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RATE OF SUBLIMATION. HISTORY OF TCl_4 CHARGES OF VARYING GEOMETRY

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RATE OF SUBLIMATION
HISTORY OF TCl_4 CHARGES OF VARYING GEOMETRY

By Manfred Mueller and Iva Streeter

1. Abstract

The experimental work described in this report tells the manner in which non-volatile matter enters into the rate of sublimation history of a charge and explains certain geometric factors which enhance, circumvent, or eliminate it.

The major conclusion is that the most satisfactory rate history is to be obtained from a charge bottle with restricted opening, this opening being fixed or variable.

2. Introduction

This work was undertaken for four reasons:

a. To obtain valid rate-quantity histories for TCl_4 charge materials, employing a method which is superior to the method described in Report Chem S 228.

b. To determine the manner in which geometric considerations enter into charge history.

c. To gather evidence which would lead to proper thinking on the role of non-volatile matter in radiant heating experiments.

d. To show experimentally at least one method of eliminating variations in rate of sublimation.

The experimental work is described in detail, as has been the custom, since it is felt that much was learned by close attention to facts which could easily have been ignored.

3. Apparatus

The apparatus used in these experiments and in those reported separately for the effect of radiant heat upon rate was a modification

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of a spring balance. In the first experiments a simple form was used, but this involved the defect that the charge moved with respect to the tube within the furnace and these movements were compensated for at intervals by raising the furnace. This apparatus was used in experiments 1, 3, 4 and 6. An improved model was built by Mr. P. H. Davidson and used with internal thermocouples in experiment 2 and 12-15. (The thermocouple was part of the spring system in experiment 2, as also in experiment 1 with the other apparatus, but was led out through mercury cups in experiments 12-15). No thermocouples were in the charges in experiments 3, 4 and 6.

The spring balance was attached directly to the furnace tube. Changes of the length of the spring were determined within ± 0.01 cm. Spring sensitivities were between 15 and 20 gm/cm. Lateral motions were no source of inaccuracy. The capacity of the balances was about 600 gm. and so permitted the study of moderately large charges.

The diagram shown on Figure 1 shows the arrangement of the apparatus.

4. Method

The charge bottles were filled and the assembly of apparatus made with dry carbon dioxide as the atmosphere wherever necessary.

After the apparatus had been assembled and vacuum applied, the final alignment was made and an initial reading taken on the scale. When the temperature of the furnace had reached a constant value, readings were begun. The spacing of the readings was determined by the rapidity of the sublimation.

At the completion of the experiment, dry carbon dioxide was admitted to the various parts, and the apparatus was carefully taken apart. The condensate on the support leading to the spring balance was weighed. The nature and condition of the remainder of the charge was noted and the materials were weighed, being separated by screening to determine the quantity of fine material which was left when this was thought necessary.

When the apparatus was left overnight for the long runs, as was necessary most of the time, the temperature was left up if the rate was low enough, and decreased to some lower value if the rate was high. The charge bottles were of stainless steel, 2" diameter by 4" length. The screens and cages were of pure nickel. Screens were 46% open area, being either 20 mesh x 0.016" or 16 mesh x 0.020". The nickel discs and sheets were cut from 0.010 to 0.015" thick sheet. The assembly of cages was completed by fastening with fine wire or by spot-welding.

The vacuum which was maintained throughout a sublimation was usually better than 1×10^{-4} mm Hg at the liquid air traps, though it is obvious that the pressure at the bottles or cages was determined by the hot TCl_4 vapor present there.

5. Plan of the Experiments

Exp. 1. It was desired to study side facing charges first. The chief interest in this experiment lay in answering the question as to whether the rate declined or remained nearly constant.

Exp. 2. To find the effect of partial closure on a side-facing charge.

Exp. 3. To contrast bottom-facing material to side-facing material. The result was conclusive.

Exp. 4. To find out what kind of improvement would be experienced by adding an 'opening-up' feature to the charge. The diagram with Figure 4 shows how this was done. There was an improvement.

Exp. 6. To find out how well an orifice would maintain constant rate with the best internal construction of charge cage used so far. The result was excellent, showing that the choice of a slightly smaller orifice would have maintained a constant rate value for over 90% of the charge. The special internal design is not a necessary feature of such bottle designs.

Exp. 12. To find out how top-facing solids compared with the others. The temperature was changed to 513 from 450 for reasons stated in notes 9-1 and 2. This threw open a whole group of possibilities and explanations, but we are not planning to push this any farther.

Exp. 13. In this and the following experiment up-facing coarse material was studied. It was not possible to use the same area to weight ratios and yet have the results correspond to the usual manner of packing charges.

Exp. 14. 15. Experiment 15 was a repetition of the incompleted No. 14. Both showed that the up-facing charges were very subject to the effect of non-volatile matter when the particle size was changed.

There still remain experiments on the study of side-facing charges of material containing fine particles. It is felt that such experiments would show a rate much improved in comparison to up-facing charges. The reason we did not study these first is that it was felt that the charge would fall out of the cage too easily. Such work will be completed when there is time for it, but will not be done until some more pressing matters are taken care of.

6. Summary of the Experiments

The experimental numbers which are omitted in Section 5 and Table I deal with studies in which internal radiant heaters were used, and these results will be reported separately.

In Table I the order of presentation is the same as that which is followed in the figures, with the exception of Exp. 12, whose Figure is placed last, the temperature of the major part of the experiment being far higher than the others. This order is based on the primary factor of the geometry, namely, the direction which the solid faces.

The experiments are summarized in Table I and in Figures 2 through 9. The bottles shown with the graphs are to the scale 1 cm equals 1 inch.

Detailed tabular and graphical records were kept on each experiment. The observed rate values showed considerable variation in many experiments in rather short time intervals. Careful study of the method showed that small variations were to be ascribed to techniques of measurement but that the larger variations were to be ascribed to small temperature variations and to rearrangements of the charge material. In order to eliminate the variations due to technique, the points shown on the figures are averaged over a sufficiently large time or quantity interval to make their uncertainty about the same as the ratio of the diameter of the circle to the maximum ordinate. Values for overnight settings can be seen at a glance by the space on either side of the points. Points which represent rates calculated by extrapolation from a lower temperature are placed in parentheses and the curve is shown dotted.

The abscissa stops abruptly at a point which is the original weight of the charge, and the correction for the material which is sublimed but not indicated on the spring balance (since it condenses on the support leading to the spring) is shown by the small arrow near the right edge of the abscissa. The small vertical line to the left of the arrow indicates the final spring balance reading.

Notes on the Figures

(The numbers refer to the Figure and the little boxed-in number on the Figure.)

2-1. Extrapolated from overnight rate at 423° C. by the ratio of vapor pressures at 423° C. and 450°.

2-2. Extrapolated from week-end rate at 404° C. by the same method.

2-3. Since the charge was completely used, there is no direct evidence on the cause of this plateau, though it is probably caused by the incidence of side pump-out due to cone formation. See Note 3-2.

3-1. These fluctuations were real. No reason has been found.

3-2. Experiment 14 was terminated on account of a short in the jacket thermocouple. It will be noted that the early history of experiments 14 and 15 was nearly identical and shows a marked difference from the slightly coarser material used in experiment 13. Experiment 15 was terminated at 55% completion since it was felt that enough had been learned and since it was of interest to see what such a charge looked like half way through. It was found to be consolidated into a truncated cone. Pump out contributions from the side of the cone appear to have been a major part of the contribution to the vapor on account of the lack of non-volatile blankets over about half of the sloping areas. This was accompanied during the run by an increase in the temperature difference between the charge thermocouple and the furnace thermocouple from 5 degrees to 10.

was accompanied during the run by an increase in the temperature difference between the charge thermocouple and the furnace thermocouple from 5 degrees to 10.

4-1. The sudden drop in rate was caused by a rearrangement of the charge sufficiently great to be noticed by violent motion of the spring balance. This indicated that the charge had maintained its position to this point and then made a single rearrangement to a lower level. The cylindrical stainless steel block which 'rode' on the top surface of the solid fell with the charge. The experiment had to be terminated soon afterwards on account of fogging up of the scale. This was prevented in later experiments by a vapor baffle.

5-1. The early rate history of this charge at 450° was not obtained, the charge having been at 430° until 26 gm were sublimed.

5-2. No direct evidence was obtained on this drop-off in rate. The cause may have been the same as noted in 4-1. If so, the subsequent small rise in rate at 80-100 gm. sublimed resulted from an increase in porosity of the charge as the surface again became less dense.

6-1. At the end of the experiment it was noticed that the individual levels of the assembly were about 1/3 full, and this was found to be the very fluffy residue. The residue weighed only 5.8 gm. and yet occupied the same space that 55 gm. of TCl_4 had occupied. Subsequent observations in Exp. 6 and by packing the residue showed that its density in packed form is about 0.3 gm/cc. Non-volatile material must be quite porous.

7-1. The line is drawn straight since the error in measurements and variations of temperature accounted for an uncertainty of 10% in the rate measurements. This experiment was the only one with quite low rate which was done on the first model of the balance.

8-1. This drop off was probably caused by a compacting and felting of the residues on the screen.

8-2. At the end of the experiment the charge bottle was removed very carefully. Upon examination with a mirror in the dry box the screen was observed to be completely felted over with light green residue ($TOCl_2$). This result was instructive, but wholly unexpected. The charge material had been chosen coarse so as to eliminate falling through of charge material. The screen had been woven by hand to be 78% open, 8 meshes to the inch. The result appears to have been caused by the felting properties of the slender filaments of the residue, but would not have been obtained without a shock-free assembly. It was clearly shown that the residue would fall through with light tapping on the body of the bottle. The underlying TCl_4 was then quickly bared. The top plate of the bottle had a deposit of large crystals on its under surface, indicating that the bottle had been pretty well closed up. Crystals will grow in such a fashion on slightly cooler surfaces.

9-1. The experiment was started at a temperature of 450° on the furnace. The average rate of 3-4 gm per hour was maintained for a few hours and then was followed by four hours in which no change in the spring balance was observed. It appears that the rate had fallen suddenly to something under 0.5 gm/hr. The explanation of this seems to be that the top layer of material sublimed well, and, when this was gone, the vapor had to diffuse through the overlying film of residue.

9-2. The temperature of the furnace was raised to 513° to find out what such a temperature rise would do. The charge temperature rose from 443° to 487°. The rate of sublimation was much higher than expected, and the reason soon became clear. It was found that a part of the non-volatile matter was being blown off the charge by TCl_4 vapor with sufficient force to travel 20 inches, mostly through a zone in which no TCl_4 vapor was left to carry it. It was subsequently found that the support wires and plate were plastered with almost 1/4 inch thickness of the residue, the width being slightly smaller than the object struck. It is thus obvious that the non-volatile residue is light enough to be transported by vapor at 0.25 mm pressure but not by vapor at 0.05 mm pressure, or whatever corresponds to these equilibrium vapor pressures in the cell of space from which the particles are moved. The observation on ejection of residue was made at 99 gm on the abscissa, but the phenomenon must have occurred at the outset of the 513° work.

9-3. At 47 grams on the abscissa it was noticed that the temperature of the charge was beginning to drop, though the rate had made a slight increase. It was written in our notes at that time that this must be caused by cone formation, since the temperature of the thermocouple could indicate a lower value only if it was more completely surrounded than before by the low temperature surface.

9-4. The effect of this on the rate is shown by the rise of the rate curve to 50 gm/hr. The lowest reading of the charge thermocouple was 459°, with the furnace at 513°. The bottle wall must have been around 490°. The decrement in rate from 120 grams on must be from a combination of causes, including blanketing by non-volatile material.

9-5. The apparatus was left at 513° all night, and upon dismantling the bottle was found to contain 6 grams of residue. Another 2 grams had been blown out. The thermocouple was not exposed.

This experiment showed that the effect of non-volatile material on the rate becomes much less important, provided the pump-out area is large, at charge temperatures above 450°, on account of partial removal of the residue and on account of the higher pressure of the vapor.

7. Discussion

In Figure 10 all the experimental curves are brought together, the ordinate being the percentage of the initial rate (which is quite arbitrary for several of the experiments) and the abscissa being the percentage of the whole charge. Too much emphasis is not to be placed on this comparison, since it would be strictly valid only if the ratio of area to charge weight were constant. Since this ratio is much larger for the side-facing charges, it must be realized that the results for these include the rather large geometric variations which occur in such cylindrical charges.

It is more proper to separate the experiments into two groups on the basis of the kind of rate which is to be expected from the particular geometry. Thus materials which face upwards are to be expected to have constant rate if they are 100% pure, and this rate would be only slightly lowered in the early part of the experiment by the decrease in particle size which is inevitable at the surface. There should be a decrement as the material becomes thinner than the minimum layer which gives a nearly maximum rate. Gross departures from this nearly horizontal rate line are to be ascribed to nonvolatile material if sintering does not occur, and to changes in the effective area of the charge if it can be shown that sintering has resulted in cone formation. In Figure 11 those experiments which should have resulted in 'constant' rate are shown together. Several facts stand out. The marked change in the rate curves upon employment of 8-10 mesh material as against 6-8 mesh material is shown in the curves marked 15 and 13. The dotted line shows what is expected of still finer material (Exp. 12) in the absence of sintering. That the effects shown are due to non-volatile residue is demonstrated by the upside down charge of slightly coarse material used in Exp. 3. The effect of sintering upon change of area of the charge is shown by the curve of the higher temperature work in Exp. 12. The corresponding effect in Exp. 13 and 15 was mentioned in notes 2-3 and 3-2.

The side-facing charges are fundamentally different than the up or down-facing charges. Suppose that a particle at the surface decreases in size and eventually becomes residue. If it does not settle down, it plugs nothing. If it falls, it will close off 1/3 of the area at the most, whether it falls on other non-volatile matter or on fresh material. Thus one would expect that the non-volatile matter would effect at most a 33% reduction in rate. However, since practically all the charge is taking part in the sublimation (for geometries and materials we used), there should be a gradual change in particle size and a settling of the mass, which should have a continuous effect upon the rate. The simplest analysis would result in the conclusion that the rate should decline constantly. If the solid does not settle continually then the rate is not likely to follow such a simple rule. In note 4-1 it is stated that the solid does not settle continuously, but at intervals, thus introducing an unsteadiness in the rate curve. In Figure 12, the various experiments with side-facing solids are brought together (not including Exp. 6), and it is seen that the combined effect of the non-volatile matter and the occasional settling is not as bad as would have been expected on the basis of settling alone.

There is no reason for which charge material containing fine particles is to be expected to have a poorer history than the coarse material, and two reasons for which it should have a better history:

1. Sintering results in a mass which does not settle;
2. The effective area of the mass will still be about 1/2 of its original amount when the charge is 3/4 consumed.

The results presented in this report permit the following conclusions:

I. For granular material, of coarse grade, at temperatures not exceeding 455° C, open charges:

  a. The non-volatile material contained in the charge is of such nature as to present no great advantage to side pump out of the charge as against top pump out for geometries such as were used. See, however, Section 7.

  b. It is easy to design charge geometries which give better histories for side pump out than for top pump out, merely on account of the increased ratio of area to weight, and the opportunity this gives of closing down the opening of the bottle.

  c. Charges pumped out from the bottom with the solid resting on a screen across which the vapor flows suffer a rapid decrement in rate due to loading of the screen. This probably will not be the case for assemblies undergoing moderate mechanical vibration.

  d. For top facing material the non-volatile material has a rapidly increasing effect as the particle size is decreased, such that statement (a.) above is true only for the coarsest material.

II. For granular material including fines, open charges:

  a. At about 450° bottle temperature there is still the rapid decline in rate for up-facing charges which one would expect at lower temperatures. This may, however, be only a temporary condition.

  b. At higher temperatures charges containing fine material will sinter in such a way as to improve their sublimation properties, due to the removal of the material closest to the walls and the consequent excellent condition of these regions for pump out. It is to be expected that the major contribution of such charges to the vapor is from the steep surfaces where the effect of the non-volatile matter is not as large.

  c. It is to be expected that for any size of particle the effect of the non-volatile material on the rate becomes of small importance at temperatures above 500 on the bottle or 460 on the surface of the subliming material. This appears to be related to both the greater rate of flow of vapor through the non-volatile matter and to the partial removal of the non-volatile matter by the vapor 'wind'.

d. See the discussion, par. 7, for side-facing charges.

III. For charges in bottles with restricted openings, the openings being small enough to give vapor pressure equilibrium in the bottle:

a. The rate is obviously a function of the temperature of the charge alone, if the opening is fixed.

b. The rate is proportional to changes in the area of the opening if the temperature is fixed.

c. It is possible to design bottles which will maintain stated rates of sublimation over as much of the charge content as is desired.

The implications of this work on radiant heat studies and on the problem of the non-volatile residue will be treated elsewhere.

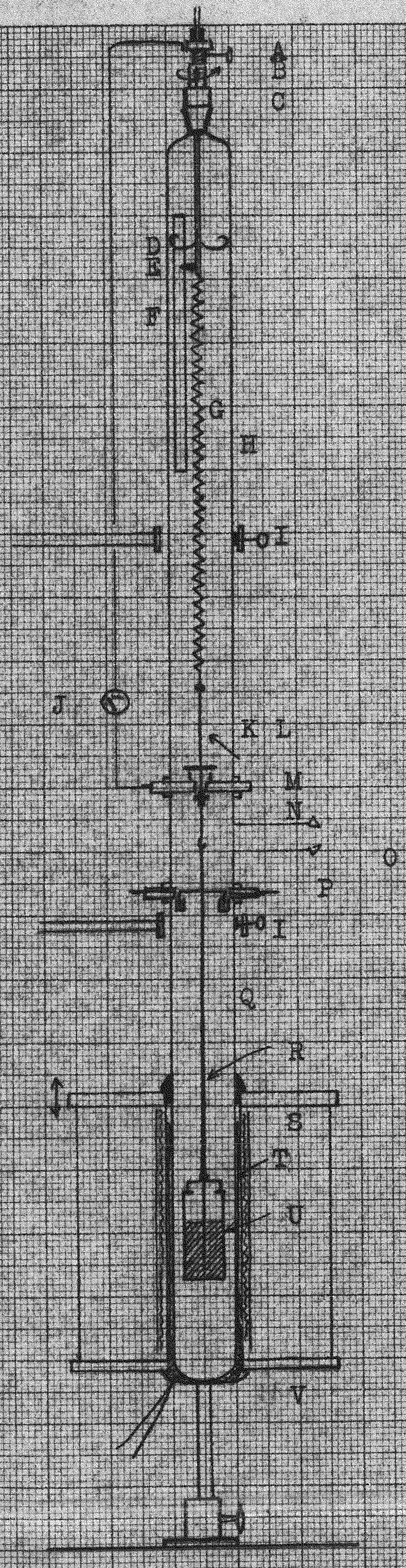
Table I

Experiment Number 12

'2	13	14	15	1	2	4	6	3
	Top	Top	Top	Side	Side	Side	Side	Bottom
ines	6-8	8-10	8-10	6-8	4-8	6-8	6-8	4-8
513 487 to 458	452 - 448 - 39	452-1/2 - 447	452-1/2 - 447-1/2	430-40 - Shorted	432 456 426 442 422 437	431-6 - -	450 - -	439-41 - -
/8"	1-7/8"	1-7/8"	1-7/8"	1-3/8"	1-3/8"	1-3/8"	1-3/8"	1-3/8"
/8"	2-3/4"	2-3/4"	2-3/4"	3"	3"	3"	2-3/4"	2-1/4"
8	17.8	17.8	17.8	84	84	82	87	17.7
6	9.6	9.6	9.6	22.5	6.4	22.5	0.596	17.7
85	1.85	1.85	1.85	3.7	13.1	3.6	146	1
091	.070	.0785	.0765	.49	.50	.465	.53	.0945
4	253.4	226.9	232.6	170.6	169	175.8	165.2	187.6
	233	-	129	76	130	151	155	109
	12.5	-	10	-	10	9	7	8
8	3.1	-	(3)	(3)	1.9 - 3	3.3	2.9	(3)

ined by weight, the non-volatile matter was estimated. The residue for experiment 4 was weighed and ontained 92% $TOCl_2$, 3.3% $CrCl_3$, 0.15% Fe_2O_3, and 4.5% other matter. It is not to be forgotten that l non-volatile residue quantity stated in reports in the amount of TO_2. $TOCl_2$ is the origin of most eported and is present in the ratio 2.4 to 1 for the TO_2.

FIGURE 1



A Coarse and fine adjustments for spring extension
B " "
C Body of Wilson Seal
D Centering tripod
E Fine flat pointer
F Scale
G Steel spring, about 100 turns of 0.031" diam. wire on .75 cm radius
H Pyrex tube, 70mm, about 30" long
I Alignment clamps and cushioned screws, cork tipped
J Detection devise, which was either a buzzer, light, or deflection meter (adapted from a resistance meter)
K Spring extension, 1/16" diam.
L Flat ground contact plate to contact tripod underneath.
M Brass disc equipped as base for the balance. The pump-out hole was 1/4" diam. and was baffled
N Pyrex connection unit
O Vacuum system: High Capacity
  Two large liquid air traps
  Manometer
  McLeod Gage
  Mercury diffusion pump
  Mechanical pump
P Brass ring, with insulated leads for thermocouples, power, and insulated mercury cups
Q Furnace tubes, 65mm. i.d., length from 15 to 30"
R Support rod, which was a porcelain thermocouple tube, 1/8" o.d. as shown but which for other models was usually a nickel wire
S 3" diameter electric furnaces of either 12" or 18" length
T 1/8" thick brass cylinder to which jacket thermocouple was attached. The length of this cylinder was 10"
U Charge bottle or cage
V Support for the furnace tube.

FIGURE 2

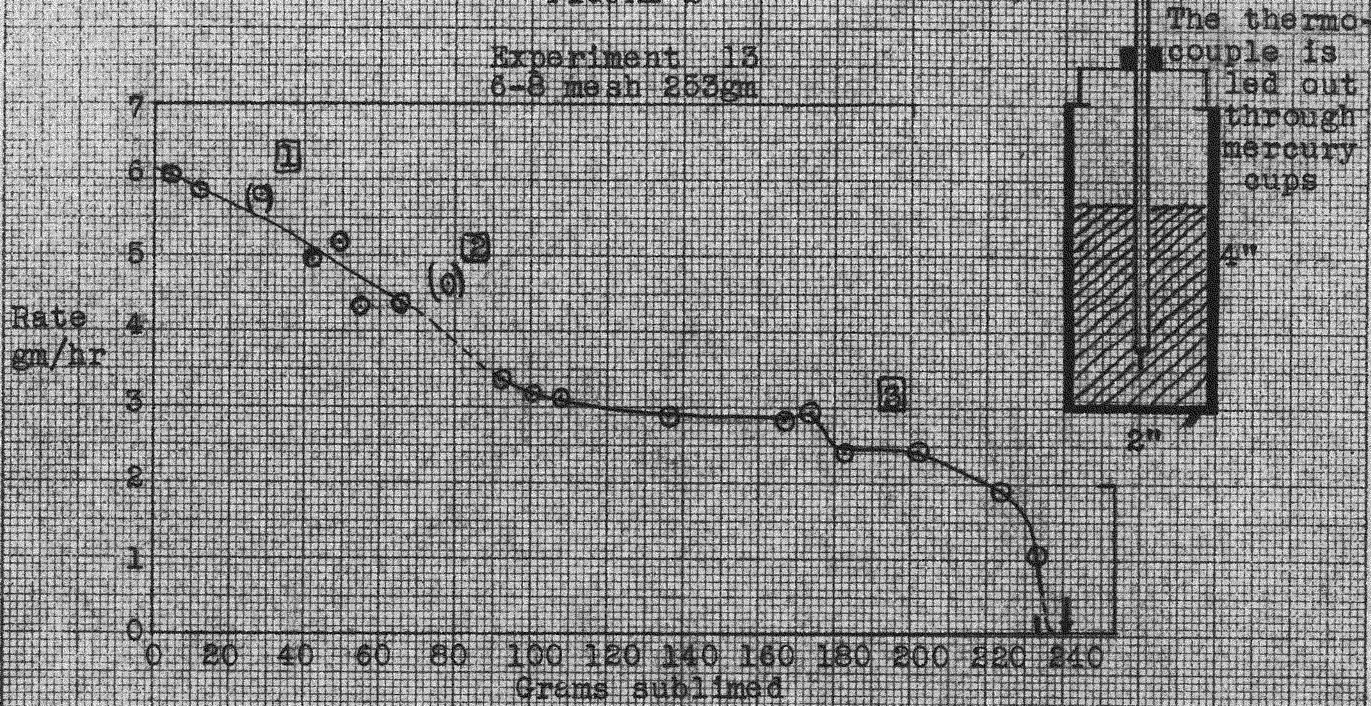


FIGURE 3

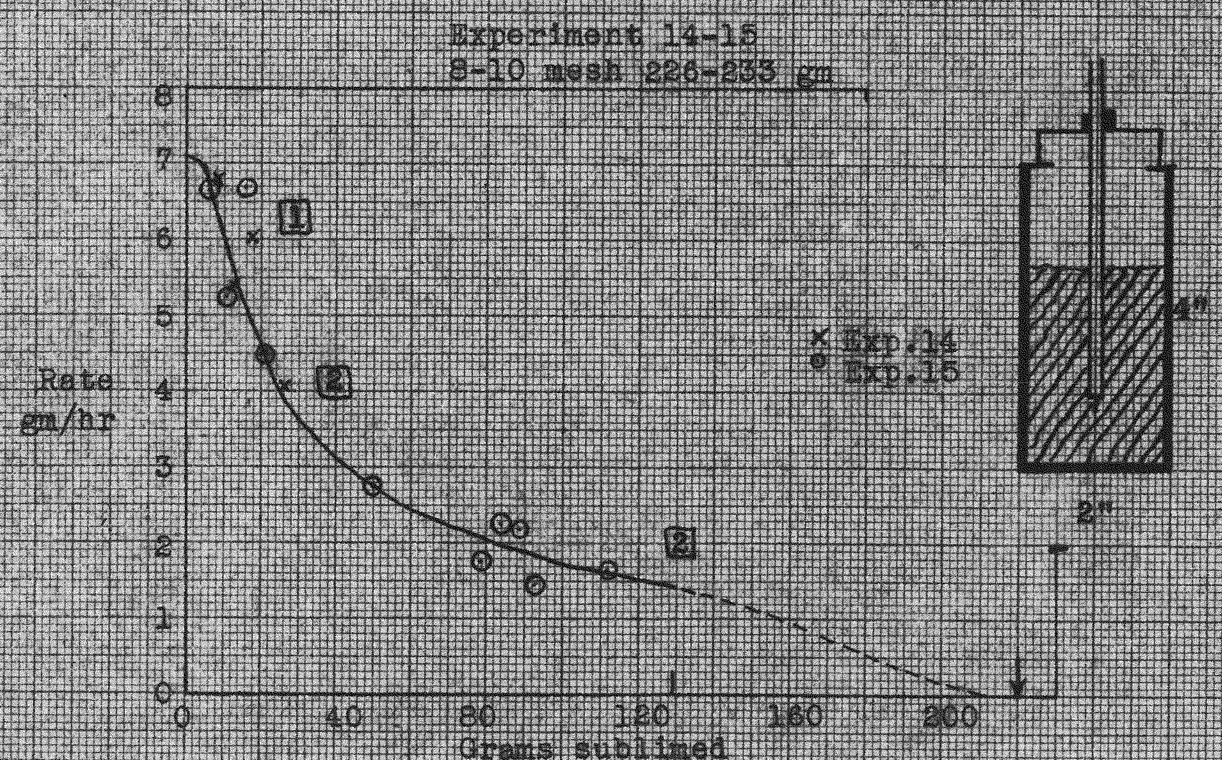


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FIGURE 4

Experiment 1
6-8 mesh 170 gm.

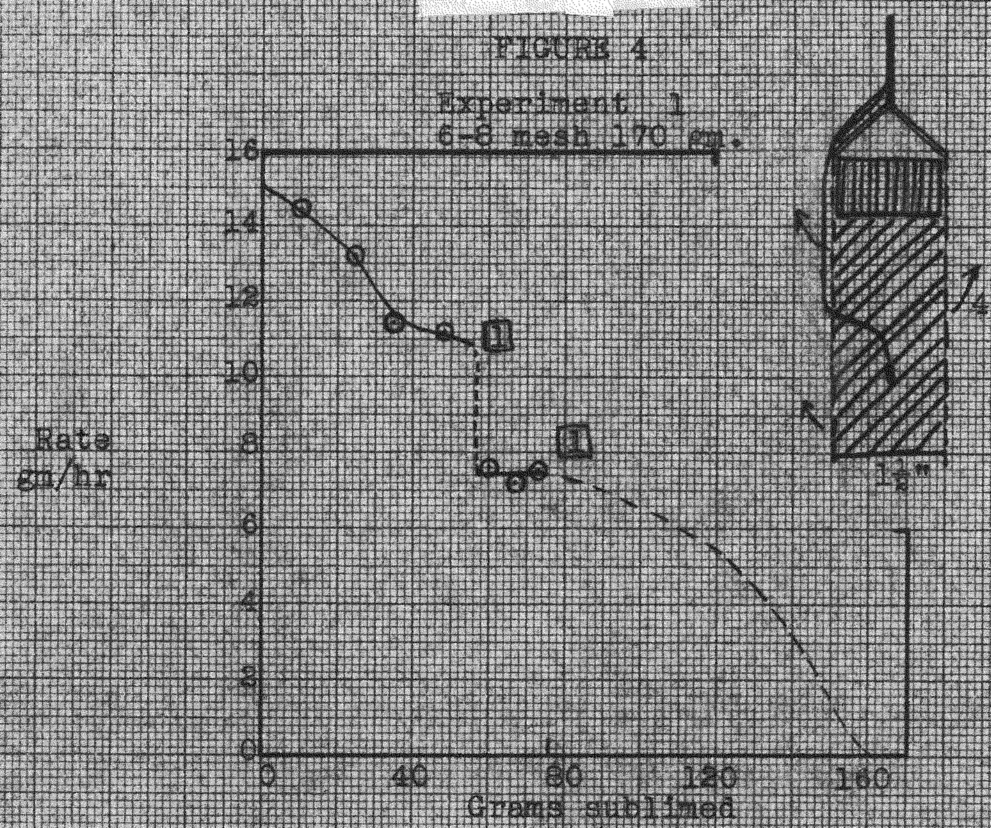


FIGURE 5

Experiment 2
4-8 mesh 169 gm

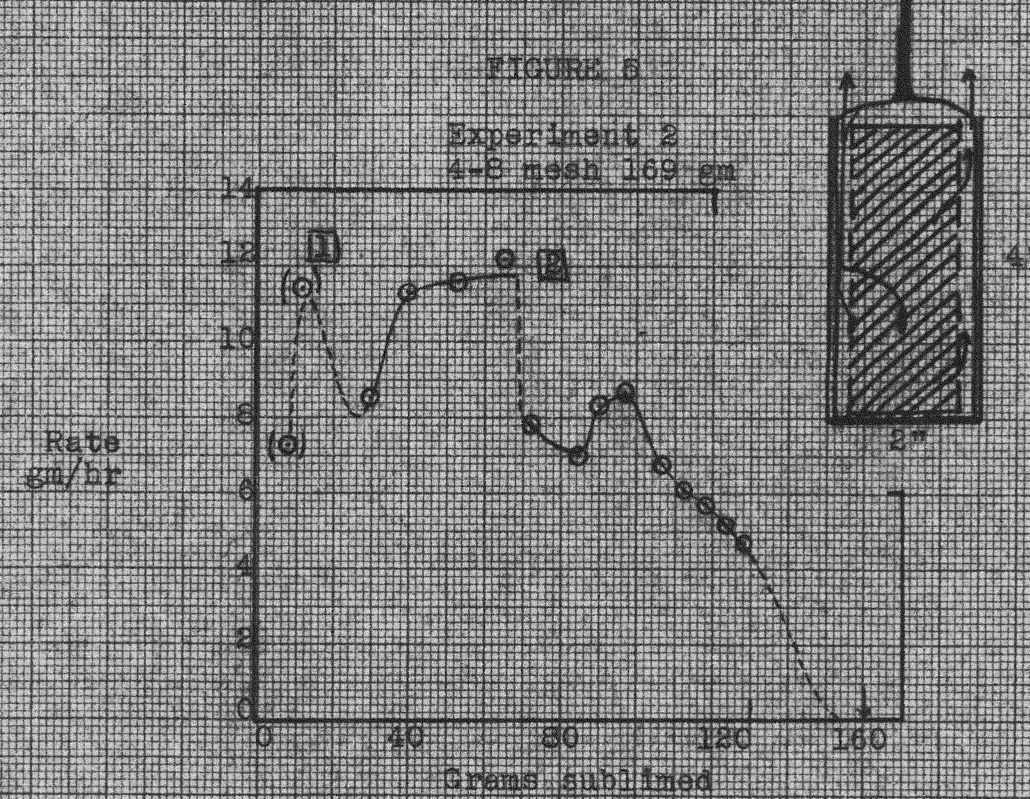
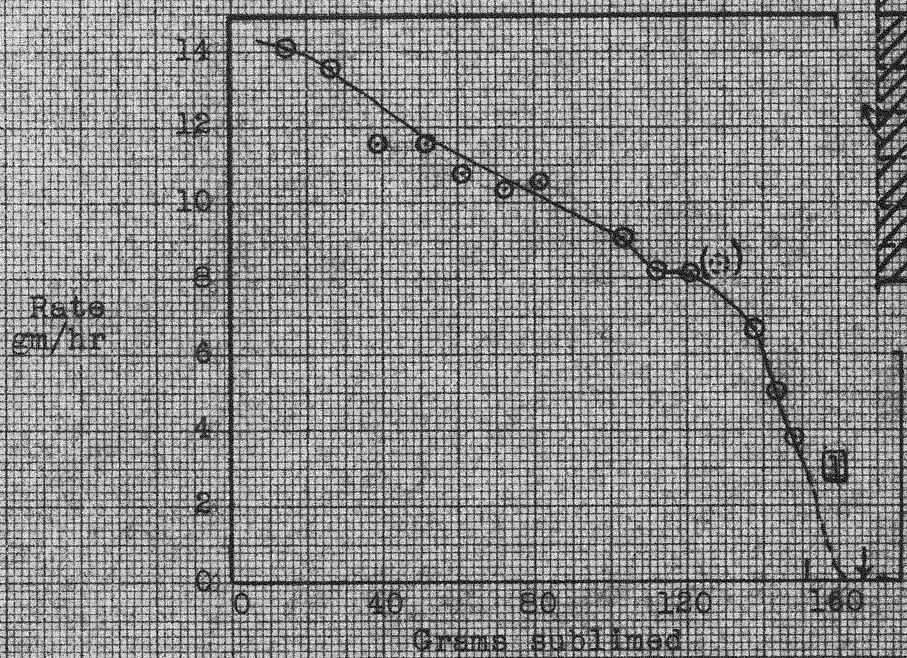


FIGURE 6

Experiment 4
6-8 mesh 176 gm



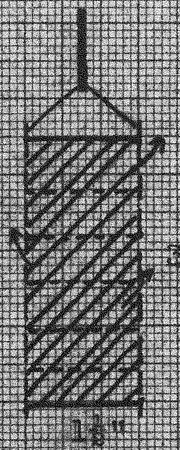
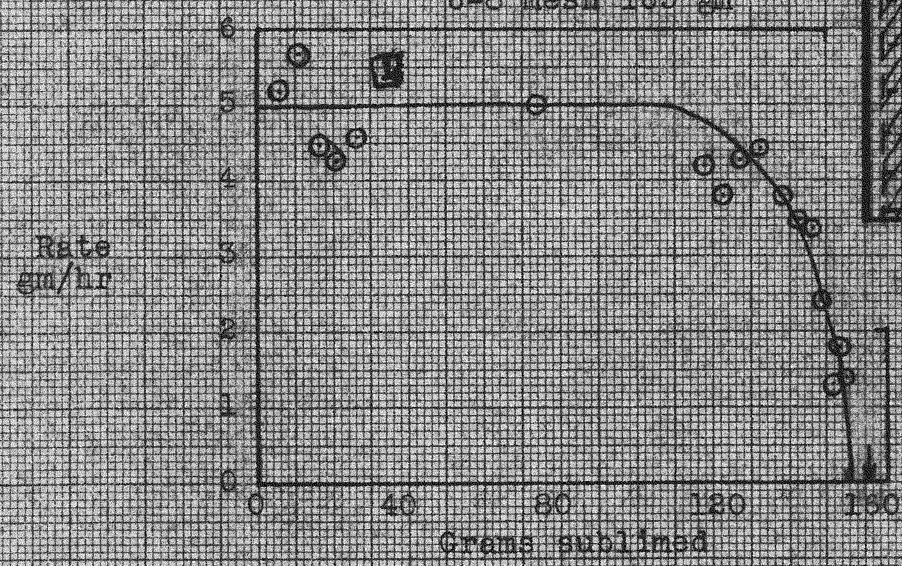


FIGURE 7

Experiment 6
6-8 mesh 165 gm



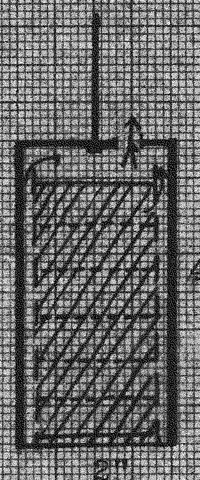


FIGURE 8

Experiment 3
4-8 mesh 188gm

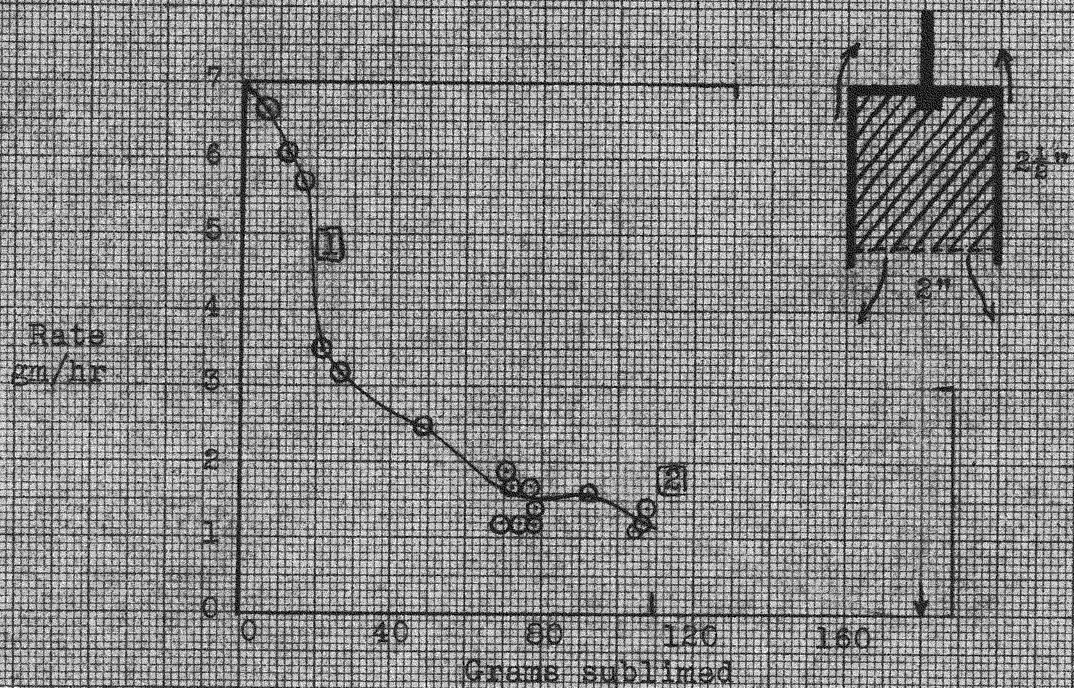
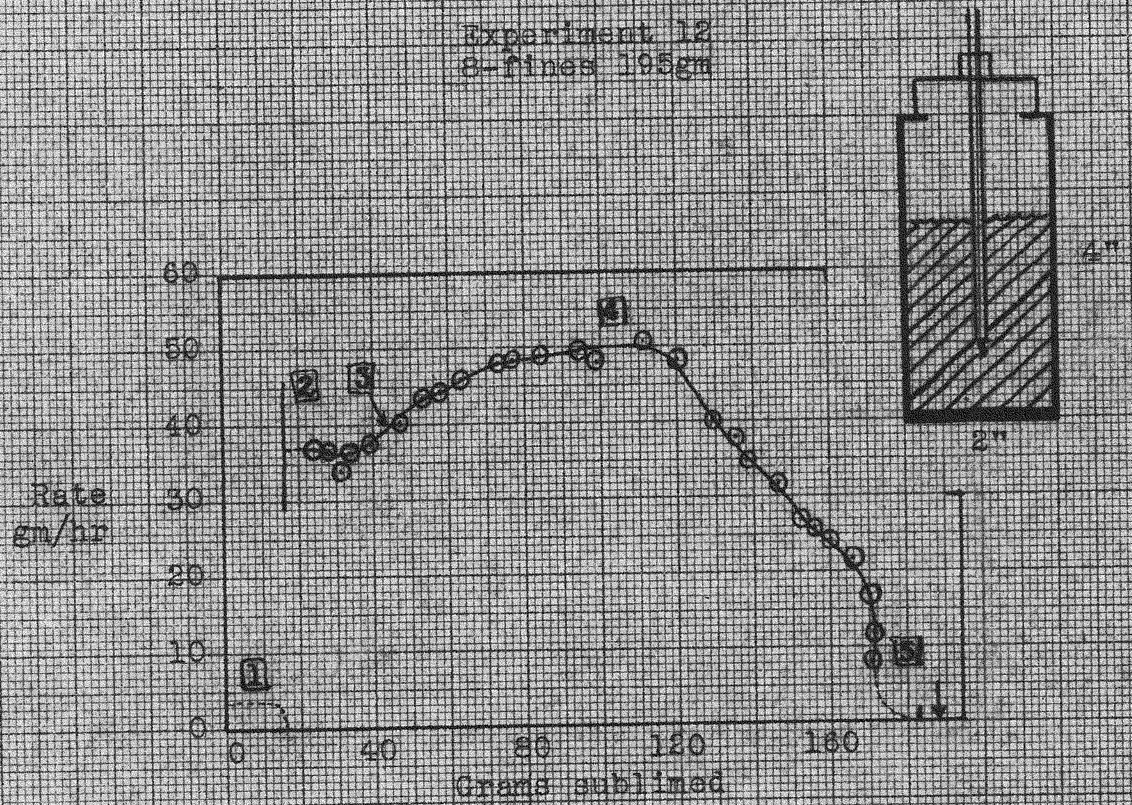


FIGURE 9

Experiment 12
8-fines 195gm



Note: The small dotted curve represents the furnace temperature at 451° whereas the main curve represents the furnace temperature at 513° C.

FIGURE 10

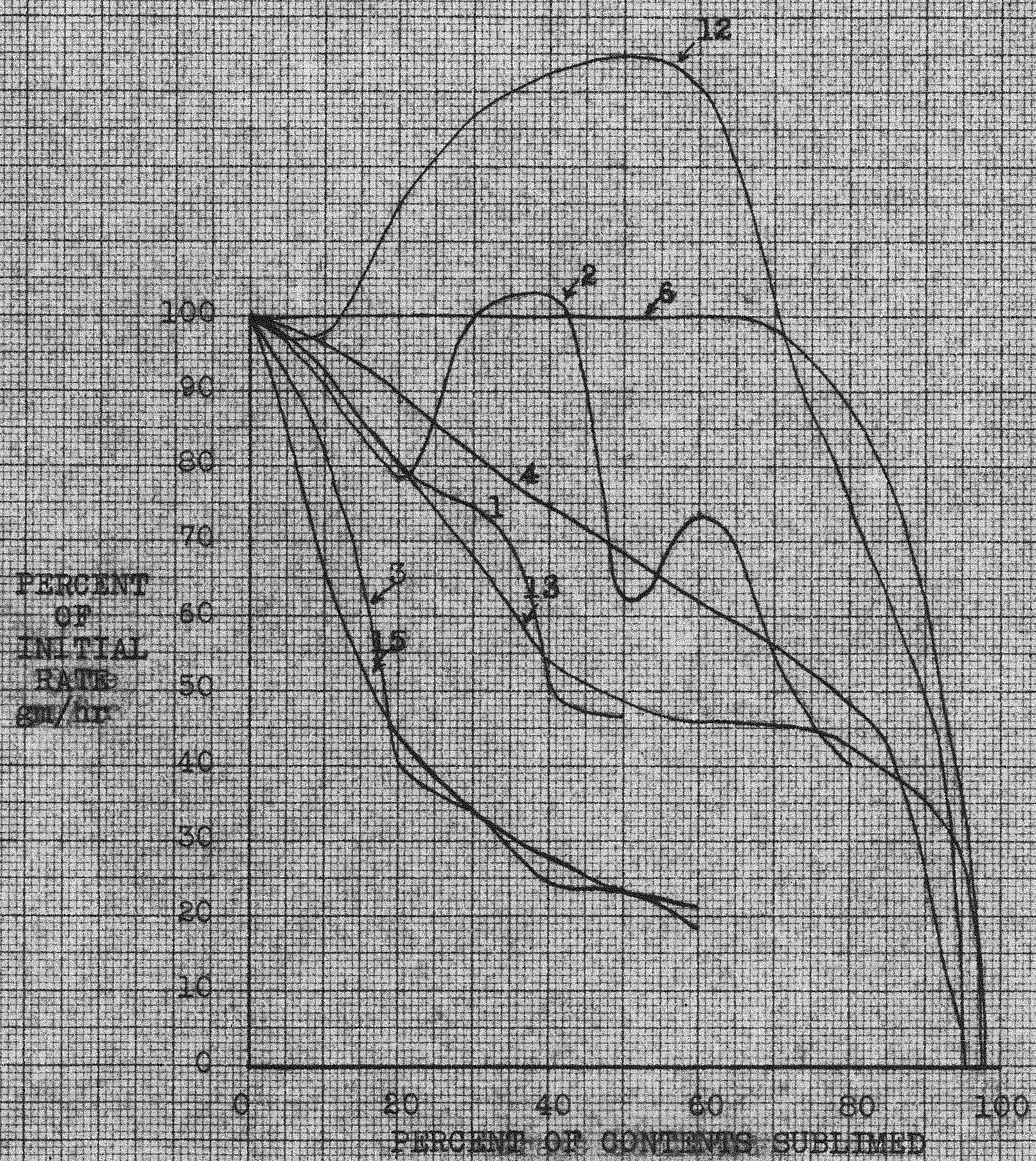


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FIGURE 11

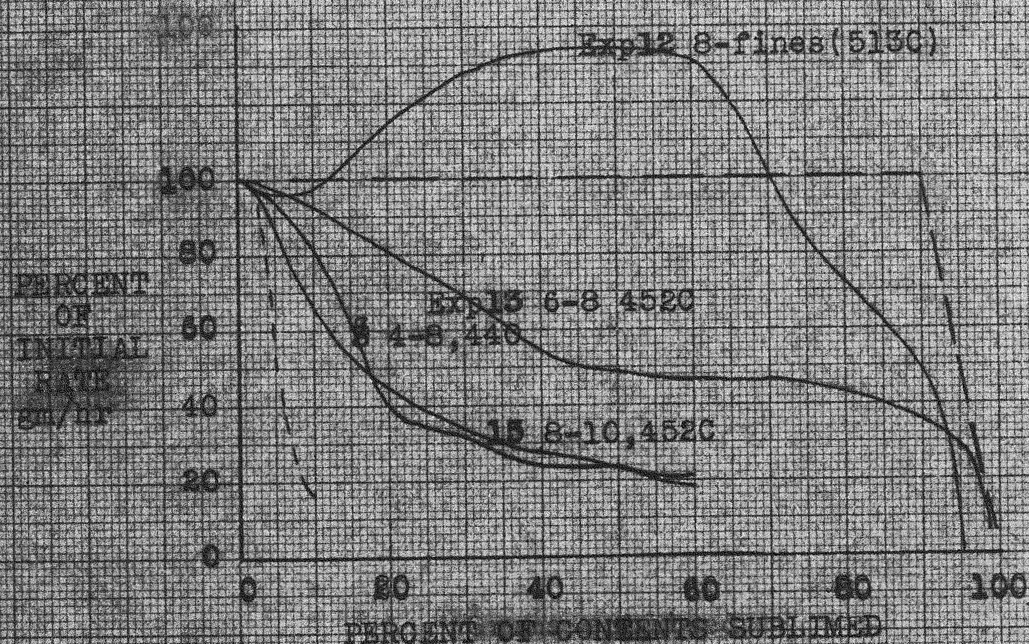

FIGURE 12