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FINAL REPORT

PART II. THE KINETICS OF DISSOLUTION OF SPECIAL TYPES
OF ZIRCONIUM AND ZIRCALLOY-II IN HYDROFLUORIC ACID

By

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FINAL REPORT

PART II. THE KINETICS OF DISSOLUTION OF SPECIAL TYPES
OF ZIRCONIUM AND ZIRCALLOY-II IN HYDROFLUORIC ACIDINTRODUCTION

As a result of preliminary work at the University of Michigan on the effect of oxidation and surface coating on the dissolution rates of zirconium and Zircalloy reported in June, 1953,¹ and recommendations made in an Engineering Research Institute progress report of September, 1953,² interest was shown in further experimentation in this field. Several selected samples with various surface coatings were received from the Phillips Petroleum Company, together with a revised schedule of research from the U.S. Atomic Energy Commission, Idaho Operations Office. These samples had various surface coatings which were to be investigated for their effect on the dissolution rate of the material.

Both zirconium and Zircalloy-II samples were received. The samples were designated as types A, B, and C: type A was Zircalloy-II with a black oxide coating, type B was a zirconium crystal bar with a white oxide coating, and type C was a zirconium crystal bar with a black oxide coating. Pure zirconium and Zircalloy-II were available here and similar tests were run on them.

The experimental runs were made at 100°C, near the refluxing temperature of the hydrofluoric acid solutions used. Gas evolution was measured for two rates of acid addition to the sample. Tables and graphs of the data taken are presented in this report along with a method of transforming the data to dissolution rates.

EXPERIMENTAL PROCEDUREPreparation of the Samples

The samples of types A, B, and C were run in the as-received condition from the Phillips Petroleum Company. They were individually wrapped in tissue when received and were handled only preceding a run when being weighed and measured. The samples of uncoated zirconium and Zircalloy-II were machined from pieces received earlier from the American Cyanamid Company. These samples were washed, degreased with acetone, and then weighed and measured.

Preparation of the Acid Solutions

In the dissolution experiments reported earlier (Progress Report 10, September, 1953) samples of metal were placed in large volumes of hydrofluoric acid solutions of given concentrations and allowed to react. In the work reported here the procedure was quite different. Each sample was immersed in distilled water which was maintained at about 100°C. At zero time strong hydrofluoric acid (about 48%) was allowed to start dropping into the water. The acid flow was continued until the total fluoride ion in the reaction vessel was 7.4 molar. This point was determined from the quantity of distilled water used, the amount of 48% acid added, and the specific-gravity-concentration tables prepared by Elving, et al.³ The total quantity of acid was dependent on the mass of the metal to be dissolved, 1 gram of 100% HF being added for every gram of metal.

The Constant-Temperature Reaction Vessel and Gas-Collecting Apparatus

A schematic diagram of the equipment used is shown in Fig. 1. A copper reaction vessel, three gas-collecting burettes, and a jacketed temperature vessel were the main pieces of equipment. Auxiliaries consisted of a hydrofluoric acid dropping funnel, a condenser, and pieces of tubing.

The hydrofluoric acid dropping funnel was constructed from a small polyethylene bottle and a 1/16-inch-ID polyethylene tube. The bottle was suspended 6 feet above the reaction vessel to minimize variation in acid rate due to hydrostatic head loss. A pinch clamp was placed in the line to control the flowrate. At a distance of 3 inches above the entrance into the reaction vessel the small tubing was joined to a 3/8-inch-ID tube in order to facilitate measurement of the acid addition rate. Drops of acid were

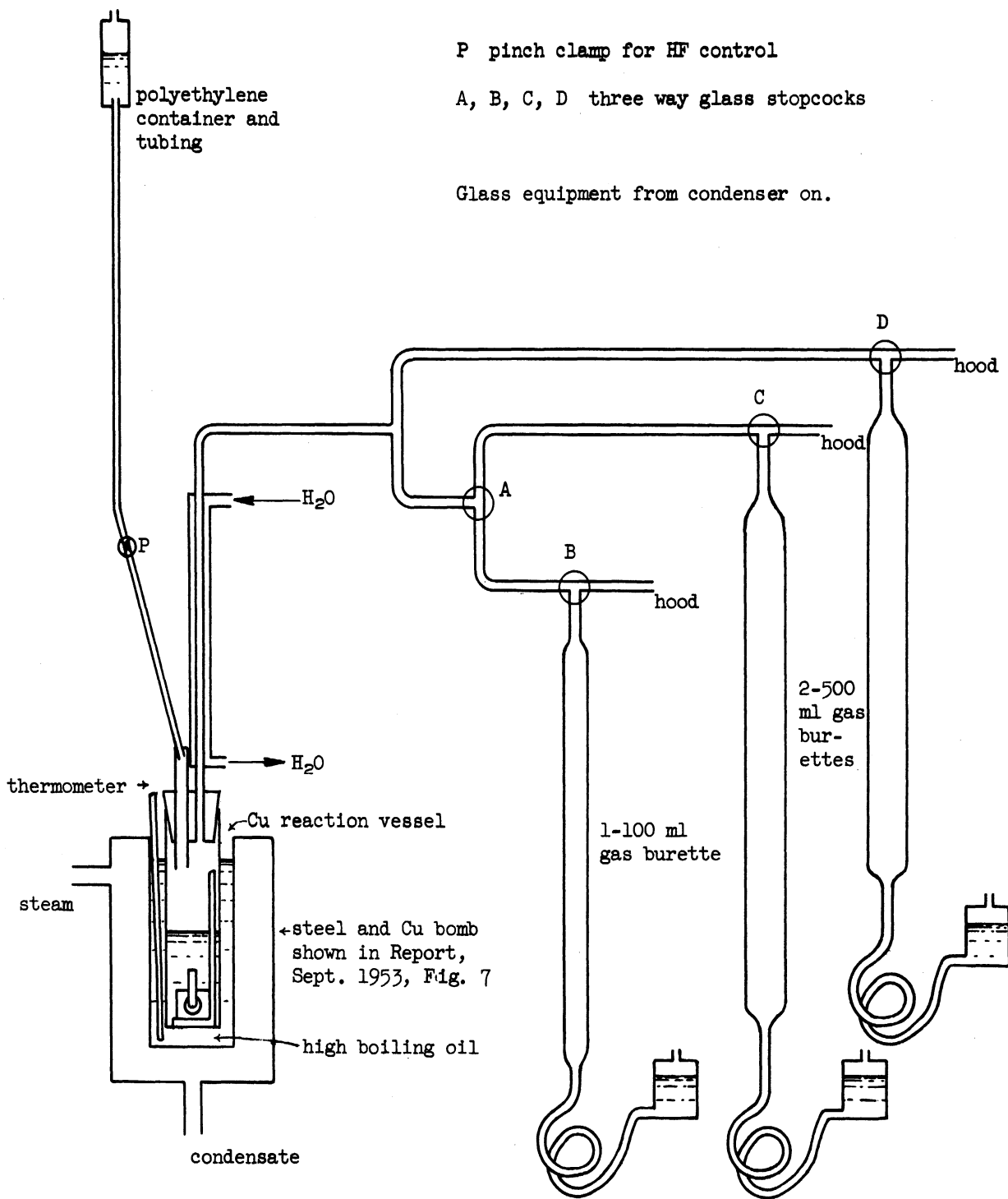


Fig. 1. Schematic Diagram of the Equipment.

counted in order to maintain a constant flowrate. The apparatus was calibrated in grams per minute versus drops per minute.

The reaction vessel was constructed from a piece of 2-inch-ID pure-copper pipe with one end sealed. A polyethylene-coated rubber stopper with openings for the acid addition tube and a glass condenser provided the top for the vessel.

The reaction vessel was placed in a bath of oil held in a steam-jacketed container (Fig. 7, in the September, 1953, Progress Report). The temperature of the oil was controlled by regulating the steam pressure to the jacket. The hydrogen evolved in the course of the reaction passed through a glass condenser to the collection burettes. Any entrained or vaporized water or hydrofluoric acid was collected on the sides of the condenser to drip back down into the reaction vessel. Although glass is subjected to attack by hydrofluoric acid, polyethylene does not have the required heat-transfer properties to condense water and hydrofluoric acid. Preliminary tests made with a glass condenser indicated that there was no appreciable attack on the glass during the length of time required for a run.

The hydrogen passed from the condenser into one of three gas-collecting burettes. At the start and conclusion of each run the gas was collected in a 100-ml burette. At these times the reaction rate, and thus gas evolution, were small enough to permit collection in the ~~100~~¹⁰⁰-ml burette without danger to the operator. During the middle portion of each run the gas was collected alternately in two 500-ml burettes, which were large enough to handle the gas safely at a fairly high rate. While gas was being collected in one burette, it was being vented to the hood from the other.

Conduct of the Run

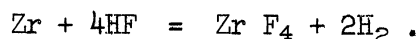
The samples were suspended in the reaction vessel by a polyethylene support that touched the sides of the sample only at two small points. The apparatus resembled a pair of ice tongs, which held the sample satisfactorily in a vertical position, allowing the acid to contact all sides of the sample.

A known amount of water was placed in the reaction vessel with the suspended sample and the stopper containing the condenser was placed in position and the condenser connected to the gas burettes. The reaction vessel was then put in the hot oil and heated to 100°C before the acid addition. A stopclock was started when the first drop of acid was observed to fall into the reactor. The acid rate was regulated to a predetermined value and the gas was collected as described previously. The acid was shut off at the time calculated from the rate of acid addition and the total amount of acid needed. The reaction was allowed to go to completion and then the reactor was

dismantled and removed from the oil bath. The final solution containing any undissolved residue was poured out for examination. The system was tested for air leaks before proceeding with the experimental run. The number of samples provided permitted only two runs to be taken at any one acid rate for any one type of coating.

DATA AND EXPLANATION OF CALCULATIONS

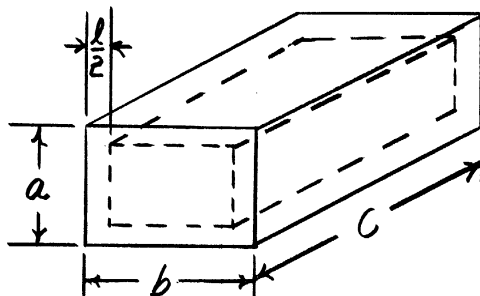
The volume of gas evolved was corrected to standard conditions from the average temperature of the gas recorded during the run. This was also checked stoichiometrically against the theoretical volume predicted by the equation for the reaction,



In checking the Zircalloy, all the sample was assumed to be pure zirconium and any reactions involving alloying constituents were neglected. In all cases reported here this balance was well within the expected error, considering the system used. In the single case where this value did not check, an appreciable air leak was found; this run is not reported.

The volume of H_2 , corrected to standard conditions, is plotted as a function of time for the acid addition rate used (see Tables III through VII and Figs. 2, 3, 4, 6, and 7). From these graphs the number of moles of zirconium dissolved is calculated from the stoichiometric reaction. The mass is then the molecular weight times the number of moles. Expressed in symbols this is

$$M_{\text{Zr dissolved}} = \frac{(\text{cm}^3 \text{ H}_2 \text{ evolved})(\text{MW}_{\text{Zr}})}{(22,400)(2)}$$



By assuming uniform attack by the acid, the mass balance around a typical sample (shown above) may be written. The mass of zirconium dissolved is the density, ρ , times the change in volume of the sample. Expressed in

TABLE I
PHYSICAL CHARACTERISTICS OF COATED SAMPLES

Type of Sample Coating	Identification Numbers	Initial Weight, gm	Initial Dimensions, in.
A-I	2 --- 7	11.0183	(0.950)(0.093)(1.173)
A-II	2 --- 6	12.3763	(0.946)(0.114)(1.083)
B-I	1 --- 8	13.6908	(0.669)(0.104)(1.905)
B-II	1 --- 9	14.4535	(0.666)(0.111)(1.891)
C-I	599T - 201	11.7636	(0.380)(0.223)(1.344)
C-III	1060 - 1828B	17.4635	(0.502)(0.213)(1.583)
Uncoated Zr-I pure P-I		9.2493	(0.595)(0.129)(1.221)
Uncoated Zr-II pure P-II		8.5742	(0.523)(0.144)(1.225)
Uncoated Zr-I ^{Zircalloy} Z A-I		8.7215	(0.478)(0.170)(1.027)
Uncoated Zr-II ^{Zircalloy} Z A-II		9.4878	(0.503)(0.169)(1.068)
A-III	2 -- 1 - 7292	12.9368	(0.877)(0.117)(1.179)
*B-III	1 --- 1	15.1692	(0.719)(0.106)(1.897)
*B-IV	1 --- 4	15.4490	(0.721)(0.108)(1.906)
C-IV	223 - 690B	18.4030	(0.480)(0.241)(1.532)
Uncoated Zr-III pure P-III		4.7194	(0.481)(0.110)(0.979)
Uncoated Zr-III ^{Zircalloy} Z A-III		8.9595	(0.581)(0.164)(0.910)

*Reaction too rapid to measure gas volume.

TABLE II

EXPERIMENTAL CHARACTERISTICS OF COATED SAMPLES

Type of Sample Coating	Theoretical Vol. of Gas Released at Std. Cond., cm ³	Acid Rate gm/min	Total Wt. 48% HF Added, gm	Total Wt. H ₂ O Present at Start, gm	Gas Temp. °K
A-I	5410	.50	21.5	57.2	314
A-II	6077	.50	23.0	64.2	309
B-I	6722	.50	26.5	71.0	320
B-II	7097	.50	28.0	75.0	311
C-I	5776	.50	22.5	61.0	312
C-III	8575	.50	33.0	90.6	315
Uncoated Zr-I pure P-I	4541	.50	18.0	48.0	301
Uncoated Zr-II pure P-II	4210	.50	16.5	45.6	314
Uncoated ^{Zircalloy} Zr-I ZA-I	4282	.51	17.8	45.3	313
Uncoated ^{Zircalloy} Zr-II ZA-II	4659	.50	18.5	49.2	311
A-III	6352	1.14	26.2	67.1	314
*B-III		1.14		78.7	
C-IV	9036	1.24	40.0	95.5	321
Uncoated Zr-III pure P-III	2317	1.20	10.2	26.8	319
Uncoated ^{Zircalloy} Zr-III ZA-III	4399	1.33	19.9	46.5	311
*B-IV		1.23		80.2	

*Reaction too rapid to measure gas volume.

TABLE III

TIME AND TOTAL VOLUME AT STANDARD CONDITIONS OF H₂ EVOLVED FOR TYPE A

A-I			A-II			A-III		
Time, min	sec	H ₂ Evolved cm ³	Time, min	sec	H ₂ Evolved cm ³	Time, min	sec	H ₂ Evolved cm ³
13	30	87	11	39	88.4	6	28	87
18	22	522	13	25	177	9	17	521
20	30	956	16	51	618	10	46	956
22	26	1391	18	32	1060	11	58	1390
24	25	1826	20	00	1502	13	08	1825
26	30	2260	21	37	1944	14	22	2259
28	58	2695	23	31	2385	15	41	2694
31	46	3130	25	55	2827	17	03	3128
35	02	3565	28	39	3269	18	34	3563
38	22	3999	31	42	3711	20	14	3997
41	50	4434	34	58	4152	22	04	4432
42	35	4521	38	30	4594	24	05	4866
47	10	4956	42	08	5036	27	47	5388
48	36	5043	46	32	5478	33	44	5822
50	40	5129	52	05	5831	35	37	5909
53	45	5216	55	00	5920	37	51	5996
56	00	5260	58	46	6008	40	36	6083
58	55	5303	62	27	6052	44	14	6170
63	13	5347	73	30	6070	49	23	6257
70	35	5390				55	40	6344
79	25	5412						

TABLE IV

TIME AND TOTAL VOLUME AT STANDARD CONDITIONS OF H₂ EVOLVED FOR TYPE B

B-I		B-II		B-III	
Time, min sec	H ₂ Evolved cm ³	Time, min sec	H ₂ Evolved cm ³	Time, min sec	H ₂ Evolved cm ³
7 33	64	10 33	88	7 14	88
8 24	85.3	11 44	176	7 30	513
10 04	171	13 13	614		
11 46	597	14 01	1053		
12 49	1024	15 01	1492		
14 08	1450	17 04	1931		
16 36	1878	20 06	2370		
18 57	2304	23 43	2809	5 23	89
21 48	2730	27 12	3248	7 45	515
24 48	3158	30 43	3687	8 20	998
28 09	3583	34 21	4126		
31 22	4008	38 00	4565		
34 38	4438	41 56	5003		
37 54	4860	45 45	5442		
41 17	5290	49 23	5881		
44 29	5718	52 54	6320		
47 53	6142	56 09	6759		
52 37	6563	62 30	7089		
56 02	6720				
60 00	6723				

TABLE V
 TIME AND TOTAL VOLUME AT STANDARD CONDITIONS
 OF H₂ EVOLVED FOR TYPE C

C-I			C-III			C-IV		
Time, min sec	H ₂ Evolved cm ³		Time, min sec	H ₂ Evolved cm ³		Time, min sec	H ₂ Evolved cm ³	
4	10	22	7	14	43	3	44	85
4	52	44	8	24	87	5	41	510
5	18	66	9	38	173	6	52	936
5	39	88	12	40	607	8	00	1361
6	35	175	14	46	1040	9	09	1786
9	27	613	16	34	1474	10	22	2211
12	02	1050	18	32	1907	11	45	2637
14	20	1488	21	00	2341	13	20	3062
17	27	1925	24	12	2774	15	00	3487
20	48	2363	27	39	3208	16	42	3912
24	30	2800	31	13	3641	18	28	4338
28	15	3238	34	50	4075	20	15	4763
32	16	3675	38	37	4508	22	03	5188
36	22	4113	42	23	4942	23	52	5613
40	30	4550	45	28	5375	25	42	6039
44	58	4988	48	29	5809	27	32	6464
51	00	5425	51	44	6242	29	29	6889
51	30	5447	55	12	6676	31	27	7314
51	58	5469	58	56	7109	33	36	7740
52	26	5491	63	00	7543	36	25	8165
52	57	5513	67	32	7976	40	52	8590
54	04	5556	72	23	8267	42	12	8675
55	23	5600	74	39	8354	44	00	8760
56	53	5644	77	46	8440	45	45	8845
58	45	5688						
61	32	5731	82	15	8527	48	15	8930
63	30	5753	84	23	8570	51	45	9015
68	30	5775				54	30	9029

TABLE VI

TIME AND TOTAL VOLUME AT STANDARD CONDITIONS OF H₂ EVOLVED
FOR UNCOATED PURE ZIRCONIUM

Uncoated Zr-I <i>P-I</i>			Uncoated Zr-II <i>P-II</i>			Uncoated Zr-III <i>P-III</i>		
Time, min sec		H ₂ Evolved cm ³	Time, min sec		H ₂ Evolved cm ³	Time, min sec		H ₂ Evolved cm ³
2	05	91	2	07	87	2	25	428
6	08	544	5	23	521	4	39	856
9	40	998	8	50	955	7	04	1284
13	44	1451	13	07	1389	10	00	1712
17	46	1908	17	19	1823	12	13	1892
21	39	2358	20	52	2257	13	46	1977
25	36	2812	24	10	2691	15	42	2063
29	34	3265	27	56	3125	18	20	2149
33	42	3719	32	12	3559	21	50	2234
34	37	3809	38	44	3993	27	09	2320
35	33	3900	41	29	4080			
36	28	3991	45	56	4166			
37	31	4082	50	30	4210			
38	50	4172						
40	32	4263						
43	14	4354						
47	58	4444						
51	40	4490						
56	48	4535						

TABLE VII

TIME AND TOTAL VOLUME AT STANDARD CONDITIONS EVOLVED
 FOR UNCOATED ~~ZIRCONIUM~~
 Zircalloy

Uncoated Zr-1 ZR-1			Uncoated Zr-2 ZR-2			Uncoated Zr-3 ZR-3		
Time, min sec	H ₂ Evolved cm ³		Time, min sec	H ₂ Evolved cm ³		Time, min sec	H ₂ Evolved cm ³	
4 12	436		1 57	88		2 43	439	
7 27	872		5 25	527		4 17	878	
10 58	1308		8 46	966		5 54	1317	
14 02	1744		12 43	1405		7 35	1756	
17 12	2180		16 53	1844		9 21	2195	
20 41	2616		20 54	2283		11 10	2634	
24 21	3052		24 50	2722		13 07	3074	
28 24	3488		28 53	3161		15 04	3512	
33 10	3924		33 04	3600		17 39	3951	
41 00	4282		37 29	4039		19 13	4127	
			39 41	4223		20 24	4214	
			41 03	4311		22 06	4302	
			42 43	4399		25 35	4390	
			44 59	4487		27 30	4404	
			48 25	4574				
			55 49	4662				

TABLE VIII

TABLE OF DISSOLUTION RATES FROM PREVIOUS WORK
AND CALCULATED VALUES FOR COATED C-III

Temp., °C	1/T, °K	Dissolution Rate, (gm/cm ² -sec) · 10 ⁵		
		0.75M _{HF}	1.05M _{HF}	0.46M _{HF}
1. Previous Work*				
30	.0033	6	11	
50	.0031	7.5	16	
80	.00283	10.5	24	
2. Calculated Values				
100	.00268	27.7	19.4	33

*Interpolated data from September, 1953, Progress Report.

the symbols used in the sketch, where a , b , and c are the initial dimensions,

$$M_{\text{Zr dissolved}} = \rho [a c l + a b l + b c l - l^3] .$$

Combining these two expressions for the mass of zirconium dissolved,

$$\frac{(\text{cm}^3 \text{ H}_2 \text{ evolved})(\text{MW}_{\text{Zr}})}{(22,400)(2)} = \rho [(a c + a b + b c) l - l^3] .$$

At any point on the curve all quantities but l are known and this may be calculated. Assume $l^3 = 0$ for the first approximation. Calculate l , and then observing that l^3 is to be subtracted from the l term, assume a slightly larger value of l , and recalculate. For the first several points on the curve the approximation $l^3 = 0$ will actually be good, as a very small amount of zirconium has been dissolved.

The area of the sample at this time will be

$$A = 2 [(a - l)(b - l) + (a - l)(c - l) + (b - l)(c - l)] .$$

The slope of the curve at this time, multiplied by the factor $(\text{MW}_{\text{Zr}})/(22400)(2)$ gives the instantaneous weight loss in gm/min. Dividing by the area gives the dissolution rate at that time. From knowledge of the rate at which acid was added in moles/min, the time, and the moles of zirconium dissolved, the acid concentration for the point can be calculated.

The point calculated for curve C-III in Fig. 4 at 10, 30, and 70 min. are plotted in Fig. 5. They are checked against previous rates reported² for pure zirconium by extrapolation of a plot of log. Dissolution rate versus $1/T$. It is seen that they are well within the range predicted by the extrapolation. The variation is probably due to the assumption of a uniform attack on the sample. At the low value of 10 min it is seen from Fig. 4 that the reaction is just starting. The attack is probably taking place at a few cracks that have appeared in the surface coating; not all of the total initial area is exposed to the attacking acid solution as was assumed. At the high value of 70 min, the area is again questionable, since any rounding of corners or pitting of the sample would change the area from the assumed value. The center portion of the curves probably represent a reacting area closest to that which was assumed.

Sample Calculation

Sample calculations for point 1 of Fig. 5, using data from curve C-III of Fig. 4 to give the reaction rate as a function of HF concentration, are shown below:

$$\text{Molecular weight of zirconium} = 91.22 .$$

Initial dimensions

$$a = 0.502 \text{ in.} = 1.275 \text{ cm}$$

$$b = 0.213 \text{ in.} = 0.541 \text{ cm}$$

$$c = 1.583 \text{ in.} = 4.021 \text{ cm}$$

$$\text{Initial weight} = 17.4635 \text{ gm.}$$

At $T = 10$ min on Fig. 4,

$$\text{cm}^3 \text{ H}_2 \text{ at Standard Conditions} = 225$$

$$\text{Slope curve C-III at 10 min} = 90 \frac{\text{cm}^3}{\text{min}}$$

From the combined expression l is calculated, neglecting the term $-l^3$ for the moment;

$$= \frac{(17.4635)(l)}{(1.275)(.541)(4.021)} \left[\frac{(225)(91.22)}{(22,400)(2)} \right] [(1.275) \cdot .541 + 1.275 \cdot 4.021 + .541 \cdot 4.021] .$$

$$l = 0.009 \text{ cm}$$

Then, $l^3 = -0.729 \times 10^{-6}$ and is negligible, as was assumed.

$$A = 2 [(1.266)(.532) + (1.266)(4.012) + (.532)(4.012)]$$

$$A = 15.774 \text{ cm}^2$$

$$\text{Dissolution Rate} = \frac{(90)(91.22)}{(44,800)(15.774)} = 0.0116 \frac{\text{gm}}{\text{cm}^2\text{-min}}$$

$$\text{Acid Rate} = 0.50 \text{ gm/min of 48\% acid for 10 min}$$

$$\text{Remaining Moles of HF} = \left[\frac{(10)(0.50)(0.48)}{20} \right] - \frac{(225)(2)}{22,400} = 0.100$$

$$\text{Molarity} = \frac{(1000)(0.100)}{90.6 + (0.5)(10)} = 1.05\text{M}$$

The term in the denominator is a volume correction for the addition of 48% acid for 10 min to the water already in the reactor.

By similar calculations the reaction rate at 30 min is found to be 0.0198 gm/cm²-min and the acid concentration is 0.46 molar. At 70 min the rate is 0.0166 gm/cm²-min at an acid concentration of 0.75M.

Observations during the Runs

In the runs with pure uncoated zirconium and uncoated Zircalloy-II, the reaction proceeded as expected with very little or no initial delay, the reaction starting immediately on addition of acid. This is shown by the immediate evaluation of gas. The reaction proceeded as a direct function of time and rate of acid addition until the acid was shut off and the area of attack became small. As expected, the faster the acid rate, the faster the reaction rate (Figs. 6 and 7).

With the coated samples, types A, B, and C, the reaction proceeded somewhat differently. There was an initial delay before the main reaction started due to the surface film's resistance to attack. During this time the acid concentration builds up to a higher value than if the reaction had been proceeding. When a crack or break in the film occurs the reaction proceeds for a time at a higher rate than the equilibrium rate. This period is represented by the first straight-line portion of the curves in Figs. 2, 3, and 4. The hump approximately one-third of the way along the curve is due to the reaction slowing down as the rate approaches the equilibrium reaction rate. The second straight portion of each curve represents the equilibrium rate, which is established by the rate of acid addition and is not primarily dependent on the initial buildup of acid. Then as the acid is shut off and the area becomes smaller, the rate dries off as shown by the curvature of the final section of the graphs. Since in all cases there was an excess of acid, the volume of gas collected goes up to the theoretical value predicted from the stoichiometric balance and stops rather than approaching an asymptotic value.

The variation in slope between two individual samples of the same type at the same acid addition rate, e.g., curves C-I and C-III in Fig. 4, may be explained by the fact that C-III has a larger surface area than C-I. This indicates that the mass transfer of H₂ from the surface to the solution or in the reverse direction has an appreciable effect. Assuming that the rate of H₂ transfer is constant, and that the metals are exactly the same below the surface coating, a greater surface area will correspond to a greater reaction rate. With no mass-transfer effects present, the rates should be exactly the same on a gm/cm²-min basis.

No external agitation was employed. The spraying action of the H₂ evolved from the reaction and the gentle refluxing supplied the only agitation.

In all the solutions containing the coated samples and the solutions containing the uncoated Zircalloy, a residue remained. In the uncoated Zircalloy-II solution the residue was a black spongy-looking material. It might be undissolved alloying constituent.

This same black spongy residue was present in the solutions from type A along with material that looked like the surface film itself. It seems that the acid, once having cracked the film, worked underneath it and caused it to peel off. Bubbles of H_2 would force off bits of coating which would drop to the bottom of the solution. The same flaky material was present in the runs from both types B and C. In the case of type B, it resembled little white granules.

At no time were these residues appreciable in relation to the sizes of the samples. They were not weighed, but it was estimated that the black spongy material weighed less than 2 percent of the total weight and the flaky residue less than 0.5 percent.

The temperature remained constant in the reaction vessel, as the copper provided good heat conduction during the reaction.

On removal of one of the samples from the reactor before the reaction was complete, it was found that the assumption of uniform attack was not completely correct. The sample was rough and pitted, possibly because of heat treatment or crystal structure variation.

CONCLUSIONS

The most important results and observations have been mentioned in the preceding section.

At an acid addition rate of 0.5 gm/min of HF, the reactions in all cases proceeded smoothly with rates that could be handled with the experimental equipment. At roughly twice this acid rate (1.14 to 1.23 gm/min) the type B samples got out of control. The initial buildup of acid started such a fast reaction that the gas could not be collected. The portions of the curves that were obtainable are presented in Fig. 3.

In all cases the delay in initiation of the reaction seems to decrease with increased acid addition rate, probably because the acid builds up more quickly to a concentration that will attack the imperfections in the coatings and cause breakdown. This speed of breakdown does not increase proportionately with the acid buildup, however, as evidenced by the extreme rate encountered with type B at the higher acid addition rate.

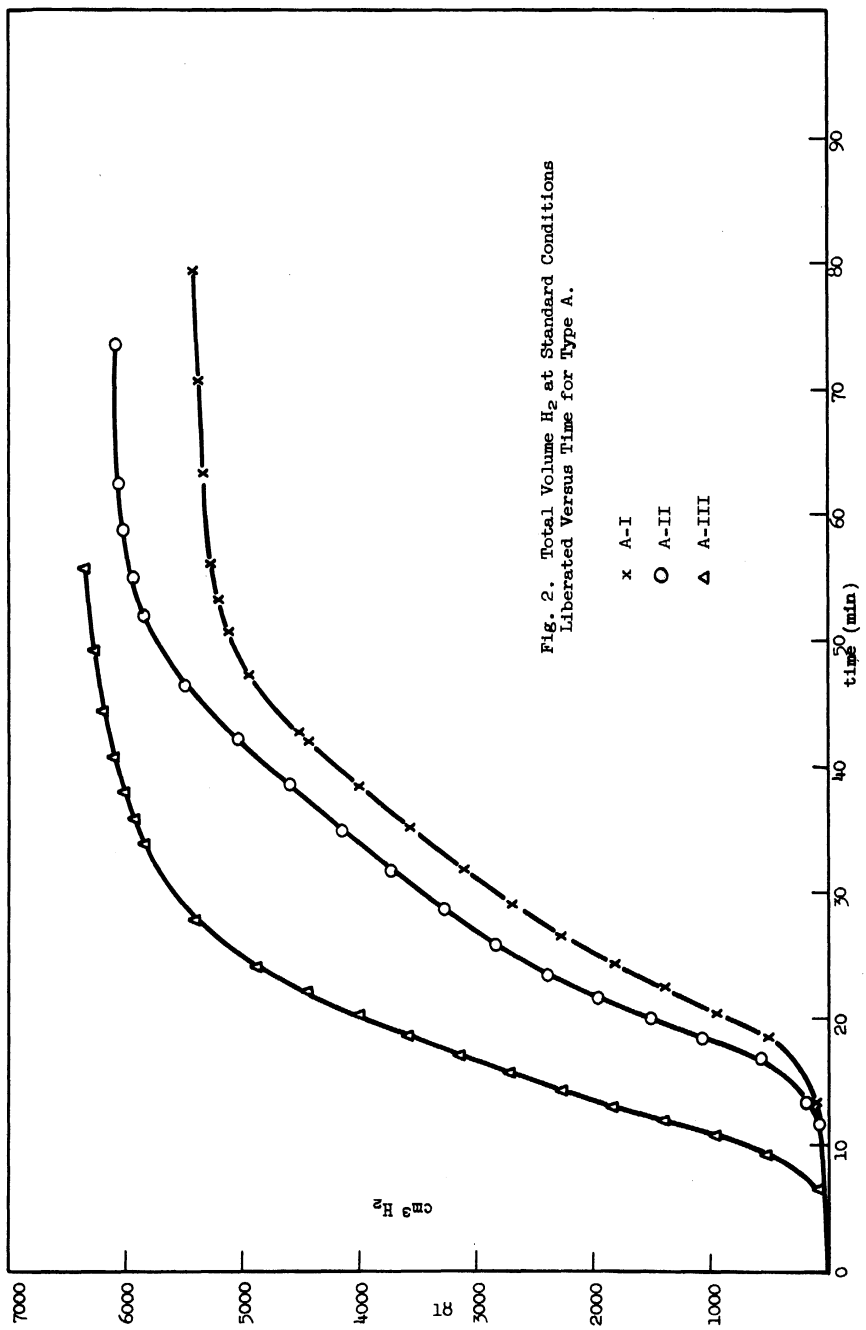
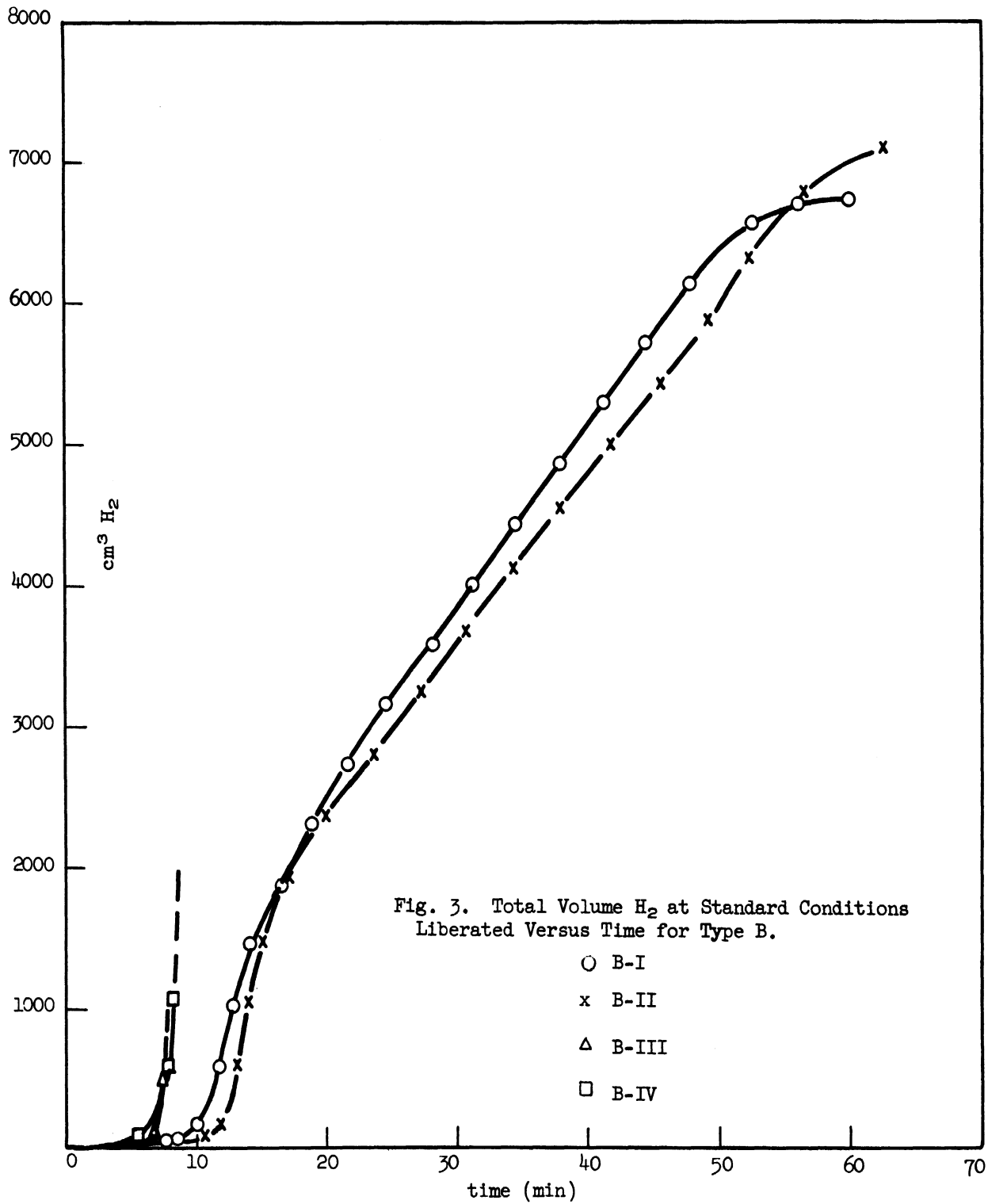


Fig. 2. Total Volume H₂ at Standard Conditions Liberated Versus Time for Type A.

x A-I
 O A-II
 Δ A-III



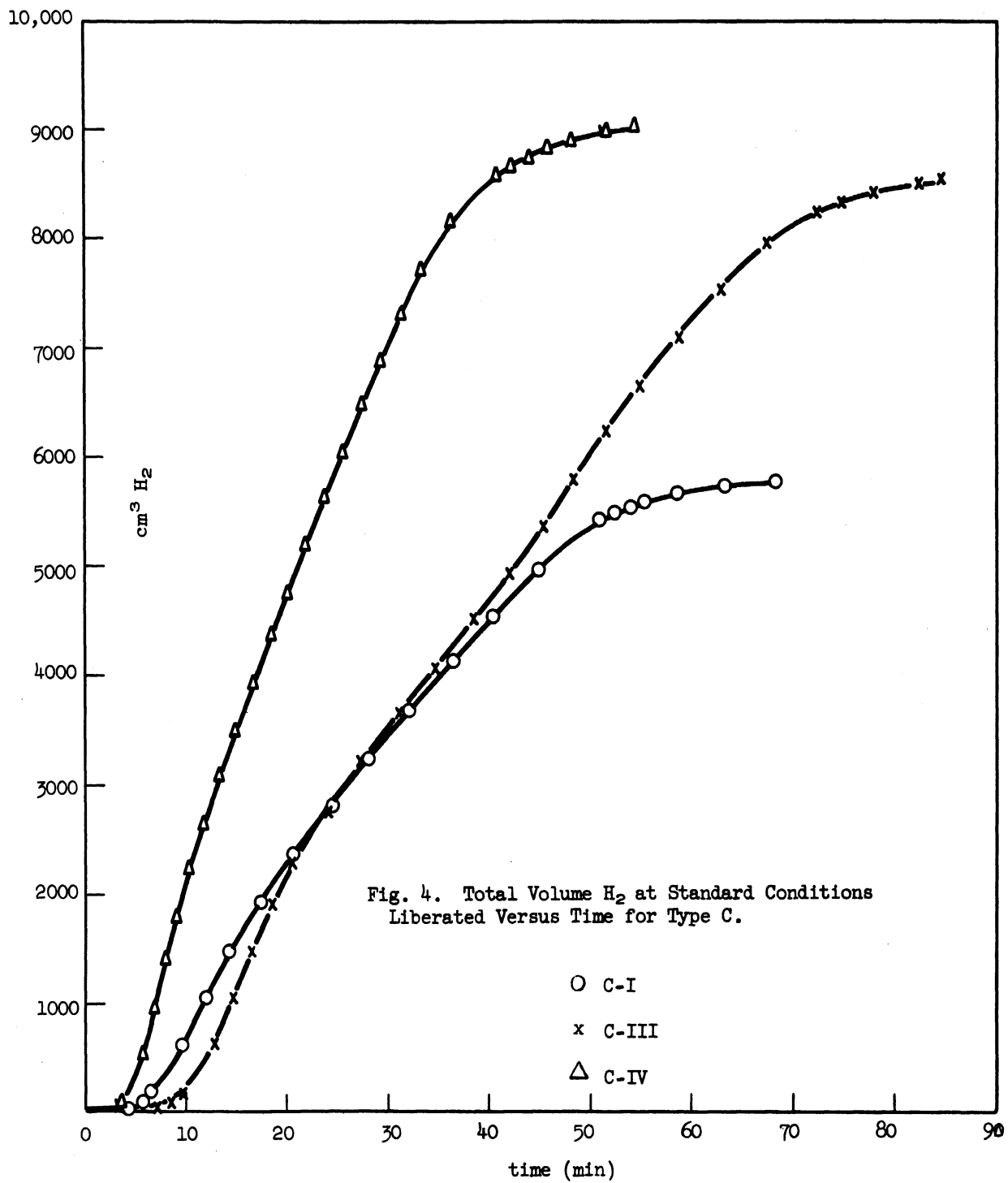
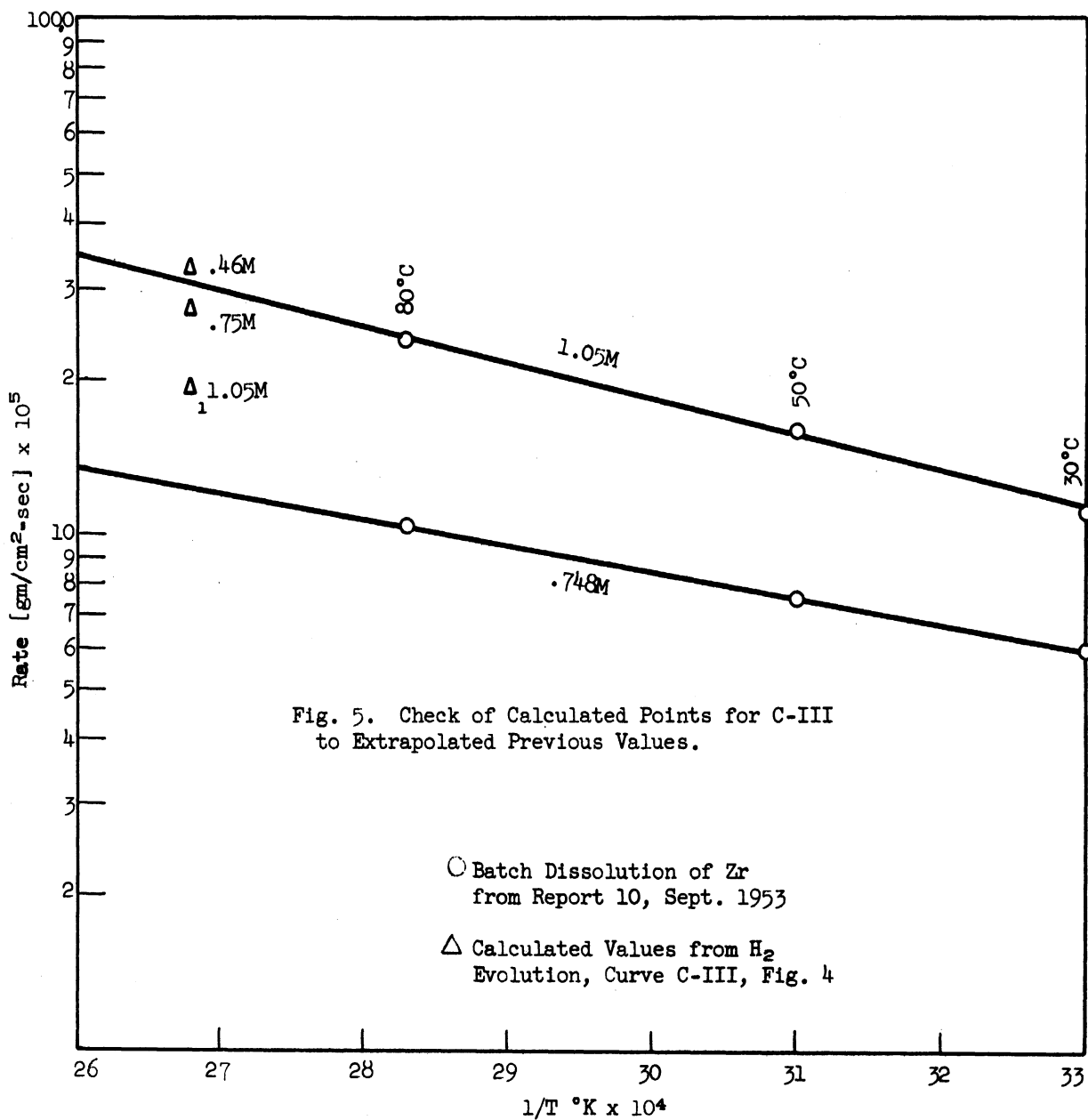
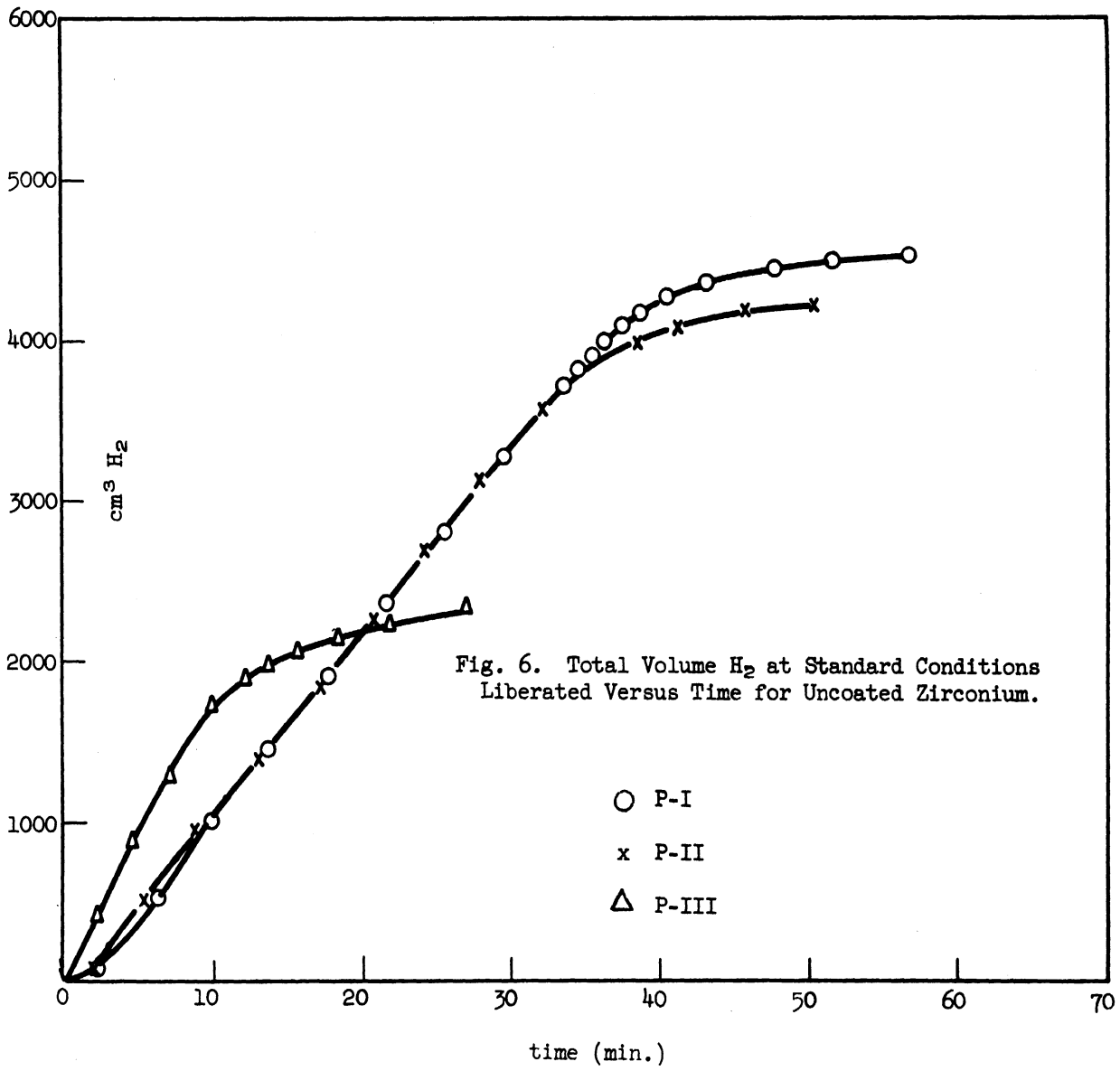
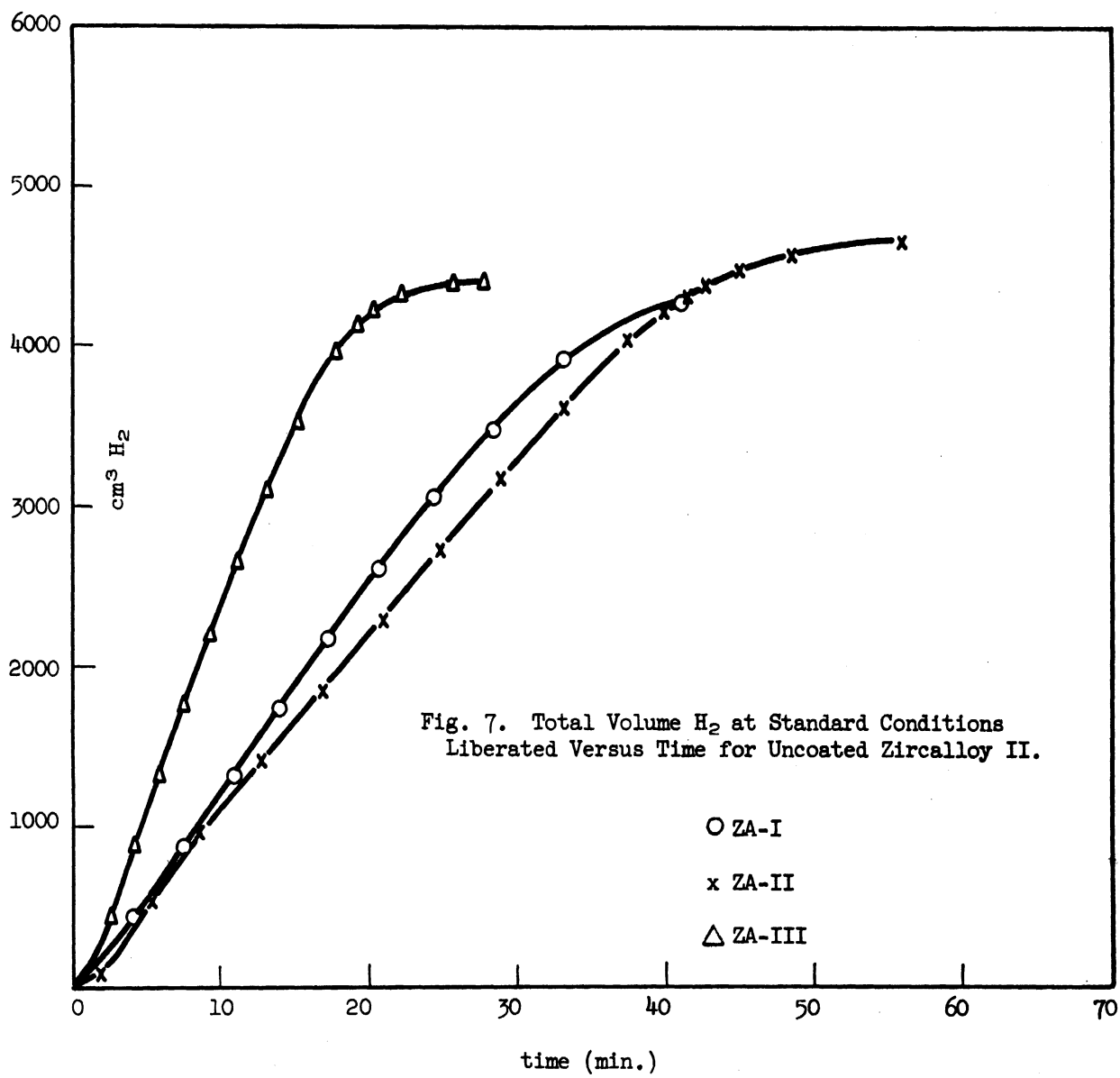


Fig. 4. Total Volume H₂ at Standard Conditions Liberated Versus Time for Type C.

- C-I
- × C-III
- △ C-IV







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