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RATES OF GAS EVOLUTION FROM THE REACTIONS OF URANIUM AND THORIUM CARBIDES WITH AQUEOUS SOLUTIONS OF HCl, H_2SO_4, NaOH, AND NH_4F

Mildred Bradley Sears
Leslie M. Ferris

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

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JUNE 1969

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ABSTRACT

Gas evolution, as a function of time, is shown graphically for the reactions of 3- to 4-g specimens of arc-cast uranium and thorium carbides with aqueous solutions of HCl, H_2SO_4, NaOH, and NH_4F.

1. INTRODUCTION

The rates of the chemical reactions of the uranium and thorium carbides are of interest in the reprocessing of nuclear reactor fuels containing these compounds, in evaluating the safety of certain nuclear reactors, and in establishing suitable procedures for manufacturing and storing the carbides.

This report presents graphs showing the volumes of gas evolved, as a function of time, during the reactions of high-purity, arc-cast uranium and thorium carbides with aqueous solutions of HCl, H_2SO_4, NaOH, and NH_4F. The products of these reactions have been discussed previously.[1-4] Because the specimens used in the experiments were irregularly shaped, the data obtained were not suitable for determining the orders and mechanisms of the reactions or for calculating rate constants.

Acknowledgment. – The authors wish to thank the following members of the ORNL Metals and Ceramics Division: R. E. McDonald and L. Queener for arc-melting the carbides, and J. P. Hammond and C. Hamby for heat-treating the uranium sesquicarbide. We are also indebted to J. F. Land for conducting some of the experiments.

2. EXPERIMENTAL PROCEDURE AND RESULTS

The data presented here were obtained in the course of our experiments on the products of the reactions of the uranium and thorium carbides with aqueous solutions

of HCl, H_2SO_4, NaOH, and NH_4F.[1-4] The preparation and compositions of the carbide specimens, the hydrolysis procedure, the method of correcting gas volumes for water and acid vapors, and the analytical procedures have been described in detail previously[1-6] and are not repeated here. The carbide specimens were irregularly shaped pieces, weighing between 3 and 4 g,* which resulted from breaking 100-g arc-cast buttons in a diamond mortar. Specimens were stored in a nitrogen-filled "dry" box with P_2O_5 as the desiccant. There were no significant differences between specimens that had been stored for one month and those that had been stored for several years.

In Figs. 1-14, the volumes of evolved gases are plotted, as a function of time, for the reactions of the uranium and thorium carbides with aqueous solutions of HCl, H_2SO_4, NaOH, and NH_4F. Most of the experiments were conducted at 80°C; however, the reactions with 6 M NaOH were also studied at 40°C and occasionally at 99°C. Only the initial part of the reaction (at least the first 6 hr) is shown for the slower reactions. The total times required for 95% of the gases to be evolved in these reactions have already been reported.[1-3]

Neither acid nor base appeared to have any strong catalytic effect on the carbide hydrolysis; this is in accordance with the results of our D_2O studies.[7] Hydrolysis was slower in H_2SO_4 solutions than in pure water (Figs. 1-6), as might be expected, since both the $U(SO_4)_2 \cdot 4H_2O$ and the $Th(SO_4)_2 \cdot xH_2O$ products form insoluble coatings on the carbide surface, and since the water concentration is lower in the H_2SO_4 solutions than in pure water. The reactions of UC and ThC with 4 and 6 M NH_4F solutions at 80°C were slower than the corresponding reactions with water (Fig. 7), again presumably due to the formation of the insoluble products $NH_4F \cdot UF_4$ and $NH_4F \cdot ThF_4$, respectively.

In general, the reactions with the HCl solutions (Figs. 1-6) were similar to those in pure water; this indicates that the formation of the soluble metal chloride instead of the insoluble oxide counterbalanced the small decrease in water concentration in going from pure water to an HCl solvent. The uranium mono- and dicarbides reacted more rapidly with water than with sodium hydroxide solutions (Figs. 8 and 9); uranium sesquicarbide and thorium monocarbide reacted at about the same rate in both media

*In a few cases, < 3-g specimens were used because larger ones were unavailable.

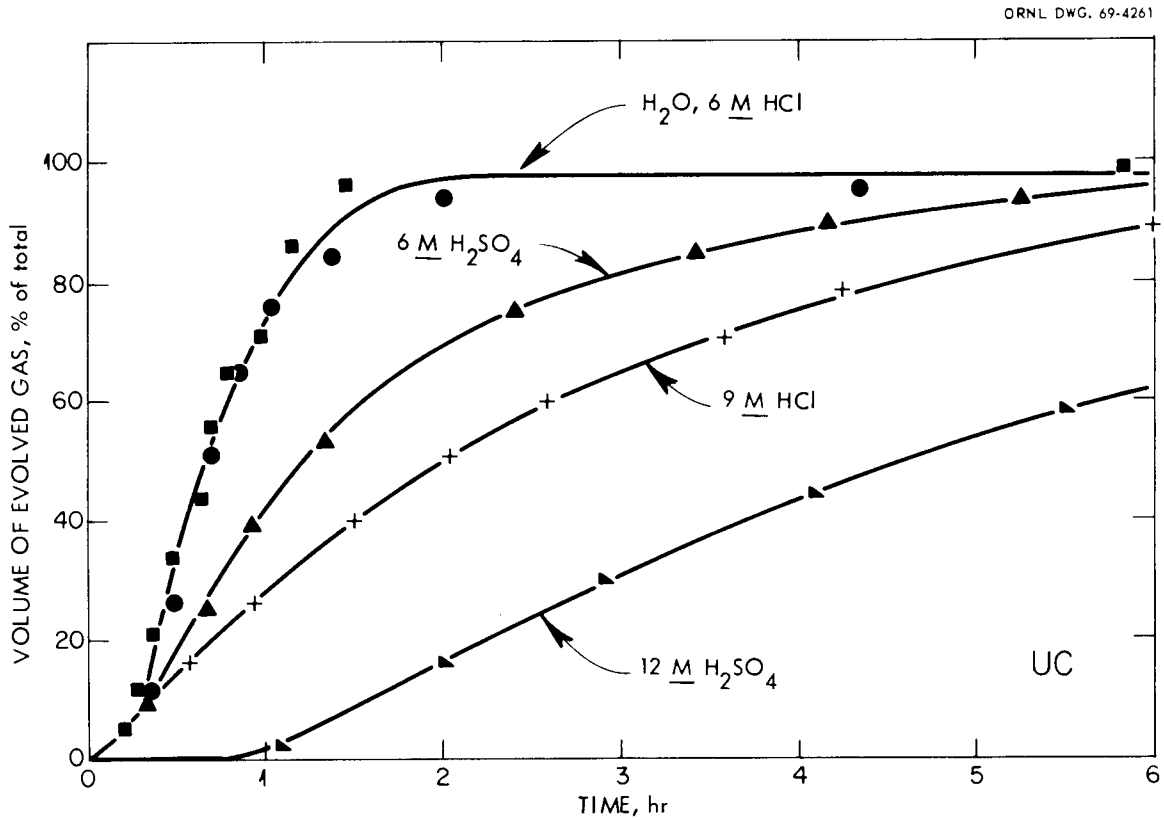

Fig. 1. Rates of Gas Evolution in the Reactions of 3- to 4-g Uranium Monocarbide Specimens with Nonoxidizing Acids at 80°C.

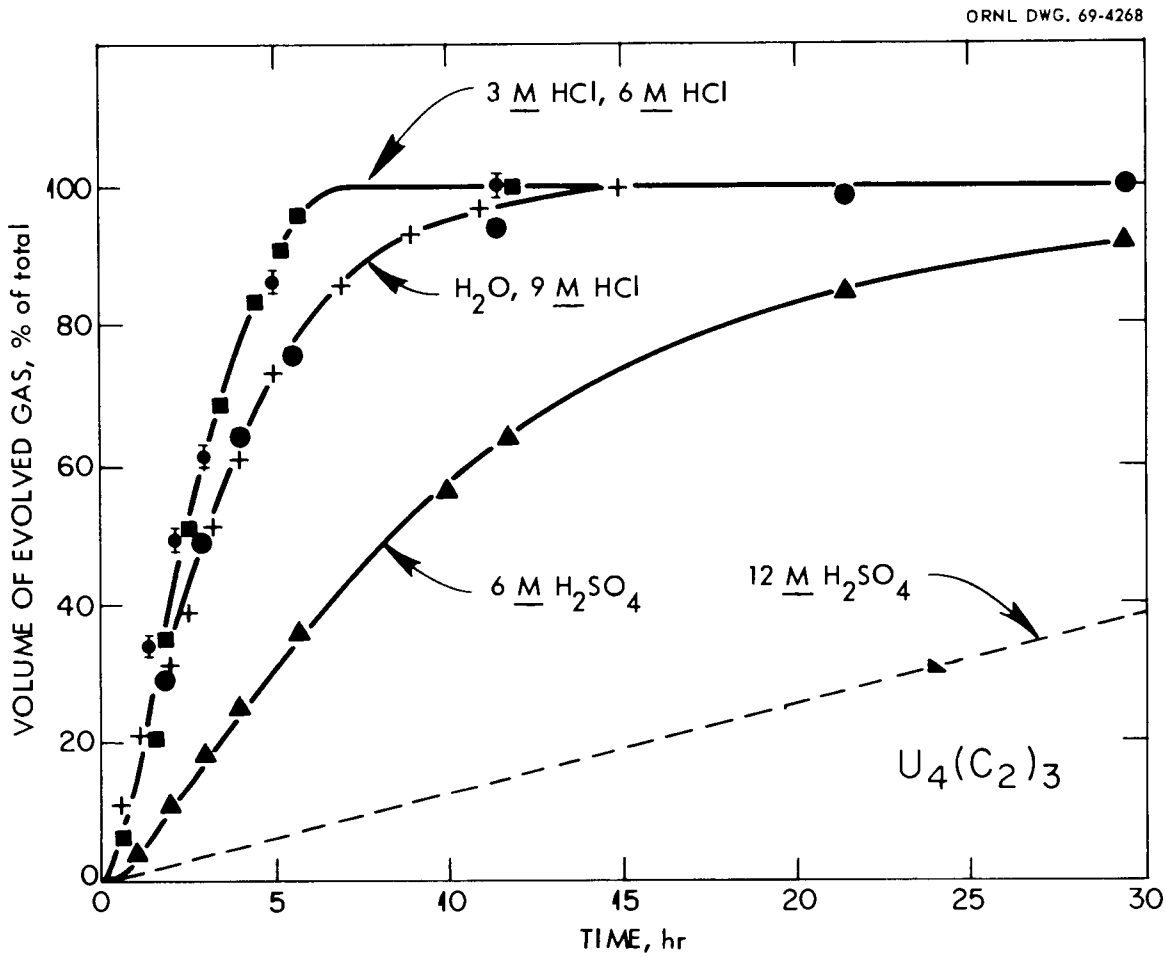

Fig. 2. Rates of Gas Evolution in the Reactions of 3- to 4-g Uranium Sesquicarbide Specimens with Nonoxidizing Acids at 80°C.

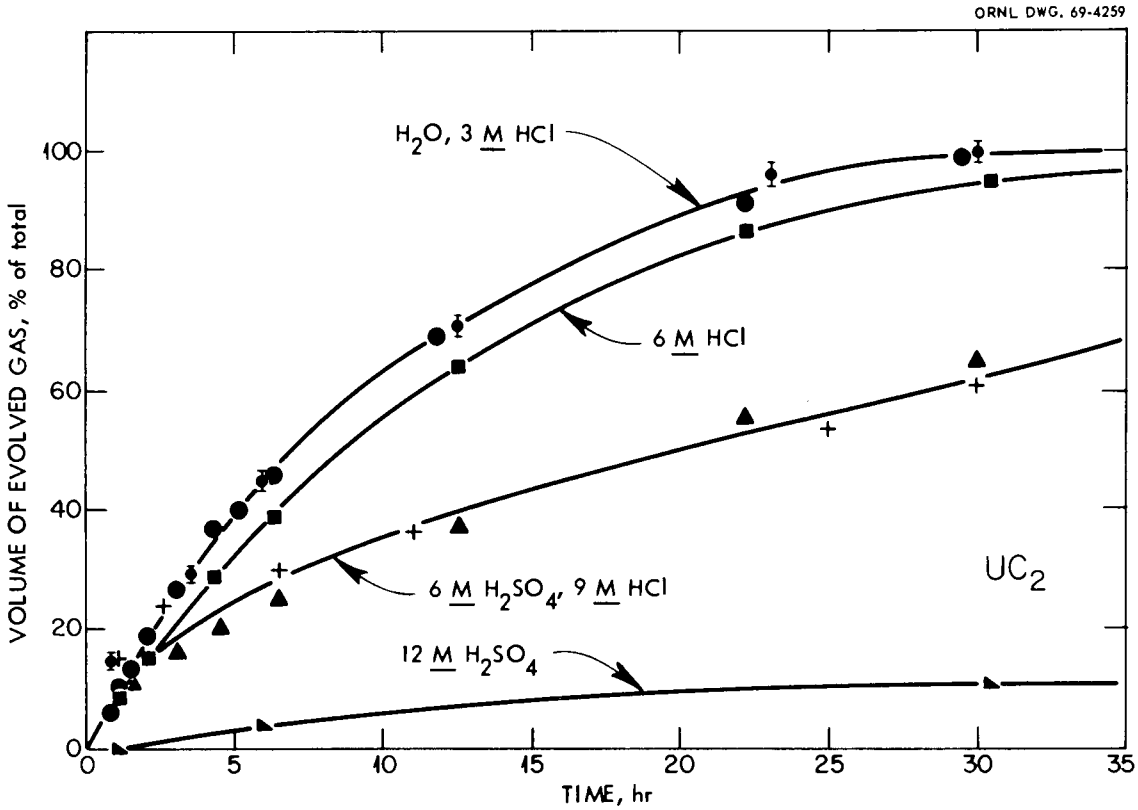

Fig. 3. Rates of Gas Evolution in the Reactions of 3- to 4-g Uranium Dicarbide Specimens with Nonoxidizing Acids at 80°C.

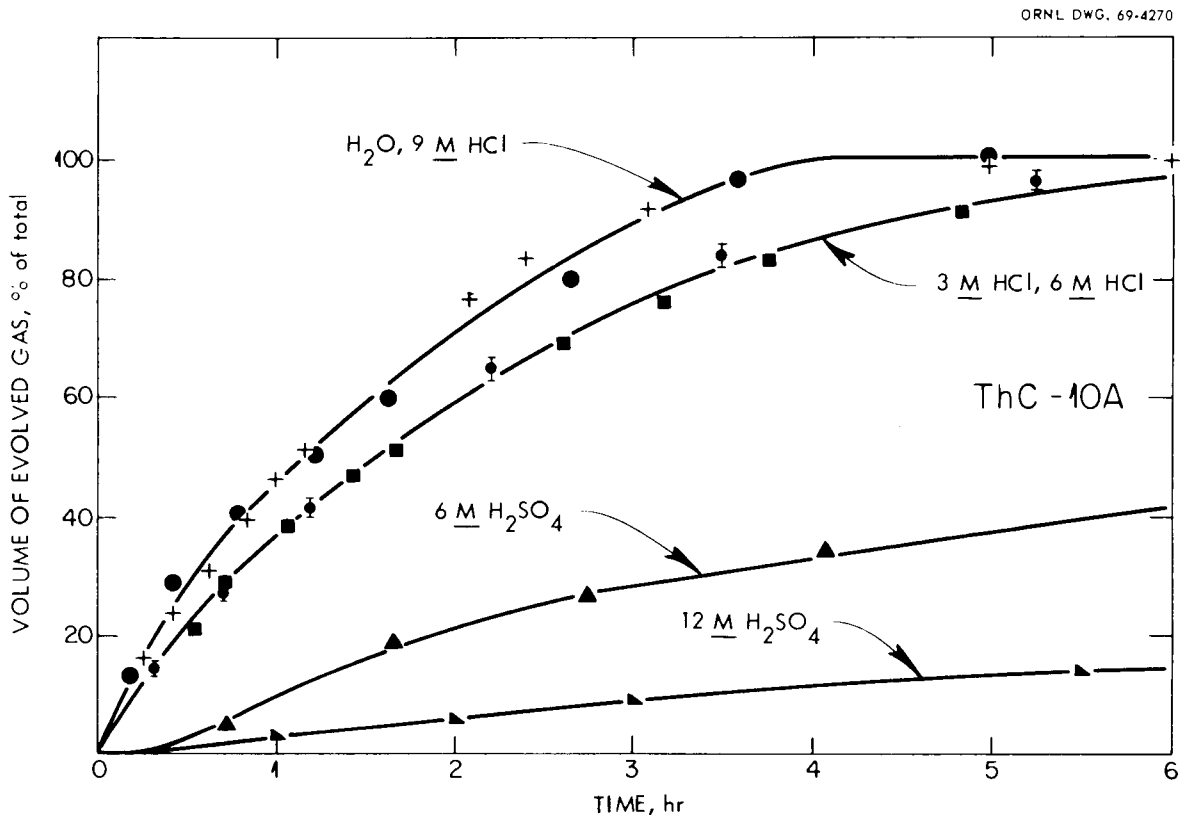

Fig. 4. Rates of Gas Evolution in the Reactions of 3- to 4-g, Single-Phase Thorium Monocarbide Specimens ($ThC_{0.92}$) with Nonoxidizing Acids at 80°C.

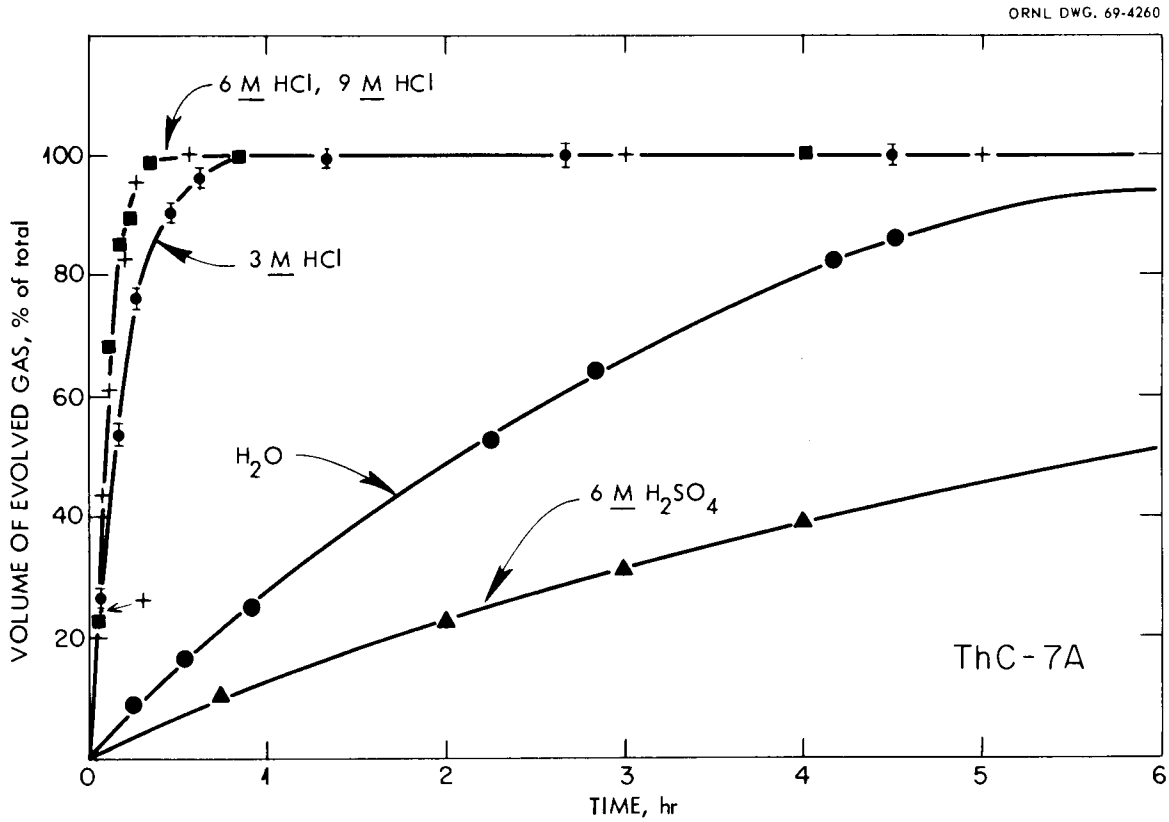

Fig. 5. Rates of Gas Evolution in the Reactions of 3- to 4-g Specimens of Thorium Monocarbide ($ThC_{0.99}$) Containing Small Amounts of Thorium Dicarbide with Non-oxidizing Acids at 80°C.

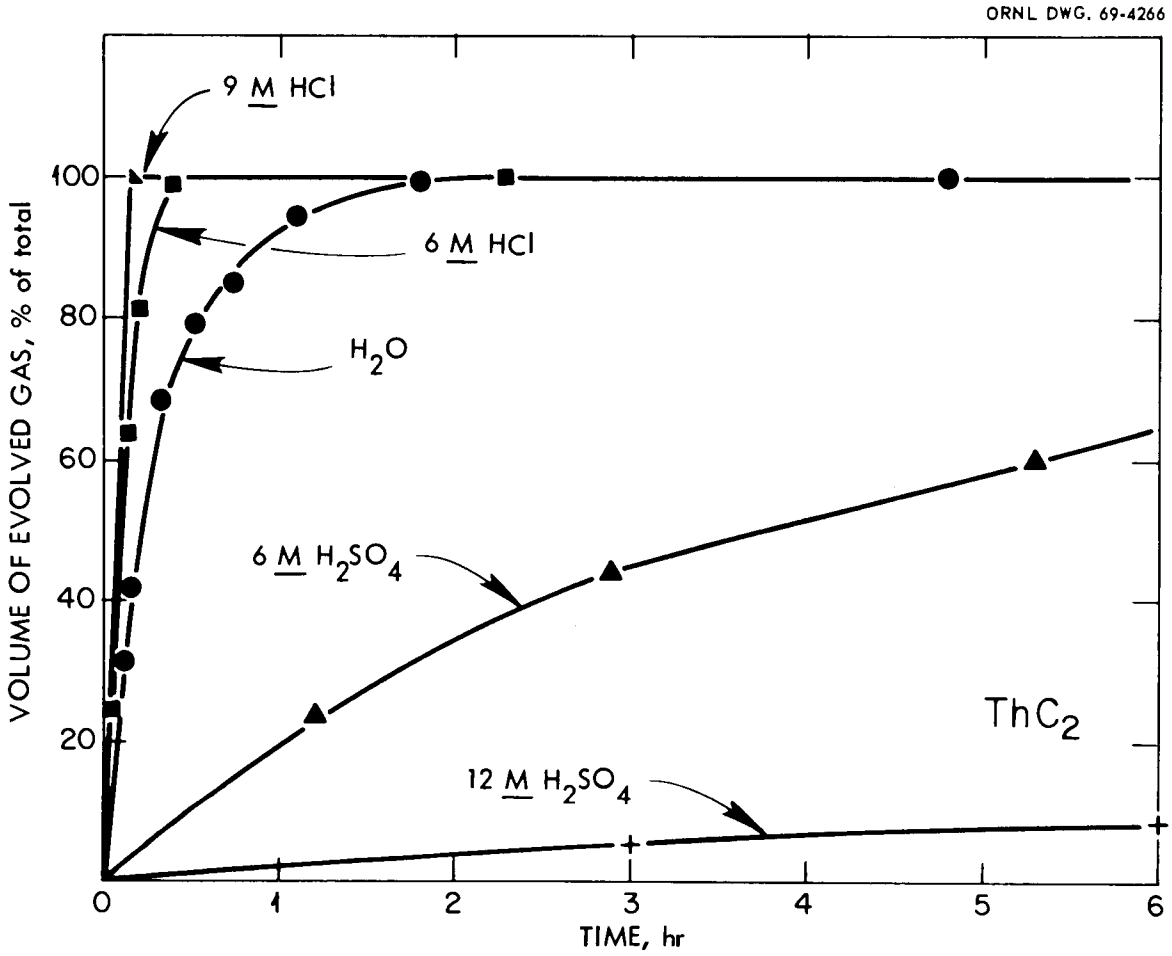

Fig. 6. Rates of Gas Evolution in the Reactions of 3- to 4-g Thorium Dicarbide Specimens with Nonoxidizing Acids at 80°C.

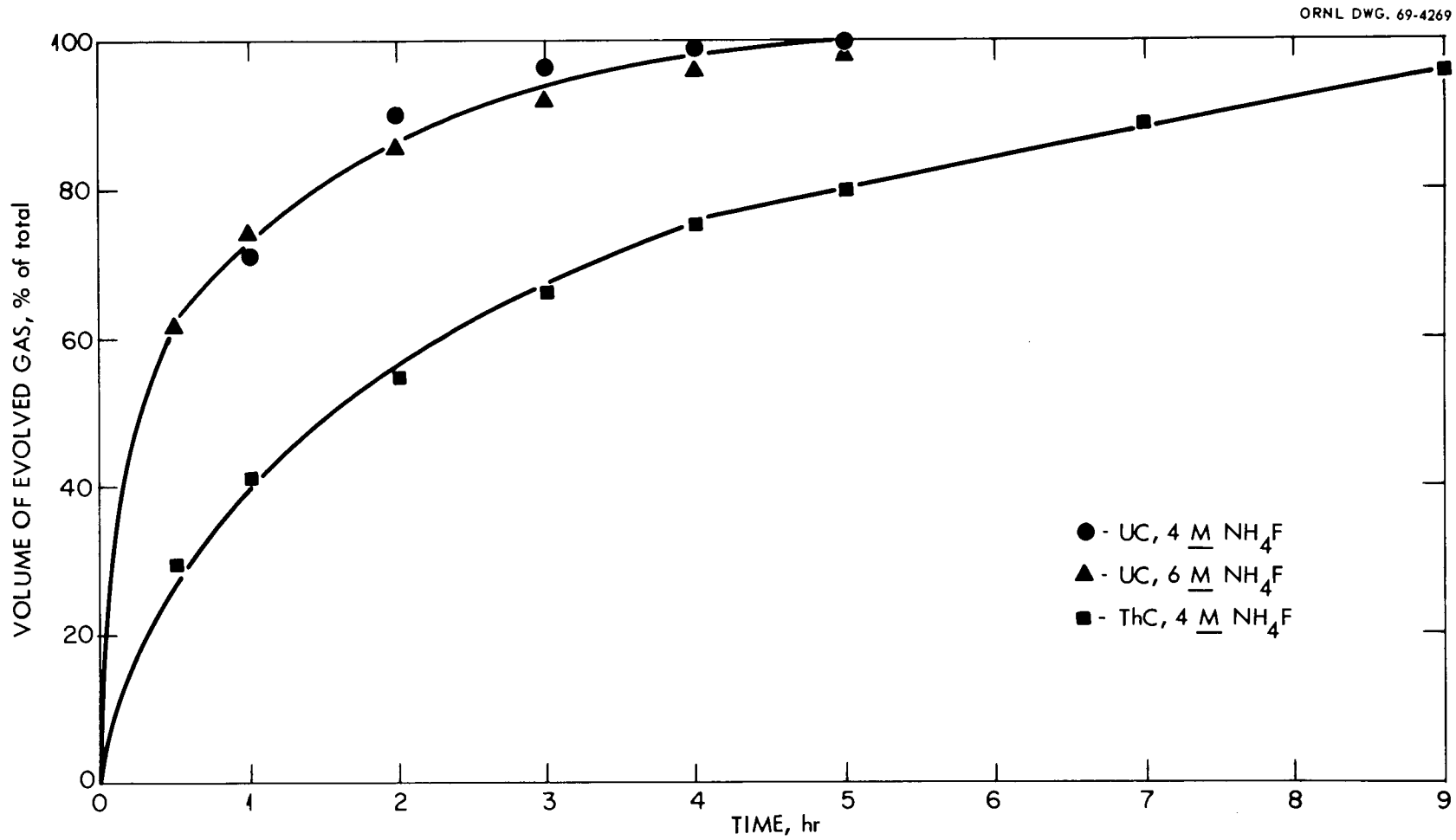

Fig. 7. Rates of Gas Evolution in the Reactions of 3- to 4-g Specimens of UC and ThC with Ammonium Fluoride Solutions at 80°C.

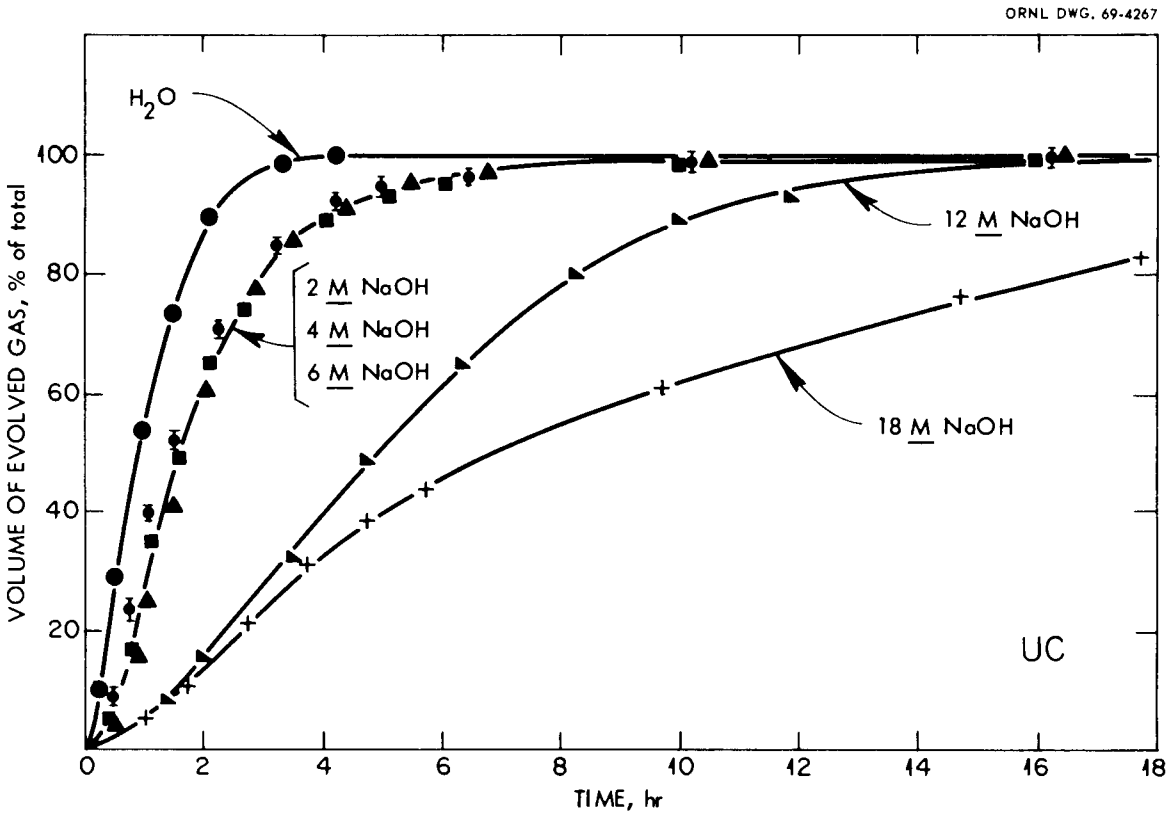

Fig. 8. Rates of Gas Evolution in the Reactions of 3- to 4-g Uranium Monocarbide Specimens with 0 to 18 M Sodium Hydroxide Solutions at 80°C.

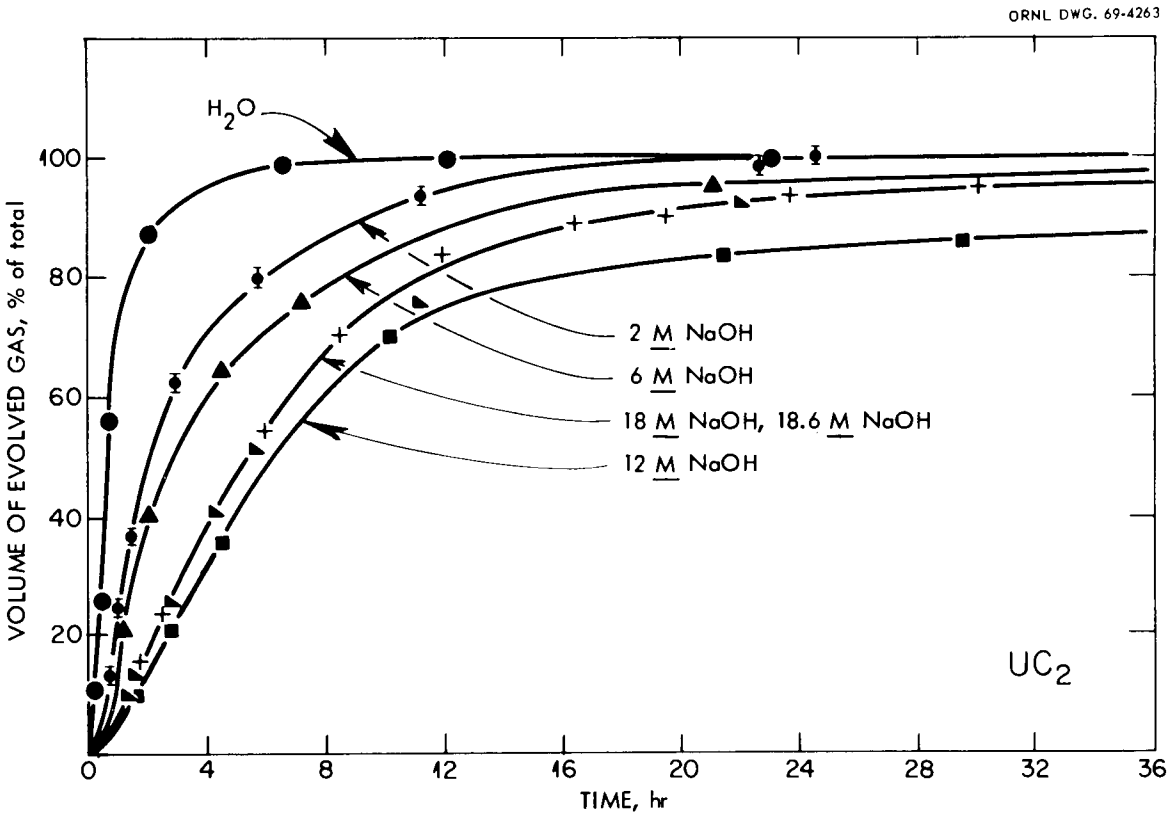

Fig. 9. Rates of Gas Evolution in the Reactions of 3- to 4-g Uranium Dicarbide Specimens with 0 to 18.6 M Sodium Hydroxide Solutions at 80°C.

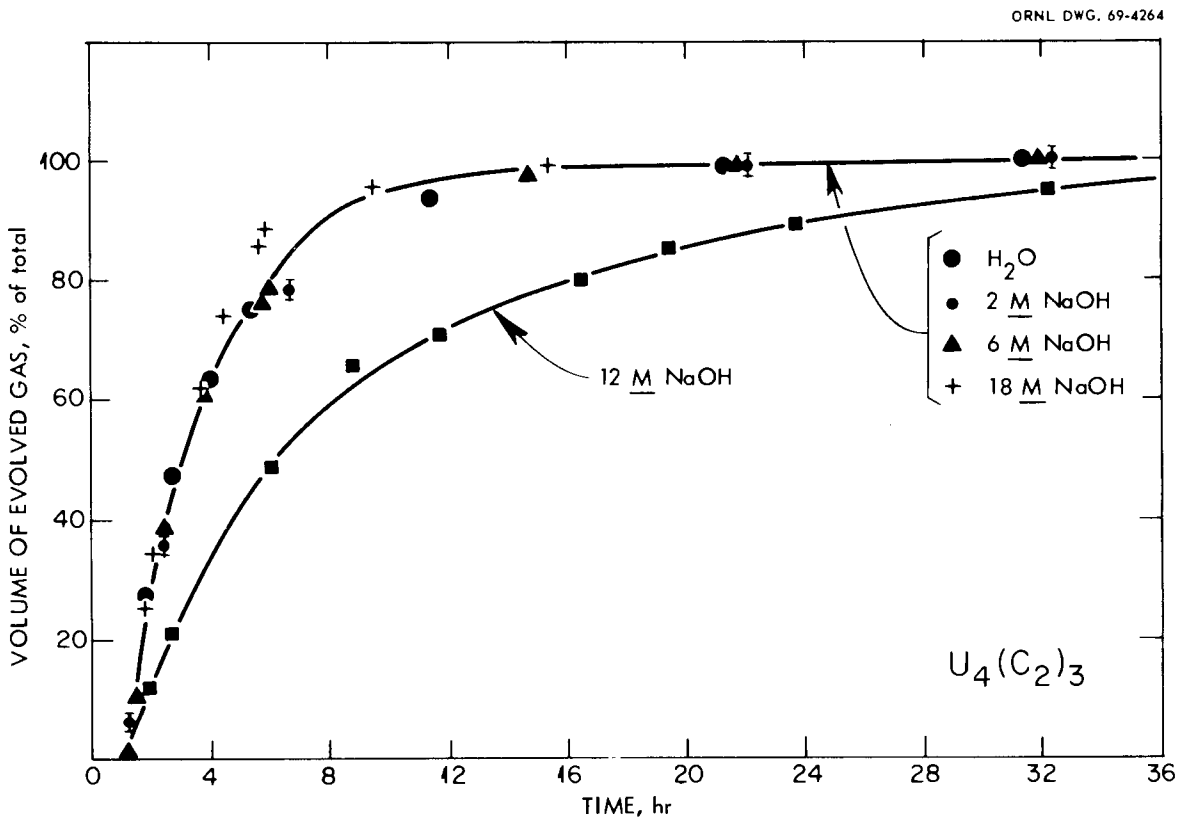

Fig. 10. Rates of Gas Evolution in the Reactions of 2- to 4-g Uranium Sesquicarbide Specimens with 0 to 18 M Sodium Hydroxide Solutions at 80°C.

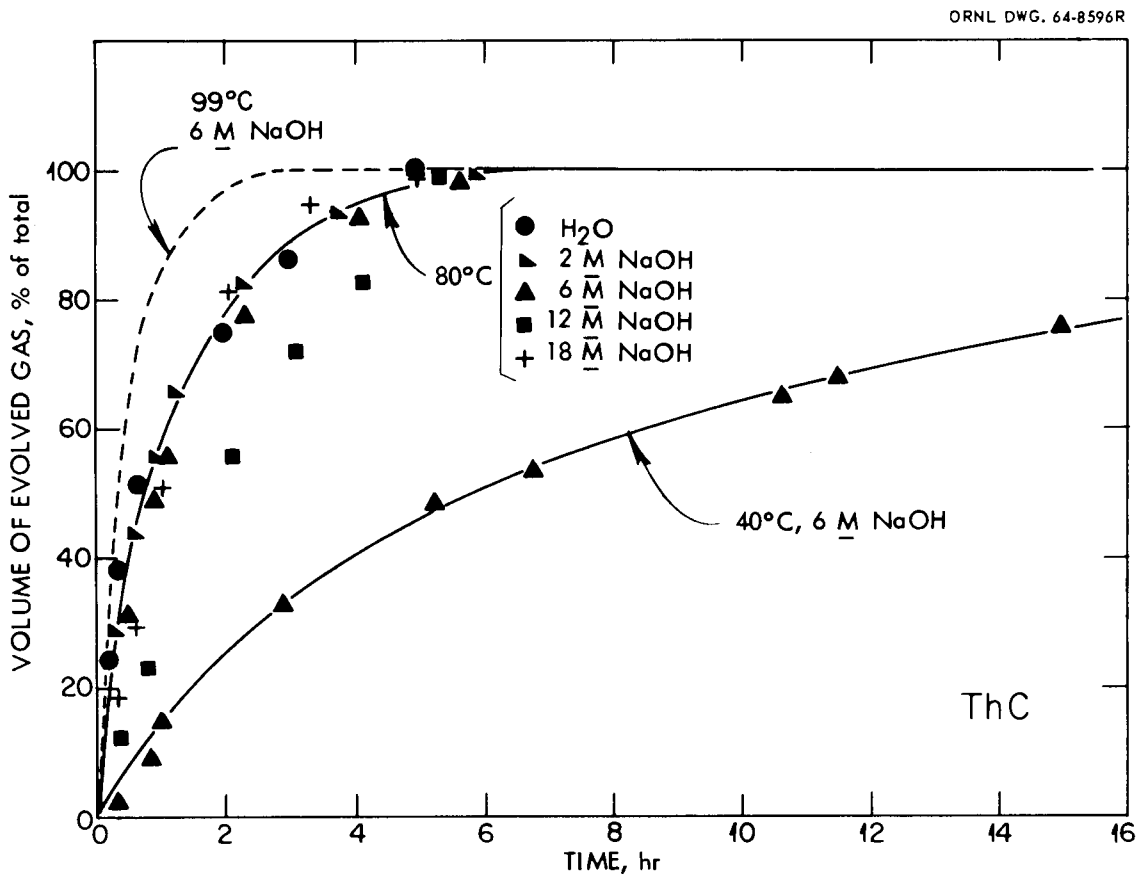

Fig. 11. Rates of Gas Evolution in the Reactions of 3- to 4-g Thorium Monocarbide Specimens ($ThC_{1.03}$) with 0 to 18 M Sodium Hydroxide Solutions.

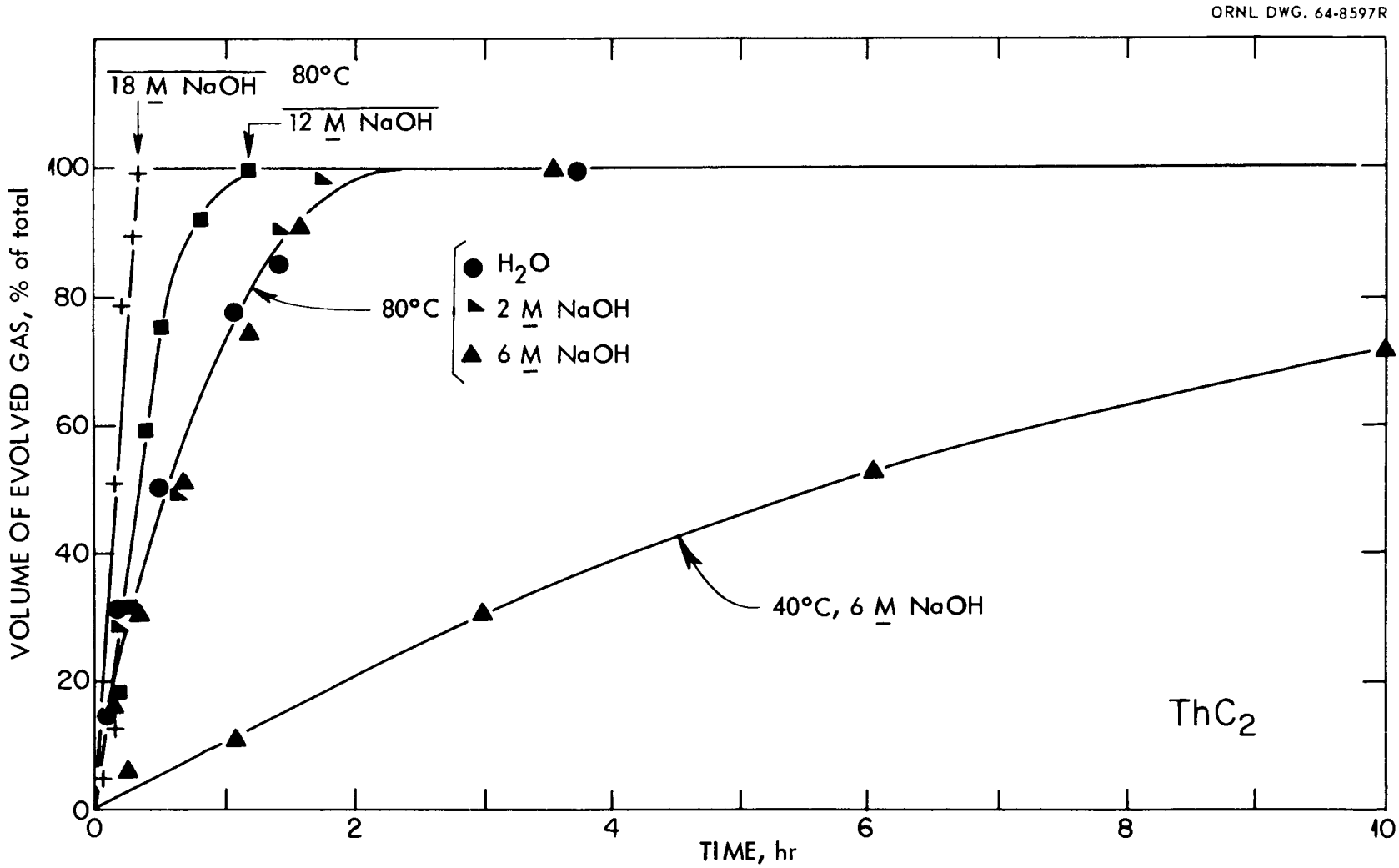

Fig. 12. Rates of Gas Evolution in the Reactions of 3- to 4-g Thorium Dicarbide Specimens with 0 to 18 M Sodium Hydroxide Solutions.

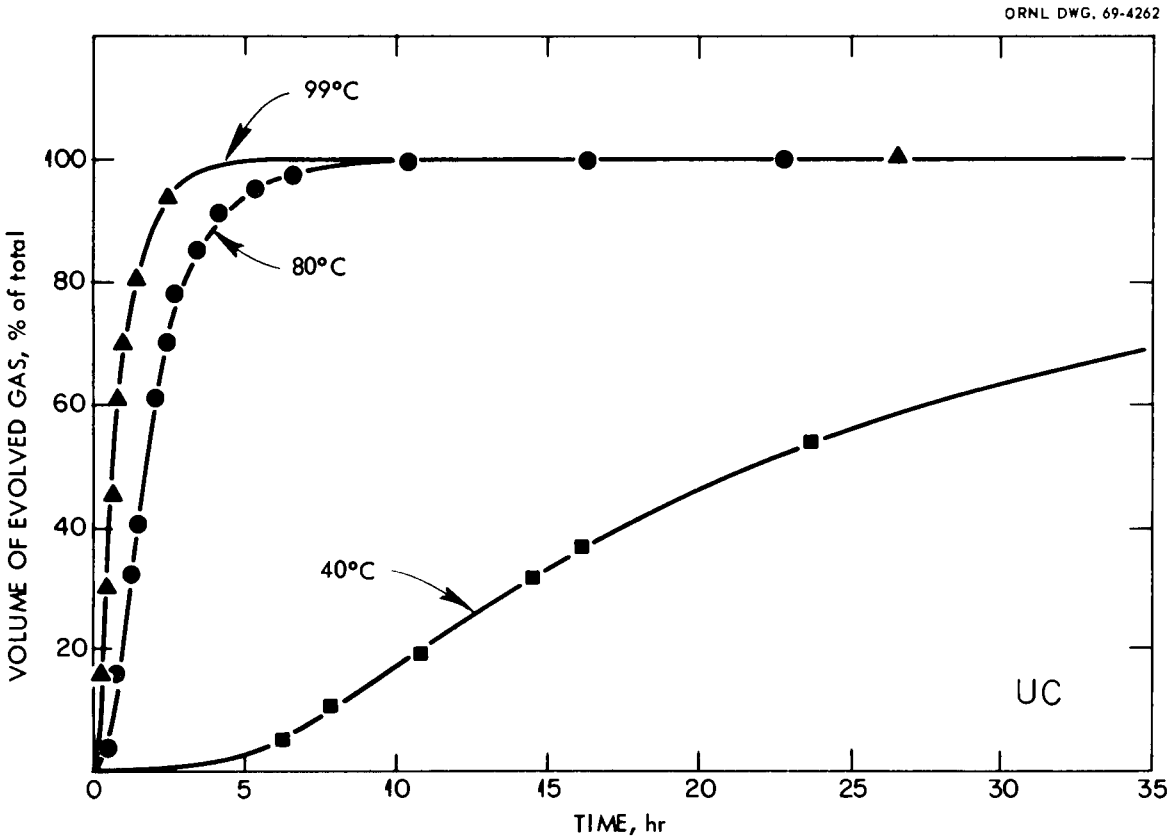

Fig. 13. Effect of Temperature on the Rate of Gas Evolution in the Reaction of Uranium Monocarbide with 6 M NaOH. Specimen sizes: 3 g at 99°C and 80°C; 1 g at 40°C.

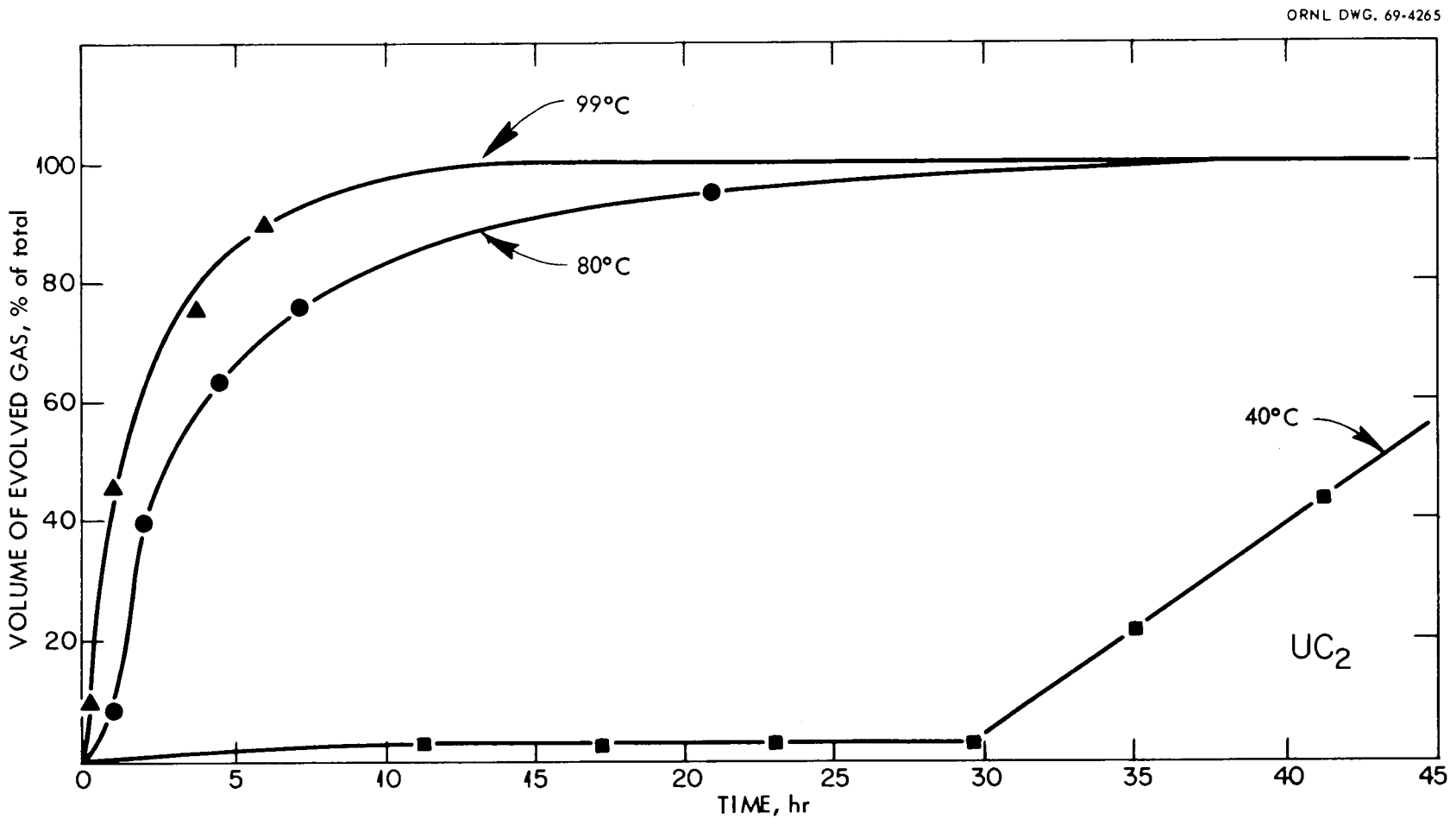

Fig. 14. Effect of Temperature on the Rate of Gas Evolution in the Reaction of 3- to 4-g Uranium Dicarbide Specimens with 6 M NaOH.

(Figs. 10 and 11), while thorium dicarbide reacted more rapidly with the more concentrated sodium hydroxide solutions (Fig. 12).

3. DISCUSSION

Even if high-purity specimens of fixed geometry had been available for these studies, it is doubtful whether any basic kinetic data could have been obtained. The uranium and thorium carbides are so reactive toward moisture that obtaining these compounds in the form of fine powders, free from surface hydrolysis, is virtually impossible. Massive specimens can be used to minimize the amount of surface hydrolysis; however, once the reaction starts, water attacks cleavage planes within the specimens and causes the specimens to disintegrate. For example, 4-g specimens of arc-cast uranium carbides disintegrated completely in water at 25°C to give a -20 mesh powder before there was much chemical reaction of the carbide.[8-10] Even without actual physical disintegration of the specimen, Murbach[11] found that exposure of uranium monocarbide to laboratory air for a few days caused an increase in its chemical reactivity toward oxygen, nitrogen, and carbon dioxide, and also an increase in the apparent surface area of about 100 cm^2 per gram. He postulated that this was caused by hydrolysis occurring along the grain boundaries. It is interesting to note that the uranium monocarbide used in our studies had properties similar to Murbach's "inert" carbide (which had been freshly arc-melted), even though our uranium monocarbide had been stored for several years. To date we have found no way to correct the experimental rate data for the change in surface area caused by attack at the grain boundaries and/or cleavage planes. Single-crystal specimens might possibly eliminate the problem; however, at present they are much too expensive for chemical studies.

Except for work reported by this Laboratory, no information about the rates of reaction of the arc-cast carbides with aqueous solutions of hydrochloric or sulfuric acids, sodium hydroxide, or ammonium fluoride could be found in the literature. Spitz[12] studied briefly the rates of gas evolution in the reactions of sintered uranium monocarbide with solutions of hydrochloric and hydrochloric-phosphoric acids. His sintered carbide was considerably more reactive toward water than the arc-cast specimens used in this study.

4. REFERENCES

1. M. J. Bradley, M. D. Pattengill, and L. M. Ferris, Inorg. Chem. 4, 1080 (1965).
2. M. B. Sears and L. M. Ferris, J. Inorg. Nucl. Chem. 29, 1548 (1967).
3. M. B. Sears and L. M. Ferris, J. Inorg. Nucl. Chem. 30, 2111 (1968).
4. L. M. Ferris, J. Inorg. Nucl. Chem. 30, 2661 (1968).
5. M. B. Sears, R. J. Gray, L. M. Ferris, and B. C. Leslie, Correlation of Composition and Heat-Treatment with the Microstructures of Uranium Carbides, ORNL-3515 (1968).
6. M. B. Sears, T. M. Kegley, Jr., L. M. Ferris, and B. C. Leslie, Metallographic Preparation of Arc-Cast Thorium Carbides and Correlation of Their Microstructures with Composition, ORNL-4354 (in press).
7. M. B. Sears and L. M. Ferris, J. Inorg. Nucl. Chem. 28, 2055 (1966).
8. M. J. Bradley and L. M. Ferris, Inorg. Chem. 1, 683 (1962).
9. M. J. Bradley and L. M. Ferris, Inorg. Chem. 3, 189 (1964).
10. M. J. Bradley and L. M. Ferris, Inorg. Chem. 3, 730 (1964).
11. E. W. Murbach, The Chemical Reactivity of Uranium Carbide, NAA-SR-11235 (1965).
12. J. Spitz, Contribution a l'Etude de l'Hydrolyse des Carbures d'Uranium, CEA-R 2350 (1964); also Premiere These, Universite de Grenoble (1963).

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