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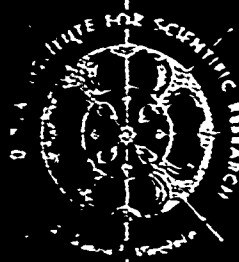
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The Accelerated Corrosion of Metals

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Covering the Period

September 16 - December 15, 1961

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Prepared By

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TABLE OF CONTENTS

	<u>Page</u>
Introduction	1
Description of Apparatus	2
Experimental Procedure	3
Results and Discussion	4
Bibliography	28

INTRODUCTION

A report is made herein of additional experiments performed on the oxidation of aluminum in contact with mercuric iodide. Previous reports (1) pointed out the important influence of relative humidity on the oxidation rate. These experiments were extended to relative humidities as low as 27% and additional experiments were carried out at 27-100% relative humidity.

X-ray diffraction studies have also been carried out for the purpose of determining the nature of the reaction products and with the hope that an insight might be obtained into the crucial role played by water vapor in the overall oxidation.

DESCRIPTION OF APPARATUS

The apparatus used in the oxidation-rate measurements was the same as described in the Eighth Quarterly Report (1).

The X-ray diffraction investigations were carried out using copper radiation and conventional powder techniques.

EXPERIMENTAL PROCEDURE

The procedure for measuring the rate of oxidation of aluminum in the presence of mercuric iodide has been given in the Seventh and Eighth Quarterly Reports. Samples of Reynolds 99.999% aluminum, having exposed surface areas of approximately 1.25 cm², were used.

The oxygen consumed during an experiment was measured by a pressure gauge; and values of ΔP in mm Hg were converted to ΔW_{O_2} in mg/cm² from the following:

$$\Delta W = \frac{VM}{1.25R} \cdot \frac{\Delta P}{T}$$

where $\frac{VM}{1.25R}$ remained constant throughout the experiments. Values of ΔW were plotted vs. time for each experiment and the slopes of the linear portions of the curves were graphically determined.

The oxides used in the X-ray diffraction studies were investigated during several periods of aging under various conditions. In all cases the oxides were X-rayed immediately after being taken from the reaction chamber. Upon aging in a) a very dry atmosphere, b) a very humid atmosphere, or c) at room conditions, for different lengths of time, the oxides were periodically X-rayed. Comparison of succeeding X-ray patterns indicated any changes in crystallinity upon aging under the different conditions used.

RESULTS AND DISCUSSION

As previously reported (1), the oxidation of aluminum occurred linearly with time in the presence of mercuric halides and water vapor. The slope of this linear curve was constant at any particular relative humidity and increased with an increase in relative humidity.

The first portion of this report presents additional data to be used in conjunction with all the previous oxidation-rate measurements. Several new saturated-salt solutions have been used to give relative humidities different from those used previously. The slopes of the oxidation-rate curves are listed in Table A along with the relative humidities obtained from the saturated-salt solutions.

Figures 1 and 2 are rate curves for experiments at 100% R. H.; Figures 3 through 5 at 92.9% R. H.; Figures 6 and 7 at 74.9% R. H.; Figures 8 through 10 at 54.2% R. H.; Figures 11 and 12 at 26.6% R. H.

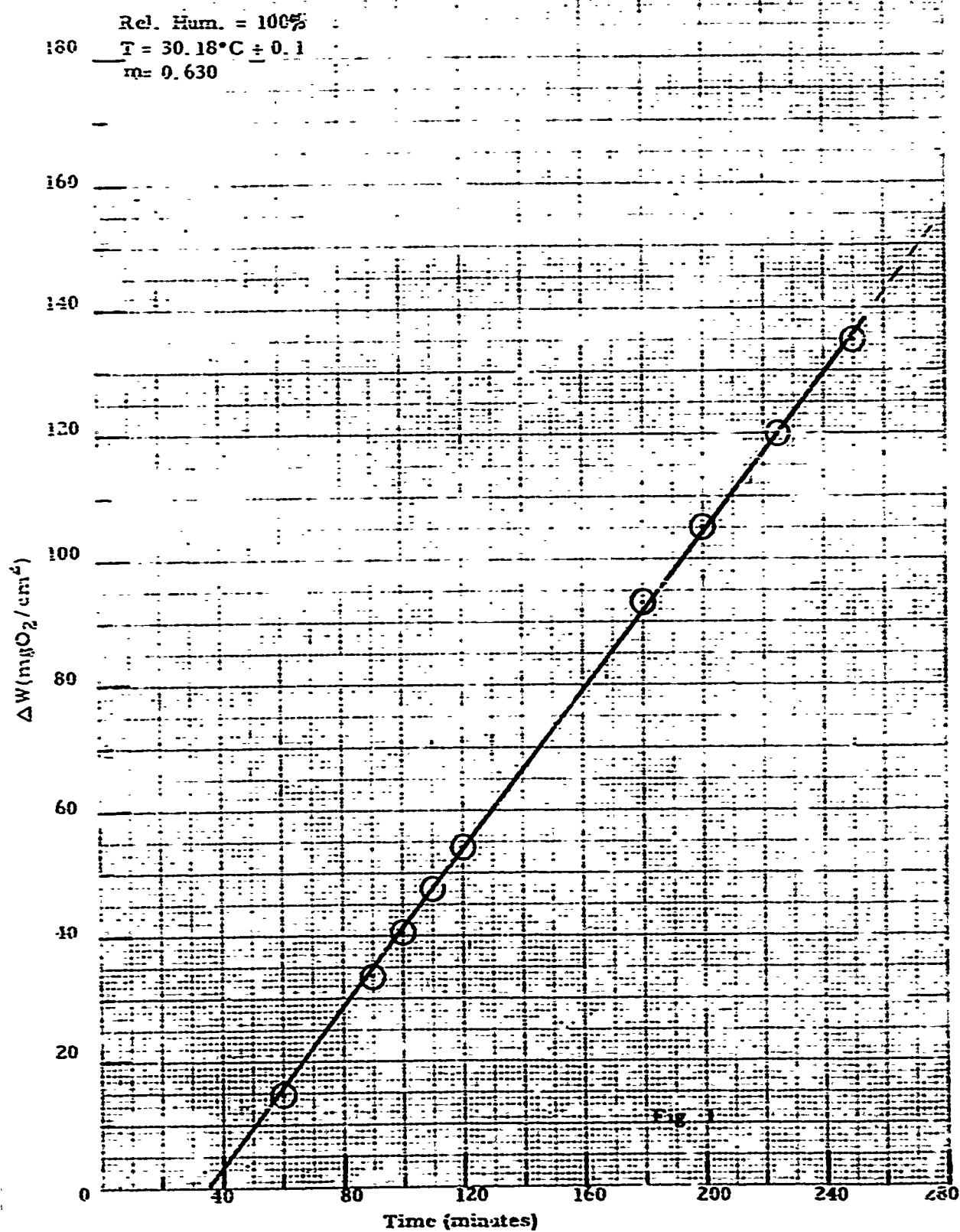
The influence of the relative humidity upon the oxidation rate is noted in Figure 13, where the average values of the different slopes ($\bar{m}$) are plotted vs. the relative humidities at which the slopes were determined. The lazy - S curve is very similar to Figure 53 of the Eighth Quarterly Report (page 34) but additional points have been included which change the shape somewhat. The rapid increase in oxidation rate is still noted in the 60-75% R. H. range.

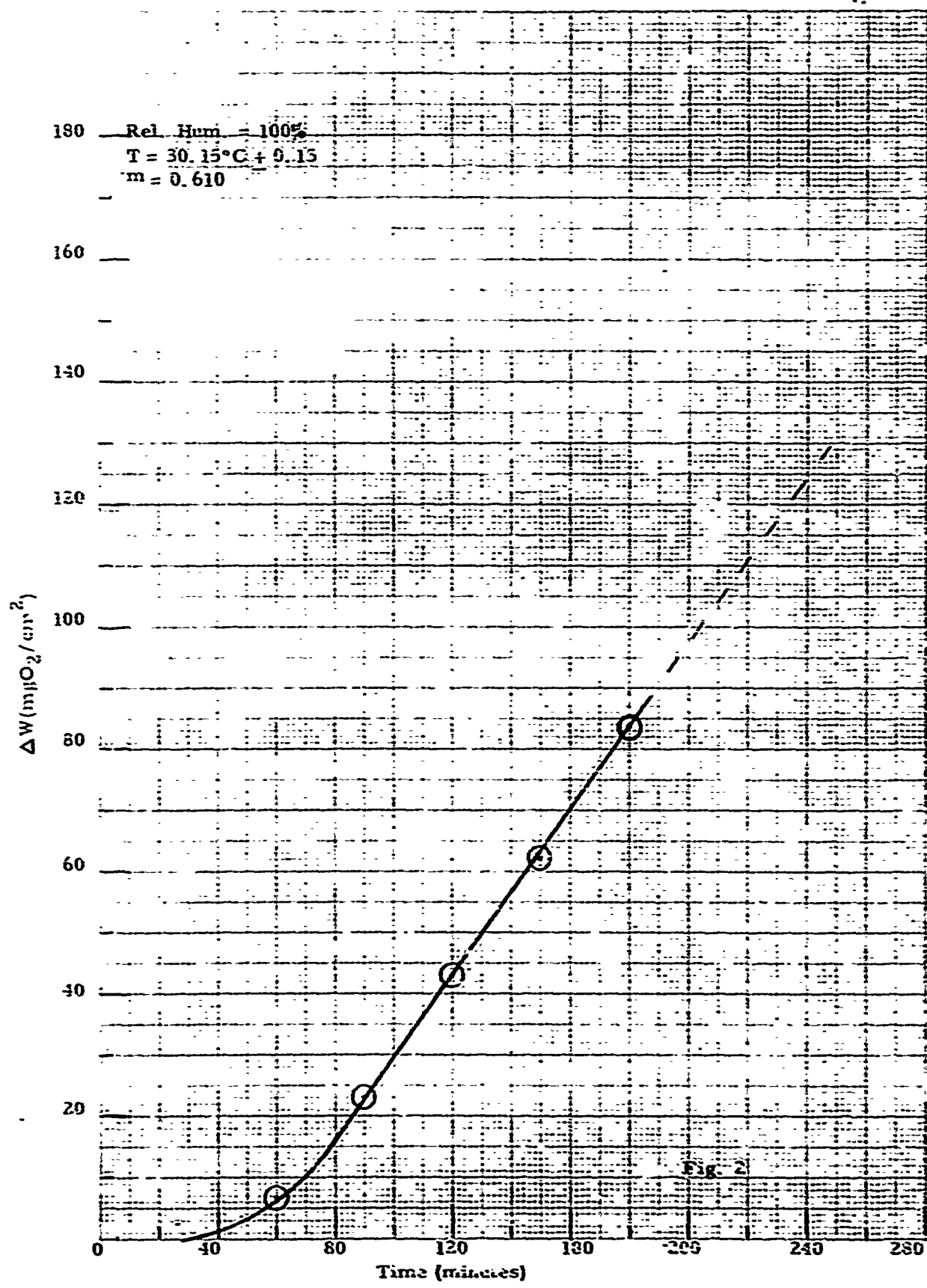
TABLE A

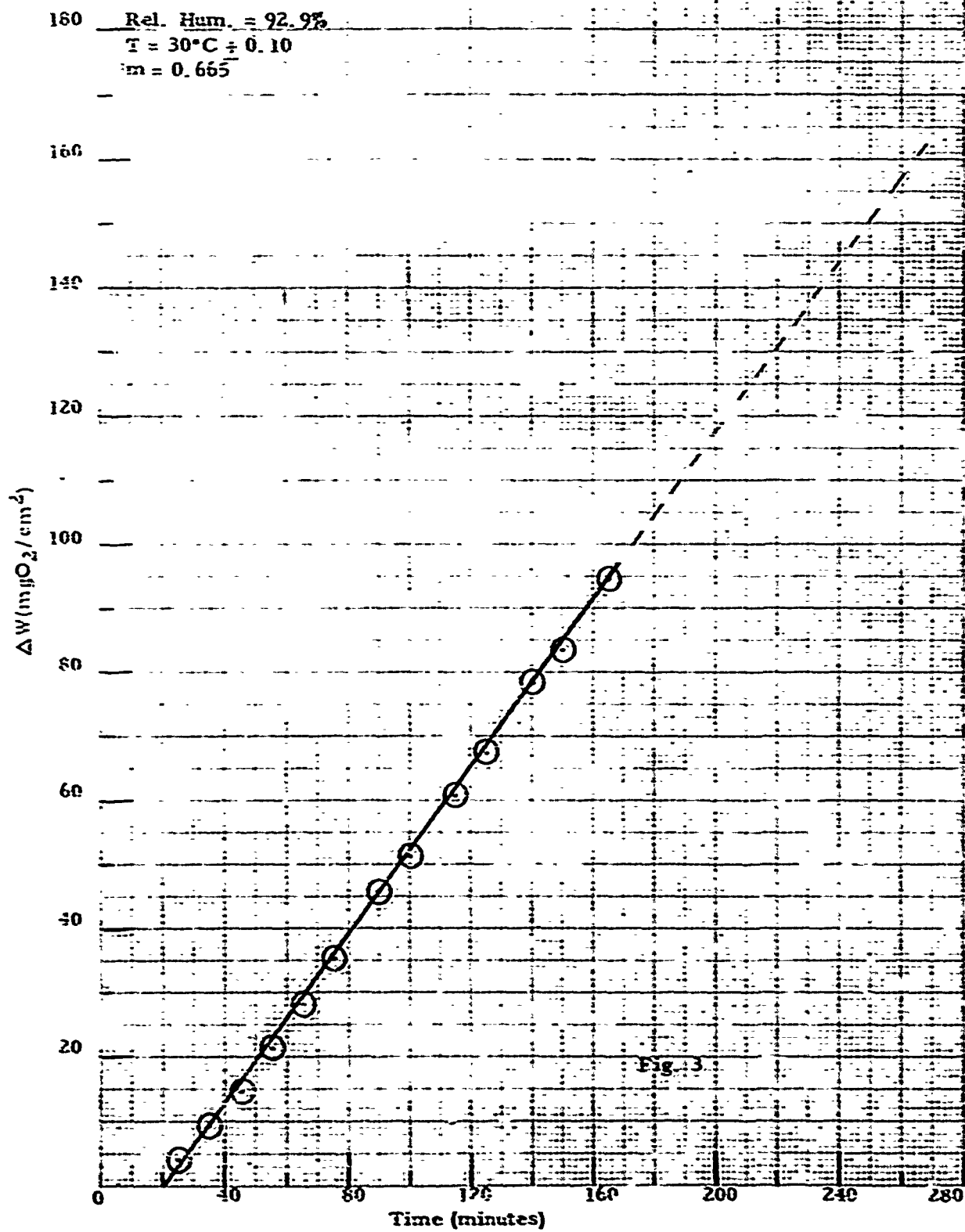
Values for the Slopes of the Oxidation Rate Curves at Different
Relative Humidities at 30°C.

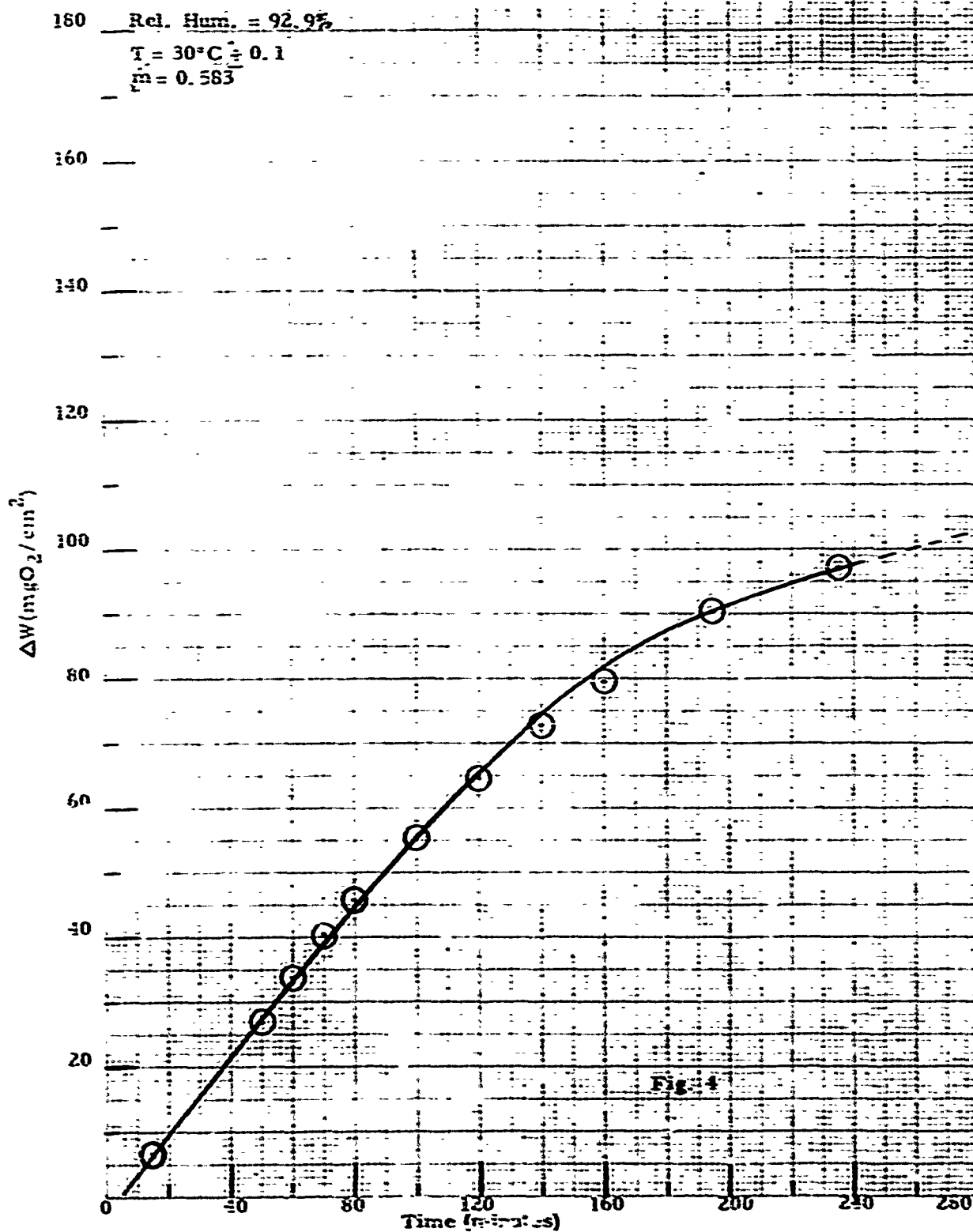
Saturated Salt Solution Used	Relative Humidity (%)	Slope (m) mgO ₂ /cm ² /min	*A g. Slope (m) mgO ₂ /cm ² /min
Distilled Water	~100.0	0.630	0.615
	~100.0	0.610	
(NH ₄)H ₂ PO ₄	92.9	0.583	0.613
	92.9	0.665	
	92.9	0.650	
BaCl ₂ · 2H ₂ O	85.0	-	0.559
(NH ₄) ₂ SO ₄	81.1	-	0.520
NaCl	74.9	0.466	0.471
	74.9	0.475	
NaNO ₃	72.7	-	0.409
NaNO ₂	63.0	-	0.271
NaBr · 2H ₂ O	56.2	-	0.213
Na ₂ Cr ₂ O ₇	54.2	0.200	0.202
	54.2	0.206	
	54.2	0.206	
CrO ₃	44.6	-	0.136
NaI · 2H ₂ O	36.4	-	0.050
KF	26.6	0.049	0.047
	26.6	0.046	

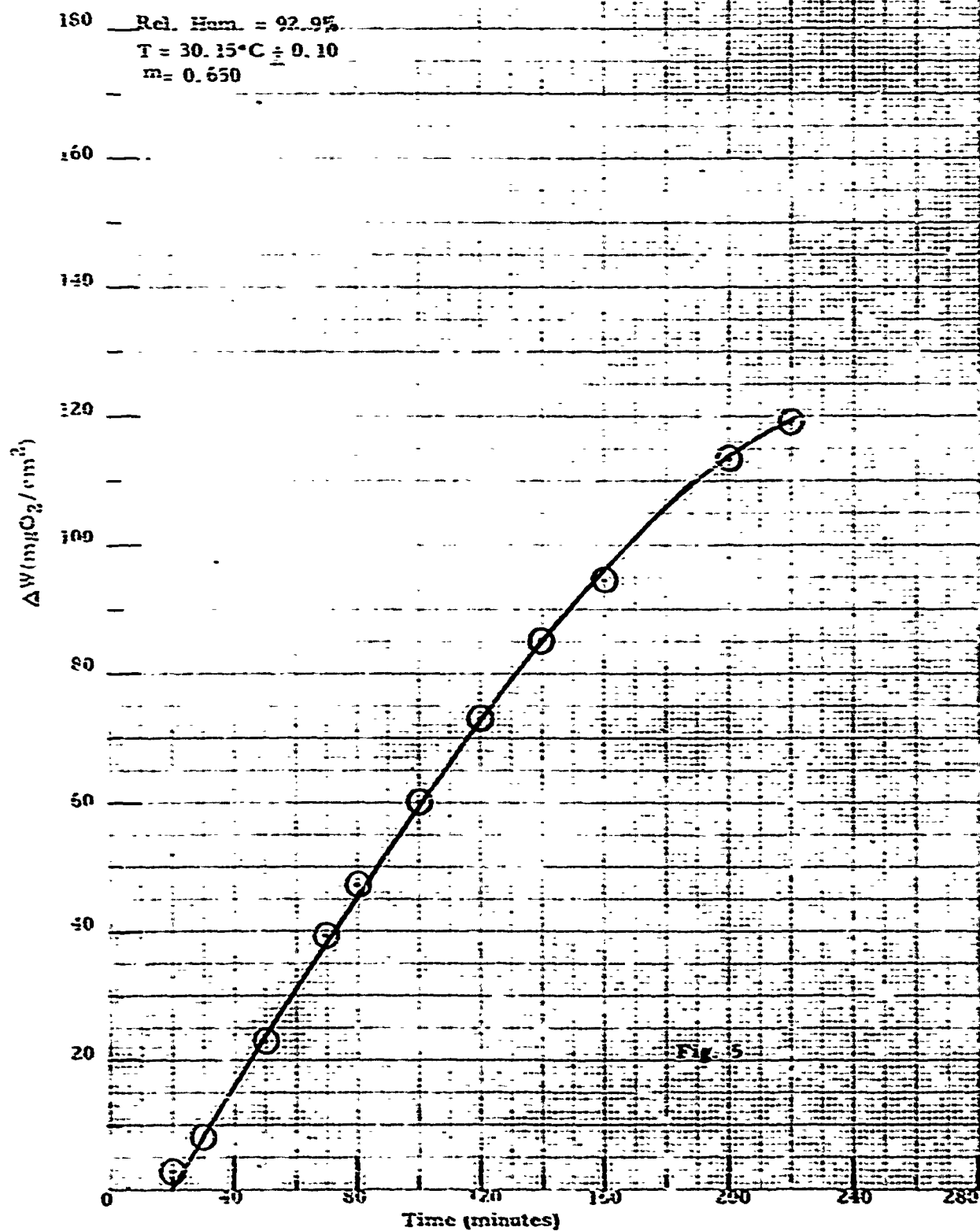
*Overall average slopes, using these data with data from page 8, Eighth Quarterly Report. The value of $m = 0.566$ for the last experiment at 100% R. H. in the Eighth Quarterly Report was omitted in calculating the average.

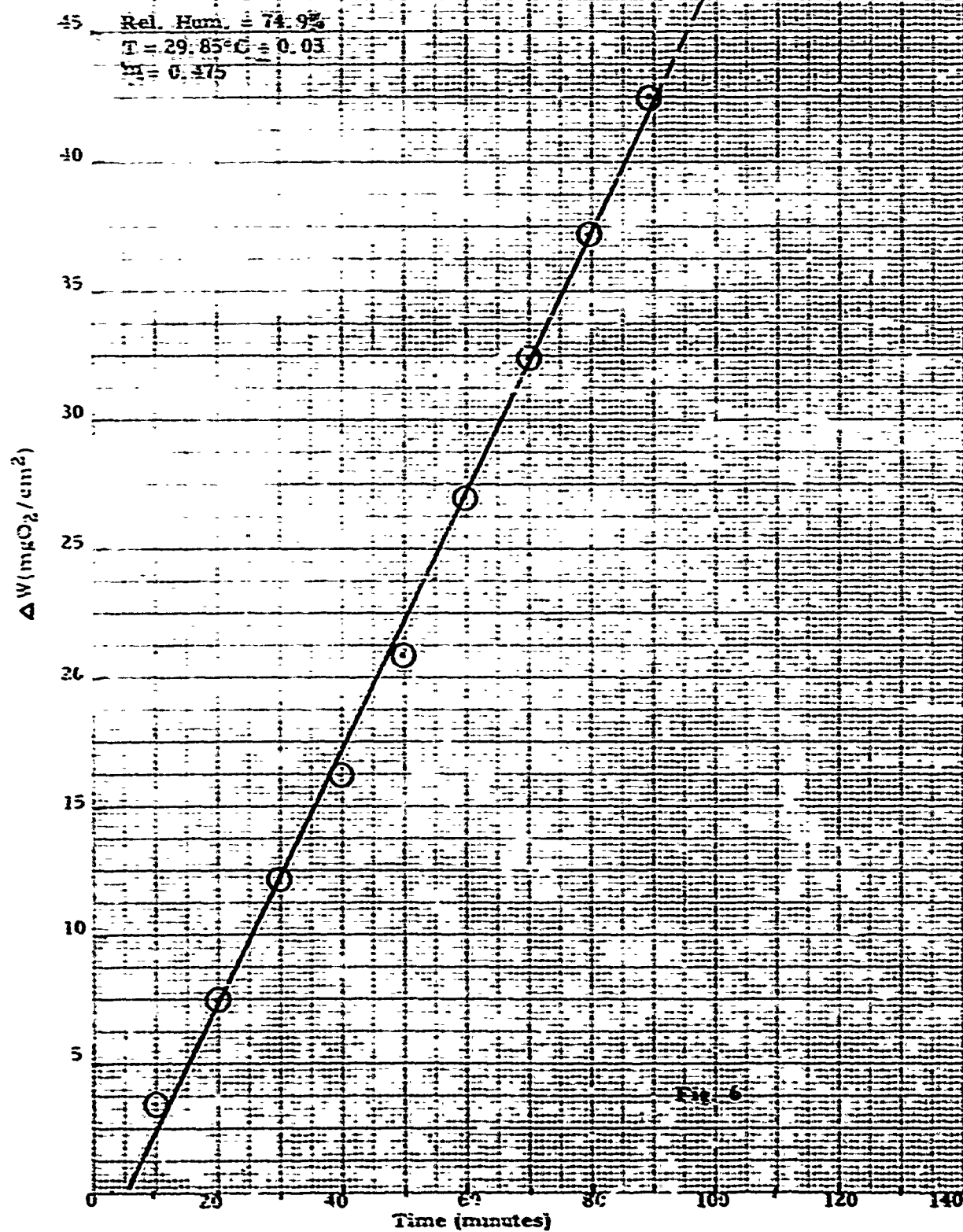


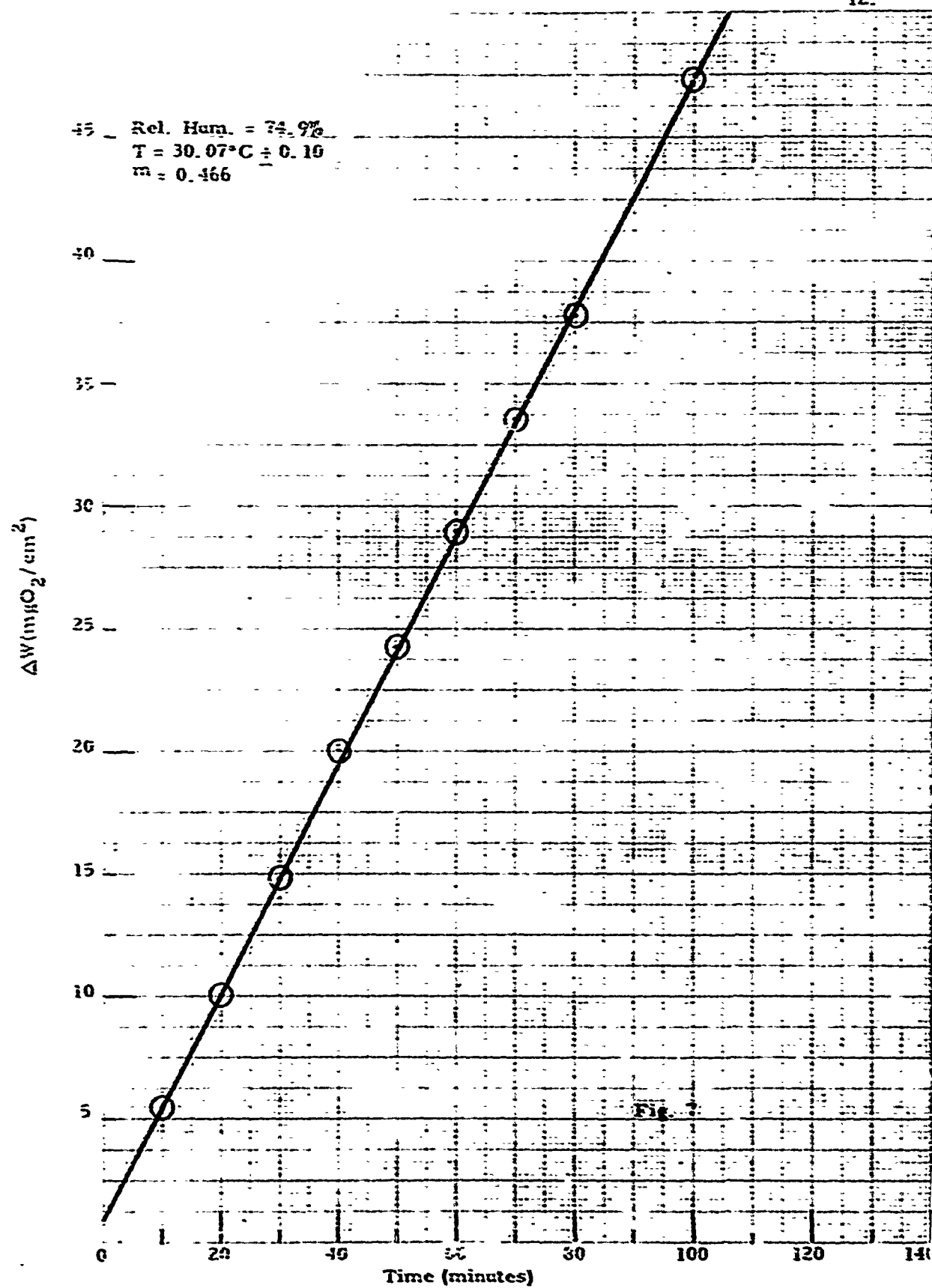




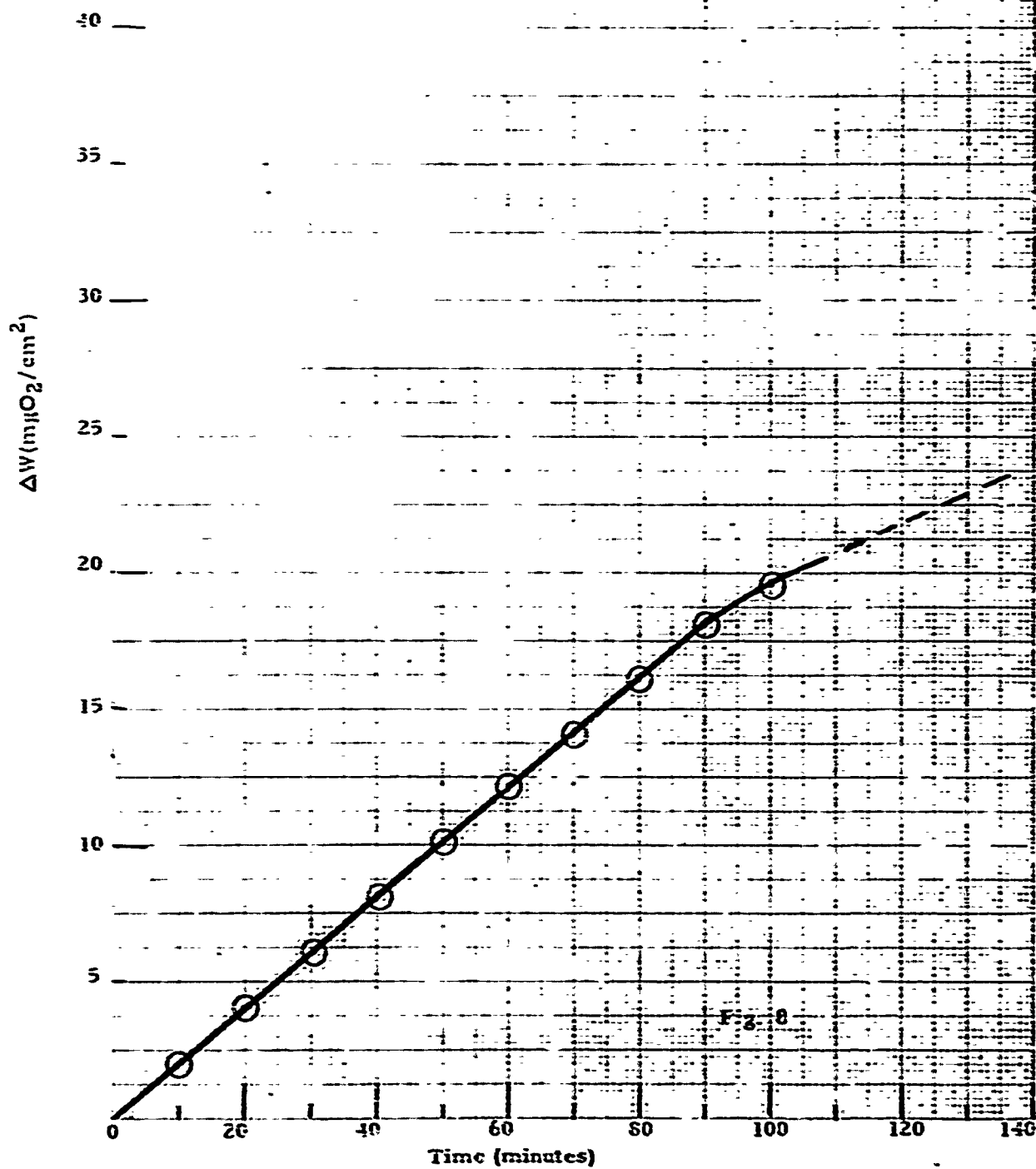




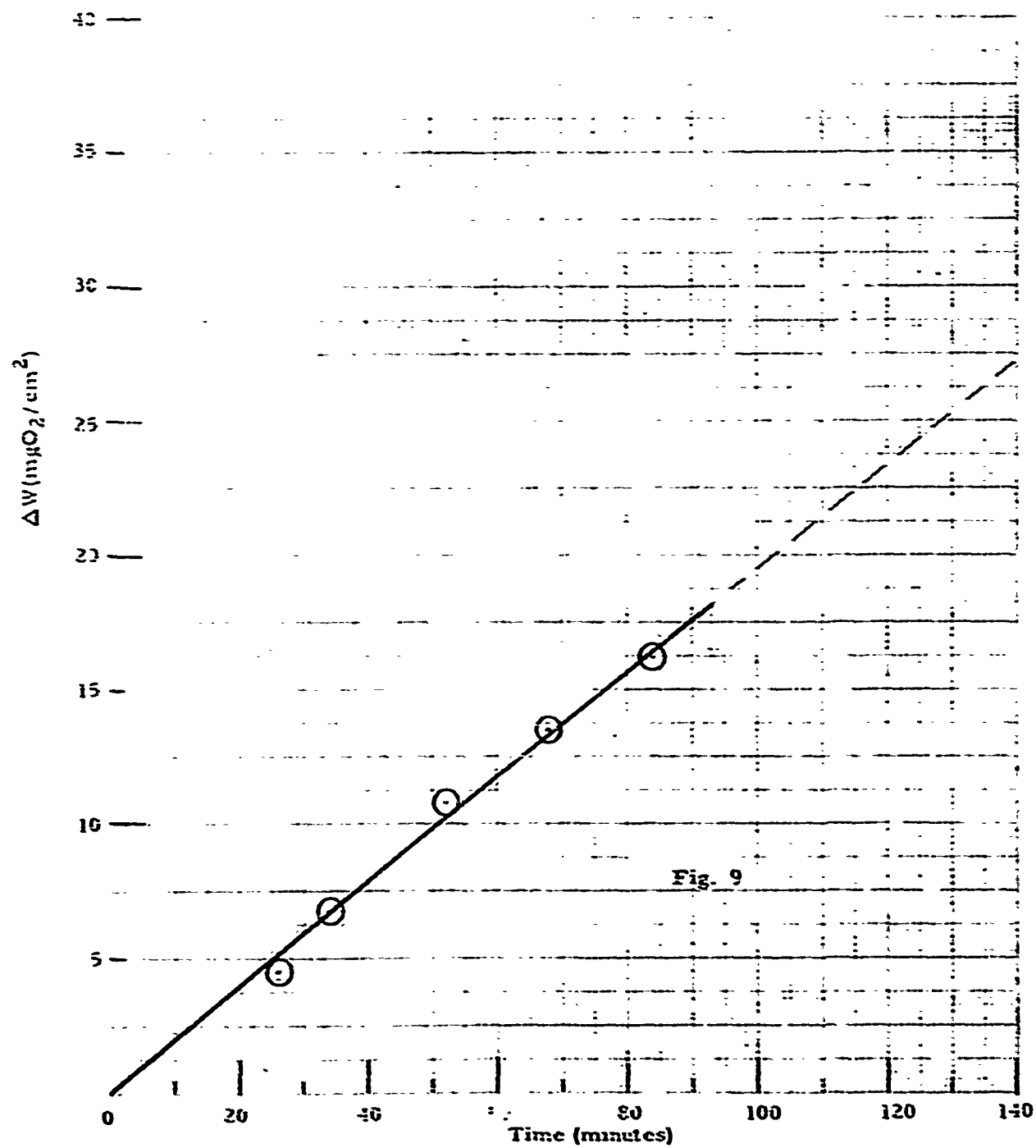




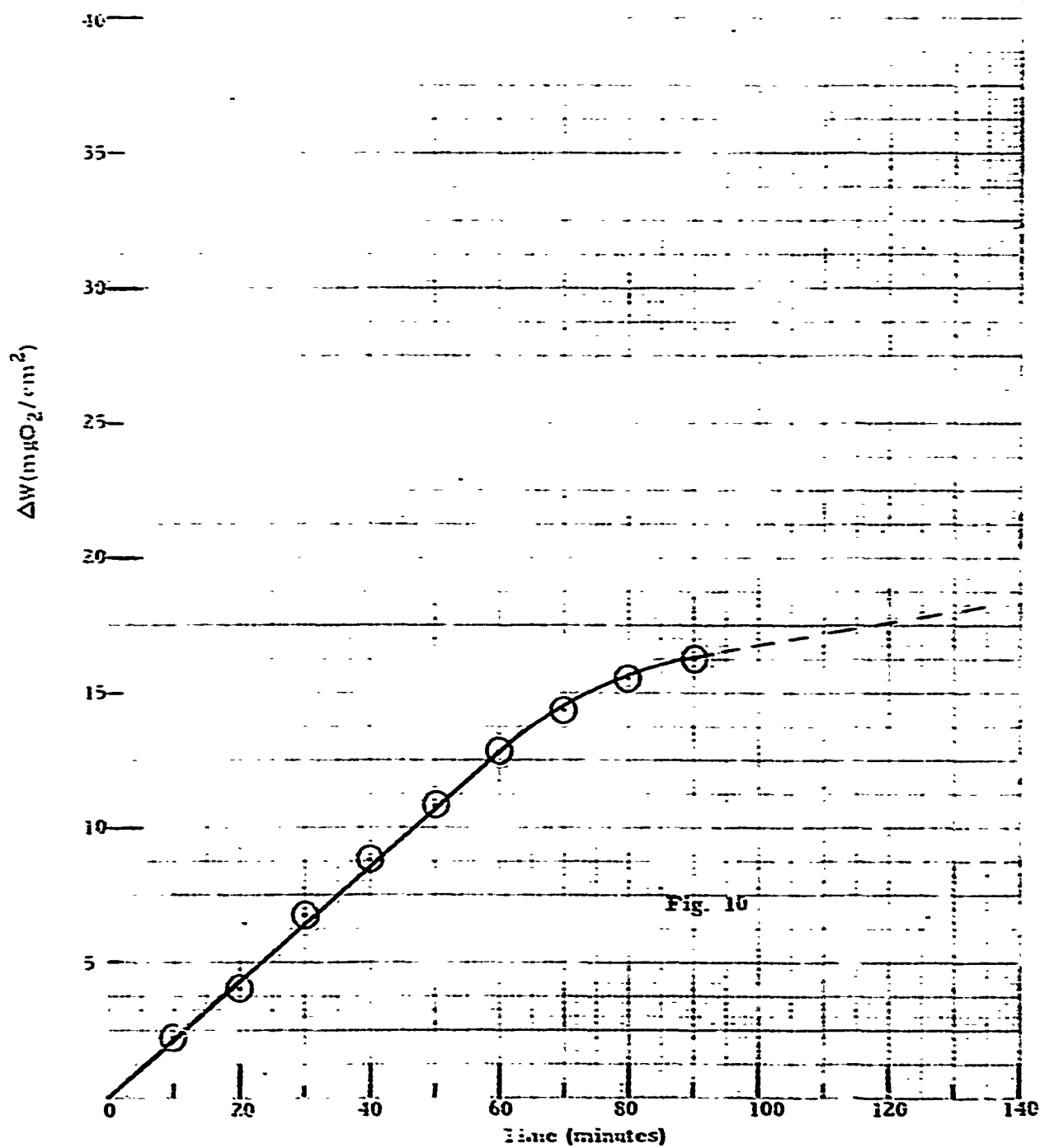
Rel. Hum. = 54.25%
 $T = 30.02^{\circ}\text{C} \pm 0.04$
 $\bar{m} = 0.200$

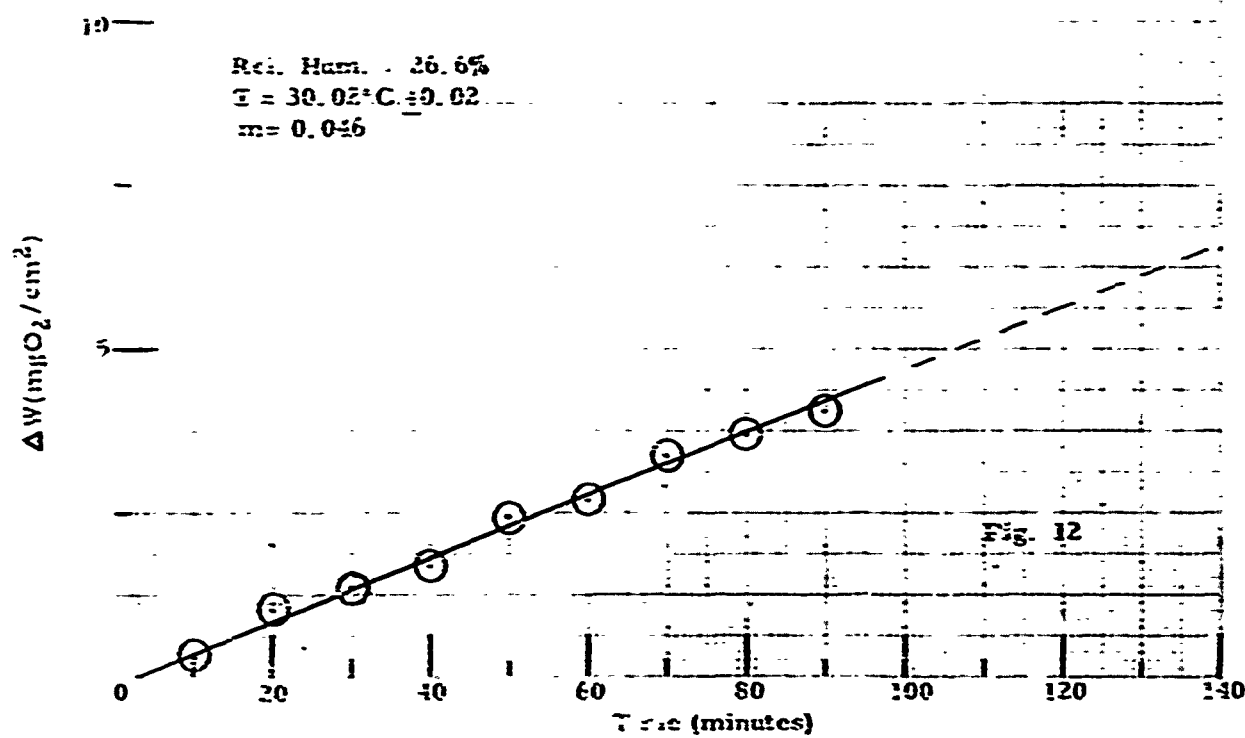
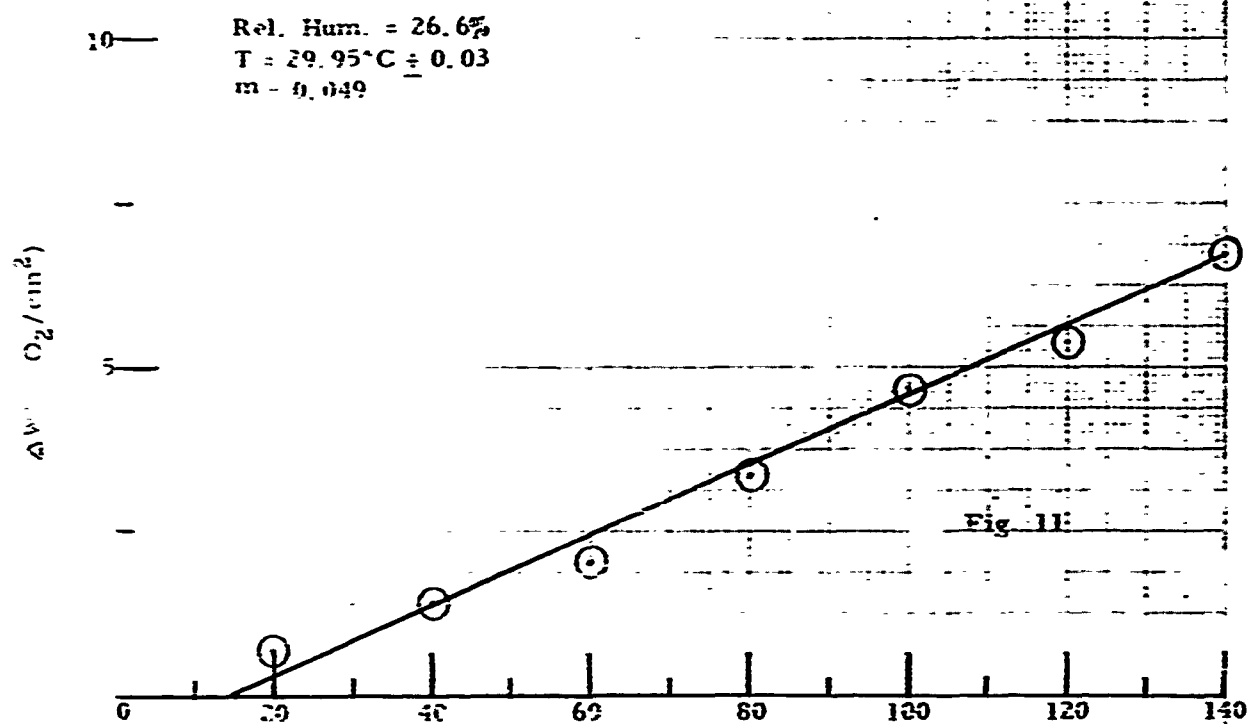


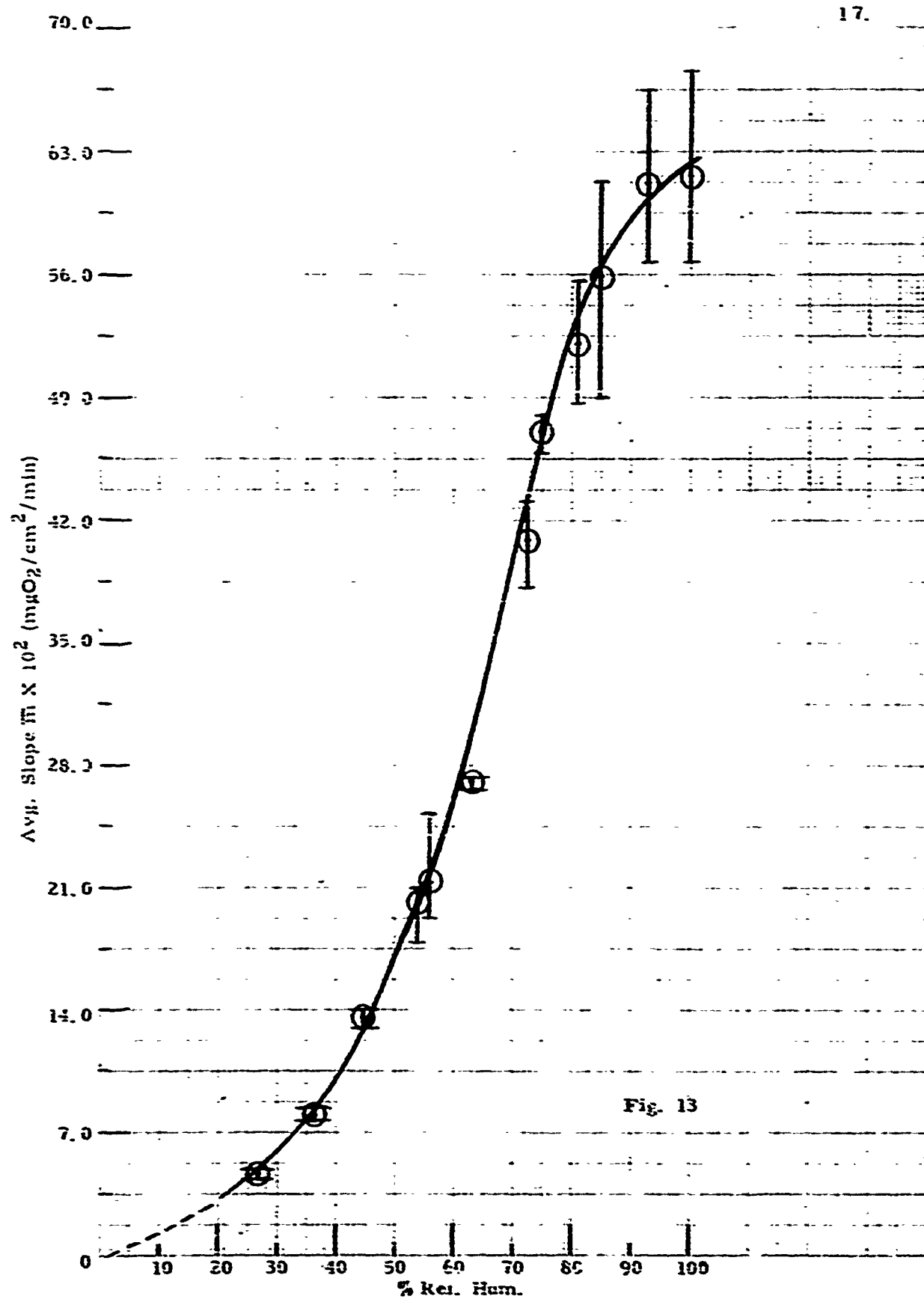
Rel. Hum. = 54.2%

 $T = 30^{\circ}\text{C} \pm 0.1$ $m = 0.200$ 

Rel. Hum. = 54.2%
 $T = 30.04^{\circ}\text{C} \pm 0.04$
 $m = 0.266$







The latter portion of this report is concerned with X-ray diffraction studies of the oxides formed at different relative humidities and under various aging conditions. Table B summarizes the X-ray data collected on a number of oxide samples.

In every case in which the oxides were X-rayed immediately after preparation, there existed one to three faint lines on the film regardless of the relative humidity at which the oxides were formed. Upon aging in the desiccator, even for long periods, the lines either became fainter or disappeared altogether. No correlations of these lines could be made with any form of aluminum oxide, mercuric iodide or metallic aluminum. The "d" spacings are as follows: 2.20 Å., 1.99 Å., and 1.75 Å.

One sample which was formed near 100% R. H. was placed in an oven at 115°C. for ten hours. There appeared to be no change in the structure of the oxide (one faint line which could not be correlated), and the small weight-loss was assumed to be due to surface water. The same sample was then placed in a high relative humidity chamber (near 100% R. H.) for seventy-one hours. The same single line at 1.99 Å. was observed. After returning this sample to the high humidity chamber and leaving it for one month, the final X-ray exhibited seven diffuse lines corresponding to

$\alpha\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. or boehmite. The physical appearance, however, did not change. Since this oxide had the tendency to form the monohydrate when kept in a high humidity chamber, the original oxide was assumed to be a more anhydrous form. This conclusion is consistent with the unchanged

TABLE B

Oxide Formed at R. H. (%)	Aging Time	Aging Conditions	No. Lines	Correlation
~ 100	O	-	3 faint	none
~ 100	16-1/2 hrs.	Desiccator	1 faint	none
81.1	O	-	1 faint	none
"	20 hrs.	Desiccator	none	none
74.9	O	-	1 faint	none
72.7	O	-	3 faint	none
"	21-1/2 hrs.	Desiccator	3 faint	none
"	92-1/2 hrs.	Desiccator	3 faint	none
92.9	O	-	none	none
"	O	Boiled in H ₂ O 5 min. & dried in air overnight	11 broad	α Al ₂ O ₃ ·H ₂ O
~ 100	O	-	1 faint	none
"	O	Boiled in H ₂ O 30 min. & dried with heat lamp	8 broad	α Al ₂ O ₃ ·H ₂ O
"	O	Boiled in 0.1M HCl for 30 min. washed in H ₂ O, EtOH & Acetone	29 sharp	indeterm. (mixture)
"	64 hrs.	Desiccator	1 faint	none
"	10 hrs.	Oven at 115°C.	1 faint	none
"	71 hrs.	~ 100% R. H.	1 faint	none
"	1 month	~ 100% R. H.	7 faint- broad	α Al ₂ O ₃ ·H ₂ O
"	O	Room	1-2 faint	none
"	60 hrs.	Room	7 faint, sharp	
"	86 hrs.	Room	17 strong, sharp	α Al ₂ O ₃ ·3H ₂ O
"	146 hrs.	Room	17 sharp	"
"	2 months	Room	22 strong, sharp	"

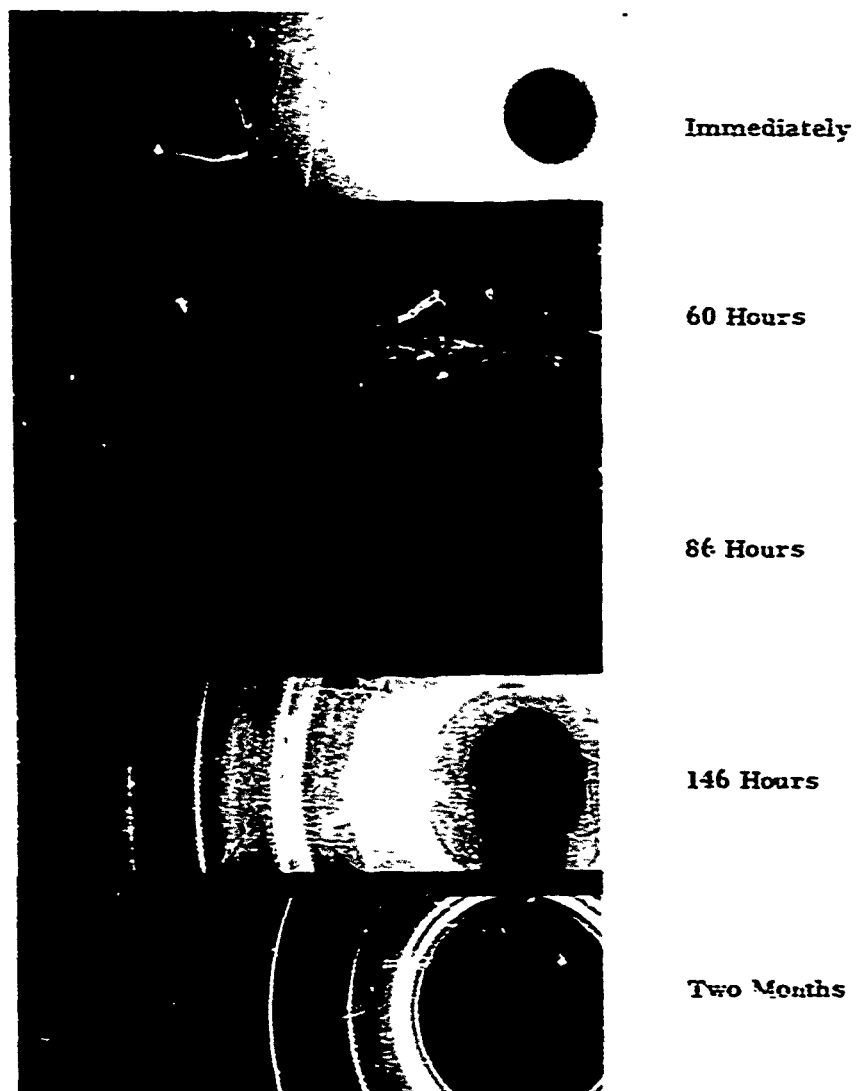
X-ray pattern of the oxide after heating in the oven at 115°C.

Another oxide sample formed at approximately 100% R. H. was boiled in water for thirty minutes and dried with a heat lamp. The X-ray pattern contained eight broad lines corresponding to $\alpha\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. This demonstration further suggested the less hydrated nature of the initial oxide, for Spooner (2) found that an isolated anhydrous oxide was converted to $\alpha\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ when boiled in water. A second oxide sample formed at 92.9% R. H. underwent the same transformation to $\alpha\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ after exposure to boiling water for five minutes and drying in air overnight. The X-ray pattern contained eleven broad lines.

The formation of the trihydrate from the amorphous oxide also has been accomplished. The oxide was prepared at 100% R. H. Two faint lines, which could not be correlated with any known aluminum oxide, were observed on the powder diffraction photograph. Upon aging at room conditions (the sample was placed in a plastic vial and left on the table top) the oxide began to crystallize slowly. After two months, the X-ray pattern contained twenty-two strong, sharp lines corresponding to the pattern of $\alpha\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. The X-ray patterns at various stages of this transformation are given in Figure 14 over the entire two-month period.

FIGURE 14

X-Ray Powder Patterns Showing the Transformation of Amorphous Aluminum Oxide Formed near 100% R. H. to $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.



Therefore, under less drastic conditions than exposure to boiling water a degree of hydration greater than the monohydrate was obtained. Huttig and Kolbl (3) similarly found a limited quantity of bayerite ($\beta\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) when anhydrous Al_2O_3 at 20°C . was left in contact with water vapor for one month. Kiselev and Smirnova (4) found that a mixture of $\alpha\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $\alpha\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ was formed when anhydrous Al_2O_3 was left in contact with saturated water vapor at 37°C . for several weeks.

Bentley and Feachem (5), on the other hand, found that the trihydrate was formed when amorphous Al_2O_3 was placed in liquid water at 20°C ., but only the monohydrate was found when the amorphous oxide was washed in liquid water for four days at 60°C . Other workers (6), (7), (8), found that the monohydrate was formed from anhydrous alumina when exposed to liquid water or water vapor at higher than room temperatures. The reason for the formation of different hydrates under similar conditions apparently is not yet understood.

The oxide samples were often kept in plastic vials which were exposed to direct sunlight for short periods during the aging. In order to determine the possible effect of aging in the presence of radiation, a few of the amorphous oxides were exposed to infrared and ultraviolet light. No effect on the chemical or crystallographic transformations was observed.

The exact nature of the original amorphous oxide may be examined by comparison of results with those of other workers. A considerable body of experimental information is available in the literature on the hydration

and dehydration of aluminum oxides. A few of the published reports which have a direct bearing on these studies will be cited.

Although some authors consider the different hydrated oxides as hydroxides, the authors of this report will use the notations boehmite and hydrargillite or bayerite as representing true hydrated oxides, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, respectively. For instance, Glenser and Riech (9) designate boehmite, hydrargillite and bayerite as $\frac{1}{2}\text{Al}_2\text{OOH}$, $\frac{1}{2}\text{Al}(\text{OH})_3$ and $\frac{1}{3}\text{Al}(\text{OH})_3$. They maintain that the phases should be considered as non-stoichiometric hydroxides with changing OH^- content. The same designation was used by Torkar (10) when he stated that the trihydroxide only exists at relatively low temperatures, and the monohydroxide at room temperature or slightly above.

In a paper concerning the thermal decomposition of the hydrates in dry air, steam and room air, Stumpf et. al. (11) state that the partially dehydrated aluminas tend to adsorb water, but do not form crystalline hydrates at room temperature. They assumed that rehydration may take place at high temperature in the presence of water vapor. The influence of hydrate particle size, water vapor content, time, temperature and purity was given with reference to the phase transformations. These authors noted that the X-ray pattern of the product formed during the thermal decomposition of $\beta\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ was identical to that obtained for the hydrated oxide formed from the action of water with amalgamated aluminum. The present studies, however, have yielded what appears to be the

α - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$; i. e. by aging an amorphous oxide formed by exposure of amalgamated aluminum to water vapor. The nature of the initially-formed amorphous oxide is still undefined, however.

In an extensive paper investigating the vacuum dehydration and subsequent rehydration of the alumina hydrates, Pappe et. al. (12) have identified a transitional phase of partially hydrated oxide which was transformed directly to the trihydrate upon rehydration. The total dehydrated product, $\text{Al}_2\text{O}_3 \cdot 0.6\text{H}_2\text{O}$, consisted of two phases: boehmite, representing approximately 25% of the product; and the transitional phase, representing 75% of the product, and having a composition $\text{Al}_2\text{O}_3 \cdot 0.45\text{H}_2\text{O}$. Upon rehydration, the boehmitic phase remained unaltered whereas the transitional phase was quantitatively transformed into bayerite, β - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. Detection of the two phases in the dehydrated product was difficult because only the boehmitic phase was easily detected by X-ray analysis. The transitional phase appeared to be practically amorphous with only one X-ray line at 1.395 Å. in the proximity of very strong lines of the over-shadowing boehmitic phase.

When the dehydration took place under atmospheric pressure, the product indicated only a very weak tendency for rehydration, and the X-ray diagrams were used to identify the transitional phase as essentially chi (χ) alumina with the main lines at 1.395 Å., 1.92 Å. (very diffuse), 2.12 Å. and 2.41 Å.

The original oxide formed in the present study near 100% R. H. and under pressures slightly less than atmospheric, aged to $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

Similarly, Papee et. al. formed a transitional phase of alumina by dehydration of hydrargillite under vacuum, which subsequently rehydrated to $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. Both the original oxide of the present study and the transitional alumina exhibit similar X-ray diffraction patterns, namely much scattered radiation and only one to three definite lines. Both these oxides also apparently contained less water than that corresponding to the monohydrate. Furthermore, a very finely divided sample of hydrargillite used in forming the transitional alumina was found by Papee to be composed of lamellar microcrystals having the dimensions of 1,000 to 10,000 Å. Heyn (13) found that the particle size of the amorphous oxide formed in this study was 100 to 2,000 Å. in size. These dimensions, then, are on the same order of magnitude.

The transitional alumina exhibited an X-ray pattern resembling that of chi (χ) alumina. The oxide formed in this study also exhibited a strong X-ray line (1.99 Å.) close to a diffuse line of chi-alumina (2.00 Å.).

Papee et. al. have proposed a mechanism for the formation of the transitional alumina based on 1) ease of water vapor transport through the oxide under varying pressures, and 2) size of pores through the oxide, and 3) the specific surface area. It was found by adsorption of C_6H_{12} on transitional alumina that the smaller the pore size the greater the degree of rehydration. This tendency for rehydration was directly related to the very large specific surface area and the small pores of the transitional alumina. Likewise for amorphous oxide formed in this study it was assumed that the finely divided material indicated a very large specific surface area.

Bernard and Randall (14) have maintained that the diffusion rate of water or water vapor through aluminum oxide layers is the governing factor in hydrated oxide growth. Therefore, not only is water transport a major factor during dehydration of a hydrated phase to transitional alumina, but it is conversely a major factor in hydration or rehydration as well. From either direction (dehydration or hydration) an intermediate material, such as transitional alumina, may exist which is the easily rehydrated phase and which is primarily dependent on the same factor, water transport. Assuming this to be true, it appears that the initially amorphous oxide may be similar to the transitional alumina described by Pappe.

On the other hand, there also exist points of dissimilarity between the two oxides. The methods of preparation are greatly different, i. e. vacuum dehydration of hydrargillite at high temperature for transitional alumina and essentially room temperature growth from amalgamated aluminum at high relative humidity for the amorphous oxide of this study. The "d" spacings for the transitional alumina (1.395 Å.) do not correspond to the main X-ray line for our oxide (1.99 Å.); and the product for the rehydration of transitional alumina was β $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, whereas the hydrated product of our oxide was α $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. Finally, the existence of chi alumina indicates a formation temperature of 400-600°C. It is unreasonable to believe that such temperatures were reached in the reaction vessel. Concerning the two methods of rehydration of these oxides, the transitional alumina was rehydrated in liquid water at 25°C., whereas our oxide was rehydrated in air under room conditions.

In summary, it appears that the transitional alumina of Papee et. al. is similar in many respects to the amorphous oxide formed in the present study. The similarity is not quantitative, however, and future studies should determine if these points of difference are one of degree or of kind.

The chief experimental fact which is lacking at the present time is the water content of the amorphous oxide. Unequivocal measurements designed to determine the composition of the product are difficult to formulate because of the possible perturbing influence of small amounts of unreacted mercuric iodide, metallic mercury, or particles of alumina on gravimetric or thermal measurements. Consideration is being given at the present time to carrying out such experiments.

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