of preferred orientation of the copper substrate.

X-ray analyses were made with copper radiation at a specimen-film distance of 3.0 cm. No filter was used since the nickel deposit served to filter out the majority of the beta radiation. The x-ray beam was directed tangentially to the surface of the deposit. The sphere was inserted in a special holder and its position was adjusted so that, when viewed with a telescope, exactly one-half of the x-ray beam intersected the surface of the specimen. This method was adopted because it was possible to obtain x-ray information about the deposit without stripping it from the base metal or without special sectioning techniques. The type of preferred orientation was determined directly by measuring the angle between the center of the intense arcs on the rings and the vertical plane. A knowledge of the angles between the various crystal planes in a face-centered cubic structure enables one to identify immediately the type of orientation.

The grain size of the deposit was typified by the terms large or small. Large grains were considered to be those having a mean diameter larger than  $10^{-2}$  mm. Such grains yield spotty diffraction rings. Small grains were considered to be those having a mean diameter in the range  $10^{-2}$  to  $10^{-4}$  mm. Within this range, the diffraction rings are sharp and continuous. Grains smaller than  $10^{-4}$  mm yield diffuse diffraction rings, and the breadth of the rings can be used in the determination of the grain size. However, in the  $10^{-2}$ - to  $10^{-4}$ -mm range, the x-ray method is not sensitive to differences in grain size. All deposits examined in this study had grains larger than about  $10^{-4}$  mm.

<sup>1</sup> Manuscript received January 3, 1953. This research was sponsored by the Harshaw Chemical Company, Cleveland, Ohio.

## RESULTS

The nickel deposit formed in an unadulterated<sup>2</sup> Watts bath at current densities in excess of 1 amp/dm<sup>2</sup> and at temperatures of 20°–70°C exhibited a grain size larger than 10<sup>-2</sup> mm and moderately strong (100) preferred orientation. At current densities below 1 amp/dm<sup>2</sup>, either no preferred orientation or a (110) orientation was detected. The typical diffraction pattern obtained at current densities above 1 amp/dm<sup>2</sup> is given in Fig. 1. The diffraction rings consist of well-defined spots, indicating a grain size larger than 10<sup>-2</sup> mm; intensity maxima occur 55° from the vertical on the (111) ring and at the meridial position on the (200) ring. A (100) preferred orientation is thus indicated. Similar results were obtained many times over a period of several years

number of organic compounds added singly to the Watts bath. A few preliminary experiments were

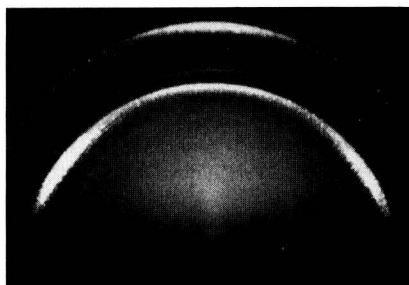


FIG. 1. X-ray diffraction photograph of nickel deposit formed in unadulterated Watts bath. Spotty nature of rings indicates a grain size larger than 10<sup>-2</sup> mm; moderate (100) preferred orientation.

TABLE I. The effect of 29 organic compounds on the appearance, ductility, grain size, and preferred orientation in nickel electrodeposits

Organic compound	Conc. in moles/l	Appearance of deposit	Ductility	Grain size*	Preferred orientation
None	—	Grainy, matte	Ductile	Large	mod (100)
<i>m</i> -Aminophenol	0.0025	Semibright	Brittle	Small	mod (211)
<i>p</i> -Aminosulfonic acid	0.004	Semibright	Ductile	Small	sl (100)
Aniline	0.001	Dull, gray	Brittle	Small	Random
Benzaldehyde	0.002	Grainy, matte	Brittle	Large	Random
Benzaldehyde <i>m</i> -sulfonate (Ni salt)	0.008	Very bright	Brittle	Small	sl (100)
<i>m</i> -Benzenedisulfonic acid (Ni salt)	0.016	Bright	Ductile	Small	s (100)
Benzoic acid	0.0025	Matte	Ductile	Small	mod (100)
Benzonitrile	0.0005	Semibright	Brittle	Small	sl (311)
Ethanolamine	0.01	Grainy, matte	Ductile	Large	mod (100)
Ethanol	0.01	Grainy, matte	Ductile	Large	mod (100)
Ethylamine	0.01	Matte	Ductile	Large	mod (100)
Ethylenecyanohydrin	0.0012	Bright	Brittle	Small	Random
Ethylenediamine	0.002	Matte, gray	Brittle	Small	Random
Naphthalene-2,7-disulfonate (Na)	0.008	Bright with haze	Ductile	Small	s (100)
Naphthalene-1,3,6-trisulfonate (Na)	0.01	Bright with haze	Ductile	Small	s (100)
1-Naphthylamine-4,8-disulfonic acid	0.0002	Bright one side Matte other side	Brittle	Small	Random
Nitrobenzene	0.001	Matte, gray	Brittle	Small	Random
Phenol	0.01	Grainy, matte	Ductile	Large	mod (211)
<i>p</i> -Phenolsulfonic acid	0.01	Grainy, matte	Ductile	Large	(100)
Piperidine	0.01	Matte	Ductile	Large	mod (100)
Propionitrile	0.003	Matte	Brittle	Large	sl (211)
Pyridine	0.001	Matte, white haze	Brittle	Small	Random
Quinaldine ethiodide	0.0005	Semibright	Brittle	Small	sl (210)
Quinoline ethiodide	0.001	Bright	Brittle	Small	mod (211)
Saccharin	0.0007	Semibright	Ductile	Small	s (100)
Succinonitrile	0.0005	Bright	Brittle	Small	(221) and (310)
Thianaphthene dioxide	0.0002	Bright, hazy	Ductile	Small	s (100)
Thiourea	0.003	Bright	Brittle	Small	sl (100)
<i>p</i> -Toluenesulfonamide	0.001	Bright, hazy	Ductile	Small	s (100)

\* Large refers to grains larger than 10<sup>-2</sup> mm, and small to grains less than 10<sup>-2</sup> mm.

† Sl—slight, mod—moderate, s—strong, random—no detectable preferred orientation.

in baths prepared from different batches of nickel sulfate, nickel chloride, and boric acid.

It was next of interest to determine the effect of a

<sup>2</sup> An "adulterated" Watts bath is defined as one to which organic compounds have been added.

carried out in order to choose a set of experimental conditions for the plating operation, and it was found that the results were essentially independent of current density between 2 and 10 amp/dm<sup>2</sup>. Further experiments were then carried out under the follow-

ing conditions: 6 amp/dm<sup>2</sup>, 60°C, pH of 4.0, stirring by a 2-blade propeller rotating at 300 rpm. The concentration of addition agent used was determined, in part, by the maximum concentration which did not cause the deposit to crack or to peel. The cathode potential results (1) were of great assistance in choosing a representative concentration.

The results of this study are summarized in Table I. In a few cases, several different concentrations of the agent were used with identical results, but, for brevity, only a single concentration is listed in the

to the naked eye over the entire arc. Several typical diffraction patterns are given in Fig. 2-5.

During this study, approximately 200 nickel electrodeposits were examined by x-ray diffraction. Since these deposits were prepared over a period of several years, all the deposits could not be examined visually at the same time. However, in several cases, lots of about 20 specimens were examined within a short period, and the surface appearance could be compared immediately with the x-ray diffraction photograph. The generalization soon emerged that there



FIG. 2. X-ray diffraction photograph of nickel deposit formed in presence of 0.002 mole/l of ethylenediamine. No detectable preferred orientation.

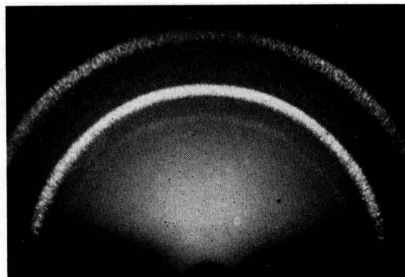


FIG. 4. X-ray diffraction photograph of nickel deposit formed in the presence of 0.003 mole/l of propionitrile. Grain size larger than  $10^{-2}$  mm; slight (211) orientation.

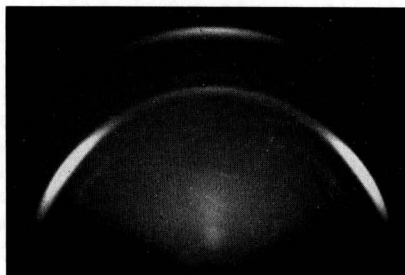


FIG. 3. X-ray diffraction photograph of nickel deposit formed in presence of 0.0007 mole/l of saccharin. Grain size less than  $10^{-2}$  mm; strong (100) preferred orientation.

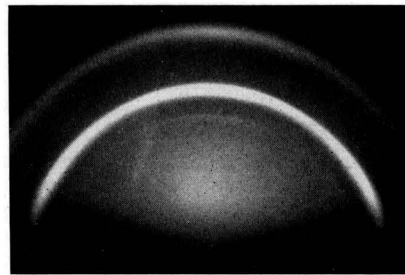


FIG. 5. X-ray diffraction photograph of nickel deposit formed in the presence of 0.008 mole/l of nickel benzaldehyde *m*-sulfonate. Grain size less than  $10^{-2}$  mm; slight (100) orientation.

table. The appearance of the deposit was noted and described by the terms grainy, matte, dull, semi-bright, bright with haze, or bright. A very qualitative measure of the ductility of the deposit was made by holding the deposit on the supporting wire up to the ear, bending the wire through an angle of 45°, and listening for a cracking sound. If cracking was heard, the deposit was termed brittle; if none was heard, the deposit was termed ductile. No attempt was made to grade the deposits in degree of ductility. The type of preferred orientation is given in the sixth column along with a qualifying phrase such as strong, moderate, or slight. The term "random" is used in cases where the rings appeared of uniform intensity

was no direct relationship between the degree or type of preferred orientation and the brightness of the surface. Both matte and bright deposits were noted with strong, preferred orientations and with complete absence of any detectable orientation. A survey of Table I shows the lack of correlation between brightness, and degree and type of preferred orientation. These results are in accord with those obtained by Clark and Simonsen (2) and by Smith, Keeler, and Read (3). On the other hand, approximately 50 per cent of the mirror-bright deposits exhibited no detectable preferred orientation when examined by x-ray diffraction. A mirror-bright deposit is considered to be one which shows no visible imperfection

in shininess when examined in a well-lighted room and in the direct beam of a flashlight in a dark room. Many bright deposits exhibit a strong haze when examined carefully in a dark room.

In order to test the foregoing conclusion, the following experiments were performed. Nine commercial, bright plating baths were obtained and were formulated according to the directions furnished by the manufacturer. Nickel was electrodeposited on the electrolytically polished copper spheres at 50°–60°C and at current densities of 2 and 6 amp/dm<sup>2</sup>. Mirror-bright deposits were obtained from each of the nine baths, although three of the deposits contained many pits on the surface. Four of the deposits exhibited no detectable preferred orientation, two of the deposits exhibited very slight preferred orientation, and two of the deposits exhibited slight orientation. These results furnish additional support for the conclusion that a large number of mirror-bright nickel electrodes show no preferred orientation.

#### DISCUSSION

In the absence of organic additives and under the conditions used in this study, the Watts bath yielded a deposit with a (100) preferred orientation. A similar orientation has been reported by other workers (4). It is known that, when nickel is electroplated from the same bath on electrolytically polished single crystals of copper and nickel, the deposit occurs as a single crystal on the (100) faces (5). For some unknown reason, the Watts solution promotes the formation of a deposit with the (100) planes parallel to the substrate. This behavior is not characteristic of the nickel deposit alone, since a (211) orientation is observed in the all-chloride bath of Wesley (6), and, as shown in this study, small amounts of organic impurities can change the type of preferred orientation completely. An understanding of the driving force for the (100) type of preferred orientation in the Watts bath is an intriguing problem.

Twenty-three of the 29 organic compounds tested had an effect on the crystal growth of the deposit as evidenced by their ability to reduce the grain size or change the type and/or degree of preferred orientation, as compared to the deposit obtained in the unadulterated Watts bath. These compounds are classed in groups 2–5 given below. Five of the compounds yielded deposits which were similar in all respects to the deposits obtained in the unadulterated Watts bath. These five compounds thus had no effect on the crystal growth of the deposit and are classed in group 1.

Group 1. The presence of the organic compound resulted in the formation of a deposit with a grain size larger than 10<sup>-2</sup> mm and with moderate to strong (100) preferred orientation.

Group 2. The presence of the organic compound resulted in the formation of a deposit with a grain size larger than 10<sup>-2</sup> mm and with a preferred orientation other than (100).

Group 3. The presence of the organic compound resulted in the formation of a deposit with a grain size smaller than 10<sup>-2</sup> mm and with moderate to strong (100) preferred orientation.

Group 4. The presence of the organic compound resulted in the formation of a deposit with a grain size smaller than 10<sup>-2</sup> mm and with only a slight (100) preferred orientation.

Group 5. The presence of the organic compound resulted in the formation of a deposit with a grain size smaller than 10<sup>-2</sup> mm and with a preferred orientation other than (100), or with no detectable preferred orientation.

The compounds falling in each of these five groups are listed in Table II.

An excellent correlation exists between the effects of the addition agents on crystal growth and the effects of the same compounds on the cathode potential (1). The following discussion is given in relation to results reported in Reference (1).

The compounds which were ineffective in changing the grain size or preferred orientation in the deposit (group 1) had a negligible effect on the cathode potential, whereas the compounds which both decreased the grain size and changed the type or degree of preferred orientation (groups 4 and 5) had a moderate to great effect on the cathode potential. The compounds which were only effective in decreasing the grain size and did not change the type or degree of (100) preferred orientation (group 3) had a small to moderate effect on the cathode potential, and yielded cathode potential curves which leveled off with further increases in concentration of the organic compound. Two of the compounds classed in group 2 (benzaldehyde and propionitrile) increased the cathode potential greatly, whereas phenol had a negligible effect on the cathode potential. The grouping of the compounds in relation to their effect on the cathode potential is given in Fig. 6 for convenience in a different form than given in Reference (1).

It appears from this correlation that the compounds which interfere only moderately with the deposition of nickel, as evidenced by a small to moderate effect on the cathode potential, are capable of reducing the grain size greatly, but are ineffective in changing the type of preferred orientation. Compounds which interfere to a great extent with the deposition of nickel are capable of both decreasing the grain size and changing the type of preferred orientation.

The compounds classed in group 3 are characterized by either acidic groups, such as the sulfonate

or carboxyl, or by groups which are neither strongly acidic nor strongly basic, such as the sulfone and sulfonamide groups. The compounds classed in groups 4 and 5 are characterized by the presence of basic groups, such as nitrogen in conjugated ring,

size did not necessarily confer brittleness. Ductile and brittle deposits were both observed with grain sizes smaller and larger than  $10^{-2}$  mm.

The primary interest of this study was to determine the effect of individual organic compounds on

TABLE II. The grouping of organic compounds according to their effects on the grain size and orientation of the deposit

Group 1. Large grain size, (100) preferred orientation	
Ethanol	Piperidine
Ethanolamine	<i>p</i> -Phenolsulfonic acid
Ethylamine	
Group 2. Large grain size, orientation other than (100)	
Benzaldehyde	
Phenol	
Propionitrile	
Group 3. Small grain size, strong (100) orientation	
<i>m</i> -Benzenedisulfonic acid (Ni salt)	Saccharin
Benzoic acid	Thianaphthene dioxide
Naphthalene-2,7-disulfonate (Na salt)	<i>p</i> -Toluenesulfonamide
Naphthalene-1,3,6-trisulfonate (Na salt)	
Group 4. Small grain size, slight (100) orientation	
<i>p</i> -Aminosulfonic acid	
Benzaldehyde <i>m</i> -sulfonate (Ni salt)	
Thiourea	
Group 5. Small grain size, random or orientation other than (100)	
<i>m</i> -Aminophenol	Nitrobenzene
Aniline	Pyridine
Benzonitrile	Quinaldine ethiodide
Ethylenecyanohydrin	Quinoline ethiodide
Ethylenediamine	Succinonitrile
1-Naphthylamine-4,8-disulfonic acid	

nitrile, and amine. The similarity of results obtained with aniline and nitrobenzene in the cathode potential and x-ray diffraction experiments suggests strongly that the nitro group is reduced under the conditions used. The greater effectiveness of the basic groups in interfering with crystal growth is not unexpected, since these compounds would presumably be attracted to the cathode by virtue of their positive charge in solution.

Fifteen of the 30 deposits recorded in Table I were graded brittle and 15 were graded ductile. In the case of the brittle deposits, 13 exhibited no preferred orientation or a preferred orientation other than (100), and two exhibited slight (100) preferred orientation. In the case of the ductile deposits, 14 exhibited (100) preferred orientation and only one exhibited another type. It appears that the compounds which were sufficiently active at the surface to change the type of preferred orientation also had a great tendency to impart brittleness to the deposit.

No correlation between brittleness and grain size was detected. A large grain size did not necessarily confer ductility to the deposit, and a small grain

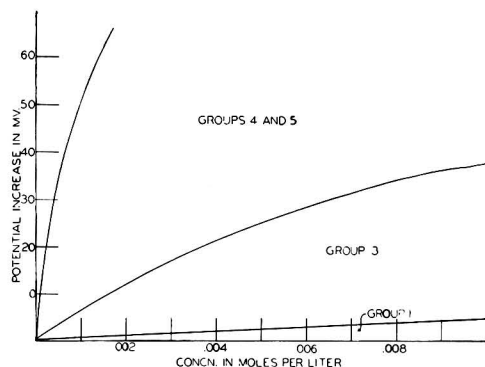


FIG. 6. Correlation of the effects of organic compounds on the cathode potential at 1 amp/dm<sup>2</sup> with their effects on crystal growth (see Table II).

the crystal growth of nickel during electrodeposition. The results, however, are also of value in assessing any relation between preferred orientation and brightness. Results with over 200 electrodeposits indicated conclusively that there is no correlation between preferred orientation and brightness. How-

ever, it was noted that a high fraction (roughly 50% in this study) of the mirror-bright deposits exhibited no detectable preferred orientation. Clark and Simonsen (2) made a similar observation, but they did not stress the fact. These workers examined 86 nickel deposits, of which 15 were bright. Eleven (73%) of these 15 bright deposits had, in their words, "a random distribution of crystals." The results of Smith, Keeler, and Read (3) are more difficult to evaluate on this basis because they compared the line intensities obtained by back reflection in order to detect orientation. These workers examined 33 nickel deposits prepared in the presence of various organic agents, of which eight deposits were considered bright by visual examination. Six of these deposits yielded line intensity ratios the same or only slightly different from that obtained from a recrystallized nickel sheet, which presumably exhibited no preferred orientation. Only two of the deposits exhibited line intensity ratios greatly different from the nickel sheet. It is thus concluded that six (75%) of the eight bright deposits studied by Smith, Keeler, and Read showed no preferred orientation.

Even though it appears true that a high fraction of bright nickel plates exhibit no preferred orientation, it is also true that the absence of preferred orientation does not necessarily lead to a bright plate. Many of the duller plates observed in this study also showed no detectable preferred orientation. The results with 1-naphthylamine-4,8-disulfonic acid afford an excellent example. The specimen was bright on one side and matte on the other, yet the x-ray diffraction photographs in both areas were identical: neither area exhibited preferred orientation and both areas had grain sizes between  $10^{-2}$  and  $10^{-4}$  mm.

The great majority of bright nickel electroplates formed in the presence of organic compounds have a small grain size, as pointed out by Zentner, Brenner, and Jennings (7). However, a small grain size does not necessarily lead to a bright deposit, as shown by Clark and Simonsen (2).

It is interesting to note that bright nickel plates can be obtained with no detectable preferred orientation and a small grain size, as well as with complete orientation and a very large grain size (single crystal), as is the case when deposition is carried out on the (100) face of copper or nickel single crystals (5). Bright plates can thus be obtained at both ends of a scale of grain size and orientation.

The lack of any preferred orientation in a high fraction of mirror-bright deposits indicates that one function of an addition agent is to minimize the differences between crystal faces at the surface. It appears that crystal growth is no longer controlled during bright plating by the nickel surface but by a film adjacent to the surface, since it is known from studies carried out by Gwathmey and coworkers at the University of Virginia and studies carried out in this laboratory that, when the rate of reaction is controlled by the surface, the reaction occurs at different rates on the various crystal faces.

#### ACKNOWLEDGMENT

The authors wish to express their deep appreciation to the laboratory staff of the Harshaw Chemical Company and especially to Mr. Andrew Aylies for their cooperation and sympathetic interest in this research.

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

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# Copper-Activated Zinc Sulfide Phosphors with Trivalent Substituents<sup>1</sup>

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## ABSTRACT

With increasing concentrations of Cu and Al in H<sub>2</sub>S-fired Zn(Al)S:Cu phosphors, the emission spectrum is shifted from green to orange under 3650 Å excitation. The emission of these triple sulfides consists of three sub-bands of such relative intensities that the presence of a single band is simulated. The bands have different temperature, decay, and excitation characteristics. Among other substituents, the elements Sc, Ce, Pr, and Nd are of interest, as they produce infrared stimulability even with high activator concentrations.

When fired in H<sub>2</sub>S with oxide additions, the phosphors with Al emit only green light and become strongly electroluminescent. The green emission persists at all frequencies from 60 to 15000 cps. Phosphors prepared with 0.1 to 0.4 per cent Cu and with 0.25 to 2.5 moles Al/mole Cu are nearly equally bright. The mole ratio Cu:Al in the brightest NaCN-washed phosphors is near 1:1.

The results lend strong support to Kroeger's theory of charge compensation. The complexity of the emission spectra leads to the conclusion that several species of Cu atoms must be present in the phosphors. The electroluminescent response is attributed to oxide barriers in, or on, the phosphors.

## INTRODUCTION

According to Kroeger and Dikhoff (1), blue and green emitting ZnS:Cu phosphors of high brightness are obtained when trivalent cations such as Al are introduced into the phosphor in place of monovalent halide ions. These results have been interpreted with the principle of charge compensation. Assuming that copper is monovalent, the incorporation of Cu into the ZnS lattice should be facilitated if pairs of monovalent copper and trivalent aluminum ions are introduced rather than copper alone, to replace pairs of divalent zinc ions at lattice sites.

Kroeger and Dikhoff's results are reported for copper concentrations from zero up to 10<sup>-4</sup> gram atoms Cu per mole ZnS, or about 0.0065 per cent Cu in the phosphor. Their results are readily reproduced with these and the lower concentrations of Cu and Al. An extension of this work to much higher Cu and Al contents, however, has disclosed the existence of a new phosphor system with emissions extending into the orange. Already summarized briefly (2), the results are reported below in greater detail. They lend even stronger support to the contention that true triple sulfides are formed on the basis of the principle of charge compensation. However, interpretation is rendered more difficult due to the complexity of the observed emission spectra and to the dual role of activator and of base modifier which copper is now found to assume in the phosphors.

This, in turn, may be related to the fact that, previously studied phosphor systems, copper has been found to be an effective activator when present in concentrations as high as 0.5 per cent Cu or more.

## CHARACTERISTICS OF PHOSPHORS FIRED IN P<sub>2</sub>H<sub>2</sub>S

### *Experimental*

The phosphors were prepared and fired in a manner described in a previous paper (3). Copper and the trivalent elements were introduced in form of several salts such as chlorides, nitrates, sulfates etc., with equally consistent results. Most of the phosphors were fired at 1100°C for ½ to 1 hour. Minor changes in the firing temperature did not produce characteristic changes in phosphor emission. When fired at 1000°C, the brightness was generally lower; when fired at 1200°C, the phosphors were coarser compared with the 1100°C materials. The presence of small amounts of air or gaseous oxides in the firing atmosphere caused relatively minor changes in emission characteristics in some cases, and very striking changes in other cases notably those involving aluminum as the substituent. For this reason, the phosphors prepared in pure H<sub>2</sub>S are considered separately from the phosphors fired in the presence of oxide additions. The phosphors with aluminum have so far been given more detailed consideration. Most of the emphasis in this report is, therefore, on materials with aluminum additions.

The emission curves were obtained with a recording spectroradiometer. In order to emphasize re-

<sup>1</sup> Manuscript received January 20, 1953. This paper was prepared for delivery before the New York Meeting, April 12 to 16, 1953.



tive changes more clearly, all emission curves have been normalized at the peak positions. Unless otherwise noted, all activator concentrations refer to the amounts of Cu and Al, etc., in per cent by weight of ZnS, that were introduced in the raw batch mixture. The excitation source was a BH4 lamp.

### Zn(Al)S Phosphors

Pure precipitated ZnS, fired in pure H<sub>2</sub>S, did not give a fluorescent response with optical excitation. The introduction of aluminum into pure ZnS resulted in a weak to medium-bright emission with 3650 Å excitation. This is shown in Fig. 1 for two concentrations of Al. Of the two fairly well resolved bands, the greener one at about 5000 Å became more prominent at the higher Al concentration when excited at room temperature. At the temperature of liquid nitrogen, the samples with Al showed only a

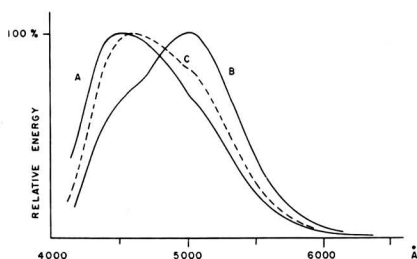


FIG. 1. Emission of H<sub>2</sub>S-fired Zn(Al)S phosphors. Curve A—0.32% Al; curve B—1.7% Al with 3650 Å excitation; curve C—1.7% Al with cathode ray excitation.

faint to weak blue emission in the 4500 Å band. At room temperature, the sample with low Al content gave a fairly long lasting green phosphorescence, while the sample with the higher Al concentration had a very short decay.

It is not clear whether the emission is due to zinc or to aluminum atoms or ions in the Zn(Al)S base material.<sup>2</sup> As is well known from the system SrS-Ce<sub>2</sub>S<sub>3</sub>, solid solutions of trivalent sulfides in divalent sulfides are capable of existence up to certain molar proportions, and without formation of thio-spinells. This appears to be the case also with ZnS-Al<sub>2</sub>S<sub>3</sub>. Almost all of the Al<sub>2</sub>O<sub>3</sub> that was formed or introduced in the raw material mix appears to have been converted into Al<sub>2</sub>S<sub>3</sub> during the firing. The phosphor with 0.3 per cent Al was almost completely soluble in dilute HCl, while the material with 1.7 per cent Al left only a small amount of insoluble residue. The

<sup>2</sup> The abbreviated notation used for these zinc-aluminum sulfide phosphors was chosen to suggest that the exact manner in which Al is incorporated in the ZnS matrix is still uncertain, and that Al probably acts chiefly as a base modifier, especially in the system with additional copper.

latter had to be calcined at 700°C in order to give the x-ray diffraction pattern of Al<sub>2</sub>O<sub>3</sub>. The formation of Al<sub>2</sub>S<sub>3</sub> took place only when the aluminum compounds were in contact with ZnS; pure Al<sub>2</sub>O<sub>3</sub>, fired in H<sub>2</sub>S at 1200°C, was not converted into Al<sub>2</sub>S<sub>3</sub>. The phosphors did not hydrolyze with water to give H<sub>2</sub>S, and the washed materials retained their luminescence unimpaired. This is taken as indirect evidence that a solid solution was formed. X-ray diffraction work is in progress to determine the phase relationships.

The optical excitation of the phosphors was due to a weak absorption band in the near u.v. at about 3800 Å. As shown in Fig. 2, this band became slightly stronger with increasing Al concentration. The phosphors did not respond to infrared stimulation or to electroluminescent excitation. Under cathode ray excitation, the same blue and green emission bands

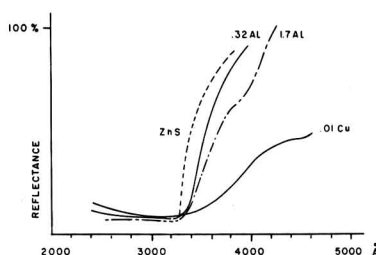


FIG. 2. Reflection spectra of H<sub>2</sub>S-fired ZnS phosphors

were obtained as with u.v. excitation, but in different relative, and very low absolute intensities. The blue band was the stronger of the two with both Al concentrations.

### Zn(Al)S:Cu Phosphors

In order to study the combinations of Cu and Al in ZnS, several different series of phosphors were prepared. For each concentration of Al several concentrations of Cu were used, representing deficiencies, equal amounts, and amounts in excess over the molar equivalents of Cu. The changes in emission that resulted from these substitutions are surveyed in the curves of Fig. 3 for 3650 Å excitation.

With copper concentrations up to about 0.05 per cent, all emissions at room temperature were substantially green, regardless of the amounts of Al introduced. This is shown by curves A, B, and C in Fig. 3. Curves B and C are identical despite a tenfold increase in Al content. They are slightly displaced compared with curve A due to a tenfold increase in the Cu activator content and the resulting suppression of the blue emission. At low Cu concentrations, therefore, Al is not a very effective modifier

of the emission spectrum. At the lowest Cu concentration, curve *A*, the usual blue band appears individually and in low intensity.

With increasing concentration of Cu, the blue band disappeared and the peak of emission shifted further toward longer wave lengths. At 0.3 per cent Cu the shift became still stronger and the effect of Al became more characteristic. Thus, curve *E* for 0.3 per cent Cu and 0.069 per cent Al (mole ratio 1:0.54) peaks at 5400 Å, curve *F* for 0.32 per cent Al (mole ratio 1:2.5) peaks at 5550 Å, and curve *G* for 0.69 per cent Al (mole ratio 1:5.4) peaks at 5740 Å in the yellow. Simultaneously the curves broaden

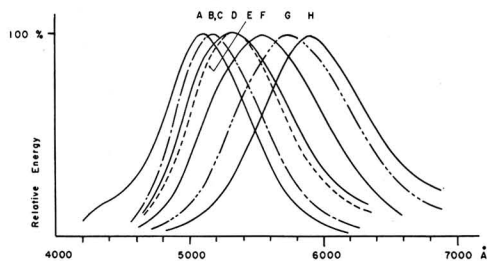


FIG. 3. Emission of  $H_2S$ -fired  $Zn(Al)S:Cu$  phosphors with 3650 Å excitation.

Curve	% Cu	% Al	Moles Al per mole Cu
A	0.005	0.0114	5.4
B	0.05	0.069	3.2
C	0.05	0.69	32.0
D	0.1	0.23	5.4
E	0.3	0.069	0.54
F	0.3	0.32	2.5
G	0.3	0.69	5.4
H	0.6	1.37	5.4

to a considerable extent, such that the half width of curve *G* is about 40 per cent greater than that of curve *A*. Curve *H* shows the emission spectrum of a phosphor with 0.6 per cent Cu and 1.37 per cent Al (mole ratio 1:5.4) which peaks at 5900 Å. With still higher Cu contents, the emission spectrum did not appear to deepen further appreciably, and the intensity of emission became too low for the spectrum to be recorded. Phosphors made with 1 per cent Cu or more (and corresponding amounts of Al) did not fluoresce at room temperature. They fluoresced only at low temperatures with u.v. excitation, and were olive colored in daylight.

Those phosphors which were prepared with molar deficiencies of Al compared with Cu contained excess free copper sulfide, which was readily removed by means of NaCN. The phosphors with molar equivalents or excess of Al over Cu did not contain any

appreciable amounts of free copper sulfide. Likewise, they did not contain any free  $Al_2S_3$  as they were not decomposed by water or weak acetic acid. However, they contained some  $Al_2O_3$  which separated out when the phosphors were dissolved in dilute HCl.

While the amount of acid-insoluble  $Al_2O_3$  increased with increasing molar excess of Al over Cu, the amount of readily soluble Al was much higher than the actual Cu equivalent. For example, three phosphors, prepared with 0.3 per cent Cu and with 2.2, 5.4, and 21.6 moles added Al per mole added Cu, gave 2.1, 3.9, and 15.8 moles soluble Al per mole Cu, as found by analysis for acid-insoluble  $Al_2O_3$ . Thus the amount of soluble Al increased in both relative and absolute amount compared with the constant amount of Cu.

It is uncertain, however, whether all acid-soluble Al was due to  $Al_2S_3$  or at least in part to some  $Al_2O_3$ . In other words, the amounts of Al that were readily soluble in acid do not necessarily represent only the amounts of  $Al_2S_3$  that were present in solid solution in ZnS, but they may also contain some acid-soluble  $Al_2O_3$ . The source for the latter product may be the excess  $Al_2O_3$  in the phosphor itself (part of it being soluble and part of it being insoluble in acid) or, as a further complication, a possible solid solution of  $Al_2O_3$  in ZnS which could also provide a homogeneous phosphor phase. The identification of separate phases in the phosphors, such as  $Al_2O_3$ , if any, is currently being attempted by x-ray diffraction. Preliminary work has shown only the diffraction lines characteristic of the ZnS wurtzite structure.<sup>3</sup>

Whether or not the conversion of the added aluminum salts into  $Al_2S_3$  stops exactly at the mole ratio Cu:Al = 1:1, or continues beyond, there is a definite effect of excess Al upon the emission spectrum. This is shown by curves *E* to *G* in Fig. 3 where Al becomes increasingly more effective after the 1:1 mole ratio has been overstepped.

The phosphors with equivalent amounts or excess of Al turned out with white to yellow to olive body colors which did not change when the materials were washed with NaCN. The depth of color increased with increasing Cu concentrations. The phosphors appeared to contain all added Cu incorporated in solid solution. Chemical analysis for retained Cu content (after an NaCN wash) showed full recovery, within the experimental error, of all added Cu in the phosphors prepared with a molar excess of Al. Thus the phosphors appeared to represent complete solid

<sup>3</sup> (Added in print) According to a recent paper by H. Hahn and G. Frank [*Z. anorg. u. allgem. Chem.*, **269**, 227 (1952)], a compound of composition  $ZnAl_2S_4$  was also found to have the wurtzite structure of ZnS when prepared above 1000°C, and the spinell structure when prepared at lower temperatures, the transformation being reversible.

solutions of (presumably)  $\text{Cu}_2\text{S}$  in the base material to form true triple Zn-Al-Cu sulfides. Expressed differently, the solubility of copper sulfide ( $\text{Cu}_2\text{S}$ ) is considerably higher in zinc-aluminum sulfide than in pure zinc sulfide.

In some respects, the new Zn(Al)S:Cu phosphor system is reminiscent of the (Zn,Cd)S:Cu system, in which an increase of the substituting sulfide produces a shift of the ZnS:Cu emission toward longer wave lengths. However, the efficiency of the yellow-orange emitting Zn(Al)S:Cu phosphors was only about one-half of that of (Zn,Cd)S:Cu phosphors of similar color. The greener materials approached the brightness of the phosphors with cadmium, while at the longer wave length side the brightness fell off much more rapidly. However, there are other characteristic differences.

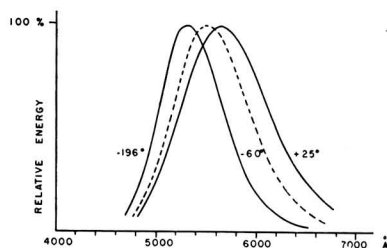


FIG. 4. Emission of phosphor *G* in Fig. 3 with 3650 Å excitation at different temperatures.

The (Zn,Cd)S:Cu system requires very small amounts of Cu activator (less than 0.01%), while the Zn(Al)S:Cu system requires up to 100 times as much Cu to produce corresponding colors. In this system, the substituting sulfide is actually a double sulfide, the pair  $\text{Cu}_2\text{S}-\text{Al}_2\text{S}_3$  apparently replacing 4 ZnS in the lattice just as 4 CdS replace 4 ZnS in the phosphors with cadmium. Hence the peculiar situation in these new phosphors where copper performs a dual role, namely, that of a matrix constituent and modifier, and that of an activator as well.

Further differences with the (Zn,Cd)S:Cu system were found in the phosphorescent decay, which is rather long and strong in this system, but comparatively brief in Zn(Al)S:Cu. Also, the phosphors with cadmium are quite temperature stable, while the phosphors with aluminum lost brightness very rapidly at elevated temperatures. They were practically extinct at temperatures of 100°–150°C. On cooling to low temperatures, they all increased in brightness and changed to green, as shown, for example, in Fig. 4 for a phosphor with 0.3 per cent Cu and 0.69 per cent Al. While the peak of emission shifted from 5740 to 5300 Å, the intensity of emission increased, and the half width decreased again by nearly 40 per cent. Even the phosphor with 1 per

cent Cu and 1.37 per cent Al was fairly bright green when excited at  $-196^\circ\text{C}$  with 3650 Å radiation.

The emission bands give the impression of being true single bands which are displaced with increasing matrix substitution, as in the case of (Zn,Cd)S:Cu. This is not so, however. It can be demonstrated that the emission consists of three sub-bands of such relative intensities that the presence of a single band is deceptively simulated.

The change in color and attendant greater change in half width with low temperature excitation are taken as one indication of a multiple band emission at room temperature. A second point is the fact that the emission spectrum is dependent upon the intensity of the exciting u.v. radiation, as shown in Fig. 5 for the phosphor with 0.3 per cent Cu and

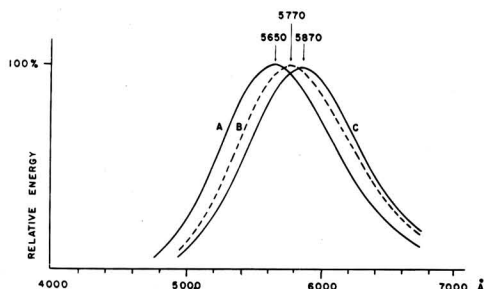


FIG. 5. Emission of ZnS (0.3% Cu, 0.69% Al) with different intensities of 3650 Å excitation. Approximate ratio of intensities A:B:C = 40:5:1.

0.69 per cent Al. An increase in the 3650 Å intensity, estimated at about fortyfold, caused the emission spectrum to move about 200 Å toward shorter wave lengths. The phosphor looked considerably greener when excited at close range, and more orange when excited at a greater distance from the BH4 lamp. This is readily explained with the postulate of two or more individual bands in the emission spectrum, the bands having different excitation sensitivities. As the intensity of the exciting radiation is increased, the longer wave length band appears to be approaching a state of saturation, while the intensity of the green band continues to build up at a regular rate. While the half width of the emissions does not change over the range of u.v. intensities used, it is not likely that the observed shift represents a mere displacement of a single band.

The strongest argument for multiple band emission, however, was found in the phosphorescent decay of these phosphors. Though not measured as yet, the decay was observed to consist of a very rapidly declining green emission and a far more slowly declining yellow-orange emission. The time constants for the two decays were estimated to differ by a factor of the order of 100.

In Fig. 3, the peak emission of the phosphor with 0.3 per cent Cu and 0.69 per cent Al is shown to be at 5740 Å. This is about intermediate compared with the results of Fig. 5 for the same phosphor. As the distance of u.v. source-phosphor-spectrograph slit was not changed while the curves for the phosphors of Fig. 3 were taken, the relative color changes due to phosphor composition as shown in that figure are approximately correct for the particular intensity of 3650 Å radiation used. The isolation of each sub-band as a function of the exciting energy and intensity remains to be undertaken.

The band at 5900 Å appears to be the longest wavelength emission which the Zn(Al)S:Cu phosphor system with high Cu contents can furnish. The green band at 5150 Å represents the other extreme. Thus, one might expect that these two bands in different

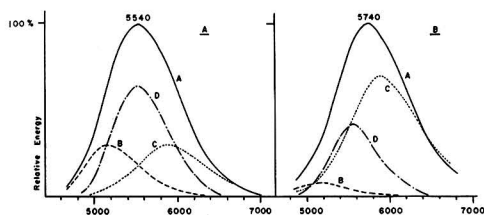


FIG. 6. Approximate intensity distribution of sub-bands in emission spectra of 3650 Å-excited ZnS phosphors with: A—0.3% Cu and 0.32% Al; B—0.3% Cu and 0.69% Al.

relative intensities should yield the observed emissions of the intermediate phosphors. This is not so. At least three bands are required to synthesize the observed emissions from simpler sub-bands.

The third band is obtained by subtracting the extreme bands (in intensities adjusted by trial to give the best fit) from the observed emission bands of the yellow phosphors. The remaining band peaks at 5550 Å, it has a normal shape, and it is always found at the same position. Its half width is slightly larger than that of the green band and slightly smaller than that of the orange band. This is shown in Fig. 6A where the reconstruction of the emission spectrum of phosphor *F* in Fig. 3 is indicated. The solid line represents the emission as recorded, from which the adjusted sub-bands *B* and *C* have been subtracted to leave the third band as the dashed line *D*. A slight discrepancy occurred only at the deep red end where the measurements were known to be less reliable (slightly too high).

Curve *B* in Fig. 6A is identical with curve *B* in Fig. 3, reduced to 30 per cent of its peak intensity; likewise, curve *C* in Fig. 6A is identical with curve *H*

in Fig. 3, also reduced to 30 per cent of its peak intensity. This leaves the differential band *D* at 5550 Å as the most intense band of the three. The sum of the sub-bands *B*, *C*, and *D* gives curve *A*, the observed emission. In this particular phosphor, therefore, the relative intensity contribution of the three sub-bands is in the approximate ratio of 1:2:1.

While the construction of curve *A* in Fig. 6A may seem obvious due to the fairly symmetrical grouping and identical height of the sub-bands *B* and *C*, the emission curves of other intermediate phosphors such as *G* in Fig. 3 can be equally well reconstructed from the same three bands. In this case, however, the ratio of peak intensities for the 5150, 5550, and 5900 Å bands must be about 1:6:10 in order to obtain a good match. This is done by adjusting the 5150 Å band to 10 per cent of peak intensity and the 5900 Å

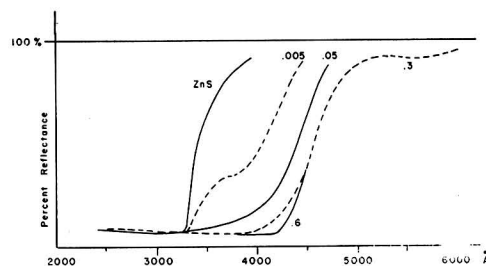


FIG. 7. Reflection spectra of H<sub>2</sub>S-fired ZnS phosphors with constant mole ratio of Cu:Al = 1:5.4. Figures next to curves indicate per cent by weight of added Cu.

band to 70 per cent of peak intensity as shown in Fig. 6B. If the adjusted bands are subtracted from the recorded band, the remaining band at 5550 Å is identical in shape with the one obtained from curve *F* above. In this phosphor the band at 5900 Å is the dominant one. For this reason, the discrepancy at the deep red end becomes slightly worse.

It is curious that the relative intensities of the three sub-bands seem to be always so adjusted that the resulting emissions as observed with average intensities of exciting radiation present the picture of normally shaped single bands. There are no humps in the curves to indicate the beginning of resolution at either room or lower temperatures. It has not been possible so far to isolate the 5550 Å band for observation by itself.

The optically excited emission of the phosphors is due to a strong absorption band in the near u.v. which extends into the visible. This band, as obtained in reflection and shown in Fig. 7, is at the same position as the bands for Cu and Al alone. It is a great deal stronger, however, and increases in strength with increasing concentrations of both Cu and Al. A

complete absorption spectrum is shown specifically for the phosphor with 0.3 per cent Cu and 0.69 per cent Al. The absorption in the blue is responsible for the yellow body color of the phosphor. The excitation spectrum for these materials will not coincide with the absorption spectrum, as neither short u.v., such as 2537 Å radiation, nor blue light, such as the strongly absorbed 4200 Å radiation, lead to any noteworthy fluorescent response of the phosphors.

When excited by 5000-volt cathode rays with moderate beam currents, all Zn(Al)S:Cu phosphors with copper contents in excess of 0.05 per cent emitted substantially green luminescence, regardless of the amount of Al present, and regardless of their color with u.v. excitation. The bands were of normal shape. The peak positions shifted from 5100 Å for the phosphor with 0.05 per cent Cu to 5300 Å for the materials with up to 0.6 per cent Cu. Aluminum played only a minor role in broadening the spectrum, in contrast to the results obtained on the same phosphors with u.v. excitation. For phosphor *G*, for example, the shift of peak with u.v. excitation amounted to 700 Å and the broadening to about 40 per cent compared with phosphor *A*; with cathode ray excitation of the same phosphor sample, the shift of peak amounted to only 200 Å and the broadening to about 15 per cent.

Practically all Zn(Al)S:Cu phosphors fired in atmospheres of pure H<sub>2</sub>S were nonresponsive to electroluminescent excitation. The only exceptions were materials prepared with molar deficiencies of Al which were fired at lower temperatures. This is discussed below. Unlike the ZnS:Cu phosphors described in the preceding paper, those prepared with additional Al did not respond to infrared stimulation.

In view of the different emission characteristics of the phosphors with u.v. and with cathode ray excitation one might suspect that the materials were not homogeneous so far as the fluorescent phase is concerned (i.e., disregarding the presence of free Al<sub>2</sub>O<sub>3</sub>). Conceivably, a shell of a certain composition and fluorescent response on each phosphor particle might surround a core of different composition and response. This was disproved, however, by subjecting the phosphors to slow and destructive dissolution in strong acid. The characteristic emissions of the phosphors under u.v. and under cathode ray excitation, respectively, persisted at all stages until the very last of the materials had been dissolved by the acid (again disregarding any Al<sub>2</sub>O<sub>3</sub>).

#### *Trivalent Substituents other than Al*

The introduction of other trivalent elements into H<sub>2</sub>S-fired ZnS:Cu phosphors with higher copper contents has been explored to a considerable extent. While a large number of experimental results have

been obtained, only a very brief and qualitative survey can be presented here. This introductory survey will be confined to only those compositions which appear to be of greater interest and novelty.

The trivalent elements may be expected to give results similar to aluminum, unless their ionic size is either much too small or much too large to permit easy entry into the ZnS lattice. The extremes in ionic radii of the trivalent group III elements are found in boron (0.2 Å) and lanthanum (1.15 Å), compared with aluminum (0.55 Å) and the next closest element, gallium (0.65 Å). Thus Kroeger and Dikhoff have found that the copper emission in ZnS phosphors with low Cu contents and any of the larger trivalent group III elements is the same position-wise and differs mainly intensity-wise.

At the higher Cu concentrations, such equivalence was no longer found. For example, phosphors with 0.1 per cent Cu and enough Ga to give mole ratios of 1:1 and 1:5 were practically devoid of any fluorescent response to either u.v., cathode ray, or electroluminescent excitation. They gave a very weak orange luminescence when excited at -196°C; this despite the fact that the materials were apparently triple sulfides like the compositions with aluminum. They were of light yellow body color, did not contain any appreciable amount of free copper sulfide, and did not hydrolyze with water or weak acetic acid.

Similarly, homogeneous materials were obtained with indium, yttrium, and lanthanum in place of aluminum, and with copper contents of 0.1 per cent. The body color of the samples with indium was a deep yellow. They gave a weak deep orange-red emission with a peak at about 6700 Å when excited by u.v. at room temperature, and a lighter and brighter emission at -196°C. With cathode ray excitation the emission was a weak deep orange. Yttrium, in equimolar amount and in excess of 0.1 per cent Cu, gave yellowish-brown body colors, a weak orange emission with 3650 Å excitation which became redder at low temperatures, and a fairly bright yellow-orange emission with cathode ray excitation. The fluorescence of the samples with La was a very weak green. Despite the low intensity of fluorescence, the phosphorescent decay was long and strong, especially in some samples made with high La contents.

While all these materials appeared to be built up according to the same principle which governed the formation of rather bright phosphors with aluminum substitution, the fluorescent response of these other materials was surprisingly poor. In particular, the lack of response in the case of gallium was of interest in view of the great chemical similarity between Ga and Al. Thallium probably does not form a trivalent sulfide at the firing temperatures in question, but

several group V elements, such as Bi or Sb, probably do. These elements, however, were ineffective in promoting the formation of triple sulfides with ZnS and Cu<sub>2</sub>S.

The remaining group III elements, including especially a few of the rare earths, were again of considerable interest. Thus, triple sulfides with bright yellow and orange luminescence were obtained with scandium in equimolar amount and in excess, and with as much as 0.3 per cent Cu or more. The materials appeared to be homogeneous and contained all added Cu in nonextractable form. They were of light tan to deeper orange-brown body colors, the colors increasing in depth with increasing Cu and Sc contents and with increasing firing temperature. The yellow to orange luminescence was obtained with u.v. as well as with cathode ray excitation, the fluorescent color likewise deepening with higher activator concentrations and higher firing temperature. It was again found that a two-band or multiple emission was involved consisting of a green and at least one orange band. The phosphorescence was very strong in all samples with scandium.

Under u.v. excitation, the phosphors with scandium showed reasonably good temperature stability of the orange band, while the green band faded much more rapidly at elevated temperatures. Thus, all phosphors emitted orange light between 100 and 200°C. The phosphors also showed a strong thermoluminescent emission of both green and orange, the orange being stronger in the materials with high scandium contents.

The phosphors with scandium were of greatest interest, however, because of their strong infrared stimulability. The emitted light was of yellow to orange color in the brightest phosphors which were made with 0.05 per cent Cu and increasing amounts of Sc. However, and this seems even more interesting, the stimulated emission was also very strong in the phosphors made with as much as 0.3 per cent Cu. The usual activator concentrations in stimutable sulfide phosphors are in the parts per million range, higher concentrations leading to quenching. The phosphors with scandium were stimutable only when fired in H<sub>2</sub>S. When prepared with NaCl flux in the usual manner, they showed no stimulability whatever, and they fluoresced green instead of yellow-orange.

Compared with the strontium sulfide infrared phosphors, the Zn(Sc)S:Cu materials were less bright in stimulation, but they showed much greater stability to atmospheric exposure. Thus, they were not attacked in over a week's contact with moist air or liquid water, indicating that the Sc<sub>2</sub>S<sub>3</sub> that was formed appeared to have been incorporated in a stable solid solution in ZnS.

Similar results were obtained when cerium, praseodymium, or neodymium were used as the trivalent substituents. Praseodymium and neodymium produced orange luminescent colors in excitation and stimulation, while the colors of the phosphors with cerium were more concentration-dependent, ranging from green-yellow to orange with increasing Ce.

The emission spectra of phosphors with these three substituents showed the appearance of narrower, resolved bands, even with room temperature excitation. Cerium gave such bands near 4400, 5000, 5500, and 6700 Å. Praseodymium and neodymium gave even sharper bands approaching line emission in width, which were superimposed upon a continuous background of orange-red emission with peaks in the red. With Pr, the bands or lines were located at 5040, 5500, 6100 (multiplet), and 6700 Å. By far the strongest of the four was the one at 6700 Å, in a phosphor with 0.05 per cent Cu and 0.22 per cent Pr (mole ratio 1:2). The 6700 Å band towered sharply over the continuous background, with its peak intensity in the deep red. In the phosphors with neodymium, the bands or lines were located at 5050, 5410, 6050 (multiplet), and 6680 Å. The strongest band here was the one at 6050 Å in a phosphor with 0.05 per cent Cu and 0.23 per cent Nd (mole ratio 1:2). When excited at -196°C, the sharp bands did not change their position or half width; the continuous background, however, moved slightly toward longer wave lengths. It is evident that the narrow bands represent the characteristic emission of the rare earths, while the background represents the characteristic red emission of Cu discussed previously (3).

While the phosphors with 0.05 per cent Cu were brighter than the compositions with 0.3 per cent Cu, it was of interest that the latter products not only fluoresced at all, but were again responsive to infrared stimulation and in some cases to electroluminescent excitation.

The results on the combination of copper with the rare earths (at high concentrations) thus parallel the results which Kroeger and Dikhoff (1) obtained with the combination of silver with the rare earths (at low concentrations). The characteristic line emission is superimposed upon a continuous background in both cases. In this connection it is of interest to note that a corresponding system of phosphors with high silver and aluminum, etc., contents could not be developed. Phosphors with amounts of Ag that are equivalent to the 0.05 to 1 per cent range of Cu concentrations reported here did not fluoresce and did not appear to form homogeneous triple sulfides.

The storage ability of the phosphors with Ce was better than that of the materials with Sc, Pr, or Nd. After storage for 15 hours in the dark, the stimulated

light was about as bright as it was immediately following the excitation by u.v. While the introduction of the other trivalent elements had produced yellow to brown body colors of the phosphors, the H<sub>2</sub>S-fired materials with Ce were pink to purple colored.

The remaining group III and rare earth elements produced little if any fluorescent response of interest, when used in conjunction with such relatively high concentrations of Cu as 0.05 to 1 per cent.

#### PHOSPHORS FIRED IN ATMOSPHERES OF H<sub>2</sub>S WITH OXIDE ADDITIONS

##### *Experimental*

As mentioned before, the characteristics of some of the phosphors discussed changed markedly when they were fired in the presence of oxide additions to the H<sub>2</sub>S firing atmosphere. These changes were especially noteworthy in the phosphors with aluminum substitution.

When the latter materials were fired in H<sub>2</sub>S with small admixtures of air, water vapor, CO<sub>2</sub>, SO<sub>2</sub>, etc., the incorporation of copper sulfide became incomplete, regardless of the amount of Al present; the body color of the phosphors changed to the usual tan-gray characteristic of ZnS-ZnO:Cu phosphors; the yellow-orange emission substantially disappeared, leaving only the green emission; and the materials became strongly responsive to electroluminescent excitation within certain ranges of activator concentrations.

The phosphors were prepared as described previously, except for the addition of the oxide gases. For most of the compositions 1100°C proved again to be the optimum firing temperature. The relative brightness under u.v., cathode ray, and electroluminescent excitation was not the same for all phosphors. Since the phosphors were prepared with much higher Cu concentrations than those reported by Kroeger and Dikhoff (1) (for pure H<sub>2</sub>S-firing), their brightness under u.v. excitation was not quite as high. Considering the large amount of Cu which was actually incorporated in the materials, however, their brightness was surprisingly high. Most of the discussion below will be devoted to the electroluminescent response which appears to be of greater interest in connection with these phosphors.

The admixture of oxide gases to the H<sub>2</sub>S was simple only in the case of water vapor. When bubbled through water or dilute Ba(OH)<sub>2</sub> solution at room temperature, a mix of H<sub>2</sub>S with about 3 per cent H<sub>2</sub>O was conveniently obtained. To prepare mixtures with lower water contents, the gas mix was passed through traps cooled to lower temperatures to freeze out excess water. The vapor pressure of the ice

formed was then assumed to determine the desired partial pressure of H<sub>2</sub>O in the emerging gas mix. To obtain mixtures with more than 3 per cent H<sub>2</sub>O, the gas was bubbled through heated water and the duct to the firing vessel was kept hot to prevent condensation.

For mixtures with air and CO<sub>2</sub>, flowing currents of these gases were mixed with H<sub>2</sub>S in a larger vessel and then led to the firing vessel after passing a trap cooled to -57°C. At this temperature, the vapor pressure of ice is 12  $\mu$ . Thus water was effectively removed to the extent of about 1 part in 65,000. The resultant mixture with such low water content acted as though it contained no water at all, i.e., the phosphors had the same characteristics as those fired in pure H<sub>2</sub>S. The amounts of air and CO<sub>2</sub> that could be dosed reasonably well by this method ranged from 2 to 20 per cent.

When the phosphors were fired in atmospheres with large additions of oxide gases (10, 20% or more), their electroluminescent response was a weak to medium bright blue, regardless of the nature of the gas. When the amounts of oxide additions were small, the response was a pure green, and varied in intensity mainly with the activator concentrations. Thus, there was no significant difference in color or brightness between the phosphors fired with air, water vapor, or other additions. Since water was so much easier to dose than the other gases, most of the experiments were carried out with this addition. It will be referred to as "wet firing."

All phosphors, whether prepared with molar deficiencies or excess of Al relative to Cu, contained free copper sulfide which was removed with NaCN. While the solubility of copper sulfide in ZnS was thus considerably lower than in the dry-fired phosphors, it was nevertheless larger than in the phosphors with Cu alone, and it was dependent upon the Al concentration, increasing slightly with increasing Al additions. The removal of copper sulfide from the fired products was necessary for the double purpose of increasing the brightness and reducing the conductivity of the phosphors, so as to allow their use in electroluminescent cells without an insulating material. The concentration of acid-insoluble Al<sub>2</sub>O<sub>3</sub> was slightly higher than in the dry-fired materials.

The exact nature of the atmosphere to which the phosphors were exposed during the firing has not been determined. It is apparent that the addition of air or CO<sub>2</sub> to H<sub>2</sub>S produces H<sub>2</sub>O and SO<sub>2</sub> in certain concentrations. Since all of these gases were equally effective in producing the reported changes, it follows that it is the oxygen constituent of the gas mix which, regardless of its nature, produced the changes in characteristics compared with the phosphors fired in pure H<sub>2</sub>S.

## Wet-Fired Zn(Al)S:Cu Phosphors

The formation of Zn(Al)S:Cu phosphors with different emission and response characteristics is a fully reversible process. One type of phosphor could be readily converted into the other type, merely by refiring for a short time in the appropriate atmosphere. Thus a dry-fired phosphor with yellow body color, orange 3650 Å-response, and lack of electroluminescent response, gave a tan-gray colored product with green u.v. and green electroluminescent response on refiring in wet H<sub>2</sub>S; this latter material, heated again in dry H<sub>2</sub>S (without removal of the excess copper sulfide) reverted to the first type, which on further firing in H<sub>2</sub>S plus air gave again the second type, etc.

TABLE I. Effect of water vapor in firing atmosphere on electroluminescent response

Water temp	Trap temp	Ratio H <sub>2</sub> O:H <sub>2</sub> S	Electrolum. response
°C	°C		
100	—	1:0	Faint blue
55	—	1:4.6	Bright green
25	—	1:33	Very bright green
25	-20	1:1000	Weak green
25	-42	1:10000	Very weak green
25	-57	1:65000	Dead

The best range for the preparation of bright green electroluminescent phosphors was about 1 to 20 per cent H<sub>2</sub>O, and about 2 to 5 per cent of either air or CO<sub>2</sub> in H<sub>2</sub>S. The effect of the concentration of water vapor upon the electroluminescent emission of a phosphor prepared with 0.3 per cent Cu and 0.35 per cent Al is shown in Table I.

It has been pointed out (3) that the H<sub>2</sub>S-fired ZnS phosphors activated with Cu alone gave an orange emission with electroluminescent excitation. When fired with oxide additions, they luminesced mainly blue at both low and high frequencies. The addition of even very small amounts of aluminum to the phosphors changed their response completely, to a pure green, when they were fired in the presence of gaseous oxides. As little as 10 mole per cent of Al relative to Cu effected the color change to green and, at the same time, increased the brightness fourfold. Larger amounts of Al gave a greater brightness increase, as shown below. It is of particular interest and importance that the luminescence remained green over the entire frequency range of 60 to 15000 cps investigated. This is in contrast to the Destria-type ZnS-ZnO:Cu phosphors and to the ZnS phosphors activated with Cu and Pb which change from green to blue at the higher frequencies (4).

The spectral emission of the wet-fired phosphors with aluminum was substantially invariant with com-

position under electroluminescent excitation. Their brightness, however, was a function of composition as well as firing temperature. This was found from several series of phosphors which were prepared with increasing amounts of Cu, each of them with a number of different Al concentrations, and each of these fired at different temperatures. The optimum firing temperature was about 1100°C. Phosphors fired at either 1000° or 1200°C were significantly less bright. The optimum copper content was about 0.15 per cent added Cu (with 0.05 % Al), although a much wider range of compositions gave nearly equally bright materials. The dependency of the brightness upon the Al concentration is shown in Fig. 8 which holds for both 60 and 5000 cps excitation of the

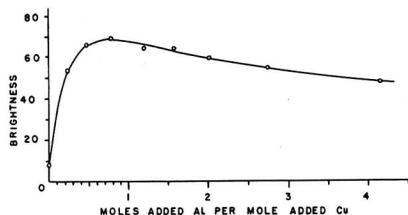


FIG. 8. Electroluminescent brightness as dependent upon Al concentration in phosphors prepared with 0.15% Cu. Excitation by 60 and 5000 cps currents.

phosphors in oil cells. The brightness ordinate is in arbitrary units. Curves of similar shape were obtained for Cu concentrations from 0.05 to 0.5 per cent added Cu, with peaks occurring at different levels of brightness.

The figure demonstrates the striking increase in electroluminescent brightness due to Al. This increase was obtained with very small amounts of Al, much less than the equivalent of added Cu, and it reached a maximum at a concentration of about 0.75 moles Al per mole added Cu. A plot of brightness vs. moles of Al per mole of retained Cu (after the NaCN wash) gave a similarly flat maximum at about 2 moles Al. Since 0.75 is known to be too low (not all added Cu was retained by the washed phosphors), and since 2 is too high (not all Al is incorporated as Al<sub>2</sub>S<sub>3</sub> in the phosphors), the true mole ratio of Cu:Al for phosphors of optimum brightness must be in between, i.e., somewhere near 1:1. It does not follow, however, that all phosphors with equimolar Cu and Al contents are electroluminescent. This is discussed below.

With respect to the optical response of the wet-fired Zn(Al)S:Cu phosphors, it was already mentioned that their emission was bright green with 3650 Å excitation. This is shown in Fig. 9 for amounts of added Cu up to 0.3 per cent. There was no further change in emission with higher concentrations of Cu,



but the intensity of emission began to decline again. The range of colors obtained was a great deal narrower than that of phosphors of the same initial composition but fired in pure  $H_2S$ . It covered a total displacement of only about 170 Å by going from 0.05 to 0.3 per cent Cu or higher, compared with the 700 Å displacement for the dry-fired materials. This was not due to the lower amounts of Cu actually incorporated in the phosphors. Thus a dry-fired product with 0.3 per cent retained Cu emitted yellow-orange, whereas a wet-fired product with 0.3 per cent retained Cu emitted green light.

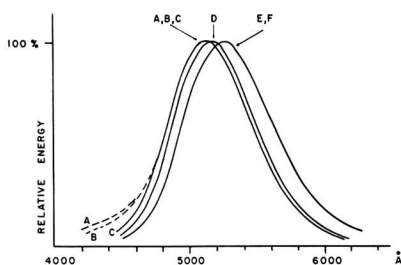


FIG. 9. Emission with 3650 Å excitation of Zn(Al)S:Cu phosphors fired at 1100°C in  $H_2S$  with 3%  $H_2O$ .

Curve	% Added Cu	% Added Al
A	0	1.7
B	0.005	0.0114
C	0.05	0.069
D	0.05	0.69
E	0.3	0.69
F	0.3	2.7

The typical blue band appeared again in low intensity in the phosphors with low Cu content. In comparing the curves for the phosphors with increasing concentrations of Cu and Al, it was found that practically all of the peak displacement was due to the increasing Cu content; Al contributed but little to the shift. The reflection (absorption) curves of the wet-fired phosphors presented about the same picture as those of the dry-fired phosphors shown in Fig. 2. An increase of the Cu content caused the absorption band to become stronger, while an increase of the Al content was relatively ineffective.

Under 5000-volt cathode ray excitation, identical emission bands were found, as already reported for the dry-fired phosphors of like composition. With increasing Cu concentration up to about 0.3 per cent, the peak of emission shifted from 5100 to about 5250 Å. The shape of the emission curves of the wet-fired Zn(Al)S:Cu phosphors was practically identical under all three forms of excitation, i.e., ultraviolet, cathode rays, and electroluminescence.

#### Wet-Fired Phosphors with Other Trivalent Cations

The phosphors with aluminum substitution underwent characteristic changes resulting from dry vs. wet firing. In surveying the effect of wet firing upon the phosphors with other trivalent substituents, it can be stated summarily that such striking changes were, in general, not observed. It was surprising to find that the electroluminescent response was hardly affected where it existed at all in the corresponding dry-fired materials, and that it was not as strikingly improved as with Al substitution. Again it was found that gallium in particular did not produce more than the faintest electroluminescent response.

With excitation by u.v., wet firing resulted generally in either slight or stronger shifts toward shorter wave lengths. In some cases, the shifts were accompanied by a change in brightness, in others, they were not. For example, the phosphors with indium, cerium, and praseodymium became dimmer as the emission shifted toward green-blue, while the phosphors with scandium became just slightly greener with little or no loss of brightness. Likewise, the infrared stimulability was generally affected adversely, and showed similar changes of color, except again in the samples with scandium whose stimulated light was slightly greener but almost as bright as with dry firing. In general, none of these phosphors was as interesting as the ones with aluminum substitution.

#### DISCUSSION

The results obtained on  $H_2S$ -fired ZnS phosphors with high copper and high trivalent cation contents are best explained with the premise that these materials are substantially true triple sulfides. So far, the x-ray diffraction patterns have shown that the materials with aluminum substitution have the structure, and very nearly the spacings, of hexagonal ZnS. Differentials in spacings between pure ZnS and the phosphors with as much as 0.3 per cent Cu and 0.69 per cent Al, for example, appear to be so small that refined analysis becomes necessary. Individual phases of  $Cu_2S$ ,  $Cu_3S$ ,  $Al_2O_3$  or  $Al_2S_3$  have not been identified on the patterns obtained, despite the fact that  $Al_2O_3$ , for example, was found analytically. Other physical and chemical characteristics make it also most plausible to regard the phosphors as triple sulfides with monovalent Cu. Thus Kroeger's (1) original hypothesis that trivalent cations facilitate the incorporation of Cu in ZnS appears to have been even better substantiated with these materials of much higher activator concentrations than Kroeger investigated.

If the presence of free  $Al_2O_3$  is disregarded in the phosphors prepared with molar excess of Al over Cu, the luminescent phase proper looks like a homogene-

ous product in which a single species of copper atoms appears to perform the dual role of base modifier and of activator. In contradiction with this conclusion, the complexity of the emission spectra leads to the opposite conclusion, namely, that two or more different species of Cu activator atoms must be present in these phosphors. This is concluded from the fact that the green emission is characterized by a different and independent excitation sensitivity, different temperature dependence, and different phosphorescent decay compared with the longer wave length emissions. It also follows from the fact that the emission spectra of phosphors of intermediate colors, such as green-yellow or yellow, cannot be built up additively from just two bands of extreme emission. A third sub-band is required to describe the observed emission fully.

The phosphors with the lower (0.05%) and higher (0.6% Cu) activator concentrations are considered to furnish two of the three sub-bands in nearly pure form. The remaining sub-band at 5550 Å could not be isolated individually.

The 5150 Å band is at the same position and of the same shape as the green emission band of conventional, hexagonal ZnS:Cu phosphors. It is suggested, therefore, that the same type of center which is operative in hexagonal ZnS:Cu phosphors, prepared with low concentrations of activator and coactivator, is also operative as an individual in the Zn(Al)S:Cu phosphors with much higher activator contents, furnishing the same green emission. This is the emission which is ultimately reached in pure form when these latter phosphors are excited at very low temperatures, or when they are excited by cathode rays at room temperature. The green emission would thus be due to only a small fraction of the number of Cu atoms in the phosphors, placed in the more common surroundings. The bulk of the Cu and Al atoms may be assumed to be aggregated in "insular" regions of higher than average concentration and thus non-random distribution throughout the phosphor crystals. The longer wave length emissions are then attributed to such "molecular island" complexes consisting of more nearly stoichiometric  $Zn_2AlCuS_4$  groupings with much higher than average concentration of Cu and Al. Such complexes may be expected to be very temperature-sensitive, consistent with the observed rapid loss of fluorescent brightness which approaches zero at temperatures as low as 100°C.

The phosphors with electroluminescent response have a much simpler emission, which is due essentially to the same type of center operative in all ZnS:Cu phosphors with green emission. However, and speaking on submicroscopic scale, the phosphors are probably heterogeneous and of more complicated

structure than the dry-fired materials. The tan-gray color of the wet-fired materials shows that the copper activator is present in some other association with the host lattice than in dry-fired phosphors of the same retained Cu content. The electroluminescent response is a direct consequence of the presence of oxides in the firing atmosphere, and its intensity depends upon the amount of these oxides. It thus seems reasonable to attribute the electroluminescent response to a solid oxide phase, providing barriers (5), which are distributed in extreme subdivision in or on the phosphor particles and in close physical contact with them. Speaking macrochemically, the "oxide" phase may be any of these possibilities: ZnO,  $Al_2O_3$ , CuS or CuO with divalent Cu, or their combinations.

Among these possibilities, it seems most plausible to associate the electroluminescent response with a separate phase of  $Al_2O_3$ . In the wet-fired phosphors, a certain amount of oxide should remain or form in accordance with the equilibrium  $Al_2S_3 + H_2O \rightleftharpoons Al_2O_3 + H_2S$ . Actually, the acid-insoluble  $Al_2O_3$  content of wet-fired phosphors was found to be higher than that of dry-fired materials, as expected. However, the  $Al_2O_3$  formed in wet firing must be considered to be in a different state than any unconverted oxide in dry-fired phosphors. The latter is a mere diluent and does not provide the type of boundaries necessary to make them responsive to electroluminescent excitation.

Thus, the following crude picture develops for the Zn(Al)S:Cu phosphors with high activator contents and with a molar excess of Al over Cu. When fired in dry  $H_2S$ , nearly all added Al is converted into  $Al_2S_3$ , which, together with all added Cu in the form of  $Cu_2S$ , forms a solid solution with ZnS, the ZnS being present in much larger amount than the compound  $Zn_2AlCuS_4$  requires. Any nonconverted Al survives in the form of separate, diluent particles of  $Al_2O_3$ . The main phosphor phase can fluoresce, but it is not responsive to electroluminescent excitation as it is homogeneous and has no oxide barriers. The formation of triple sulfides probably continues beyond the concentrations of Cu and Al that were investigated here; however, these materials cease to be phosphors.

Upon firing in atmospheres with oxide additions, the Al additive survives in form of two functional phases: most of the Al is converted into sulfide which is necessary to hold relatively large amounts of Cu in solid solution in the base material; it is not essential for the electroluminescent excitation itself. A smaller but significant portion of the added Al survives as  $Al_2O_3$  in extreme subdivision in or on the phosphors; it does not contribute to the solubility of  $Cu_2S$ , but it is essential to provide the heterogene-

ous barriers for the electroluminescent excitation of the phosphors. Since only a portion of the added Al is converted into  $\text{Al}_2\text{S}_3$ , not all of the added Cu can be taken into solid solution. The balance survives the firing as free copper sulfide, which can be washed out. Although the solubility of  $\text{Cu}_2\text{S}$  in the wet-fired phosphors is lower than in the dry-fired materials, it is appreciably higher than in the phosphors without aluminum.

It was mentioned before that some dry-fired phosphors did give a response to electroluminescent excitation. These were materials prepared with molar deficiencies of Al which were fired at lower temperatures. This may be explained on the basis of the picture outlined above. The temperatures were not high enough to effect the complete conversion of  $\text{Al}_2\text{O}_3$  into  $\text{Al}_2\text{S}_3$ . The concentrations of Al and the temperature were too low to allow particle growth of free, diluent  $\text{Al}_2\text{O}_3$  to occur. Thus, sufficient  $\text{Al}_2\text{O}_3$  could remain in the phosphors in suitable subdivision to provide the heterogeneous barrier phase and the condition for the electroluminescent response of the phosphors.

The response of the  $\text{Zn}(\text{Al})\text{S}:\text{Cu}$  phosphors is thus

attributed to a small amount of oxide in the phosphors. A similar situation seems to exist in the Destriau-type  $\text{ZnS-ZnO}:\text{Cu}$  phosphors which are, in fact, prepared with a deliberate, although much larger, addition of oxide.

#### ACKNOWLEDGMENT

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

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# Electrical Conductivity and Density of Molten Cryolite with Additives<sup>1</sup>

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## ABSTRACT

The electrical conductivities at 1000°C, expressed as per cent of the cryolite value, for cryolite containing 10 weight per cent of the following substances are: sodium fluoride 112, calcium fluoride 96, aluminum fluoride 91, and alumina 83. For pure sodium fluoride at 1000°C, conductivity is 5.52  $\text{ohm}^{-1}\text{cm}^{-1}$ , compared to 2.80  $\text{ohm}^{-1}\text{cm}^{-1}$  for cryolite. Molar conductance decreases linearly with mole per cent sodium fluoride, aluminum fluoride, alumina, or calcium fluoride addition to cryolite. The activation energy for conductance, calculated from a plot of the Arrhenius equation, is about 4.3 kcal/mole for the systems of cryolite with sodium fluoride, aluminum fluoride, and alumina, as well as for pure sodium fluoride, but is slightly higher for the cryolite-calcium fluoride system. This value agrees reasonably with the 4.48 kcal/mole for pure chryolite. Densities in these systems change linearly with temperature, that for pure sodium fluoride following the equation  $2.567 - 0.610 \times 10^{-3} t$ . The stability of the complex  $\text{NaF} \cdot \text{Na}_2\text{AlF}_6$  is indicated by a density maximum.

## INTRODUCTION

The first paper (1) in this series reported the electrical conductivity of cryolite as measured by improved techniques. In the Hall process for electrolytic production of aluminum, the electrolyte, while largely cryolite, usually contains an excess of either sodium fluoride or aluminum fluoride, along with calcium fluoride and varying quantities of dissolved alumina. Consequently, the effect on conductivities and densities of these additives to cryolite has been measured over a considerable composition range.

Literature values for the electrical conductivity of cryolite were summarized in the earlier work (1). No values are available for the electrical conductivity of pure molten aluminum fluoride inasmuch as it sublimes before melting. Arndt and Kalass (2) listed the specific conductance of sodium fluoride at 1000°C as 3.15  $\text{ohm}^{-1} \text{cm}^{-1}$ , and asserted that the equivalent conductances of sodium fluoride and of cryolite are nearly equal. In the temperature range of 1000°–1100°C, calcium fluoride and alumina are both solids and insulators.

## EXPERIMENTAL

*Materials.*—Hand-picked crystals of pure Greenland cryolite were crushed to 20 mesh and any associated particles of galena were removed. Sodium fluoride was Baker's C.P. powder. Aluminum fluoride was distilled and was presumed to be pure, except for a 0.9 per cent loss on ignition at 600°C. The alumina was Alcoa A-14, a high purity, calcined product containing less than 0.2 per cent water with

other impurities not exceeding 0.1 per cent. Calcium fluoride was hand-picked fluorspar, ground to a fine powder. These materials were heated for one hour

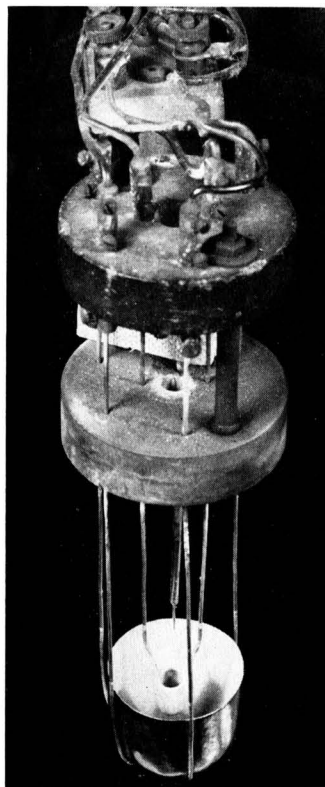


Fig. 1. Conductivity cell

<sup>1</sup> Manuscript received March 30, 1953.

in a platinum crucible at 400°C before weighing for each determination.

**Electrical conductivities.**—The procedure was to weigh out the desired mixture, grind the components together, and determine the resistance between hemispherical platinum electrodes immersed in the molten liquid. The cell pictured in Fig. 1 was immersed in a platinum crucible containing the stirred molten salt, with frequent adjustment to a fixed depth below the surface. The cell constant was taken as  $0.0835 \text{ cm}^{-1}$  as in the work with pure cryolite (1). Resistance was measured with a Kelvin bridge to eliminate errors from lead resistance. Frequencies from 600 to 4000 cycles/sec were employed and

Equivalent conductance

$$= \frac{(\text{eq wt}_A \times \text{wt fract}_A + \text{eq wt}_B \times \text{wt fract}_B)}{\text{density of melt}} \times \text{specific conductance of melt}$$

The equivalent weight of cryolite has been taken as one-third the formula weight ( $\text{Na}_3\text{AlF}_6$ ), that of calcium fluoride as one-half the formula weight.

#### POLARIZATION

There is no satisfactory criterion for knowing whether the additives to cryolite are causing appreciable errors in the extrapolation of resistance to infinite frequency. In the present work with the sub-

TABLE I. Densities of cryolite with several additives

Composition by weight	Density g/cm <sup>3</sup>	Range of measurement °C
100% Cryolite.....	$3.032 - 0.937 \cdot 10^{-3}t^*$	1000-1080
5% NaF-95% cryolite.....	$3.051 - 0.950 \cdot 10^{-3}t$	996-1080
10% NaF-90% cryolite.....	$3.024 - 0.920 \cdot 10^{-3}t$	1007-1078
15% NaF-85% cryolite.....	$3.016 - 0.910 \cdot 10^{-3}t$	988-1080
20% NaF-80% cryolite.....	$3.015 - 0.910 \cdot 10^{-3}t$	978-1080
40% NaF-60% cryolite.....	$2.867 - 0.790 \cdot 10^{-3}t$	947-1074
100% NaF-0% cryolite.....	$2.567 - 0.610 \cdot 10^{-3}t$	1003-1076
5% Al <sub>2</sub> O <sub>3</sub> -95% cryolite.....	$2.942 - 0.880 \cdot 10^{-3}t$	1009-1093
10% Al <sub>2</sub> O <sub>3</sub> -90% cryolite.....	$2.852 - 0.810 \cdot 10^{-3}t$	976-1079
15% Al <sub>2</sub> O <sub>3</sub> -85% cryolite.....	$2.753 - 0.720 \cdot 10^{-3}t$	998-1085
5% AlF <sub>3</sub> -95% cryolite.....	$2.986 - 0.910 \cdot 10^{-3}t$	1007-1086
8% AlF <sub>3</sub> -92% cryolite.....	$2.992 - 0.930 \cdot 10^{-3}t$	1008-1094
5% CaF <sub>2</sub> -95% cryolite.....	$3.012 - 0.890 \cdot 10^{-3}t$	992-1083
10% CaF <sub>2</sub> -90% cryolite.....	$3.027 - 0.870 \cdot 10^{-3}t$	993-1084
15% CaF <sub>2</sub> -85% cryolite.....	$3.057 - 0.870 \cdot 10^{-3}t$	997-1099
20% CaF <sub>2</sub> -80% cryolite.....	$3.060 - 0.840 \cdot 10^{-3}t$	987-1085
40% CaF <sub>2</sub> -60% cryolite.....	$3.172 - 0.840 \cdot 10^{-3}t$	1015-1096
5% Al <sub>2</sub> O <sub>3</sub> -10% CaF <sub>2</sub> -85% cryolite.....	$2.929 - 0.810 \cdot 10^{-3}t$	1000-1080

\*  $t$  in °C.

resistance vs. frequency<sup>-1</sup> was extrapolated to the infinite frequency value which has been used throughout this work to minimize polarization errors. Temperature was measured with a platinum, platinum-10 per cent rhodium thermocouple immersed a fixed distance in the molten salt.

**Densities.**—Density was determined with a platinum sinker (calibrated from the room temperature density and the coefficient of expansion of platinum) suspended from an analytical balance by a fine platinum wire. Equations for density as a function of temperature are given in Table I.

**Definitions.**—For a mixture of components A and B:

Molar conductance

$$= \frac{(\text{mole wt}_A \times \text{mole fract}_A + \text{mole wt}_B \times \text{mole fract}_B)}{\text{density of melt}}$$

× specific conductance of melt

merged platinum cell, the frequency dependence seemed to be unaffected to any major degree by the sodium fluoride, aluminum fluoride, calcium fluoride, or alumina additives, and the slopes of the resistance extrapolations against frequency<sup>-1</sup> were taken the same as for cryolite measured with the cell platinization in an equivalent state. As was the case in earlier experiments with pure cryolite, the platinum cell was platinized only at the start of the work. There was an erratic tendency for the slopes of the plots of resistance vs. frequency<sup>-1</sup> to increase as the work proceeded. Temperature changes in the range of these measurements, 1000° to 1080°C, had little influence on the slope of the frequency curves.

#### CONDUCTIVITY OF CRYOLITE WITH ADDITIVES

The specific conductances are plotted in Fig. 2 as per cent of the cryolite value vs. weight per cent of added sodium fluoride, calcium fluoride, aluminum fluoride, and alumina. To achieve maximum conductivity, the bath should contain an excess of

sodium fluoride, and it should have minimum amounts of alumina and calcium fluoride. Additional data on these systems are shown in Table II.

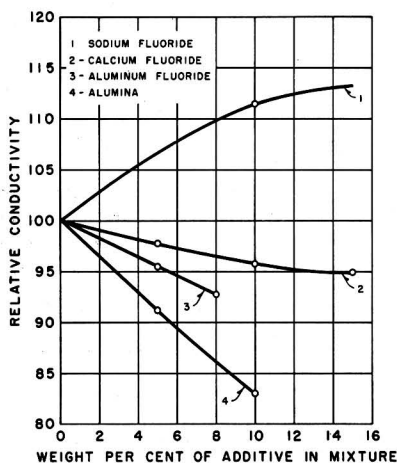


FIG. 2. Electrical conductivity of cryolite systems relative to pure cryolite.

at high concentrations in cryolite makes measurements on this system unreliable.

Pearson and Waddington (3), using the data of Batashev (4), found a linear decrease in molar conductance plotted against mole per cent on addition of either sodium fluoride or aluminum fluoride to cryolite. The authors' data and those of Vayna (5) plotted by this method give general confirmation of the linearity of these plots, although the absolute values throughout the system are altered (Fig. 3).

Equivalent conductance vs. mole per cent additive for the system cryolite-sodium fluoride has a slight break in the graph (not shown) at a concentration corresponding to the formula  $\text{NaF} \cdot \text{Na}_3\text{AlF}_6$ . For the system cryolite-aluminum fluoride, the long extrapolation of equivalent conductance gives a value of about  $40 \text{ ohm}^{-1}$  for the hypothetical pure molten aluminum fluoride.

The densities at  $1000^\circ\text{C}$  in the system sodium fluoride-aluminum fluoride show a maximum (Fig. 4) at a composition corresponding approximately to  $\text{NaF} \cdot \text{Na}_3\text{AlF}_6$ , in agreement with the data of Abramov and Kozunov (6) and of Lundina (7). However,

TABLE II. Electrical conductivity of cryolite containing sodium fluoride, aluminum fluoride, alumina, and calcium fluoride

Additive		Specific conductance			Energy of activation of conductance kcal/mole	Conductance $1000^\circ\text{C}$	
wt %	mole %	$1000^\circ\text{C} \text{ ohm}^{-1}\text{cm}^{-1}$	$1040^\circ\text{C} \text{ ohm}^{-1}\text{cm}^{-1}$	$1080^\circ\text{C} \text{ ohm}^{-1}\text{cm}^{-1}$		molar $\text{ohm}^{-1}$	equivalent $\text{ohm}^{-1}$
Cryolite							
0	0	2.79 <sub>9</sub>	2.90 <sub>1</sub>	2.99 <sub>7</sub>	4.48	281	94
Sodium fluoride							
10	35.7	3.12 <sub>2</sub>	3.23 <sub>3</sub>	3.33 <sub>3</sub>	4.30	223	100
16.67	50.0	3.18 <sub>9</sub>	3.30 <sub>1</sub>	3.40 <sub>8</sub>	4.30	191	99
40	76.9	3.85 <sub>5</sub>	3.99 <sub>8</sub>	4.13 <sub>5</sub>	4.30	150	109
100	100.0	5.51 <sub>8</sub>	5.74 <sub>4</sub>	5.95 <sub>3</sub>	4.30	118	118
Aluminum fluoride							
5	11.6	2.67 <sub>7</sub>	2.77 <sub>3</sub>	2.85 <sub>6</sub>	4.19	252	88
8	17.9	2.60 <sub>0</sub>	2.68 <sub>4</sub>	2.76 <sub>2</sub>	4.19	236	84
Alumina							
5	9.7	2.55 <sub>1</sub>	2.63 <sub>8</sub>	2.71 <sub>9</sub>	4.20	247	83
10	17.2	2.32 <sub>7</sub>	2.40 <sub>9</sub>	2.48 <sub>6</sub>	4.20	218	74
Calcium fluoride							
5	12.3	2.73 <sub>5</sub>	2.84 <sub>7</sub>	2.95 <sub>0</sub>	4.69	250	88
10	23.0	2.68 <sub>0</sub>	2.79 <sub>1</sub>	2.89 <sub>7</sub>	4.69	223	83
15	32.3	2.65 <sub>7</sub>	2.76 <sub>6</sub>	2.87 <sub>2</sub>	4.69	203	79
Alumina 5 wt %, 8.4 mole %—calcium fluoride 10 wt %, 22.0 mole %							
15	30.4	2.44 <sub>0</sub>	2.54 <sub>9</sub>	2.65 <sub>3</sub>	4.92	198	66

*Sodium fluoride, aluminum fluoride.*—For the systems cryolite-sodium fluoride and cryolite-aluminum fluoride, conductivity decreases continuously from sodium fluoride through cryolite toward aluminum fluoride. The extreme volatility of aluminum fluoride

Vayna's densities (8) at  $1000^\circ\text{C}$  show a maximum between pure cryolite and  $\text{NaF} \cdot \text{Na}_3\text{AlF}_6$ .

*Alumina.*—The molar conductances measured by Batashev (4), for the system cryolite-alumina, were extrapolated to zero conductivity at pure alumina

when plotted against mole per cent added alumina by Pearson and Waddington (3). The authors' values and Vayna's (5) for molar conductance vs. mole per cent added alumina are shown in Fig. 5 in comparison with these values. The evidence from the present work is that molar conductance falls off

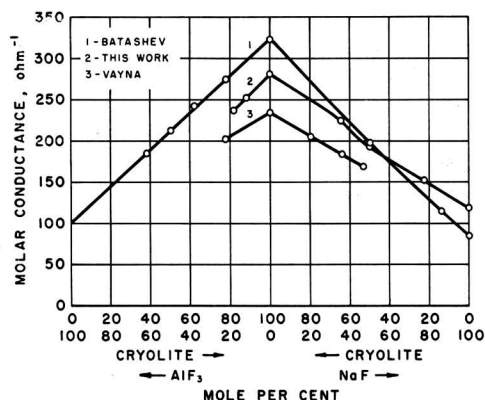


FIG. 3. Molar conductance of cryolite-aluminum fluoride and cryolite-sodium fluoride.

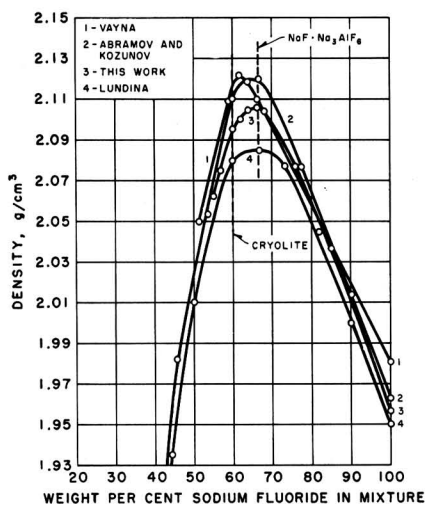


FIG. 4. Density of the system sodium fluoride-aluminum fluoride.

more rapidly than would be anticipated if the alumina were inert in this system.

The density at 1000°C of the cryolite-alumina system (Fig. 6) decreases with the first alumina additions, another indication of an interaction between alumina and cryolite, inasmuch as the density for hypothetical molten alumina at 1000°C would be much greater than that of cryolite. The density of molten alumina near its melting point (2040°C) was

determined as 2.5 g/cm<sup>3</sup> by Wartenberg and co-workers (9).

This system is particularly difficult to measure because of the slow solution of alumina in cryolite

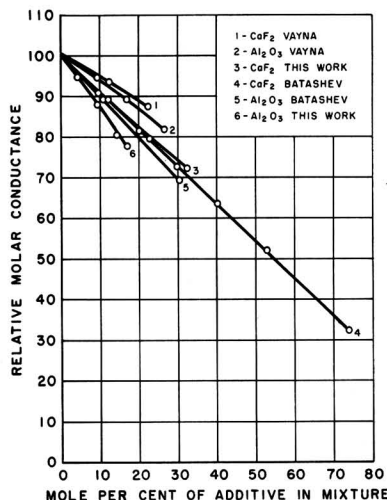


FIG. 5. Molar conductance of cryolite-calcium fluoride and cryolite-alumina relative to pure cryolite.

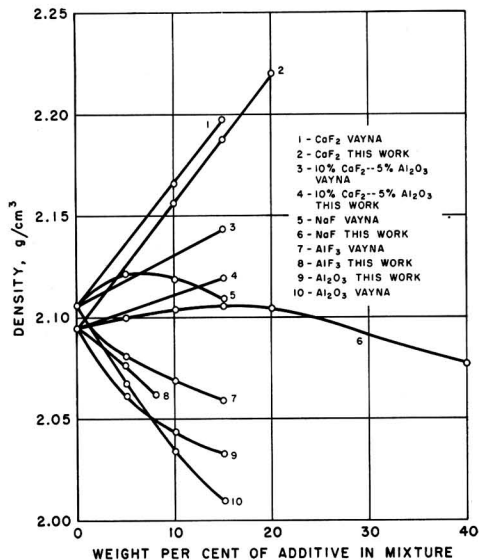


FIG. 6. Density of cryolite with additives

at high alumina concentrations, and the extrapolation of results from low alumina concentrations to pure alumina is subject to inaccuracies.

*Calcium fluoride.*—Pearson and Waddington (3) reported a linear decrease of molar conductance with

mole per cent calcium fluoride for the cryolite-calcium fluoride system. Vayna's (5) data are again in marked disagreement. The authors' values for this system are not quite linear (Fig. 5). Equivalent conductance plotted (not shown) against mole per cent also lacks linearity. The extrapolated equivalent conductance of calcium fluoride is  $50 \text{ ohm}^{-1}$ .

Density of the melt at  $1000^\circ\text{C}$  increases almost linearly with weight per cent added calcium fluoride (Fig. 6) up to 40 per cent, the limit of these measurements, where the value is  $2.333 \text{ g/cm}^3$ . Inasmuch as both the density and conductivity plots (on the equivalence basis) are ideal, it appears that calcium fluoride does not react with cryolite.

*Calculation of ternary mixtures.*—The specific conductance at  $1000^\circ\text{C}$  of a mixture containing 5 per cent alumina and 10 per cent calcium fluoride in cryolite is  $2.44 \text{ ohm}^{-1} \text{ cm}^{-1}$ . It is interesting that this value would be predicted from the curves for the binary mixtures cryolite-alumina and cryolite-calcium fluoride.

#### TEMPERATURE DEPENDENCE OF CONDUCTIVITY

All the conductivity data can be plotted linearly as log equivalent conductance,  $\Lambda$ , against reciprocal absolute temperature,  $T$ , where  $\Lambda = KE/d$ , with  $K$  the specific conductance,  $E$  the equivalent weight (equivalent weight of a mixture is defined in this work as the equivalent weight of pure component  $A$  times the weight per cent of component  $A$  in the mixture, plus the equivalent weight of pure component  $B$  times the weight per cent of component  $B$  in the mixture, etc.), and  $d$ , the density. Values of the activation energy for conductance (10, 11) in kcal/mole, are listed in Table II for sodium fluoride, aluminum fluoride, alumina, and calcium fluoride separately added to cryolite. The activation energy ap-

pears to be consistent within the limits of error at  $4.3 \text{ kcal/mole}$  over the measured range of sodium fluoride, aluminum fluoride, and alumina compositions. With calcium fluoride addition, however, the value increases to  $4.7 \text{ kcal/mole}$ . This increase is in accord with the general rule that energies of activation increase with increased size of the cation. The ternary mixture, 5 per cent alumina, 10 per cent calcium fluoride in cryolite, has a higher activation energy,  $4.9 \text{ kcal/mole}$ , than the binary mixtures.

#### ACKNOWLEDGMENT

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

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# Correlation of Limiting Currents under Free Convection Conditions<sup>1</sup>

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## ABSTRACT

Limiting currents were measured for deposition of copper on plane vertical cathodes from unstirred solutions. Electrolyte composition ranged from 0.01 to 0.7 molal CuSO<sub>4</sub>, 1.38 to 1.57 molal H<sub>2</sub>SO<sub>4</sub>, and 0 to 6.38 molal glycerol. Cathode heights varied from 0.25 to 3.0 in. Limiting current densities were from 0.4 to 108 ma/cm<sup>2</sup>. A general correlation of the data may be represented by the equation:  $Nu' = 0.673 (ScGr)^{1/4}$ , where  $Nu'$ ,  $Sc$ , and  $Gr$  are the mass transfer Nusselt, Schmidt, and Grashof numbers, respectively. This result is in good agreement with that predicted from the boundary layer theory for mass transfer by free convection.

## INTRODUCTION

This paper is concerned with limiting rates of deposition of copper ions at a vertical cathode in an unstirred solution. In such a system, natural convection, or "spontaneous stirring," results from density changes which accompany concentration changes in the region of the electrode. The limiting process is controlled by the maximum rate of mass transfer of copper between bulk solution and the electrode surface. A more detailed discussion of mass transfer phenomena in electrochemical problems has been presented in an earlier paper (1).

Natural convection usually involves laminar motion of the fluid so that the over-all process requires consideration of the simultaneous action of molecular diffusion and convective flow. In steady-state free convection, the main resistance to mass transfer is associated with a relatively small region of fluid in the vicinity of the electrode, and the concentration of the bulk solution remains constant. It is convenient to describe the rate of transfer between any point on the electrode surface and the surrounding solution in terms of a mass transfer coefficient for free convection as given by the relation:

$$(N_D)_x = k_x(C_o - C_i) \quad (I)$$

where:  $(N_D)_x$  = local rate of mass transfer, gram moles/cm<sup>2</sup>-sec;  $k_x$  = local mass transfer coefficient at height  $x$  on the electrode surface; and  $C_o$  and  $C_i$  = concentration of reacting species in bulk solution and at electrode surface, respectively, gram moles/cm<sup>3</sup>.

The total local rate of mass transfer, excluding migration, is determined by the current density:

$$(N_D)_x = \frac{I_x(1-t)}{nF} \quad (II)$$

where:  $I_x$  = current density at height  $x$ ;  $n$  = valence charge of reacting ion;  $F$  = the Faraday; and  $t$  = transference number of reacting ion averaged over the mass transfer path.

To describe the rate of mass transfer per unit area averaged over the entire electrode, an average mass transfer coefficient may be defined by the equation:

$$N_D = k_L(C_o - C_i) = \frac{I(1-t)}{nF} \quad (III)$$

where:  $N_D$  = average mass transfer rate, gram moles/cm<sup>2</sup>-sec;  $k_L$  = average mass transfer coefficient, cm/sec; and  $I$  = average current density, amp/cm<sup>2</sup>, i.e., total current ÷ electrode surface area.

## Limiting Current and Concentration Polarization

The mass transfer coefficient has a value characteristic of the system and current density under consideration, so that the average current density is given by rearrangement of equation (III):

$$I = \frac{nF(C_o - C_i)k_L}{(1-t)} \quad (IV)$$

The theoretical maximum current density is that which would reduce  $C_i$  to zero. This theoretical limiting current density cannot be fully reached in practice because of the development of electrode polarization associated with depletion of the reacting ions in the region of the electrode. This polarization is approximately equal to the emf of a concentration cell formed between two solutions containing the reacting ion at concentrations  $C_o$  and  $C_i$ , respectively. Thus:

$$\Delta E = \frac{RT}{nF} \ln \frac{a_o}{a_i} \approx \frac{RT}{nF} \ln \frac{C_o}{C_i} \quad (V)$$

where  $\Delta E$  = concentration polarization, volts. As the current density is increased toward the theoretical limit, the applied potential must increase as a

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result of the polarization, so that, in general, before the theoretical maximum current can be reached, some competing electrode reaction such as hydrogen evolution occurs. However,  $C_i$  often can be reduced in practice to an essentially negligible value before the onset of a successive reaction. For example, in the deposition of a copper ion at 25°C, a concentration polarization of 0.087 volt will require the ratio  $C_i/C_o$  to be  $10^{-3}$ . In view of the possibility of successive reactions, it is necessary to define the limiting current density as the maximum current density which may be utilized exclusively for the production of a desired electrode reaction.

Equations for prediction of mass transfer coefficients and general correlation of data may be developed by analogy to solutions of the corresponding problem of heat transfer to vertical surfaces by free convection. In another paper (2), the authors have applied the boundary layer equations of Squires (3), as outlined by Eckert (4), to the present mass transfer problem. This procedure leads to the following results in the form of dimensionless groups:

$$(Nu')_x = 0.508Sc^{1/4}(0.952 + Sc)^{-1/4}Gr^{1/4} \quad (VI)$$

where:  $(Nu')_x$  = local Nusselt number for mass transfer;  $Sc$  = Schmidt number; and  $Gr$  = Grashof number.

The Nusselt, Schmidt, and Grashof numbers are given by

$$(Nu')_x = \frac{k_x x X_f}{D} \quad (VII)$$

where:  $k_x$  = mass transfer coefficient at height  $x$ , cm;  $x$  = vertical height on electrode surface, cm;  $D$  = effective diffusion coefficient of cupric ion,  $\text{cm}^2/\text{sec}$ ;  $X_f$  = "film factor" for diffusion of cupric ion analogous to film pressure factor in gases (5, 6), equal to the log mean volume fraction of nondiffusing species in the present case.

$$Sc = \frac{\mu}{\rho D} \quad (VIII)$$

where:  $\mu$  = average liquid viscosity, g/cm-sec, and  $\rho$  = average liquid density, g/cm<sup>3</sup>.

$$Gr_x = \frac{g(\rho_o - \rho_i)\rho^2 x^3}{\rho_i \mu^2} \quad (IX)$$

where:  $\rho_o$  and  $\rho_i$  = fluid densities in bulk solution and at the electrode surface, respectively, g/cm<sup>3</sup>, and  $g$  = acceleration of gravity, cm/sec<sup>2</sup>.

It is convenient to relate the density difference,  $\rho_o - \rho_i$ , to the concentration difference,  $C_o - C_i$ , by the specific densification coefficient,  $\alpha$ , defined by the relation:

$$\alpha = \frac{\rho_o - \rho_i}{\rho_i(C_o - C_i)} \quad (X)$$

The specific densification coefficient does not vary greatly with concentration and, therefore, provides a convenient method for correlation of density data for use in these equations.

At the limiting current, assuming  $C_i$  to be negligible over the entire electrode,  $k_x$  varies inversely as the  $1/4$  power of  $x$ . By integration over the electrode, the average mass transfer coefficient over height 0 to  $x$  can be related to the local value at height  $x$  by the equation:

$$k_L = 4/3k_x \quad (XI)$$

Assuming  $X_f = 1$  and the number 0.952 negligible compared to  $Sc$ , equations (VII), (VIII), and (XI) may be combined to give the general equation for correlation of mass transfer coefficients in liquid systems:

$$Nu' = \frac{k_L x}{D} = 0.677 (Sc Gr)^{1/4} \quad (XII)$$

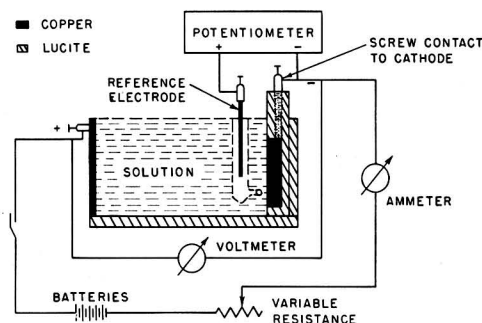


FIG. 1. Cell and circuit diagram

#### APPARATUS AND MATERIALS

The apparatus consisted essentially of an electrolytic cell for copper deposition and auxiliary equipment for measurement of total current and cathode potential relative to the bulk solution in the cell. Fig. 1 is a schematic diagram of the apparatus.

The cell was a rectangular container 7.6-cm wide and 10-cm high, formed of several sections of Lucite so that the distance could be varied between the cathode and anode located at opposite ends. Fig. 2 and 3 illustrate these features. A copper plate formed one of the end walls and served as anode. The copper cathodes were mounted in various Lucite holders as shown in Fig. 4. These holders permitted use of electrodes of four different heights: 0.634 cm, 2.54 cm, 3.75 cm, and 7.6 cm, and facilitated exchange of electrodes for repetition of the experiments. All cathodes were equal in width to the inner dimension of the cell, i.e., 7.6 cm. The sides of the cathodes were insulated with Glyptal lacquer so that only the side facing the anode conducted current. The cathode

circuit was completed by means of a contact screw, as indicated in Fig. 1. A fresh electrode was used for every limiting current determination, each electrode having been abraded and preplated by a standard procedure to assure uniformity of surface properties. Care was taken to obtain smooth alignment of the cathode surface with the vertical cell wall formed by the Lucite holder.

As reference electrode, a copper rod was immersed in a solution of the same composition as the bulk liquid in the cell and connected to the cell through a capillary of  $\frac{1}{2}$ -mm outside diameter, located in the corner of the cell at the centerline of the cathode at a distance of 1 mm from the surface. Data were not corrected for the small error in potential caused by ohmic resistance of the solution between the capillary tip and the electrode.

Potentials between the cathode and the reference electrode, i.e., total cathodic polarization, were measured with a type K-2 potentiometer, and current was measured with a range of calibrated ammeters.

Fifteen different solutions of  $\text{CuSO}_4$  in approximately 1.5M sulfuric acid were investigated.  $\text{CuSO}_4$  concentration varied from about 0.01M to 0.74M, and  $\text{H}_2\text{SO}_4$  varied from 1.38M to 1.57M. The electrolyte composition remained essentially constant in any one experiment. The cell liquid was analyzed frequently during the course of the study;  $\text{Cu}^{++}$  by the iodine-thiosulfate method, and  $\text{SO}_4^-$  by standard gravimetric procedure. C.P. chemicals were used for preparation of all solutions.

#### EXPERIMENTAL PROCEDURE FOR LIMITING CURRENT

The principal limiting current experiments are described below. Certain auxiliary experiments are discussed in a later section.

With the electrodes in place, the cell was filled with liquid to a depth of 10 cm, completely covering the cathode in all cases. Current was then passed through the cell and increased in small increments until the limiting current was attained, and usually increased further to the point of hydrogen evolution. Potential readings and new current settings were made at intervals of approximately 1 minute. These time intervals permitted the current and potential to reach essentially steady-state conditions at each rheostat setting, as demonstrated in preliminary experiments. Current-potential measurements were made with each electrode and electrolyte composition, and repeated three or four times, using freshly prepared cathodes. Reproducibility of successive limiting current determinations was within 1-2 per cent. The limiting current density for each experimental condition was determined by plotting the average current density over the electrode vs. potential, as determined by the reference elec-

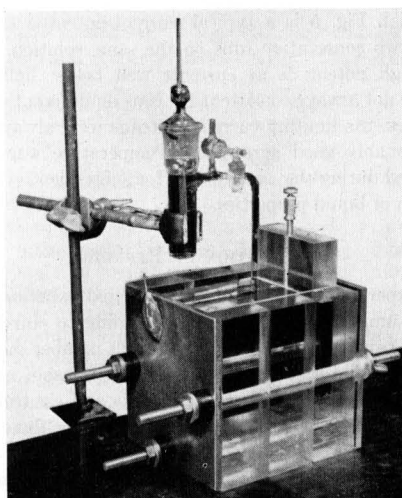


FIG. 2. Assembled cell and reference electrode

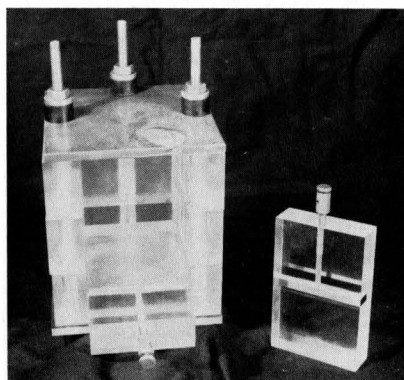


FIG. 3. Cell resting on end, anode at top

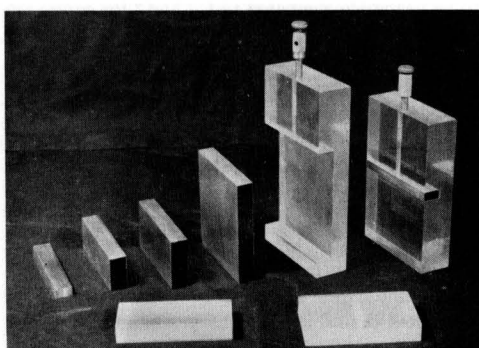


FIG. 4. Various cathodes and holders

trode, and observing the "plateau" where the current density became essentially independent of po-

tential. Fig. 5 is a typical current-potential curve for two consecutive runs on the same solution. Although potentials at currents well below limiting were not always consistent for runs on different electrodes, the limiting current plateaus were always in reasonably good agreement. Temperature was observed during the experiments for subsequent evaluation of liquid properties.

#### CORRELATION OF RESULTS

Experimental data for the principal experiments are summarized in Table I. According to equation (XII) and related theory, the Nusselt number should be a unique function of the Schmidt-Grashof number product for all electrode heights and electrolyte compositions. The procedure for obtaining these dimensionless groups is outlined briefly.

*Mass transfer coefficients.*—Average mass transfer coefficients were calculated by substitution of ex-

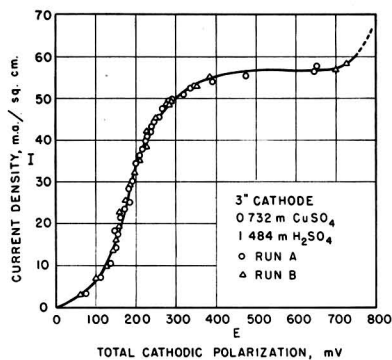


Fig. 5. Typical current potential curve

perimental quantities in equation (III), assuming  $C_i$  to be negligible compared to  $C_o$ , and  $t$  for cupric ion to be zero. Estimates based on ionic mobilities at infinite dilution and corrected for concentration by comparison with similar systems indicated that the average value of  $t$  over the boundary layer probably did not exceed 0.015 for even the most concentrated  $\text{CuSO}_4$  solutions. In absence of a rigorous theory for treating transference over the present concentration profiles further refinement of the analysis did not seem justified.

*Film factor for cupric ion.*—Due to the small volume of the cupric ion, ( $X_f$ ) in equation (VII) was never less than 0.997 for the maximum concentrations and was, therefore, assumed unity in all calculations.

*Diffusion coefficients.*—The effective diffusion coefficient for cupric ion was assumed to be the value for  $\text{CuSO}_4$  since sulfate was the only anion present.

Numerical values were based on the experimental data of Gordon and Cole (7) corrected for temperature, viscosity, and ionic strength of the solution. Hydrogen ion and sulfate ion were assumed to diffuse as sulfuric acid since the cupric ion concentration was relatively small in all cases. Sulfuric acid diffusivities were derived from data of Gordon (8) and Thovert (9), utilizing temperature and viscosity corrections in a similar manner to the procedure for  $\text{CuSO}_4$ . Diffusion coefficients and viscosities entering the final correlation were evaluated at the arithmetic mean composition between the bulk solution and electrode-solution interface. Numerical values are given in Table I.

*Interfacial composition.*—The cathode reaction and migration effects result in a net movement of sulfuric acid toward the interface. Eventually, a steady state is reached in which acid is transported away from the electrode by convective mass transfer at the same rate it is carried toward the electrode. The concentration difference thus developed between the electrode and bulk solution is expressed by the relation:

$$I_{t_{H^+}} = k_{H_2SO_4}(C_i - C_o)_{H_2SO_4} \quad (\text{XIII})$$

where  $t_{H^+}$  = transference number for hydrogen ion, and  $k_{H_2SO_4}$  = mass transfer coefficient for sulfuric acid. According to equation (XII), the mass transfer coefficients for the various species vary as the  $3/4$  power of the respective diffusion constants for any given electrode and solution. Therefore, the mass transfer coefficients for  $\text{H}_2\text{SO}_4$  were calculated from the relation

$$k_{H_2SO_4} = \left[ \frac{D_{H_2SO_4}}{D_{CuSO_4}} \right]^{3/4} \cdot k_{CuSO_4} \quad (\text{XIV})$$

From the known bulk solution sulfuric acid concentration, the electrolyte composition at the interface could be calculated for each experiment. Trial and error procedure was required in the solution of equations (XIII) and (XIV) since the average film composition, and, hence, the diffusion constant, was not known in advance.

*Viscosities.*—Viscosities were measured with an Ostwalt viscosimeter for sulfuric acid and copper sulfate solutions over the range of temperature and composition of interest. Results for pure sulfuric acid solutions were in agreement with the data of Vinal and Craig (10).

*Densities.*—Densities were measured with a special pycnometer of large volume for various solutions covering the range of compositions used in the experiments. A general correlation of  $\alpha$  values for  $\text{CuSO}_4$  and  $\text{H}_2\text{SO}_4$  in water and aqueous glycerol solutions was developed which permitted the calcu-

lation of the density difference between bulk solution and the electrode-solution interface for each

*General correlation.*—Using the mass transfer coefficients and property values developed as discussed

TABLE I. *Experimental data and results for deposition of copper from CuSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> solutions on vertical electrodes*

Run No.	Electrode height, in.	CuSO <sub>4</sub> molarity	H <sub>2</sub> SO <sub>4</sub> molarity	Lim. current density ma/cm <sup>2</sup>	Mass transfer coefficient $\times 10^3$ cm/sec	Temp. °C	Avg. viscosity centipoise	Avg. density g/cm <sup>3</sup>	Avg diffusion coefficient $\times 10^5$ cm <sup>2</sup> /sec	$\Delta C_{H_2SO_4}$ moles/liter	$\rho_0 - \rho_i$ g/cm <sup>3</sup>	$Nu'$	$Sc$	$Gr \times 10^{-6}$
1	0.25	0.01002	1.530	0.602	0.3113	24.7	1.197	1.0898	0.628	0.0031	0.00139	31.43	1749	0.00264
2	0.25	0.0270	1.561	2.12	0.4068	23.7	1.220	1.0919	0.615	0.0083	0.00371	41.94	1817	0.00680
3	0.25	0.0498	1.498	4.20	0.4370	23.0	1.260	1.0933	0.593	0.0153	0.00675	46.72	1943	0.01167
4	0.25	0.0688	1.523	6.44	0.4850	23.7	1.242	1.0924	0.604	0.0209	0.00926	50.91	1882	0.01641
5	0.25	0.0813	1.501	7.67	0.4890	23.7	1.229	1.0918	0.610	0.0247	0.0109	50.82	1845	0.01969
6	0.25	0.0966	1.508	9.63	0.5010	23.7	1.263	1.0968	0.594	0.0301	0.0133	53.47	1939	0.02290
7	0.25	0.189	1.573	20.69	0.5671	23.7	1.300	1.1034	0.580	0.054	0.0248	62.00	2031	0.04078
8	0.25	0.247	1.465	27.55	0.5778	20.5	1.396	1.1056	0.533	0.071	0.0319	68.73	2369	0.04575
9	0.25	0.376	1.450	48.68	0.6710	22.5	1.400	1.1150	0.537	0.103	0.0478	79.25	2338	0.06936
10	0.25	0.467	1.471	66.45	0.7373	22.5	1.438	1.1282	0.525	0.123	0.0594	89.01	2428	0.08345
11	0.25	0.624	1.424	92.44	0.7675	26.0	1.385	1.1328	0.522	0.156	0.0791	88.13	2215	0.1211
12	0.25	0.660	1.502	94.65	0.7435	21.5	1.576	1.1406	0.480	0.160	0.0845	98.21	2578	0.1006
13	0.25	0.732	1.484	108.2	0.7658	23.7	1.559	1.1447	0.490	0.174	0.0938	99.09	2779	0.1151
14	0.25	0.739	1.384	105.3	0.7376	23.7	1.536	1.1397	0.495	0.177	0.0941	94.47	2773	0.1186
15	1.00	0.0113	1.522	0.495	0.2270	22.9	1.218	1.0906	0.613	0.0035	0.00157	94.06	1822	0.1852
16	1.00	0.0270	1.561	1.46	0.2802	24.9	1.186	1.0913	0.635	0.0083	0.00371	112.1	1711	0.4625
17	1.00	0.0498	1.498	2.76	0.2872	21.0	1.317	1.0942	0.536	0.0153	0.00675	129.6	2138	0.6867
18	1.00	0.0813	1.501	5.00	0.3187	20.4	1.320	1.034	0.561	0.0247	0.0109	144.3	2152	1.101
19	1.00	0.189	1.573	13.05	0.3578	20.5	1.392	1.1050	0.536	0.0540	0.0249	169.5	2350	2.295
20	1.00	0.247	1.465	17.58	0.3688	20.1	1.404	1.1058	0.528	0.071	0.0319	177.4	2405	2.910
21	1.00	0.376	1.450	28.8	0.3969	19.4	1.495	1.1168	0.498	0.103	0.0479	202.4	2688	3.924
22	1.00	0.467	1.471	44.9	0.4982	24.0	1.390	1.1272	0.546	0.123	0.0593	231.7	2258	5.733
23	1.00	0.660	1.502	66.3	0.5252	25.0	1.466	1.1375	0.523	0.160	0.0844	255.0	2464	7.437
24	1.00	0.732	1.484	74.65	0.5284	21.3	1.654	1.1465	0.458	0.174	0.0939	293.1	3150	6.597
25	1.50	0.0113	1.522	0.45	0.2063	22.4	1.231	1.0910	0.605	0.0035	0.00137	127.9	1865	0.5839
26	1.50	0.0270	1.561	1.29	0.2476	25.5	1.171	1.0911	0.645	0.0082	0.00371	143.9	1664	1.528
27	1.50	0.0305	1.522	1.53	0.2599	22.0	1.265	1.0920	0.588	0.0094	0.00418	165.8	1970	1.476
28	1.50	0.0498	1.498	2.60	0.2705	22.5	1.276	1.0936	0.584	0.0153	0.00675	173.7	1998	2.351
29	1.50	0.0813	1.501	4.58	0.2919	20.0	1.331	1.0936	0.556	0.0247	0.0109	196.9	2188	3.485
30	1.50	0.189	1.573	12.05	0.3304	20.4	1.395	1.1051	0.535	0.054	0.0249	231.6	2359	7.354
31	1.50	0.247	1.465	16.6	0.3486	22.3	1.345	1.1046	0.557	0.071	0.0319	234.7	2186	10.18
32	1.50	0.376	1.450	26.2	0.3610	20.0	1.474	1.1168	0.506	0.103	0.0478	267.6	2608	12.99
33	1.50	0.467	1.471	39.5	0.4383	22.7	1.432	1.1280	0.527	0.123	0.0594	311.9	2409	17.41
34	1.50	0.660	1.502	49.2	0.3863	19.0	1.700	1.1417	0.441	0.160	0.0846	328.5	3376	17.93
35	1.50	0.732	1.484	66.8	0.4728	23.7	1.558	1.1448	0.490	0.174	0.0937	361.8	2777	23.85
36	3.00	0.0113	1.522	0.397	0.1820	22.3	1.231	1.0909	0.605	0.0035	0.00157	228.7	1865	4.860
37	3.00	0.0270	1.561	1.07	0.2053	24.8	1.190	1.0914	0.633	0.0082	0.00371	246.5	1722	12.31
38	3.00	0.0305	1.522	1.24	0.2107	22.4	1.256	1.0918	0.593	0.0094	0.00418	270.0	1940	12.46
39	3.00	0.0498	1.498	2.09	0.2175	21.2	1.310	1.0942	0.567	0.0153	0.00675	291.5	2117	18.59
40	3.00	0.0813	1.501	3.55	0.2263	20.4	1.320	1.0934	0.561	0.0247	0.0109	306.5	2152	29.48
41	3.00	0.189	1.573	9.91	0.2717	20.4	1.395	1.1051	0.535	0.054	0.0249	385.9	2359	61.22
42	3.00	0.247	1.465	14.05	0.2947	22.1	1.351	1.1048	0.554	0.071	0.0319	404.3	2207	84.03
43	3.00	0.376	1.450	20.7	0.2853	19.0	1.504	1.1171	0.494	0.103	0.0478	438.8	2725	103.9
44	3.00	0.467	1.471	29.7	0.3295	18.0	1.612	1.1308	0.461	0.123	0.0595	543.2	3092	114.9
45	3.00	0.660	1.502	44.1	0.3462	22.8	1.546	1.1396	0.491	0.160	0.0844	535.9	2763	179.7
46	3.00	0.732	1.484	56.6	0.4003	27.2	1.429	1.1422	0.540	0.174	0.0937	563.3	2317	235.1

Note: Transference numbers of H<sup>+</sup> varied from 0.75 to 0.81.

experiment. This procedure is outlined in detail elsewhere (11). Density data based on these  $\alpha$  values are presented in the data tables pertaining to the various experiments.

above, the Nusselt, Schmidt, and Grashof groups were evaluated for each experiment as presented in Table I. Fig. 6 is a log-log plot of the Nusselt group vs. the Schmidt-Grashof product. All of the data

correlate very satisfactorily in the manner indicated by the theory to a straight line corresponding to the equation:

$$Nu' = 0.673(ScGr)^{1/4}. \quad (XV)$$

The constant 0.673 was evaluated by averaging the constants calculated for individual experiments, assuming the Schmidt-Grashof product to enter as the  $1/4$  power. Such close agreement between equation (XV) and equation (XII) is no doubt fortuitous, but, nevertheless, the result appears to be a very encouraging indication of the general validity of the methods employed.

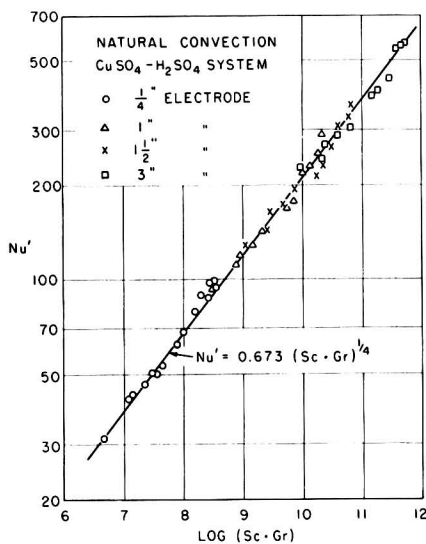


Fig. 6. General correlation of free convection data

## DISCUSSION

### Comparison of Results with other Theories and Experiments

*Diffusion layer theory.*—As originated by Nernst (12), this theory assumes transfer of ions to occur by diffusion through a "diffusion layer" of thickness  $B'$  defined for dilute solutions by the relation:

$$N_D = \frac{C_o - C_i}{B'} D. \quad (XVI)$$

The diffusion layer is thus a hypothetical layer of stagnant fluid by means of which the total rate of mass transfer by all mechanisms acting over the actual mass transfer path may be expressed by an equivalent rate equation for pure diffusion. This concept has been widely used in the chemical engineering literature, with  $B'$  usually designated as the "effective film thickness." From equations (III), (XV), and (XVI), the diffusion layer thickness is given by:

$$B' = 1.48x(ScGr)^{-1/4}. \quad (XVII)$$

Equation (XVII) indicates that  $B'$  is not constant, but varies with electrode height, electrolyte composition, and other factors which influence the Schmidt-Grashof number product. For the experimental results obtained in this study,  $B'$  ranged, in agreement with the theory, from 0.0064 cm to 0.0332 cm. Some authors (13, 14) have recommended use of an average value of 0.05 cm for  $B'$  in unstirred systems, a procedure which is theoretically unsound and which may be very seriously in error, as indicated by the present results.

*Analogy to the Schmidt-Pohlhausen-Beckmann development for heat transfer* (15).—As recommended for electrochemical systems by Agar (16) this theory gives the result:<sup>2</sup>

$$Nu' = 0.525(ScGr)^{1/4}. \quad (XVIII)$$

Although the numerical coefficient in this equation disagrees with that derived from more exact theories and the present experimental result, the essential form of the equation is the same for large values of  $Sc$ . The disagreement is to be expected since the original solution of the differential equations by Pohlhausen was based upon Beckmann's experimental result for heat transfer to air from vertical plates. The numerical coefficient of equation (XVIII) can be considered applicable only to systems with Schmidt or Prandtl numbers of numerical value near to the Prandtl number for air, i.e., about 0.73.

*Equations of Levich.*—Levich (17) has developed an approximate solution to the differential equations for the free convection boundary layer which may be put into the form of equation (XII) as follows:

$$Nu' = 0.51(ScGr)^{1/4}. \quad (XIX)$$

Again, although the exact numerical coefficient differs, this theory leads to an equation of the same general form as those previously described.

*Equations of Wagner.*—A detailed treatment of the free convection problem in relation to electrode processes has been presented by Wagner (18). Wagner uses the method of the boundary layer, assuming that the boundary layers for velocity and for diffusion of the various ionic species do not necessarily coincide. By assuming certain functions for the distribution of velocity and concentration between the electrode and point of maximum velocity, equations are developed to apply specifically to the system  $CuSO_4-H_2SO_4-H_2O$ . This result may be expressed in the following form for comparison with equation (XII):

$$Nu' = 0.805(ScGr)^{1/4}. \quad (XX)$$

<sup>2</sup> Inspection of the equations as presented by ten Bosch indicates that the coefficient of equation (XVIII) should be 0.518.

As a consequence of assuming the boundary layer thickness for diffusion of  $H^+$  to be greater than for diffusion of  $Cu^{++}$ , Wagner obtains an expression for calculation of the density difference between bulk solution and the electrode surface which differs from the result obtained in this paper. Direct comparison of the methods is, therefore, complicated.

When  $\alpha$  may be assumed constant at an average value for each species, equations (IV) and (XIII) to (XV) lead to the following result for the average limiting current density over an electrode of height  $x_0$ :

$$I = \frac{0.673nF\Delta C_0}{x_0(1 - t_{Cu^{++}})} \left[ \frac{gx_0^2 D^2 \Delta C_0 (\alpha_{CuSO_4} - \alpha_{H_2SO_4} t_{H^+} |D_{CuSO_4}/D_{H_2SO_4}|^{3/4})}{\mu^2} \right]^{1/4} \quad (XXI)$$

Equation (XXI) may be compared directly with equation (XLVI) of Wagner's paper. Limiting cur-

TABLE II. Limiting current densities at copper cathodes in 0.1M  $CuSO_4$  + 1.0M  $H_2SO_4$  at 25°C

Electrode height, cm	Average limiting current density, amp/cm <sup>2</sup>			
	Experimental result (18)	Calculated <sup>1</sup> equation (XXI) (physical properties, this study)	Calculated <sup>2</sup> equation (XXI) (physical properties of Wagner)	Calculated, Wagner
1	0.0103	0.0099	0.0083	0.0094
4	0.0067	0.0070	0.0058	0.0066
16	0.0052	0.0050	0.0041	0.0047

<sup>1</sup>  $D_{CuSO_4} = 0.657 \times 10^{-5}$  cm<sup>2</sup>/sec;  $\alpha_{CuSO_4} = 143.6$  cm<sup>3</sup>/mole;  $\alpha_{H_2SO_4} = 51.9$  cm<sup>3</sup>/mole.

<sup>2</sup>  $D_{CuSO_4} = 0.5 \times 10^{-5}$  cm<sup>2</sup>/sec;  $\alpha_{CuSO_4} = 166$  cm<sup>3</sup>/mole;  $\alpha_{H_2SO_4} = 68$  cm<sup>3</sup>/mole.

rent data for deposition of copper from 0.1M  $CuSO_4$  in 1.0M  $H_2SO_4$  are presented by Wagner for three electrodes of heights 1, 4, and 16 cm. These observations are given in Table II, along with values calculated by the method of Wagner, and calculated by equation (XXI) above. Equation (XXI), in conjunction with physical properties evaluated by the correlations developed for this paper, gives a very satisfactory prediction of the measurements, with an average deviation of 3.9 per cent between calculated and observed values. Use of physical properties recommended by Wagner, however, leads to a much less satisfactory result. The principal disagreement with respect to physical data lies in the values of the diffusion coefficient for  $CuSO_4$  and in the densification coefficients for  $CuSO_4$  and  $H_2SO_4$ , as indicated in Table II.

*Equations of Keulegan.*—Keulegan (19) presents the differential equations for motion and diffusion in the boundary layer for mass transfer in a manner similar to that used by Pohlhausen (15) for heat

transfer. An approximate solution is developed by assuming the distribution of velocity and concentration to be arbitrarily selected sine functions of distance through the boundary layer perpendicular to the electrode surface. The resulting solution may be extended into the general form corresponding to equation (XV) as follows:

$$Nu' = 0.628(ScGr)^{1/4} \quad (XXII)$$

Keulegan compares density reductions between bulk solution and the electrode for deposition of copper and nickel, calculated by equations based on this theory, with experimental results determined in freezing experiments by Brenner (18). The agreement obtained between calculation and theory is sufficient to constitute a strong indication of the correctness of the concepts which have been assumed in the boundary layer theory. Keulegan's presentation does not consider effects of migration and resultant increase in concentration of acid at the electrode on the developed density difference between the interface and bulk solution; however, the resultant error is not sufficient to alter the general agreement of the theory with the interpretation of Brenner's experiments.

*Equations of Ostrach for heat transfer.*—An excellent comprehensive treatment of heat transfer by free convection to vertical plates has been presented by Ostrach (19). The convection-diffusion equations are developed to give differential equations of the form used by Pohlhausen. By use of an IBM Card Programmed Electronic Calculator, solutions of these differential equations were obtained for various values of Prandtl number to give useful tabular functions from which Nusselt numbers, temperature, and velocity distributions can easily be obtained. These equations are adaptable to the mass transfer problem by substitution of Schmidt number for Prandtl number. For the average mass transfer Nusselt number over a plate of height  $x_0$ , the result of Ostrach may be expressed as follows:

$$\frac{Nu'}{(Gr)^{1/4}} = 0.943 f(Sc) \quad (XXIII)$$

where  $f(Sc)$  is a function of the Schmidt number, tabulated by Ostrach as the function  $-H'(0)$  of Prandtl number. Equations (VI) and (XI) give:

$$\frac{Nu'}{(Gr)^{1/4}} = \frac{0.677(Sc)^{1/2}}{(0.952 + Sc)^{1/4}} \quad (XXIV)$$

A comparison of numerical values of equations (XXIII) and (XXIV) for various  $Sc$ , using  $f(Sc)$  from the tables of Ostrach, indicates that satisfactory agreement is over the range of Schmidt numbers above 0.73, with the two methods almost coinciding in the region of high Schmidt numbers such

as usually prevails in liquid systems. Both of these methods indicate equations of the simple form of equation (XVIII) to be theoretically inadequate over an extended range of Schmidt numbers for mass transfer or of Prandtl numbers for heat transfer.

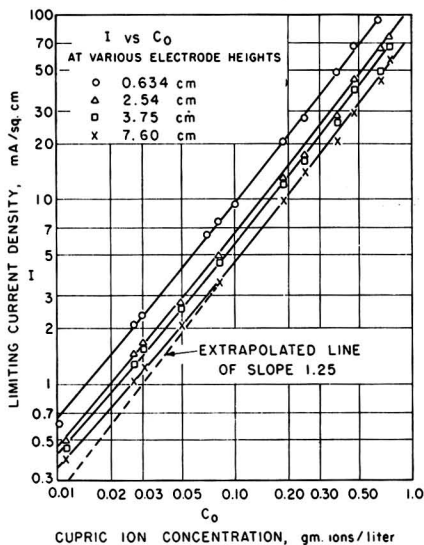


Fig. 7. Variation of limiting current with bulk cupric ion concentration.

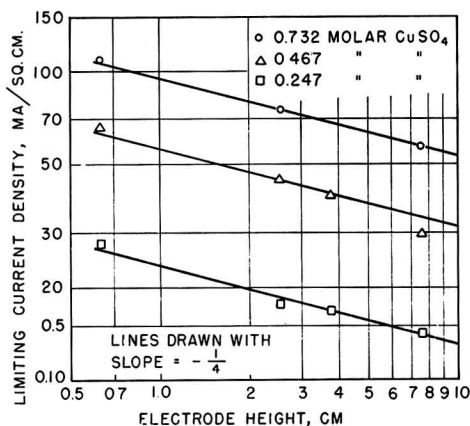


Fig. 8. Effect of electrode height on average limiting current density.

This limitation of equation (XVIII) has apparently been overlooked by ten Bosch, Agar, and others, who have postulated its application for all Prandtl and Schmidt numbers. A detailed discussion of these equations and comparisons with experimental heat transfer data is given by Ostrach.

### Effect of Experimental Variables on Limiting Current Density

**Bulk concentration of reacting species.**—Equation (XXI) indicates the effect of all variables on the limiting current density when  $\alpha$  may be assumed constant. If variation of other properties with electrolyte composition is not significant for a given system, the limiting current density should vary with the  $5/4$  power of the bulk concentration of reacting species. In Fig. 7, limiting current densities for the present experiments are plotted against concentration of cupric ion in the bulk electrolyte. A straight line of slope  $5/4$  passes through the data very well at concentrations greater than  $0.1M$ . However, at lower concentrations, the relationship breaks down, due to failure of the assumption of constancy of  $\alpha$  and other properties. Thus it may be concluded that limiting current density may vary as the  $5/4$  power of concentration in certain cases, but that the rule is not universal.

**Electrode height.**—According to equation (XXI), the average limiting current density over an entire electrode should vary inversely as the  $1/4$  power of total electrode height. This relationship is substantiated in Fig. 8, which is a log-log plot of current density vs. electrode height for three different  $CuSO_4$  concentrations. As a further consequence of this relationship, the total current passing to an electrode increases as the  $3/4$  power of electrode height.

### Effect of Free Convection on Limiting Current Distribution

Equation (XXI) gives the local value of limiting current density at height  $x$  on a given electrode when the total height  $x_0$  in the equation is replaced by local height  $x$  and the numerical constant is reduced to 0.508. According to this result, the local current density varies inversely as the  $1/4$  power of distance from the bottom of the electrode. This effect has been demonstrated by Wagner (18), who measured the current distribution for deposition of copper. Fig. 9 shows the theoretical current distribution for one of the present experiments. To investigate the extent of nonuniformity of current distribution at current densities below the limiting value, two experiments were conducted in which copper was deposited at a steady state rate of  $19.5 \text{ ma/cm}^2$  on an electrode of  $7.6 \text{ cm}$  height. After a given run, the fresh metal deposit was stripped off, and its weight per  $1 \text{ cm}^2$  measured as a function of position on the electrode. This, in turn, permitted the calculation of local current density. At heights above  $2 \text{ cm}$ , the current distribution was fairly uniform. At lower heights, a significant distortion of current distribution is evident, indicating that the effect of free con-



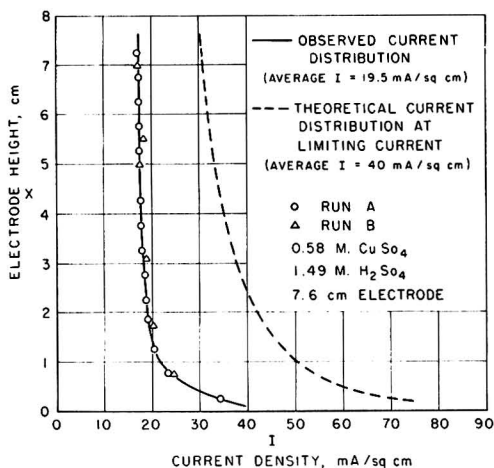


FIG. 9. Current distribution in free convection

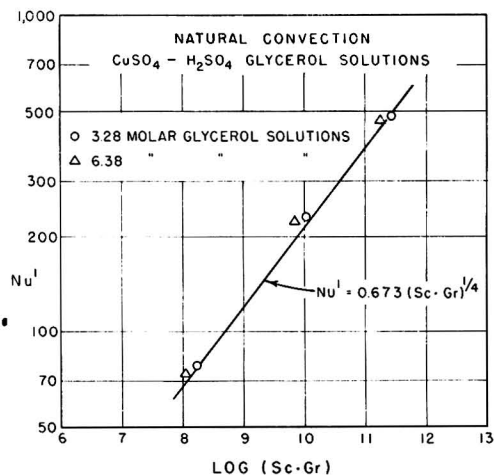


FIG 10. Comparison of data for glycerol solutions with general correlation.

SPECIAL EXPERIMENTS

In order to illustrate certain additional features of the problem and to test further the general application of the correlation a number of special experiments were conducted as follows.

Copper Deposition from Aqueous Glycerol Solutions

In order to obtain a greater variation in properties of the electrolyte, particularly a variation in viscosity and diffusion coefficient, various H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O solutions were prepared containing glycerol in amounts ranging from 3.28 to 6.38 moles/liter. This increased the viscosity of the liquid and reduced the diffusion constant, respectively, by a factor of ten. Limiting current data were obtained for 1/4-in., 1-in., and 3-in. electrodes in the manner previously described. Table III presents the experimental results. Fig. 10 shows the comparison of Nu' as a function of ScGr for these solutions with the line obtained in the general correlation, Fig. 6. This agreement is believed to be very satisfactory and an encouraging indication of the general validity of the correlation.

Study of Full-End Electrodes

In the preceding experiments, the electrodes were placed in Lucite holders and centered approximately midway between the floor of the cell and upper surface of the electrolyte. It seemed desirable, therefore, to study an electrode extending over the entire end-wall of the cell, since this arrangement represents the opposite extreme in cell geometry. Accordingly, the entire Lucite end of the cell was replaced by a copper plate which served as the cathode. Limiting current measurements were made with liquid filling the cell at various levels from 2.5 cm to 10.0 cm. Experimental results are compared with the general correlation in Fig. 11. Although the best line through the data might be placed a few per cent below th-

TABLE III. Data and results for copper deposition from CuSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub>-glycerol solutions on vertical electrodes

Run No.	Electrode height, in.	CuSO <sub>4</sub> molarity	H <sub>2</sub> SO <sub>4</sub> molarity	Glycerol molarity	Lim. C.D. ma/cm <sup>2</sup>	Mass transfer coeff. X 10 <sup>3</sup>	Temp. °C	Avg viscosity centipoise	Avg density g/cm <sup>3</sup>	Avg diffusion coeff. X 10 <sup>5</sup> cm <sup>2</sup> /sec	ΔCH <sub>2</sub> O <sub>2</sub> moles/l	ρ <sub>0</sub> - ρ <sub>i</sub> g/cm <sup>3</sup>	Nu'	Sc	Gr X 10 <sup>-6</sup>
47	0.25	0.3679	0.751	6.38	9.32	0.1313	23.4	10.02	1.1983	0.113	0.153	0.0472	73.67	73,976	0.001437
48	0.25	0.5702	1.145	3.28	35.5	0.3226	22.5	4.254	1.1755	0.264	0.204	0.0719	77.47	13,708	0.01204
49	1.00	0.3679	0.751	6.38	7.12	0.1003	23.5	9.991	1.1983	0.114	0.153	0.0472	224.4	73,784	0.09284
50	1.00	0.5702	1.145	3.28	25.5	0.2317	21.5	4.392	1.1762	0.255	0.204	0.0719	230.8	14,643	0.7272
51	3.00	0.3679	0.751	6.38	4.58	0.0645	22.1	10.596	1.1992	0.106	0.153	0.0472	462.5	83,357	2.215
52	3.00	0.5702	1.145	3.28	18.65	0.1695	22.9	4.197	1.1752	0.268	0.204	0.0719	480.6	13,326	21.29

<sup>1</sup> Measured in diaphragm cell (23).

vection persists at current densities well below limiting in these systems.

line based on Fig. 6, the deviation is not very significant. It may, therefore, be concluded that the posi-

tion of the electrode with respect to the floor of the cell or with respect to the liquid surface is relatively unimportant insofar as limiting current is concerned.

#### Position of Electrode Relative to Floor of Cell

To observe further the effect of variation in electrode location, additional experiments were conducted with two electrodes 0.634 and 2.54 cm in height, respectively. In a series of runs, these electrodes were each placed at distances of 0, 1.3, 3.2,

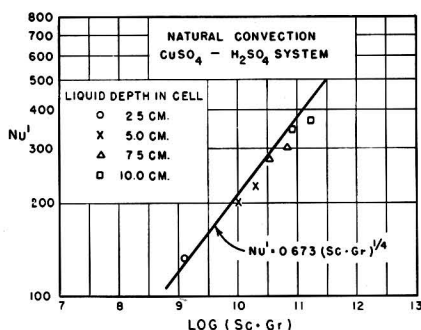


FIG. 11. Data for full-end electrodes

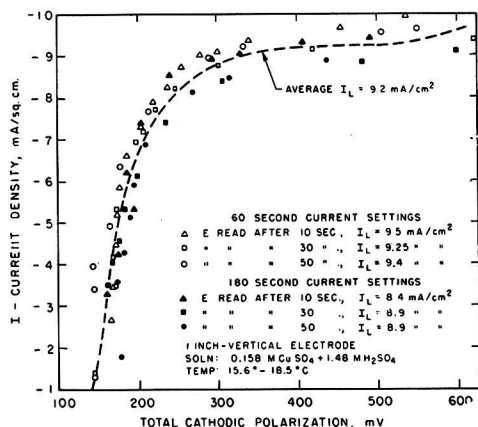


FIG. 12. Effect of time intervals between current settings and potential reading and between successive current settings upon the limiting current.

and 5.7 cm from the cell floor with the cell filled to a depth of 7.6 cm. Several solutions ranging from 0.042 to 0.732 in  $\text{CuSO}_4$  molarity were used in these tests. For a given electrode and solution, variations in the observed limiting currents from the average for the series never exceeded 1.5 per cent over the range of electrode positions.

#### Effect of Window Baffles between Anode and Cathode

In the majority of experiments, the electrolyte between anode and cathode presented a larger cross

section perpendicular to the direction of current flow than did the cathode. Under these conditions, some nonuniformity of current distribution might be expected, particularly at the upper and lower edges of the cathode. To determine the extent to which such nonuniformity of current density might affect the limiting current data, several experiments were conducted using specially designed window-type Lucite baffles placed parallel to and near to the cathode. Two parallel baffles were used with windows of the same size as the electrode and located at the same elevation. Limiting current data were obtained for a 1-in. cathode at various elevations in the cell filled to a depth of 7.6 cm, with the baffles placed at distances of  $\frac{1}{4}$  in. and 1 in., respectively, from the electrode. Limiting current results obtained with and without baffles were identical within limits of experimental accuracy.

#### Variation in Technique of Obtaining Current-Potential Curves

In order to establish the validity of the experimental techniques which was finally adopted, various ways of obtaining current-potential curves were studied. The objective of these studies was to determine any effect on the limiting current of altering the time intervals between successive current settings, and of altering the time at which the potential was measured following a given current setting. In one series of experiments, the time of electrolysis at each current setting was held constant at 60 seconds, and potentials were measured following each current setting at intervals of 10, 30, and 50 seconds, respectively, in successive runs. In another series of runs, the electrolysis time was held at 180 seconds between current settings, and the potentials were measured at the same intervals as in the preceding series. The data for these runs, giving six different current-potential curves for identical electrolyte compositions and electrodes, are shown in Fig. 12. The maximum deviation of the limiting currents from the average value of 9.22  $\text{ma/cm}^2$  is 3.2 per cent. Irreproducibility of polarization of copper cathodes should be expected in view of results of other studies (22). However, the limiting current density appears to be independent of the initial shape of the current-potential curve, in agreement with the concept of mass transfer being the controlling process at the limiting current point.

#### ACKNOWLEDGMENT

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

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# Thermodynamics of the Acid Weston Cell and the Acid Clark Cell<sup>1</sup>

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## ABSTRACT

The dependence of the potential of the saturated Weston cell on the concentration of sulfuric acid is calculated thermodynamically in satisfactory accord with experimental results. In the case of the Clark cell, the observed dependence of the potential on the concentration of sulfuric acid is somewhat greater than the calculated value. A modified acid Weston cell is suggested in order to eliminate the dependence of the potential on acid concentration.

### THERMODYNAMICS OF THE ACID WESTON CELL

Most Weston cells are prepared with a small amount of sulfuric acid in order to prevent hydrolysis of mercurous sulfate (1). Presence of sulfuric acid lowers the electromotive force. According to Obata (2), the electromotive force  $E$  of a Weston cell saturated with  $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$  decreases linearly with the concentration of sulfuric acid according to the empirical equation

$$\delta E / \delta c = -0.855 \cdot 10^{-3} \text{ volt / (equivalent } \text{H}_2\text{SO}_4 \text{ / liter)} \quad (\text{I})$$

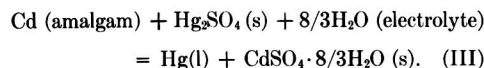
where  $c$  is the concentration of  $\text{H}_2\text{SO}_4$  in equivalents per liter. Measurements made by Vosburgh (3) confirm equation (I). Ishibashi and Ishizaki (4) have obtained the slightly different relation

$$\delta E / \delta c = -0.833 \cdot 10^{-3} \text{ volt / (equivalent } \text{H}_2\text{SO}_4 \text{ / liter)}. \quad (\text{II})$$

The dependence of the electromotive force on the concentration of sulfuric acid may be derived from thermodynamic considerations as is shown in the following:

The virtual cell reaction for passing two faradays ( $=2\mathbf{F}$ ) across the Weston cell

$\text{Cd amalgam} \mid \text{electrolyte saturated with } \text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}, \text{Hg}_2\text{SO}_4 \mid \text{Hg}$  may be written as



Hence the electromotive force  $E$  equals

$$E = -[\mathbf{F}_{\text{Hg}} + \mathbf{F}_{\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}} - \mathbf{F}_{\text{Cd}} - \mathbf{F}_{\text{Hg}_2\text{SO}_4} - (8/3)\mathbf{F}_{\text{H}_2\text{O}}] / 2\mathbf{F} \quad (\text{IV})$$

where the molar free energies of liquid mercury and  $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O} (\text{s})$  and the partial molar free energies of Cd and  $\text{H}_2\text{O}$  are denoted by  $F$  and  $\bar{F}$  with the corresponding subscripts, respectively. Addition of

$\text{H}_2\text{SO}_4$  to the electrolyte decreases  $\bar{F}_{\text{H}_2\text{O}}$  and thus, according to equation (IV), also decreases the potential  $E$ .

The components of the electrolyte,  $\text{H}_2\text{O}$ ,  $\text{CdSO}_4$ , and  $\text{H}_2\text{SO}_4$ , will be denoted as 1, 2, and 3, and their numbers of moles by  $n_1$ ,  $n_2$ , and  $n_3$ , respectively. Presence of  $\text{Hg}_2\text{SO}_4$  in the electrolyte is disregarded, since its concentration is relatively low. The Gibbs-Duhem equation reads

$$[n_1 d\bar{F}_1 + n_2 d\bar{F}_2 + n_3 d\bar{F}_3 = 0]_{P,T}. \quad (\text{V})$$

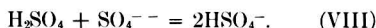
If the solution is saturated with  $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$  the sum  $\bar{F}_2 + (8/3)\bar{F}_1$  is constant, i.e.,

$$[d\bar{F}_2 + (8/3)d\bar{F}_1 = 0]_{P,T}. \quad (\text{VI})$$

Upon combining equations (V) and (VI), it follows that

$$d\bar{F}_1 = - \frac{n_3/n_1}{1 - (8/3)(n_2/n_1)} d\bar{F}_3. \quad (\text{VII})$$

If  $\text{H}_2\text{SO}_4$  is added to the electrolyte, the following reaction takes place



In view of the large excess of cadmium sulfate in the saturated solution, the activity of  $\text{SO}_4^{--}$  and the activity coefficient of  $\text{HSO}_4^-$  are virtually constant for small additions of  $\text{H}_2\text{SO}_4$ . Consequently, the activity of  $\text{H}_2\text{SO}_4$  is essentially proportional to the square of its concentration. Thus, if  $n_3 \ll n_1$ ,

$$d\bar{F}_3 = 2RT d \ln (n_3/n_1). \quad (\text{IX})$$

Substitution of equation (IX) in equation (VII) yields

$$d\bar{F}_1 = - \frac{2RT d(n_3/n_1)}{1 - (8/3)(n_2/n_1)}. \quad (\text{X})$$

Upon combining equations (IV) and (X), it follows that

$$dE = - \frac{8}{3} \frac{RT/\mathbf{F}}{1 - (8/3)(n_2/n_1)} \frac{dn_3}{n_1}. \quad (\text{XI})$$

<sup>1</sup> Manuscript received January 7, 1953.

According to Hulett (5) and Cohen and Sinnige (6) one liter of a solution saturated with  $\text{CdSO}_4 \cdot 8/3 \text{H}_2\text{O}$  at  $25^\circ\text{C}$  contains 3.36 mole  $\text{CdSO}_4$  and 50.8 mole  $\text{H}_2\text{O}$ . Hence

$$\frac{n_3}{n_1 - (8/3)n_2} = \frac{\frac{1}{2}c}{50.8 - (8/3)3.36} = 0.0120c \quad (\text{XII})$$

where  $c$  is the concentration of  $\text{H}_2\text{SO}_4$  in equivalents per liter.

Substitution of equation (XII) in equation (XI) yields for  $25^\circ\text{C}$

$$(\delta E/\delta c)_{c=0} = -0.82 \cdot 10^{-3} \text{ volt/} \\ (\text{equivalent } \text{H}_2\text{SO}_4/\text{liter}) \quad (\text{XIII})$$

in close accordance with equations (I) and (II).

Uhlig (7) has pointed out that a cadmium amalgam electrode reacts with acid,  $\text{Cd} + 2\text{H}^+ = \text{Cd}^{++} + \text{H}_2$ , and thus the potential of a cadmium electrode is slightly more noble than the true equilibrium potential. This effect increases with increasing acid concentration but is only of the order of a microvolt and therefore insignificant in comparison to the shift of the equilibrium potential calculated in equation (XIII).

#### THERMODYNAMICS OF THE ACID CLARK CELL

The effect of sulfuric acid on the electromotive force of the Clark cell

$\text{Zn}$  amalgam | electrolyte saturated with  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{Hg}_2\text{SO}_4$  |  $\text{Hg}$  may be calculated in a similar way. Since the solid salt contains 7 moles  $\text{H}_2\text{O}$  per mole  $\text{ZnSO}_4$ , the analogue to equation (XI) is

$$dE = - \frac{7RT/F}{1 - 7(n_4/n_1)} \frac{dn_3}{n_1} \quad (\text{XIV})$$

where  $(n_4/n_1)$  is the molar ratio of  $\text{ZnSO}_4$  and  $\text{H}_2\text{O}$  in the electrolyte.

According to Hulett (5), a solution saturated with  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  at  $25^\circ\text{C}$  contains 3.36 mole  $\text{ZnSO}_4$  and 52.7 mole  $\text{H}_2\text{O}$ . Hence,

$$\frac{n_3}{n_1 - 7n_4} = \frac{\frac{1}{2}c}{52.7 - 7 \times 3.36} = 0.0171c. \quad (\text{XV})$$

Substitution of equation (XV) in equation (XIV) yields for  $25^\circ\text{C}$

$$\delta E/\delta c \\ = -3.1 \cdot 10^{-3} \text{ volt/}(\text{equivalent } \text{H}_2\text{SO}_4/\text{liter}) \quad (\text{XVI})$$

whereas Hulett (5) found experimentally

$$\delta E/\delta c \\ = -4.1 \cdot 10^{-3} \text{ volt/}(\text{equivalent } \text{H}_2\text{SO}_4/\text{liter}). \quad (\text{XVII})$$

The difference between the calculated and the experimental value may be due to the reaction between

zinc amalgam and acid, whereby the potential of the zinc amalgam electrode is shifted to a slightly more noble potential (8). For the Clark cell this effect is far more significant than for the Weston cell since the single electrode potential of a zinc amalgam electrode is 0.4 volt less noble than that of a cadmium amalgam electrode and, accordingly, the rate of hydrogen evolution and dissolution of metal is about 1000 times greater.

#### SUGGESTION OF A MODIFIED ACID WESTON CELL

At either side of the saturated Weston cell there are four phases, viz., two metallic phases, solid  $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ , and aqueous solution at the negative electrode; and liquid mercury, solid  $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ , solid  $\text{Hg}_2\text{SO}_4$ , and aqueous solution at the positive electrode. In the acid Weston cell there are five components, e.g.,  $\text{Hg}$ ,  $\text{Cd}$ ,  $\text{CdSO}_4$ ,  $\text{H}_2\text{O}$ , and  $\text{H}_2\text{SO}_4$ . Hence, applying the Gibbs phase rule to either half cell (9, 10), there are three degrees of freedom, e.g., temperature, pressure, and the activity of sulfuric acid.

To obtain the greatest possible stability of the potential at a given temperature, it seems desirable to reduce the number of degrees of freedom to two so that the electromotive force is determined by only two independent variables, i.e., temperature and pressure. To this end, one may add  $\text{K}_2\text{SO}_4$  as a new component and two other phases, e.g., the solid salt  $3\text{CdSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$  described by Benrath and Thönnessen (11) and a solid acid potassium sulfate, possibly  $\text{KHSO}_4$ . Cells of this type although without  $\text{KHSO}_4$  have been investigated by Vosburgh, Derr, Cooper, and Pettengill (12). Eventually, however, the rather high hydrogen concentration in cells involving solid  $\text{KHSO}_4$  may cause too high a rate of hydrogen evolution at the cadmium amalgam electrode, which is undesirable in the first place because of an irreversible potential change according to Uhlig (7), and in the second place because of the dependence of the potential on total pressure. According to Cohen and Sinnige (6) the potential of the saturated Weston cell increases by 6 microvolts when the pressure is increased by one atmosphere.

As an alternative possibility for reducing the number of degrees of freedom, one may add an organic acid as a new component and two other phases, e.g., solid acid  $\text{HX}$  and solid salt  $\text{CdX}_2$  or its hydrate. Eventually, 1- or 2-naphthalenesulfonic acid may be suitable, but at the present no definite proposal can be made.

#### ACKNOWLEDGMENT

The author is indebted to Dr. H. H. Uhlig for stimulating discussions.

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

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## Iron Contamination of Storage Batteries<sup>1</sup>

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### INTRODUCTION

Small amounts of iron are present in all lead-acid storage batteries. The raw materials usually contain iron, and the manufacturing is carried out in iron equipment. The amount of iron present in the battery is usually estimated by analyzing the electrolyte, and the amount so found is usually less than 0.01 per cent.

The exact amount which a battery can tolerate without damage has not been accurately determined. Gillette (1) found that when 0.01 per cent was added to the electrolyte, there was no perceptible influence, but that 0.10 per cent caused a high rate of self-discharge. Vinal (2) found that there was a perceptible influence on self-discharge when 0.012 per cent was added to the electrolyte.

Vinal's tests were carried out under rather special conditions. He used single plates, suspended them in a large excess of acid, and followed changes by weighing the plates while suspended in the acid.

In view of the limited nature of this information, it was decided to redetermine the effect of iron under conditions which more closely conform to actual battery practice.

### EXPERIMENTAL

For this test, a series of 67 test batteries was prepared. These were standard 100-amp-hr, 15-plate, six-volt automobile units prepared from commercial materials. The separators were a commercial type, consisting of a polystyrene bonded diatomaceous earth, supported on a glass mat and having a conventional ribbed surface and a glass mat facing the positive plates. After the first charge, usually described as the formation, the cells were drained, rinsed with a solution of reagent grade sulfuric acid to remove most of the dissolved iron, and then filled with reagent grade acid which had been adjusted to a specific gravity of 1.270. They were then charged to secure thorough mixing of the acid, and the iron

content of the electrolyte determined. This averaged 0.007 per cent on several typical cells.

Ferrous sulfate was then added to some of the cells in accurately measured amount to adjust the iron content of the electrolyte to the desired value. Thirteen batteries of each of five iron contents were prepared.

Duplicate batteries were then given each of the customary performance tests according to the specifications of the Society of Automotive Engineers as published in 1952 (3). Three different laboratories carried out the tests, using either four or five batteries of each of the five iron contents.

### RESULTS

The averaged results are summarized in Table I for three significant iron contents. In general, iron affected the performance in two ways. Most obviously, it shortened the battery life when the battery was given repeated cycles of charge and discharge. At 0.1 per cent by weight of added iron, the life was seriously reduced.

The rate of self-discharge was also affected by iron content. At 0.1 per cent added iron, the rate of self-discharge was measurably greater than that of a battery with no added iron. When the self-discharge was measured in terms of a loss of specific gravity, 0.1 per cent iron increased the loss 1.5 times. When the residual capacity was measured, the loss was only 1.15 times.

Where less than 0.1 per cent of iron was added to the electrolyte, no definite harmful effects were observed. Tests were run at 0.00, 0.012, 0.020, 0.030, and 0.100 per cent iron. The results of the first four iron contents are substantially identical, so that of these only the 0.00 and 0.030 per cent results are tabulated. Although it appears that there is some effect at the latter level, the differences are within the expected variation of experimental results and are not considered significant.

<sup>1</sup> Manuscript received February 24, 1953.

TABLE I. *Effect of iron*

Iron content, % of electrolyte*	0.000	0.030	0.100
Self-discharge—28-day loss in sp gr @ 80°F			
Laboratory A	0.033	0.032	0.053
Laboratory B	0.041	0.046	0.057
Laboratory C (% residual capacity)	70	72	66
20-hr capacity, amp hr @ 5 amp @ 80°F			
Laboratory A	103.8	100.7	96.5
Laboratory B	100.6	99.4	96.6
Laboratory C	101	100.0	95.0
SAE life, cycles, 4 charge-discharge cycles per day			
Laboratory A	—	—	—
Laboratory B	360	360	214
Laboratory C	453	417	123
Overcharge life, weeks @ 9 amp			
Laboratory A	8	8	7
Laboratory B	6	6	6
Laboratory C	6	7	7
Cold test capacity, min at 300 amp			
Laboratory A	4.41	3.93	3.67
Laboratory B	3.8	3.40	3.70
Laboratory C	3.58	3.55	3.63
5-sec voltage, at start of cold test			
Laboratory A	4.38	4.44	4.39
Laboratory B	4.48	4.41	4.40
Laboratory C	4.38	4.32	4.22
End of charge volts			
Laboratory A	7.53	7.53	7.56
Laboratory B	—	—	—
Laboratory C	7.36	7.30	7.25

\* Grams Fe per 100 g electrolyte. Added as an equivalent amount of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .

TABLE II. *Iron summary as percentage of electrolyte*

Added to acid	0.000	0.030	0.100
Total in cell	0.007	0.037	0.107
Found in acid			
Found—after 3 cycles	0.009	0.025	0.130
after 60 days stand	0.007	0.018	0.045
after cycle life test	0.006	0.021	0.077
after overcharge life test	0.004	0.007	0.034
Found in lead peroxide after overcharge life test			
(Calculation to % in acid)	—	0.030	—

### Iron Analyses

Although carefully weighed amounts of ferrous sulfate were added to the test batteries, analysis of the electrolyte for iron gave low results. The missing iron was found in the lead peroxide upon dismantling

the test cells. The results are summarized in Table II.

### DISCUSSION

Two aspects of the action of iron are important. First, there is the practical matter of the iron tolerance of a battery; and second, there is the technical question of why iron affects battery performance.

The mechanism of the action of iron in the storage battery can be discussed only briefly. Vinal has shown that iron is oxidized at the positive plate to the ferric state, and this diffuses to the negative plate where it is reduced and returned to the positive plate. The net result is a transfer of an electrical charge between the plates without the passage of an external current, and constitutes self-discharge. On this basis, the contribution of iron to self-discharge should be proportional to the iron content of the electrolyte.

The appearance of iron in the positive active material is certainly evidence that ferric iron is dissolved in, or is adsorbed by, lead peroxide.

The effect on SAE life is interesting since, in this test, life is limited by the shedding, or sloughing off, of the positive active material. During periodic charge-discharge cycles, the lead peroxide is converted to crystalline lead sulfate and back to lead peroxide repeatedly. During this process, the active material gradually softens, and finally drops to the bottom of the battery as a finely divided lead peroxide sediment. Since iron accelerates this process considerably, it seems probable that iron is adsorbed on the peroxide crystals, and prevents fresh peroxide formed during charge from attaching itself firmly to the underlying lead peroxide.

The effect of large amounts of iron on the 20-hr rate capacity can be explained by the same mechanism. This test capacity is usually limited by the rate at which acid can reach the interior of the positive plate. Since iron reduces the capacity, it probably influences the plate structure to retard diffusion. In view of the structural differences postulated in connection with the SAE cycling life test, it is anticipated that iron would gradually reduce the capacity measured at the 20-hr rate.

The test data are not sufficiently precise to establish this gradual deterioration of capacity, but they are at least suggestive of such a deterioration.

On the basis of the above tests, it is concluded that iron is harmless to the automobile battery when 0.037 per cent is present initially in the electrolyte, but that 0.10 per cent is somewhat harmful. Further, it is concluded that an analysis of the electrolyte is not a reliable method of measuring the iron content of the battery since part of the iron is removed from



the electrolyte by the lead peroxide of the positive plate.

To avoid uncertainty, it appears desirable to consider the total iron content of the cell, that is, both the electrolyte iron and the iron in the lead peroxide. The above results can be expressed by saying that the battery can tolerate a total iron content equal to 0.037 per cent of the weight of acid, but to test the cell it is necessary to analyze both acid and lead peroxide.

This conclusion is based on the standard bench testing of automotive batteries only. It manifestly

cannot be applied to specialty batteries, or special service conditions, such as calcium alloy telephone batteries where self-discharge offers a different kind of problem, or industrial truck batteries where shedding rates must be controlled more carefully than in automobile batteries.

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# FUTURE MEETINGS OF The Electrochemical Society



Chicago, May 2, 3, 4, 5, and 6, 1954

Sessions on

Electric Insulation, Electronics, Electro-Organic  
Chemistry, Industrial Electrolytics, Theoretical  
Electrochemistry

Headquarters at the La Salle Hotel

★ ★ ★

Boston, October 3, 4, 5, 6, and 7, 1954

Headquarters at the Statler Hotel

★ ★ ★

Cincinnati, May 2, 3, 4, and 5, 1955

Headquarters at the Sheraton-Gibson Hotel

★ ★ ★

Pittsburgh, October 9, 10, 11, 12, and 13, 1955

Headquarters at the William Penn Hotel

Papers are now being accepted for the meeting to be held in Chicago. Five copies of each abstract (not exceeding 75 words in length) are due at the Secretary's Office, 216 West 102nd Street, New York 25, N. Y., *not later than January 15, 1954*. Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at the same address.



## On the Electrochemistry of Ion-Exchange Resins

### A Review of Recent Work

K. S. Spiegler<sup>1</sup>

#### ABSTRACT

Electrochemical properties of ion-exchange resins such as specific conductances, ionic mobilities in the resins, and potentials across resinous membranes have been measured recently. A review of these measurements and their correlation to the general thermodynamic treatment of ion-exchange resins is presented. Applications such as the use of resinous membranes as ionic sieves, electrolytic regeneration of ion-exchange resins, and the use of ion-exchange resins as media for electrophoretic separations are discussed.

#### Introduction

Synthetic ion-exchange resins have been known for about 15 years and, apart from their use in a great variety of applications, several points of theoretical interest such as adsorption isotherms and exchange kinetics have been investigated. While the electrochemical properties of natural ion-exchange materials and different synthetic materials of low capacity had been investigated previously, the study of the electrochemistry of the synthetic resins and the correlation of the data to the resin equilibria have developed only during the last few years. These studies are reviewed here. Ionic migration in the resins proper is discussed first, followed by the electrochemistry of systems containing both resins and solutions.

The methods used so far in these studies are very similar to those used in previous researches dealing with other materials. Thus, ion-exchange membrane potentials have been measured by standard methods as applied previously to collodion-base membranes, and the conductance of ion-exchange resins was determined in cells like those used for aqueous solutions. To interpret their results, investigators have drawn extensively on well-known theories such as Kohlrausch-Weber's equations of electromigration and the Gibbs-Donnan theory of membrane equilibria. However, as the exchange-resins are solid in the gross physical sense and yet act in almost all other respects like solutions of electrolytes, the results are of a particular nature and point to interesting future applications.

The results of these investigations confirmed the structural model of ion-exchange resins (1, 2). They are solid poly-electrolytes consisting of a hydrocarbon crosslinked skeleton to which polar groups are attached. Thus the motion of one charge type of ion is restricted. In nuclear sulfonic cation-exchange resins, such as Dowex-50, the bound groups are the  $-\text{SO}_3^-$  anions. The counter-ions, in this case cations, may be considered dissociated from this skeleton—similar to the dissociation of an ionized salt in concentrated solution. Because of electrostatic attraction, the small cations remain in the vicinity of the polyanion and can move into water or a

solution only to the extent determined by the relation between their thermal energy to electrostatic attraction. They can, however, move freely inside the resin. In other words, the resin may be visualized as an anionic sponge filled with cations, the latter being replaceable by a mechanism similar to musical chairs (3).

If an electrical field is applied to a cation-exchange resin, one would expect the mobile cations to migrate in the direction of the current, while the anions are immobile, since they are bound to the hydrocarbon skeleton. Similarly, in an anion-exchange resin, the current should be carried by the mobile anions. This conclusion is indeed borne out by experiments.

#### Conductance of Exchange Resins

Measurements of the specific conductance of resin plugs were made by packing the wet, granular materials between electrodes connected to a Wheatstone bridge (4-6a). The conductance depends somewhat on the pressure applied to the plug, but at light pressures, just sufficient to insure good contact, conductance readings are reproducible within a few per cent. Conductance measurements in resinous membranes reproduce better. These measurements are made by clamping the wet membrane, which is protected from moisture loss, between the electrodes of a conductance cell (7-9).

Dry exchange resins are very poor conductors. With increasing moisture content, the specific conductance increases abruptly (4). The conductance of commercial granular resins, which have a high capacity, is predominantly ionic; conductances of granular Dowex-50 measured with direct current are almost identical with those measured at 60 and 100 cycles alternating current (6). In resins of low exchange-capacity, the ionic contribution is less, and hence the impedance depends appreciably on the frequency of the applied potential. Albrink and Fuoss (10) analyzed the a-c electrical properties of an anion-exchange membrane of low capacity and calculated a-c and d-c components. The d-c conductance of the membrane changed with the electrolytic environment, but the a-c properties were substantially unaffected. The conductance of a phenolsulfonic acid formaldehyde polymer was found to increase appreciably with the frequency of the applied potential (10a).

Heymann and O'Donnell (5) measured the specific conductances of a phenolsulfonic resin (Amberlite IR-100) in different forms. The resin was placed in conductivity water.

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A representative set of their results is listed in Table I, which shows the equivalent conductance  $\Lambda = k/c_R$ ,  $c_R$  representing the capacity of the resin (in equivalents of exchangeable hydrogen per ml cell space), and  $k$  the specific conductance of the resin plugs (in mho  $\text{cm}^{-1}$ ), which is an average conductance of swollen resin plus free water. These values are compared to the equivalent ionic conductance,  $l_c^\circ$ , at infinite dilution for an aqueous solution at 18°C.

TABLE I. Conductance of Amberlite IR-100 in different forms at 18°C (5)\*

Resin particle size: 0.2-1.0 mm; plug: 1.35 cm diam, 4.0 cm length; cell constant = 2.79;  $c_R = 0.764$  meq/ml column space or 2.9 meq/gram gel water

Ion	Resistance, $R$ (ohm)	Eq. conductance, $\Lambda$ (mho $\text{cm}^2 \text{eq}^{-1}$ )	Ionic conductance in water (infin. dil.), $l_c^\circ$	$l_c^\circ/\Lambda$	Ionic conductance in 2.9 molar nitrate solution, $l_c$	$l_c/\Lambda$
H <sup>+</sup>	200 ± 5	18.3	313.9	17.2	(191)†	(10.4)
Li <sup>+</sup>	2505 ± 10	1.46	33.3	22.8		
Na <sup>+</sup>	1849 ± 5	1.98	43.4	22.0	(19.5)	(9.9)
K <sup>+</sup>	1375 ± 5	2.66	64.6	24.3	(32.3)	(10.2)
NH <sub>4</sub> <sup>+</sup>	1153 ± 5	3.17	64.7	20.4		
Ag <sup>+</sup>	8600 ± 100	0.42	54.0	130	(26.4)	(63.8)
Mg <sup>++</sup>	7000 ± 100	0.52	45.9	90		
Ca <sup>++</sup>	7300 ± 100	0.50	51.9	100	(16.5)	(33)
Ba <sup>++</sup>	12700 ± 200	0.29	55.4	190		
La <sup>3+</sup>	45000	0.07	61.0	900		
Th <sup>4+</sup>	74000	0.05	23.5	1000		

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† Values in brackets are calculated from available data (13) by interpolation and extrapolation.

TABLE II. Conductance of Dowex-50 in different forms at 27.5°C (6)\*

Resin particle size: 80-100 mesh (dry basis); plug: 1.6 cm diam, length 10 cm;  $c_R = 1.96$  meq/ml column space or 5.3 meq/gram gel water

Ion	Specific conductance $k$ (mho $\text{cm}^{-1}$ )	Eq. conductance, $\Lambda$ (mho $\text{cm}^2 \text{eq}^{-1}$ )	Ionic conductance of cation in an aqueous chloride solution, 5.3 molar (18°C) $l_c^\circ$	$l_c^\circ/\Lambda$
H <sup>+</sup>	$10.0 \times 10^{-3}$	5.1	(135)	(26.4)
Na <sup>+</sup>	$1.22 \times 10^{-3}$	0.62	(14)	(22.6)
Zn <sup>++</sup>	$0.60 \times 10^{-3}$	0.306	(7.5)	(24.5)

\* Values in brackets are calculated from available data (13) by interpolation and extrapolation.

Table II shows some conductance measurements with Dowex-50 (6) and in Table III the specific conductances of some ion-exchange membranes are listed for comparison (8, 11, 12).

It is seen that the conductances can be classed in four groups; the hydrogen resin having the highest conductance, followed by the alkali metal resins, whose conductances are comparable and increase with the atomic weight as in aqueous solution, the silver and alkaline earth resins whose conductances are considerably lower, and, finally, the lanthanum and thorium resins, which are very poor conductors.

Heymann and O'Donnell (5) compared the equivalent conductance,  $\Lambda$ , of the resin to the ionic conductance,  $l_c^\circ$ , of the

same ion in an aqueous solution at infinite dilution. Their values for the ratio  $l_c^\circ/\Lambda$  are listed in Table I. It is seen that this ratio is about equal for the alkali metal and hydrogen ions, and increases with the valency of the ion. By comparing the equivalent conductance of a resin to the ionic conductance,  $l_c^\circ$ , of the same ion in a comparable aqueous solution of the same molality as the resin, one can obtain an idea about the strength of binding of the ions in the resin. For if all resin salts were completely dissociated and the presence of the crosslinked matrix acted merely as a viscous factor, increasing the frictional resistance of the medium on the moving particle, the migration of all types of cations would be slowed down to the same extent, and the ratio  $l_c/\Lambda$  would be equal for all cations. If the resin were a labyrinth of fine pores, similar to a sponge, the ratio  $l_c/\Lambda$  would represent a measure for the tortuosity of the path of the ions, similar to the formation factor used in soil science (14). It will be shown later, how-

TABLE III. Specific conductance of ion-exchange membranes in various forms

Membrane	Type	Mobile ion	Temp (°C)	Specific conductance, $k \times 10^3$ (mho $\text{cm}^{-1}$ )	Reference
Nepton CR-51*	Homogeneous phenolsulfonic cation-exchanger	Na <sup>+</sup>	23	7.8	(11)
		Zn <sup>++</sup>	27	3.7	(11)
		Ca <sup>++</sup>	27	4.4	(11)
Nepton ARX-44*	Homogeneous moderately basic anion-exchanger	Cl <sup>-</sup>	25	9.0	(8)
Amberplex C-1†	Nonhomogeneous sulfonic acid cation-exchanger	Na <sup>+</sup>	25	0.48	(12)
		H <sup>+</sup>	25	3.6	(12)
Amberplex A-1†	Nonhomogeneous strongly basic anion-exchanger	Cl <sup>-</sup>	25	0.46	(12)
		OH <sup>-</sup>	25	1.1	(12)
		SO <sub>4</sub> <sup>==</sup>	25	0.34	(12)

\* Product of Ionics, Inc., 152 Sixth St., Cambridge, Massachusetts. The "Nepton" resin membranes were previously called "Permionic."

† Product of Rohm and Haas Company, Washington Square, Philadelphia, Pennsylvania.

ever, that some properties of the resin can be explained more adequately by a one-phase, solid electrolyte model.

Since it is found that the ratio  $l_c/\Lambda$  varies with the types of ions considered, one may conclude that the higher this ratio, the less the dissociation of the respective resin salt. It would be logical to compare the resins to the corresponding monomeric solutions, for instance, sodium Dowex-50 to a solution of sodium toluyl sulfonate of equal molality. Since sufficient conductance data on such solutions are not available, the resin forms in Tables I and II have been compared to nitrate and chloride solutions, respectively. It is seen that the general trend of the ratios  $l_c/\Lambda$  for Amberlite IR-100 confirms the qualitative conclusions drawn from the ratios  $l_c^\circ/\Lambda$ , indicating that the strength of binding increases with the valency of the cation. The monovalent silver ion is seen to be bound considerably stronger than the alkali metal ions.

The data for Dowex-50 are not sufficiently extensive to allow definite conclusions. In this case, the value of the ratio  $l_c/\Lambda$  is almost the same for the three ions tabulated, suggesting that the dissociation of the hydrogen, sodium, and zinc

forms of Dowex-50, which contains no phenolic groups, is about equal.

These considerations have a direct bearing on the question of electrophoretic separations in the resin phase. For if the resinous polyanion shows specific interaction with certain cations, this effect may increase differences in the mobility of two ions and make their separation easier. It must, however, be borne in mind that the methods used in the measurement of the conductance of resin plugs are rather crude and, therefore, the conclusions drawn from them must be considered merely qualitative. As soon as precision measurements of conductances of resins become available, a more satisfying correlation between binding strength and conductance should be possible.

#### Correlation of Self-Diffusion Coefficients in Resins to the Electrical Conductance

Self-diffusion in the resins is invariably smaller than for the same ions in water, and decreases with increasing ionic charge (15).

From the measured conductance of an ion-exchange membrane, it is possible to calculate the self-diffusion coefficient of an ion,  $D$ , ( $\text{cm}^2 \text{sec}^{-1}$ ) in the resin by means of the Nernst-Einstein formula (16), which in the case of ion-exchange resins assumes a particularly simple form, since the current is carried only by one charge type of ion (11, 16).

$$D = RTm/ZF = 2.66 \times 10^{-7} \Lambda/Z \text{ at } 25^\circ\text{C}$$

where  $R$  is the gas constant ( $\text{watt sec deg}^{-1} \text{mole}^{-1}$ ),  $T$  the absolute temperature,  $F$  Faraday's constant ( $\text{coul eq}^{-1}$ ),  $Z$  the valency of the ion,  $m$  its electrical mobility ( $\text{cm}^2 \text{volt}^{-1} \text{sec}^{-1}$ ), and  $\Lambda$  the equivalent conductance of the resin ( $\text{mho cm}^2 \text{eq}^{-1}$ ).

These values can be compared to those obtained from the observed spread of radiotracers on ion-exchange membranes (11) and to those computed from the rate of isotopic exchange between a resin and a solution (16, 17). A comparison of these values is shown in Table IV.

It is seen that the agreement is fairly good except for calcium, and the data show that the mechanisms of diffusion and electrical conductance in the resin are similar. All the values computed from the electrical conductance are higher than those obtained from the radioactive tracer method. This discrepancy is believed to be due to electroosmosis, and is discussed in a later section.

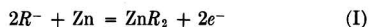
Both specific conductance (18) and self-diffusion rates (15, 19) diminish considerably with increasing crosslinking of the resin matrix, and it may be possible to develop an analytical method for the determination of the degree of crosslinking based on conductivity measurements.

So far, it has been assumed that the transference number of the mobile ions in a resin salt, with respect to the macromolecular immobile matrix, is unity. This assumption was proved by the study of electromigration in the resins analogous to the moving boundary method used in solutions and also by the measurement of potentials in systems containing ion-exchange resins. These experiments have a number of further implications and are discussed in the following paragraphs.

#### Electromigration in Ion-Exchange Resins

When current flows through an ion-exchange resin, electrode reactions occur and often cause chemical changes in the resin. However, one can use electrode materials which do not cause such changes. For instance, if the zinc form of Dowex-50 is electrolyzed between zinc electrodes, an amount of zinc

ions equivalent to that which is removed from the resin at the cathode is supplied at the anode by the reaction:



(where  $R$  represents one gram-equivalent of resin anion) and the resin remains in the zinc form.

Electromigration in this system was studied by the "moving boundary method," tagging a thin lamina of the resin column with  $250d \text{ Zn}^{65}$ , observing its progression by means of radioactive counting equipment, and correlating it to the total amount of charge passed (6). If the very small differences between the ionic mobilities of the zinc isotopes are neglected, the rate of progression of the lamina,  $dz/dt$ , should equal the ratio between the flux of cations,  $n_c$ , and the concentration:

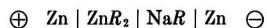
$$\frac{dz}{dt} = \frac{n_c}{c_R} = \frac{T_c i}{F c_R}$$

where  $z$  is the length coordinate in the direction of the current,  $t$  the time,  $c_R$  the capacity of the resin ( $\text{meq/ml}$  column space),  $T_c$  the transference number of the cation with respect to the resin matrix,  $i$  the current density ( $\text{ma cm}^{-2}$ ), and  $F$  is Faraday's constant ( $\text{coul. eq}^{-1}$ ).

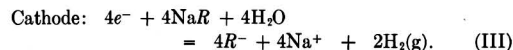
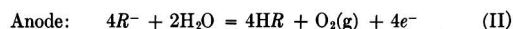
TABLE IV. Self-diffusion coefficients,  $D$ , in phenolsulfonic ion-exchange resins as determined by different methods (11)

Cation	Resin	$\zeta$ Temp.	Self-diffusion coefficient, $D \times 10^6 \text{ cm}^2 \text{ sec}^{-1}$		
			Ki- netic	Radioactive tracer spread	Electrical conductance
Sodium	Amberlite IR-1	30	2.1		
	Nepton CR-51	23		$1.95 \pm 0.25$	$2.15 \pm 0.20$
Zinc	Nepton CR-51	27		$0.41 \pm 0.05$	$0.48 \pm 0.05$
	Nepton CR-51	27		$0.31 \pm 0.05$	$0.58 \pm 0.05$

$T_c$  was found to be unity, and this result was confirmed by measuring the progression of a traced zinc lamina at the zinc-sodium boundary of the system:



If sodium Dowex-50 is electrolyzed between platinum electrodes, the following electrode reactions occur (5, 20):



Reaction (II) produces continuously the hydrogen form of the resin, and hence the resin can be regenerated by electrolysis without the use of acid solutions. The current yield decreases, however, as electrolysis proceeds, for the hydrogen ions formed at the anode penetrate the whole sodium layer, eventually reaching the cathode, when the following reaction completes with reaction (III):



Hence, the current yield (as eq. HR formed per faraday) decreases as soon as this reaction starts. Analogous phenomena were observed in anion-exchange resins. In this case, hydroxyl ions are formed at the platinum cathode. The mobility of iodine was measured by a radiotracer method, and the progress of the hydroxyl ions measured by the use of phenolphthalein indicator (9).

It was found that if a sharp boundary exists initially between two forms of the resin, such that the slower cation is

behind the faster with respect to the direction of the current, the boundary remains sharp during electromigration. In the reverse case, mixing occurs. This is analogous to the behavior of boundaries in aqueous solutions. By virtue of reaction (II), the anode is equivalent to an initial  $HR | NaR$  boundary.

Spiegler and Coryell (6) applied Weber's electromigration equations (21), and presented a simplified treatment of this phenomenon, treating the resin as a homogeneous medium. They neglected diffusion, as in their experiments the electrical force on the ions caused by the applied potential was much larger than the osmotic force causing diffusion.

From the general equations, derived under the assumption that the ratio of the mobilities of the adsorbed ions is independent of the composition of the resin, one can calculate the distribution of hydrogen and sodium ions at any point and at any time during the electrolytic regeneration process of the sodium resin, described by equations (II) and (III).

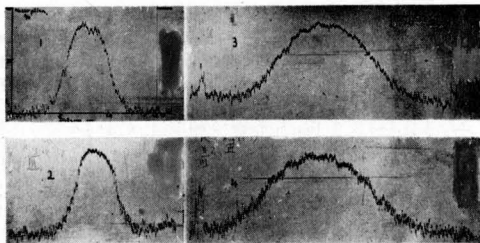


Fig. 1. Comparison of densitographs of autoradiographs of a Nepton CR-51 membrane (product of Ionics, Inc., Cambridge, Mass.) in the sodium form containing a lamina traced with  $2.6\mu Na^{22}$ . Sections 1 and 2 represent the initial activity distribution in the two halves of the membrane, respectively; sections 3 and 4 show the distribution after 8 hr, section 3 in the upper half, which was left in distilled water, and section 4 in the lower half, which was electrolyzed. Autoradiographic exposure: sections 1 and 2, 5 min; sections 3 and 4, 12 min; all on Kodak Medical X-ray Film (No-Screen). Total migration of peak in section 4: 4.9 cm.

After an electrolysis period of  $t$  seconds, the following three regions are found in the resin: (a) a zone adjacent to the anode which contains only  $HR$ :

$$z < it/Fc_R M,$$

where  $z$  is the distance from the anode (cm),  $i$  the current density (ma  $cm^{-2}$ ),  $t$  the time (sec),  $F$  Faraday's constant (coul.  $eq^{-1}$ ),  $c_R$  the resin capacity (meq  $ml^{-1}$ ), and  $M$  the mobility ratio  $m_{H^+}/m_{Na^+}$ ; (b) a mixed zone containing both  $HR$  and  $NaR$ :

$$it/Fc_R M < z < itM/Fc_R,$$

in which the concentration of  $HR$  equals

$$c_{HR} = \frac{1}{M-1} \left[ (itc_R M/Fz)^2 - c_R \right]$$

The length of this mixed zone increases linearly with time; and (c) a zone adjacent to the cathode containing only  $NaR$ :

$$z > itM/Fc_R$$

Thus an approximate picture of the efficiency of the electrolytic regeneration process can be obtained.

While no direct determination of the concentrations along the column was made, the theory was applied to the progression of a traced lamina of the sodium resin. As electrolysis

proceeds, the rate of progress of the activity maximum decreases and the band spreads, owing to penetration of hydrogen ions into it. Comparison of the observed rate of migration of the activity maximum to the calculated values showed that the progress is faster than predicted under the assumption of independent ionic mobilities.

In the electrolysis of the sodium form of carboxylic exchange resins, such as Amberlite IRC-50, a sharp boundary between the anodic hydrogen form of the resin and the sodium form is maintained during electrolysis, as the net mobility of hydrogen ions in these resins is lower than of the sodium ions. This case is analogous to the boundary acetic acid | sodium acetate in aqueous solution which remains very sharp during electromigration (22). However, hydrolysis of the resin salt is appreciable, and the specific resistance of the hydrogen form of the resin is very high because the degree of dissociation of the carboxylic groups is low.

### Separations by Electromigration in Ion-Exchange Resins

The use of solid media for electromigration separations has found increasing attention in recent years (23). Filter paper (24, 25), silica jelly (26), and agar gel (27) have been used, and ion-exchange resins, in particular in the form of membranes, may now be added to this list. While the accurate optical methods of analysis used in aqueous solutions cannot be applied to them, they offer other advantages such as stoichiometric ion-binding, low diffusion rates, the possibility of direct cooling by flowing water, and, as in other solid media, the absence of convection.

In principle, two methods of separation seem possible. In the first, which is used extensively for electrophoretic separations in solutions (28), a small amount of the mixture to be separated is placed in a large excess of "supporting electrolyte." The function of the latter is to keep the potential gradient constant and thus prevent "boundary anomalies."

Electromigration under such conditions is illustrated by the experiment described in Fig. 1. A thin lamina of a cation-exchange membrane ("Nepton CR-51," product of Ionics, Inc., Cambridge, Massachusetts) in the sodium form was traced by adsorbing a small amount of  $2.6\mu Na^{22}$  and the membrane electrolyzed between zinc electrodes. The activity of the traced lamina was determined by autoradiography. The optical density of the autoradiographs was subsequently recorded by a recording densitometer. The activity distribution in the electrolyzed half of the membrane is compared to a blank kept in distilled water for an equal period of time. It is seen that both bands spread by diffusion and their shape is almost the same.

Were the resin membrane material proper not homogeneous,<sup>2</sup> the spread of the migrating band would be larger. Thus the difference between the diffusion spread and the spread associated with electromigration is considerably larger in columns of granular resin particles than in resinous membranes.

If two kinds of ions of different mobility are absorbed, the peaks will migrate at different rates and separation can be achieved.

In the second method of separation, the mixture is placed between layers of other electrolytes such that the ions of lower mobility migrate behind those of higher mobility. Thus, to separate sodium from potassium, the mixture is adsorbed on a lamina of an ion-exchange membrane such that it is sand-

<sup>2</sup> The membranes are backed by a Lumite screen, the effects of which can be seen in the densitograph. The screen represents the only inhomogeneity of the system.

wiched between an anodic section of  $ZnR_2$  and a cathodic section of  $HR$ , and a current is passed through the membrane using zinc electrodes. In the experiment described in Fig. 2, the sodium had been traced with  $2.6\mu Na^{22}$ . As the band progressed, the boundaries remained sharp, and partial separation of sodium from potassium occurred. The discontinuities of the curves are due to the presence of the Lumite screen backing material.

A similar technique had been used previously by Kendall (29) in electroseparations in agar gel. He was able to separate ions of very similar properties such as the rare earths, but did not succeed in separating isotopes. Because of their mechanical stability, ion-exchange resins offer possibilities which were absent in the soft gels.

For instance, such separations can be carried out on a rotating wheel (30). The ions to be separated are adsorbed on a thin section of a resin membrane belt mounted on a wheel, and, while they migrate, the wheel rotates in the opposite direction with a speed equal to the average of the speeds of the ions to be separated. The principle of this arrangement is similar to the "squirrel wheel." It represents an infinite path length for electromigration separations and, since the electrodes are applied in the vicinity of the boundaries of the

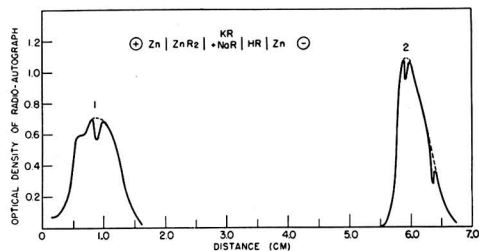
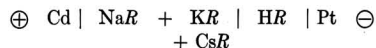


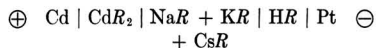
FIG. 2. Partial separation of sodium and potassium by electromigration in a Nepton CR-51 membrane. Sodium traced with  $2.6\mu Na^{22}$ . Figure shows densitographs of membrane radioautographs.

region of the ions to be separated, only a minimum of electric power is dissipated in the remainder of the membrane.

The wheel is shown in Fig. 3. A mixture of alkali ions is adsorbed in the top section of the resin belt which rests on the wheel.<sup>3</sup> The anode consists of cadmium amalgam (5% cadmium) held in a cell whose bottom is made of 66-gauge Nylon hose, and makes electrical contact with the resin belt. The cathode is a platinum sheet. At the start, the position of the zones is represented by the following scheme:



As the current flows, cadmium "dissolves" in the resin by a reaction similar to (I):



This increases the resistance between the electrodes, since  $HR$  conducts better than  $CdR_2$ . The current is kept constant by an electronic current regulator, and hence the voltage increases. This voltage signal is fed back into an electronic motor controller accelerating a motor which, through a gear

<sup>3</sup>The author is greatly indebted to Dr. A. A. Kasper of Ionics, Inc., for the belts of "Nepton CR-51" resin. These belts contained no backing material.

train, turns the wheel from right to left until the alkali ion band is about in the middle between the electrodes. Henceforth the feedback mechanism controls the position of the alkali ion band at this spot during the passage of the current.

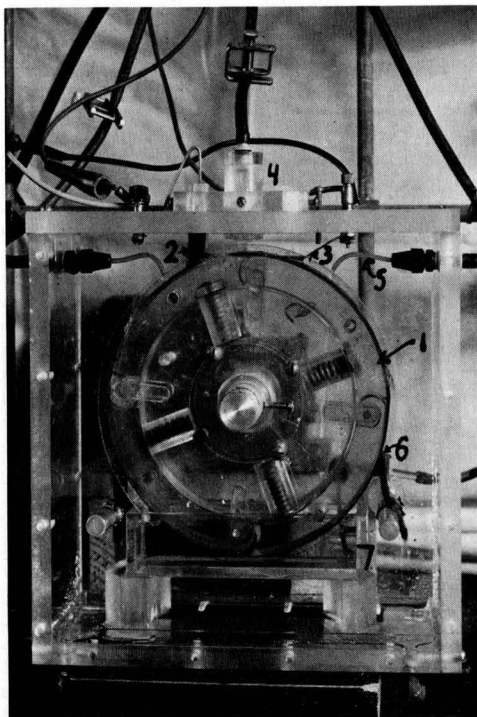


FIG. 3. Apparatus for ion separation on a rotating ion-exchange membrane belt. Figure shows the circular membrane belt [1] held on a Lucite wheel under spring tension, liquid cadmium amalgam anode [2], platinum cathode [3], rinsing system consisting of a shower head [4], side sprinklers [5], and water deflectors [6]. The acid regenerating vessel [7] is seen at the bottom. Wheel diameter: 7 in.

When separation is complete, the zones are represented as follows:



Successful separations of alkali metal ions by this method have been reported (30), but, for the time being, this work is still in a development stage.

Such separations are also possible in beds of granular resins (6, 31, 32). For instance, partial separation of cupric from cobaltous ions, both adsorbed on Amberlite IRC-50, was observed when the column was electrolyzed (31). In this case, the progress of the separation could be observed visually, as the resin is white and both cations colored.

#### Difusion of Electrolytes into the Resin

The solid polyelectrolyte model of ion-exchange resins also proved very useful in the interpretation of potential measurements which provided further insight into ion-exchange resins, in particular systems containing both resins and solutions, as compared to the work discussed in the previous paragraphs which dealt mainly with ion-exchange resins in a medium of pure water.

In the theoretical interpretation of these data, account has to be taken of the penetration of electrolytes from the solution into the resin. When the resins are in equilibrium with solutions of electrolytes, they are no longer ideal cation or anion conductors, respectively.

Diffusion of electrolytes into resins had been observed in industrial ion-exchange practice and numerous data compiled on the need for "leaching" resin columns long before fundamental studies of this effect were undertaken.

Were the ion-exchange particle an inert, rigid sponge without surface activity, the amount of solution taken up by it would be independent of the concentration. From this viewpoint, there is more or less void space in the resin and this is occupied by solution of essentially the same composition as externally. Thus, in the case of Dowex-50, there would be two "types" of sodium ion in the resin phase, namely, at the exchange site position and in the interstitial solution (33). One would expect that the ratio,  $r$ , between the concentration of an electrolyte inside the resin (in meq ml<sup>-1</sup>) to the concentration of the same electrolyte in solution would be constant and equal to the fractional pore volume of the resin. The same effect would result from the presence of cracks in the resin particles.

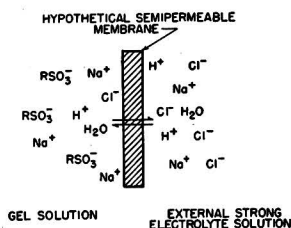


FIG. 4. Schematic representation of electrolyte partition between a strong acid cation exchanger and an external aqueous phase. (Reproduced by permission of *Annual Reviews, Inc.*, Stanford, Calif.) (2)

Experiments show that as the concentration of the electrolyte increases,  $r$  increases, and the resin shrinks. These phenomena cannot be accounted for satisfactorily by the two-phase sponge model. They can be explained (34-36) by extending to ion-exchange resins the theory of membrane equilibria developed by Gibbs (37) and Donnan (38).

In the Gibbs-Donnan model, the ion-exchanger particle may be regarded as a macromolecule acting as its own membrane. It is permeable to the ions found in the solution, but impermeable to the fixed ionic groups bound to its lattice. Thermodynamically, it can be treated as a concentrated solution. This situation is illustrated in Fig. 4 for sodium Dowex-50 in equilibrium with a solution of sodium chloride. As soon as electrolyte is taken up, the sodium ions that enter the resin phase from the solution, together with the chloride ions and the sodium ions which had been previously in the resin and held in stoichiometric proportion to the fixed anionic groups, are no longer treated as different from each other.

Conductivity measurements of resinous membranes are in better agreement with the Donnan than with the sponge model. Data on conductivity and equilibrium distribution of NaCl for "Nepton CR-51" cation-exchange membrane have been reported by Juda and coworkers (7, 39). They equilibrated a sulfonic acid cation-exchange membrane in the sodium form with a solution of sodium chloride, determined the conductance of the resin, and also separated the membrane from the solution and determined by analysis the

amount of sodium chloride that had diffused into the resin. One can calculate the specific conductance: (a) assuming that the resin does not interact with the pore solution (two phase concept; sponge with straight, wide pores); (b) assuming that the electromigration of the sodium and chloride ions is subject to the same "viscous" resistance in the resin (characterized by the ratio  $l_c/\Lambda$ ) as is the sodium ion in the pure sodium form of the resin in the absence of chloride (one phase, Donnan concept). As shown in Fig. 5, it is then found that values calculated under assumption (a) are much higher than under (b). The experimental values (39) are near to the values calculated under assumption (b), but a little higher which may be due to the presence of a small amount of the external solution in cracks or adhering to the resin surface. Therefore, it seems reasonable to consider this particular resin as a one-phase system with a small correction for two-phase behavior.

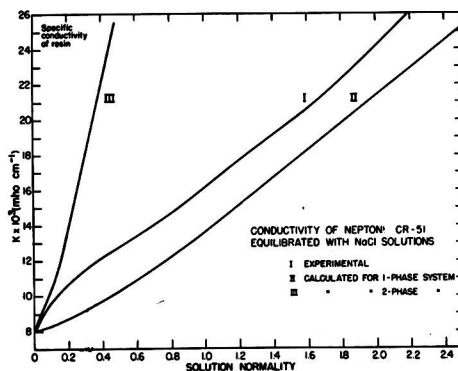


FIG. 5. Conductivity of Nepton CR-51 equilibrated with NaCl solutions.

It might be conjectured that the approximate agreement of the experimental data with those computed by method (b) is no proof for the Donnan model, for even for the sponge model one would expect lower conductivities than calculated under assumption (a) because of the lower value of the mobility in the capillaries than in a free solution. For instance, in a certain type of wet filter paper, the mobility of albumin was found to be approximately 30 per cent less than in water (24). This reduction, however, is far too small to account for the low values of the observed resin conductivities, and hence, if capillaries exist, they must be extremely narrow. Possibly their cross section is of molecular dimensions. In this case, the resin can no longer be treated as a two-phase system, and its properties must be expected to approach those of the one-phase model. A similar viewpoint has been applied recently by Schmid to the interpretation of the electrical properties of collodion membranes (40). Recent electron micrographs of different ion-exchange materials (40a) show that the pore size in synthetic resins is indeed very small. The pore diameter of a synthetic cation-exchange resin was found to be of the order of 10 Å units, whereas in an inorganic synthetic ion-exchange gel it was several orders of magnitude larger. It is, therefore, not surprising that significant differences in electrolyte distribution characteristics were found in the study of different ion-exchange materials.

#### Gibbs-Donnan Model of Ion-Exchange Resins

The quantitative treatment of the one-phase "Donnan" model of the resin follows closely along the exact thermodynamics of membrane equilibria developed by Donnan and Guggenheim (41), and only some of its most fundamental



features are briefly outlined in the following. The model is schematically represented in Fig. 4, showing the resin and solution phases separated by an imaginary membrane which is impermeable to the sulfonic groups. Phase equilibrium between two electrolyte solutions in the same solvent and of unequal concentration is possible if there is a difference in the pressure to which the phases are subjected. The components inside the resin particle are assumed to be subjected to the pressure of the strained hydrocarbon network of the solid polyelectrolyte while no such pressure acts in the solution.

Gibbs has shown (37) that if a system of this kind is in equilibrium, the temperature is constant and the chemical potentials,  $\mu$ , of any component that can pass through the membrane are equal in the two phases:

$$\mu^s(p^s, T) = \mu^r(p^r, T)$$

where  $p$  is the pressure,  $T$  the absolute temperature, and the superscripts,  $s$  and  $r$ , refer to solution and resin phase, respectively.

The activity,  $a$ , of a component is defined by the equation,

$$\mu = \mu^0(p, T) + RT \ln a$$

where  $\mu^0(p, T)$  is the standard chemical potential of this component. We chose the same standard state of the component in the solution and resin phase, namely, at unit pressure and at the prevailing temperature,  $T$ . The variation of the chemical potential with pressure is given by the well-known relation,

$$\left(\frac{\delta\mu}{\delta p}\right)_T = \bar{v} \quad (V)$$

where  $\bar{v}$  is the partial molar volume of the component. Substituting these relations in the Gibbs equation we obtain

$$\begin{aligned} \Delta\mu^0(1, T) + \int_1^{p^s} \bar{v} dp + RT \ln a^s \\ = \mu^0(1, T) + \int_1^{p^r} \bar{v} dp + RT \ln a^r. \end{aligned}$$

If the compressibility of the component is considered negligible, i.e., its partial molar volume is independent of the pressure, this equation reduces to

$$\ln \frac{a^s}{a^r} = \bar{v}(p^r - p^s)/RT = \bar{v}\pi/RT \quad (VI)$$

where  $\pi$ , termed the swelling pressure, is defined as the difference between the pressure in the resin and the solution which is in equilibrium with it.

Equation (VI) is valid for each component of the system that can pass through the membrane. Combining two equations for the electrolytes  $MX$  and  $NX$ , respectively, and using the definition of the activities of the ions,

$$(a_{M^+})(a_{X^-}) = a_{MX}; \quad (a_{N^+})(a_{X^-}) = a_{NX}$$

one obtains

$$\begin{aligned} \ln \frac{(a_{M^+}^s)(a_{N^+}^s)}{(a_{M^+}^r)(a_{N^+}^r)} &= \ln \frac{(m_{M^+}^s)(m_{N^+}^s)(\gamma_{M^+}^s)(\gamma_{N^+}^s)}{(m_{M^+}^r)(m_{N^+}^r)(\gamma_{M^+}^r)(\gamma_{N^+}^r)} \\ &= \frac{\pi(\bar{v}_{M^+} - \bar{v}_{N^+})}{RT} \equiv K \quad (VII) \end{aligned}$$

where  $a$  stands for the ionic activities,  $m$  the molalities, and  $\gamma$  the ionic activity coefficients of the ions.  $K$  is a real constant only to the extent that the swelling pressure is independent of the ion activities. There is no way to measure the individual ionic activity coefficients without further assumptions.

To test equations (VI) and (VII) one has to know the activity coefficients of the components in the resin and in the solution and the swelling pressure,  $\pi$ . The activity coefficients in the solution are often known, but the activity coefficients in the resin have to be estimated.

To determine the swelling pressure,  $\pi$ , in sulfonic acid resins, Glueckauf (42) compared the partial pressure of water vapor of these resins to the partial vapor pressure of water of a very slightly crosslinked resin of equal molality. (These two resins are not in thermodynamic equilibrium.) As the water molecules in the highly and the weakly crosslinked resin are in similar media except for the different pressure prevailing in these resins, the observed difference of the partial vapor pressure of water is attributed to this pressure difference. From these data, pressure differences of the order of several tens to several hundreds of atmospheres were computed, depending on the volume of the resin and on the degree of crosslinkage. If the resin of low crosslinkage is considered essentially strainless, the computed pressure difference between the two resins represents the pressure prevailing in the highly crosslinked resin particles. The volume of the resin was found to decrease linearly with increasing pressure.

The importance of the swelling pressure term in equations (VI) and (VII) has been discussed by Gregor (36) and a theory developed which is based on the linear relationship between swelling pressure and resin volume. This term is very important in the interpretation of swelling phenomena of the resin. However, if one wants to predict from equations (VI) and (VII), respectively, the amount of electrolyte in the resin in equilibrium with the solution, or the exchange equilibrium constant for two ions, one has to estimate the activity coefficients of the ions in the resin, and the uncertainty involved in the estimation of the logarithm of this factor is often of the same order of magnitude or larger than the whole swelling pressure term (19, 34). Since there is no exact theory by which the activity coefficients in such concentrated systems as ion-exchange resins can be estimated, activity coefficients in aqueous solutions of 1-1 electrolytes of equal ionic strength have been used or empirical rules applied.

Thus measuring the uptake of KCl by anion-exchange membranes and neglecting the swelling term on the right side of equation (VI), Manecke and Bonhoeffer (9) reported fair agreement between the measured values and the values calculated under the assumption that the mean ionic activity coefficients of KCl in the resin are equal to those of aqueous solutions of KCl of equal ionic strength.

Several investigators (34, 43, 44) used Harned's rule (45) for the estimation of mean ionic activity coefficients in the resin. This rule had proved of great value in the estimation of activity coefficients in mixed concentrated aqueous solutions from activity coefficients in the solutions of their components. A detailed discussion of these researches is outside the scope of this paper, but a few further remarks on the application of the Donnan theory to the diffusion of electrolytes into the resin will be made.

Applying equation (VI) to the equilibrium between a solution of a chloride,  $MCl$ , and a cation-exchange resin in the  $M$  form,  $MR$ , one can again split the activity of  $MCl$  into the ionic activities and obtains:

$$\begin{aligned} \ln \frac{(a_{M^+}^s)(a_{Cl^-}^s)}{(a_{M^+}^r)(a_{Cl^-}^r)} &= \ln \frac{(m_{MCl}^s)^2(\gamma_{\pm}^s)^2}{(m_{M^+}^r)(m_{Cl^-}^r)(\gamma_{\pm}^r)^2} \\ &= \pi\bar{v}_{MCl}/RT \quad (VIII) \end{aligned}$$

where  $(\gamma_{\pm})^s$  and  $(\gamma_{\pm})^r$  are the mean ionic activity coefficients of  $MCl$  in the solution and the resin, respectively.

The distribution of  $MCl$  between the resin and the solution is not equal, and considering that the right hand term of equation (VIII) is positive, it is seen that the presence of a considerable concentration of mobile  $M^+$  ions in the exchanger causes the activity and the concentration of the chloride ion in the exchanger to be smaller than in the solution.

Thus, electrolytes are partially excluded from the resin, while the equilibrium distribution of nonelectrolytes of low molecular weight between resin and solution is roughly equal on a molality basis. This ion exclusion principle has been used to separate electrolytes from nonelectrolytes (46). To test equation (VIII), Boyd and Larson (34) determined by neutron activation analysis the diffusion of  $HCl$ ,  $LiCl$ , and  $HBr$  into nuclear sulfonic cation exchangers of the sulfonated polystyrene-divinylbenzene copolymer type. Their results for  $HCl$ , illustrating the strong dependence of the phenomenon on the degree of crosslinking, are shown in Fig. 6. The

low concentration. They provide an indication that the resins are not quite ideal homogeneous single-phase systems and that some allowance must be made for two-phase behavior.

#### Potential Measurements Across Synthetic Ion-Exchange Membranes

The connection between the ion-exchange properties of a membrane material and its permselectivity, i.e., its ability to transfer only certain kinds of ions, in particular positive or negative ions, had been known even before synthetic ion-exchange resins became available and was treated quantitatively by Teorell (47, 48) and by Meyer and Sievers (49, 49a). This subject is of considerable interest in the biological sciences because of the permselective properties of many biological membranes.

If a solid is able to exchange ions readily with a solution and this ability extends to layers beneath the solid surface, this evidently proves that the exchanging ions can migrate freely in the solid. Consequently, when a membrane made of an ion-exchange material is placed between two solutions and a potential is applied, exchangeable ions are transferred from one solution to the other. Nonexchangeable ions can pass through the membrane only to the extent that they can enter the membrane by a mechanism different from ion-exchange. For instance, if the membrane has comparatively wide channels which can fill with solution, nonexchangeable ions can pass through these channels from one side of the membrane to the other. Synthetic membranes made of ion-exchange resins have, in general, no wide pores. In equilibrium with dilute solutions the resins were shown to take up only very small amounts of electrolytes.

If a cation-exchange membrane is placed between dilute solutions and an electrical potential applied across it, the current is carried primarily by the cations, because the anions from the solution are almost completely excluded from the resin and the fixed anion groups of the resin are immobile. Thus, in dilute solutions, cation-exchange membranes are almost impermeable to anions, acting as "ionic sieves" which screen out the anions. Similarly, anion-exchange membranes are impermeable to cations.

As the concentration of the solutions increases, electrolytes from the solutions are taken up by the membrane. Both cations and anions participate now in the transport of current across the membrane and hence its permselectivity decreases with increasing electrolyte concentrations.

To obtain fundamental data on resin behavior in such systems, electrical potentials were measured across two reference electrodes in contact with solutions of different concentrations which are separated by an ion-exchange membrane. These measurements represent a continuation of extensive previous researches on permselective membranes of biological origin, of clay (50) and collodion which were recently reviewed by Sollner (51). The main advantages of the synthetic resinous membranes are their low specific resistance, high capacity, and mechanical stability, which may lead to industrial applications where other material failed.

Consider a cell consisting of silver-silver chloride electrodes in aqueous solutions of  $KCl$  of activities  $a_1^{KCl}$  and  $a_2^{KCl}$ , respectively, separated by a membrane. Neglect the transport of water associated with the transfer of ions. If the membrane is ideally permselective and transfers only potassium ions, the reversible passage of one Faraday involves the transfer of one mole of  $KCl$  from one solution to the other. As the

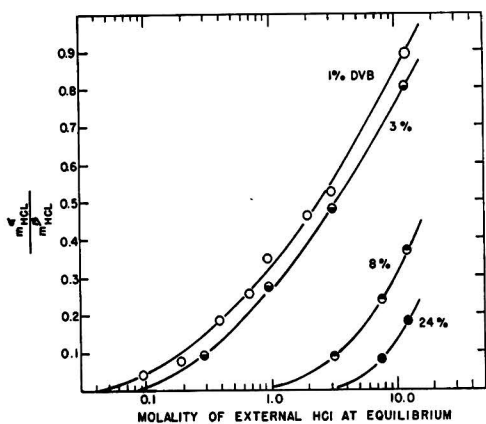


Fig. 6. Variation of distribution of diffusible chloride ion in polystyrene DVB copolymers with external concentration and crosslinking. Electrolyte:  $HCl$  (Reproduced by permission of Dr. G. E. Boyd.)

degree of crosslinking is indicated by the nominal divinylbenzene (DVB) content of the resin. The ratio of the molalities of  $HCl$ ,  $m^r/m^s$ , in the resin and solution phases is plotted against the logarithm of the molality. Analyzing these curves and estimating  $\pi$  at roughly 100 atm, they reached the conclusion that the osmotic free energy term in equation (VIII) is small compared to the logarithm of the activity coefficient of  $HCl$  in the resin. In other words, ionic interaction plays a more important part than the osmotic free energy in determining diffusion of these electrolytes into the resin.

Equation (VIII) leads to the postulate that the values of  $m^r/m^s$  should approach zero at infinite dilution when plotted against  $\log m^s$  as in Fig. 5. It is seen that this is indeed the case. In previous studies (1, 7, 8) of this and other types of resins, similar results were obtained, but the values of  $m^r/m^s$  approached a constant low value, but not zero, at low values of  $m^s$ . These findings may have been due in part to incomplete phase separation or to small cracks and channels in the resin particles. They were reported for both cation and anion-exchange (46a) resins, and lead to abnormally low activity coefficients,  $\gamma_{\pm}$ , in resins in equilibrium with solutions of

reversible electrical work equals the difference of the chemical potentials of KCl in the two solutions, we obtain:

$$E = \frac{RT}{F} \ln \frac{a_1^{\text{KCl}}}{a_2^{\text{KCl}}} = \frac{RT}{F} \ln \frac{a_1^{\text{K}^+}}{a_2^{\text{K}^+}} + \frac{RT}{F} \ln \frac{a_1^{\text{Cl}^-}}{a_2^{\text{Cl}^-}} = E_{\text{K}^+} + E_{\text{Cl}^-} \quad (\text{IX})$$

where  $E$  is the measured potential,  $F$  Faraday's constant,  $R$  the gas constant,  $T$  the absolute temperature, and  $a^{\text{K}^+}$  and  $a^{\text{Cl}^-}$  are the ionic activities of potassium and chloride ions, respectively. The ionic activities cannot be measured separately. The measured potential can be considered split into two parts,  $E_{\text{Cl}^-}$  and  $E_{\text{K}^+}$ , the first of which is attributed to the sum of the electrode potentials and the second to the membrane. In the following reasoning in this section the ionic activities of the potassium and chloride ions will be set equal to each other, since this is convenient, and since, from a thermodynamic viewpoint, the magnitude of the measured potentials, e.g.,  $E$ , of a complete cell does not depend on the manner in which the potential difference is distributed within the cell. The potentials  $E_{\text{K}^+}$  and  $E_{\text{Cl}^-}$  are then equal. They will be designated as  $E_0$ . When this treatment is extended to solutions other than potassium chloride, this assumption must be kept in mind.

If calomel electrodes are used instead of silver-silver chloride electrodes, and if the sum of the liquid junction potentials between them and the potassium chloride solutions is negligible, the potential difference between the calomel electrodes equals  $E_0$ , the membrane potential of the ideally permselective membrane:

$$E_0 = \frac{RT}{2F} \ln \frac{a_1^{\text{KCl}}}{a_2^{\text{KCl}}} = \frac{RT}{F} \ln \frac{c_1(\gamma_{\text{K}^+})_1}{c_2(\gamma_{\text{K}^+})_2} \quad (\text{X})$$

where  $\gamma_{\text{K}^+}$  is the ionic activity coefficient of potassium, which was set equal to the mean activity coefficient of potassium chloride.

In general, the membranes are not ideally permselective and only a fraction  $\bar{T}_{\text{K}^+}$  of the current is carried by the potassium ions. Hence the potential between the silver-silver chloride electrodes equals:

$$E = (\bar{T}_{\text{K}^+}) \frac{RT}{F} \ln \frac{a_1^{\text{KCl}}}{a_2^{\text{KCl}}} = 2(\bar{T}_{\text{K}^+})E_0 = E_M + E_0 \quad (\text{XI})$$

where  $E_M$  is the membrane potential of the non-ideal membrane and hence:

$$\bar{T}_{\text{K}^+} = \frac{E_M}{2E_0} + 0.5.$$

Thus the average transference number,  $\bar{T}_{\text{K}^+}$ , of the potassium ions in the membrane, as defined by equation (XI), can be determined from the measurement of the potential  $E$ , provided the activities of the electrolyte in the solutions are known. The average transference number is the quantitative measure for the permselectivity of the membrane under the given conditions.

In general, it is found that the transference number of the exchangeable ion equals unity at low concentrations of the solutions and decreases with increasing solution concentration. This fact is due to the diffusion of electrolyte into the resin which causes a certain proportion of the current to be carried by the nonexchangeable ions.

If the Donnan concept is applied to the ion-exchange material as discussed in the previous section, and if the concentrations are so small that the activity coefficients are unity,

the membrane potential can be predicted from the capacity of the resin  $c_R$ , the concentrations of the electrolytic solutions on the two sides of the membrane,  $c_1$  and  $c_2$ , respectively, and the ratio of the mobilities  $m_+$  and  $m_-$  of the two ions in the membrane. Neglecting the osmotic pressure terms in the membrane equilibrium equations, the following expression for the membrane potential was obtained in the case of a 1-1 electrolyte (47, 49):

$$E_M = \frac{RT}{2F} \ln \frac{x_2 + c_R}{x_2 - c_R} - \frac{RT}{2F} \ln \frac{x_1 + c_R}{x_1 - c_R} + \frac{RT}{F} U \ln \frac{x_1 + U c_R}{x_2 + U c_R} \quad (\text{XII})$$

where

$$x_1 \equiv \sqrt{c_R^2 + 4c_1^2}, \quad x_2 \equiv \sqrt{c_R^2 + 4c_2^2}, \quad \text{and } U \equiv \frac{m_+ - m_-}{m_+ + m_-}$$

Usually the mean ionic activity coefficients of the electrolyte  $(\gamma_{\pm})^r$  and  $(\gamma_{\pm})^s$  in the resin and solution, respectively, cannot be assumed to equal unity, and equation (XII) has to be modified by substituting  $c_R(\gamma_{\pm})^r$  for  $c_R$ , and  $c(\gamma_{\pm})^s$  for  $c$  (9, 52). This is done under the simplifying assumption that  $(\gamma_{\pm})^s$  is constant throughout the membrane. An alternative derivation, based on the general flow equations in electrolytic systems, has been discussed by Schloegl (53, 54), and by Lange and Schuecker (54a).

The three terms in the expression for the membrane potential [equation (XII)] can be considered as the two "Donnan" potentials at the interfaces between the membrane and the solutions and the diffusion potential within the membrane. Combining equations (XI) and (XII), it is seen that the permselectivity of the membrane should decrease with increasing solution concentration and increase with increasing capacity,  $c_R$ , of the ion-exchange material. It is the latter property that makes the synthetic ion-exchange resins of high capacity particularly suitable as permselective materials. Hence considerable effort has been spent to prepare ion-exchange resins in the shape of membranes and to measure potentials across them.

Potential measurements across ion-exchange resins have been carried out in solutions of KCl, NaCl, LiCl, and HCl, using membranes made completely of ion-exchange materials (9, 39, 52, 55-61) and membranes containing ion-exchange resins and inert resinous binders (12, 62, 62a).

The main result of all these researches is that in dilute solutions the average transference number of the cations approaches, indeed, unity within a few per cent. Some results for the inhomogeneous membranes of Wyllie and Patnode are shown in Table V (62).

It is seen that, in dilute solutions of HCl, the response of the membranes to hydrogen ions is very similar to that of a glass electrode.

The measurement of potentials across membrane electrodes can be used to determine activities of sodium and other ions by the use of a modified form of equation (X) by methods analogous to the pH measurement with a glass electrode. As for the concentration range in which equation (X) is claimed to be valid, considerable differences are found in the literature for different types of membranes. Kressman (56) reported a linear relationship between membrane potentials and the logarithm of the ratio of the activities of the alkali metal ions up to activities of 2.0, and Wyllie and Patnode (62) state that the agreement between the mean potentials given by some of their membranes and the potential computed under the assumption of unit transference number for the cation

may be considered reasonably satisfactory in the case of 3.000*M* and 0.462*M* NaCl solutions, and fair in the case of 4.000*M* and 0.700*M* NaCl solutions.

Juda and coworkers (7) found for a phenolsulfonic resin membrane (Nepton CR-51) that the ideal membrane equation (X) was satisfied within seven per cent up to sodium chloride concentrations of the order of 0.1*M*. As the solution concentration increases, however, the discrepancies become appreciable. This may be compared to the potentials measured by Sollner (51) across permselective collodion membranes. He computed a cation transference number,  $T_+$ , of 0.971 from the membrane potential measured between potassium chloride solutions of 0.2*M* and 0.1*M* and, for 0.4 and 0.2 solutions,  $T_+$  was found to be 0.935. The specific resistance of the permselective collodion membranes is between ten and one hundred times higher than of the homogeneous Nepton CR-51 material.

In the evaluation of all these measurements, water transport across the membranes was neglected.

There also seems to exist a lower limit to the applicability of equation (X). Discrepancies were observed at solution concentrations lower than of the order of  $10^{-4}$ *M*.

TABLE V. Potentials obtained at 22°C using bonded Amberlite IR-100 and methyl methacrylate plastic and hydrochloric acid solutions of pH approximately 0.0 and 1.1\* (62).

Electrode No.	Comp. of membrane by weight %	Thickness of membrane mm	Mean emf obs mv	emf obs with glass electrode mv
H1	20 H Amberlite 80 Plastic	2.0	65.3 ± 0.1	64.3
H2	20 H Amberlite 80 Plastic	2.0	65.4	64.3
H3	20 H Amberlite 80 Plastic	2.0	63.9	64.3
Na4	25 Na Amberlite 75 Plastic	3.5	65.4	64.3
Na5	25 Na Amberlite 75 Plastic	2.5	65.4	64.3
Na6	25 Na Amberlite 75 Plastic	3.0	64.7	64.3

\* Reproduced by permission of the *Journal of Physical Chemistry*.

† Difference between potentials measured first in one hydrochloric acid solution and then in the other with a Beckman glass electrode and a saturated calomel reference electrode.

The use of cation-exchange membrane electrodes for the measurement of cationic activities is seriously limited by the interference of other cations. If more than one type of cation is present in the solution on one side of the membrane, the relationship between potential and activity of any particular ion is complex. In some cases, membrane electrodes may still prove useful, if properly calibrated, but, in general, their degree of specificity is low if compared to the specificity of the glass electrode for hydrogen ions.

Analogous results were obtained for anion-exchange membranes (8, 9, 60).

By measuring the membrane potentials as a function of the activities of the solutions on the two sides of the membrane, the mean activity coefficient ( $\gamma_{\pm}$ )<sup>r</sup> of the mobile ions in the resin can be determined from modified equation (XII), if the capacity of the resin is known. Bonhoeffer and coworkers (9, 52, 60) estimated the activity coefficients of different 1-1 electrolytes in different resins by this method.

Using some simplifying assumptions, they compared the exchange-equilibrium constants predicted from these potential measurements to the values found by experiment. For a cation-exchanger with strongly acid groups (Wofatit 21), the agreement was within the limit of error of the measurements. (The limit of error in the determination of ( $\gamma_{\pm}$ )<sub>r</sub> was estimated at 15 per cent.) For a polyfunctional cation-exchange resin with weakly acid groups (Wofatit 24) and a polyfunctional anion-exchange resin (Wofatit 35), equation (XII) cannot be expected to hold and, while the activity coefficients estimated from the membrane potentials predicted qualitatively which ions are preferred by the exchange-resin under given conditions, quantitative agreement with the exchange-adsorption data was no longer found. It was also established from the measurements that for KCl, NaCl, and LiCl the mobility ratio  $m_+/m_-$  in the exchanger is about the same as in aqueous solutions, although the absolute values of the mobilities are much lower.

A somewhat different method was used by Juda and collaborators (7, 8) to evaluate potential measurements across a cation-exchange membrane (Nepton CR-51) and an anion-exchange membrane (Nepton ARX-44), and to correlate them to conductivity data and to the amount of electrolyte in the membrane determined by direct analysis. The conclusion was reached that the exchange groups in Nepton CR-51 are strongly acid and in Nepton ARX-44 they are weakly basic.

#### Water Transport Across Ion-Exchange Membranes

In the previous considerations of this article, the water transport associated with the ion transport through ion-exchange materials has been neglected. Water can be transported through the ion-exchanger as hydration water of the mobile ions, which represents water strongly bound to the ions, and as water carried along with the ions and not tightly bound to them, viz., electroosmotic transfer of water. Any exact electrochemical theory of ion-exchange resins must take this phenomenon into account. A discussion of this effect, based on experiments with collodion membranes, has been presented by Schmid (40, 63-65).

When electric current passes through a solution of an electrolyte, a viscous drag is exerted on the solvent by both cations and anions. Since the force exerted by the migrating ions is equal but in opposite directions, no net transfer of solvent occurs except for the effect of the water of hydration. In an ion-exchange resin, however, one type of ions is immobile. The force exerted on the solvent by the mobile ions would not be counter-balanced if the solvent were to stay at rest and, therefore, the solvent moves in the same direction as the mobile ions and at a rate determined by the friction between itself and the ions and the resin matrix, respectively.

While the theory of electroosmosis in ion-exchange membranes has been discussed in considerable detail (64), and direct measurements made of the electroosmotic transfer of water across membranes of collodion (65) and other membrane materials, very few measurements have been reported for synthetic ion-exchange resins. According to Rosenberg (66) the water transport between very dilute solutions of sodium chloride across a Nepton CR-51 membrane in the sodium form is about 300 ml/equivalent of sodium ions. In other words, each sodium ion transports about seventeen water molecules.

This effect must be taken into account in the interpretation of ion-exchange membrane potentials and of resin conductivity data. If current is drawn from two silver-silver chloride

electrodes placed in two sodium chloride solutions of different activity which are separated by an ion-exchange membrane, sodium chloride is transferred from the concentrated solution to the dilute one. Since the electroosmotic transport of water is in the same direction, water is simultaneously transported from a solution more dilute with respect to water to a more concentrated one. The electroosmotic transport therefore decreases the ideal membrane potential. The general equations for the electromotive force which take self-transport into account have been developed and discussed by Scatchard (58). The complete expression for the membrane potential,  $dE$ , between two solutions of sodium chloride of activity  $a$  and  $a + da$  is

$$dE = \frac{RT}{F} [-d \ln a_{Na} + (T_{Cl} + 0.018m'_{Cl} T_w)d \ln a_{Na} a_{Cl}]$$

where  $T_{Cl}$  and  $T_w$  are the number of moles of chloride ion and of water transported per Faraday, and  $m'_{Cl}$  is the molality of the solution with respect to sodium chloride. The first term on the right side represents the contribution of the transport of sodium ions to the potential, the second that of the chloride ions in the resin, and the third is due to the electroosmotic transport of water.

The occurrence of electroosmosis explains why the values of ionic self-diffusion coefficients computed from the specific conductance by the Nernst-Einstein formula are lower than those measured directly from the spread of radioactive tracers. When the mobile cations migrate under the action of an electric field, their linear velocity with respect to the fixed anions is higher than with respect to the electroosmotic flow of water. Therefore, the measured conductance,  $k$ , is higher than the conductance,  $k^*$ , corresponding to a state where the water is at rest with respect to the fixed anions. When self-diffusion occurs in a resin, no electroosmosis takes place, and hence if  $k$  instead of  $k^*$  is used to calculate the self-diffusion coefficient by the Nernst-Einstein formula, the computed values are too high.

Since the electroosmotic permeability of an ion-exchange membrane (in ml water transported per volt and second),  $L_{EP}$ , is a measure of the frictional force between the water molecules and the resin through which they migrate, it is related to the hydraulic permeability,  $D_H$ , (in ml solvent passing through the membrane per second and pressure difference of one dekabar; 1 dekabar  $\equiv 10^7$  dynes/cm<sup>2</sup>) which also depends on this force. ( $D_H$  refers here to the permeability measured in the absence of a streaming potential.)  $L_{EP}$  is also related to the electrical conductance,  $L$ , (in mho) of the membrane, because the latter, in turn, is related to this frictional force. The relationship between electroosmotic permeability, hydraulic permeability, and conductance appears in the general equations for the flow of current,  $I$ , and water,  $V$ , through a membrane between two solutions to which both an electrical potential,  $E$ , and a pressure differential,  $P$ , are applied. It can be shown by elementary considerations (63, 64) or in a quite general manner by the methods of the thermodynamics of irreversible processes (67, 68) that the same membrane constant,  $L_{EP}$ , appears in both equations:

$$I = LE + L_{EP}P \quad (XIII)$$

$$V = L_{EP}E + D_H P \quad (XIV)$$

where  $I$  is the current through the membrane (amp),  $E$  the potential applied to it (volt),  $P$  the pressure difference between the two sides of the membrane (dekabar), and  $V$  the flow of water through the membrane (ml sec<sup>-1</sup>).

The first equation states that the current flowing through

the membrane is composed of two parts, namely, the regular current which is proportional to the applied electrical potential, and a convection current proportional to the pressure difference. The second equation states that the water flow through the membrane is composed of the regular flow, proportional to the pressure difference and the electroosmotic flow, proportional to the applied electrical potential. Each of these statements is almost self-evident, but it is important that the same constant,  $L_{EP}$ , appears in both equations.

Equations (XIII) and (XIV) are true for any membrane model. Schmid (40) has shown that if the membranes are considered as one-phase systems rather than a network of microscopic pores (sponge model), the following simple relation holds between  $L_{EP}$  and  $D_H$ :

$$L_{EP} = FAD_H \quad (XV)$$

where  $F$  is Faraday's constant (coul.eq<sup>-1</sup>) and  $A$  the molal resin capacity (eq. per ml water). It is assumed that the active groups in the resin are completely ionized and that their electrostatic interaction is negligible. If this is not so,  $A$  must be replaced by  $f_\lambda A$ , where  $f_\lambda$  is the conductivity factor.

By means of equation (XV) it is possible to obtain a rough estimate of the electroosmotic permeability of resinous membranes from their hydraulic permeability and vice versa, provided the molal resin capacity is known. Moreover, if the conductance of the membrane is known, all other electrokinetic properties such as streaming potentials and streaming currents can then be calculated by combination of equations (XIII), (XIV), and (XV).

It is known that the hydraulic permeability of commercial synthetic ion-exchange membranes is very low, but only few quantitative data are available. Rosenberg (66) reported that the specific hydraulic permeability<sup>4</sup> of Nepton CR-51 membrane in the sodium form at room temperature was  $2.3 \times 10^{-7}$  cm<sup>2</sup> dekabar<sup>-1</sup> sec<sup>-1</sup>. This value was obtained by measuring the flow of water through a membrane under a pressure differential but without applying an external short circuit between the solutions on the two sides of the membrane. It is much lower than the specific hydraulic permeability of the collodion membranes used by Schmid (63, 64). The capacity of the membrane was about 0.002 eq. per ml water. If it is assumed that the conductivity coefficient,  $f_\lambda$ , equals 0.5, which is a reasonable value at this molality, modified equation (XV) yields the value of 2.2 volts<sup>-1</sup>cm<sup>2</sup>sec<sup>-1</sup> for the specific electroosmotic permeability. Since the specific conductivity of the membrane was 0.008 mho cm<sup>-1</sup>, the time necessary to pass one Faraday was  $1.21 \times 10^7$  sec, and hence the amount of water transported was 265 ml per Faraday, while direct measurement of the electroosmotic transport gave a value of 300 ml (66). The agreement is rather good in spite of the crudeness of the estimate of  $f_\lambda$  and of the use of a permeability value uncorrected for the "electroviscous effect" (63), resulting from the absence of an external short circuit. (In these calculations ml and cm<sup>2</sup> were set equal.)

#### Practical Applications of Ion-Exchange Membranes

These researches provide the theoretical background for the application of ion-exchange membranes as ionic sieves which are able to screen out one charge-type of ions. The use of ion-exchange membranes for electrodialysis processes of this kind offers a number of promising possibilities. So far,

<sup>4</sup> The specific hydraulic permeability is defined as the flow of water (in ml sec<sup>-1</sup>) through a membrane cube 1 x 1 x 1 cm and per pressure difference of 1 dekabar.

only little work has been published on practical applications of these membranes, but it is believed that considerable effort is being expended in this field (69, 69a, 69b, 70).

For instance, salt removal from sea water or other brines can be effected by electrolysis of systems of the following kind:

Inert anode, solution	anion-ex- change membrane	middle chamber: sea water	cation-ex- change membrane	solution inert cathode
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If a current is passed, the anions and cations will move from the middle chamber to the anion and cation chambers, respectively, while almost no movement of anions from the cathode to the middle chamber or of cations from the anode to the middle chamber is possible, because of the selective permeability of the cation and anion-exchange membranes for cations and anions, respectively. Hence the sea water in the middle chamber is being demineralized.

Similar systems containing less permselective membranes had been used previously to produce electrolyte-free water from tap water (72, 73).

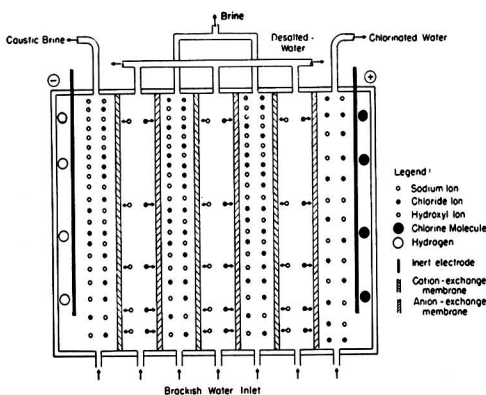
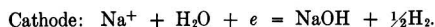
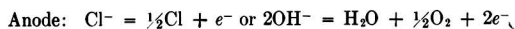


Fig. 7. Schematic representation of salt removal from brackish water in a multicompartiment electro dialysis cell containing ion-exchange membranes.

The thermodynamic minimum requirement of electrical energy to reduce the salinity of 1000 gal of sea water containing about 3.5 per cent dissolved salts by a factor of one hundred, i.e., to a drinking water level is about 2.5 kwhr. This value corresponds to the free energy of the dilution process and, therefore, refers to a completely reversible process. In practice, electrical energy is always lost by irreversible transformation into Joule heat and as a consequence of processes occurring at the electrodes. For instance, in a representative experiment, a magnetite anode and a nickel cathode were used, and the potential drop at the electrodes alone was found to be about three volts (73). A portion of the energy corresponding to this potential drop is required for the electrode reactions, in this case the following:



The rest is due to irreversible electrode processes which cannot be reduced below a certain minimum. It is hard to prepare completely reversible electrodes giving a sufficiently long period of useful service.

However, improved power economy can be achieved by

passing the current through a series of cells separated by alternating anion and cation-exchange membranes with electrodes only at the terminal points of the series (71) as shown in Fig. 7. In this case, the loss of energy at the electrodes per equivalent of salt removed from the salt water will be reduced to a minimum.

The diffusion of electrolytes into the membranes and electroosmotic water transport play an important part in the power economy of the process. Both reduce the efficiency, the first because it causes some ion transport from the concentrated into the dilute solutions, and the latter because it causes the flow of pure water from the fresh water into the brine compartments. Both effects decrease with increasing crosslinking of the membrane material, but the higher electrical resistance of highly crosslinked ion-exchange resins requires a compromise in the extent of crosslinking (74).

At relatively low production rates, practical energy requirements for this process have been estimated at 20-30 kwhr/1000 gal of fresh water produced (70, 71). The latter figure is only one-third that of the most efficient vapor compression units available. On the other hand, the initial investment may be considerable. Little is known about the stability of the membranes over a considerable period of time. The cost of the fresh water may be determined largely by the development of stable and sturdy membranes.

For the demineralization of waters of lower salinity than sea water, the economical prospects of this process seem attractive even at this stage. An idea about the power requirements and size of such units may be obtained from the following figures for a pilot model offered by one manufacturer (75).

A unit for the demineralization of 200 gal/hr of brackish water containing 2000 ppm (parts per million) of sodium chloride to a level of 400 ppm uses a power input of 0.6 kw. The size of the unit is 4 ft.<sup>3</sup>

Where fresh water and concentrated brine are available, the system shown in Fig. 7, operating in reverse, may be used for the production of direct current, utilizing the free energy of dilution of the brines (76, 77).

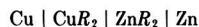
The potential  $E'$  of each cell unit consisting of a brine compartment, anion-exchange membrane, fresh water compartment, and cation-exchange membrane in series, is given by

$$E' = (T_+^c - T_+^a) \frac{RT}{F} \ln \frac{a_B}{a_S}$$

because the passage of one Faraday involves the reversible transfer of  $(T_+^c - T_+^a)$  moles of NaCl from the brine to the fresh water compartment.  $a_B$  and  $a_S$  are the activities of NaCl in brine and fresh water, respectively, and  $T_+^c$  and  $T_+^a$  the average transference numbers of the sodium ion through cation and anion membranes, respectively.

In practice,  $E'$  cannot reach high values, because at high values of  $a_B$  the membranes lose their permselectivity and  $(T_+^c - T_+^a)$  becomes small, while at low values of  $a_S$  the inner resistance of the cell is high. It remains to be seen if it is possible to achieve practical results by arranging in series a large number of such cells with very narrow spaces between the membranes, through which brine and dilute solutions flow.

It is also possible to obtain a resin analogue of the Daniel cell:



whose potential depends on the type of cation exchanger, R, used. Measured potentials were often higher than 1 volt

(18). Permselective diaphragms made of ion-exchange membranes can be used to advantage in primary electric cells. They prevent mixing of anolyte with catholyte, and yet offer little resistance to the passage of the current. Thus an anion-exchange resin membrane in the sulfate form was used to separate the zinc and copper sulfate solutions in a cell of the Daniel type (10a).

Continuous separations of ions in solution can be carried out using the membranes as "ionic sieves" in electro dialysis processes in which selective transmission of ions from one solution to another is desired. For instance, if a potential is applied to a cell containing mixed solutions of sodium and potassium salts separated by a membrane, enrichment of potassium in the cathode chamber will occur. This effect can be magnified by cascading a number of such cells as shown in Fig. 8 (78). This multistage system is analogous to a distillation column with the feeding stock entering at one of the middle plates and with reflux from the cathode chamber. The engineering calculations for such a column are very similar to those developed for stills.

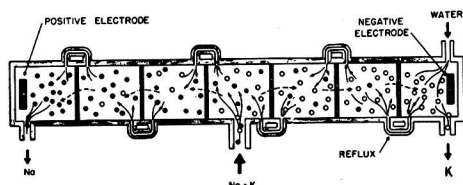


FIG. 8. Continuous separation of sodium from potassium by multistage membrane cell.

### Conclusion

Different aspects of the electrochemistry of both cation and anion-exchange resins lead to the conclusion that the solid polyelectrolyte model of the resins is essentially consistent with the electrochemical data. While solid in the gross physical sense, the wet resins act like solutions of electrolytes whose properties are modified by the binding of one charge type of ion to a macromolecular, immobile hydrocarbon matrix. It is reasonable to assume that the development of the electrochemistry of concentrated solutions will be associated with the development of ion-exchange resin theory. There is little doubt, however, that work on practical applications will make headway even before this is achieved.

### Acknowledgments

Thanks are due to Professors G. Scatchard and C. D. Coryell for many valuable discussions, and to Professor J. A. Beattie and Dr. M. R. J. Wyllie for their helpful suggestions. This work was partly supported by the Atomic Energy Commission and the Weizmann Institute Postdoctoral Fellowship.

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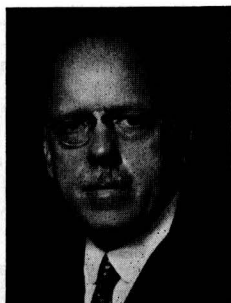
## Death of Dr. Colin G. Fink

It is with great regret that the JOURNAL records the death on September 16th of Dr. Colin G. Fink, 14th president and for 26 years secretary of The Electrochemical Society and editor of its TRANSACTIONS. A memorial service was held in the Chapel of Columbia University on October 9th.

Colin Garfield Fink was born in Hoboken, New Jersey, on December 31, 1881. After graduation from Columbia University in 1903, he went to Leipzig for graduate study. Here he received the Ph.D. degree with highest honors. Returning to America he joined the research staff of the General Electric Company. In 1917 Dr. Fink became chief chemist for the Chile Exploration Company and he went from this position, in 1921, to Columbia where he became head of the division of electrochemistry. Following retirement from active teaching in 1950, he was appointed emeritus professor of chemical engineering.

Dr. Fink joined The Electrochemical Society in 1907 and immediately became active in its affairs. He published many papers in the TRANSACTIONS over the years. He was elected president in 1918 and became secretary upon the death of Joseph W. Richards in 1921. Upon retirement from the latter office in 1947, Dr. Fink was made Secretary Emeritus of the Society. At a dinner given in his honor during the fall convention in October 1947, Dr. Fink was presented with a scroll in appreciation and grateful recognition of his great services to the Society. On that occasion his many students in all parts of the world presented him with a bound volume of their letters of greeting.

The professional career of Dr. Fink was threefold in character—scientist, educator, and executive secretary-editor. In each, his achievements were notable. Among his best-known research projects were those that led to ductile



COLIN G. FINK

tungsten for incandescent lamp filaments, an insoluble anode for the electrowinning of copper, an electrolytic process for the faithful restoration of corroded ancient bronzes, the development of hot dipped aluminum coatings, the electrodeposition of metals, and, in particular, a commercial process for chromium plating.

As teacher to a generation of students, the influence of Dr. Fink will endure for a long time. His infectious enthusiasm, insatiable curiosity, and energetic drive inspired all who came in touch with him. These qualities account for Dr. Fink's great popularity as a teacher. His students have become leaders in science and engineering in this country and abroad, both in academic and industrial circles.

Sharing the early optimism of the founders of this Society, Dr. Fink foresaw the important part that electrochemistry was to play in modern life. This led to his whole-hearted devotion to the purposes and the affairs of the Society. From early morning until late evening, every moment that could be spared from teaching and research was spent on Society matters. Not only secretarial correspondence, bookkeeping, financial reports, meeting arrangements, and Board meetings claimed attention, but

editorial problems, translations, revisions, and the styling of manuscripts for the printer were taken care of personally. At no time did Dr. Fink receive a salary or any other form of monetary compensation for his services. When presented with the \$1000 Acheson prize in 1933 he promptly returned it to the Society's Roebor Research Fund. A fierce loyalty to the Society and to the profession of electrochemistry seems to have urged him on. He admitted that "Our entire social life was centered around the Society." No one has ever been more intimately identified with the Society and no one ever made a greater contribution to its welfare than Dr. Fink. Without this generous devotion it is doubtful that the organization would have survived in 1921 and during the depression period of the early 1930's. It was the faith and loyalty of Dr. Fink that made continued existence possible.

Beyond the conduct of current affairs, Dr. Fink found time for constructive, longer range matters. Largely through his efforts the Acheson Medal, Weston Fellowship, and the Roebor Research funds were created. He had much to do with the establishment of sustaining membership and personally secured practically all of the first fifty sustaining members.

Among the many honors received by Dr. Fink were the Acheson Medal in 1933 and the Perkin Medal in 1934. He was the recipient of an honorary D.Sc. degree and was elected to honorary membership in The Electrochemical Society in 1946. He was the author of over 200 papers and held many patents.

Dr. Fink leaves a wife, Lottie Muller Fink, and two sons, Dr. Harold K. Fink of New York, and Frederick W. Fink of Columbus, Ohio. To them the Board of Directors has extended a resolution of sympathy on behalf of the Society.—RMB

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## DIVISION NEWS

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### Electronics—Instrumentation Symposium Scheduled for Chicago

The Instrumentation group of the Electronics Division will hold its third biennial symposium at the Chicago Meeting, May 2-6, 1954. Emphasis for this symposium will be placed on instrumentation of particular interest to the electronics industry.

Five copies of the abstract (not to exceed 75 words) should be sent to Society headquarters, 216 West 102nd Street, New York 25, N. Y., not later than January 15, 1954.

In addition, the 75-word abstract and a longer abstract of 1000-1200 words (2½-3 double-spaced pages) should be submitted to the Chairman of the Instrumentation Symposium, A. E. Martin, % Sylvania Electric Products Inc., Sylvania Center, Bayside, N. Y., as soon as possible, with a final deadline of January 15, 1954.

The extended abstract of about 1000 words is "printed, but not published" in a booklet which will be available, at cost, during the meeting. Abstracts of other Electronics Division papers (luminescence, screen applications, semiconductors, etc.) will also appear in this booklet.

Participation in the 1954 Instrumentation Symposium is cordially invited.

### Industrial Electrolytic Spring Meeting Plans

The Industrial Electrolytic Division is planning sessions at the Chicago Meeting of the Society, May 2-6, 1954. As outlined at present, the program of this Division will include a technical session with papers on industrial electrolysis, a business session and luncheon, and a round-table conference on "Compression of Halogen Gases" with special emphasis on the history of chlorine compressors and discussion of types of compressors in use at present. The Division further plans a joint symposium with the Rare Metals group of the Electronics Division and with members of the Electrodeposition Division on "Fused Bath Electrolysis."

Additional papers on any of the above subjects are being solicited.

Authors having material appropriate for these sessions 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 F. W. Koerker, Chairman, Industrial Electrolytic Division, The Dow Chemical Company, Midland, Mich., or notify the Vice-Chairman of the Division, A. R. Orban, Niagara Alkali Company, Niagara Falls, N. Y., as soon as possible and certainly no later than January 15, 1954.

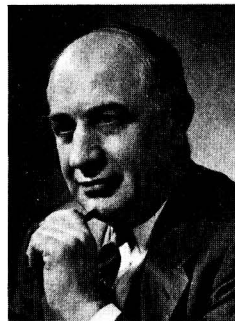
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## SECTION NEWS

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### Niagara Falls Section

The 1953-54 season of the Niagara Falls Section began September 9th at the Youngstown Yacht Club with an informal "mixer" meeting. The members and guests spent an enjoyable evening which included speed boat rides,



C. C. FURNAS

refreshments, a buffet supper, and an informal talk, "Trends in Modern Aircraft," by Dr. C. C. Furnas, Director of the Cornell Aeronautical Laboratory.

Dr. Furnas briefly reviewed the very rapid development of aircraft from the first flight, half a century ago, to the present status of a weapon carrier which, in the time of war, can make possible total global war. Dr. Furnas then described the trends in aviation for the next fifty years, predicting future changes in fuels, propulsion systems, speeds, helicopters, and commercial aircraft. The future of commercial aviation is very promising indeed, with an estimated air travel of the order of 100 billion passenger miles being predicted by the year 2000. The meeting was closed with a discussion of guided missiles and rockets.

J. E. CURREY, *Secretary*

### India Section

#### Symposium on Electrolytic Alkali-Chlorine

This symposium was given by the India Section during February 1953 and the papers presented there have been published in the *Bulletin of the India Section of The Electrochemical Society*, Volume 2, No. 3, 1953 (June Journal, page 166C).

\* \* \*

#### Symposium on Non-Ferrous Metal Industry

The National Metallurgical Laboratory, Jamshedpur, has arranged for a Symposium on "Non-ferrous Metal Industry in India" in January 1954. The topics for discussion cover extraction and refining, melting and foundry technique, thermal treatment and fabrication technique, powder metallurgy, protective coatings, expansion of the industry, economics.

T. L. RAMA CHAR

### International Council for Electrodeposition

The International Council is making plans for the International Conference of 1954 to be held in London, April 21 to 24. Participation by overseas delegates is anticipated, including a strong contingent of scientists and technicians from the States. The Council hopes to organize a special session to discuss the latest American practice in electrodeposition.

#### William Blum To Be Honored

Dr. William Blum has been invited by the Council of the Institute of Metal Finishing to give the Hothersall Memorial Lecture for 1953-54 on the eve of the International Conference. This lecture will be under the auspices of the I.M.F. Dr. Blum is well-known for his numerous researches in the field of electrodeposition covering many years of active study of electrochemical processes and problems.

#### Aims of the Council

At its first, recent meeting, the International Council considered such questions as the mutual interchange of publications between countries, and further concluded that such questions as universal standards of electroplating and universally-agreed nomenclature and definitions of terms used in electrodeposition should be explored and would well repay future study.

### Fifth Dinner of Chemical Profession in Cleveland

The fifth annual dinner of The Chemical Profession in Cleveland will be held at the Hollenden Hotel on November 11. Professor Harold C. Urey, of the Institute of Nuclear Studies, University of Chicago, will speak on "Cosmic Chemical Engineering." The dinner is sponsored jointly by the Cleveland sections of the American Chemical Society, Alpha Chi Sigma, American Institute of Chemists, The Electrochemical Society, and The American Institute of Chemical Engineers.

### Conference on Luminescence

The Electronics Group of the Institute of Physics is organizing a conference on luminescence, with particular reference to solid inorganic phosphors, to be held in Cambridge, England, from April 7 to 10, 1954. Communications regarding the meeting should be sent to Dr. S. T. Henderson, The Institute of Physics, 47, Belgrave Square, London, S.W. 1, England.

### PERSONALS

JAMES H. MOORE has been named general manager of Vacuum Metal Corporation, Cambridge, Mass. Mr. Moore was previously with the National Research Corporation in Cambridge.

HUGH V. ALESSANDRONI has been promoted from manager of research to assistant technical director, National Lead Company, Titanium Division, Perth Amboy, N. J.

THOMAS HAZEN, Bakelite Company, Division of Union Carbon & Carbide Corporation, Bloomfield, N. J., is now located at the Bakelite plant in Bound Brook, N. J.

MORRIS FEINLEIB, Division of Metallurgical Research, Kaiser Aluminum & Chemical Corporation, Spokane, Wash., has transferred to the Permanente Research Laboratory at Permanente, Calif.

A. F. GARCIA, Kaiser Aluminum & Chemical Corporation, Chalmette, La., has been transferred to the company's Oakland, Calif., office.

MILW. KREJCI, formerly of Reconstruction Finance Corporation, Tin

Division, Washington, D. C., is now engaged in consulting metallurgical work. After December 1 he will be located in Newark, Del.

CHRISTIAN AALL, Development Director, Phosphate Division, Monsanto Chemical Company, is now at the company's St. Louis, Mo., office. Dr. Aall had been at Anniston, Ala.

RUSSELL H. AXSOM, Michigan Chrome & Chemical Company, Detroit, has been appointed Vice-President of the Company. He was general manager.

H. A. CATALDI, formerly with the Standard Oil Company in Chicago, is now with the General Electric Company in Schenectady, N. Y.

JOSEPH L. COLLINS has opened an office as consulting engineer in the Statler Building, Boston, Mass. Mr. Collins was previously connected with Aerovox Corporation, New Bedford, Mass.

NORMAN H. KIRK, Works Manager, Park Bros., Ltd., Blackburn, Lancs, England, has joined the Bankfield Works in Blackburn, England.

ROBERT A. OLER of Solvay Process Division, Allied Chemical & Dye Corporation, Syracuse, N. Y., has transferred to the company's plant at Moundsville, W. Va.

CLARENCE G. OZAR of Cowles Chemical Company has been transferred from Cleveland, Ohio, to Syracuse, N. Y.

CARLTON M. DEAN, Monsanto Chemical Company, St. Louis, Mo., has been named manager of the engineering sales department of the company's Organic Chemical Division. Mr. Dean has been associated with Monsanto since 1917.

THOMAS M. RODGERS, Hanson-Van Winkle-Munning Company, Matawan, N. J., was appointed sales representative for the territory south of Wilmington, with headquarters in Baltimore. Mr. Rodgers previously served the company in eastern Pennsylvania.

S. KRISHNAMURTHI, chemist at the Indian Telephone Industries, Ltd., Bangalore, India, has been elected an Associate of the Royal Institute of Chemistry, London.

### NEW MEMBERS

In September 1953, the following were elected to membership in The Electrochemical Society:

#### Active Members

- JAMES H. BATTLE, National Lead Research Labs., 105 York St., Brooklyn, N. Y. (Corrosion)
- CHARLES R. BRUMMETT, Acheson Plant, National Carbon Co., Niagara Falls, N. Y. (Industrial Electrolytic)
- ARTHUR A. CLINE, Great Lakes Carbon Corp., mailing add: Rt. 2, Box 19-D, Morgantown, N. C. (Electrothermic)
- STANLEY M. DAVIS, American Cyanamid Co., Calco Chemical Division, Bound Brook, N. J. (Electro-Organic and Theoretical Electrochemistry)
- PHILIP B. DETTMER, Cobalt Chemicals Ltd., Cobalt, Ont., Canada (Electrothermic and Industrial Electrolytic)
- ROBERT L. DILLON, General Electric Co., mailing add: 623 Cottonwood, Richland, Wash. (Corrosion)
- JOHN L. EVERHART, Materials & Methods, 330 W. 42 St., New York, N. Y. (Corrosion and Electrodeposition)
- DANIEL R. FRANKL, Sylvania Electric Products Inc., Physics Labs., Bayside, N. Y. (Electronics)
- JAMES F. HUNT, Great Lakes Carbon Corp., mailing add: 200 Park St., Morgantown, N. C. (Industrial Electrolytic)
- HILLARD J. JENDRZYNSKI, General Motors Corp., Research Lab. Div., 485 W. Milwaukee, Detroit, Mich. (Electrodeposition and Theoretical Electrochemistry)
- MYER KRULFELD, Metallurgy Div., Naval Research Laboratory, Washington, D. C. (Corrosion, Electrodeposition, and Theoretical Electrochemistry)
- MALCOLM McLOUD, United States Rubber Co., 1230 Sixth Ave., New York, N. Y. (Battery and Electric Insulation)
- ARTHUR E. MIDDLETON, Battelle Memorial Institute, Columbus, Ohio (Electronics)
- JAMES L. MILLER, National Carbon Co., mailing add: 8465 Usher Rd., Olmsted Falls, Ohio (Corrosion and Industrial Electrolytic)
- JOHN W. PEARCE, S. C. Johnson & Son, mailing add: 5106 Wind Point Rd., Racine, Wis. (Electro-Organic)
- JOHN J. STOKES, JR., Aluminum Co. of America, mailing add: Station St.,

Box 212, Unity, Pa. (Battery and Industrial Electrolytic)

#### Reinstatement

EDWIN M. SHERWOOD, Battelle Memorial Institute, Columbus, Ohio (Electrothermic)

#### Associate Members

KEITH G. BLANTON, Naval Ordnance Laboratory, mailing add: 1444 Kana-wha St., Apt. 101, Hyattsville, Md. (Battery)

NORMAN C. CRAIG, Harvard University, mailing add: 6513 Barnaby St., Washington, D. C. (Theoretical Electrochemistry)

VAUGHN S. HARRIS, Owens-Corning Fiberglas Corp., Research & Dev. Labs., Newark, Ohio (Battery)

SUNDARESA SOUNDARARAJAN, General Chemistry Dept., Indian Institute of Science, Bangalore, India (Electro-Organic)

#### Student Associate Members

MYRON O. DAVIES, Western Reserve University, mailing add: 13436 Harlan Ave., Lakewood, Ohio (Battery and Theoretical Electrochemistry)

ROBERT C. GRIFFIS, Western Reserve University, mailing add: 25340 Lakeshore Blvd., Euclid, Ohio (Electrodeposition and Theoretical Electrochemistry)

ROBERT S. JOHNSON, Dept. of Chemistry, Ohio State University, Columbus, Ohio (Electro-Organic)

ROBERT W. PENN, Western Reserve University, mailing add: 2060 Cornell, Cleveland, Ohio (Electrodeposition and Theoretical Electrochemistry)

FRANK L. SAUNDERS, Western Reserve University, mailing add: 9805 Manor Ave., Cleveland, Ohio (Theoretical Electrochemistry)

ROMEO R. WITHERSPOON, Western Reserve University, mailing add: 11215 Wade Park Ave., Cleveland, Ohio (Battery)

J. Vernon at the Chemical Research Laboratory, Teddington, England, devised a passivity test for low alloy steels which might well be improved by the use of impulsive current.

A particular difficulty of accelerated corrosion tests of the intermittent spray type seemed to be that of correctly placing in an order of merit those steels (e.g., the chromium bearing steels) which depend for their resistance upon an inherent tendency to passivity. It was found that such steels became passive in different strengths of nitric acid and the behavior of a steel in a critical concentration of acid enabled a correction to be applied which was successful in bringing the results into line with those found on normal atmospheric exposure.

The steel, after the nitric acid dip, was plunged into sodium carbonate solution. Timing and temperature were very critical and the test was some what "messy." The use of impulsive currents might result in a far more elegant test.

JOHN A. LEWIS  
Widnes, Lancashire,  
England

altered to include new knowledge, to amplify certain chapters dealing with subjects that are of great topical interest, and to correct typographical errors. No attempt has been made to describe in detail the new techniques of analytical chemistry such as polarography, chromatography, flame photometry, mass spectrometry, etc., for this is not a book of special techniques, but one devoted primarily to separations and reactions that are fundamental to analytical chemistry.

The chapters on niobium and tantalum, tin, and the platinum metals have been entirely rewritten to bring them up to date, but because of space limitations no attempt has been made to expand the chapter on uranium in proportion to the new material made available in the last decade.

The portion of the 1929 book on Silicate and Carbonate Rock Analysis has been retained fundamentally unchanged, but the part that dealt with the Analysis of Soda-Lime Glass, Bauxite, and Refractories has been omitted to permit the introduction of new material throughout the book without increasing it to an unwieldy size.

The book is well bound and printed in "easy to read" type. Altogether this is a very welcome addition to the analyst's library.

C. L. LUKE

## BOOK REVIEWS

APPLIED INORGANIC ANALYSIS (2nd ed.) by W. F. Hillebrand and G. E. F. Lundell; second edition revised by G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, 1034 pages. John Wiley & Sons, Inc., New York, and Chapman Hall, Limited, London, \$15.00.

Those of us to whom Applied Inorganic Analysis is an indispensable reference text are, I am sure, profoundly grateful to have this revision of Hillebrand and Lundell's monumental work. It is doubtful whether any other published text has been as valuable to the practicing analytical chemist in the past two decades as has this one. Its value lies in the fact that it is a critical summation of the important methods of analysis of metals rather than a comprehensive, noncritical accumulation of methods. The authors have "separated the wheat from the straw," as it were, and in doing so have performed an invaluable service for their fellow analysts.

In the present revision, the basic value and the elegance of presentation of the 1929 edition have been preserved. At the same time, the text has been

TEXTBOOK OF QUANTITATIVE INORGANIC ANALYSIS, 3rd Ed., by I. M. Kolthoff and E. B. Sandell. The Macmillan Company, New York, 1952. xv plus 759 pages, \$6.50.

The third edition has been expanded somewhat. The authors have added the Bronsted theory of acid and bases, a discussion of separation by coprecipitation, and brief description of some physical methods, namely, flame photometry, fluorescence and radioactivity measurements, mass spectrometry, Raman spectrography, and x-ray diffraction and absorption.

The sections on organic reagents, chromatography, and spectroscopy have been expanded, and the sections on indeterminate errors and colorimetry and spectroscopy revised. In some chapters problems have been added or changed. One procedure from the revised edition has been omitted and a procedure for fluorine in rocks added.

The format has been changed to provide a better appearance. This new format is noticeably harder to read. The lines are longer and the type is larger than in the revised edition.

## LETTER TO THE EDITOR

### Iron Passivation in Nitric Acid

Dear Sir:

S. Aronow, in his letter on this subject in the April issue of your JOURNAL, called attention to the effect of a current pulse on passive films. The undersigned, when working with W. H.

The book remains a very useful reference book for instructors and students. It is doubtful whether many freshman chemistry courses enable students to use this book as a text in their second year.

PAUL D. GARN

## RECENT PATENTS

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

June 23, 1953

Cox, G. C., 2,643,222, Method of Cathodically Descaling and Electrode Therefor

Notvest, R. W., 2,643,223, Apparatus for Electrolytic Analysis

Niccoli, P., 2,643,224, Ozonizers  
Jones, H. F., and Colby, H. R., 2,643,225, Electroplating Rack

Salauze, J., 2,643,276, Negative Electrode for Alkaline Storage Batteries and Method of Manufacturing the Same

Falkenthal, E. E., 2,643,277, Photo-voltaic Cell

Simpson, A. W., 2,643,278, Dry Cell

Bradley, J. C., 2,643,279, Separator Protector

June 30, 1953

Fischer, J., 2,643,959, Process for the Protective Treatment of Iron

Neish, R. A., 2,643,975, Method of Lead Coating a Ferrous Article

Hamister, V. C., 2,644,020, Graphization of Carbon Articles

Moulton, J. D., Schweitzer, E. F., and Briggs, T. R., 2,644,022, Alkaline Storage Battery with Negative Iron Electrode

Rasch, C. H., 2,644,023, Storage Battery Paste With Amino Dye as Ion Exchange Expander

Schumacher, E. A., and Heise, G. W., 2,644,024, Anode Assembly for Primary Galvanic Cell

Dunham, L. R. S., 2,644,025, Air-Depolarized Primary Cell

July 7, 1953

Bonn, T. H., and Wendell, D. C., Jr., 2,644,787, Electrodeposition of a Magnetic Coating

Shenk, W. J., Jr., 2,644,788, Electrodeposition of Nickel

Zinc

Cadmium

Germanium

Gallium



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Shenk, W. J., Jr., 2,644,789, Electrodeposition of Nickel

Tapke, K. W., 2,644,851, Thermocouple

Dunlap, W. C., Jr., 2,644,852, Germanium Photoceel

July 14, 1953

Herres, S. A., and Redden, T. K., 2,645,575, Chromium-Nickel Titanium Base Alloys

Madorsky, S. L., and Brewer, A. K., 2,645,610, Process for the Separation of Isotopic Ions

Axtell, W. G., 2,645,611, Method of and Bath for Electrolytic Polishing

Taylor, R. D., 2,645,612, Sacrificial Anode

Walton, H. F., 2,645,635, Method of Regenerating Electrolytic Polishing Solutions

Arvin, M. J., 2,645,675, Thermoelectric Generator and Method for Production of Same

Emériat, R., 2,645,676, Method of Assembling and Insulating Flat Dry Cells

Morin, F. J., 2,645,700, Semiconductor of Mixed Nickel Manganese and Iron Oxides

Kerridge, F. E., Belham, M., and

Pearce, G., 2,645,701, Electrical Resistor and Resistance Elements Therefor

July 21, 1953

Dean, R. S., 2,646,396, Method of Making Electroformed Articles

Wean, R. J., 2,646,397, Electroplating Zinc Using Titanium Containing Electrolyte

Henderson, H. P., 2,646,398, Electroprocessing Apparatus

Herold, V., 2,646,454, Process for the Manufacture of Battery Electrodes and the Resulting Electrodes

Jeannin, R. A. A., 2,646,455, Electrolytic Cell and Battery

Jacquier, P. A. C., 2,646,456, Fabrication of Storage Battery Plates

Jacquier, P. A. C., 2,646,457, Electrode for Alkaline Batteries

Walz, H. P. H., 2,646,458, Galvanic Cell

Gill, W. L., 2,646,459, Electric Storage Battery Venting System

July 28, 1953

Homer, H. H., 2,647,066, Phosphor Suspension and Method of Applying  
Williams, P. D., 2,647,067, Electron Emitter for Electron Tubes

Burnham, J., 2,647,079, Production of Insulated Condenser Electrodes

Joyce, R. M., 2,647,080, Light-Stabilized Photopolymerization of Acrylic Esters

Doering, W. v. E., and Knox, L. H., 2,647,081, Photochemical Preparation of Tropilidenes

Kent, D. W., 2,647,082 Electrolytic Cells of the Tank Type

Homer, H. H., 2,647,086 Methods of Phosphor Manufacture

Fortney, D. F., 2,647,087 Improved Calcium Fluorophosphate Phosphor Containing Aluminum

Guerry, W. R., 2,647,153 Protector Skid for Thermocouples

Rupp, J. L., Diekover, M. W., Willihnganz, E., and Snyder, A. H., 2,647,154, Storage Battery

Dyer, C. A., 2,647,155, Primary Electrolytic Cell or Group of Cells

Booth, F., 2,647,157, Electrical Storage Battery

Booth, F., 2,647,158, Method of Making Acid Resisting Microporous Material for Storage Battery Separators

Lighton, L. E., 2,647,159, Storage Battery Filling and Venting Structure

Brown, B. B., 2,647,216, Dispenser Cathode

Foulke, T. E., 2,647,217, Electric Discharge Lamp

## RESEARCH TEAM NEEDED

**NOW FORMING RESEARCH TEAM** to continue classified development of new chemical process. This group to possess a sound background in physical chemistry, physics, inorganic and analytical chemistry, theoretical electrochemistry, physics of metals, and chemical engineering.

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Chemical engineers

The personnel in this team should have the ability to reduce complex problems to simple principles, to produce not only research papers but to achieve practical results. A strong theoretical background, ingenuity, perception, versatility, and the capacity for independent, creative thinking are more essential than experience.

Results of the research will be reduced to commercial production. This is an outstanding challenge and an opportunity for qualified people to advance with the growth of this process in a small company.

Immediate attention will be given and replies made to all applications which state full details of training, experience, scholastic standing, references, and salary required. Correspondence kept in confidence. Location: Detroit. *Reply to Box A-249.*

Require CHEMIST qualified as STENOGRAPHER. 70% analytical work, 30% of time in library research, record keeping, correspondence, purchasing, and invoicing. State experience and salary required. *Reply to Box A-250.*

Ludvika, A. A., 2,647,226, Dry Rectifier Valve Plate

Lacey, W. M., 2,647,227, Dry-Plate Rectifier

August 4, 1953

Cook, N. E., and Norteman, S. L., 2,647,304, Process of Terne Coating Metal and Terne Coated Product

Cook, N. E., and Norteman, S. L., 2,647,305, Process of Tight Coat Hot Dip Galvanizing and Hot Dip Galvanized Product

Perl, M. L., and Elliott, J. R., 2,647,841, Preparation of Luminescent Screens

Goffredo, D. L., 2,647,864, Etching Process

Freud, H. M., 2,647,865, Brightening Aluminum and Aluminum Alloy Surfaces

Brown, H., 2,647,866, Electroplating of Nickel

Schaltegger, H., 2,647,867, Process for Production of Cholesteryl Esters Brominated in Position 7

Dean, F., 2,647,868, Color Removal from Esters

## LITERATURE FROM INDUSTRY

**HIGH VACUUM PUMPS.** Two Kinney midget vacuum pumps are described and illustrated in a 4-page bulletin, featuring high pumping speed; low absolute pressures to 0.2 micron; small, standard motors; rugged construction; quiet operation; no discharge oil vapor; automatic lubrication: compact, entirely self-contained; light weight, easily portable. Model CVM 3153, smallest pump in the Kinney line, is specially designed for laboratory projects, industrial installations, refrigeration service applications, and wherever a very compact pump of high pumping speed is required. Widely used alone or as a fore pump for small diffusion pumps. Efficient mechanical seal prevents oil seepage at the main drive shaft and excludes atmospheric air. Model CVM 3534 has high pumping speed and dependability designed for small industrial applications, and research and processing operations. Minimum attention required. Double rotary shaft seal with independent oil reservoir prevents atmospheric air leakage into the pump. Kinney Manufacturing Co.

P-157

**SONICLEAN PROCESS.** A special technical folder illustrates and describes the

new Detrex Soniclean Process, the application of ultrasonic energy for the cleaning of metal parts. It can be applied to nonabsorbent materials such as metals, glassware, and molded products; removes iron oxide residues to a degree previously not obtainable; and quickly removes soils from cavities, shallow indentations, small holes, interiors of hypodermic needles, and other precision finished surfaces. Detrex Corp. P-158

**THERMOCOUPLE TABLES.** New reference tables for iron-constantan thermocouples, covering a very broad range—from  $-310^{\circ}$  to  $+1600^{\circ}\text{F}$ —constitute an important step toward uniformity in this field. Recommended by the Scientific Apparatus Makers of America for adoption as a tentative standard. National Bureau of Standards. P-159

**RUBBER TUBING CHART.** A rubber tubing wall chart has been designed for maximum convenience and instant reference for use in storerooms and laboratories. Includes 18 actual-size illustrations of amber and black tubing, giving inside and outside dimensions, physical properties, and prices. Arthur S. La Pine & Co. P-160

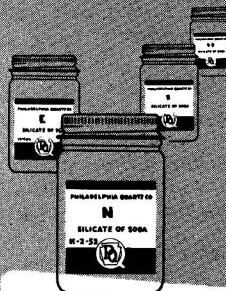
**GUIDE OF TESTING INSTRUMENTS.** A new 16-page buyer's guide provides data on such instruments as hook-on volt-ammeters, hook-on wattmeters, hook-on power-factor meters, portable recorders, voltmeters and ammeters, phase-sequence indicators, hand pyrometers, surface roughness scales, insulation-resistance meters, and others. Includes application data, features of each instrument, and prices. General Electric Co. P-161

**THERMAL CONDUCTIVITY UNITS.** Illustrated bulletin is available on Gow-Mac thermal conductivity cells. Contains information on specifications, applications, sampling, accuracy, repairs, etc. Gow-Mac Instrument Co. P-162

**SIMPLIFIED RECORDING POTENTIOMETER.** A new booklet fully illustrates and describes all features of the simplified Weston Recording Potentiometer, which is of completely new design with all parts interchangeable, with a universal slide wire that never needs changing, and which permits chart speeds to be changed on-the-line by a simple screwdriver adjustment. Weston Electrical Instrumental Corp. P-163

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**TV PICTURE TUBE COMPONENTS.** Tungsten and chemical components for television picture tubes are described in a 4-page booklet. Also described are screen phosphors, potassium silicate for screen settling, tungsten wire for cathode heaters, triple carbonate cathode coatings, stranded tungsten coils, and filaments for vacuum metallizing. Sylvania Electric Products Inc. P-164

**ACID-PROOF COATINGS.** New bulletin covers DURO-KOTE acid-proof coatings. These materials give the highest type of vinyl and butadiene styrene acid-proof resin protection against acids, alkalis, and many solvent actions. Planned primarily as acid-proof and alkali-proof maintenance paints useful in metal finishing, chemical, synthetic fiber, textile dye house, tannery, coal mine, metallurgical and electrometallurgical, and food plants. Electro Chemical Engineering & Mfg. Co. P-165

**DIAL THERMOMETERS.** A new 16-page, illustrated bulletin describes dial thermometers for long distance measurement. It emphasizes the variety of ranges, and the bulbs, tubing, and accessories available, and provides

complete data on temperature indicators of the vapor pressure and gas pressure types. The Foxboro Co. P-166

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 25, N. Y.

Please print your name and address plainly.

## NEW PRODUCTS

**MASS SPECTROMETER.** A new mass spectrometer designed to meet process instrumentation requirements in the gas, petroleum, pharmaceutical, and chemical fields has been announced. The new instrument uses the principle of ion resonance. In addition, a sample inlet system allows direct connection to a stream or process line, thus permitting continuous sample introduction. General Electric Co. N-28

**CRC DIODE TESTER.** A rugged, precision instrument for testing both

## ADVERTISERS' INDEX

Bell Telephone Laboratories	292C
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Lea-Ronal, Incorporated	Cover 3
Eagle-Picher Sales Company	321C
Philadelphia Quartz Company	323C
Rapid Electric Company	294C
E. H. Sargent & Company	290C

dynamic and static characteristics of crystal diodes has been developed. The new CRC Diode Tester (Model 136) tests both forward and back characteristics, indicating how the diode will perform before mounting it in the circuit. Can also be used for periodic circuit checks to detect potential diode failures before they occur. Is adaptable to high speed, volume testing, and operates on 115-volt, 60-cycle current, using 100 watts or less. Computer Research Corp. N-29

**NEW TEMPERATURE LIMITED DIODES.** Two new tubes have been added to the line of "Kalotron" diodes. These diodes have temperature limited emission characteristics where the anode current is a direct function of filament voltage. Due to the use of a pure tungsten filament, the specified ratings are maintained throughout the normal life of the tube. Thermosen, Inc. N-30

## EMPLOYMENT SITUATION

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# The Electrochemical Society

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Address all correspondence to the Editor,  
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FORM

**Manuscripts** submitted for publication should be in triplicate to expedite review. They should be typewritten, double-spaced, with 2½–4 cm (1–1½ in.) margins.

**Title** should be brief, followed by the author's name and his business or university connection.

**Abstract** of about 100 words should state the scope of the paper and give a brief summary of results.

ILLUSTRATIONS

**Drawings** will be reduced to column width, 8 cm (3¼ in.), and after reduction should have lettering at least 0.15 cm (⅙ in.) high. Original drawings in India ink on tracing cloth or white paper are preferred. Curves may be drawn on coordinate paper only if the paper is ruled in blue. All lettering must be of lettering-guide quality. See sample drawing on reverse page.

**Photographs** must be glossy prints and mounted flat.

**Captions** for all figures must be included on a separate sheet. Captions and figure numbers should not appear in the body of the figure.

**General**—Figures should be used only when necessary. Omit drawings or photographs of familiar equipment. Figures from other publications are to be used only when the publication is not readily available, and should always be accompanied with written permission for reprinting.

REFERENCES

Literature and patent references should be listed at the end of the paper on a separate sheet, in the order in which they are cited. They should be given in the style adopted by *Chemical Abstracts*. For example:

R. Freas, *Trans. Electrochem. Soc.*, **40**, 109 (1921).

H. T. S. Britton, "Hydrogen Ions," Vol. 1, p. 309, D. Van Nostrand Co., New York (1943).

H. F. Weiss (To Wood Conversion Co.), U. S. Pat. 1,695,445, Dec. 18, 1928.

UNITS OF MEASUREMENT

Metric units should be used throughout but, where desirable, English units may be given in parentheses.

Corrosion rates in the metric system should preferably be expressed as milligrams per square decimeter per day (mdd), and in the English system as inches penetration per year (ipy).

As regards algebraic signs of potentials, the standard electrode potential for  $\text{Zn} \rightarrow \text{Zn}^{++} + 2e$  is negative; for  $\text{Cu} \rightarrow \text{Cu}^{++} + 2e$ , positive.

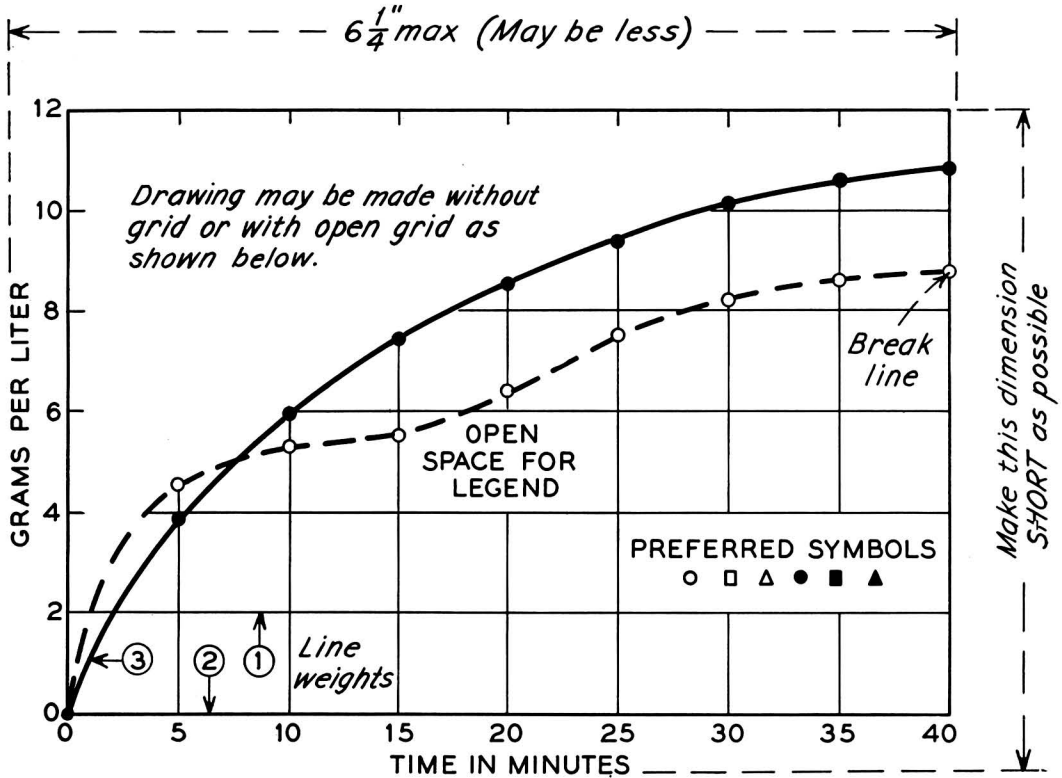
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