ELECTROLYSIS OF CHROMIC ACID SOLUTIONS CONTAINING HYDROFLUOSILICIC ACID

Thesis for the Degree of M. S.

Kurt Kannowski

1937

Chromic acid
Hydrofluosilicic acid
(New)
Make up in Desk file (mgt)

Title

Chemistry

ELECTROLYSIS OF CHROMIC ACID SOLUTIONS CONTAINING HYDROFLUOSILICIC ACID

by

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A THESIS

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Chemistry Department
East Lansing, Michigan

1937

Chromium is electrodeposited from baths containing chromic acid and small amounts of sulphate or hydrofluorosilic acid and a variable concentration of tri valent chromium. The latter is derived from the partial reduction of the chromic acid. When Faraday made his famouns investigation on the electrolysis of aqueous solutions, he and his contemporaries did not fail to notice that complications will often arise, not only at the anode, but also - and perhaps more commonly - on the cathode. These purely chemical complications are caused by side reactions, due to the new products formed on the electrodes and the changes which occur in the composition of the solution in the immediate neighborhood of the cathode under the influence of the current.

Liebrisch[1] states that these chemical reactions can arise in two ways: first, the electrolyte may react with the metal of the cathode, even when no current is flowing, or second, - and this is the more important case - the pH value of the solution may increase near the cathode owing to passage of current, thus producing complexes of a colloidal character in the solution, which are catephoretically conducted to the cathode. The increased hydroxyl ion concentration can give rise to the formation, on the surface of the cathode, of basic salts or hydroxides of the metal. An increase of polarisation follows in consequence of an increased transfer resistance, together with a larger consumption of energy for cleaning the cathode by chemical reduction or mechanical removal of the products by the hydrogen bubbles

leaving the surface. All of the above effects have a direct influence on the form of the metallic deposits. Since the current efficiency of the process for the electrodeposition of chromium depends on the metallic deposit all variables effecting the current efficiency are of importance. The effects of such factors as current density, temperature, and concentration on the current efficiency have been studied for the sulphate bath by D. T. Ewing, J. O. Hardesty and Te Hsia Koa[2]. The effect of the same variables of current density, temperature and concentration for hydrofluosilic acid baths on the current efficiency is reported in the following work.

APPARATUS AND MATERIALS.

The apparatus with the exception of some changes is the same as that used by J. O. Hardesty[2].

Diagram 1 shows the apparatus used. A porous cup (J) separated the anolyte from the catholyte. Sheet lead (10 x 17.5 cm.) bent to fit the cup loosely was used for the anode. The cathode (L) was a steel plate, (.1 sq. ft.) copper and nickel plated with a mirror finish. The plate is fastened by means of a small bolt to a heavy copper holder (1 cm. wide) which is insulated with an acid resisting lacquer. The holder is bent in a V-shape to keep the plate under the funnel (K). In series with the chromic acid cell is a carbon resistance (R), 30 ampere ameter (A), a copper coulometer (H), a switch (T) and the connection to 15 volt D. C. line. Across the cell is a 30 vole voltmeter ( ).

The solutions of varying concentrations consisted of

c. p. commercial chromic anhydride and hydrofluosilicic acid (29.8%).

Constant temperature was maintained within .5° C of each determination during the experiment. The cell was partially immersed in a sixteen gallon aquarium of water. The temperature was raised by means of a resistance heating coil, and lowered by a copper cooling plate.

The flask (A) has a calibrated capacity of 537.35 cubic centimeters. This capacity includes both tubes, (x) and (y) to the marks indicated by (O) on the drawing. Stopcocks, (B), (F) and (E) are of pyrex. The manometer (mn) is attached to the leveling tube (S). The jar, (Z), surrounding flask (A) is a constant temperature bath so arranged to determine the temperature of the collected gas.

The coulometer consisted of a four liter jar with a copper cathode (36 x 18 cm.) hanging between two copper anodes. The coulometer solution is composed of 1000 parts by weight of water, 150 parts of copper sulphate, 50 parts of concentrated sulfuric acid and 50 parts of alcohol.

EXPERIMENTAL PROCEDURE.

While procuring data for this report 222 determinations have been made. All of this data has been recorded, but some has been discarded as unreliable because of temperature changes during the determination. Other data will not be used because it has no direct bearing on the principles to be discussed.

Since the accuracy of the determinations depended

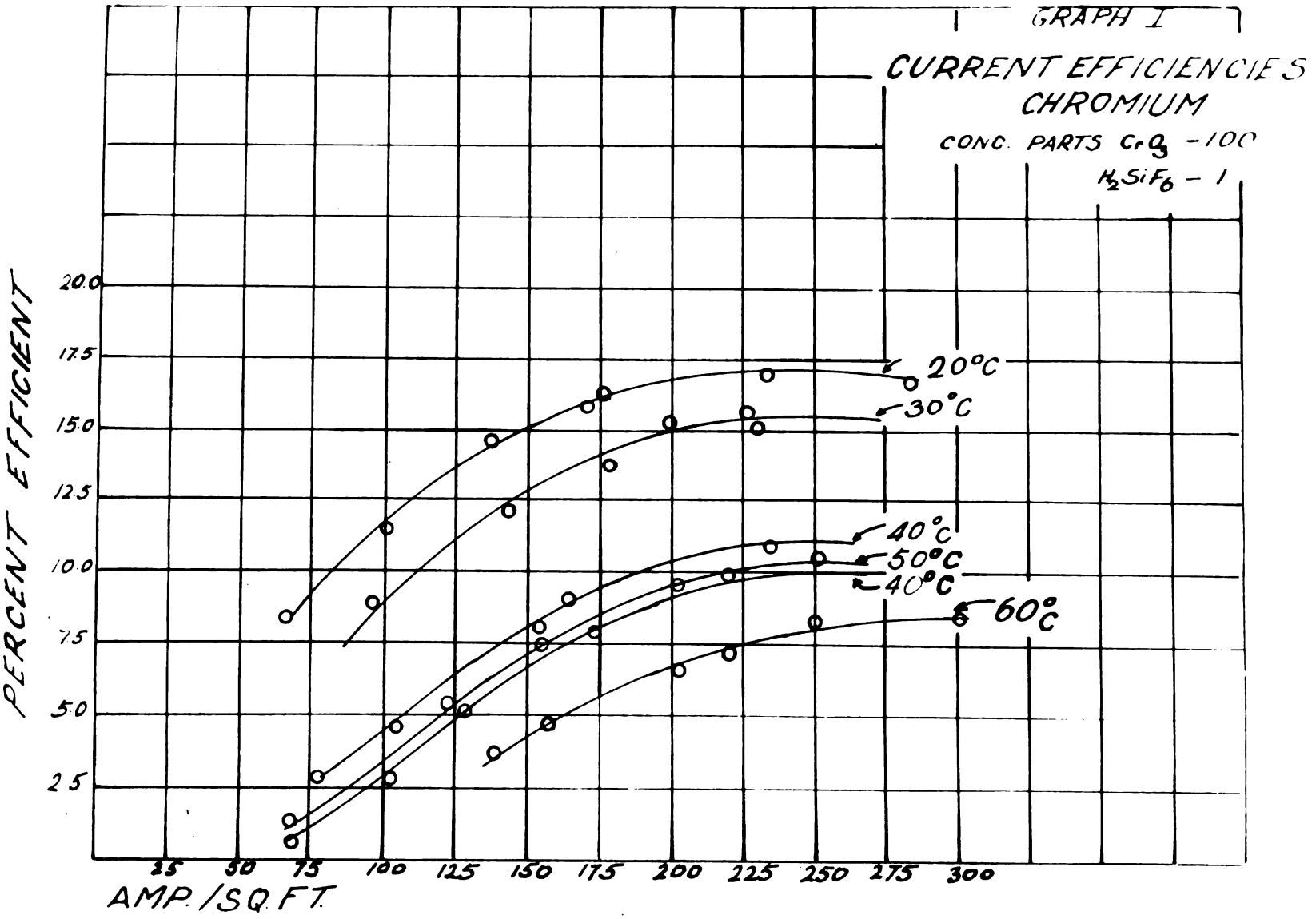
on the method of weighing special emphasis has been put on the preparation and cleaning of the cathodes. The steel plates were copper and nickel plated, polished and buffed to a mirror like finish. Each plate was electrocleaned in an alkaline cleaner, rinsed and examined for water breaks. The plate is then rinsed in hot distilled water and dried at 110° C, and weighed. The copper coulometer plate is rinsed in hot distilled water, dried at 110° and weighed.

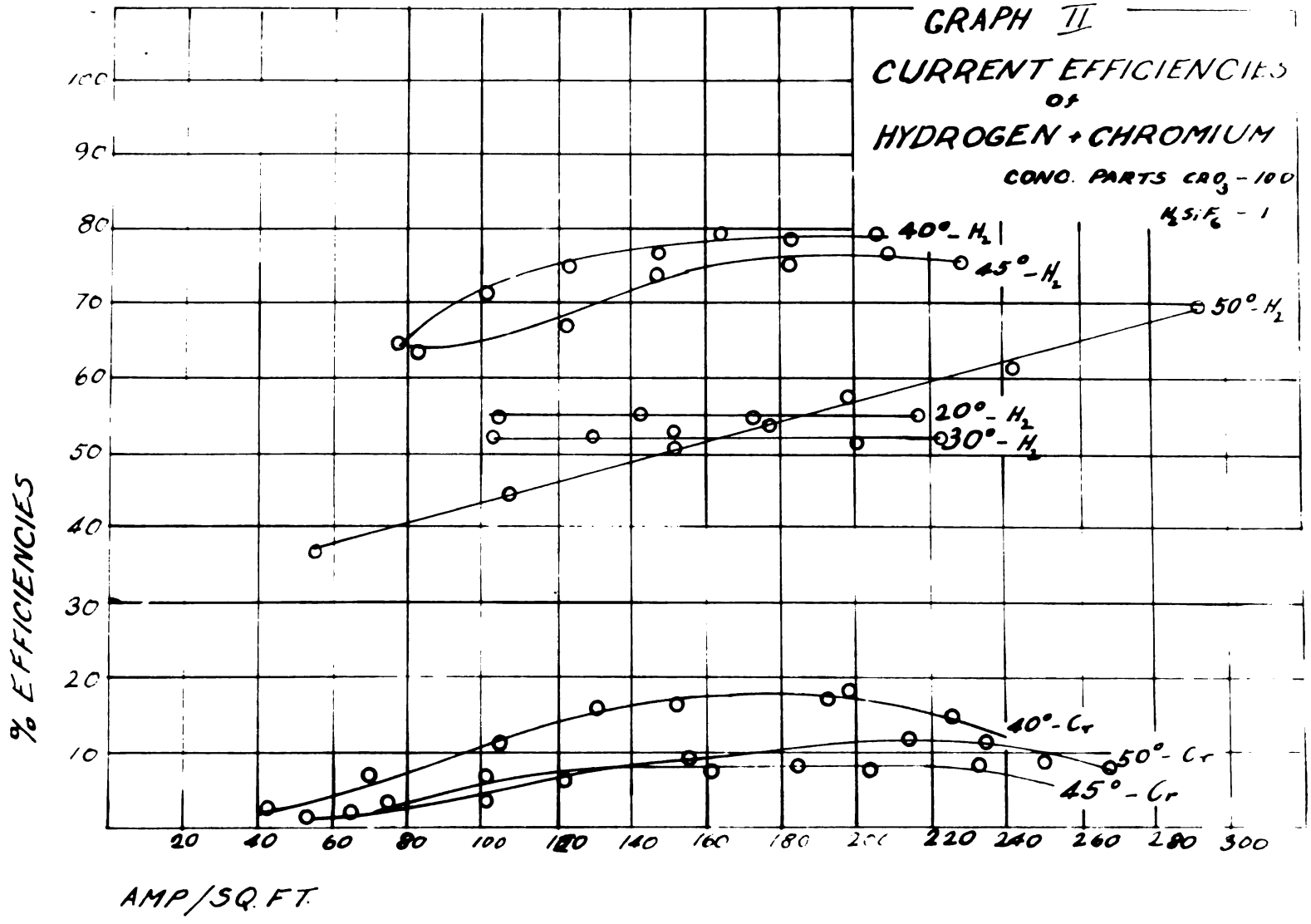
The time for each determination is determined by means of a stopwatch.

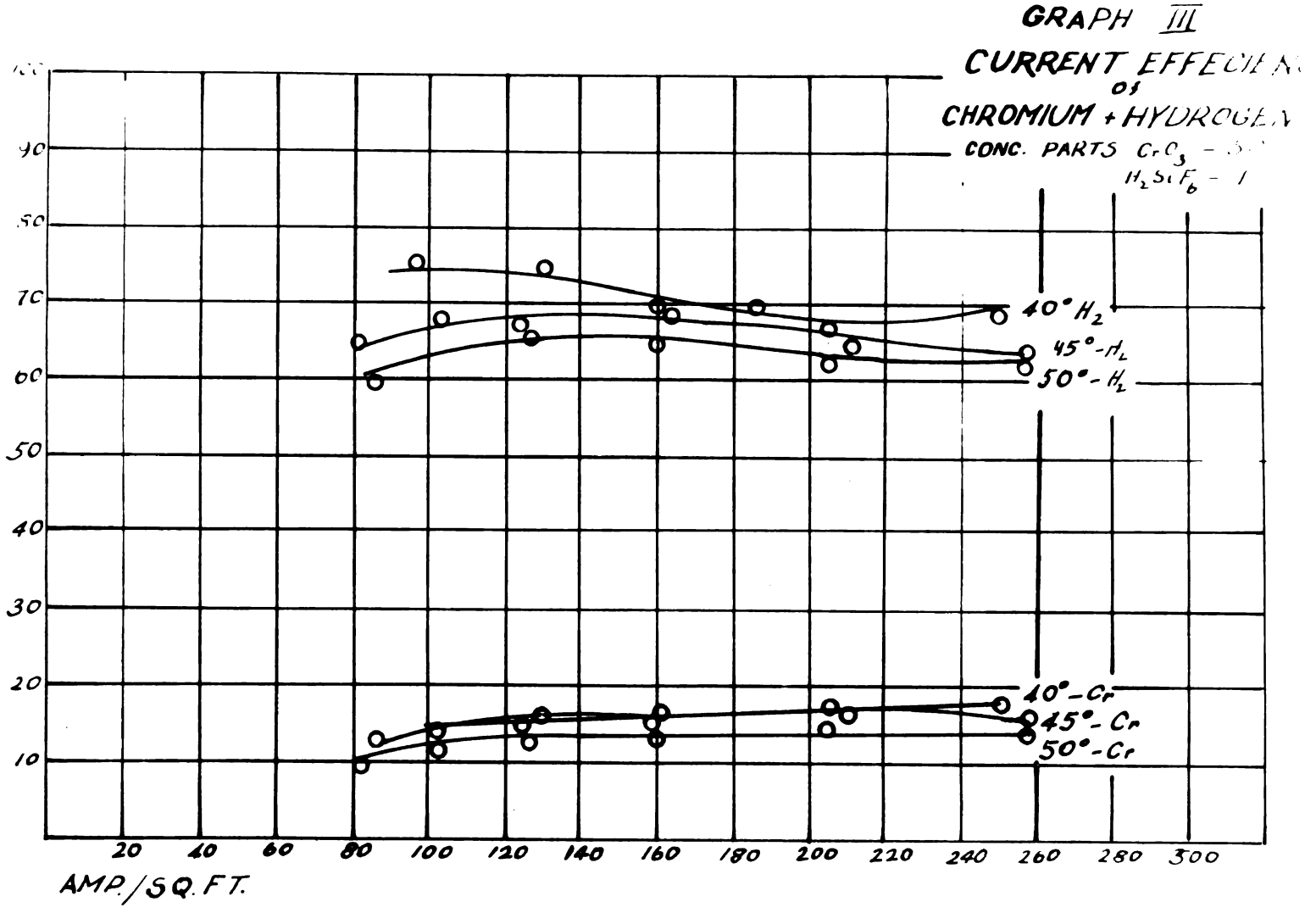
Amounts of current are regulated approximately by the use of the variable resistance and the ammeter.

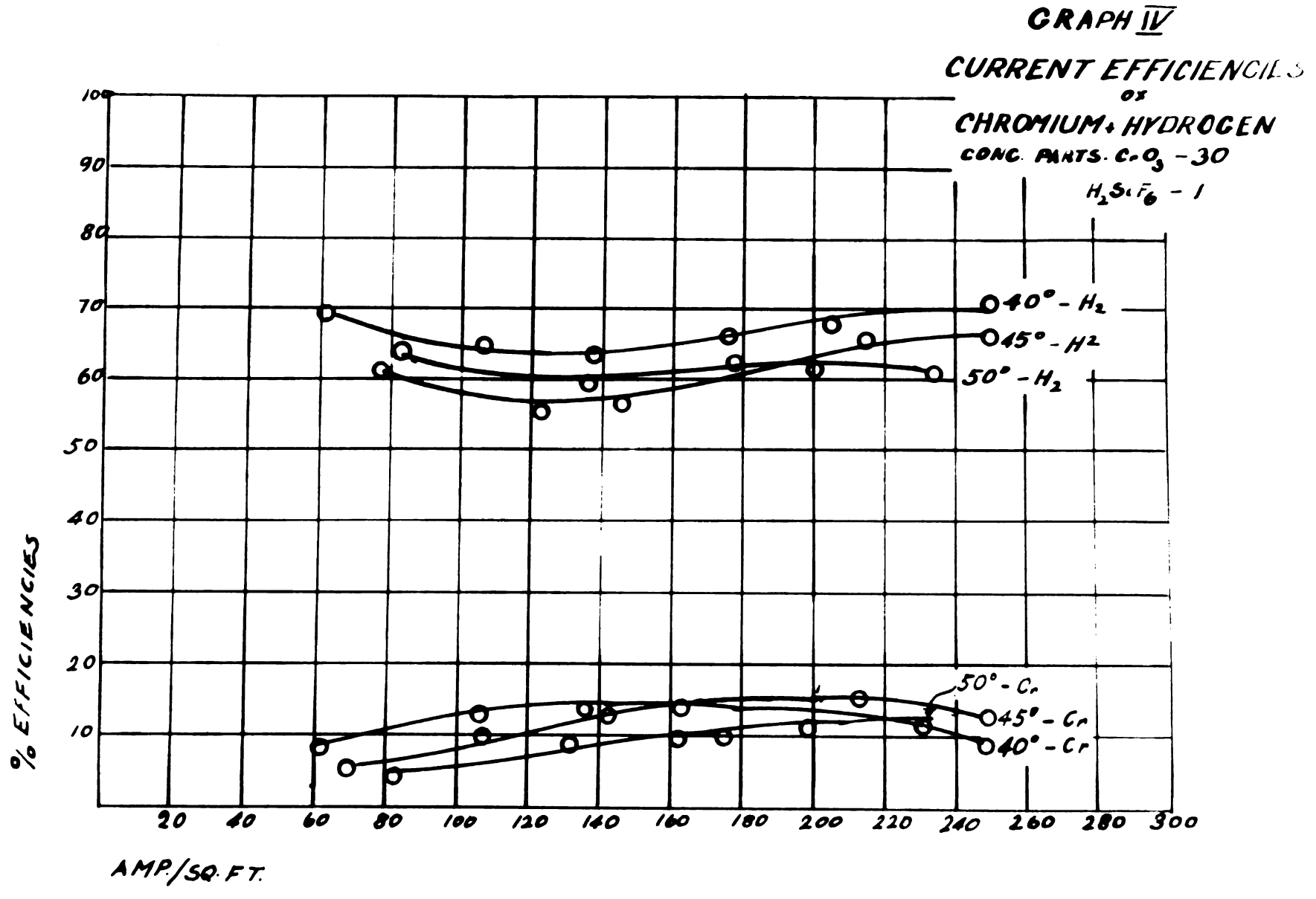
After the cathode is introduced into the solution the gas collecting funnel is placed over the former. By lowering the leveling bulb the plating solution is drawn into tube (x). Adjusting stopcocks and raising the leveling bulb all of the air in (A) is displaced by water. As soon as the current is passed this water will be displaced by hydrogen evolved at the cathode. When the hydrogen reaches the graduation mark at (0) the circuit is broken. The manometer stopcock is then opened and by means of the leveling bulb the exact difference of manometer readings is determined.

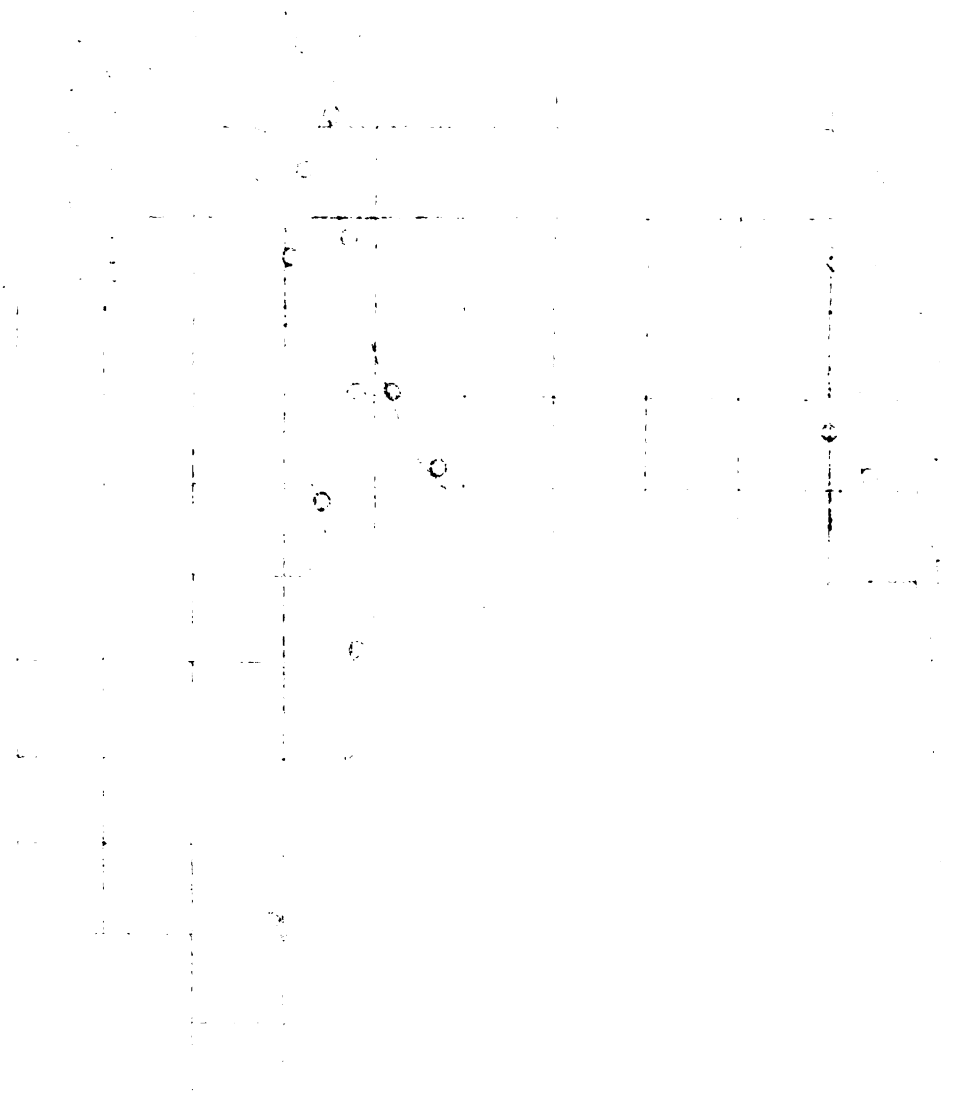
This difference in manometer levels, read in millimeters, divided by the density of mercury is the deviation from atmospheric pressures. The cathode and the copper coulometer plate are removed and rinsed in hot


GRAPH I
CURRENT EFFICIENCIES
CHROMIUM
CONC. PARTS CrO_3 - 100
H_2SiF_6 - 1
PERCENT EFFICIENT
20.0
17.5
15.0
12.5
10.0
7.5
5.0
2.5
20°C
30°C
40°C
50°C
40°C
60°C
25
50
75
100
125
150
175
200
225
250
275
300
AMP./SQ.FT.

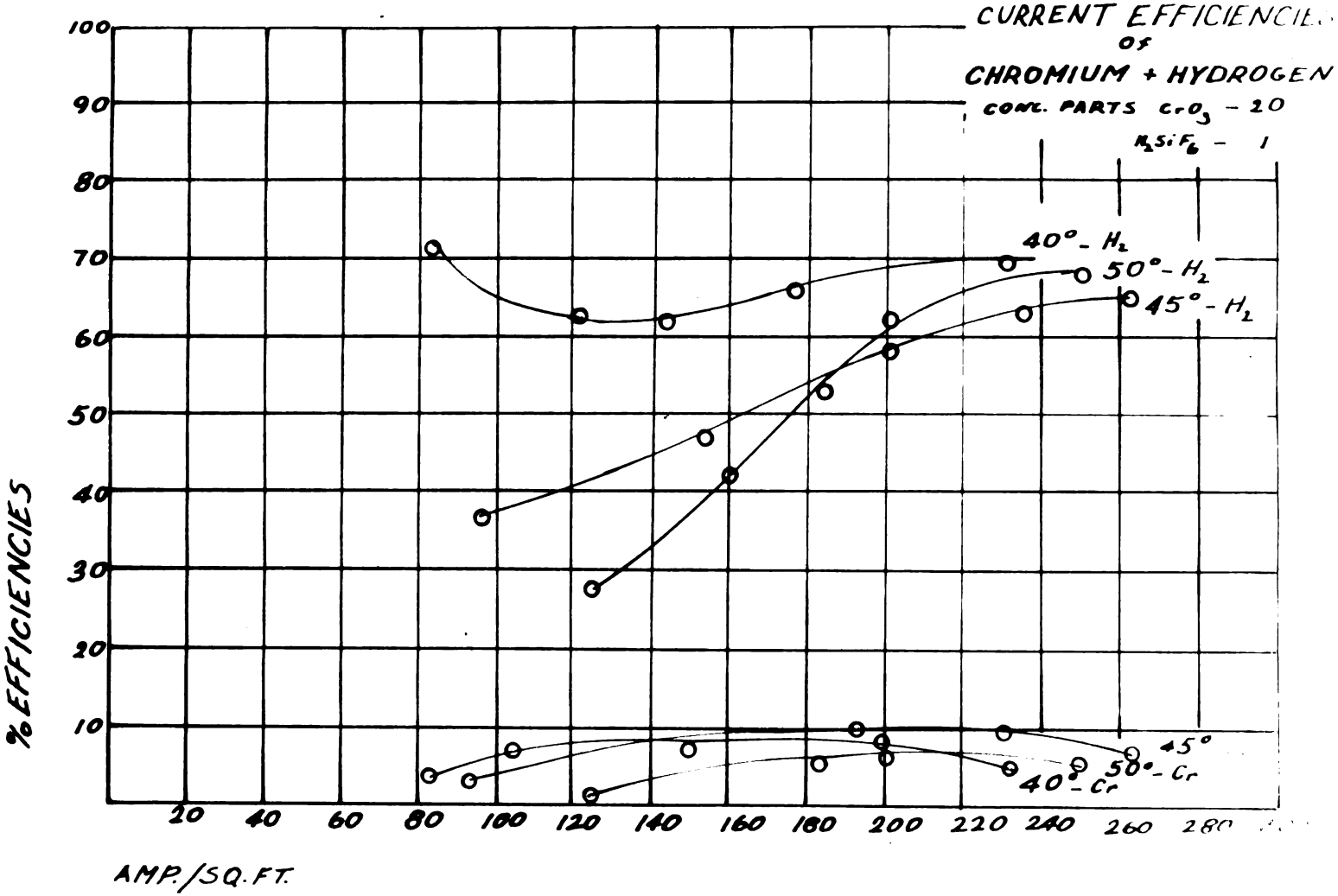

GRAPH II
CURRENT EFFICIENCIES
OF
HYDROGEN + CHROMIUM
CONC. PARTS CrO_3 - 100
H_2SiF_6 - 1
40° - H_2
45° - H_2
50° - H_2
20° - H_2
30° - H_2
40° - Cr
50° - Cr
45° - Cr
% EFFICIENCIES
AMP/SQ.FT.
100
90
80
70
60
50
40
30
20
10
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300

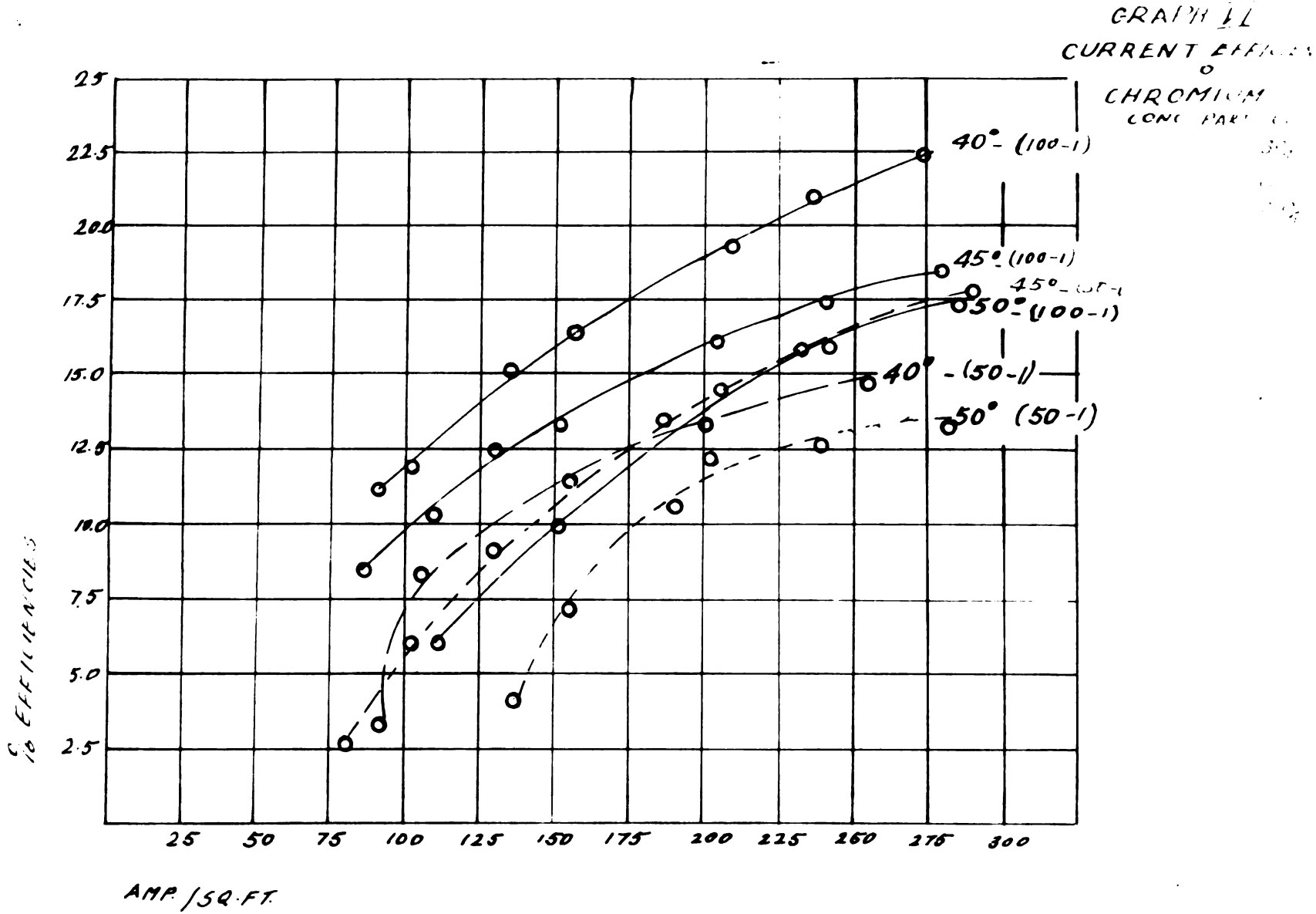

GRAPH III
CURRENT EFFICIENCIES
of
CHROMIUM + HYDROGEN
CONC. PARTS CrO_3 - 300
H_2SiF_6 - 1
90
80
70
60
50
40
30
20
10
% EFFICIENCIES
40° H_2
45° H_2
50° H_2
40° Cr
45° Cr
50° Cr
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
AMP./SQ.FT.


GRAPH IV
CURRENT EFFICIENCIES
OF
CHROMIUM & HYDROGEN
CONC. PARTS. Cr_2O_3 - 30
H_2SiF_6 - 1
40° - H_2
45° - H_2
50° - H_2
50° - Cr
45° - Cr
40° - Cr
% EFFICIENCIES
AMP./SQ. FT.
100
90
80
70
60
50
40
30
20
10
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300



GRAPH V


CURRENT EFFICIENCIES
OF
CHROMIUM + HYDROGEN
CONC. PARTS CrO_3 – 20
H_2SiF_6 – 1
% EFFICIENCIES
AMP./SQ.FT.
100
90
80
70
60
50
40
30
20
10
20
40
60
80
100
120
140
160
180
200
220
240
260
280
40° – H_2
50° – H_2
45° – H_2
45°
50° – Cr
40° – Cr


GRAM
CURRENT
CHROMIUM
40° - (100-1)
45° (100-1)
45° - (50-1)
50° (100-1)
40° - (50-1)
50° (50-1)
% EFFICIENCIES
25
22.5
20.0
17.5
15.0
12.5
10.0
7.5
5.0
2.5
25
50
75
100
125
150
175
200
225
250
275
300
AMP / SQ. FT.

Exp. No.	g. of Cr. Depos.	cc H_2 collected	Amp. Min.	Amp. /Sq. ft.	H_2 efficiency %	Cr efficiency %	Remarks
			$CrO_3 - H_2SiF_6$ (100 - 1)				
			30° C				
1	.0879	467.10	122.5	95.0	77.0	9.21	gray
2	.0806	472.0	131.6	103.2	51.9	11.32	gray
3	.1028	478.5	113.1	131.6	51.8	14.51	gray
4	.1109	472.0	149.9	227.0	51.9	15.50	bright, edges gray
5	.1123	484.6	117.7	128.5	50.0	15.00	gray
6	.1165	483.0	138.0	200.0	50.1	15.6	bright
57	.0794	485.13	108.6	178.5	64.08	13.53	bright, center dull
58	.0537	485.8	108.7	153.1	64.02	9.14	bright
			20° C				
7	.0833	478.1	115.5	101	59.2	13.4	dull
8	.0879	498.0	124.8	105	54.8	13.1	dull
9	.1098	484.0	128.2	154	52.6	15.8	dull
10	.1070	467.1	128.8	153	54.0	15.4	dull
11	.1063	472.0	125.9	174	52.3	15.7	dull
12	.1133	467.5	126.6	176	53.2	16.5	dull
13	---		---	---	---	---	loose connection
53	.0805	486.48	100.0	159	68.5	14.89	dull
54	.0498	483.11	109.3	65.8	63.67	8.45	dull
55	.0718	485.8	97.5	108.5	72.38	13.63	dull
56	.0902	478.39	149.5	285.6	65.62	16.74	dull
			40° C				
14	.0310	484.0	122.0	104.0	51.0	4.70	dull
15	.0304	481.0	120.4	88.8	52.9	4.75	gray
16	.0419	478.0	98.1	152.5	51.0	4.7	bright center
17	.0325	473.1	110.6	106.0	52.9	4.75	dull

Exp. No.	g. of Cr. Depos.	cc H_2 collected	Amp. Min.	Amp. /Sq. ft.	H_2 efficiency %	Cr efficiency %	Remarks
18	.0315	468.8	104.3	98.9	70.4	7.9	gray
19	.0128	472.2	108.5	40.9	60.9	2.18	dull
20	.0130	472.1	110.2	43.1	61.2	2.45	dull
21	.0478	472.3	115.6	101.6	57.9	7.71	bright
22	.0435	473.1	114.5	100.5	56.2	7.43	bright
23	.0741	472.9	122.1	151.0	55.4	8.40	bright
24	.0743	473.2	122.9	151.6	54.8	8.60	bright
25	.1141	474.5	117.2	194.0	59.8	17.57	bright, corners burned
26	.1150	474.8	115.9	189	60.1	18.00	bright, corners bt
27	.0972	477.2	127.9	236	53.6	10.65	bright, corners bt
28	.0969	477.6	128.5	240	56.2	11.20	bright, corners burned
68	.0206	476.3	113.4	101	71.3	3.36	bright
69	.0264	475.7	73.5	128	44.7	5.16	bright
70	.0424	480.0	86.4	164	81.30	9.1	bright, corners burned
71	.0609	480.0	101.8	199	69.0	11.2	bright, edges burned
72	.0459	482.1	90.6	217	76.0	9.42	burnt, center bright
				50° C			
29	.0107	483.8	183.8	54 .7	36.6	1.08	dull
30	.0111	484.3	185.1	55.0	40.5	.99	dull
31	.0304	475.9	147.5	108.5	44.8	3.82	bright
32	.0312	475.4	147.4	108.6	45.2	3.86	bright
33	.0526	476.2	127.6	161.4	60.2	7.60	bright
34	.0531	476.8	130.2	167.5	60.5	7.93	bright
35	.0661	475.8	123.2	202.0	55.4	9.94	excellent
36	.0701	474.2	122.8	199.8	56.1	10.01	excellent
37	.0767	482.9	131.2	250	60.7	8.55	bright, burnt

Exp. No.	g. of Cr. Depos.	cc H_2 collected	Amp. Min.	Amp. /Sq. ft.	H_2 efficiency %	Cr efficiency %	Remarks
38	.0725	483.3	129.5	245	60.5	10.7	bright, burnt
63	.0333	483.4	93.7	174	66.7	8.06	excellent
64	.0422	483.1	99.7	207	68.27	9.20	excellent
				60^{o} C			
39	.0363	472.3	240.0	101.6	28.2	2.80	dull
40	.0371	473.5	241.2	106.2	27.8	2.06	dull
41	.0281	476.2	372.5	157.0	26.8	4.64	bright
42	.0293	475.1	372.8	160.1	26.4	4.72	bright
43	.0386	482.3	198.2	206	45	6.35	bright
44	---	---	---	---	---	---	loose connection
45	.0452	481.0	164.7	256	52.2	8.04	bright
46	.0461	480.9	163.2	248	52.8	7.95	bright
47	.0590	484.2	167.6	304	51.3	8.98	bright, corners burnt
48	.0592	484.3	161.8	300	51.8	8.50	bright, corners burnt
49	---	---	---	---	---	---	excessive peeling
50	---	---	---	---	---	---	of Cr deposit
51	---	---	---	---	---	---	of Cr. deposit
52	---	---	---	---	---	---	of Cr deposit
73	.0219	480.1	114.0	133	61.6	3.68	bright
74	.0352	478.4	86.4	222	75.0	7.2	bright, burnt
65	.0516	486.48	96.4	220.0	72.8	9.93	excellent
66	.0497	476.0	95.2	234.0	77.28	9.70	excellent
67	.0188	467.1	249.6	64.2	69.6	11.7	excellent
59	.0132	464.0	204.5	64.5	69.02	11.9	bright
60	.0230	478.2	215.6	63.0	32.67	7.9	bright
61	.0318	484.0	101.5	122.3	69.02	5.77	excellent

Exp. No.	g. of Cr Depos.	cc H_2 collected	Amp. Min.	Amp. /Sq. ft.	H_2 efficiency %	Cr efficiency %	Remarks
62	.0388	480.3	102.5	154.0	42.67	7.56	excellent
		24° C		CrO_3 - H_2SiF_6 (100 - 1)			New Bath
111	.0463	482.5	90.0	78.0	77.0	9.56	dull
112	.0724	476.1	94.3	99	71.8	14.1	dull
113	.0720	478.5	90.1	123.6	75.9	14.76	dull
114	.0803	480.0	97.6	147.5	73.9	15.75	dull
115	.0759	479.1	95.7	184	78.8	14.7	dull
116	.0819	481.6	95.6	207	79.1	15.9	dull
117	.0795	480.0	98.4	246.0	68.9	15.2	dull
				45° C			
118	.0318	473.8	85.1	70	78.7	6.93	excellent
119	.0478	476.0	145.2	152	79.0	8.79	excellent
120	.0343	475.0	141.7	200	59.0	6.93	bright, slightly burnt
121	.0474	469.1	91.0	147.5	73.3	9.54	excellent
122	.0403	478.2	95.4	185.0	74.0	8.10	excellent
123	.0403	179.1	89.4	204.0	76.7	8.34	bright, slightly burnt
124	.0279	483.0	89.0	252.0	75.2	5.79	bright, burnt
				50° C			
125	.0938	482.6	92.9	75	74.0	8.7	dull
126	.0451	474.0	144.0	154	47.0	8.9	excellent
127	.0474	473.8	144.1	200	55.0	9.1	excellent
128	.0478	leakage	151.0	207.5	---	9.42	excellent

Exp. No.	g. of Cr Depos.	cc H_2 collected	Amp. Min.	Amp. /Sq. ft.	H_2 efficiency %	Cr efficiency %	Remarks
129	.0515	482.0	92.4	239	75.4	10.3	bright, slightly burnt
130	.0746	478.9	97.0	273	71.0	14.2	bright, burnt
				40° C			
131	.0679	465.0	103.5	76	64.2	12.3	dull
132	.0852	469.6	91.3	100	73.6	17.2	bright
133	.0817	473.0	99.4	131	68.5	15.2	excellent
134	.0827	478.5	95.8	152	71.5	16.0	excellent
135	.0840	470.5	91.7	200	73.4	16.9	excellent
136	.0843	480.0	91.2	227	75.4	17.0	burnt, slightly hard
		(45° C)	CrO_3 - H_2SiF_6		(50 - 1)		
137	.0677	469.3	103.1	78	65.0	12.8	excellent
138	.0752	470.9	103.2	103	67.0	13.8	excellent
139	.0787	465.0	99.25	125	65.1	14.2	excellent
146	.0890	475.0	172.5	259	63.0	15.6	bright, edges burnt
147	.0950	475.0	106.5	205	64.1	16.5	bright, edges burnt
148	.0887	479.1	61.0	161	69.7	16.6	excellent
				50° C			
140	.0618	474.9	111.6	82	60.8	10.2	excellent
141	.0651	470.5	100.8	103	66.8	12.0	excellent
142	.0720	473.2	103.7	126	65.3	12.8	excellent
143	.0757	476.1	100.3	159	66.6	13.6	excellent
144	.0933	478.0	109.4	205	62.6	15.8	excellent

Exp. No.	g. of Cr Depos.	cc H_2 collected	Amp. Min.	Amp. /Sq. ft.	H_2 efficiency %	Cr efficiency %	Remarks
145	.0856	477.0	108.0	258	63.3	14.7	excellent
				40° C			
149	.0493	474.6	105.2	94.5	69.6	8.73	excellent
150	.0762	476.2	96.8	96.0	77.4	14.6	excellent
151	.0841	475.0	104.5	129.6	77.0	14.88	excellent
152	.0755	479.0	99.1	159.0	69.3	14.1	excellent
153	.1019	477.9	107.2	206.0	69.0	17.65	excellent
154	.0899	479.8	97.6	250.0	70.8	17.1	excellent
				$CrO_3 - H_2SiF_6$ (30 - 1) 40° C			
155	.0426	468.9	95.6	60	69.0	8.22	bright
156	.0698	472.0	104.0	107	64.8	12.4	excellent
157	.0744	472.0	107.2	138	63.2	12.86	excellent
158	.1262	475.5	94.7	170	65.1	13.96	excellent
159	.0667	475.6	100.4	207	66.7	12.3	bright, loose deposit
160	.0471	474.3	95.8	250	70.4	9.0	bright, loose deposit
161	.0349	478.2	112.6	79.0	61.6	5.82	excellent
162	.0639	483.0	125.0	108,0	55.4	9.50	excellent
163	.1727	487.5	118.7	143.6	57.8	11.36	excellent
164	.0622	483.5	105.6	162.0	59.4	9.90	bright, loose deposit
165	.0881	481.9	102.8	214	67.2	15.85	bright, loose deposit
166	.0714	484.8	104.0	245	65.6	12.72	bright, loose deposit

Exp. No.	g. of Cr Depos.	cc H_2 collected	Amp. Min.	Amp. /Sq. ft.	H_2 efficiency %	Cr efficiency %	Remarks
				50° C			
167	.0288	478.2	156.8	82.6	64.1	3.51	bright, edges burnt
168	.0458	487.1	126.6	121	55.0	7.38	loose deposit
169	.0529	478.4	116.7	133	59.3	8.65	loose deposit
170	.0514	481.1	105.6	175	65.6	9.05	loose deposit
171	.0662	482.5	110.4	200	62.7	11.2	loose deposit
172	.0615	489.0	95.9	230	62.6	11.85	loose deposit
				CrO_3 + H_2SiF_6 (20 - 1) 45° C			
173	.0283	481.0	183.9	93.5	37.6	2.96	excellent
174	---	---	---	---	---	---	excessive anode
175	---	---	---	---	---	---	corrosion
176	.0502	488.9	117.4	200	59.4	7.95	bright, loose deposit
177	.0423	490.1	107.2	264	65.0	7.30	bright, loose deposit
178	.0578	487.9	78.9	155	57.1	8.75	bright, loose deposit
				50° C			
179	.0452	482.0	130.5	183.0	52.8	6.4	bright, loose deposit
180	.0152	480.0	246.7	124.1	27.92	1.14	bright, loose deposit
181	.0432	488.9	140.0	200.0	63.3	6.1	bright, loose deposit
182	.0381	489.0	135.8	250	67.8	6.00	bright, loose deposit
				40° C			
183	.0416	473.8	107.4	145	62.9	6.94	excellent
184	.0450	472.0	114.4	108	59.1	7.50	excellent

Exp. No.	g. of Cr. Depos.	cc H_2 collected	Amp. Min.	Amp. /Sq. ft.	H_2 efficiency %	Cr efficiency %	Remarks
185	.0440	477.9	98.0	200	70.0	8.35	bright, loose deposit
186	.0316	478.1	101.0	234	68.4	5.65	bright, loose deposit
187	.0262	470.0	103.6	83.2	72.0	4.46	excellent
			$CrO_3 - SO_4$ (100 - 1)				
			40° C				
188	.0803	473.2	133.0	84.5	50.95	11.15	bright
189	.0834	474.0	130.6	101	51.6	11.74	excellent
190	.1108	471.0	133.6	136	50.6	15.3	excellent
191	.1233	473.9	136.4	157	49.7	16.7	excellent
192	.1453	474.0	137.0	210	48.8	19.6	bright, corners burnt
193	.1671	471.1	137.9	275	48.9	22.4	bright, burnt
				45° C			
194	.0645	471.0	133.6	84.4	50.04	8.88	bright
195	.0765	471.2	132.0	109.5	51.2	10.7	excellent
196	.0859	472.2	130.2	129.2	51.9	12.2	excellent
197	.0902	471.0	126.4	152.5	53.5	13.2	excellent
198	.1160	473.8	132.3	204	51.5	16.1	bright, corners burnt
199	.1343	475.0	134.0	280	51.0	18.5	bright, burnt
200	.0159	471.1	116.2	80	58.1	2.54	excellent
201	.0413	475.0	127.0	102	54.7	6.0	excellent
202	.0409	470.1	125.3	129.6	53.6	6.06	excellent
203	.0780	471.9	128.0	157	52.8	11.1	bright, corners burnt
204	.1048	473.0	134.3	207	51.2	14.4	bright, corners burnt
205	.1164	476.5	123.6	284	55.2	17.5	bright, burnt

Exp. No.	g. of Cr. Depos.	cc H_2 collected	Amp. Min.	Amp. /Sq. ft.	H_2 efficiency %	Cr efficiency %	Remarks
			$CrO_3 - SO_4$ (50 - 1)				
			50° C				
206	.0510	479.8	216.2	141	31.7	4.36	excellent
207	.1072	487.2	106.5	206	41.2	12.4	bright, loose deposit
208	.0461	480.0	289.2	106	23.7	3.0	excellent
209	.1074	482.6	153.2	283	45.4	13. 0	bright, loose deposit
210	.0630	481.1	156.4	155	43.9	7.45	excellent
			45° C				
211	.0574	481.0	206.2	81.5	32.9	5.20	excellent
212	.0610	481.2	204.9	110	36.5	6.0	excellent
213	.0985	499.0	176.5	150	40.7	10.4	excellent
214	.1235	479.0	159.2	202	41.8	14.2	bright, loose deposit
215	.1311	482.1	151.8	259	45.6	13.1	bright, loose deposit
216	.1447	482.8	99.4	296	46.1	17.9	bright, loose deposit
			40° C				
217	.0669	477.9	374.8	91.2	18.0	3.30	excellent
218	.0870	478.0	199.4	106	34.0	8.05	excellent
219	.1094	477.8	172.9	155	49.8	11.60	bright, loose deposit
220	.1182	480.3	159.0	200	42.9	13.61	bright, loose depos
221	.1279	481.0	156.1	253	44.2	15.12	bright, loose depos
222	.1592	485.0	159.6	295	43.6	18.50	bright, loose depos

DISCUSSION.

In this investigation determinations were made for the following concentrations of CrO_3 and H_2SiF_6 respectively 100 parts to 1 part, 50 to 1, 30 to 1 and 20 to 1. 250 g. of CrO_3 were dissolved in 1 liter of water. The range of current densities considered was from 75 amps. per sq. ft. to 250 amps. per sq. ft. The temperatures for each concentration were 40°C, 45°C and 50°C. One general determination for the effect of a temperature change from 20°C to 60°C with the concentration of 100 parts CrO_3 to 1 part of H_2SiF_6 has been made.

In order to understand some of the facts brought out by the experimental procedure one of the theories of chromium deposition from a chromic acid - sulphate bath will be given.

Sargent[3] recognized a number of important variable factors namely, that the cathode film is only slightly acid at high current densities, that reduction of chromic acid at high current densities must occur through the medium of the chromic - chromous couple, that sulphate is necessary for metal deposition, and that pure chromic acid can be reduced at low but not at high current densities. The latter factor was attributed to a colloidal layer which was designated as non-permeable, though Sargent tacitly assumed it to be permeable to hydrogen ions. The mechanism of the action of sulphate has not been set forth. Kasper[4] advances the following theory. Deposition of bright chromium

depends upon maintaining in the cathode film a definite hydrogen ion concentration. This must be sufficiently low to permit metal deposition and yet sufficiently high to prevent hydrolysis and thus yield oxide-free deposits. At low current densities direct reduction of hexavalent or trivalent chromium undoubtedly occurs. At high current densities, which require cathode potentials sufficient to liberate hydrogen gas, the conditions are vastly different. On account of the high migration velocity of the hydrogen ion in the cathode film, the latter becomes relatively alkaline. If the hydrogen ion concentration drops, a basic electropositive dispersoid of $Cr(OH)_3 \cdot Cr(OH)CrO_4$ exists. In the absence of the sulphate ion the dispersoid migrates to the cathode and covers it with a colloidal layer which prevents reduction of the constituents except hydrogen to which it is permeable. The action of the sulphate is to decrease the electrophoretic velocity of the colloid by adsorption; which causes a reduction of the positive charge and prevents the formation of a dense, adherent colloidal layer. Other ions can reach the cathode and be reduced.

Liebreich[1] has advanced a theory which is identical with the latter. He has investigated the effects of acids on the colloid film surrounding the cathode. The nature of the deposit depends largely on the degree of solubility of the film. He states that it is important that by a certain degree of solubility, the film should form and dissolve

continually, maintaining a certain definite thickness. This follows from the fact that in cases where, at ordinary temperatures greyish deposits are obtained, bright deposits are obtained at higher temperatures (30°, 40° or 50°C). This form of deposit, again is confined to certain limits of current density.

Miller[5] discusses the above named film formation in relation to current densities. According to his determination the continual formation of the film is effected by the concentration of the SO_4 ion. With an increase of the concentration the film formation slows down hence a lowering in current density.

The above fact will explain the lowering in efficiency of the sulphate bath investigated in this work. Table (6) and graph (6) show the decrease in efficiency with increase of sulphate from the ratio - 100 parts CrO_3 to 1 part SO_4 - to the ratio of 50 parts CrO_3 to 1 part SO_4. The temperature effects shown in the graph were explained by D. T. Ewing, J. O. Hardesty and Te Hsia Kao.[2]

From the data obtained in this work it can be concluded that the effect of H_2SiF_6 is the same as the SO_4 for chromic acid bath of the same composition.

The following effects of the chromic acid bath with hydrofluosilicic acid are the same as that of the sulphate bath.

1. A decrease of current efficiency with an increase of temperature.

2. A decrease of current efficiency with an increase of H_2SiF_6.

3. A low efficiency at a low current density with a relatively sharp rise in efficiency at a higher current density. A leveling off of the efficiency curve at higher current densities.

From these facts it may be concluded that the previously stated theories hold true also for chromic acid solution with hydrofluosilicic acid although the magnitude of effect of varying factors gives relatively different results.

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