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The Accelerated Corrosion of Metals

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Contractor: Army Chemical Center
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Eighth Quarterly Report

Covering the Period

June 16 - September 15, 1961

Title: THE ACCELERATED CORROSION OF METALS

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September 26, 1961

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INTRODUCTION

In previous reports (1), the oxidation of aluminum in contact with mercuric halides has been studied, and the influence of relative humidity on the oxidation rate was noted. In this report period the Al-HgI₂ system has again been used for continued quantitative measurements of the oxidation rates. The rate of oxidation of aluminum in air in the presence of HgI₂ has been studied over a relative humidity range of 36.4-100% at a constant temperature of 30°C. A great increase in rate of oxidation has been noted in the 60-80% RH range.

DESCRIPTION OF APPARATUS

The apparatus described in the Seventh Quarterly Report has been further modified to include a pressure gauge (Fig. 1; B), which was calibrated against the mercury manometer (C). This bellows-type gauge was specifically designed to measure the small internal pressure decrease in the reaction chamber; atmospheric pressure was the reference point. Once the gauge was calibrated, the manometers were disconnected, and the system resealed. All values of ΔW_{O_2} in this report are based on pressure readings obtained by this gauge.

A photograph of the entire apparatus is seen in Figure 1. The vacuum pump (J) was used intermittently to check the system for small leaks. A detailed diagram of the reaction chamber (A) may be found in the previous reports (1).

Figure 1 - Oxidation Apparatus



Description of Apparatus for Figure 1

- A. Reaction Chamber
- B. Pressure Gauge
- C. Water and/or Mercury Manometer (now not in use)
- D. Barometer
- E. Constant Temperature Bath Control Unit
- F. Fan and Lamp Control; Barometer Adjustment Indicator
- G. Constant Temperature Water Bath
- H. Variable Speed Water Pump
- I. Variac for Water Pump
- J. Vacuum Pump

EXPERIMENTAL PROCEDURE

Reynolds 99.999% aluminum cylinders 1/2" in diameter and 1/4" thick were degreased in acetone and ether. Exposed surface areas of these samples measured approximately 1.25 cm².

The oxidation of the aluminum samples was initiated by the attack of HgI₂ which was quickly reduced to metallic mercury. The manipulation of the apparatus for this is described in previous reports(1). Upon amalgamation, the oxidation proceeded; the rate being greatly determined by the relative humidity inside the reaction chamber. The desired relative humidities were obtained by placing various saturated salt solutions in the reaction chamber. Both thermal and humidity equilibrium were facilitated by the use of a small fan which maintained the internal atmosphere in a continual state of movement. Upon reaching equilibrium, the reaction was begun as described above. The oxygen consumed during the reaction was measured by the decrease in pressure inside the chamber. Since pressure was the measured parameter, close temperature control inside the chamber was essential. Temperatures were maintained at 30.00°C ± 0.30 throughout all the experiments. Measurements of time, temperature and pressure were made at 5 to 10 minute intervals until the oxidation slowed or completely stopped. Corrections necessitated by changes in barometric pressures were made.

Values of ΔP in mm Hg were converted to ΔW_{O_2} in mg/cm² from the following:

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

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

Several saturated salt solutions and the associated relative humidities under equilibrium conditions are listed in Table A.

TABLE A

Relative Humidities of Several Saturated Salt
Solutions (4) at 30°C

<u>Solution</u>	<u>R. H. (%)</u>
Distilled water	100
$(NH_4)_2H_2PO_4$	92.9
$BaCl_2 \cdot 2H_2O$	85
$(NH_4)_2SO_4$	81.1
$NaNO_3$	72.7
$NaNO_2$	63.0
$NaBr \cdot 2H_2O$	*56.2
CrO_3	44.6
$NaI \cdot 2H_2O$	36.4

* - Extrapolated value (2), (3), (4)

RESULTS AND DISCUSSION

Whereas in earlier experiments, the linear portions of the oxidation rate curves were usually preceded by low-rate induction periods, in the present experiments no great induction period seemed to exist except in one or two cases at high relative humidities.

By plotting time vs. values of ΔW_{O_2} obtained from pressure readings, each rate curve exhibited a characteristic linear portion from which the slopes were graphically determined. The slopes of the linear portions of the rate curves were approximately the same at any particular relative humidity. However, as the relative humidity decreased, the slopes of the rate curves also decreased. The slopes of the rate curves are listed in Table B, with the existing relative humidities obtained from the saturated salt solutions.

At low relative humidities (50% RH and below), the extent of oxidation was very small, and the associated slopes for the rate curves could only be determined from the first few measurements in the 120 minute time intervals.

Figures 2 through 7 are rate curves for experiments at 100% R. H.; Figures 8 and 9 at 92.9% R. H.; Figures 10 through 12 at 81.1% R. H.; Figures 13 through 16 at 72.7% R. H.; Figures 17 through 20 at 65% R. H.; Figures 21 through 26 at 56.2% R. H.; Figures 27 through 30 at 44.6% R. H.; Figures 31 and 32 at 36.4% R. H. Since the variation in the extent of oxidation was wide, three different scales were necessary to plot accurately the oxidation time curves.

TABLE B

Values for the slopes of oxidation rate curves at different relative humidities at 33°C

Saturated Salt Solution Used	Relative Humidity (%)	Slope (m) mgO ₂ /cm ² /min.	Ave. Slope (n) mgO ₂ /cm ² /min.
Distilled Water	100	*0.630	
"	"	*0.675	
"	"	*0.640	
"	"	0.570	
"	"	0.622	0.614
"	"	0.616	
"	"	0.591	
"	"	0.567	
"	"	0.566	
(NH ₄) ₂ H ₂ PO ₄	92.9	0.600	
"	"	0.566	0.583
BaCl ₂ · 2H ₂ O	85	*0.613	
"	"	*0.556	
"	"	*0.565	0.559
"	"	*0.500	
(NH ₄) ₂ SO ₄	81.1	*0.540	
"	"	*0.515	
"	"	*0.555	0.520
"	"	0.527	
"	"	0.496	
"	"	0.487	
Na(NO ₃)	72.7	0.425	
"	"	*0.429	
"	"	*0.400	0.409
"	"	0.381	
Na(NO ₂)	63.0	0.270	
"	"	0.270	
"	"	0.273	0.271
"	"	0.269	
NaBr · 2H ₂ O	56.2	*0.193	
"	"	*0.218	
"	"	0.180	
"	"	0.209	
"	"	0.205	0.212
"	"	0.240	
"	"	0.210	
"	"	0.255	

Table B (continued)

Saturated Salt Solution Used	Relative Humidity (%)	Slope(m) mgO ₂ /cm ² /min.	Ave. Slope ($\bar{m}$) mgO ₂ /cm ² /min.
CrO ₃	44.6	0.137	6.136
"	"	0.130	
"	"	0.139	
"	"	0.138	
Na ₂ SO ₄	36.4	0.083	6.086
"	"	0.076	

* Values taken from Seventh Quarterly Report

$\bar{m}$ Short-term oxidation

ϕ Extrapolated value (2), (3), (4)

The influence of the relative humidity on the oxidation rates is easily noted in Figure 33, where the average values of the different slopes are plotted vs. the relative humidities at which the slopes were determined. The change in slopes with change in relative humidity has the appearance of a lazy-S curve. In the 60%-75% R. H. range, there is a well-defined increase in oxidation rate.

The average values for the slopes at high % R. H. (particularly near 100% R. H.), as well as the wide ranges at each %R. H. leads the authors to believe that the gradual tailing-off of the curve was due to the increasing difficulty with which equilibrium was obtained. It is believed that the most likely path for the curve to follow in this region is somewhat higher than shown, and should approach the higher limits of the individual ranges.

The extent of oxidation in the 60-75% R. H. range indicated a more pronounced increase than is shown by $\bar{m}$ values in Figure 33. Variation of

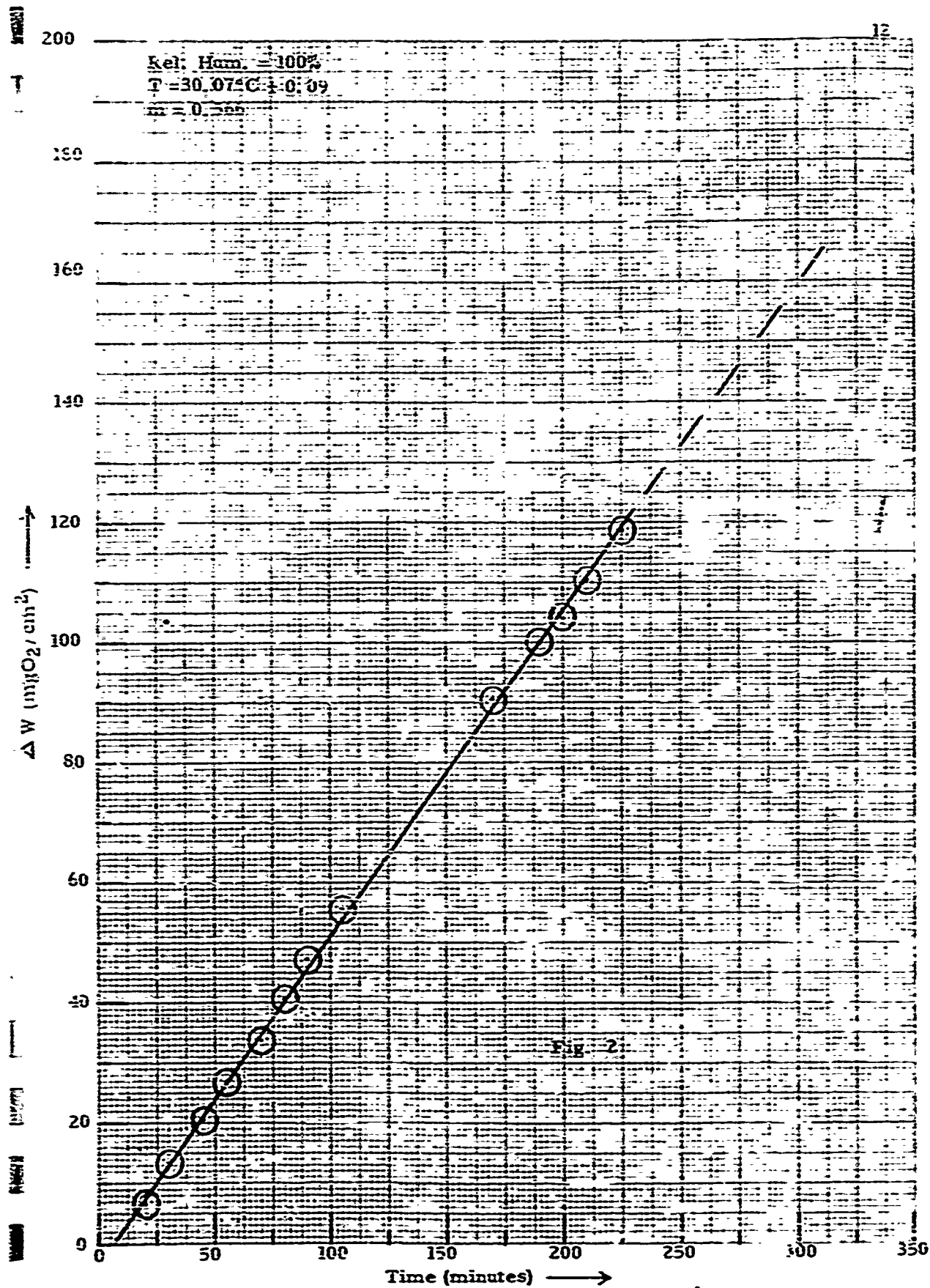
oxygen-consumed with %R. H. during a 150 minute effective oxidation period (disregarding induction periods and by extrapolation of the ΔW vs. time curves for short-term reactions) indicated that little significant oxidation occurred until the relative humidity reached 60% R. H. At approximately 60% R. H., the amount of oxygen consumed suddenly increased with increasing R. H.; i. e. at 40% R. H. an average of only 7 mg oxygen were consumed in 150 minutes, whereas near 100% R. H. approximately 83 mg oxygen were consumed in the same period.

A time-lapse 16 mm movie was made of two aluminum samples simultaneously oxidizing at different relative humidities; one sample near 80% R. H. and the other near 100% R. H. Even though there was a noted difference in reaction, a more striking difference was desired for the time-lapse films. This will be accomplished at a later date by photographing experiments near 45% R. H. and 100% R. H.

Preliminary microscopic investigations at room conditions on the oxidation of aluminum initiated by HgI_2 were begun. A polished aluminum sample was cemented to a slide and observed as a tiny crystal of HgI_2 was brought in contact with the sample. The reaction appeared to take place in several steps. First, the salt seemed to react instantly causing a dark area to form, which in turn spread rapidly from the point of contact over a relatively large area. This dark area appeared to be a clear liquid under which small bubbles of gas soon developed and came to the surface. The length of time this gas evolved depended on whether the point of contact of the salt was on the edge of a sample, or on a flat surface far removed from

the edge. Gas evolution lasted longer when the salt was placed in the central part of the sample.

As the gas evolution diminished, the metallic appearance of mercury developed. A thin layer of clear liquid still covered the surface of the mercury at this point. Soon, this clear liquid disappeared followed by uniform formation of a film over the surface, causing the metallic luster to be dulled greatly. This film grew more and more opaque until the presence of the white oxide was apparent as the film thickened. This oxide formation was more rapid at the extremities of the darkened area, especially if the area was at the edge of a sample.



250

Rel. Hum. = 100%

T = 70.2° C = 158.4° F

m = 0.567

180

160

140

120

100

80

60

40

20

0

50

100

150

200

250

300

350

 (m, ρ, cm^3)

Time (minutes) →

Fig. 13

100%
 75%
 50%
 25%
 0%

100%
 75%
 50%
 25%
 0%

1974

200

14

Rel. Hum. = 100%
 $T = 30.99^\circ \text{C} \pm 0.4$
 $m = 0.591$

$\Delta W (\text{mgO}_2/\text{cm}^2)$

180

160

140

120

100

80

60

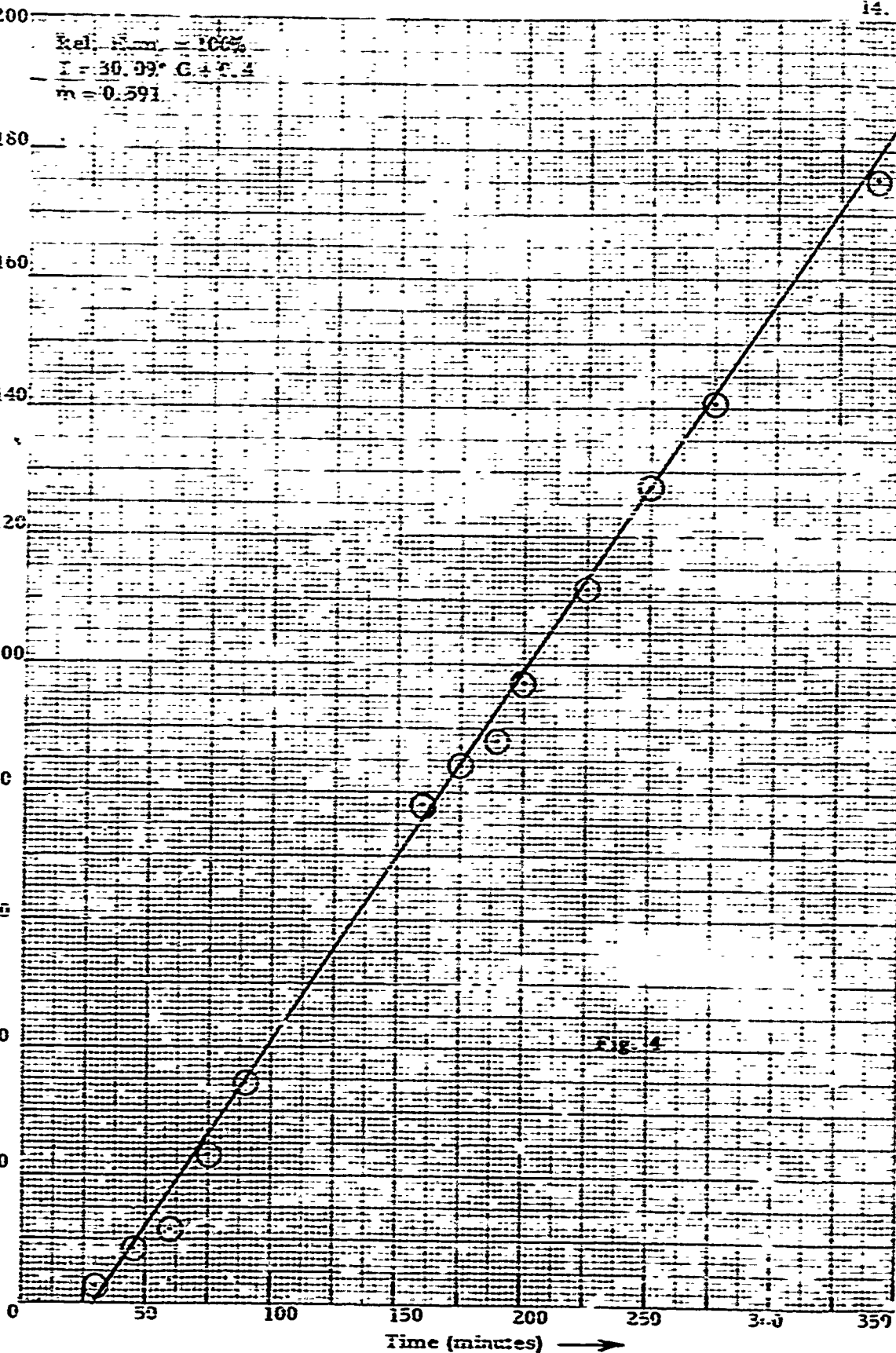
40

20

0

Time (minutes)

Fig. 4



15.

200

Rel. Hum. = 100%

T = 30.0°C ± 0.03

m = 0.015

180

160

140

120

100

80

60

40

20

0

ΔV (mV/cir.)

Time (minutes) →

15.

15.

15.

15.

15.

15.

15.

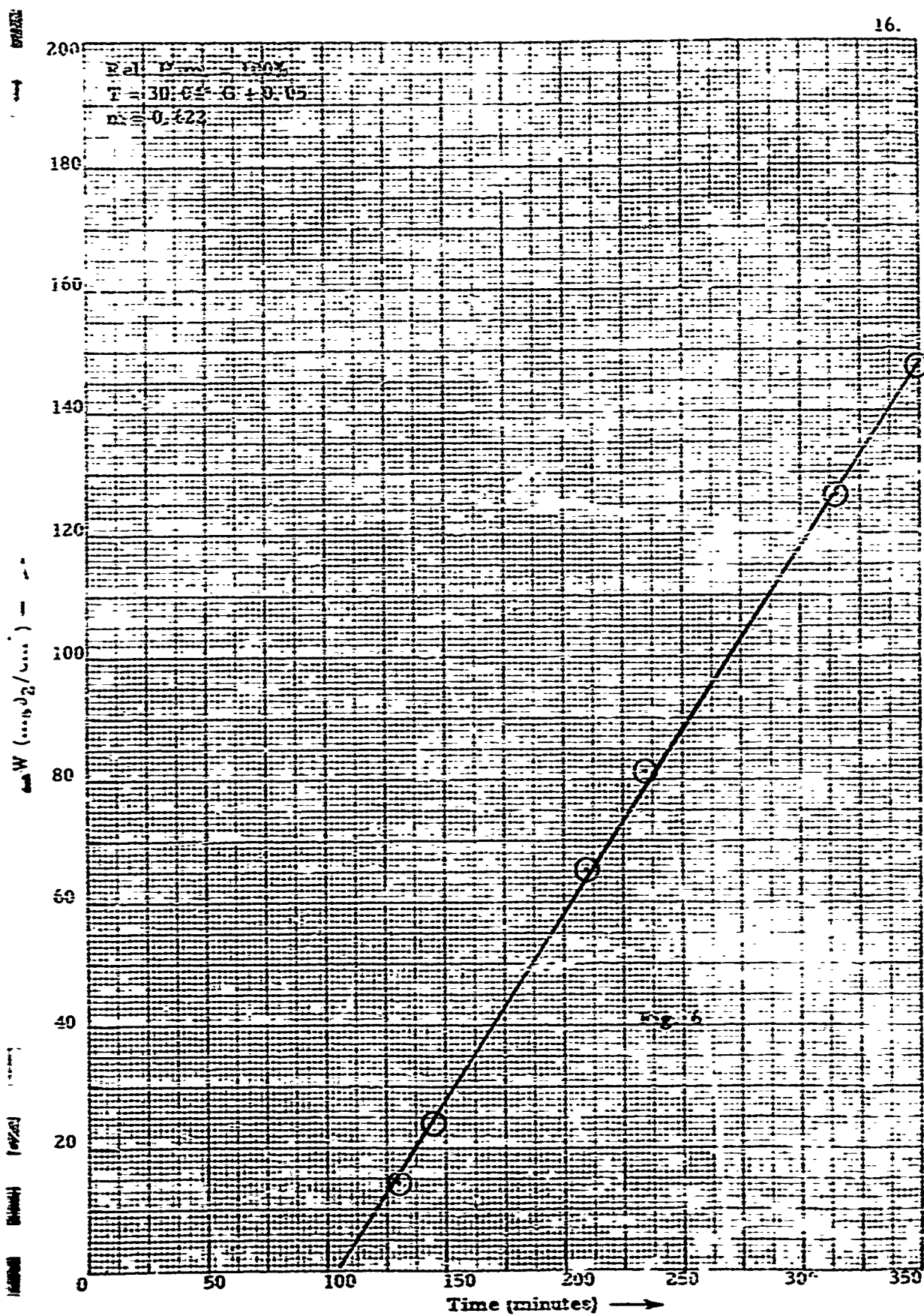
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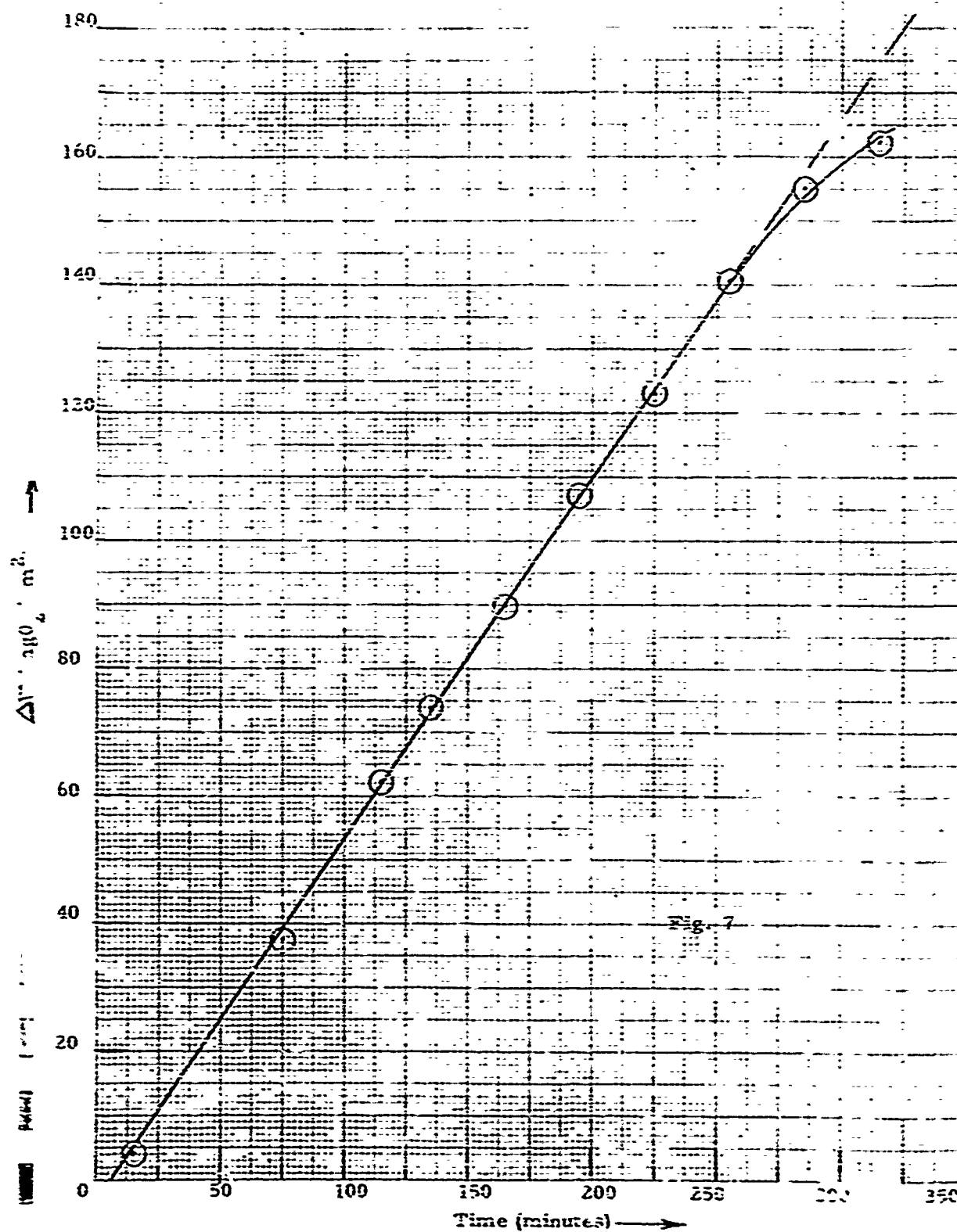
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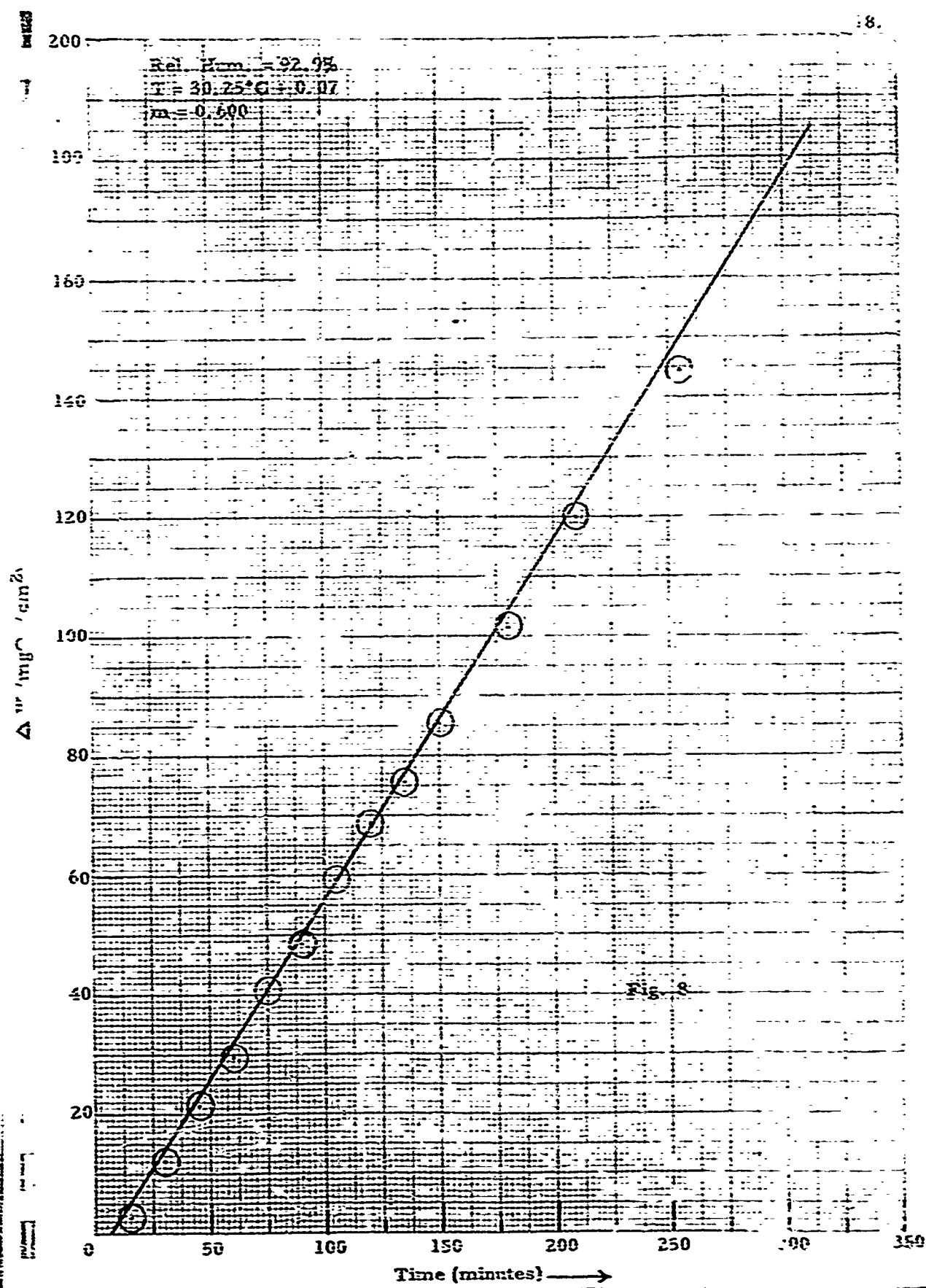


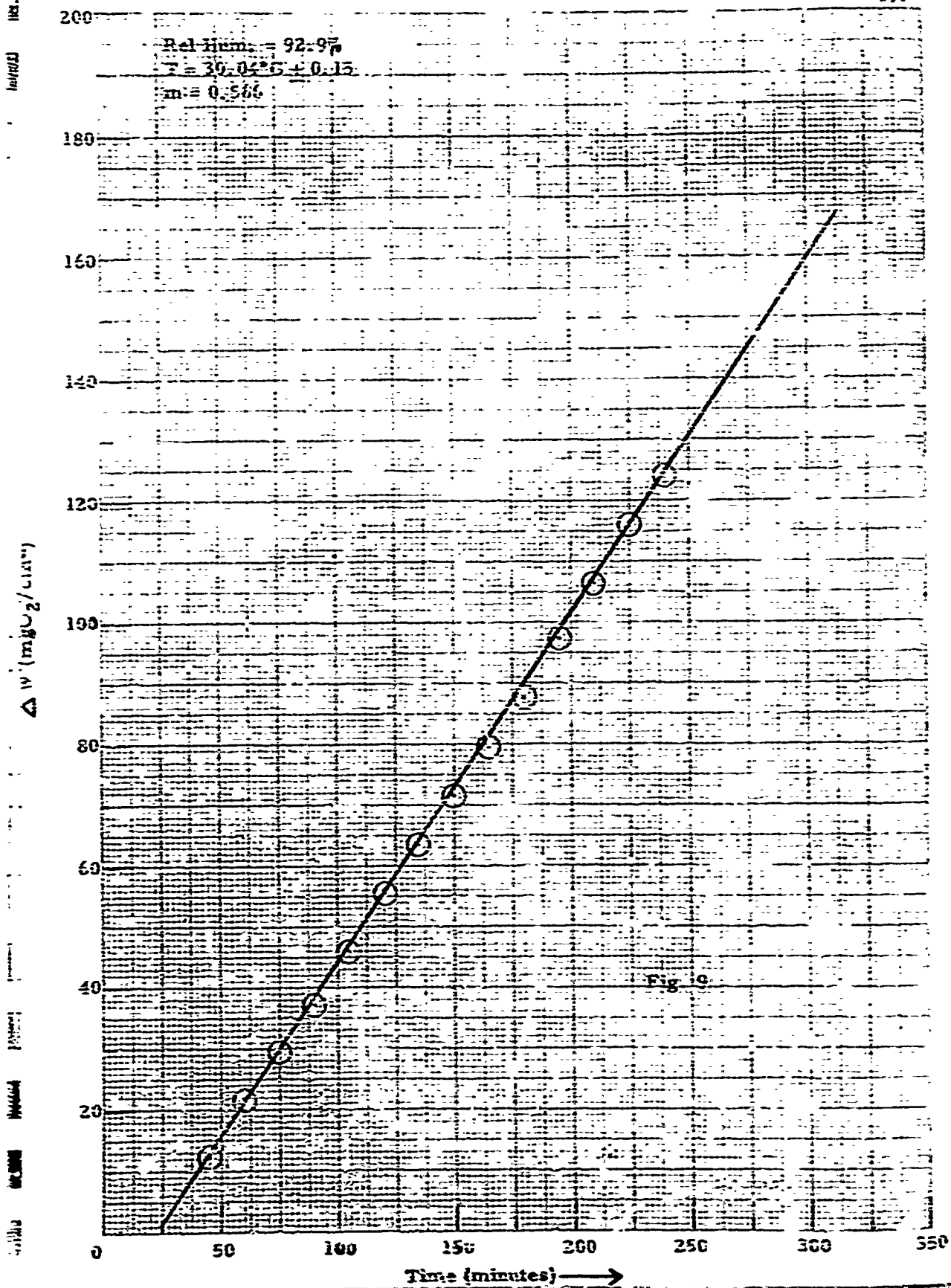
Ref. Hum. = 100%

$T = 29.99^{\circ}\text{C} \pm 0.09$

$H = 0.579$







Wet (g)

200

Rel. Hum. = 81.15
T = 29.39° C ± 0.08
m = 0.496

180

160

140

 ΔW (mgO₂/cm²)

120

100

80

60

40

20

0

Time (minutes) →

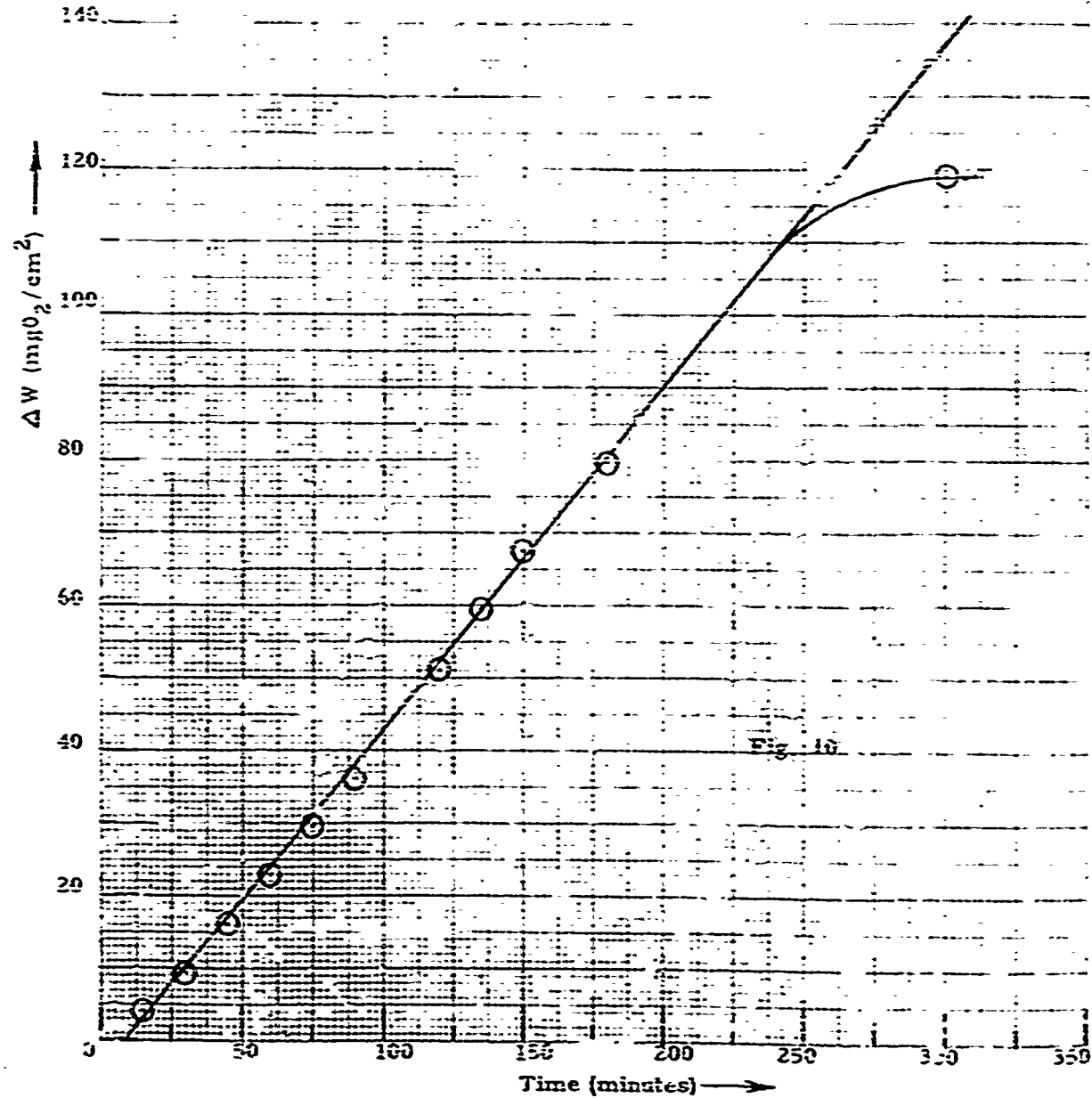


Fig. 10

100

Rel. Hum. = 84.1%
T = 29.98° C = 85.96° F
m = 0.527

30

60

 ΔW (mg O_2 / cm 2)

20

0

20

40

60

80

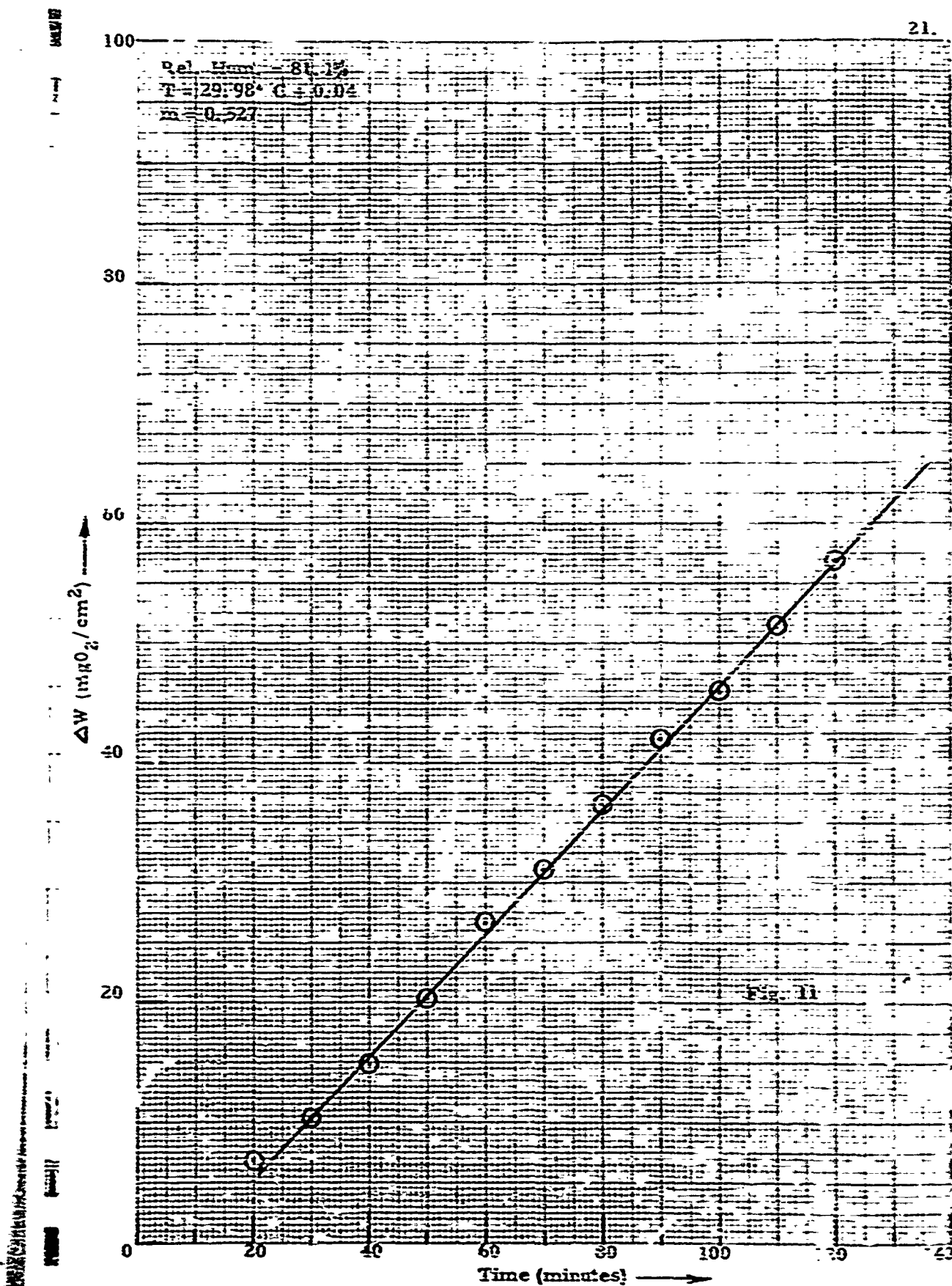
100

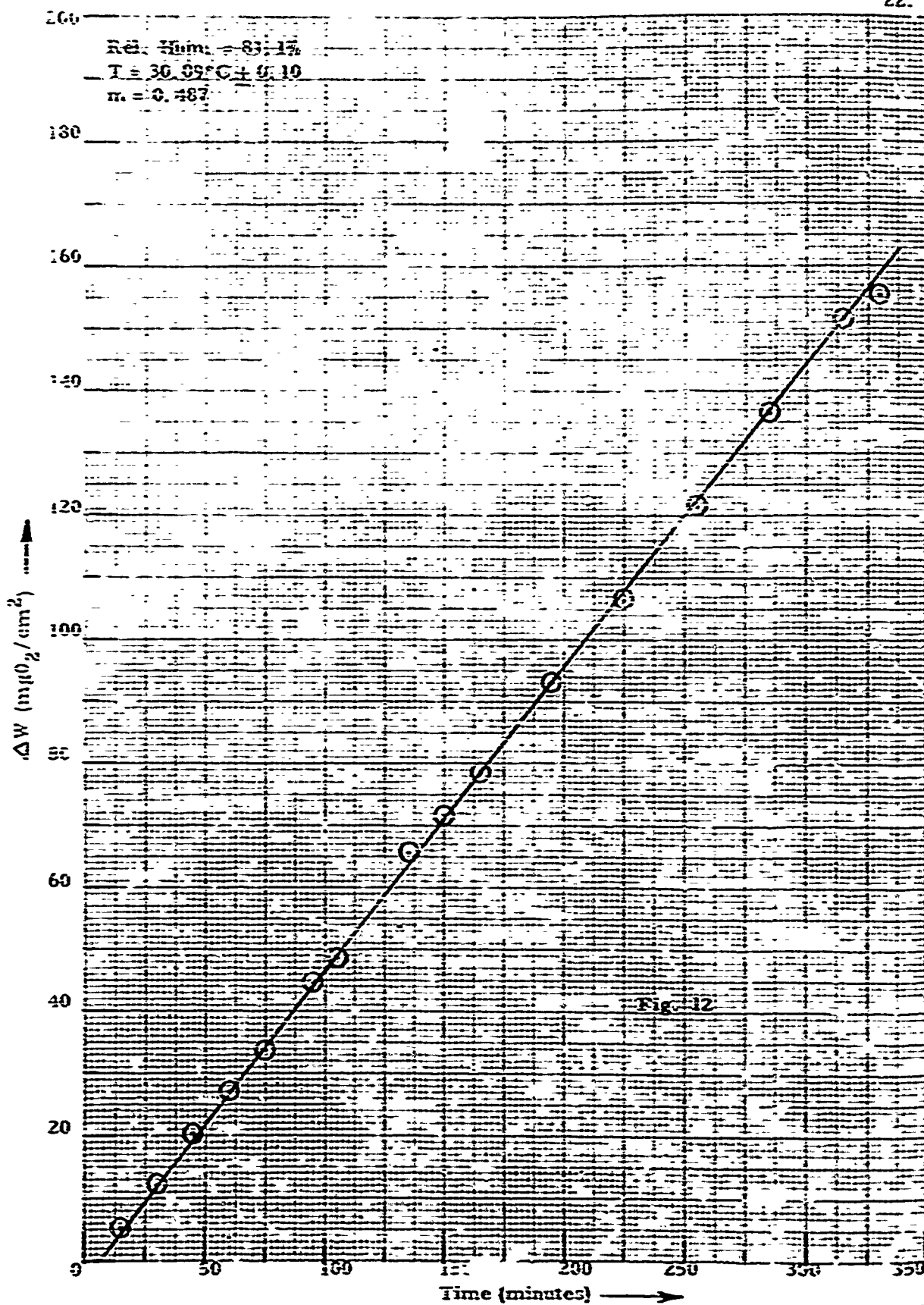
120

140

Time (minutes)

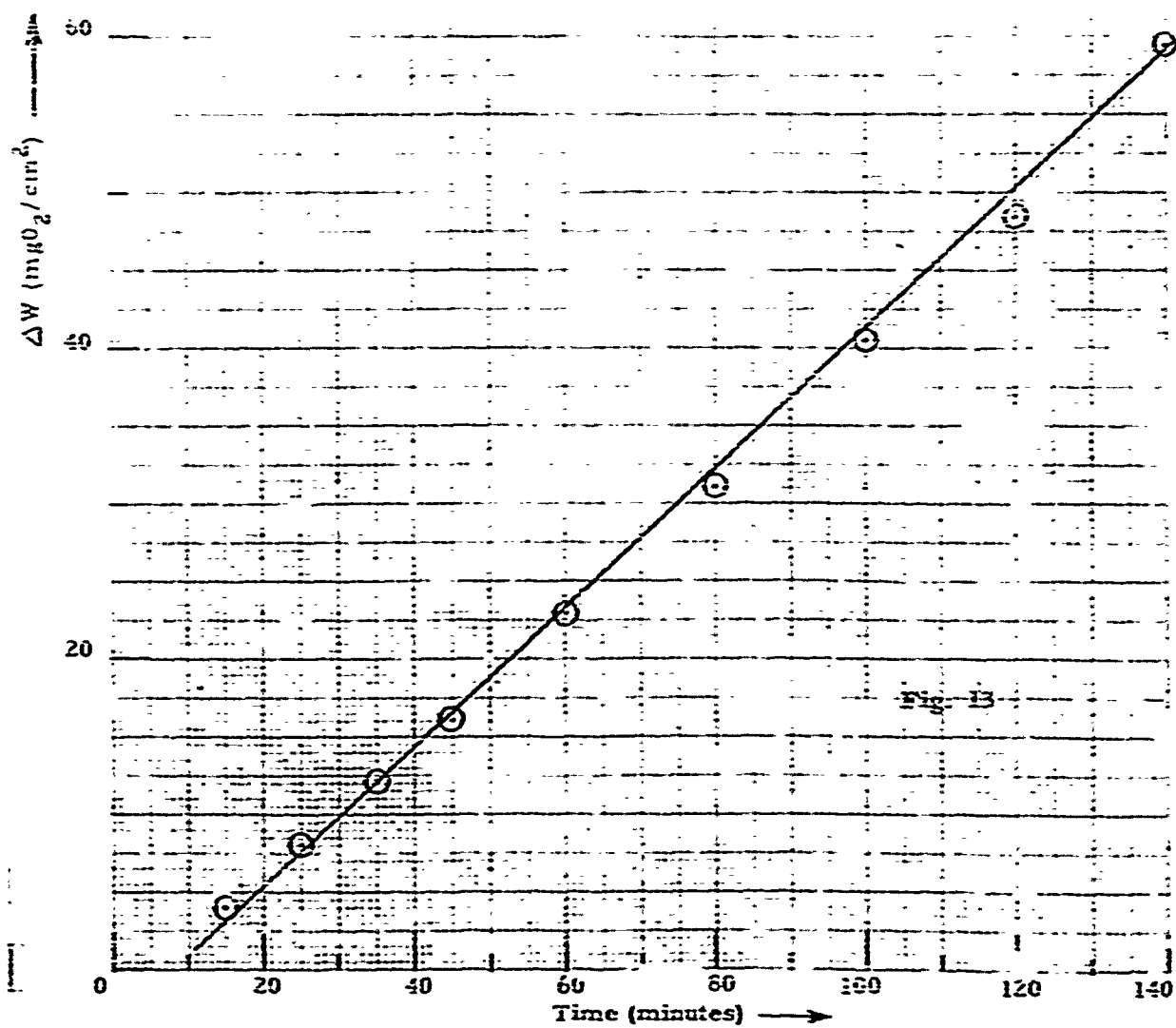
Fig. 11

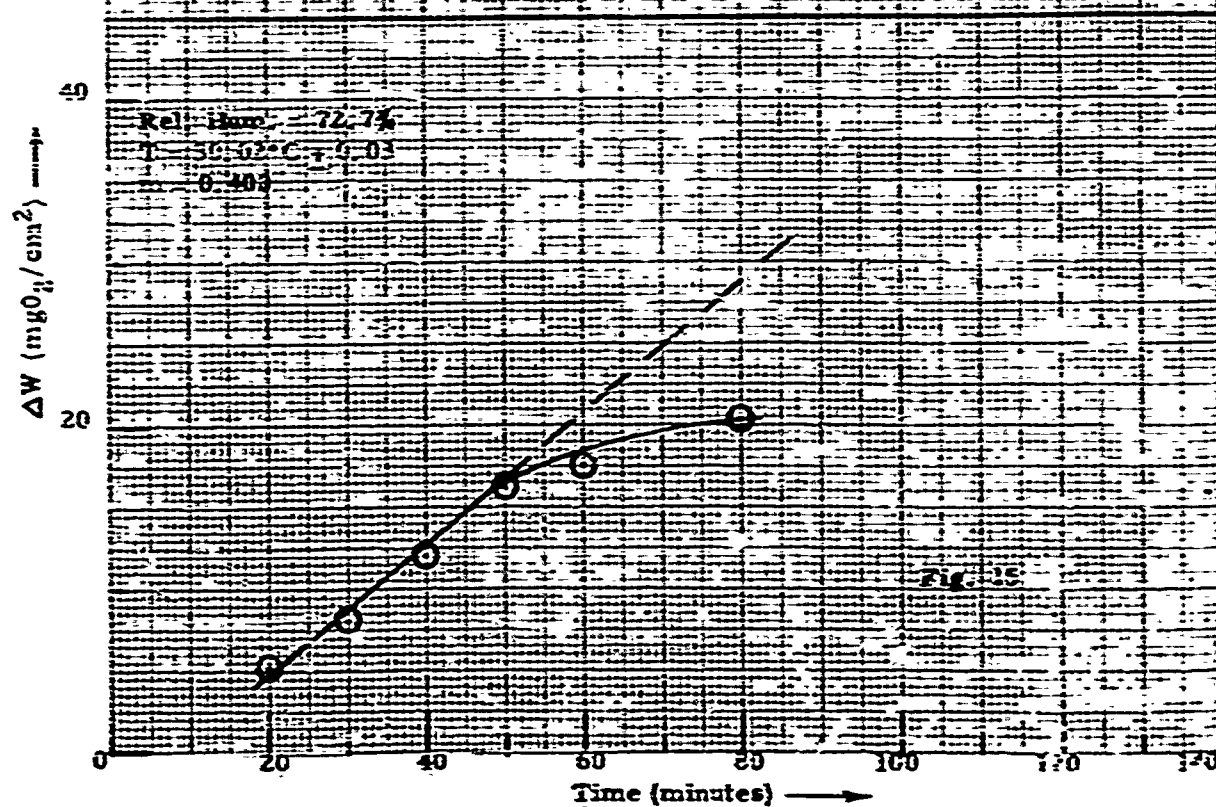
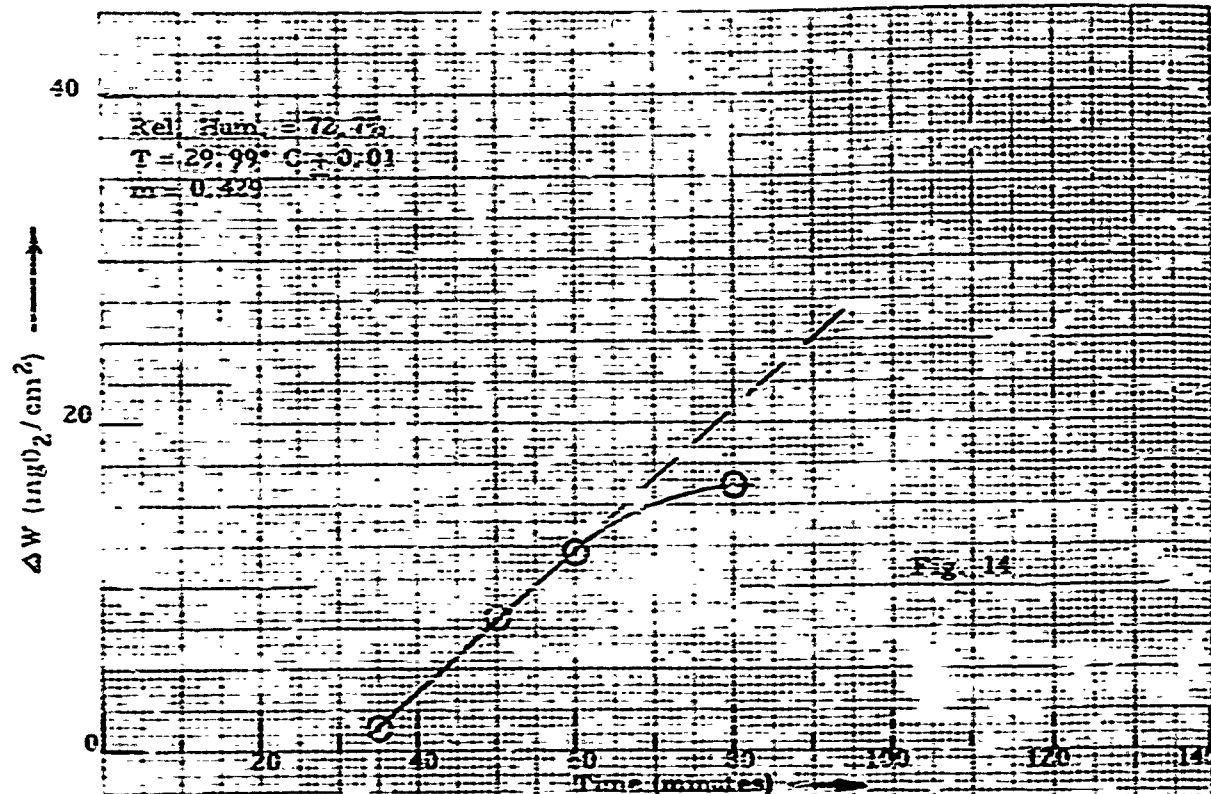


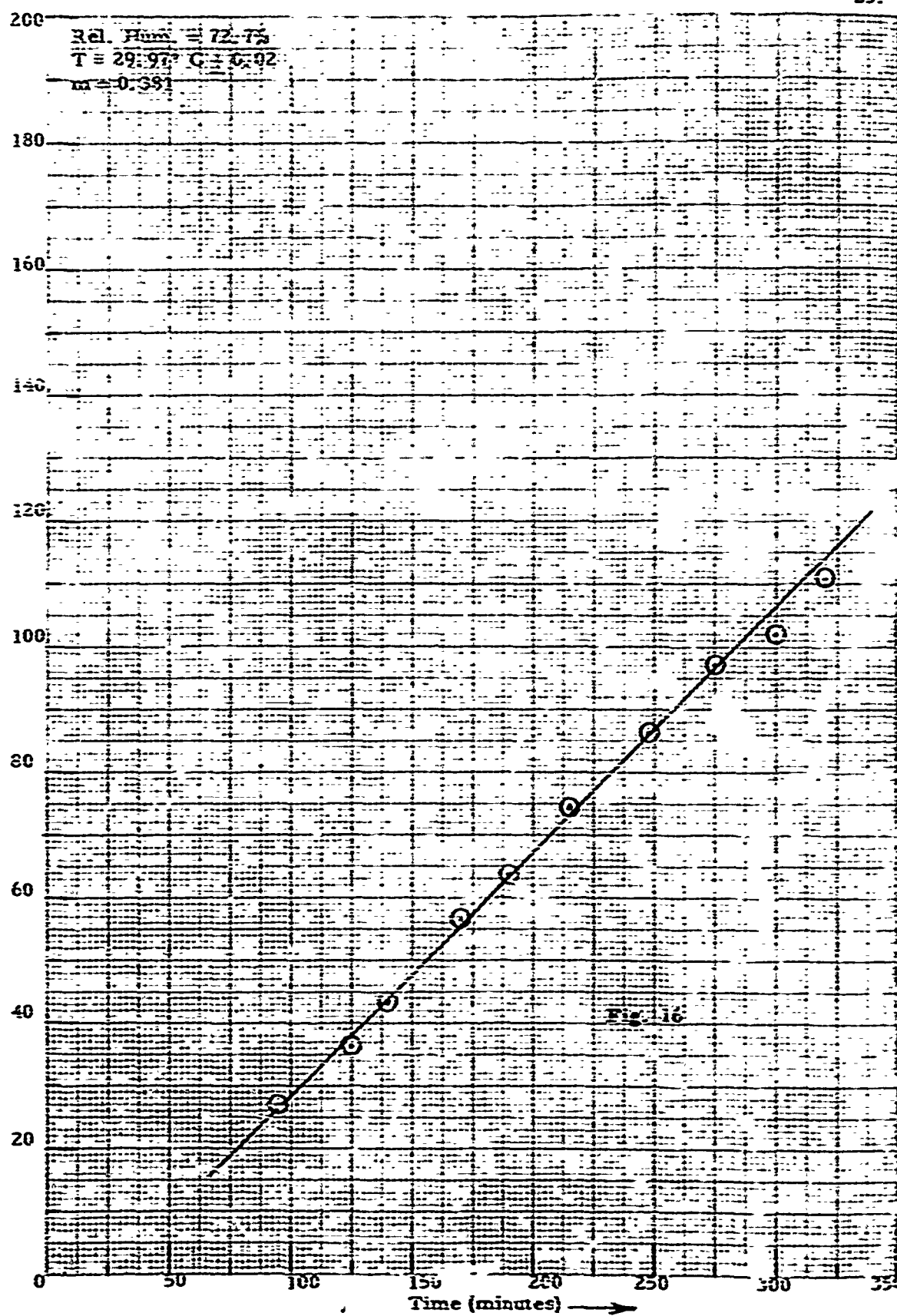


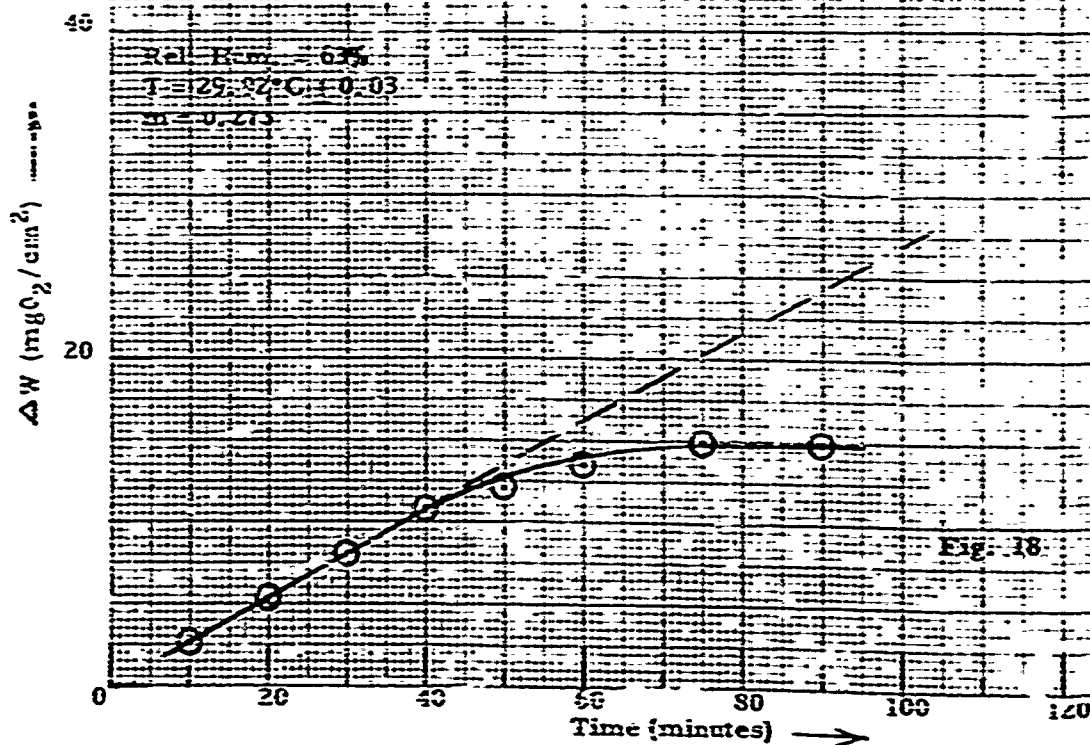
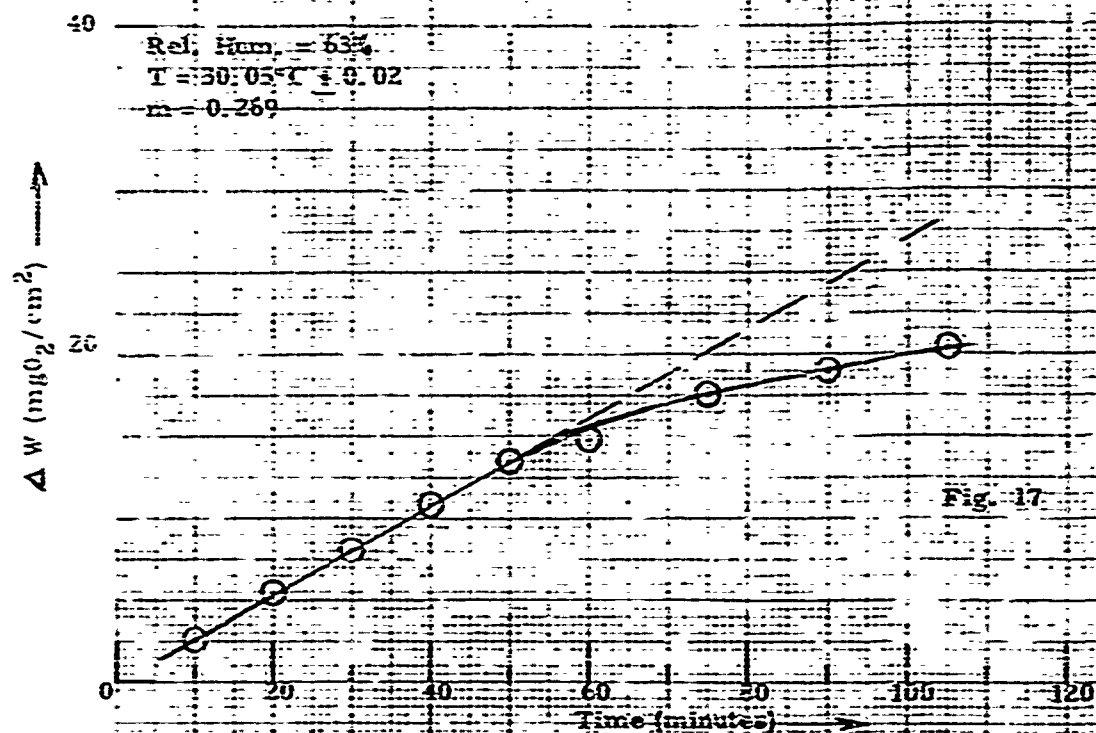
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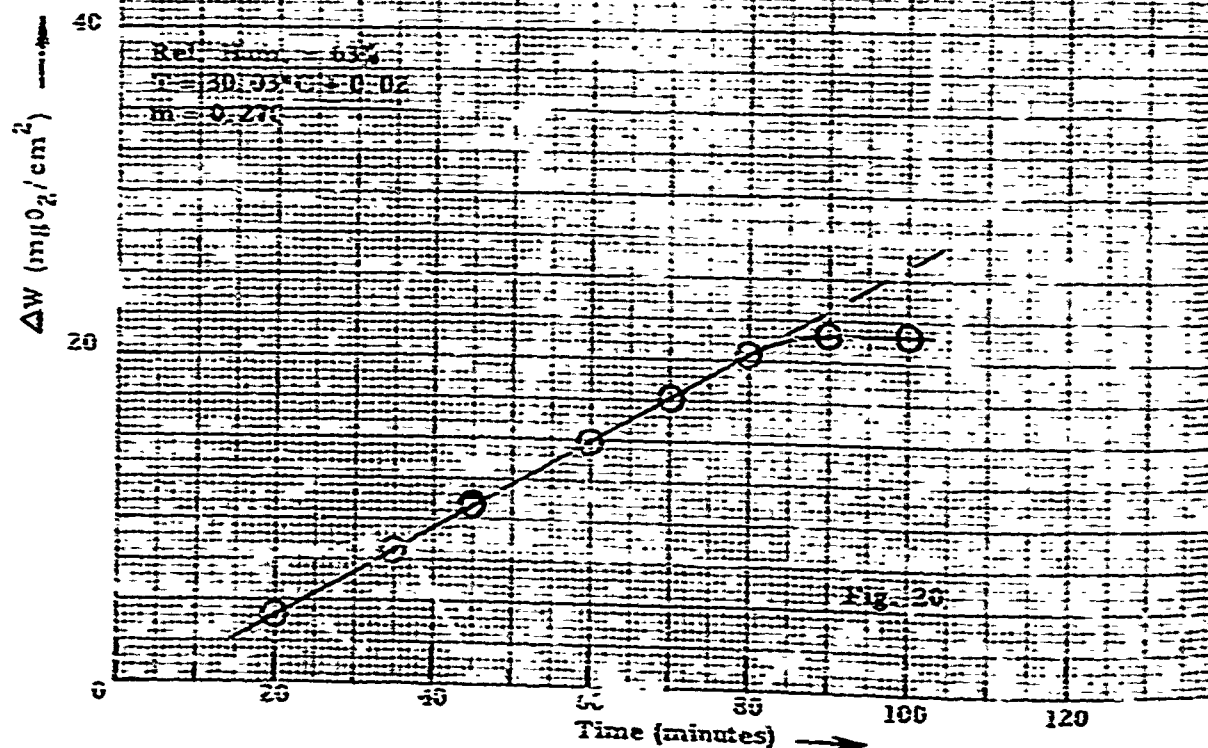
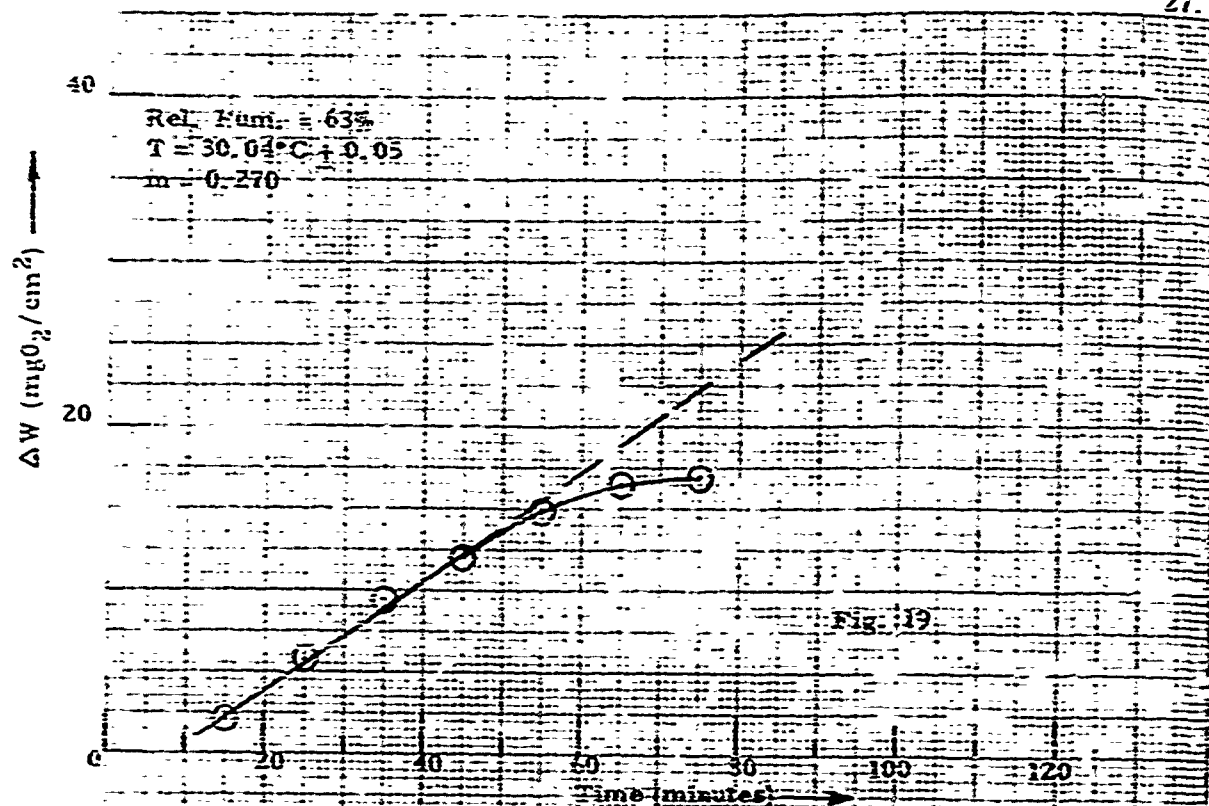
Rel. Hum. = 72.7%

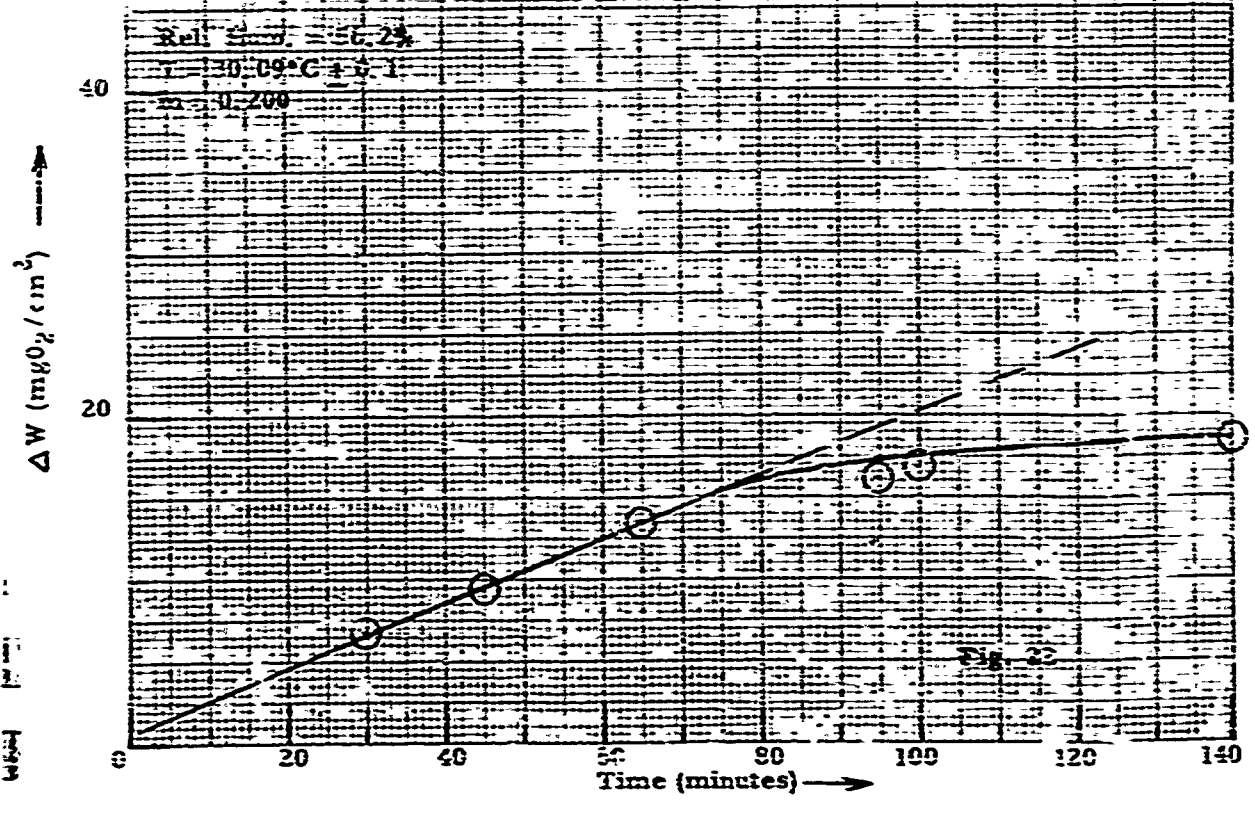
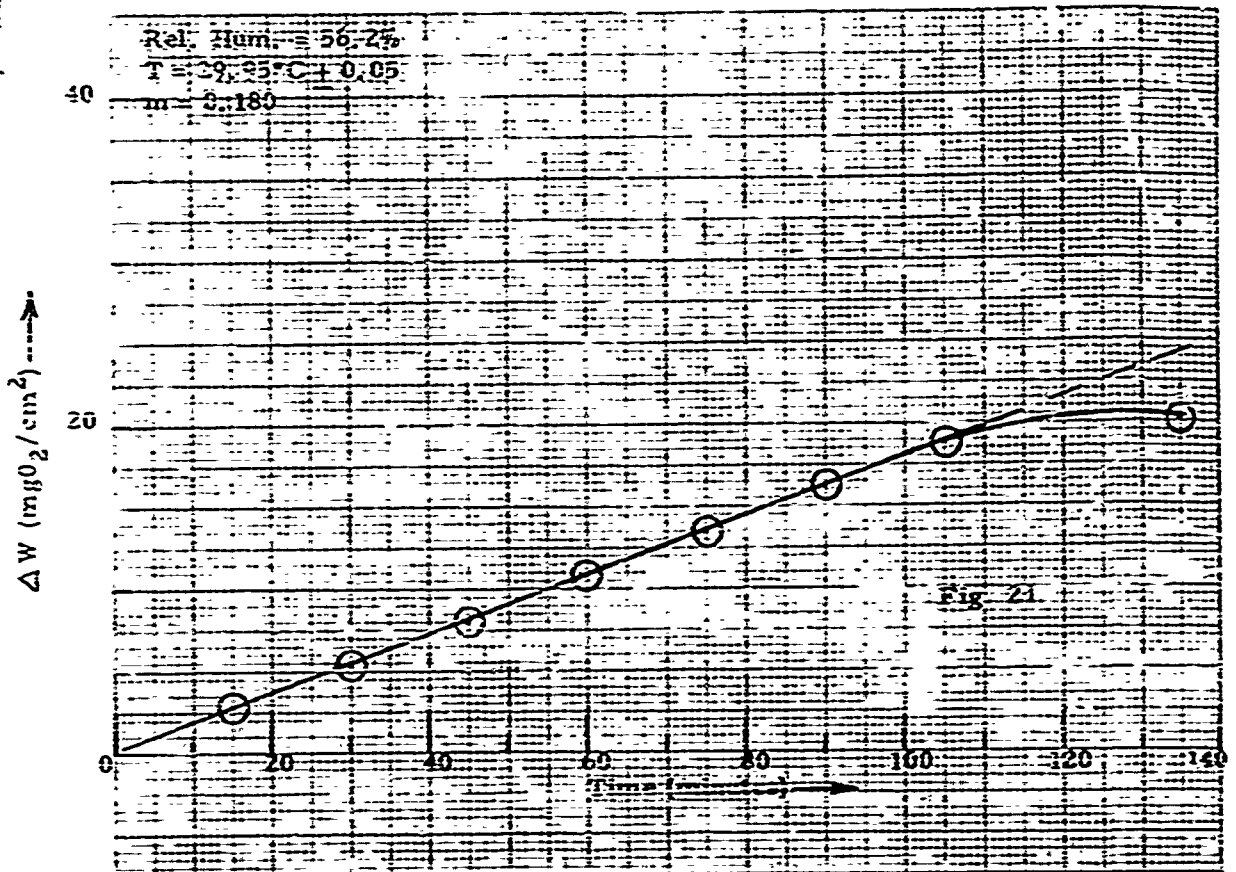
 $T = 30.16^{\circ}\text{C} \pm 0.07$ $m = 0.425$ 



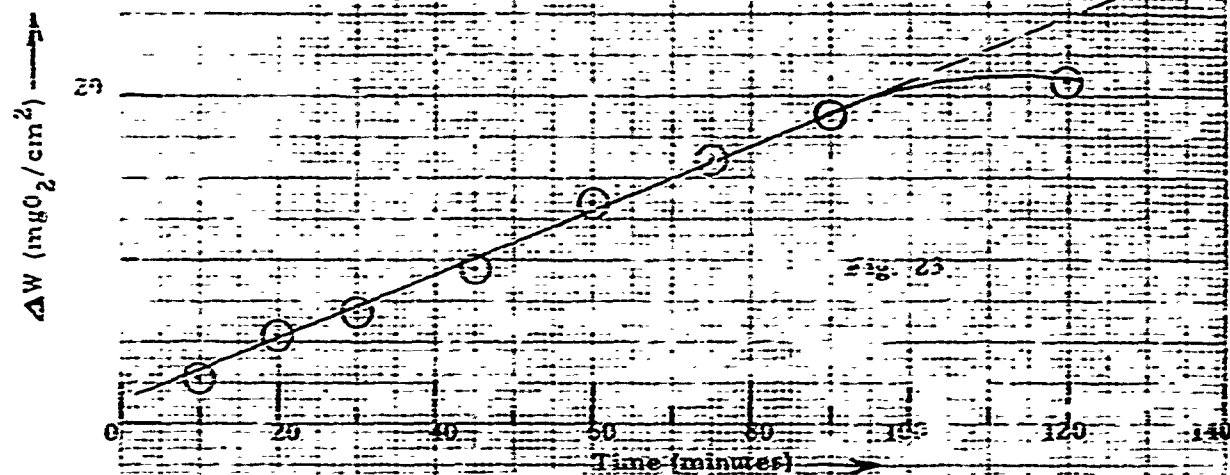




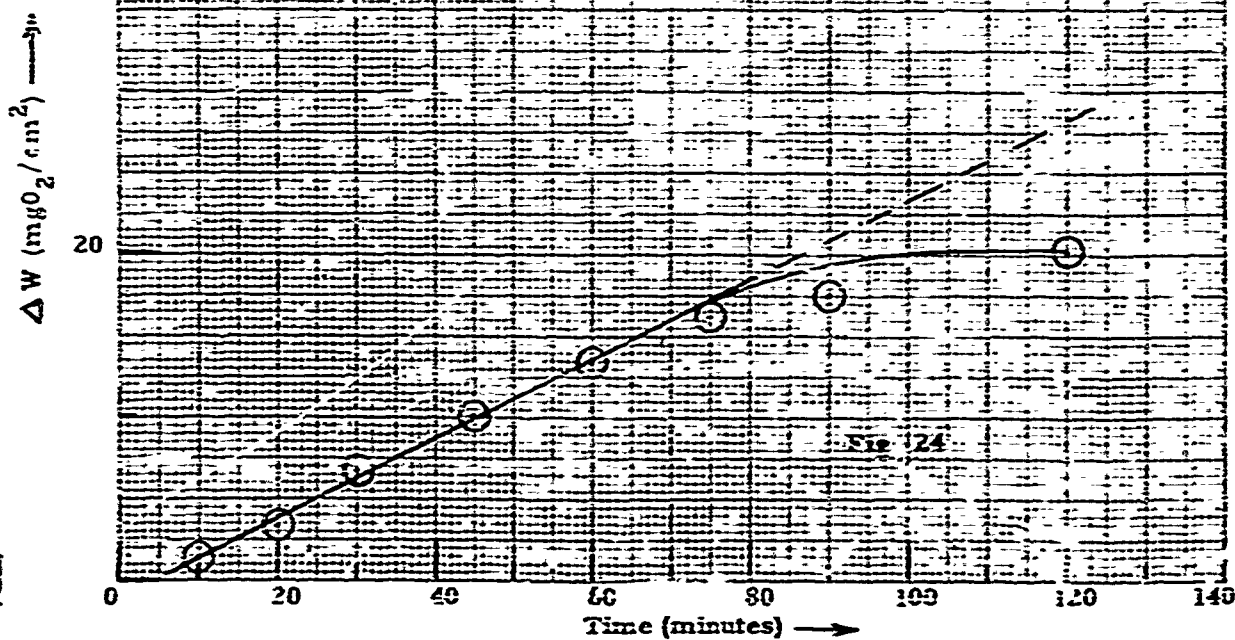


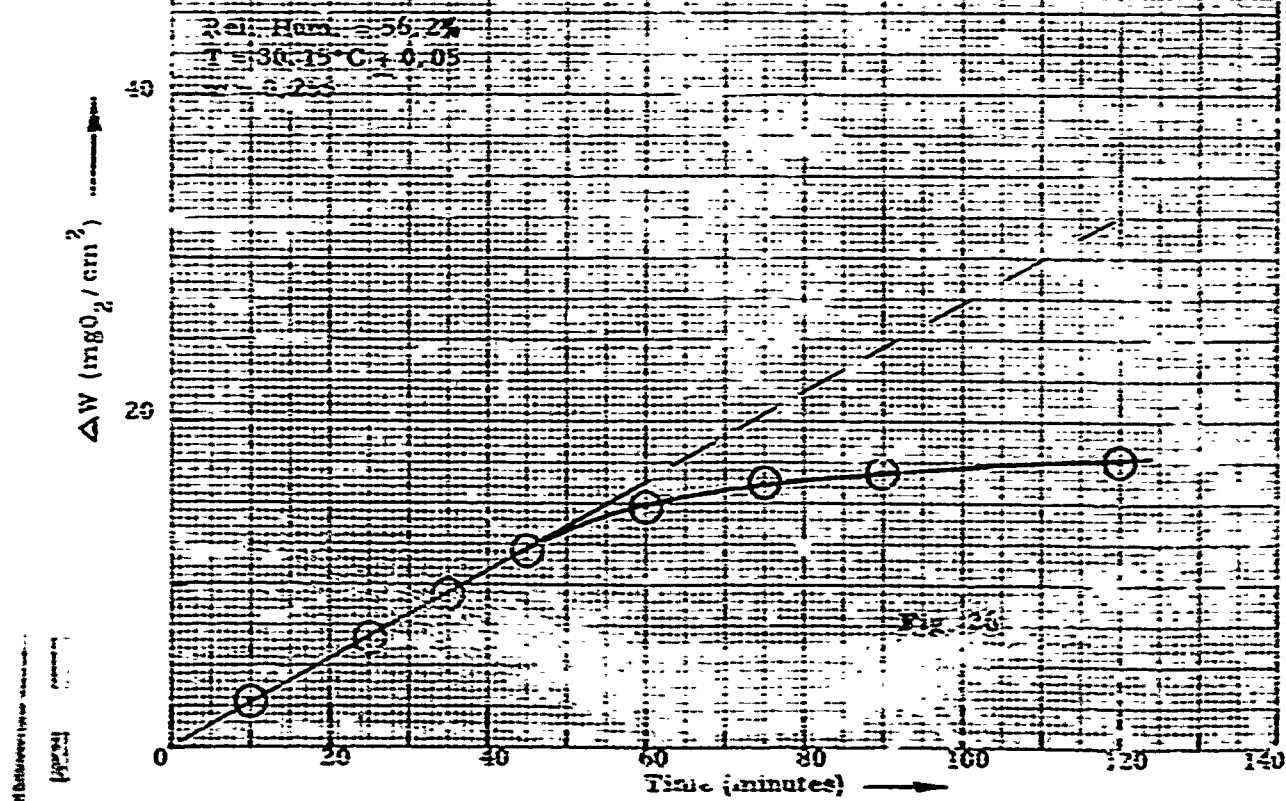
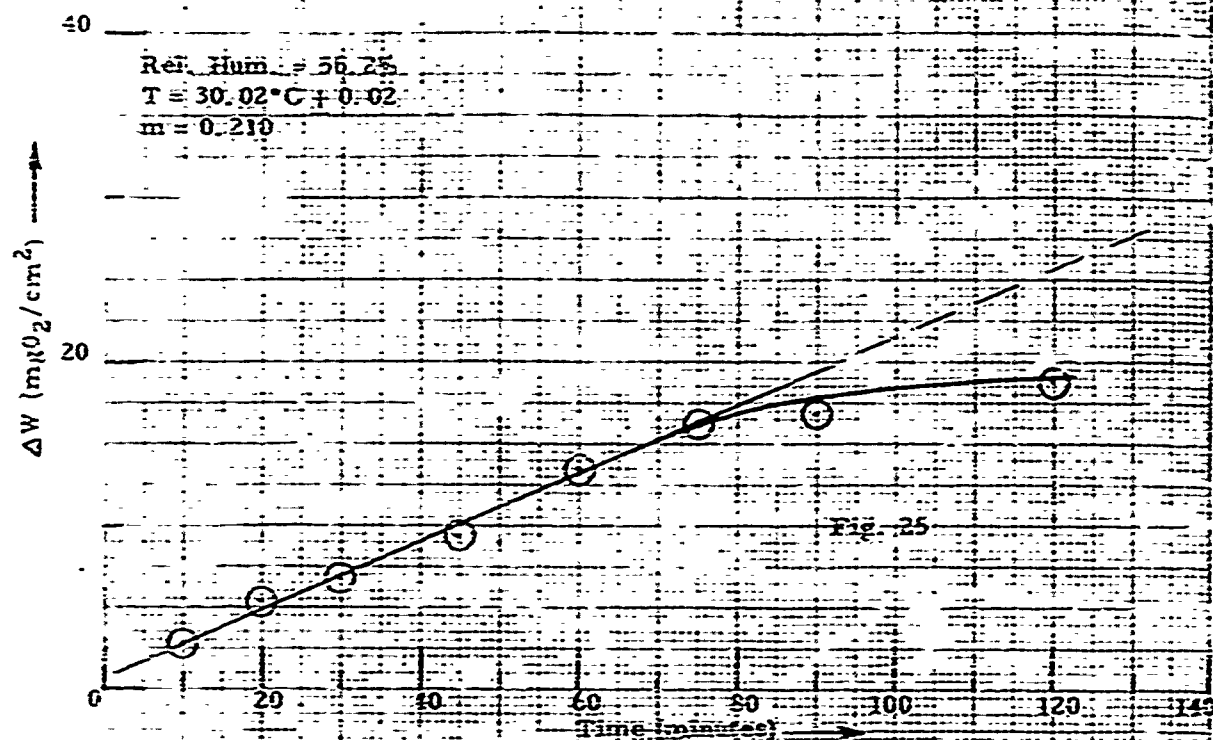


Rel. Hum. = 55.2%
 $T = 29.97^\circ\text{C} \pm 0.02$
 $m = 0.202$



Rel. Hum. = 55.2%
 $T = 29.97^\circ\text{C} \pm 0.02$
 $m = 0.242$





Rel. Hum. = 44.6%
 $T = 30.02^{\circ}\text{C} \pm 0.02$
 $m = 0.138$

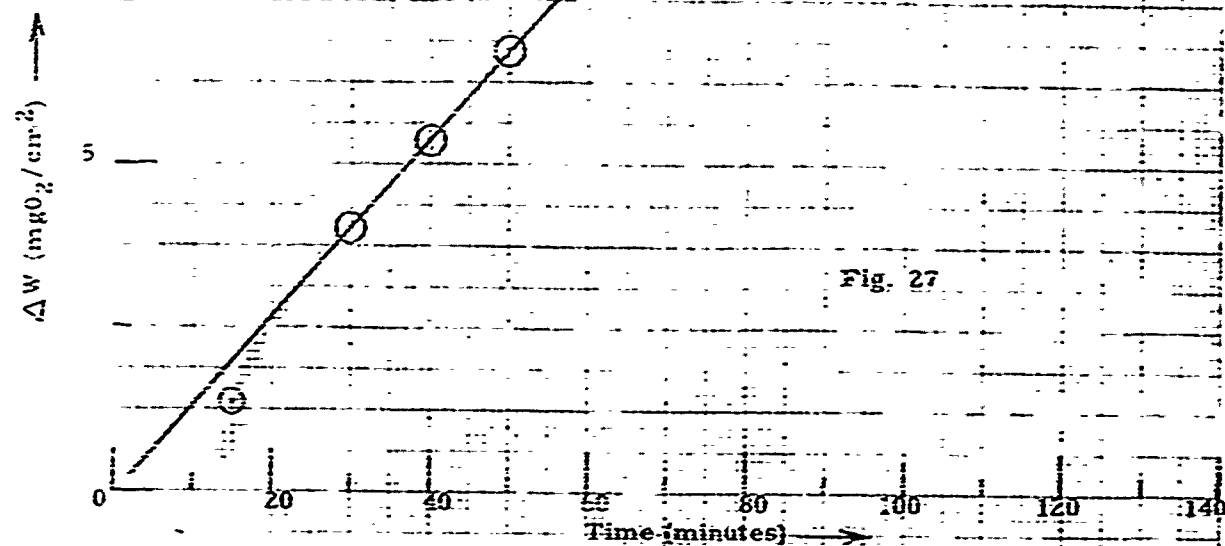


Fig. 27

Rel. Hum. = 44.6%
 $T = 30.65^{\circ}\text{C} \pm 0.05$
 $m = 0.139$

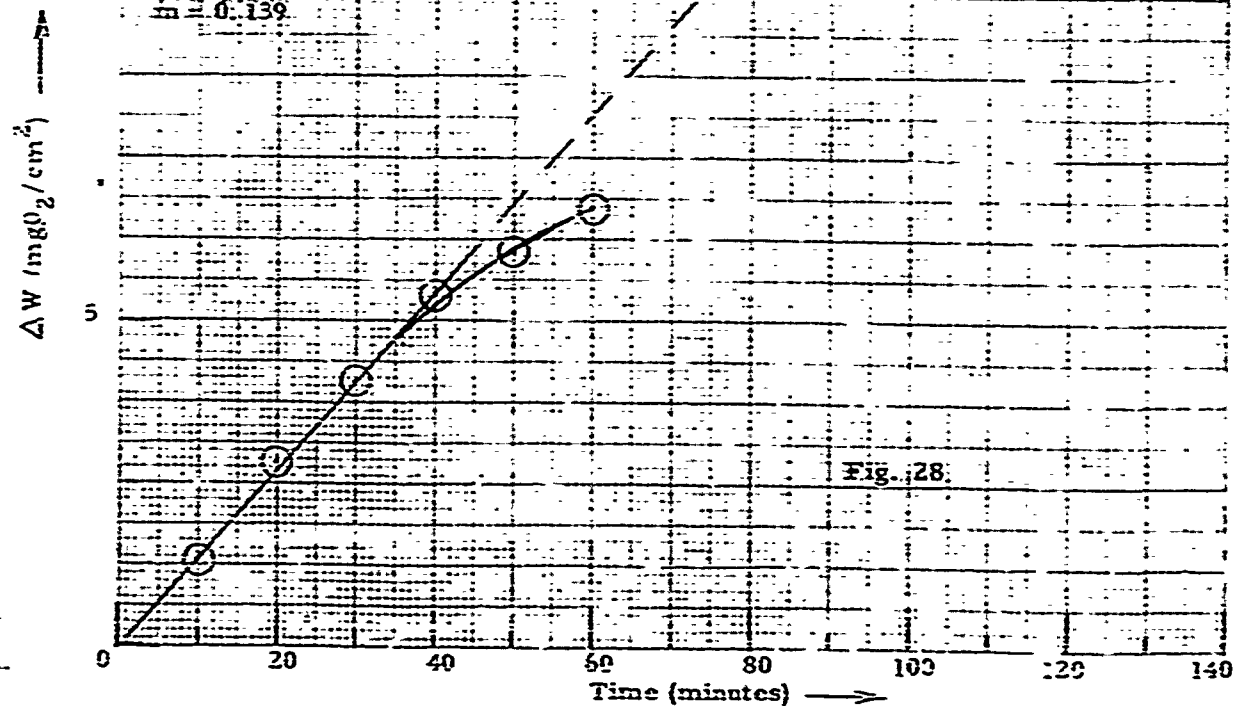
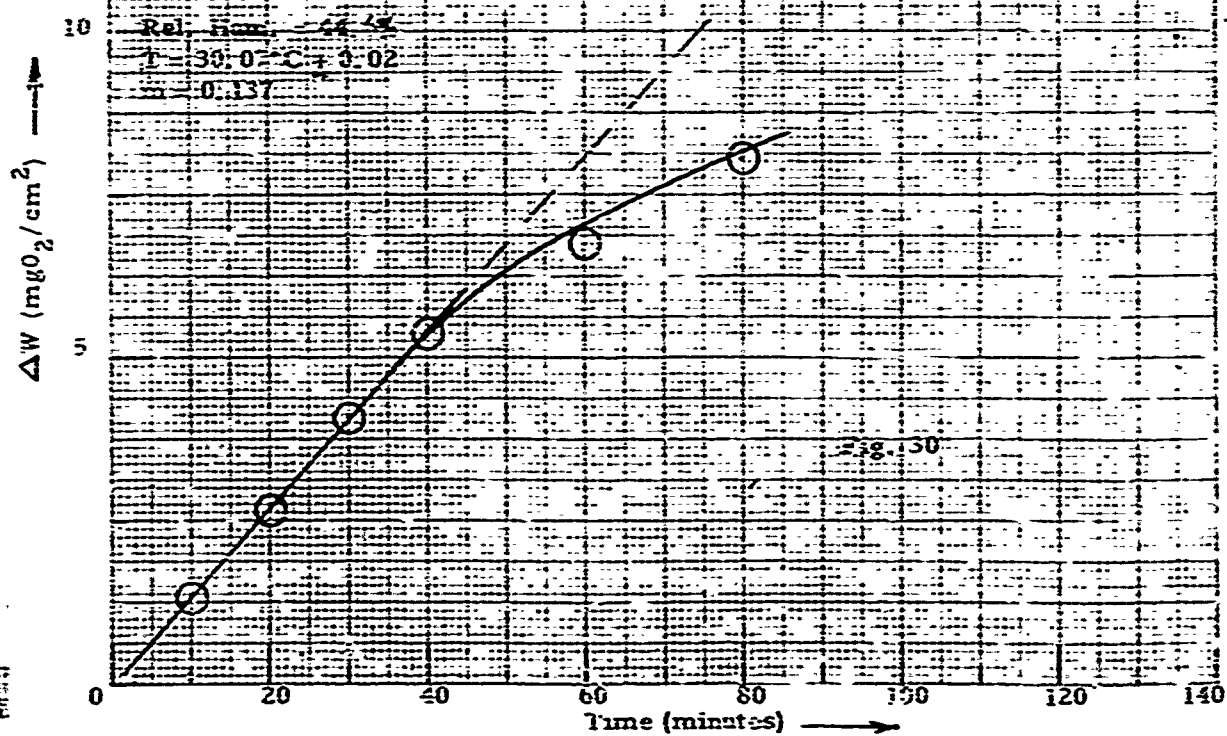
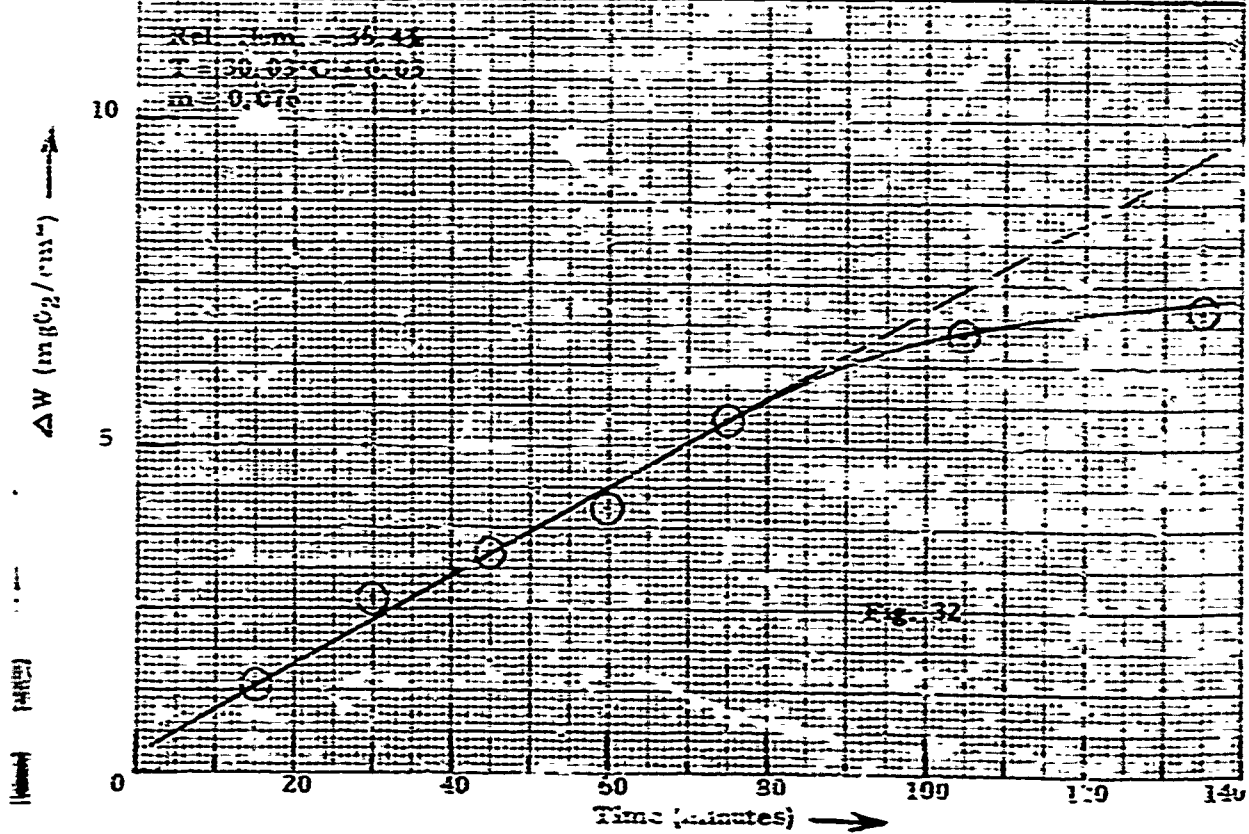
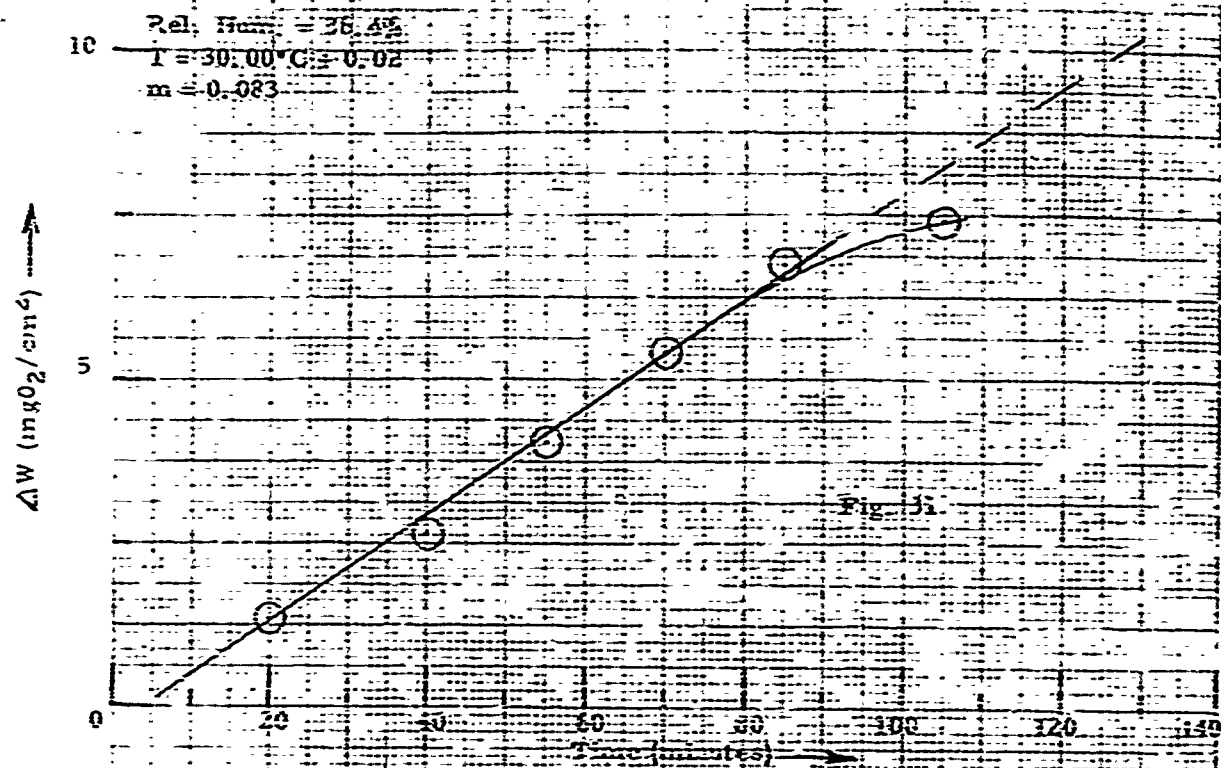
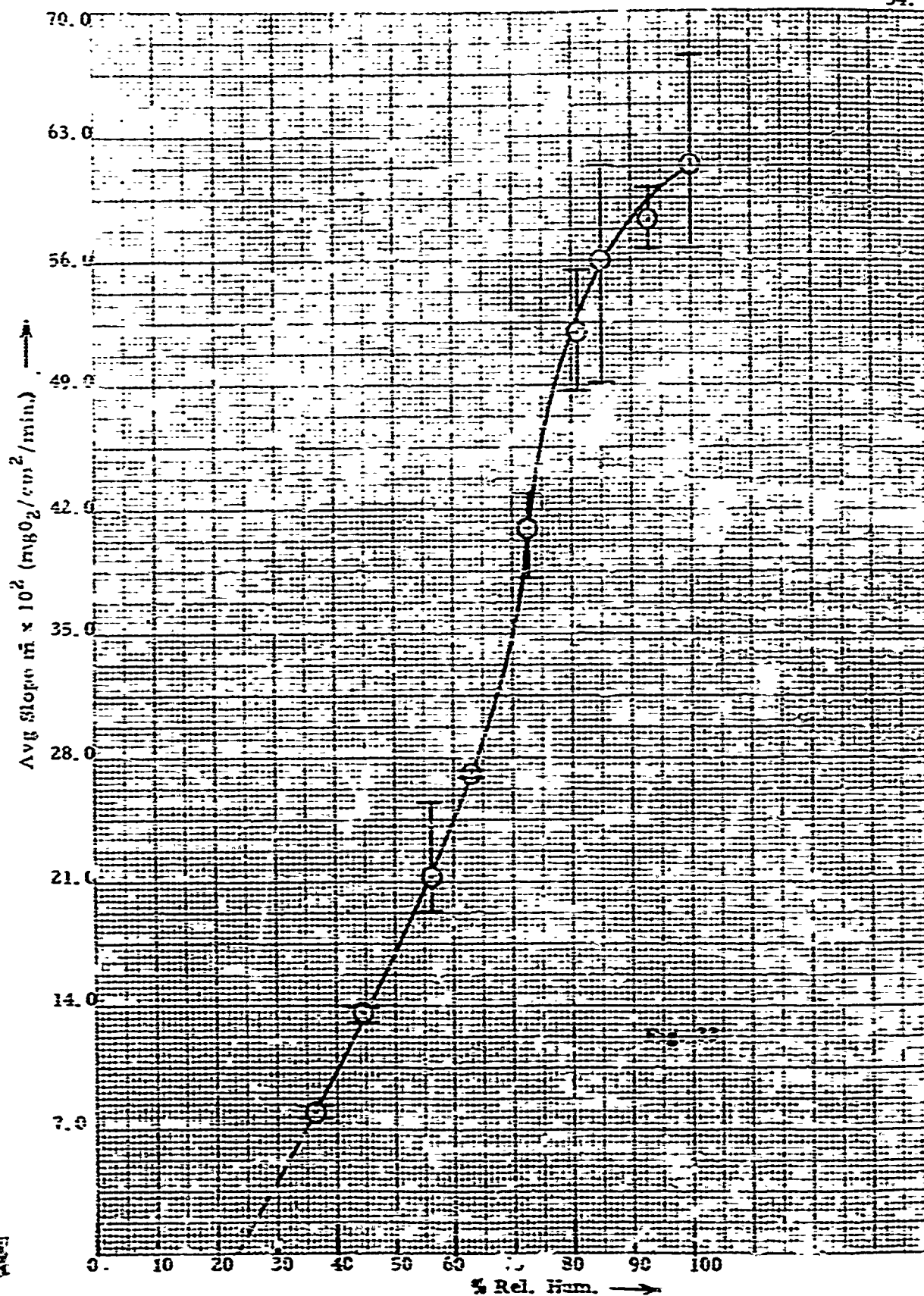


Fig. 28







EXPERIMENTS PLANNED FOR THE NEXT QUARTER

The objective of this work is to obtain as full an understanding as possible of the accelerated oxidation of aluminum in the presence of mercury. Research reported during the past two quarters has demonstrated the critical role played by water vapor. As a step towards understanding this critical role, it is planned to carry out the following two series of experiments.

(1) X-Ray diffraction studies will be made of the oxidation product formed at different relative humidities. It is known from past electron microscope, electron diffraction, and X-ray diffraction studies that the product formed at approximately 82% relative humidity has a small particle size and yields a diffraction pattern typical of amorphous materials. It is desired to determine if this product has a similar non-crystalline nature over the entire humidity range. A few diffraction studies will also be made of the oxidation product after aging at room temperature at low relative humidity.

(2) Chemical studies will be made in an effort to determine the amount of water contained in the oxidation product. Such studies will be very difficult because simple heat treatment will also possibly remove some mercury trapped in the product as it is formed. The exact procedure to be followed will be based on preliminary experiments in which the product will be heated at 110°C. for 18 hours and the weight loss will be determined. Gravimetric studies, in which the product will be desiccated at room temperature, will also be carried out.

Quantitative experiments on the rate of oxidation of aluminum in the presence of HgI_2 have been limited to pure aluminum. A few studies will be carried out during the next quarter on less pure aluminum and on aluminum alloys. The extent of this work will be determined by preliminary results.

It is well known that iron has a moderate rate of oxidation (or rusting) in highly humid atmospheres. During the next quarter preliminary and qualitative experiments on iron will be begun to determine the rate of rusting of iron in humid atmospheres in the presence of various metal salts.

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