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SUBLIMATION OF TCl_4 [UCl_4].

Summary of Experimental Studies on Variables Which Enter into Sublimation

By
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DISCLAIMER

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Introduction

It has been the purpose of these studies to determine the relationship between the variables which enter into sublimation, and to obtain numerical data which would make it possible to predict the performance of TCl_4 charges under various conditions.

Previous reports* have dealt with the effect of water vapor, thickness of layer of charge material, particle size, and surface impurities on the rate of sublimation. Additional information has been gathered on the last three of these variables, and is reported in sections which follow. New results have been obtained on various geometric factors which bear directly on the design of charge bottles and on the theory of sublimation.

A section is devoted to statements of the types of apparatus employed and to facts about their geometries, and to the conditions existing in the experiments.

PART I

EXPERIMENTAL ARRANGEMENTS

A 12-inch long, 3-inch inside diameter furnace was used for

*Chem S Reports 213, 214, 215 and 228.

arrangements A to D. A similar 18-inch unit was used in arrangements E to H. The two halves of each furnace were practically identical in resistance. It was found after some time that the temperature of the two halves differed by a few degrees and that near the spaces between the halves there was a considerably cooler region. These conditions were not tolerable for much of the later work, and were rectified by a $\frac{1}{8}$-inch thick brass cylinder, 10 inches long, placed symmetrically. Losses of heat from the ends were minimized by packing with asbestos ribbon.

The arrangements were as follows:

A. Four small samples of about 10 cm^2. total area arranged symmetrically in vertical tube of 33 cm^2. cross section. Temperature measured in axial thermocouple.

B. Four small samples as in A, but set in copper heat-distributing block, the block being inside the evacuated space.

C. Arranged as in A, but with each sample set on a spindle which contained its own thermocouple.

D. (AD, BD, CD) Same as in A, B, C, but with $\frac{1}{8}$ inch brass shell distributing heat uniformly about outside of glass furnace tube, with thermocouple in a slot on the inside of the brass jacket.

E. Twelve samples set in 2-$\frac{1}{2}$" diameter truncated nickel-plated copper cylinder, 6" long, with axial hole for thermocouple tube. The furnace tube had a cross section of 33 cm^2. The minimum cross section in the evacuated hot region was 7 cm^2. Maximum area of solid which could be exposed was 31 cm^2. Brass shell as in D.

F. Same as E, but with light-weight hollow boat for rapid heating and cooling.

G. Furnace tube with sample bottles of 2" outside diameter laid on their side. Cross section for exit of gases was 33 cm^2. if the opening of the bottle faced the evacuated side, but was 12.5 cm^2. if the gas had to pass over the bottle.

H. Same as E, F, G with a radiation baffle placed in the hot region. The area for passage of the gas through the baffle was 16 cm^2.

The arrangement of the vacuum system for E, F and G is the same as was described in Chem S 228.

PART II

SUMMARY OF EXPERIMENTS: TEMPERATURES, PRESSURES, etc.

Table I provides general information on each experiment. The data are given here without further reference in the report.

The calculated average space pressure value was determined from the quantity of gas which had to escape through the minimum cross sectional area during the time of the experiment, and is probably correct to within 25%. The experimental temperature is the average value for 90% of the sublimation taking place during the experiment. The time of the experiment is listed for the temperature of interpretation. Temperature measurements were correct within 1°C, and all adjustments for proper integration of times and temperatures to within 2%.

The values given under Total Exposed Area which are marked with an asterisk (*) contain some glass covered samples which are included as half exposed, which is somewhat in excess of the actual condition.

PART III

MATERIAL TRANSFER WITHIN SOLID AGGREGATES

The amount of material transfer is determined by the same factors which govern the flow of gas through a granular mass, the density gradients of the gas in the spaces between the solid particles being set up by temperature inequalities. Due to evaporation and recondensation the transfer of material from one place to another is essentially one of transferring heat, and, under certain conditions of temperature, particle size, pressure, and time, the process results in the sintering together of the material. Such sintering has been observed a great many times.

We have observed sintering under very nearly isothermal conditions in fairly short times at 450°C. In experiment 16, each of six bottles varying in thickness of material from 4 mm to 24 mm, and 17 mm diameter, yielded slightly conical cakes of sintered material, 13-15 mm wide and 2-3 mm thick, the particle size being 32-60 mesh. Under identical conditions, six bottles containing 6-10 mesh material showed no sintering. The fact that the sintering exists under nearly isothermal

Table I

Exp. No.	Apparatus Type	No. of Samples	Total Charge Area cm^2.	Total Exposed Area cm^2	Minimum Area for Escape of gas	Calc. Ave. Space Pressure mm Hg	Vacuum Maintained mm Hg	Exp. Temperature °C	Temp. of Interpretation °C	HCl evolved gm.	Type of Study See Table II	Length of Experiment hours
16	E	12	26	26	7	$8 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	446	450	1.06	2a,b,3a	2.1
17	E	12	26	26	7	$2.4 \cdot 10^{-3}$	$3 \cdot 10^{-4}$	408	410	0.64	2a,6a	1.58
18	E	12	26	26	7	$3.6 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	427	430	0.108	2a,6a	2.74
19	E	12	26	26	7	$3.2 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	427	430	0.084	2a,6a	2.64
20	E	12	26	26	7	$2.8 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	432	430	0.090	2a,6a	2.80
21	E	12	26	26	7	$2.1 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	426	430	0.048	2a,6a	2.74
22	E	12	26	26	7	$2.4 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	426	430	-	2a,6a	2.95
23	E	12	26	20.5*	7	$3.3 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	429	430	.135	3a,6c	2.82
24	E	12	26	20.5*	7	$1.9 \cdot 10^{-3}$	$5 \cdot 10^{-4}$	427	430	.014	3a,6a,c	2.69
25	E	12	26	17.6*	7	$0.7 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	426	430	.159	3a,6a,c	3.3
26	E	12	26	17.6	7	$0.7 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	426	430	$.003_5$	3a,6a,c,4a	3.42
27	E	12	26	25*	7	$1.6 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	412	410	1.00	2ab,3a,4a	3.87
28	E	12	26	25*	7	$1.1 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	411	410	.076	2ab,3a,6a,4a	4.06
29	E	12	26	13*	7	$.37 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	406	410	.053	6c,7a	3.66
30	HF	6	13	6-½*	7	$9 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	502-½	510	negligible	4a,6c,7a	1.25
31	HE	12	26	13*	7	$2.1 \cdot 10^{-4}$	$3 \cdot 10^{-5}$	408	410	.014	6a,c,7a	3.72
32	HE	12	26	13*	7	$2.4 \cdot 10^{-4}$	$5 \cdot 10^{-5}$	409.5	410	negligible	6a,c,7a	4.61
33	HE	12	26	12.5*	7	$7.2 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	414	410	.054	6a,c,d,8a	4.11
34	HE	10	23	19	7	$5 \cdot 10^{-3}$	$5 \cdot 10^{-5}$	429	430	.041	3a,7b	3.16
35	HE	9	22	2.5	7	$1.6 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	431	430	.257	8a,9a	2.97
36	HE	6	15	.05	7	$(8 \cdot 10^{-3})$	$1 \cdot 10^{-4}$	430	430	$.005_4$	6d,8a,9a	5.78
37	HE	6	15	.05	7	$1.3 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	429	430	negligible	6d,8a,9a	5.89
38	G	4	69	4.7	12.5-33	$5.7 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	431.5	430	.116	8a,9a	3.2
39	HG	2	34.4	3.8	12.5-16	$5.1 \cdot 10^{-3}$	$2 \cdot 10^{-4}$	427	430	.027	8a,9a	2.2
40	HG	1	17.3	.6	16	$1.1 \cdot 10^{-5}$	$2 \cdot 10^{-4}$	430.5	430	-	8a,9a	3.1
41	HG	3	52	6.6	12.5-16	$3.9 \cdot 10^{-5}$	$2 \cdot 10^{-4}$	430	430	.115	8a,9a	2.4
42	HG	3	52	.32	12.5-16	$6.6 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	432	430	-	8a,9a	8.0
43	HG	2	63	5.0	12.5-16	$5.4 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	432	430	.176	8a,9a	2.8
44	HG	2	63	2.2	12.5-16	$3.7 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	433	430	.009	8a,9a	2.16
45	HE	11	27	11.1	7	$3.3 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	430	430	.054	8a,9a	5.3
46	HF	8	18.8	.72	7	$1.3 \cdot 10^{-2}$	$1 \cdot 10^{-4}$	494	490	.130	8a,9a	2.95
47	HF	8	18.8	.72	7	$9 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	466	470	.164	8a,9a	2.09
48	HF	8	18.8	.72	7	$1.5 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	389	390	.002	8a,9a	21.9
49	HE	8	18.8	.72	7	$1.4 \cdot 10^{-4}$	$< 1 \cdot 10^{-4}$	388	390	.027	8a,9a	17.3
50	HE	8	18.8	.72	7	$2.5 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	359.5	360	.007	8a,9a	19.5
51	HE	7	16.9	.29	7	$2 \cdot 10^{-3}$	$2 \cdot 10^{-5}$	357	357	.0102	8a,9a	45.9
52	HE	7	16.9	.29	7	$7 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	421.5	425	negligible	8a,9a	4.4
53	HE	7	16.9	.29	7	$2 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	359	360	.012	8a,9a	38.5
54	HF	7	16.9	.29	7	$4 \cdot 10^{-5}$	$2 \cdot 10^{-4}$	468-½	470	.015	8a,9a	2.47

Table II—Classifications Under Which Experimental Information Falls
(Types of Study)

1. a. Material transfer within solid aggregates.
   b. Temperature distribution and surface temperatures. (to be made the subject of studies now in progress).
   Part III.
2. a. Variation of rate of sublimation with thickness of solid layer.
   b. Effect of particle size.
   Part IV.
3. a. Variation of rate of sublimation with particle size.
   Part V.
4. a. Variation of rate of sublimation with temperature.
   b. Effect of particle size.
   c. Effect of inert material.
   Part VI.
5. a. Variation of rate of sublimation with surface water contamination.
   b. Effect of particle size. (not included. See Report Chem S 214).
6. a. Variation of rate of sublimation with quantity removed.
   b. The effect of inert material.
   c. The effect of surface layers of glass.
   d. The effect of geometric changes.
   Part VII.
7. a. Variation of rate of sublimation with the amount of inert material on the surface.
   b. The effect of screens and perforated discs.
   Part VIII.
8. a. The effects of orifice and charge areas on the rate of sublimation. The control by each.
   Part IX.
9. a. Transport of material through orifices. The vapor pressure.
   Part X.
10. a. Variation of the rate of sublimation with the manner of support of the material. (This work is in progress and is not included in this report).

conditions indicates that the removal of material from the surface of a charge results in marked cooling of that surface, and the size of the sintered region indicates that the temperature gradient in 32-60 mesh material at 450° does not extend over a great distance, probably 4 mm at the most.

In a recent set of experiments, not listed in Table I, it was found that slight variations in temperature within a charge bottle resulted in rates of sublimation varying by ± 50% for material of identical particle size.

The question of material transfer within a bottle has recently been brought forward sharply by experiments on R-1, with 'Pete' bottles. These bottles were built with cylindrical screen support for the solid and a radiant heater in the axis of the bottle. In run No. 157, such a bottle containing 1.2 Kg. of 2-$\frac{1}{2}$ to 10 mesh material was operated for 70 hours at about 435°C with up to 50 watts of heat into the central heater. This central heating resulted in marked material transfer within the bottle. Upon removal of the bottle it was found that there were no masses of the original material. There was, however, about 400 gm. of TCl_4 on the bottom, caked into one mass, the 'density' of this being considerably in excess of that of the original charge.

TEMPERATURE DISTRIBUTION AND SURFACE TEMPERATURE

Information of a quantitative nature is now being obtained from experiments.

PART IV.

VARIATION OF THE RATE OF SUBLIMATION WITH THICKNESS OF THE SOLID

This topic was the subject of Report Chem S 215 (10/12/43), but additional information has been obtained, and these new data are here presented with the old. There is no significant change in results.

It is now well established that the solid which is subjected to vapor removal lies within fairly thin regions facing the evacuated space. The evidence of weight losses is quite satisfactory in itself, and the

conclusions based on it are supported by evidence obtained visually (see the report mentioned above) and by a temperature gradient study, a portion of which has been completed.

The experimental data are shown in Figures 1 and 2. The first shows the rate as a function of thickness, and the second the minimum thickness estimated to give maximum rate for varying particle sizes.

It is interesting to note that for sizes up to about $\frac{1}{5}$ inch diameter (4 mesh) only about 4 layers are necessary to give maximum rates of sublimation. For smaller particle sizes the material contributing to vapor removal occupies only the first layer. It seems probable that material finer than 60 mesh loses practically all of the vapor from the surface of the layer which faces the evacuated space.

Measurements are to be desired on the character of this relationship at different external pressures of TCl_4 vapor, and at different temperatures.

Some results obtained so far show that the effective thickness (Fig. 2) does not change substantially in the region from 400° to 500°C.

PART V.

RATE OF SUBLIMATION AS A FUNCTION OF PARTICLE SIZE.

The initial report of this topic was made in Chem S 213. The results presented here are entirely new, and have been obtained under nearly isothermal* conditions from nine separate experiments.

It seems rather strange that there should be a particle size effect upon the rate of sublimation, just from the consideration of the upper surface areas alone. A theory which would account for the observed effect would probably have to explain the accompanying effect of thickness of the charge layer. (See Part IV) An elementary explanation of the existence of the particle size effect is that the coarser material is acted upon through a greater depth, and consequently offers a larger area for sublimation.

The experimental method employed for these determinations is likely to give somewhat lower rates than would be obtained from abso-

*This does not mean that the solid surface temperatures are the same as the surroundings.

lutely pure material. (See the section on the variation of rate with quantity removed, Part VII).

An attempt to determine the change in rate with varying external pressures for different particle sizes was begun but was discontinued on account of the large effect of small temperature differences.

The experimental results are given in Figure 3. Note that there is about a five-fold increase in rate of sublimation in going from fine to coarse material.

A heterogeneous mixture of sizes may be expected to exhibit a rate which is closer to that of the fine particles in it than to the coarse.

Since the work shown at 410° and 450°C is rather limited, no emphasis should be placed on discrepancies in slope and displacement of the 410° and 450° lines from that of the 430° lines.

PART VI.

VARIATION OF THE RATE OF SUBLIMATION WITH TEMPERATURE

That there should be some relationship between the vapor pressure and the rate of sublimation is to be expected, but it need not be expected that the rate should be strictly proportional to vapor pressure. The data presented in Figure 4 are for nearly open charges, and, for such, the equilibrium conditions of vapor pressure vs. temperature do not hold. The surface is lowered in temperature by the sublimation, and the rate of sublimation is governed by the temperature, and thus the pressure, existing there. For material lying beneath the surface (insofar as this material contributes to the sublimation at all) the rate will also be affected by the number and size of the apertures available for flow of the vapor.

In Figure 4 the vapor pressure line is the uppermost, the next family of lines is that of the open charges, and the lowest family is that for glass chip covered charges. By a reduction of the rate vs. temperature data by the method

$$\frac{\text{Rate at T}}{\text{Rate at 410}} \times \frac{\text{Equilibrium Transport at 410}}{\text{Equilibrium Transport at T}}$$

a single point of intersection at 410°C is obtained, and the relationship of the rate to the vapor pressure is shown. Figure 5 shows the result of this reduction.

The chief conclusion to be gathered from Figure 5 is that the rate of sublimation is approximately proportional to the vapor pressure for rather large temperature changes. It is shown in Part X that the vapor pressure changes 110-fold from 360°C to 450°C. The departure of the rate of sublimation from proportionality with vapor pressure is not greater than ½-fold in the same temperature range.

From Figure 4 it may be gathered that the rate of sublimation for open charges is about $\frac{1}{20}$ of the corresponding transport calculated from the usual vapor effusion equations.

A method of measuring the rate of sublimation continuously has been developed and should rapidly increase our information on the effect of temperature. It is expected that the results will reveal an even closer proportionality to the vapor pressure than is shown in Figure 5.

PART VII.

RATE OF SUBLIMATION AS A FUNCTION OF THE QUANTITY REMOVED

The first report on this topic was contained in the report, Chem S 228 (11/12/43), and it was stated there that the changes in rate originated primarily with the non-volatile impurity which accumulated on the upper surfaces as the charge was consumed. Most of the effect was removed by intermittent shaking of the charge.

The information presented here supplements that already reported by showing the variation with particle size and with surface coverings, such as glass chips.

The main fact to be derived from these results is that the decrement in rate is gradual for rather coarse granular material but is rapid for finer material.

The work with glass covers was undertaken with the hope that it would be possible to eliminate all differences between charges by providing a surface covering. However, this did not work out very well. There was some improvement, but not as much as was desired. It may be seen from the graphs that the decrement in rate due to pile-up of residue within the charge is not completely obscured.

Much work remains to be done on the effect upon rate of the non-

volatile residues, with particular reference to the effect of changing external geometries. This is now being studied.

Figures 6 and 7 show the results of the experimental work at 430° and 410° and are self-explanatory. The $TCCl_2$ content of the materials did not exceed 3%, and therefore the NVR (non volatile residue) did not exceed about 1.5%.

PART VIII.

THE EFFECT OF SURFACE COVERINGS ON RATE OF SUBLIMATION

Since it has been found that both particle size and the non-volatile content of the material affect the rate, it was hoped that inert surface coverings could be employed to eliminate differences in the rate of sublimation. This work was partially successful, but it was not found possible to completely eliminate differences. The lack of complete success is apparently caused by insufficiently high resistance to flow of the covering material.

Work was started by taking two samples of 6-10 mesh material which had been subjected to prior sublimations. (Samples A-20mm and B.16mm, See Report 228, page 5) The A sample had a prior rate of 0.207 gm/cm^2/hr. The B sample one of 0.063. Upon being covered with 5-$\frac{1}{2}$ layers (19mm) of 2.9mm glass beads, and again subjected to sublimation, the rates were 0.051 and 0.036, respectively. In terms of the ratio of rates of the two samples the change was from 3.3 to 1 to 1.4 to 1. In another case, shown in Table III below, a similar improvement was noted.

Table III

Sample No.	Exp. 23	Exp. 24 Rates gm/cm^2/hr		Exp. 25
No. 18 (4-6 mesh)	.254	.151	(shaken)	.031 with 9.1mm glass
No. 19 (32-60 mesh)	.112	.069	(unshaken)	.0165 with 10 mm glass
Ratio 18:19	2.3:1	2.2:1	3.7:1	1.9:1

Since sample 18 was shaken up, its prior rate may be assumed to have been 0.254, giving the ratio 3.7:1. With the 14-20 mesh glass the reduction of the ratio to 1.9:1 may be regarded as having effected elimination of 50% of the difference between the samples. This is not as good as might have been expected.

The nature of the relationship between the rate of sublimation and the thickness of the layer of material lying on top of the TCl_4 was determined in several experiments, summarized by the heavy lines in Figure 8. Curves 1 and 2 are for 4-6 mesh material, curves 3 and 4 for 10-22 mesh. It may be observed that the particle size of the covering material changes the rate of sublimation for a given material. The variation of rate with thickness of the layer involves no rapid changes, nor an approach to a condition where the change of rate is small; (there is thus a basic dissimilarity in the conditions of flow and pressure between inert material and actively subliming material).

The groups of points represented by 5 and 6 on the graph indicate attempts at removing the differences between material of different particle size. The initial spread of 2.3:1 for uncovered material compares with a spread of 1.4:1 for the covered material in Group 5, and 2.5:1 compares with 1.4:1 for the covered samples in Group 6.

Altogether then, with reasonably thin layers of moderately coarse covering material elimination of differences arising either from prior sublimation or particle size is about 50% to 70% complete. Since it was felt that this was not good enough, our attention was directed to work on the control of charges by restricting the openings above the charge. (PART IX).

Figure 9 shows the reduction in rate effected by 6 mm and 12 mm layers of different sized inert material, the values being taken from the preceding figure. In preparing this graph the chips are given diameters such as they would have if they were spherical. It is probable that the curves appear better than the data warrant. Insofar as this figure tells the truth, it appears from the relationship between the 12 and 6 mm lines that it takes an equal number of layers to give the same reduction in rate, and thus 6 mm thickness of 1mm particles is equal to 12 mm thickness of 2mm particles in reducing the rate, and therefore each layer of particles is equivalent.

Data on the glass particles used is given in Table IV.

Table IV

	2.9mm bead	2.2 mm bead	10-14 chip	14-20 chip	48 mesh beads
Ave. diam., cm.	.29	.22	(.125)	(.09)	.0295
Wt. each, gm.	.031	.013	.0038	.00144	
Packing density, gm./cc.	1.3	1.31	1.25	1.205	
Space occupied	59%	63%	60%	58%	60%
Ave. open area	41%	37%	40%	42%	40%

THE EFFECT OF SCREENS AND PERFORATED DISCS

A screen and a perforated disc are equivalent to a single layer of particles of equal open cross-section. The effect of such a resistance upon the rate should be noticeable, but not very great. In a single experiment, open samples of 8-10 mesh material were compared at 430°C with two samples covered with stainless steel screen of 44% open area (.022" holes) and a perforated brass disc of 29.5% open area (.027" holes). Both were approximately .020" thick. The results were as follows:

		Transport (gm./cm^2 open area)
Rate, 8-10 mesh, open	0.274	.274
with SS screen	0.234	.54
with SS screen	0.230	.53
with brass disc	0.185	.70

This shows that it is permissible to enclose charge material with wire screen supports and obtain rates of sublimation nearly as high as are obtained from open surfaces.

PART IX.

THE EFFECTS OF ORIFICE AND CHARGE AREAS ON THE RATE OF SUBLIMATION

Attention was next directed to obtaining control over charges of varying character by means of apertures above the surface of the charge.

The method employed was as follows: Small cylindrical bottles of about 17 mm inside diameter and 30 mm tall were equipped with tightly fitting screw caps bearing orifices which were sharp-edged for all sizes under $^3/_8$ inch diameter and shaped so that the face toward the solid was flat, that to the exterior bearing an angle of less than 30 degrees from the horizontal. Bottles were made of stainless steel for most of the work, though a small nickel bottle and cap and also a gold-plated copper bottle and cap were used. A series of similar one-piece glass bottles were used for some of the work. Larger size bottles were 2 inch diameter and both 2 and 4 inches long, stainless steel, equipped with screw caps which would take any of the interchangeable orifices used on the smaller bottles.

The work reported here is imperfect insofar as we did not employ thermocouples for measuring the charge temperatures directly. Uncertainties arising from this in the work with the larger bottles may amount to 20% (i. e., those in which the arrangement was described as G in Part I).

The data are summarized graphically in Figures 10 and 11, and are all for the same material, 4-8 mesh size Harshaw TCl_4. Since the method employed was the usual one of over-all weight loss in an experiment, certain limitations were encountered. For one, the character of the solid was not quite constant during an experiment (see Part VII), and at higher temperatures the rates would be so high as to nearly exhaust the charge, and thus render the measurement invalid.

However, as summarized in Figures 10 and 11, the data clearly show that complete control over the solid is obtained by the orifice when the ratio of areas of charge to orifice is above 40 at lower temperatures and above 100 at higher temperatures. Not shown in the data is the fact that the effective area ratio is subject to change as the solid is used up; therefore the area conditions which would offer control up to nearly complete utilization of charge are probably in excess

of a ratio of 100 to 1. Changing from coarse material to fine is not likely to change the area ratio for obtaining complete control by more than a factor of 3 or 4.

The information shows that for satisfactory operation of vapor valves area ratios of charge to opening should be above a ratio of 40 from the completely closed to the completely open position. The control over the charge by the orifice seems to be rapidly lost by changing the ratio from 40 to 20 at lower temperatures, and from 200 to about 50 at higher temperatures.

In Figures 10 and 11 the same data are treated in two ways, and an inspection of these figures will reveal the merits of each form of expression.

Interpretation in terms of the ability of the charge to produce vapor.

In Figure 3 the variation of charge rate with particle size is shown. It may be assumed that a heterogeneous charge containing all particle sizes, such as is usually supplied in charge bottles, will have an initial rate at 430°C of about 0.1 gm/cm^2/hr. For an area of 250 cm^2, the total charge rate would then be a maximum of 25 gm/hr. From the 430 curve of Figure 11 it is found that the orifice has complete control only when its transport is 4.3 gm/hr per cm^2 of opening, and it may also be observed that control is nearly gone when the transport is reduced to about 3 gm/hr/cm^2. Cross reference to Figure 10 shows that at this value, 3 gm/hr/cm^2 for the orifice, about $\frac{1}{2}$ of the charge rate is obtained. Therefore 12.5 gm divided by 3 gm/cm^2 yields a permissible opening of slightly over 4 cm^2 for the orifice. Further opening, say to 8 cm^2, would yield not more than 30% more vapor. It is clear that further increases in opening of the orifice would be impractical.

As the charge deteriorates, due to accumulation of non-volatile residues on its surface, and later a general decrease in area, its ability to produce vapor may be cut in half by the time the charge is half gone. Therefore the bottle should have been operated with its valve open to only 2 cm^2 at first, rather than 4, thus providing an over-all rate of about 9 gm/hr.

If it is desired to make such a charge bottle operate at higher rates the only alternative remaining is a change in temperature. It may be assumed that for small changes in temperature the rate change will be 5% per degree, or 100% for 15 degrees in the region 400 to 500°C.

THICK vs. THIN ORIFICES

That the geometric characteristics of the orifice are of extreme importance is shown by the additional data gathered together in Figure 12. A $\frac{1}{32}$" diameter orifice which is $\frac{1}{8}$ inch thick, compared to one which is thin-edged transports about 20% as much vapor. At $\frac{1}{16}$" diameter the comparison shows a 30-50% value, and at $\frac{1}{8}$" diameter about 65%. The effect of the $\frac{1}{8}$" thickness may be assumed to become unimportant only at diameters greater than $\frac{1}{4}$".

PART X.

DETERMINATION OF THE VAPOR PRESSURE OF TCl_4

The vapor pressures which have been in use up to the present are based on the work of Thomsen and Schelberg, as reported in UCRL Chem S Report No. 4. It has been of continuing interest to us that the data obtained by them above 400°C were considerably above the line extrapolated from their lower temperature work. Furthermore, as far back as December 1943 we were obtaining results which indicated transports across openings which were in keeping with the higher experimental results but not with the extrapolated vapor pressures. It was therefore thought desirable to determine vapor pressures by the conventional vapor effusion methods, but with sufficient variation of the openings to prove that the values determined were true equilibrium values. It was, however, also taken for granted that it would not necessarily be possible to change over the information obtained on transports to the corresponding vapor pressures.

So the point of view with which these data were obtained was the practical one of determining the transports, so that such values could be applied directly to charge bottle design and from these transports, if possible, to determine the vapor pressures.

At the same time that the data were obtained an analysis of the work of M. Knudsen on the flow of carbon dioxide (see Figures 14 and 15) showed that for carbon dioxide, and for the particular orifices used, a relationship between experimental transports and the transport obtained under conditions where the effusion law strictly holds

could be set up graphically, the value of the resulting ratio ranging from 1 to 1.63 over a very wide pressure range. Knudsen showed on theoretical grounds that it was to be expected that the ratio for any gas would have a maximum value of 1.52, and he claimed that his data showed it to be so, though our graphical analysis indicates the slightly higher ratio of 1.63. Furthermore, his data show that the value of the ratio of transports is determined by the ratio of mean free path of the gas to the diameter of the opening.

In Figure 14 the analysis of his higher pressure data is shown, providing the conclusion that the ratio of transports approaches an upper value of about 1.63 as the gas flows into regions of much lower pressure. In Figure 15 those data of his which are of sufficiently broad scope to provide the information sought show that there is a consistent relationship between the mean free path to diameter ratio and the transport ratio.

The chief burden of the experimental work was to prove that the transports obtained were those for which the solid was in equilibrium with its vapor and that the orifices used were sufficiently close to an infinitely thin opening, and these transports would then be corrected on the basis of the analysis of Knudsen's data. The first condition is reached if bottles made of different material and having a variety of openings all give the same transport at some sufficiently small opening. The second condition was reached by trial, some of the data providing the information for Figure 12. It was found to be permissible to employ orifices whose side facing the solid was flat, and whose other side was slightly conical. The edge of the hole had to be trimmed to about 0.001 to 0.002 inch thickness to give the best results with the $\frac{1}{32}''$ hole bottles. The charge area was 2.08 cm^2 for glass bottles, 2.43 cm^2 for metal bottles.

The experimental results were obtained for a variety of solids, including 4-8 mesh Harshaw, and several varieties of once and twice sublimed granular material of a size which it was possible to introduce through the openings of the one-piece glass bottles.

It was found that the nature of the solid had no effect upon the determination of the equilibrium value.

Since TCl_4 is extremely hygroscopic and when hydrated loses HCl (and therefore weight) upon being heated, the TCl correction was carefully determined for each experiment and assigned on a weight basis for a first heating and thereafter equally between the samples. It is

therefore certain that the weight losses ascribed to loss of TCl_4 are reasonably correct. The reaction of the TCl_4 vapor with stainless steel was sufficiently great to have made us decide before this work was done that bottles with $\frac{1}{32}$" openings were not to be constructed of stainless steel. Results with the all nickel bottle were the best, but one spuriously high result had to be discarded even for this bottle. This high results was caused by slight leakage past the threads of the cap, and was prevented in later work by calking the crack between the cap and the body of the bottle with a very small amount of talcum.

The graphical analysis of the data shown in Figure 13 should suffice to show that equilibrium transport values were determined at each of the stated temperatures.

The thermocouples used in this work were iron-constantan and chromel-alumel couples. The temperatures stated for the data are correct within 1°C.

Tables V, VI and VII, which follow, indicate the manner in which the data were treated to obtain vapor pressures.

The vapor pressures which were obtained in Table VII have been plotted against reciprocal absolute temperature in Figure 16.

The RMS deviation of the data from the straight line drawn through them is 8%, which is just about within the limits of reproducibility of the experiments themselves.

The results which we have determined for the transports are about the same as would have been calculated from the high temperature transport data of Thomsen and Schelberg; however, our values are significantly different from theirs at the lower temperatures of 390 and 360, temperatures where the corrections applied on the basis of Knudsen's work are insignificant. This was not expected. It is unfortunate that a careful description of the apparatus and methods of Thomsen and Schelberg is not available.

The data which have been determined and are presented in Part X of this report bear an internal consistency and agreement which warrants confidence in them, and it is probable that the vapor pressures obtained from Figure 16 are in error by less than 10%. The validity of the 'Knudsen correction' is open to some doubt, but it seems fairly certain that it is correct in direction and approximately correct in magnitude.

In Table VIII some vapor pressures read from Figure 16 are presented.

Table V—Estimation of the Correction to Transport Data

T °C	Estimated Free Path cm λ	Largest Diameter giving Equilibrium amount cm	$\frac{\lambda}{d}$	Knudsen Factor (Ratio by which Exp. Transport exceeds Molecular Effusion Value)
360	4.4	.26	17	1.03
390	1.0	.24	4.3	1.07
425	.24	.21	1.15	1.26
430	.17	(.20)	.85	1.33
470	.044	.145	.3	1.58
490	.022	.118	.185	1.62

Table VI

T °C	Experimental Transport gm/hr/cm^2.	Corrected Value for use in calculating Vapor Pressure gm/hr/cm^2.
356.5	.078	.075
359.5	.088	.085
390.2	.46	.43
425.7	3.02	2.4
430	4.3	3.0
470.3	30	19
490.4	82	50

Table VII—Calculation of Vapor Pressures

$$P = \frac{G}{At}\sqrt{\frac{2\pi RT}{M}}$$

T °A	G	P dynes	P mm Hg	$1/T_0 \times 10^3$ Abs
629.5	.075	.614	.00046	1.5885
632.5	.085	.698	.00052	1.5810
663.2	.43	3.74	.0026	1.5075
698.7	2.4	20.7	.0155	1.4310
703	3.0		.021	1.4225
743.3	19	169	.127	1.3452
763.4	50	452	.339	1.3100

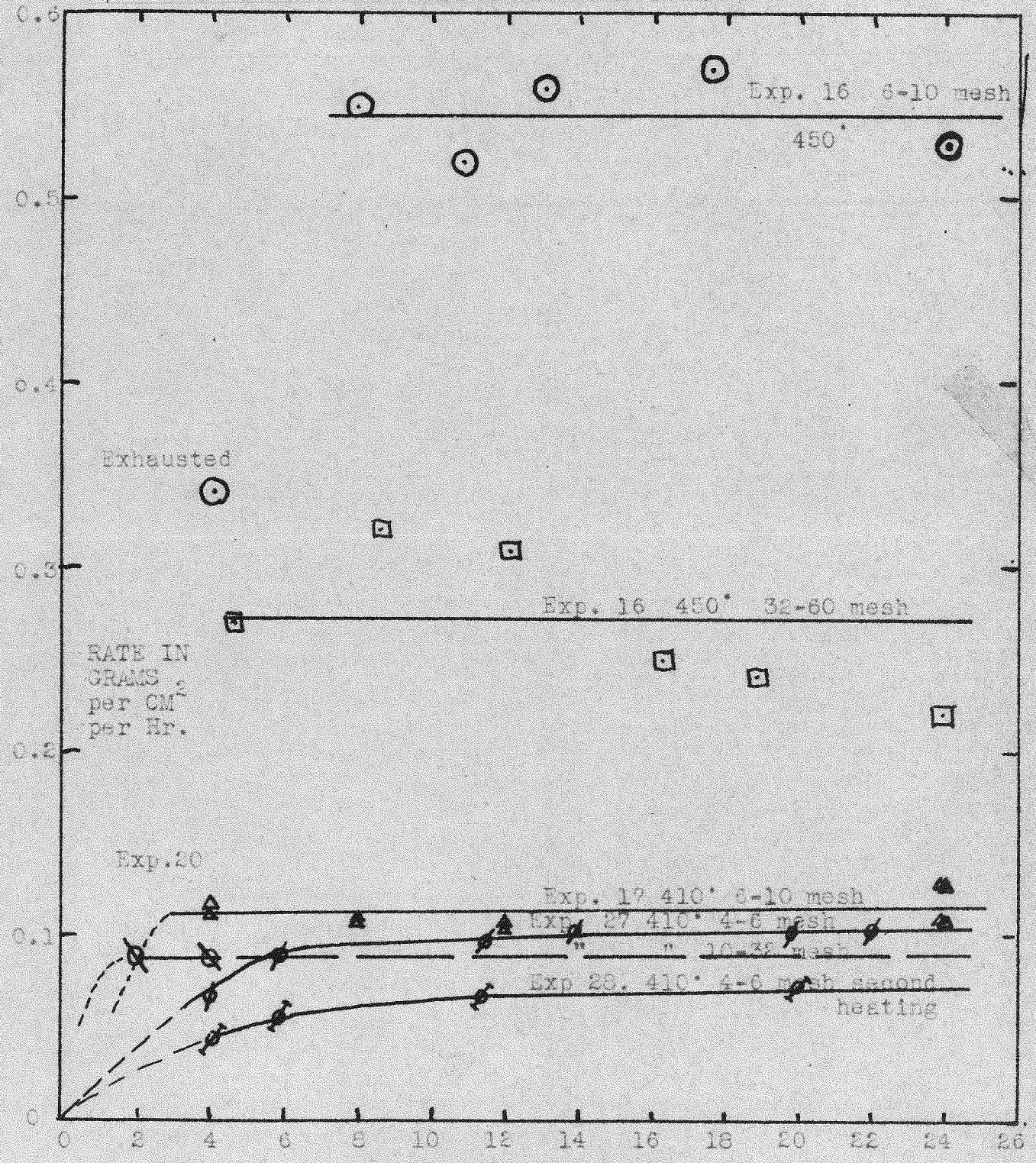
The heat of vaporization determined from Figure 16 is 123.3 cal./gm., which is 17 cal. higher than the value obtained from previously used values.

Table VIII—Vapor Pressure of TCl_4
(from Figure 16)

T °C	P mm Hg
360	.0005
390	.0029
410	.0082
430	.022
450	.055
470	.134
490	.31
510	.67

Fig. 1 21

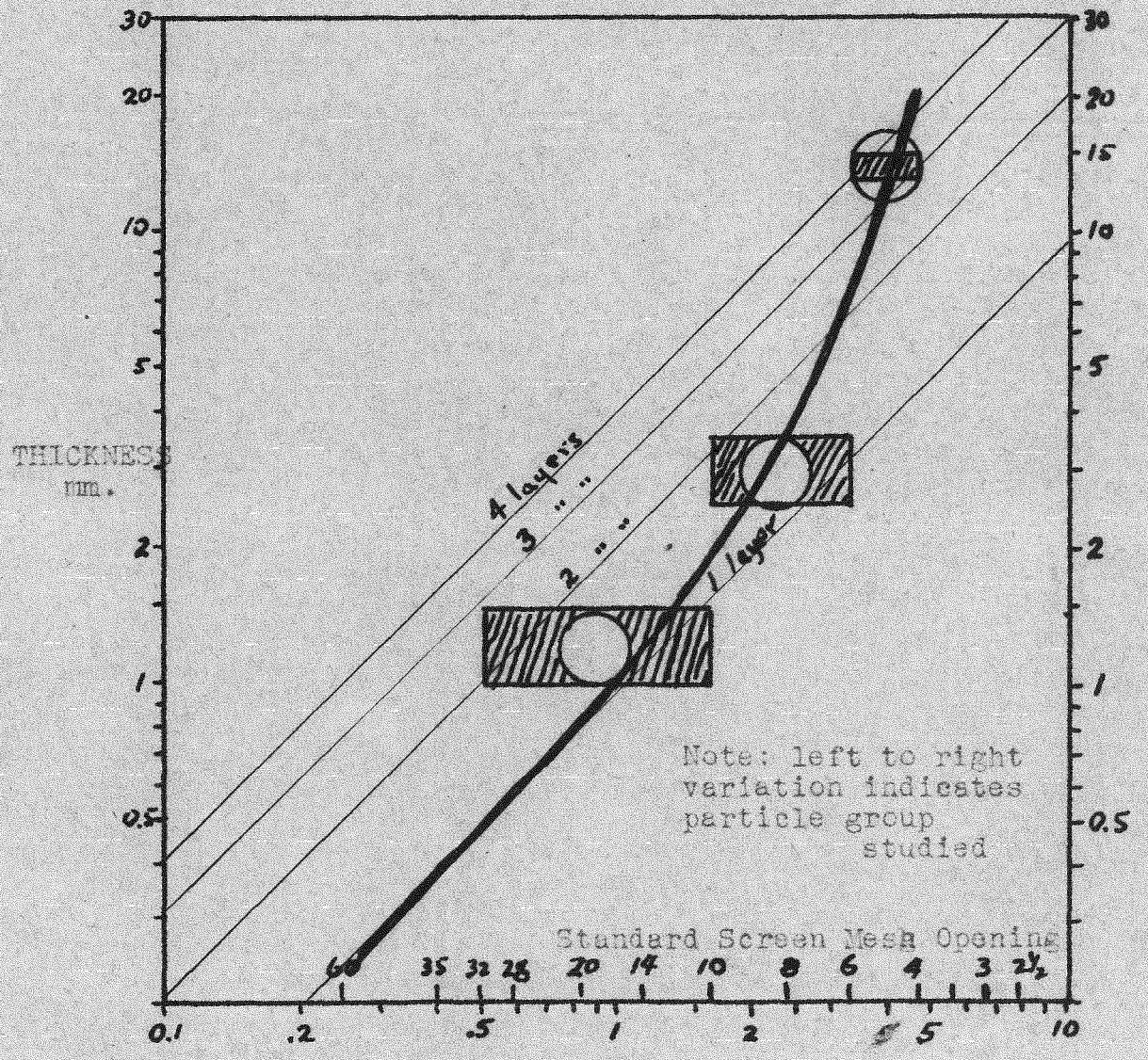
VARIATION OF RATE OF SUBLIMATION WITH THICKNESS



22

Fig. 2

MINIMUM THICKNESS OF MATERIAL
REQUIRED FOR NEARLY MAXIMUM RATE
VS.
APPROXIMATE PARTICLE DIAMETER
OR SCREEN MESH
(410 - 450 °C)



RL-4.6.257

Fig. 3

23

RATE OF SUBLIMATION
vs.
PARTICLE SIZE

(410- 450°C)

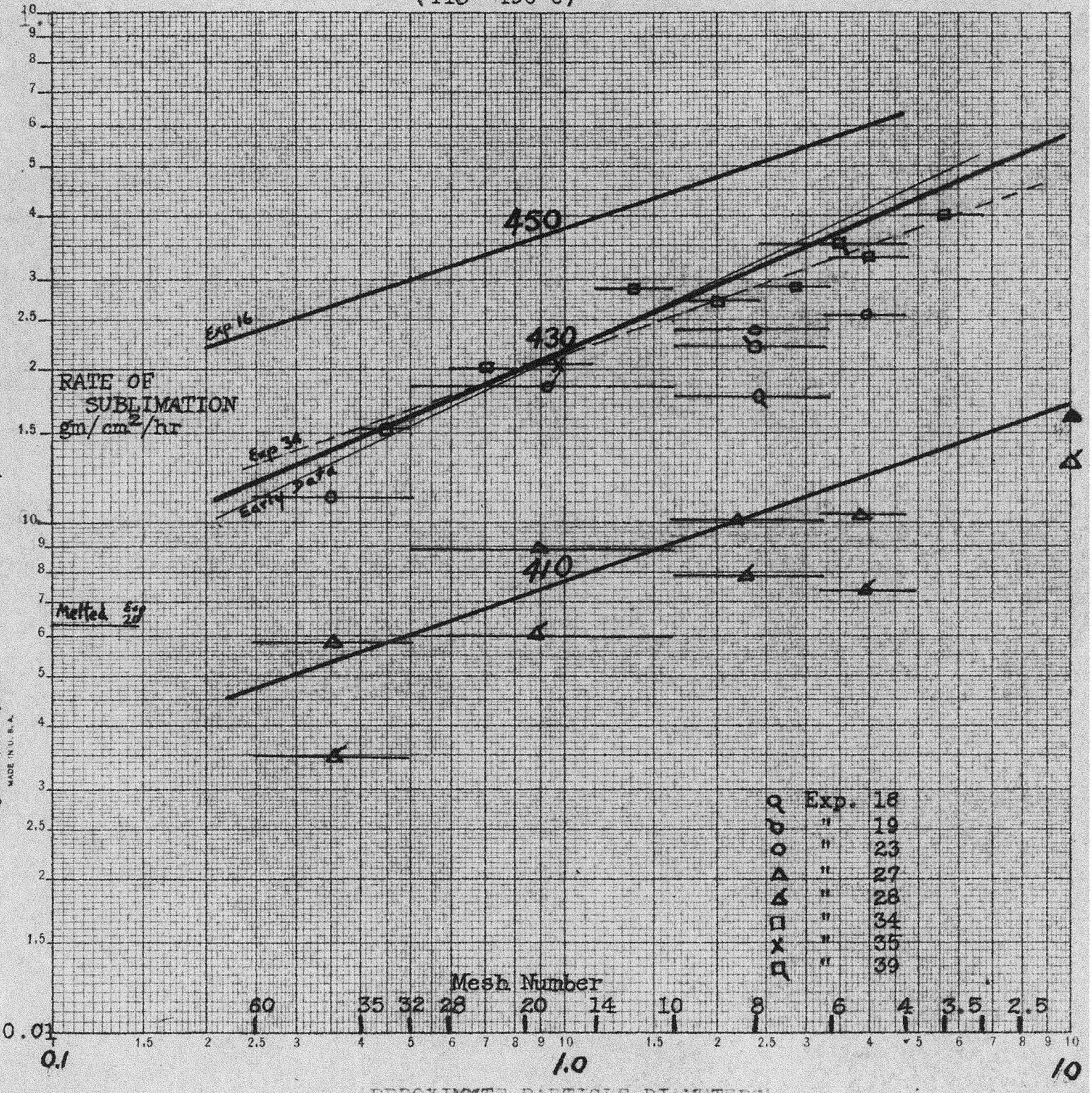
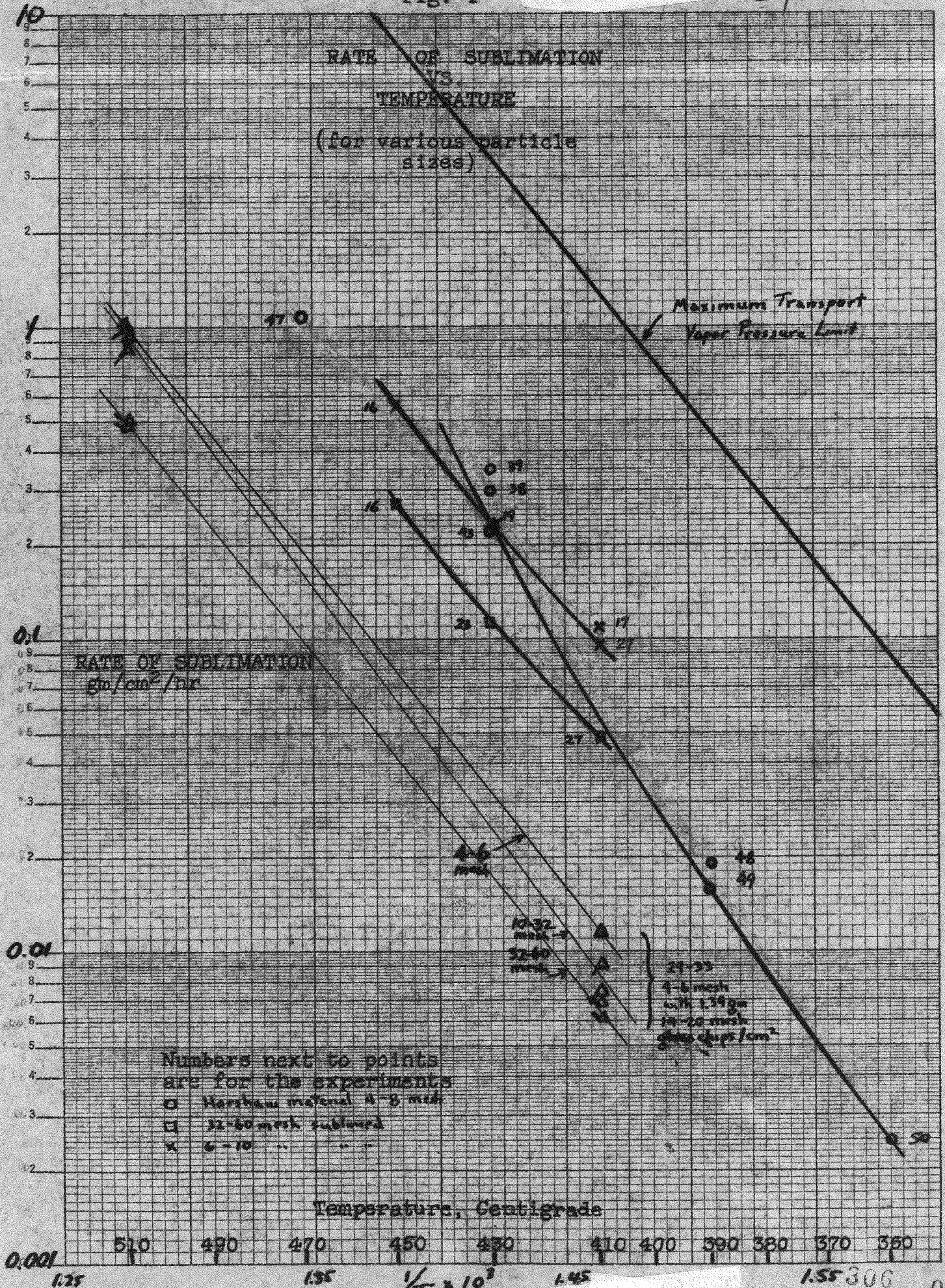


Fig. 4

24



25

Fig. 5

Graph,
showing departure of rate of sublimation from proportionality to the vapor pressure, all data being given a common point of intersection at 410 Centigrade.

The points have the same meaning as in Figure 4.

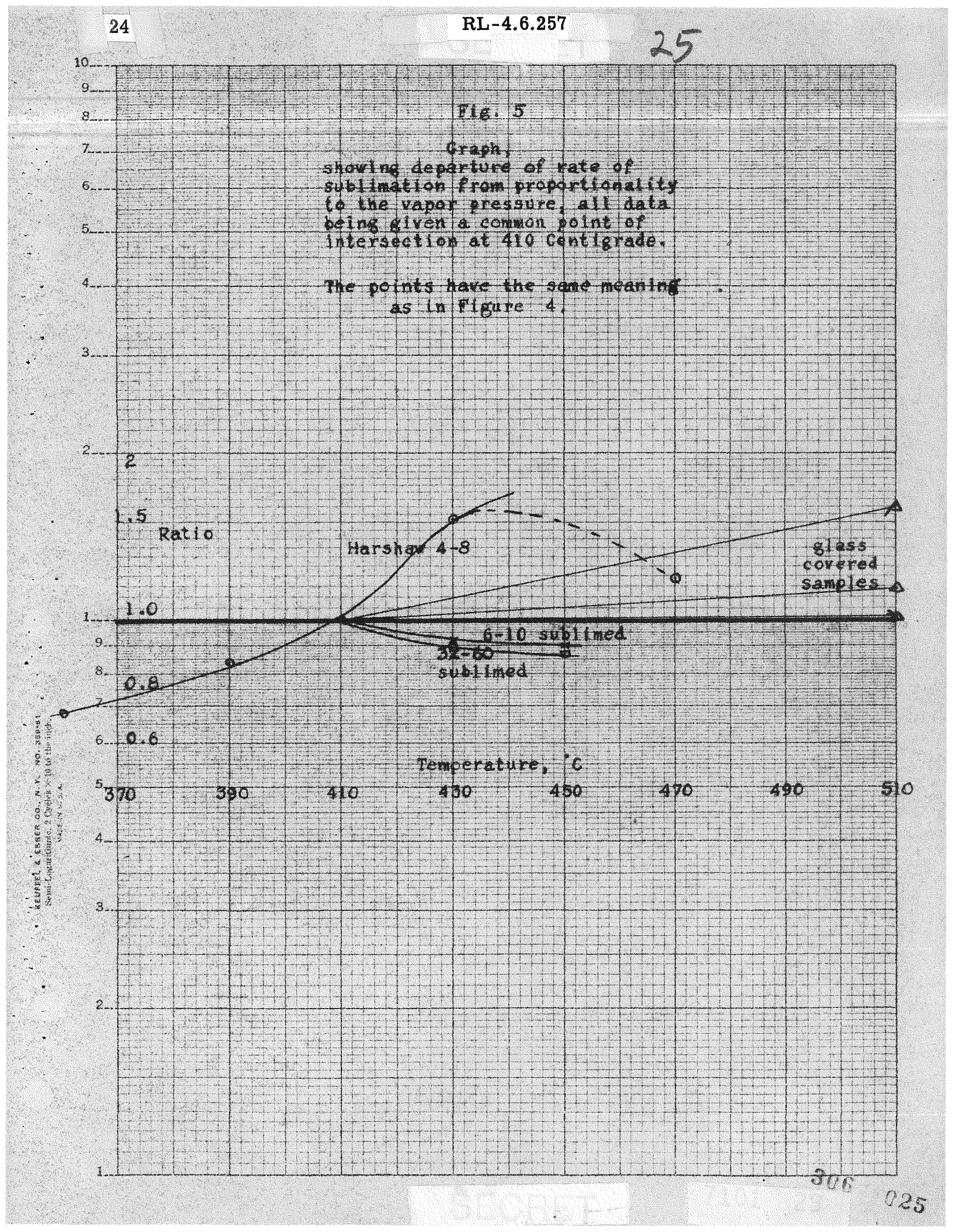


Fig. 6

26

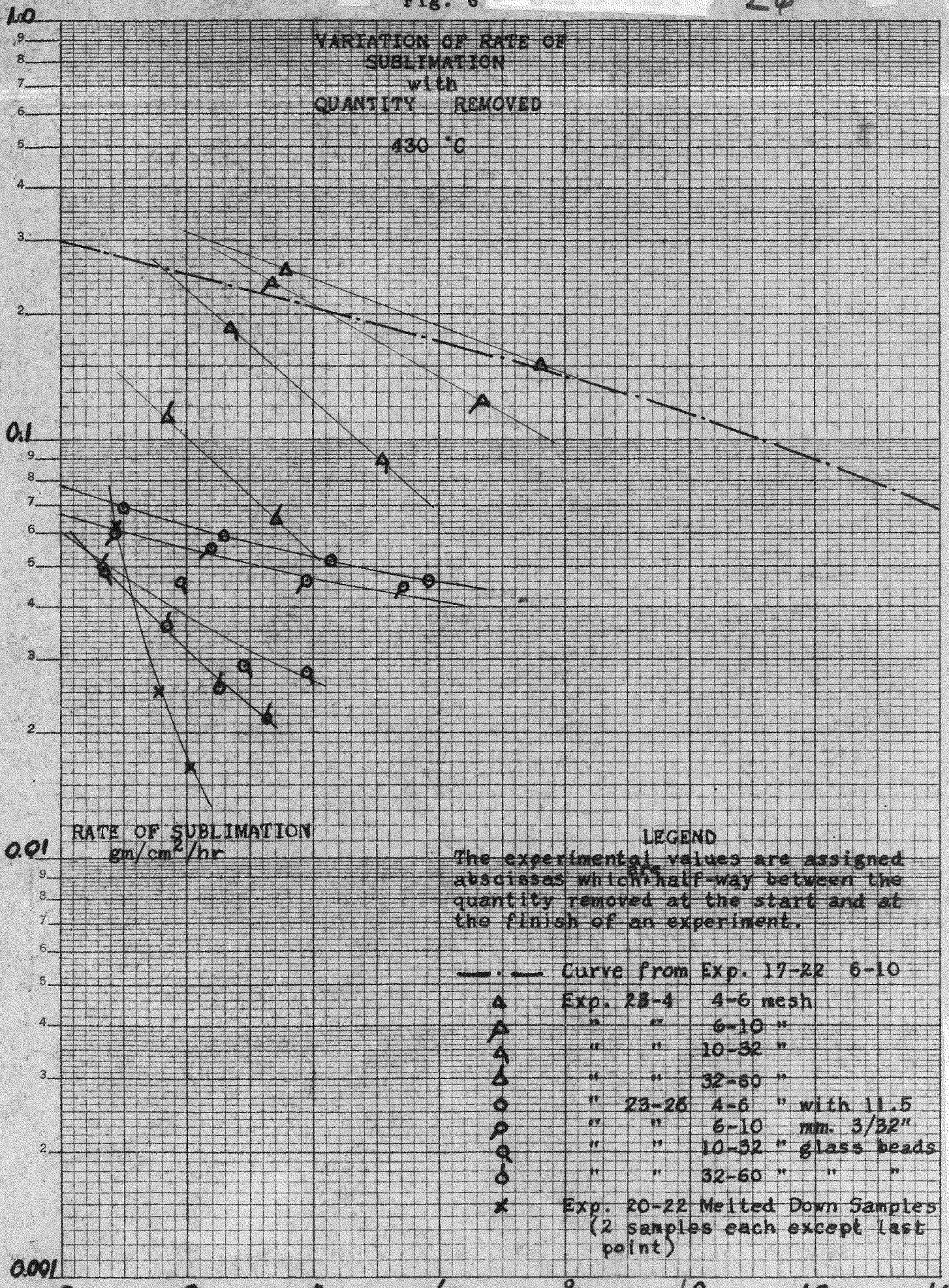


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Fig. 7

27

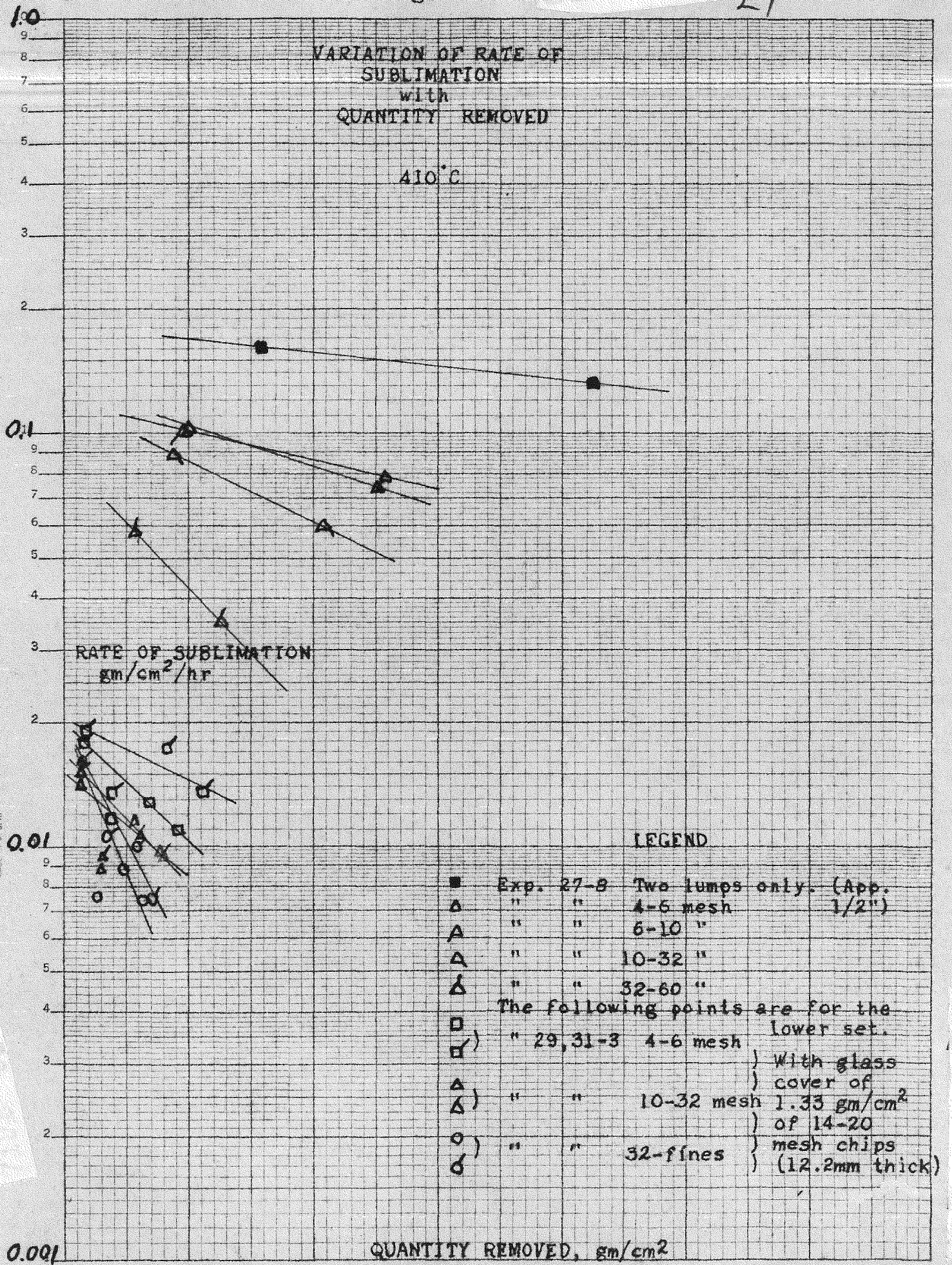


Fig. 8

RATE OF SUBLIMATION
vs.
AMOUNT OF SURFACE COVERING

The temperatures and type of glass coverage are shown for each curve.

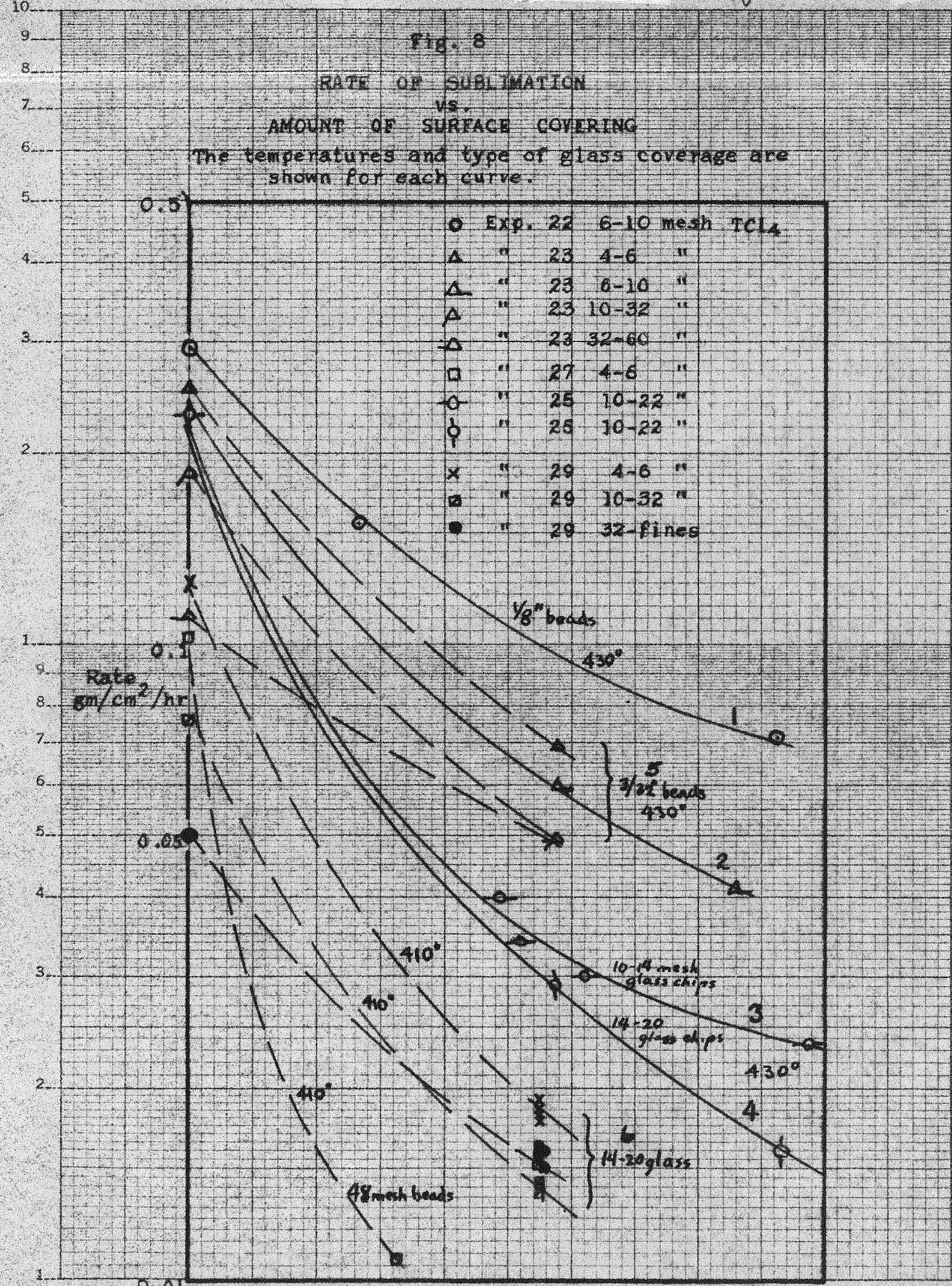
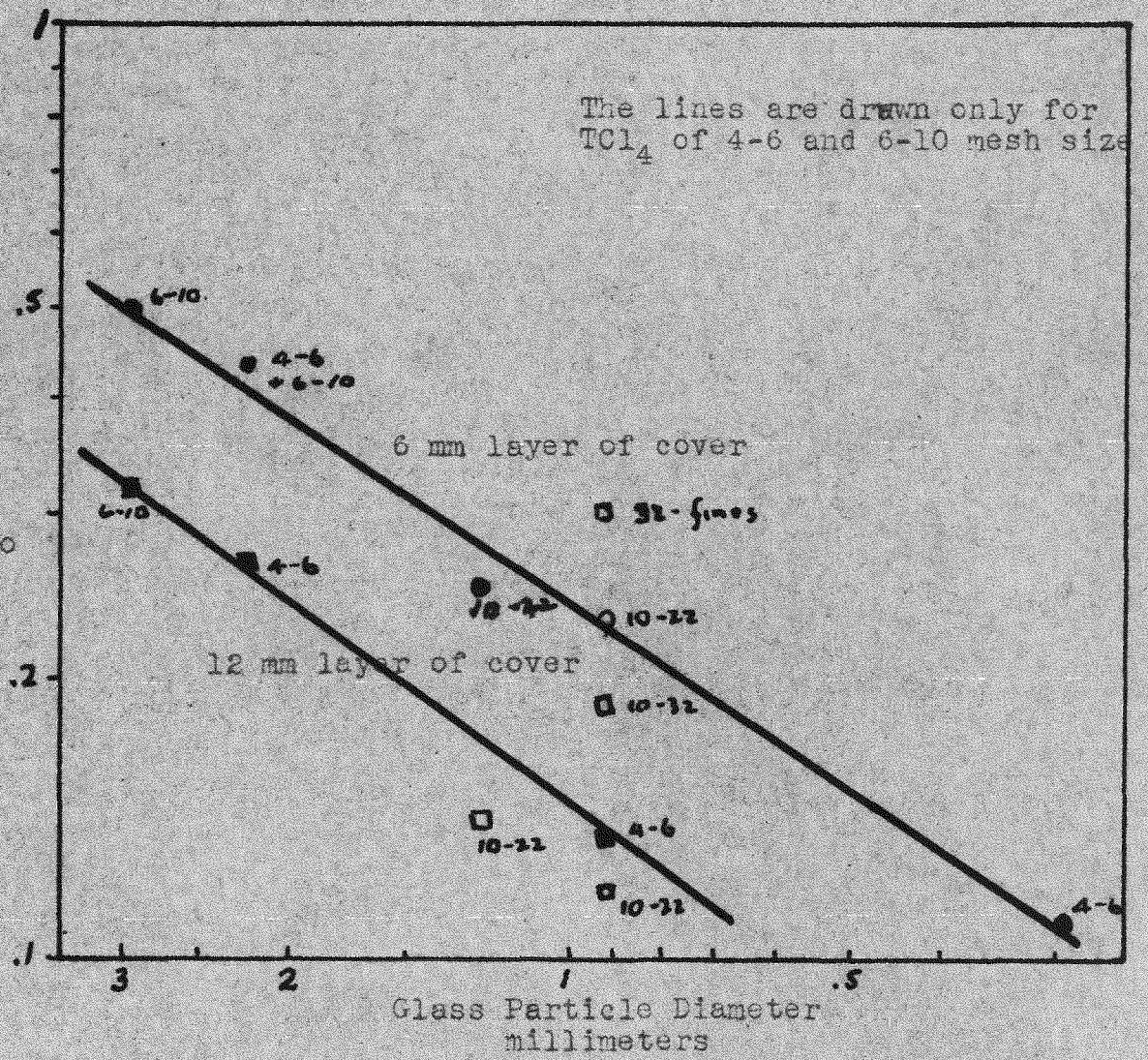


Fig. 9

29

Ratio of Observed Rate to Rate Without Cover vs. Glass Particle Diameter



30

10

1

0.1

0.01

0.001

0.0001

FIGURE 10
RATE OF SUBLIMATION PER UNIT AREA OF CHARGE vs. RATIO OF CHARGE AREA TO ORIFICE AREA

Rates for smaller area ratios were not determined at 490 and 470 since they would have been too low. They were not determined at 330 and 360 since those experiments were intended as vapor pressure determinations.

All points on this graph are for 4-8 mesh material of approximately 97% volatile content. Materials of other size and purity will vary in the point of departure of the curves from the 45 degree lines at the left which represent maximum transport due to vapor pressure. See other parts of this report for the effects of purity and particle size.

490°

470°

430°

425

390

360

357

Rate of Sublimation of Charge
gm/cm²/hour

Curve showing approximately the rate at which the orifice acquires complete control over the charge

LEGEND

Curve	Point	Exp.	Comments
490	⊙	46	
470	⊙	47	
	Q	54	Decrease in rate caused by exhaustion of chg.
430	⊙	36-7	Low values due to partly clogged orif.
	⊡	38-44	17 cm² charges
	△	43-4	46 cm² charges
	Q	45	Low value at left due to partly clogged orifice or reaction with stainless steel. Values at right differ because of charge
425	b	52	
390	⊙	48	Upper set
	⊙	49	Lower set
360	⊙	50 and 53	
357	Q	51	

1000 100 10 1

Ratio of Charge Area to Orifice Area

31

32

FIGURE 11

TRANSPORT BY ORIFICES VS. RATIO OF CHARGE AREA TO ORIFICE AREA

The notes and legend of figure 10 apply also to this figure.

Additional data on transport by orifices are given in figure 13, where data for material other than 4-8 mesh TCl_4 are included.

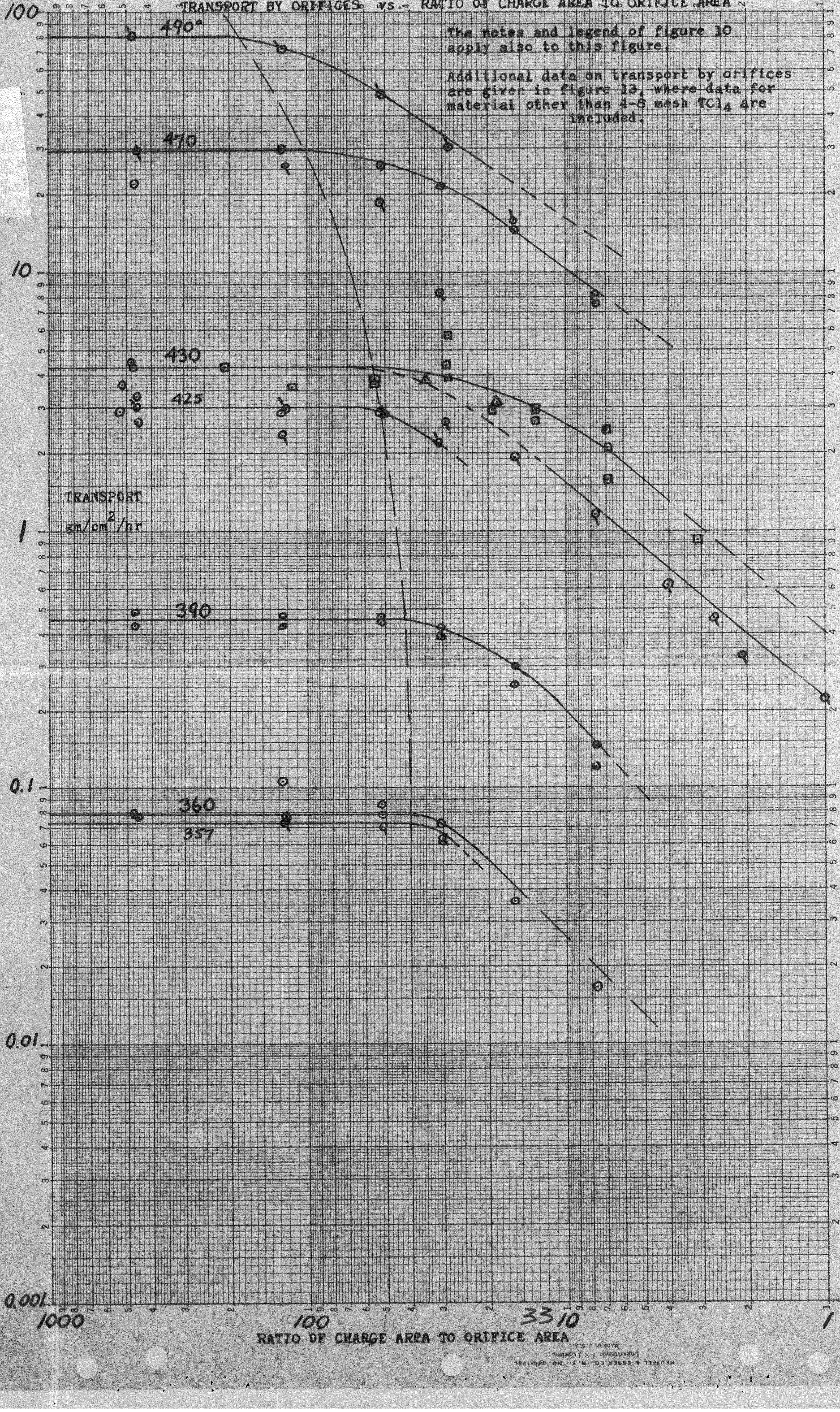
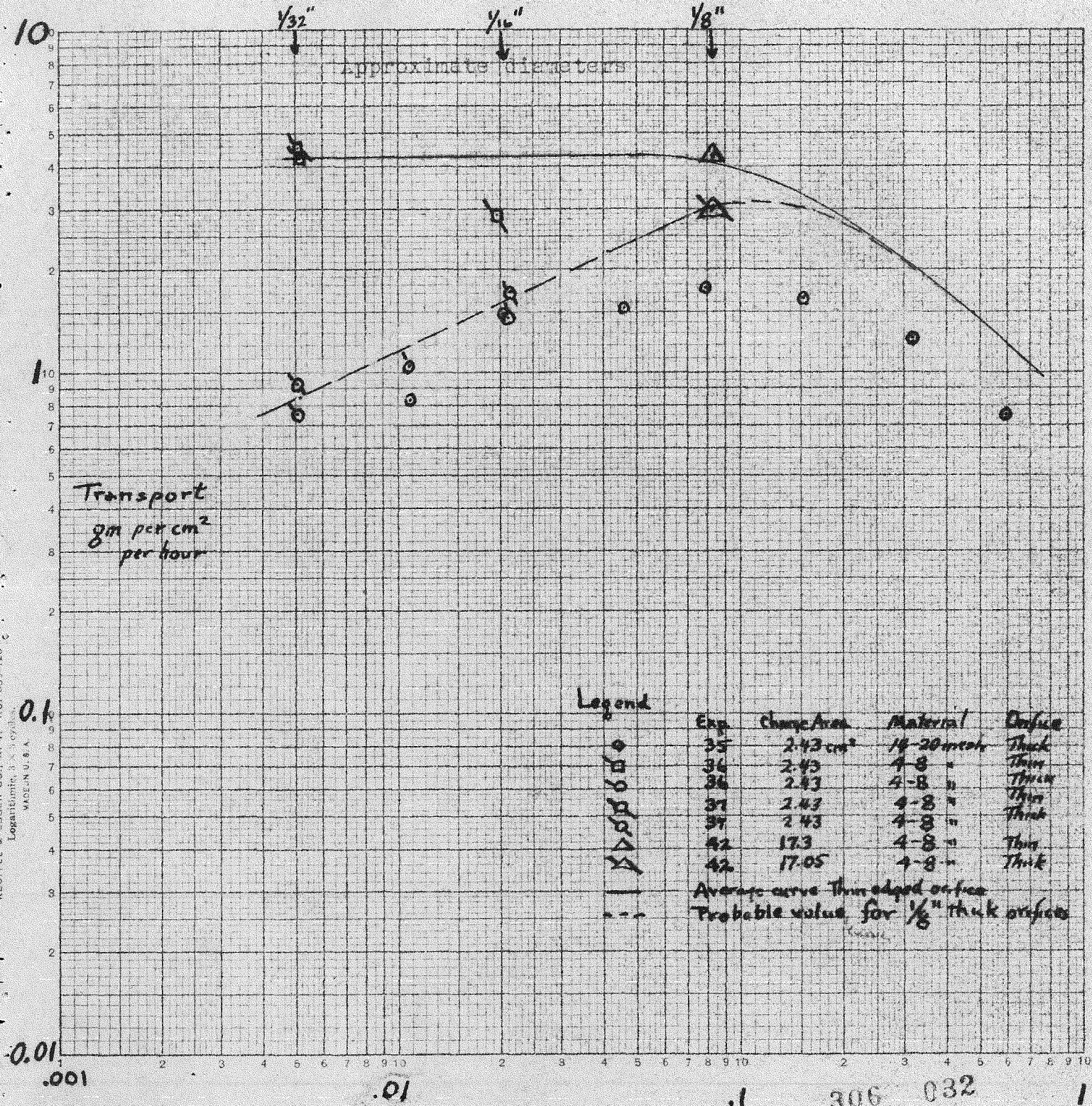


Fig. 12

34

COMPARISON OF THE TRANSPORTS THROUGH ONE-EIGHTH INCH THICK, AND THROUGH THIN-EDGED ORIFICES



306 032

Area of Orifice
cm²
except for △ points

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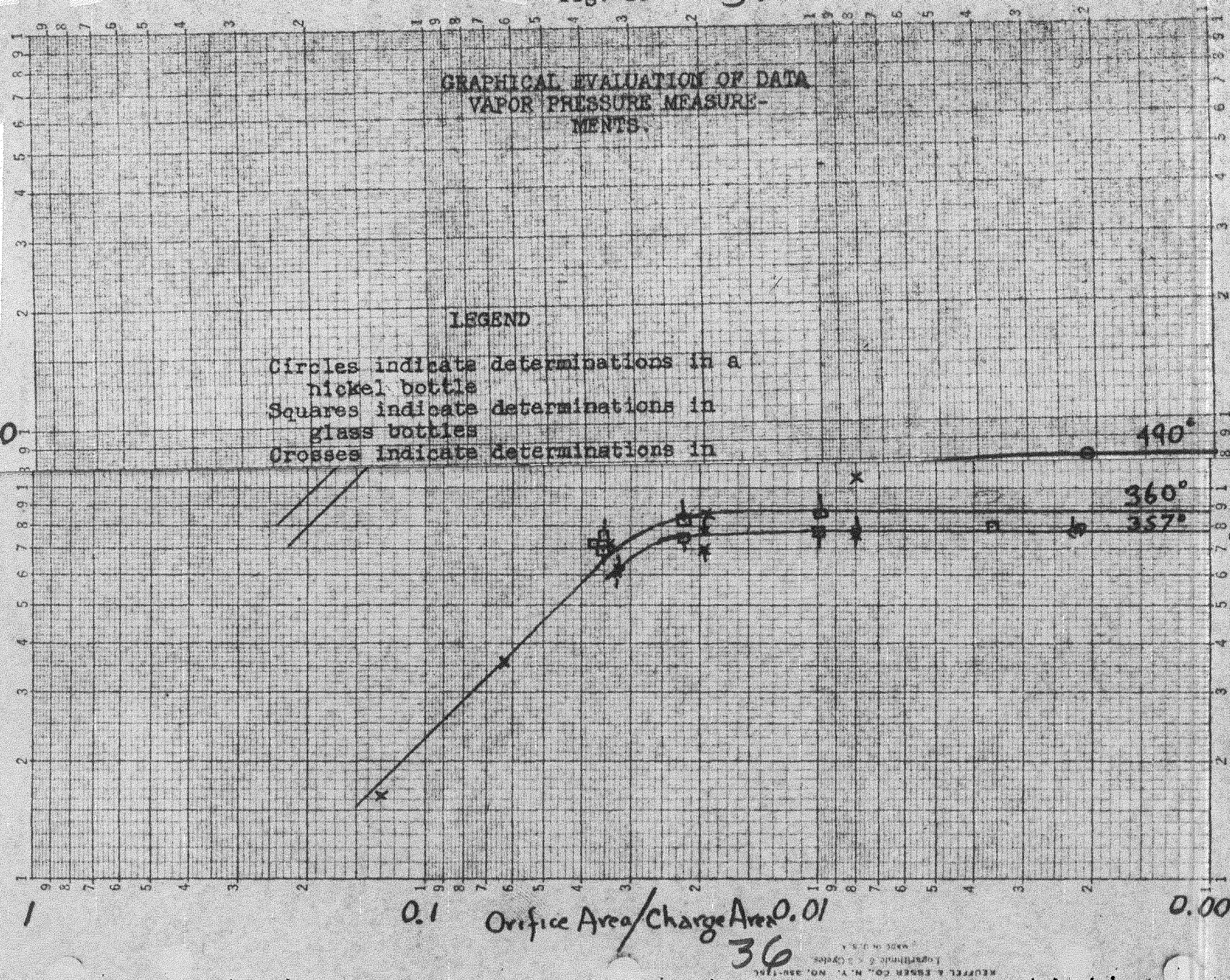
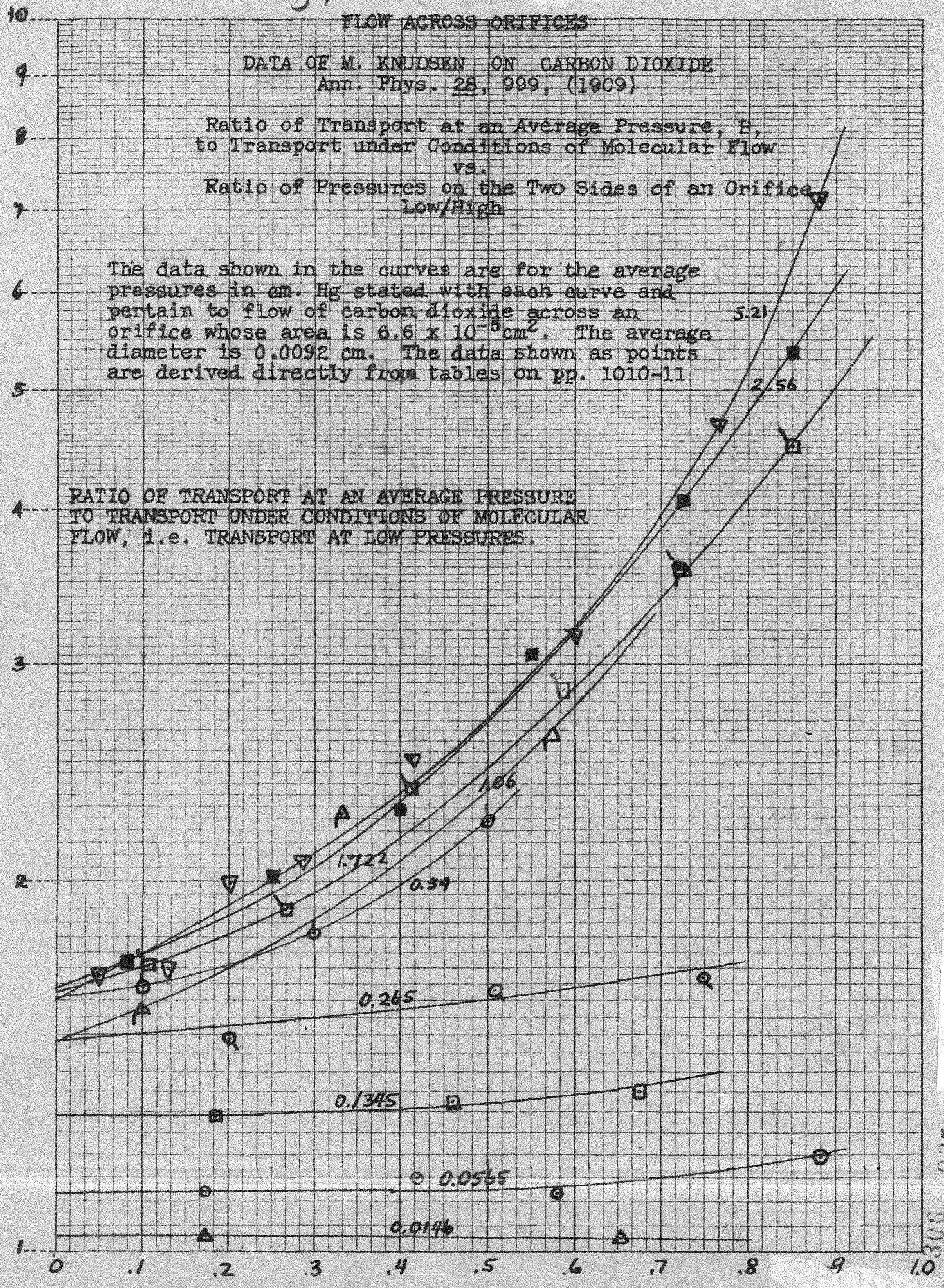
Fig. 13



37

Fig. 14



F.19-15

FIGURE 15
FLOW ACROSS ORIFICES

DATA OF M. KNUDSEN ON CARBON DIOXIDE
Ann. Phys. 28, 999 (1909)

RATIO OF TRANSPORT FROM A REGION OF PRESSURE, 2P, INTO A REGION WHERE THE PRESSURE IS SMALL IN COMPARISON TO THE TRANSPORT UNDER CONDITIONS OF MOLECULAR FLOW.
vs.
AVERAGE PRESSURE P

CURVE A is for a orifice of 6.6×10^{-5} cm^2 area, B for one of 5.2×10^{-6} cm^{-2} area. The λ=nd statements indicate the approximate location of the indicated relationship of mean free path to diameter of the particular orifice.

The points given with triangles and circles are derived from the data of p. 1009 of Knudsen's paper. Those given as squares are taken from Fig. 14 of this report.

These curves clearly show the changes in transport across an orifice as the mean free path of the gas passes from values much smaller than the orifice diameter to values much larger. The displacement in the abscissas of the two curves shows that the transport ratio is dependent on the diameter, and thus on the λ=nd value.

THE VARIATION IN FLOW FROM A PRESSURE, 2P, INTO A VACUUM AS A FUNCTION OF PRESSURE, ORIFICE DIAMETER BEING FIXED.

TRANSPORT RATIO

AVERAGE PRESSURE, cm.

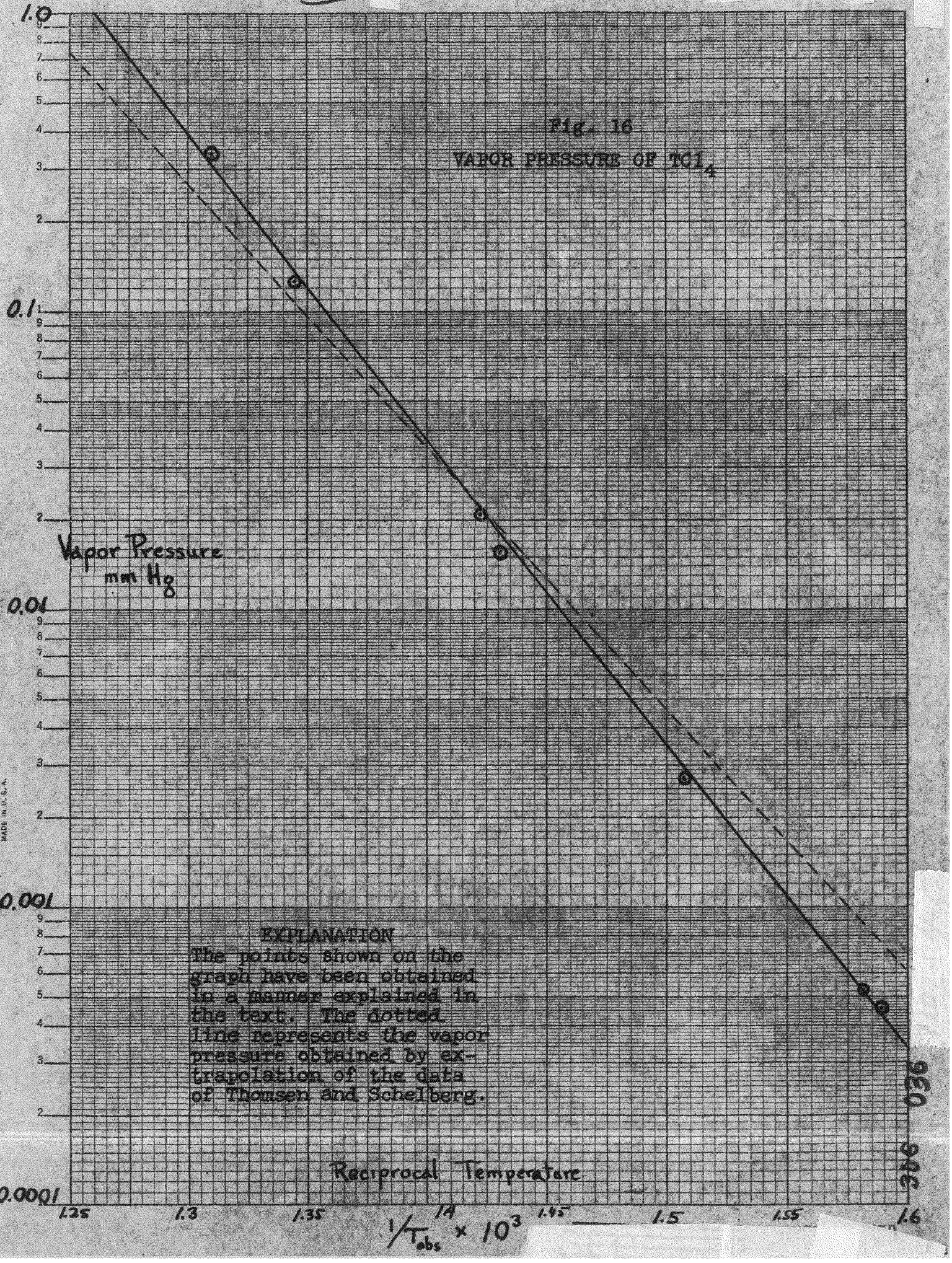


Fig. 16

VAPOR PRESSURE OF TCl_4

EXPLANATION

The points shown on the graph have been obtained in a manner explained in the text. The dotted line represents the vapor pressure obtained by extrapolation of the data of Thomsen and Schelberg.