AIP | The Journal of Chemical Physics

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Citation: The Journal of Chemical Physics **43**, 994 (1965); doi: 10.1063/1.1696883
View online: http://dx.doi.org/10.1063/1.1696883
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/43/3?ver=pdfcov
Published by the AIP Publishing

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to indicate that impurities cannot play a dominant role. Take, for instance, Fig. 5, which is based on at least seven independently grown samples. If traces of water should have a marked effect on the results, it would not be very probable that all samples would have the same amount of water, which would make it possible for the points to lie on a reasonably smooth curve. Note that the deviation from the curve for a particular sample is nearly the same for both temperatures. This indicates that these deviations are not due to accidental errors of measurement but must be due to a particular property of the sample itself. It is quite possible that this might be the amount of impurities or other lattice defects. If this is true, Fig. 5 gives an indication of the errors caused in these measurements by sample imperfections.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 43, NUMBER 3 1 AUGUST 1965

Kinetics of the Hydrofluorination of Thorium Dioxide*

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(Received 19 February 1965)

Uniformly colored and optically isotropic interference films of thorium tetrafluoride were formed on the polished trigonal faces of single crystals of thorium dioxide by reaction with gaseous hydrogen fluoride. The kinetics were determined spectrophotometrically at six temperatures in the interval 218°–327°C. The reaction is diffusion controlled with the film thickness proportional to the square roots of pressure of HF(g) and time corrected for an incubation period. The rate constant is $\beta=7.0\times10^2\exp(-6630/RT)$ $\text{Å}/(\text{sec}\cdot\text{Torr})^{\frac{1}{2}}$ within an error (75% confidence) of ±280 cal/mole for the heat of activation.

INTRODUCTION

The hydrofluorination of thoria,

$$4\text{HF}(g)+\text{ThO}_2(s)\rightarrow\text{ThF}_4(s)+2\text{H}_2\text{O}(g), \qquad (1)$$

is exothermic with a heat of reaction of 42.7 kcal/mole at 550°C.[1] A previous study[2] of the analogous reaction of HF(g) with urania has shown the feasibility of examining this reaction spectrophotometrically.

Cleavage faces of large single crystals of thoria were polished to a fine finish, given further chemical preparation to remove mechanically introduced surface damage, and under closely controlled conditions reacted with HF(g) to form interference layers. The extent of reaction was determined spectrophotometrically by the measurement of interference wavelength.[2] On the flat surfaces of reacted large crystals, it was possible with a metallurgical microscope to examine directly the uniformity of reaction by the uniformity of color of the interference layer. In the temperature interval 218°–327°C, first-, second-, and third-order interference films of fluoride product on thoria were brightly colored and optically isotropic. The interference peaks were sharp so that the second-order wavelengths of maximum interference were measurable to within ±15 Å. Both the film and substrate are transparent so that the net discontinuous phase jump is zero. Thus the interference relationships and consequently the optically derived kinetic equations are not complicated by extinction coefficients.[3] The interference wavelengths were translated into actual thicknesses by means of the refractive indices of the product layer which had been determined previously by immersion spectrophotometry.[4]

Both the kinetic constants and the incubation periods were obtained as functions of temperature. Metallographic examinations were routinely performed on each specimen in order to judge the quality of the film.

EXPERIMENTAL

The apparatus and reaction procedures have been described previously.[2,4] Surface preparation of the reactant $\text{ThO}_2(s)$ has also been reported.[4] In addition to the procedure described in Ref. 4, some crystals of $\text{ThO}_2(s)$ were given further treatment prior to surface preparation. As received from the Norton Refractories Division,[5] the single crystals of thoria were either clear

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[1] F. L. Cuthbert, *Thorium Production Technology* (Addison-Wesley Publishing Company, Inc. Reading, Massachusetts, 1958), p. 147.

[2] W. P. Ellis and B. W. Roberts, J. Chem. Phys. **39**, 1176 (1963).

[3] W. P. Ellis, J. Chem. Phys. **39**, 1172 (1963).

[4] W. P. Ellis and R. M. Lindstrom, Opt. Acta **11**, 287 (1964).

[5] Refractories Division, the Norton Company, Worcester, Massachusetts.

with a slight smoky cast, pale pink, or translucent whitish-pink. The translucence was the result of microscopic internal fracturing along the (111) planes, and although it is not certain, the discoloration appeared to be the result of a carbon impurity. Small deviations from stoichiometry or radiation damage are other possible causes of the pale color. Surfaces for reaction were prepared on the (111) faces of cleaved crystals. The back sides were uncleaved in order to minimize extraneous specularly reflected light. An anneal in Ar at approximately 2400°C to remove strain and radiation damage caused some specimens to turn black because of microscopically dispersed opaque precipitates visible at high magnifications with transmitted light in crushed fragments. Because of their small surface area, these inclusions were not seen by light reflected on the surface. Apparently they had no measurable effect upon the hydrofluorination kinetic constants derived from second-order films. Subsequent oxidation at 800°C for 1 h in flowing O_2 caused these blackened fragments to become clear without discoloration. Similar oxidation of unannealled crushed pieces had no visible effect upon the discoloration. Reaction specimens were prepared from the unannealled translucent and smoky crystals, a blackened crystal originally almost clear with only a slight smoky cast, a blackened crystal that had been oxidized to clarity in O_2 at 800°C, and a slightly smoky crystal that was unannealled but oxidized in O_2. X-ray photographs of pieces from the above five specimens showed them all to consist of a single detectable phase, to be face-centered cubic, and to have the lattice dimension $a_0 = 5.5968 \pm 0.0004$ Å. For comparisons, one can cite a value of 5.5961 ± 0.0001 Å for 99.99% pure ThO_2 measured by Lambertson, Mueller, and Gunzel,[6] and a value of 5.5973 ± 0.0003 Å by Ackermann *et al.* for 99.9% ThO_2.[7] Substoichiometric $ThO_{1.998}$ was observed by Ackermann when originally stoichiometric thoria was heated *in vacuo* above 2800°K.[7] Heating caused their crystals to assume a grayish cast which disappeared on heating in air at 1200°K. The composition of our crystals as received was determined chemically to be $ThO_{2.15 \pm 0.15}$. A spectroscopic analysis of the same material as received gave a total cationic impurity of less than 73 ppm.

The interference wavelengths were measured on a Cary 14X spectrophotometer at an angle of incidence of 7°. Each layer was inspected either on a Bausch & Lomb research metallograph or on a Zeiss metallurgical microscope. Representative areas of specimens reacted under varying conditions were routinely photographed on the metallograph with Ektacolor "L" film.

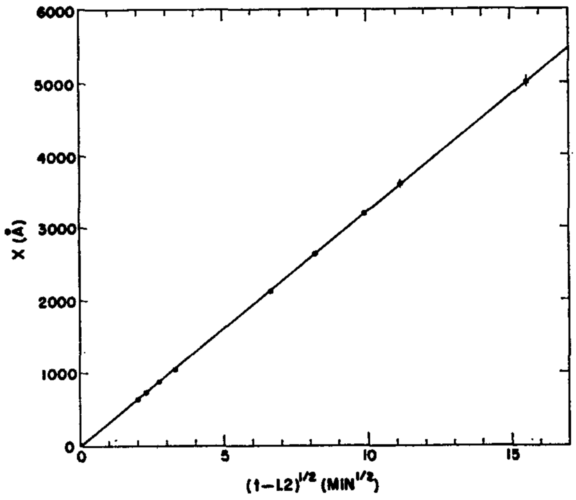

FIG. 1. Film thickness versus square root of time corrected for an incubation period. $HF(g)+ThO_2(s)$, $P(HF)=400$ Torr and 300°±1°C, respectively.

DISCUSSION OF RESULTS

Kinetics

The relationship between film thickness X, refractive index η, angle of incidence Φ, and interference wavelength λ_k is

$$X=\lambda_k(2K+1-\theta/\pi)/4(\eta^2-\sin^2\Phi)^{\frac{1}{2}}, \qquad (2)$$

in which θ is the net discontinuous phase jump, and K is an integer equal to 0 for first-order films, 1 for second-order, 2 for third-order, etc. The refractive index of the film η in Eq. (2) is at λ_k and is given in Ref. 4. In the visible region, η of these films varies from 1.55 in the blue to 1.53 in the red. For a transparent all-dielectric interference system at near-normal incidence, $\theta=0$,[8] and thus for a high-order film, the interference wavelengths divided by $4(\eta^2-\sin^2\Phi)^{\frac{1}{2}}$ are in the inverse ratio of $(2K+1)$. For fluoride films produced on thoria by hydrofluorination, within a small fraction of a percent, the values for $\lambda_k/4(\eta^2-\sin^2\Phi)^{\frac{1}{2}}$ are in the ratios of $(2K+1)^{-1}$. Additional confirmation that the film does not absorb is that within the uncertainty of the determinations, the interference wavelengths in acetone are the same as in air. If the film absorbed, λ_k would decrease with immersion according to the magnitude of the extinction coefficient of the film.[4] The above two observations are in agreement with the fact that powders of both $ThO_2(s)$ and $ThF_4(s)$ are white. Thus, since $\theta=0$, no correction has to be made in the kinetically derived optical equation as was the case with analogous fluoride films on urania.[3]

If the hydrofluorination of thoria follows the same kinetics as the analagous reaction with urania, the

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[6] W. A. Lambertson, M. H. Mueller, and F. H. Gunzel, Jr., J. Am. Ceram. Soc. **36**, 397 (1953).

[7] R. J. Ackermann, E. G. Rauh, R. J. Thorn, and M. C. Cannon, J. Phys. Chem. **67**, 762 (1963).

[8] F. A. Jenkins and H. E. White, *Fundamentals of Optics* (McGraw-Hill Book Company, Inc., New York, 1957), 3rd ed., p. 514.

TABLE I. Summary of experimental data.[a]

T (°C)	Rate constant, β [Å/(sec·Torr)$^{\frac{1}{2}}$]	Incubation period, t_0 (min)
218±1	0.771±0.031	30±3
240	1.098±0.016	11±2
262	1.332±0.012	3.9±0.8
286	1.768±0.035	2.35±0.4
300	2.07±0.03	1.2±0.2
327	2.724±0.035	0.85±0.2
327	*2.78±0.07	*1.7±0.3

[a] For all data, $P(\mathrm{HF})=400$ Torr, except starred values for which $P(\mathrm{HF})=200$ Torr. Standard deviations are given for β; for t_0 are given maximum error limits estimated from standard deviations.

relation between X, the pressure of gas P, and time t, is $X=\beta(Pt)^{\frac{1}{2}}$ where β is the rate constant. With fluoride films on thoria, the plot of X^2 vs t is a straight line, which does not pass through the origin, but intercepts the abscissa at a positive value, t_0. With the intercept t_0 subtracted from t, the parabolic relation holds for all K's as well as $K=0$ according to

$$X=\beta P^{\frac{1}{2}}(t-t_0)^{\frac{1}{2}}. \tag{3}$$

Figure 1 is a plot of X versus $(t-t_0)^{\frac{1}{2}}$ at 300°C and $P=400$ Torr which is a straight line passing through the origin and connecting points for $K=0$, 1, 2, and 3. Equation (3) is correct within one percent at 300°C for films up to 2 μ in thickness. The quantity, t_0, is taken as the incubation period of the reaction. In the following metallography section are discussed the optical observations which support this interpretation.

At each of the six temperatures, t_0 was determined at various wavelengths for $K=0$ and $P(\mathrm{HF})=400$ Torr. The kinetic constant, β, was then obtained from data for second-order films. At 327° C, the kinetics were studied also at 200 Torr. In Table I are listed the values of β and t_0 at each temperature. In Fig. 2 are presented the data for log β versus $1/T$. (For comparison, the data for urania are shown by the dashed line.) The reasonably straight line shows the correctness of writing β as $\beta=\beta_0 \exp(-Q/RT)$. A least-squares analysis gave an activation energy of $Q=6630\pm280$ cal/mole and $\log_{10} \beta_0(\text{Å}/\sec^{\frac{1}{2}}\cdot\text{Torr}^{\frac{1}{2}})=2.845\pm0.115$, where the limits are for the 75% confidence interval. For comparison, the analogous values for uranium dioxide are $Q=6930$ cal/mole and $\log_{10}\beta_0$ $(\text{Å}/\sec^{\frac{1}{2}}\cdot\text{Torr}^{\frac{1}{2}})=2.914$.[2]

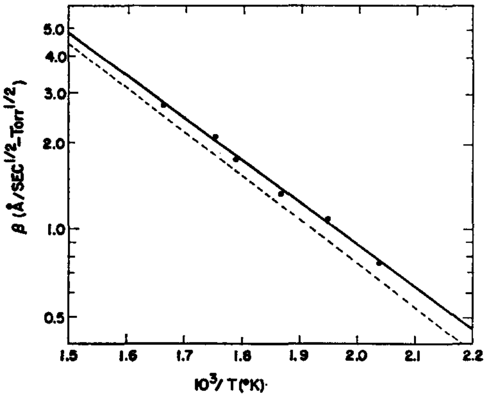

FIG. 2. Logarithmic plot of rate constant β, versus $1/T$. $\mathrm{HF(g)+ThO_2(s)}$. Dashed line represents kinetic data for $\mathrm{HF(g)+UO_2(s)}$.

In Fig. 3 are plotted the values of log t_0 at 400 Torr versus $1/T$. The experimental errors are rather large as shown by the limits. A least-squares analysis of the data on the assumption that $t_0=t' \exp(-Q/RT)$ gave $Q(t_0)=-19.5\pm2.0$ kcal/mole and $\log_{10}t'$ (min)$=-7.278\pm0.831$ where the limits are for the 75% confidence interval. The plot appears to have curvature, however, so that it may be incorrect to assume that the processes occurring during the incubation period are simply activated and thus may be represented by an Arrhenius equation.

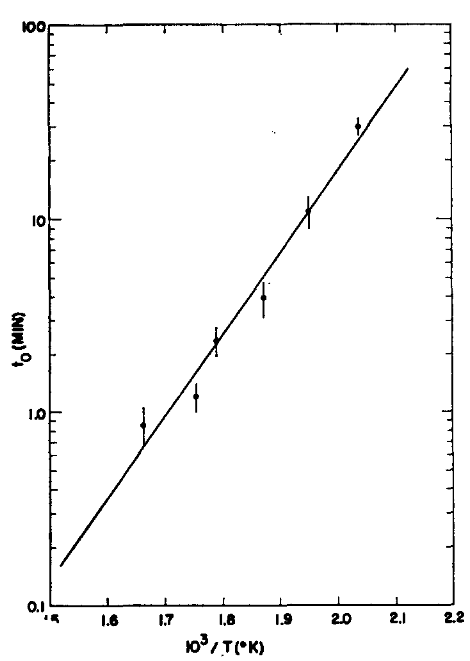

FIG. 3. Logarithmic plot of the incubation period t_0, versus $1/T$. $\mathrm{HF(g)+ThO_2(s)}$.

Unless there is an unexpected and at present unexplained discontinuous phase jump upon reflection, the value of t_0 cannot be interpreted optically by a disorganized layer at the film–substrate interface. Undoubtedly such a layer does exist. However, multilayer reflection analyses[9] have shown that the discrepancy between true film thickness of a transparent, two-layer model and that assumed for a simple single layer is a factor of 10 to 20 less than that required by the experimental data. The wavelength independence

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[9] O. S. Heavens, *Optical Properties of Thin Solid Films* (Academic Press Inc., New York, 1955), p. 82 *et seq.*

of the data in Fig. 1 and the fact that both ThO_2 and ThF_4 are electrical insulators suggest that a thin electrical double layer is not responsible.[10] Finally, the value of the refractive index of the substrate calculated by optical theory from the immersion data in Reference 4 ($\eta_2=2.119\pm0.017$ at 4840 Å) agrees with the interpolated value obtained by the minimum deviation method ($\eta_2=2.122\pm.005$ at 4840 Å). This latter result implies that in this particular system either there are compensating effects or else the optical parameters at the product-substrate interface do not differ greatly from the values of the bulk of the film or the bulk of the reactant solid.

Metallography

First-order interference films of fluoride produced on thoria by Reaction (1) are not uniform in general. The basic color itself does not vary however except in intensity. The surfaces have whitish splotches varying in intensity from white (i.e., no interference) to just a very faint paling of color. Most of the surface is a smoothly interfering film. These splotches are in the range 10–100 μ and vary in distribution within a given film and between crystals of ThO_2 but are on all first-order films to some degree. As observed metallographically, the thinnest films with λ_k $(K=0)$ $\sim$4000 Å appear the worst, blue thicker films are much more uniform, and second-order layers are completely isotropic and uniform for the temperature range 218°–327°C. Within the uncertainties of measurement, different sample treatments yielded the same kinetics. However, the uncertainties are quite large in first-order films because of the variation in distribution of whitish splotches. Some specimens consistently gave a λ_k lower than the average. The spread in $\lambda_k(K=0)$ is greatest at 218°C and least at 327°C. By reflecting a greater portion of incident light, white areas broadened the peaks which, with the background curves in this study, had the effect of lowering the measured interference wavelength. The values of t_0 in Table I and Fig. 3 are for those films in which the splotching was at a minimum. By comparison of λ_k with degree of whitish discoloration, the λ_k used in deriving the reported t_0 was estimated to be within a percent or two of the hypothetical λ_k that would be measured with no splotching. The error limits in t_0 reflect the uncertainty of this particular measurement. However the rate-constant β was obtained from measurements on uniform second-order films. Since the time to produce a second-order layer is 20 times as long as t_0 on the average, a 40% variation in t_0 is a 2% error in $(t-t_0)$ for a second-order film and thus results in a 1% uncertainty in β.

The color nonuniformities, or blemishes as they have been called, produced on urania by hydrofluorination which were discussed in Ref. 2 and in greater detail in Ref. 11 are produced also on thoria at higher temperatures. Thus 300°C is the upper useful limit with urania, whereas films produced at 327°C with thoria are completely uniform. There appears to be an approximate 50°C difference in the temperatures at which similar birefringent microstructures form in the two systems.

Scratch and edge experiments were both performed in an attempt to identify the reaction site (see Ref. 2). Because ThO_2 is transparent, the microfine scratches in these particular specimens could not be photographed with long exposures under dark-field illumination. With less sensitive oblique light, it was seen that a film with a thickness of 2 μ did not fill the scratches. From this observation alone it appeared that deposition of $ThF_4(s)$ occurred at the film-substrate interface. However, to the contrary, sharp edges of microcrystals were unmistakably smoothly coated, and from this observation it appeared that deposition of $ThF_4(s)$ occurred at the gas–film interface. Thus, the same contradiction occurs in the hydrofluorination of thoria as in the analogous reaction of urania.

ACKNOWLEDGMENTS

The authors wish to express appreciation to R. M. Douglass for determining the lattice parameters of thoria, to R. J. Bard for reviewing the manuscript, and to the Analytical Chemistry Group for the composition and spectroscopic analyses.

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[10] R. C. Plumb, J. Phys. **25**, 69 (1964).

[11] W. P. Ellis and Dana L. Douglass, Technical Document Number LA-3183 (1964) (available from Clearing House for Federal Scientific and Technical Information, National Bureau of Standards, U. S. Department of Commerce, Springfield, Virginia).