

RATE OF HYDRATION OF BORON TRIOXIDE GLASS

RATE OF HYDRATION
OF BORON TRIOXIDE GLASS

By

WILLIAM RUSSELL WILLIS

Bachelor of Science

West Virginia Wesleyan College

Buckhannon, West Virginia


1948


Submitted to the Department of Chemistry
Oklahoma Agricultural and Mechanical College
In Partial Fulfillment of the Requirements
For the Degree of
MASTER OF SCIENCE

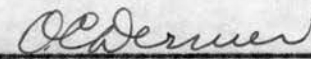
1950

OKLAHOMA
AGRICULTURAL & MECHANICAL COLLEGE
LIBRARY
APR 24 1950

APPROVED BY:


Chairman, Thesis Committee


Member of the Thesis Committee


Head of the Department


Dean of the Graduate School

250920

ACKNOWLEDGEMENT

The author desires to express his gratitude to Dr. Irving Johnson for suggesting this problem and for advising and directing the research.

STRATHMORE

STRATHMORE PARCHMENT

100% RAG U.S.A.

TABLE OF CONTENTS

| | Page |
|--|------|
| I. Introduction | 1 |
| II. Experimental | 2 |
| A. Preparation of boron trioxide glass | 2 |
| B. Instrumentation | 3 |
| III. Data | 4 |
| IV. Discussion of Data | 9 |
| A. Surface condition | 9 |
| B. Size factor | 10 |
| C. Pressure effect | 11 |
| D. Temperature effect. | 12 |
| V. Theoretical Treatment of Data. | 13 |
| VI. Summary. | 15 |
| Bibliography. | 17 |

RATHMORE PARCHMENT

100% RAG U.S.A.

I. INTRODUCTION

There have been two previous studies of the hydration of B_2O_3 glass reported in the literature. One of these, by Lorenz¹, was a semi-quantitative study in which the author made no attempt to analyze the data using the methods of chemical kinetics. The remaining study, reported by Myers², was a quantitative study. The author suspended samples of powdered boron oxide contained in glass buckets in a moist atmosphere. He then followed the hydration reaction by periodic weightings of the sample to determine the amount of water sorped. Myers concluded that the hydration was a stepwise reaction, proceeding first to metaboric acid in a unimolecular manner and then to the final orthoboric acid in an undetermined complex manner.

The reaction studied in this research is that of B_2O_3 glass with water vapor, a heterogeneous reaction of the general type



Heterogeneous reactions present the possibility of being kinetically controlled by the transport of the reactants, as well as by the rate of the chemical reaction. In this particular case the presence of a solid layer of product on the face of the reacting oxide leads to a diffusion process which may be the rate determining step in the reaction. The use of water vapor as a reactant introduces a sorption step which may also control the reaction rate. Thus the reaction rate may be controlled chemically, by adsorption, or by diffusion.

Considering the three processes mentioned above the adsorption seems unlikely as a rate controlling step. Mc Bain³ states that,

"True adsorption is nearly instantaneous. Any lag at present can be accounted for by the time required for the dissipation of the heat evolved, or the comparative inaccessibility of a portion of the surface of a porous adsorbing agent."

When the surface of the boron oxide has reacted giving a coating of acid, it would be expected that the sorption process would be adsorption. A calculation for an average sample has shown that the amount of water gained in one minute is sufficient to cover the geometric surface approximately 150 times.

A very common method of deciding between diffusion and chemically controlled reactions is by measuring the temperature coefficient of the reaction. Diffusion processes are relatively insensitive to temperature changes, while a chemical process would be expected to yield a temperature coefficient of 2-4 per 10° C. rise in temperature. In the present reaction a knowledge of the isosteres for the adsorption process would have to be known in order to utilize the method of temperature coefficients. This follows from the fact that the diffusion process should be studied with a constant concentration gradient. This condition does not exist in isobaric reactions.

II. EXPERIMENTAL

The general experimental technique was to allow prepared samples of B_2O_3 glass to hydrate under controlled conditions of temperature and water vapor pressure. The extent of hydration was determined by weighing the sample at intervals to ascertain the amount of water reacted.

A. Preparation of B_2O_3 Glass. Boron trioxide glass was prepared by fusing crystals of C. P. grade boric acid in a platinum crucible. The glass was fined by prolonged heating at 1000° C. in an electric furnace. Some samples were fined by heating with a Meeker burner operating at full blast. No difference could be detected in the results using the different methods. Samples were drawn from the glass in the form of circular cylinders. To accomplish this a simple mechanism was utilized, consisting of a sharpened brass rod mounted in a long glass tube by brass bushings. A line from the end of the rod ran over a pulley mounted in the ceiling and then to the drum

of a gear reduction box. This was connected to a cone drive stirring motor the speed of which was regulated by a "Variac" inserted in the circuit. In order to prevent rotation of the rod, it was allowed to travel along a wire which passed through off-center holes drilled in the bushings. This rod was lowered into the molten glass and then drawn out at a rate of approximately one cm./sec. It was found that by varying the temperature of the melt and speed of drawing, the diameter of the glass filament could be controlled to some extent. The maximum variation in diameter of any filament was about 3% and this was accepted only when the filament varied in a regular manner showing a constant taper. A comparison of density has been made for all filaments and shows a precision of 0.9%. After drawing, the filaments were cut into lengths of approximately 4 inches and then flashed in an incandescent nichrome coil to remove the slight surface hydration. One end of the filament was allowed to soften over the coil, forming a hook. The sample was then weighed immediately and suspended by the hook in the reaction vessel.

B. Instrumentation. Temperature was controlled by placing the reaction vessel in a constant temperature bath regulated to 0.02°C . The temperature was read by a mercury thermometer graduated to 0.05°C .

Pressure was controlled by using solutions of sulfuric acid of known density, as determined by a Westphal balance. The pressure was determined by data of water vapor pressure above these solutions as taken from the International Critical Tables⁴.

The reaction vessel consisted of a large test tube (65 mm. O.D.) equipped with a rubber stopper in which was mounted a glass rod with a hook bent on one end. The vessel was partially filled with either water or sulfuric acid and lined with asbestos paper. This was then placed in the water bath and allowed to come to equilibrium. Great care was taken to see that the filaments did not touch the side of the vessel at any time. One difficulty

encountered was that of condensation on the stopper which occurred when room temperature was such as to set up a gradient across the stopper. It was found that this could be eliminated most easily by suspending an infrared lamp over the bath at the proper height.

All weighings were performed on a chainomatic balance, type D.L.B. manufactured by William Ainsworth and Sons. It is believed that this balance gives results which are reproducible to at least ± 0.05 mg. for difference weighings.

III. DATA

During the course of this study rate of hydration determinations were made for over sixty samples of B_2O_3 . Of these sixty experiments only twenty yielded results which are considered intercomparable. The reasons for this will be considered in the next section. These twenty filaments were drawn from four separate batches of B_2O_3 glass. Values of the gain in weight have been tabulated as milligrams gained per unit length of the filament, i. e., mg. per inch.

The length of an experiment varied from six to eight hours. Experiments were conducted at temperatures of 25° , 30° and 35° C. and at water vapor pressures of 23.8, 31.7 and 42.2 mm. Hg. The data could be combined to give one isobaric (23.7 mm.) and one isothermal (35° C.) series.

The experimental data are presented in the following tables. Graphs of the data may be found in the discussion section which follows the tables.

Table I
Experimental Conditions

$T = 35^{\circ} \text{C.}$

$P_{\text{H}_2\text{O}} = 42.2 \text{ mm. Hg.}$

Filament #1
Batch A
 $d=0.0322(\text{in.})$

| t(min.) | w(mg./in.) |
|---------|------------|
| 0 | 0.000 |
| 13 | 0.467 |
| 22 | 0.657 |
| 31 | 0.832 |
| 41 | 0.940 |
| 53 | 1.13 |
| 65 | 1.29 |
| 76 | 1.45 |
| 87 | 1.60 |
| 105 | 1.84 |
| 124 | 2.04 |
| 159 | 2.44 |
| 206 | 3.00 |
| 290 | 4.01 |
| 349 | 4.78 |
| 409 | 5.57 |
| 461 | 6.25 |
| 503 | 6.87 |
| 539 | 7.33 |

Filament #2
Batch A
 $d=0.0439(\text{in.})$

| t(min.) | w(mg./in.) |
|---------|------------|
| 0 | 0.000 |
| 8 | 0.432 |
| 17 | 0.702 |
| 27 | 1.01 |
| 41 | 1.33 |
| 52 | 1.58 |
| 63 | 1.84 |
| 75 | 2.08 |
| 93 | 2.43 |
| 111 | 2.73 |
| 146 | 3.17 |
| 199 | 3.81 |
| 283 | 4.90 |
| 341 | 5.67 |
| 402 | 6.48 |
| 453 | 7.18 |
| 496 | 7.75 |
| 531 | 8.25 |

Filament #3
Batch A
 $d=0.0325(\text{in.})$

| t(min.) | w(mg./in.) |
|---------|------------|
| 0 | 0.000 |
| 13 | 0.365 |
| 23 | 0.484 |
| 32 | 0.571 |
| 41 | 0.640 |
| 89 | 1.02 |
| 155 | 1.61 |
| 216 | 2.06 |
| 276 | 2.72 |
| 326 | 3.23 |
| 368 | 3.63 |
| 390 | 3.84 |
| 449 | 4.42 |
| 512 | 5.02 |
| 552 | 5.43 |

Filament #4
Batch A
 $d=0.0300(\text{in.})$

| t(min.) | w(mg./in.) |
|---------|------------|
| 0 | 0.000 |
| 10 | 0.303 |
| 19 | 0.447 |
| 28 | 0.567 |
| 77 | 1.07 |
| 142 | 1.68 |
| 193 | 2.16 |
| 263 | 2.82 |
| 314 | 3.30 |
| 354 | 3.64 |
| 378 | 3.85 |
| 436 | 4.38 |
| 492 | 4.86 |
| 541 | 5.09 |

Filament #5
Batch A
 $d=0.0321(\text{in.})$

| t(min.) | w(mg./in.) |
|---------|------------|
| 0 | 0.000 |
| 12 | 0.363 |
| 22 | 0.493 |
| 33 | 0.611 |
| 50 | 0.759 |
| 80 | 0.994 |
| 148 | 1.50 |
| 250 | 2.39 |
| 291 | 2.78 |
| 323 | 3.05 |
| 357 | 3.36 |
| 398 | 3.65 |
| 435 | 3.96 |
| 486 | 4.45 |

Filament #6
Batch A
 $d=0.0229(\text{in.})$

| t(min.) | w(mg./in.) |
|---------|------------|
| 0 | 0.000 |
| 11 | 0.272 |
| 21 | 0.404 |
| 39 | 0.573 |
| 69 | 0.799 |
| 137 | 1.32 |
| 237 | 2.20 |
| 280 | 2.56 |
| 311 | 2.80 |
| 346 | 3.05 |
| 384 | 3.38 |
| 423 | 3.91 |
| 475 | 4.13 |

Table II
 Experimental Conditions
 $T = 35^{\circ} \text{C.}$
 $P_{\text{H}_2\text{O}} = 31.7 \text{ mm. Hg.}$

| Filament #7 Batch B $d=0.0294(\text{in.})$ | | Filament #8 Batch B $d=0.0295(\text{in.})$ | |
|--|---------------------|--|---------------------|
| $t(\text{min.})$ | $w(\text{mg./in.})$ | $t(\text{min.})$ | $w(\text{mg./in.})$ |
| 0 | 0.000 | 0 | 0.000 |
| 14 | 0.204 | 14 | 0.230 |
| 27 | 0.269 | 32 | 0.260 |
| 39 | 0.292 | 55 | 0.320 |
| 71 | 0.354 | 85 | 0.380 |
| 97 | 0.394 | 160 | 0.456 |
| 167 | 0.466 | 293 | 0.600 |
| 300 | 0.603 | 434 | 0.738 |
| 442 | 0.713 | | |

Table III
 Experimental Conditions
 $T = 35^{\circ} \text{C.}$
 $P_{\text{H}_2\text{O}} = 23.8 \text{ mm. Hg.}$

| Filament #9 Batch B $d=0.0465(\text{in.})$ | | Filament #10 Batch B $d=0.0313(\text{in.})$ | |
|--|---------------------|---|---------------------|
| $t(\text{min.})$ | $w(\text{mg./in.})$ | $t(\text{min.})$ | $w(\text{mg./in.})$ |
| 0 | 0.000 | 0 | 0.000 |
| 10 | 0.134 | 11 | 0.114 |
| 20 | 0.230 | 20 | 0.179 |
| 39 | 0.344 | 37 | 0.256 |
| 70 | 0.385 | 81 | 0.338 |
| 125 | 0.418 | 125 | 0.363 |
| 396 | 0.446 | 184 | 0.390 |
| | | 337 | 0.438 |
| | | 446 | 0.460 |
| | | 591 | 0.477 |

| Filament #11 Batch B $d=0.0200(\text{in.})$ | | Filament #12 Batch B $d=0.0202(\text{in.})$ | |
|---|---------------------|---|---------------------|
| $t(\text{min.})$ | $w(\text{mg./in.})$ | $t(\text{min.})$ | $w(\text{mg./in.})$ |
| 0 | 0.000 | 0 | 0.000 |
| 11 | 0.078 | 12 | 0.050 |
| 23 | 0.115 | 24 | 0.077 |
| 35 | 0.127 | 35 | 0.082 |
| 48 | 0.152 | 157 | 0.169 |
| 163 | 0.244 | 247 | 0.241 |
| 254 | 0.328 | 364 | 0.274 |
| 370 | 0.407 | 555 | 0.329 |
| 562 | 0.505 | | |

Table IV
 Experimental Conditions
 $T = 30^{\circ} \text{C.}$
 $P_{\text{H}_2\text{O}} = 23.7 \text{ mm. Hg.}$

| Filament #13 Batch C $d=0.0254(\text{in.})$ | | Filament #14 Batch C $d=0.0230(\text{in.})$ | |
|---|---------------------|---|---------------------|
| $t(\text{min.})$ | $w(\text{mg./in.})$ | $t(\text{min.})$ | $w(\text{mg./in.})$ |
| 0 | 0.000 | 0 | 0.000 |
| 12 | 0.183 | 12 | 0.210 |
| 27 | 0.261 | 24 | 0.230 |
| 41 | 0.286 | 37 | 0.293 |
| 60 | 0.319 | 64 | 0.340 |
| 78 | 0.338 | 87 | 0.380 |
| 102 | 0.376 | 134 | 0.436 |
| 153 | 0.439 | 214 | 0.517 |
| 206 | 0.477 | 264 | 0.570 |
| 247 | 0.512 | 307 | 0.578 |
| 369 | 0.590 | 374 | 0.622 |
| 511 | 0.647 | 421 | 0.650 |

| Filament #15 Batch C $d=0.0221(\text{in.})$ | | Filament #16 Batch C $d=0.0266(\text{in.})$ | |
|---|---------------------|---|---------------------|
| $t(\text{min.})$ | $w(\text{mg./in.})$ | $t(\text{min.})$ | $w(\text{mg./in.})$ |
| 0 | 0.000 | 0 | 0.000 |
| 12 | 0.187 | 15 | 0.182 |
| 26 | 0.225 | 30 | 0.212 |
| 52 | 0.260 | 49 | 0.227 |
| 81 | 0.302 | 66 | 0.290 |
| 127 | 0.332 | 105 | 0.390 |
| 207 | 0.398 | 130 | 0.437 |
| 257 | 0.452 | 206 | 0.560 |
| 302 | 0.462 | 273 | 0.603 |
| 367 | 0.496 | 335 | 0.645 |
| 415 | 0.515 | 434 | 0.718 |

Table V
 Experimental Conditions
 $T = 25^{\circ} \text{C.}$
 $P_{\text{H}_2\text{O}} = 23.7 \text{ mm. Hg.}$

| Filament #17 Batch C $d=0.0221(\text{in.})$ | | Filament #18 Batch C $d=0.0326(\text{in.})$ | |
|---|------------|---|------------|
| t(min.) | w(mg./in.) | t(min.) | w(mg./in.) |
| 0 | 0.000 | 0 | 0.000 |
| 11 | 0.280 | 10 | 0.351 |
| 22 | 0.453 | 23 | 0.577 |
| 34 | 0.567 | 35 | 0.725 |
| 65 | 0.738 | 70 | 0.892 |
| 94 | 0.860 | 93 | 1.05 |
| 134 | 1.05 | 123 | 1.23 |
| 218 | 1.53 | 164 | 1.53 |
| 294 | 1.97 | 214 | 1.84 |
| 355 | 2.27 | 252 | 2.07 |
| 438 | 2.71 | 316 | 2.49 |
| | | 370 | 2.88 |
| | | 443 | 3.37 |
| | | 499 | 3.77 |

| Filament #19 Batch D $d=0.0316(\text{in.})$ | | Filament #20 Batch D $d=0.0229(\text{in.})$ | |
|---|------------|---|------------|
| t(min.) | w(mg./in.) | t(min.) | w(mg./in.) |
| 0 | 0.000 | 0 | 0.000 |
| 12 | 0.317 | 10 | 0.299 |
| 22 | 0.473 | 21 | 0.449 |
| 32 | 0.555 | 32 | 0.542 |
| 45 | 0.685 | 37 | 0.574 |
| 65 | 0.763 | 59 | 0.679 |
| 86 | 1.00 | 79 | 0.795 |
| 132 | 1.27 | 126 | 1.05 |
| 180 | 1.54 | 173 | 1.32 |
| 220 | 1.70 | 213 | 1.54 |
| 257 | 1.95 | 252 | 1.82 |
| 304 | 2.22 | 301 | 2.02 |
| 365 | 2.58 | 360 | 2.36 |
| 432 | 3.03 | 424 | 2.73 |

IV. DISCUSSION OF DATA

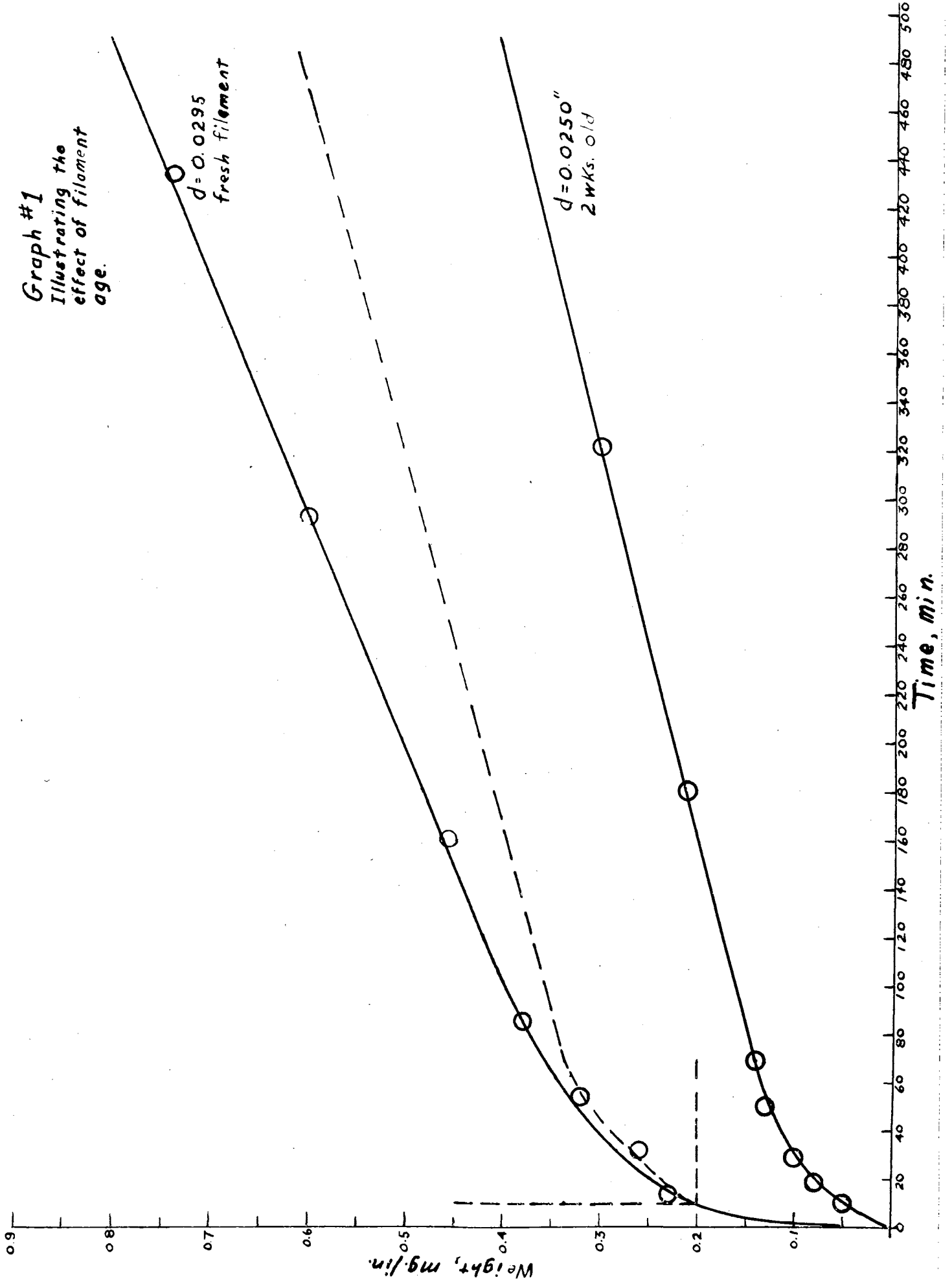
The hydration of B_2O_3 glass is a slow reaction, the total amount of water gained in eight hours varying from 0.5 to 8 mg./in. depending upon the experimental conditions. This is approximately 2 to 20% of the total weight of the B_2O_3 filament. In general, a plot of the weight gained versus time will show two distinguishable portions, (1) a very rapid initial growth which merges smoothly into (2) a practically linear growth. The initial rapid growth is not a purely exponential function as is shown by plots of the logarithm of the weight gain versus time. The linear growth rate extends for as much as twenty-four hours and does not exhibit a change in slope until two or three days have elapsed.

It is assumed that four main factors control the rate of hydration. These are, (1) the condition of the surface prior to the hydration, (2) the size of the filament, (3) the partial pressure of the water vapor in the atmosphere, and (4) the temperature.

A. Surface Condition. It is not claimed that the differences in initial surface conditions have been completely eliminated nor that a method of producing a completely reproducible surface has been developed. It is believed that the method of preparation finally adapted, while it does not completely eliminate surface effects, does reduce their variations sufficiently to allow a semi-quantitative study of the three other factors.

One very large source of variation would result from hydration of the filament prior to the actual experiment. In the original technique, it was believed that this condition could be eliminated by the flashing operation. It was found, however, that when filaments were kept for long periods in a P_2O_5 desiccator the hydration penetrated the filament in such a way as not to allow a complete dehydration by flashing. This condition can be seen if

Graph #1
Illustrating the
effect of filament
age.



results from filaments of different ages are compared (Graph 1). To eliminate this effect filaments were drawn and the measurement of the rate of hydration started within an hour. A study of figure 1 shows that the effect of prior hydration is to suppress the rapid initial growth. It is in effect a shifting of the axes of the curve.

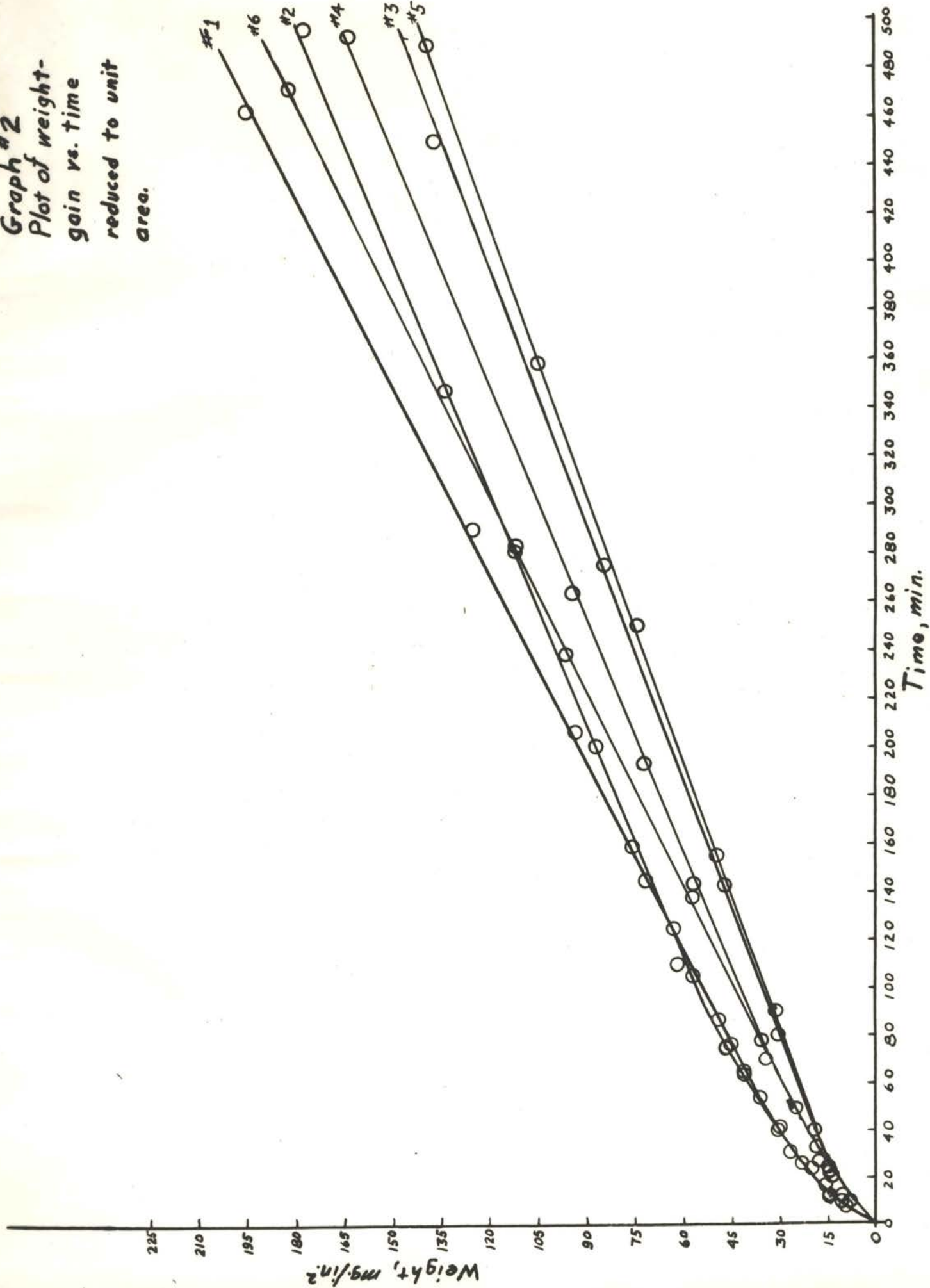
Another source of variation is that of uneven dehydration of the glass. This would lead to a smaller weight gain which should be distributed more evenly throughout the hydration than the effect mentioned above. As was pointed out in the experimental section, two methods of fining the glass were employed, and no differences could be distinguished in the final product. For example, in Table V the data are shown for filaments hydrated at the same experimental conditions and drawn from two batches. Batch C was fined in an electric furnace, Batch D by strong heating over a Meeker burner.

A source of variation which is difficult to assess is that of surface strains. The filaments cooled rapidly since heat was removed from the melt before the operation began and the filaments were of small diameters. This would be expected to lead to some mechanical strain. Filaments were sometimes seen to "shatter" so that they were split into long lengths extending halfway up their length. It was noticed that hydration was very nearly complete in these portions.

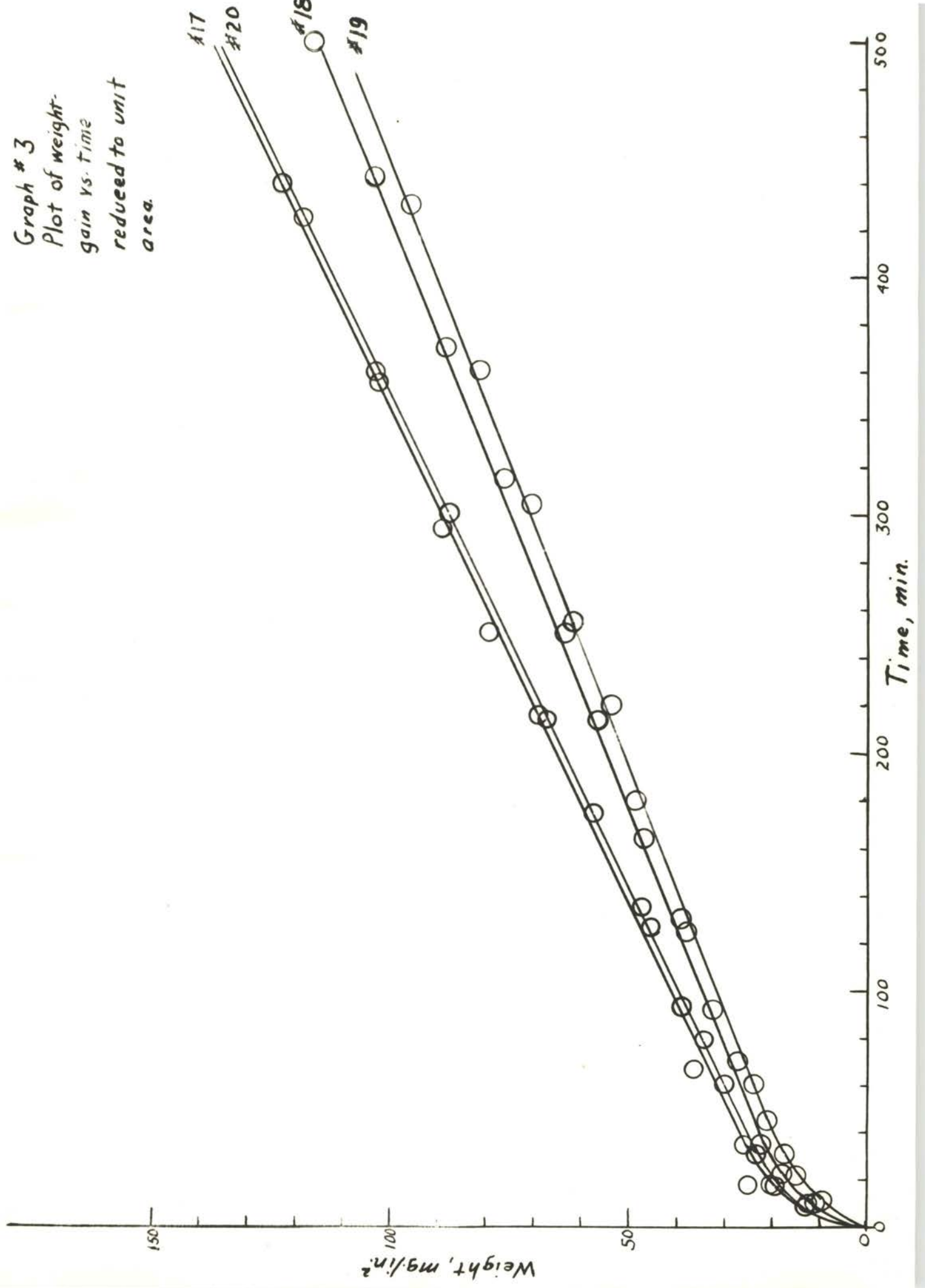
The problem of excessive hydration at the ends was also encountered. This was most likely due to marring of the surface during the cutting operations. These sources of variation led to the discarding of more than half of the filaments studied (Page 4).

B. Size Factor. At first glance the data seem to give very scattered results with reference to the filament size. A great many methods of analysis have been tried with very little success. The most obvious method of analysis

Graph #2
 Plot of weight-
 gain vs. time
 reduced to unit
 area.



Graph # 3
Plot of weight-
gain vs. time
reduced to unit
area.



is to reduce to parameters of the curve of weight gain versus time by using a function of the diameter. Such functions as d , $d^{\frac{3}{2}}$, d^2 have been tried but the results did not seem consistent.

If this reaction is considered as a diffusion phenomena, then it may be said that as a rough approximation, the process may be considered as a one dimensional diffusion problem. If this were true, it would be expected that the size factor would involve the area of the filament.

The final method used to study the data as a function of size was to replot the data as weight gain per unit area versus time. This has been done for groups I and V (Graphs 2 and 3).

As may be seen there the weight gain per unit area shows a slower rate of reaction as the filament becomes larger. The only exceptions are filaments 1 and 2. These filaments were drawn and run at the same time and show the above relation between them, so that it seems logical to assume that this difference is a surface variation.

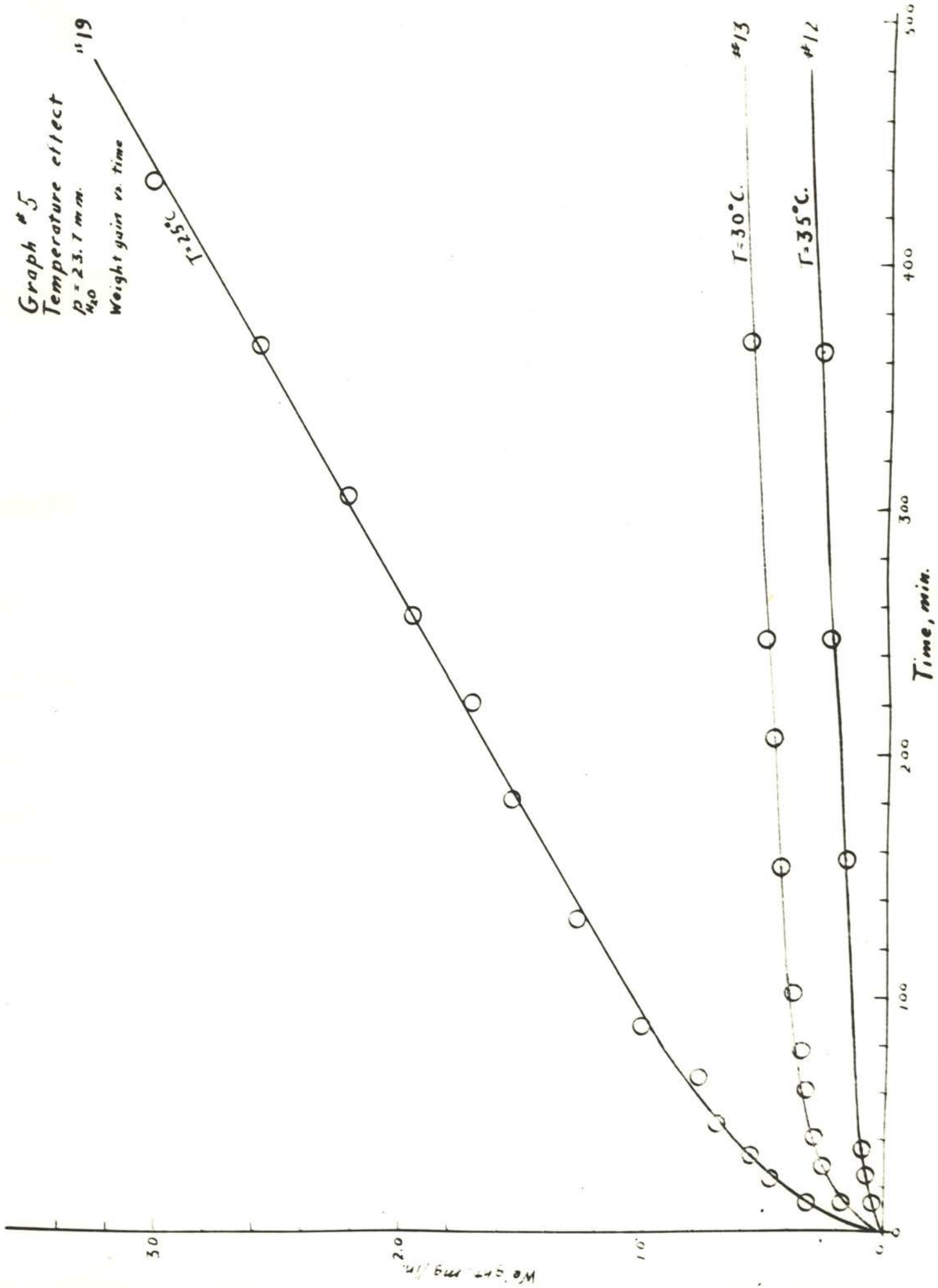
6. Pressure Effect. The effect of pressure is large, showing generally an increase in weight gained with an increase in pressure. Here again the largest change is reflected in the slope of the final portion and in the rate at which the initial slope falls off. In order to relate the parameters of the weight gain versus time curve reference must be made to the discussion of rate controlling steps of heterogeneous reactions in the introduction to this study. It was pointed out that even if the adsorption step did not control the rate of the reaction it would still have an effect in that the amount of H_2O adsorbed would determine the concentration gradient and thus the diffusion rate of H_2O through the layer of product on the surface of the filaments. It would be in this manner that pressure would be expected to have an effect.

Graph #5
Temperature effect

$p = 23.7 \text{ mm. H}_2\text{O}$

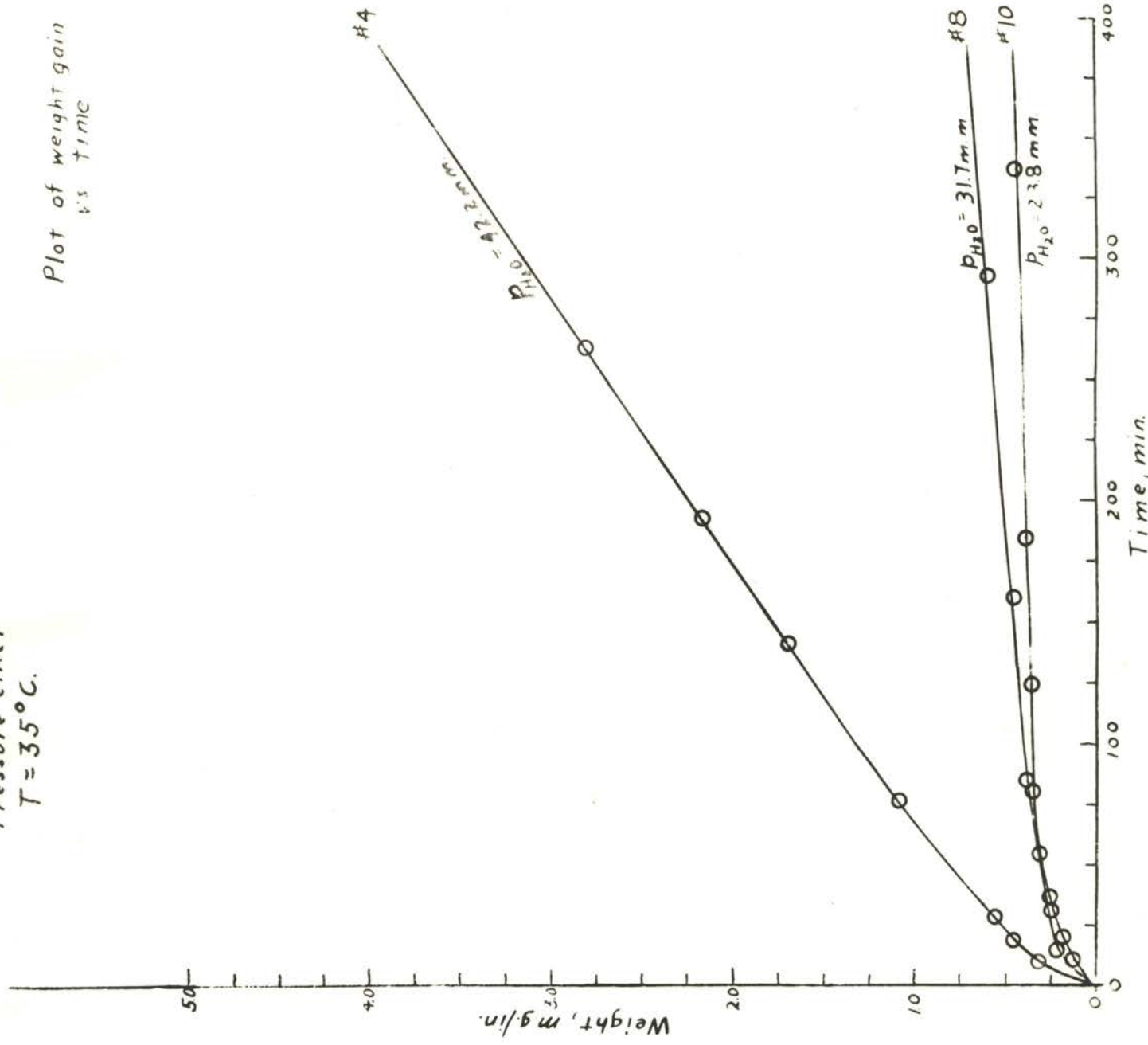
Weight gain vs. time

#19

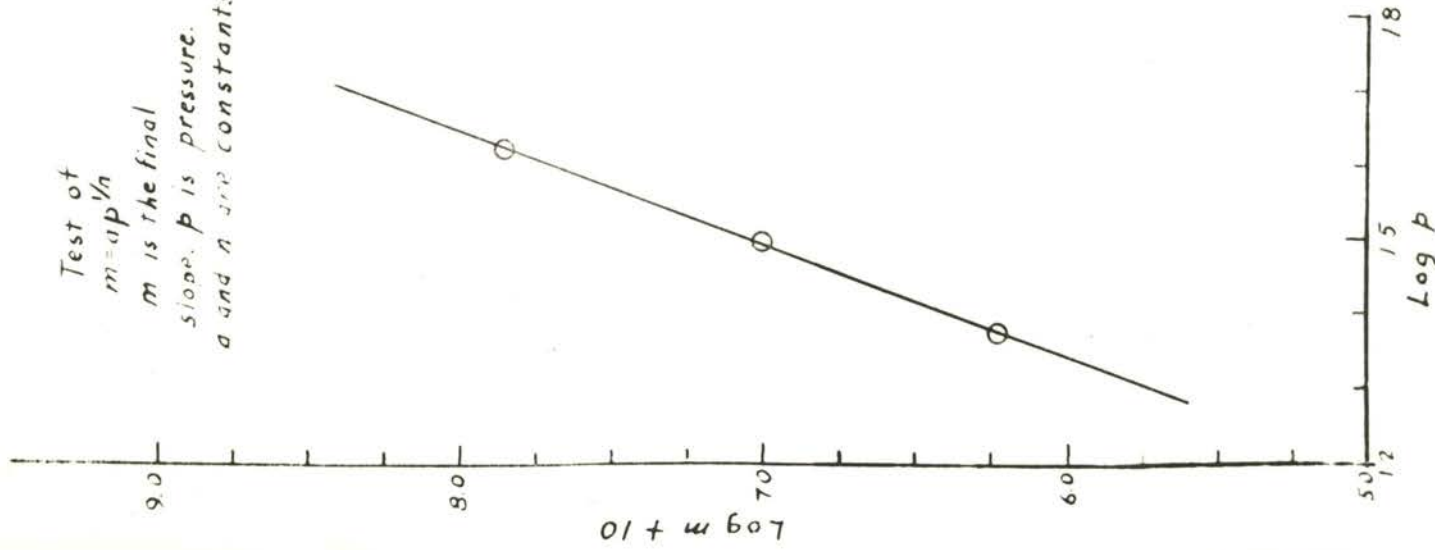


Graph 7
 Pressure effect
 $T = 35^{\circ}\text{C}$.

Plot of weight gain
 vs time



Test of
 $m = ap^{1/n}$
 m is the final
 slope, p is pressure.
 a and n are constants.



Many theories of adsorption have been developed with the best known probably being those of Langmuir⁵ and Brunauer, Emmet and Teller⁶. In all of these, however, much more data would be required to attempt an explanation of the results found. Also, the data are not believed to be accurate enough to warrant attempting a detailed analysis. As a rough approximation, it was considered that the Freundlich isotherm would define the amount of H₂O adsorbed. If it is assumed that this amount is reflected directly in the slope (k) of the final line in the weight versus time curves, then

$$k = ap^{1/n} \quad 1.$$

where a and n are constants and p is the pressure.

The results of these calculations, shown in Graph 4 indicate that the pressure effect is roughly as indicated by this equation.

D. Temperature Effect. Considering the above reasoning for the effect of the adsorption step on the reaction rate, it would be expected that temperature would also affect the weight gained by affecting the amount of water adsorbed. As was pointed out in the introduction, this effect would be expected to obscure the effect of an increase in the diffusion rate or the rate of the activated process, since it would give a negative temperature coefficient⁷. Generally, adsorption shows a large negative temperature coefficient. Taking again the final slope as an indication, a value of approximately -18 is found for the range 25° to 35° C.

As in the effect of pressure it is found that the initial slope is relatively little affected while the rate at which this slope falls off is larger as the temperature is increased.

V. THEORETICAL TREATMENT OF DATA

A primary fact, upon which any theory of the hydration of B_2O_3 glass must rest, is that the experimental data show two distinct types of growth. The second of these is clearly linear, or closely approximate to linear, in the region studied. The first portion of the growth has roughly the appearance of an exponential growth and many attempts were made to fit an equation to this curve. It was found that an equation of the form

$$w = b(1 - e^{-kt}) \quad 2.$$

would fit this first portion if b were properly chosen. Assumed values of b of the proper magnitude were found to be the value of w at points a little below the value at which the straight line merges into the initial curve.

Guided by the above facts, and by the results of Myers², it was assumed that the reaction of B_2O_3 and H_2O is a stepwise process, going first to the metaboric acid and then to orthoboric acid. Then the initial growth curve is associated with the formation of HBO_2 , while the final period is principally due to the formation of H_3BO_3 .

Since penetration of water into the B_2O_3 filaments is never very large in the experiments reported here, it was assumed that the fast reaction to HBO_2 could not be an activation controlled reaction, but rather diffusion controlled. This point would not be very important in deriving an equation however, since the diffusion equation can be reduced to the form of a first order reaction equation by logical assumptions. As the interface between HBO_2 and B_2O_3 moves into the filament it would be expected that the concentration gradient of H_2O would decrease thus slowing down the conversion of B_2O_3 to HBO_2 . This process is further aided by the slow reaction of HBO_2 to H_3BO_3 in the region behind the interface. Such a mechanism continues until the movement of the interface is extremely slow.

The second step of the conversion of B_2O_3 to H_3BO_3 must be a slow reaction. It may be either an activated or diffusion controlled reaction. Due to the difficulties in obtaining a constant concentration gradient through the layer of HBO_2 (Page 11) it is impossible to decide this point. It does, however, depend upon the concentration of HBO_2 . For reactions of this type, chemical kinetics demands that

$$C_{H_3BO_3} = a \left[\frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1} \right] + a \quad 3.$$

where k_1 and k_2 are the rate constants for the first and second steps respectively and a is a constant.

If k_1 is very great compared to k_2 then

$$C_{H_3BO_3} = a(-e^{-k_2 t} + 1) = a(1 - e^{-k_2 t}) \quad 4.$$

This may be approximated by

$$C_{H_3BO_3} = a(-1 + k_2 t - \dots + 1) = ak_2 t \quad 5.$$

Considering the above facts, we may write

$$w = b(1 - e^{-k_1 t}) + a(1 - e^{-k_2 t}) \quad 6.$$

This equation will reduce to three forms depending on the value of t .

These are:

I. $k_1 \gg k_2$

t is small

$$1 - e^{-k_2 t} = 0 \quad 7.$$

and

$$w = b(1 - e^{-k_1 t}) \quad 8.$$

II. Moderate values of t

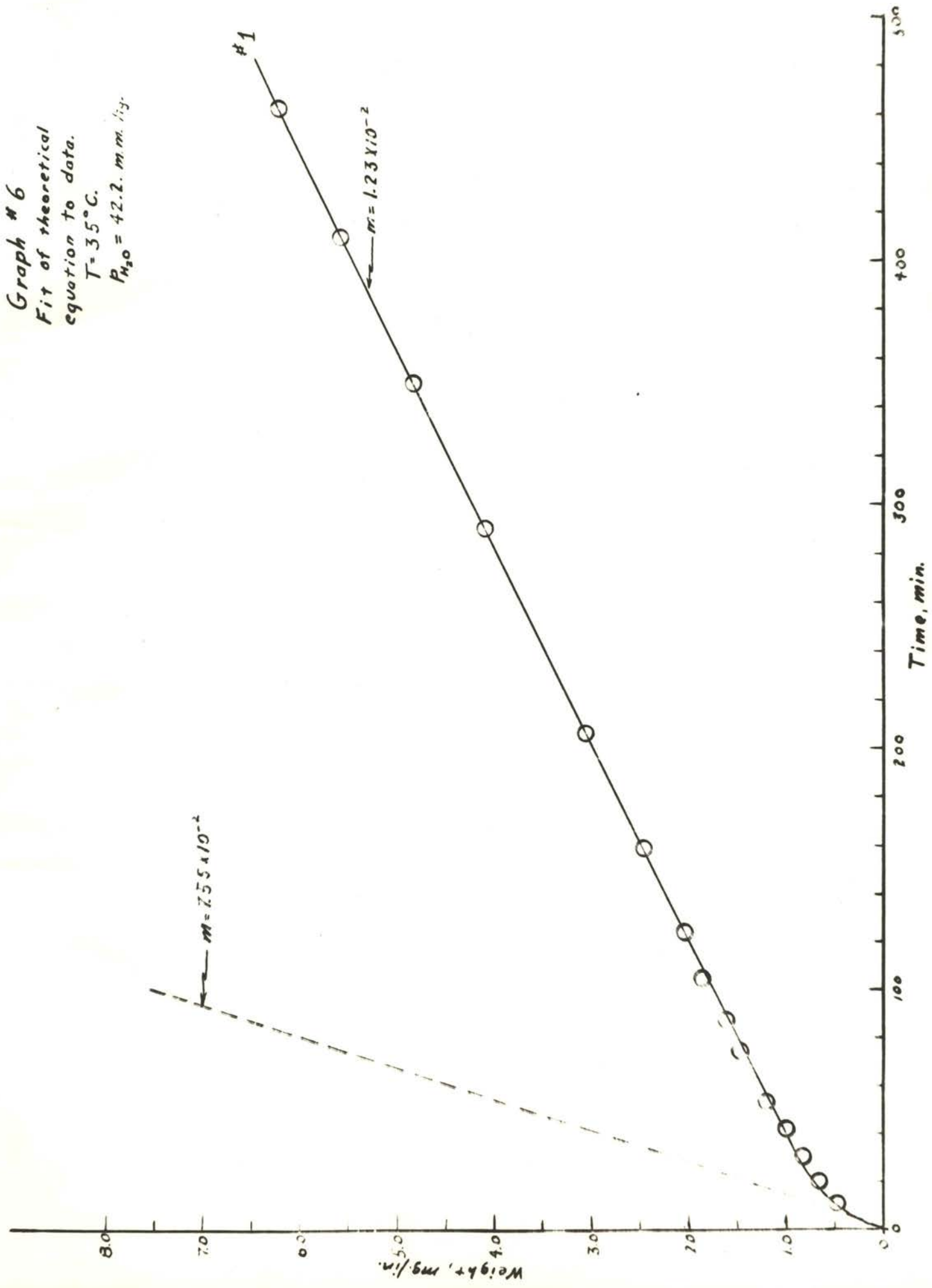
$$w = b(1 - e^{-k_1 t}) + ak_2 t \quad 9.$$

Graph # 6

Fit of theoretical equation to data.

$T = 35^{\circ}\text{C.}$

$P_{\text{H}_2\text{O}} = 42.2 \text{ m.m. Hg.}$



III. When t is very large

$$w = a(1 - e^{-k_2 t}) \quad 10.$$

All of the data in this study fit into periods I and II.

Graph 6 shows the fit of an equation of this form to experimental data.

In order to evaluate the constants involved, the equation (6) was differentiated with respect to time. Thus:

$$\frac{dw}{dt} = bk_1 e^{-k_1 t} + ak_2 e^{-k_2 t} \quad 11.$$

When $t = 0$

$$\left(\frac{dw}{dt}\right)_{t=0} = bk_1 + ak_2 \approx bk_1 \quad 12.$$

giving a value of b and k_1 in terms of the initial slope. If the equation is to fit the experimental data, then

$$(1 - e^{-k_1 t}) = 1 \quad 13.$$

when t is large. From this it is found that b is the intercept and ak_2 is the slope of the straight line portion. From equations 12 and 13

$$k_1 = \frac{\left(\frac{dw}{dt}\right)_{t=0}}{b} \quad 14.$$

VI. SUMMARY

Measurements of the rate of hydration of B_2O_3 glass were made at temperatures of 35° , 30° and 25° C. and water vapor pressures of 42.2, 31.7 and 23.7 mm. Hg. The dependence of the rate upon surface condition, size of filament, pressure and temperature were studied.

It was found that the reaction proceeds in a stepwise manner as reported by Myers, with both steps being first order kinetically. The surface factor was undetermined but was partially eliminated. The main characteristic was a dependence upon age.

The size of the filament gave a small effect depending mainly upon the filament area. It was found that the smaller the filament the greater the weight gain per unit area.

Pressure affected the rate of hydration by determining the amount of water adsorbed on the surface and thus the concentration gradient of water within the filament. The slope of the weight gain versus time curve can be related to the pressure by

$$n = ap^{(1/n)}$$

Temperature affected the rate of reaction by affecting the amount adsorbed and possibly by affecting an activation process. A negative temperature coefficient was found.

The results may be described by the equation:

$$w = b(1 - e^{-k_1 t}) + ak_2 t.$$

which equation is consistent with the assumption that (1) there is a rapid reaction to H_2O_2 , controlled by the diffusion of water into the filament, followed by (2) a slow reaction to H_3BO_3 which is possibly activation controlled.

BIBLIOGRAPHY

- (1) Lorenz, R., Maebig's Ann. 247, 250 (1888)
- (2) Meyers, J. E., J. Chem. Soc. 111, 172 (1917)
- (3) McBain, J. W., Trans. Far. Soc. 14, 202 (1919)
- (4) Washburn, E. W., Ed. International Critical Tables. New York: McGraw-Hill Book Company, 1928. Vol. III, P. 303.
- (5) Langmuir, I., J. Am. Chem. Soc. 40, 1361 (1918)
- (6) Brunauer, S., Emmett, P. H., and Teller, E., J. Am. Chem. Soc. 60, 309 (1938)
- (7) Brunauer, S. The Adsorption of Gases and Vapors. Princeton: Princeton University Press, 1945. Vol. I, P. 21.

Also

Barrer, R. M. Diffusion In and Through Solids. Cambridge: The Cambridge University Press, 1941.

STRATHMORE PARCHMENT

100% RAG U.S.A.

VITA

William Russell Willis was born in Moundsville, West Virginia on February 14, 1926. He was educated in the public schools there and graduated from Moundsville High School in May, 1943. In July of that year he entered Bethany College, Bethany, West Virginia as an Apprentice Seaman in the Navy V-12 program. While at Bethany College he became a member of Alpha Psi Omega.

In March, 1946 he was designated as a naval aviator and commissioned as ensign in the United States Naval Reserve. In April, 1946 he was ordered to inactive peace-time duty.

On June 14, 1946 he married Jean Louise Evans of Moundsville, West Virginia.

After leaving the service he enrolled as a student at West Virginia Wesleyan College, Buckhannon, West Virginia. He was awarded the degree of Bachelor of Science in August, 1948.

In September, 1948 he came to Oklahoma Agricultural and Mechanical College where he was employed as a graduate fellow in the Department of Chemistry.

PARCHMENT

U.S.A.

Typed by:

Mrs. William R. Willis

STRATHMORE PARCHMENT

100% RAG U.S.A.