SOME ASPECTS OF DIFFERENTIAL THERMAL ANALYSIS EXPERIMENTS APPLIED TO THE ANTRIM AND BEDFORD-BEREA SHALES FROM OAKLAND COUNTY, MICHIGAN

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SOME ASPECTS OF DIFFERENTIAL THERMAL ANALYSIS EXPERIMENTS APPLIED TO THE ANTRIM AND BEDFORD-BEREA SHALES FROM OAKLAND COUNTY, MICHIGAN

By

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ABSTRACT

A gray noncarbonaceous and a black carbonaceous shale were subjected to a series of differential thermal analysis experiments. It was determined that although a simple procedure was sufficient to produce consistent results with the gray shale, this was not true of the black shale.

The black shale was then subjected to further experiments designed to establish the effects of sieve size, mass, degree of packing, volume, and atmosphere on the major thermal reactions, and it was found that these variables produced, within limits, predictable trends which could be observed on the thermal curves. Possible causes of the major peaks were also discussed.

ACKNOWLEDGMENTS

The author wishes to express sincere thanks for the cooperation of the staff of the Department of Geology of Michigan State University, and especially to Dr. B. T. Sandefur and Dr. H. B. Stonehouse for their valuable advice and assistance.

He is also indebted to Mr. G. Uehara and the staff of the Department of Soils of Michigan State University for assistance with the differential thermal analysis apparatus, located in that department, and to Mr. Mantek of the Michigan Geological Survey for assistance in locating material.

THESIS

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INTRODUCTION

Discussion

Differential thermal analysis is a method of study that determines the temperatures at which thermal reactions take place in a material to which heat is added at a constant rate, and the character and intensity of these reactions. The reactions may involve physical changes such as dehydration, recrystallization, volatilization, and melting, or chamical changes such as oxidation and reduction.

The results are plotted as a continuous curve with furnace temperature on the horizontal axis and thermal reactions on the vertical axis and with exothermic reactions, by convention, expressed as upward deflections and endothermic reactions as downward deflections from a horizontal base line. At a given furnace temperature, the divergence of the curve from the base line is a measure of the difference in temperature between the sample and the furnace and is therefore a measure of the intensity of reaction.

Although differential thermal analysis has been used on such materials as coal, sulfides, carbonates, and quartz, the method has

been applied for the most part to the study of clay minerals and known mixtures of clay minerals.

It has been found from these experiments that dehydration and loss of crystal structure are endothermic reactions, whereas chemical reactions, oxidation, and phase changes are exothermic reactions.

For further informaton on theory of differential thermal analysis see Grim, Clay Mineralogy (New York: McGraw-Hill Book Co., 1953), pages 194-210.

Purpose

The original purpose of this research was to investigate the possibility of applying differential thermal analysis to the correlation of shales. It was found, however, after several trials (experiments 2 through 4) that results were not consistent, due to several variables.

It is therefore the purpose of this thesis to determine the nature of, and the variables involved in, the thermal curves of a shale by means of a series of experiments using differential thermal analysis.

MATERIAL

The material used in this thesis was obtained from the following wells:

1. Grey and White #18967

   L. Miller #1 30 - 1 N - 7 E

   Oakland County NE 1/4, SE 1/4, SE 1/4

   Interval: 810 ft.-850 ft. Black cherty carbonaceous Antrim shale of Basal Mississipian age.

2. Smith Pet. Co. #1236

   Smith #1, 1932 5 - 1 N - 7 E

   Oakland County SW 1/4, SW 1/4, NW 1/4

   Interval: A. 335 ft.-340 ft. Gray cherty noncarbonaceous Bedford-Berea shale of Lower Mississippian age.

   B. 390 ft.-470ft. Black cherty carbonaceous Antrim shale.

Samples taken from these intervals in the Antrim and Bedford-Berea formations were used because they are typical representatives of black and gray shale.

APPARATUS

The reactions in a differential thermal analysis apparatus take place in a sample-holder, which is a nickel cylinder drilled with two holes, one for a thermally inert material and the other for the sample; each hole is capable of holding about 0.3 gm. Small holes for the thermocouples are drilled through the side of the cylinder into the spaces designed to hold the sample and the intert material. A nickel disk the same diameter as the holder is used as a cover. Aluminum oxide was used in this research for the ''inert'' (a common term used in place of ''inert material''). The rate at which the temperature of the sample-holder increased was governed by a program-controller, a motor-driven auto-transformer which increased the voltage to the furnace. The thermocouples of the platinum-platinum 10 percent rhodium type were hooked up to a reflecting galvanometer through a variable resistance. Variations in the direction of the light beam from the galvanometer were plotted as a continuous thermal curve by an automatic recording device. A continuous curve was also plotted of furnace temperature against time by another automatic recorder.

The sensitivity of the apparatus could be changed with the variable resistance mentioned above which was set at 150 ohms for all experiments.

A cover, designed to contain atmospheres other than air at normal pressure, could be placed over the furnace. These atmospheres were applied to the furnace through a series of tubes leading into the cavity between the furnace and cover or through a porous plug at the base of the sample. Two additional porous plugs were available which could be placed, if desired, on top of the sample and inert.

For a more extensive treatment of the apparatus see Grim, Clay Mineralogy (New York: McGraw-Hill Book Co., 1953), pages 194-210.

The following were used for cleaning the sample-holder and transferring material:

Rubber vacuum syringe with rubber tube and glass nozzle.

Camels hair brush.

A fine wire.

Spatula.

Small glass funnel.

Small screw-top bottles.

The following items were used for preparation and treatment of samples:

Metal rod about six inches long.

Glass rod weighing 5.6611 gm.

Knife.

Diamond mortar.

Porcelain mortar and pestle.

Chainomatic balance.

The following set of micro sieves, made by the Precision Scientific Company, were used to obtain samples consisting of particles within desired size grades:

Mesh	Opening in mm.
60	0.25
80	0.20
100	0.15
120	0.13
150	0.10
200	0.08
pan	<0.08

GENERAL PROCEDURE

Iron was first removed with a small magnet. The shale to be tested was then broken down mechanically to pass the 60-mesh sieve by either grinding in the porcelain mortar, or crushing in the diamond mortar and then grinding in the porcelain mortar.

This material was passed through the required sieves and then placed in labeled bottles.

The left-hand hold of the sample-holder was filled with the inert which was completely settled by tapping the side of the holder about thirty times with the metal rod. This procedure lowered the top of the inert sufficiently to insert a small porous plug which prevented the inert from spilling when the sample was subsequently placed in the right-hand hold of the sample-holder and subjected to the controls of the experiment. When uniform packing was required throughout several trials of an experiment, each sample was initially packed by tapping the side of the sample-holder thirty times with a short metal rod. A glass rod was then set vertically on top of the sample; the weight of the rod was sufficient to produce the final packing. Since the sample was a variable distance from the top of the holder, a porous plug was not used. Finally the nickel cover was placed on the sample-holder and the furnace lowered into position.

The furnace was heated from room temperature to 1000°C. in about an hour and a half. An additional three hours were then required for the furnace to cool sufficiently to remove the sample and replace it with another.

The furnace heating rate is shown on all thermal curves, and a typical curve of furnace temperature against time is shown in the conclusion.

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Experiment 1

Purpose

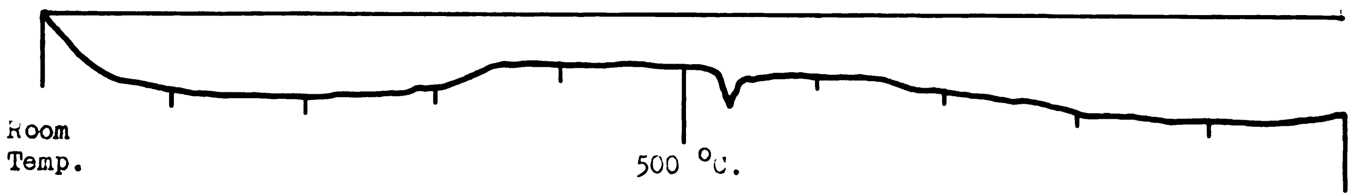
The purpose of this experiment was to determine the nature of the thermal curve when the inert material is used in both sides of the sample-holder.

Procedure

Both sides of the sample-holder were filled with aluminum oxide, which was then thoroughly settled by tapping the side of the holder thirty times with a metal rod. A porous plug was then placed at the top of each hole.

Conclusion

Using inert material in both sides of the sample-holder produced a thermal curve which closely approximates a horizontal line with an endothermic peak at about 530°C. The cause of this peak is not apparent.



Experiment 1

Experiment 2

Purpose

The purpose of this experiment was to find if a simple procedure is sufficient to produce consistent results using the same material.

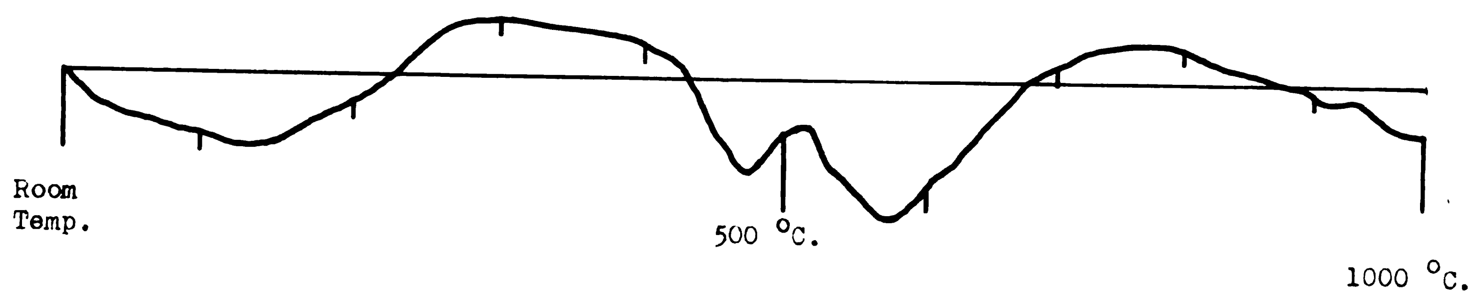
Procedure

The experiment was divided into two trials, the procedure being the same for each. Material taken from the 380 ft.-390 ft. interval of well #1236 was crushed and ground and then poured into the sample-holder. After tapping the side of the sample-holder two or three times with the handle of a knife, the material was smoothed flat with the blade.

Conclusion

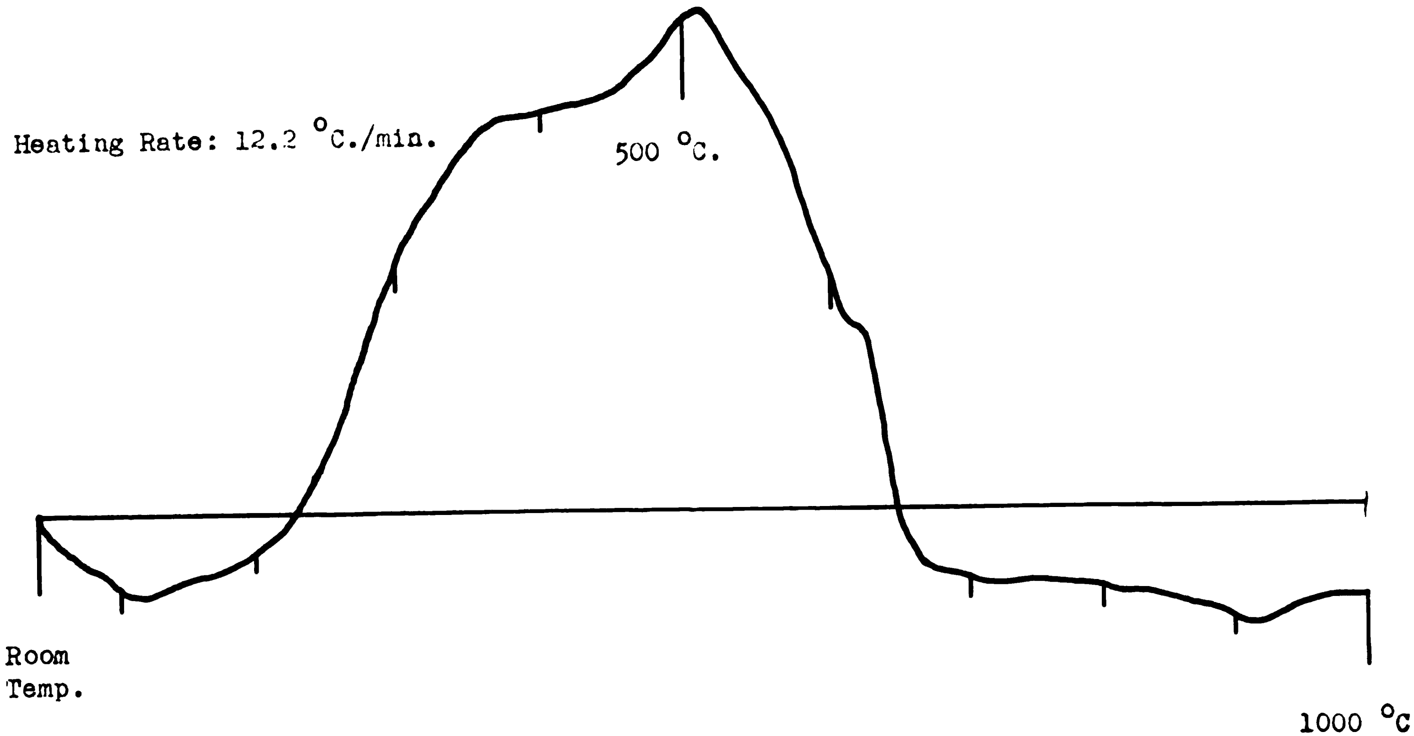
Since the two curves are dissimilar, this type of procedure is not sufficient to produce consistent results.

Heating Rate: 13.8 °C./min.



Experiment 2

Trial 1



Experiment 2

Trial 2

Experiment 3

Purpose

The purpose of this experiment was to find how changes in the quantity of material used and the degrees of packing affect the thermal curve of a shale.

Discussion

The experiment was divided into three parts--A, B, and C--each representing a different shale; each part was divided into three trials. The corresponding trials of each part are qualitatively identical.

Trial 1. Sufficient material was used just to fill the sample-holder.

Trial 2. The same weight of material was used as in Trial 1. However, this material was subjected to a certain degree of packing.

Trial 3. A different weight of material was used, but this material was subjected to the same degree of packing as in Trial 2.

A summary of the material is given in Table 1.

TABLE 1

SUMMARY OF THE MATERIAL USED

Shale	Well Permit Number	Interval (ft.)	Description
A	18967	810-850	Black cherty carbonaceous shale
B	1236	335-430	Gray cherty shale
C	1236	440-445	Black cherty carbonaceous shale

Procedure

Preparation of material. Iron was removed from each sample, which was then crushed and ground and placed in a separate labeled bottle.

In order to determine the quantity of material required to fill the sample-holder, the bottle containing the sample to be tested was weighed before and after the filling, and the difference in weights was the amount used. These values are shown in Table 2.

TABLE 2

WEIGHT OF MATERIAL REQUIRED TO FILL THE SAMPLE-HOLDER

Shale	Weight of Bottle + Material Before (gms.)	Weight of Bottle + Material After (gms.)	Weight Required to Fill Holder (gms.)
A	7.6985	7.5009	0.1976
B	8.3463	8.0927	0.2536
C	8.4825	8.1728	0.3097

Trial 1. The weight of material indicated in Table 2 was poured into the sample-holder and a thermal curve obtained.

Trial 2. The same weight of material was used as in Trial 1. The material was initially packed by tapping the side of the sample-holder thirty times with a short metal rod. A glass rod was then set vertically on top of the sample; the weight of the rod was sufficient to produce the final packing.

Trial 3. A different weight of material was used than in Trials 1 and 2, but the same degree of packing was used as in Trial 2.

The procedure is summarized in Table 3.

Shale	Tri
A	1
	2
B	
C	

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TABLE 3

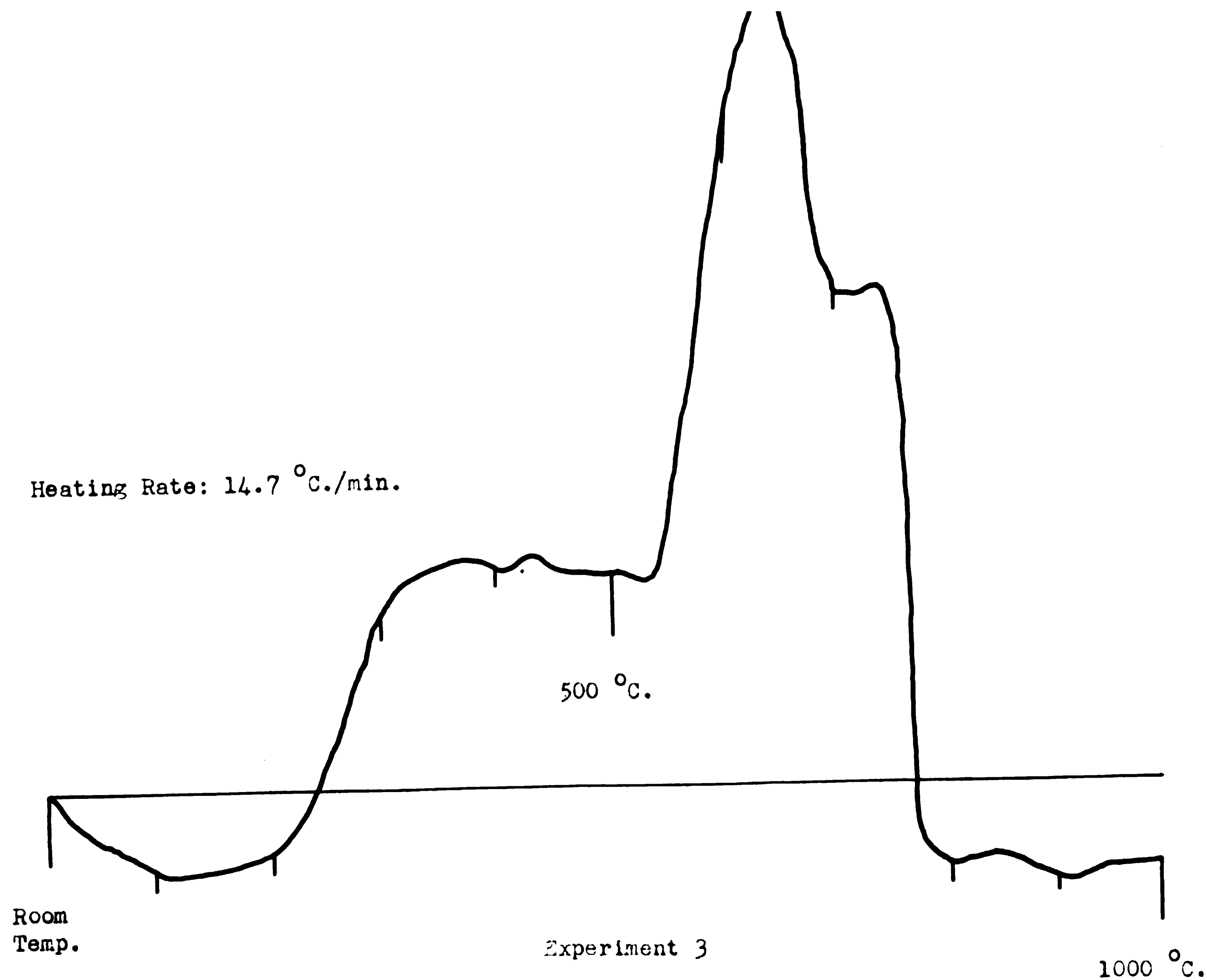
SUMMARY OF PROCEDURE

Shale	Trial	Weight of Material Used (gms.)	Packing
A	1	0.1976	none
	2	0.1976	30 taps + glass rod
	3	0.2476	30 taps + glass rod
B	1	0.2536	none
	2	0.2536	30 taps + glass rod
	3	0.2036	30 taps + glass rod
C	1	0.3097	none
	2	0.3097	30 taps + glass rod
	3	0.2597	30 taps + glass rod

Conclusion

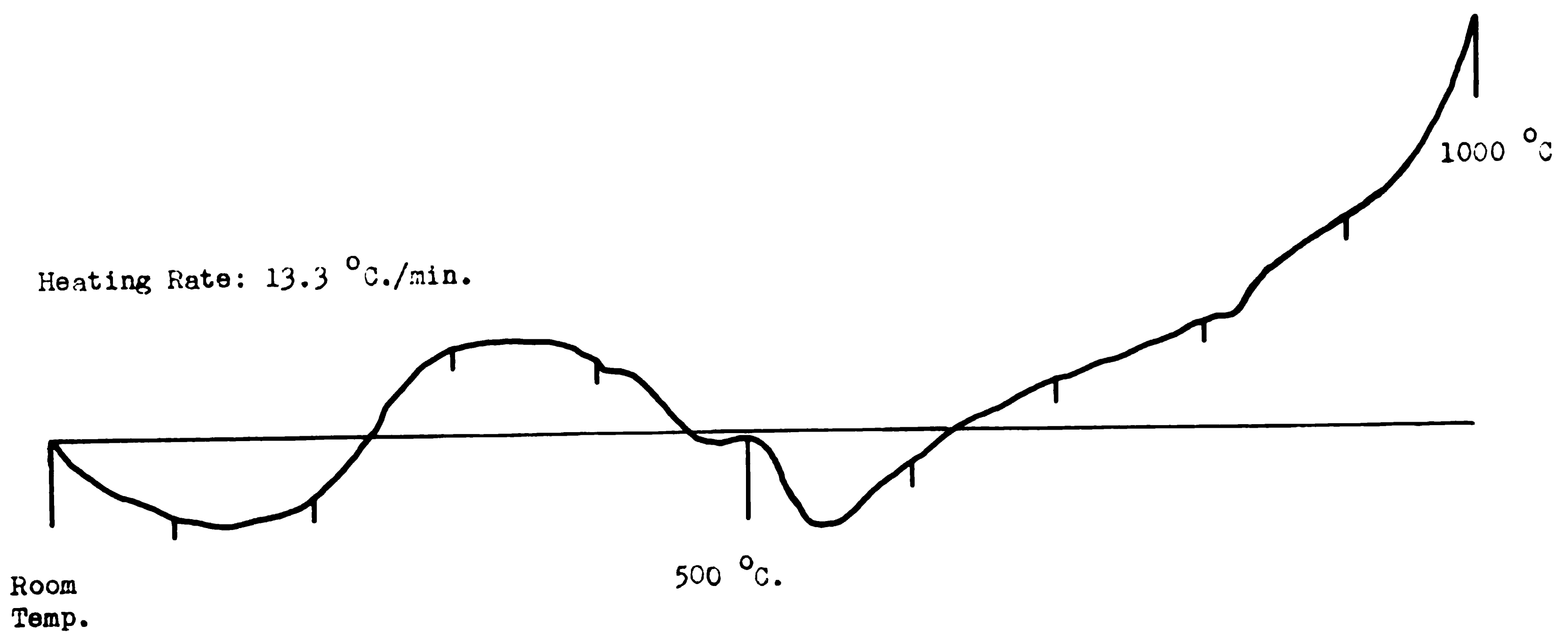
Parts A and C--black cherty carbonaceous Antrim shales. Changes in the quantity of material used and the degree of packing have a pronounced effect on the thermal curves of the shales. By comparing the curves for Trial 1 to those of Trials 2 and 3, it can be seen that a change in packing has a more profound effect than a change in quantity of material.

Part B--grey cherty noncarbonaceous Bedford-Berea shale. Changes in quantity of material and degree of packing have very little effect on the thermal curves of this shale.



Experiment 3

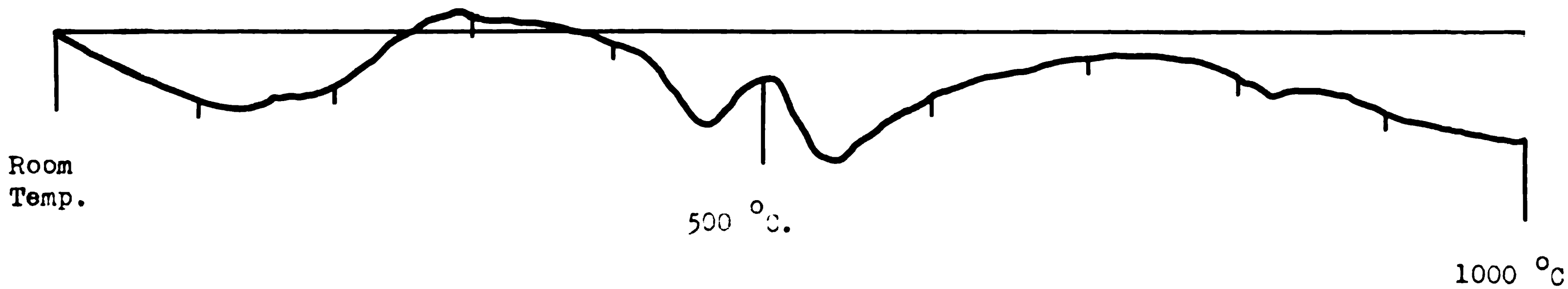
Part A Trial 1



Experiment 3

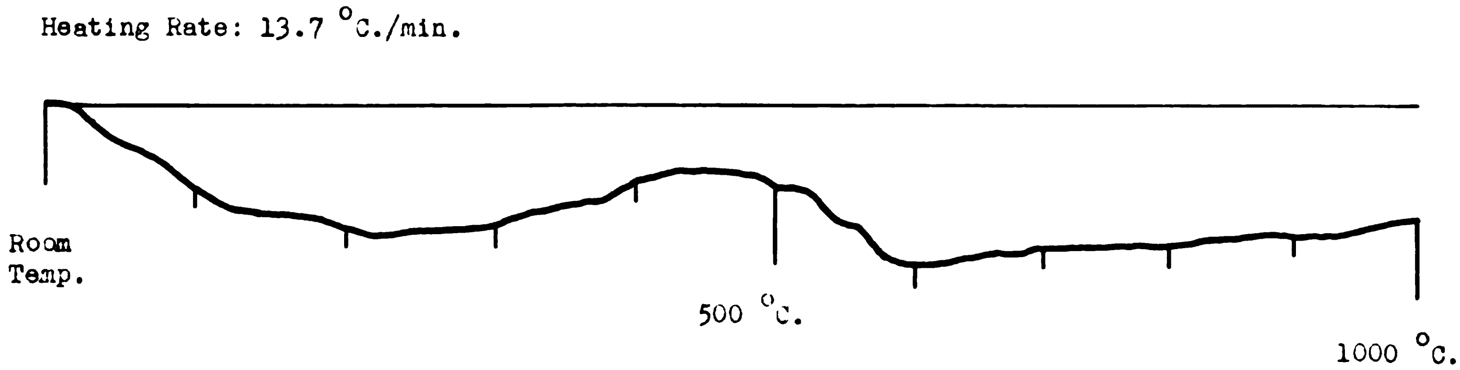
Part [illegible] Trial 2

Heating Rate: 12.9 °C./min.



Experiment 3

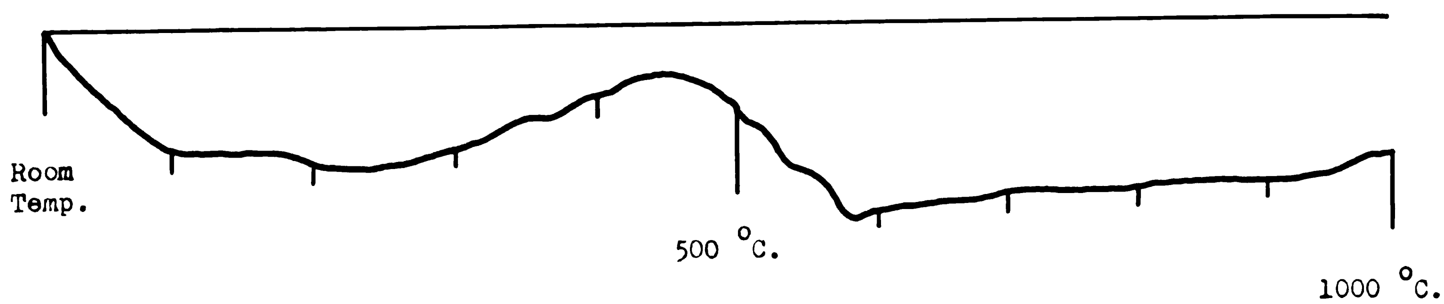
Part A Trial 3



Experiment 3

Part B Trial 1

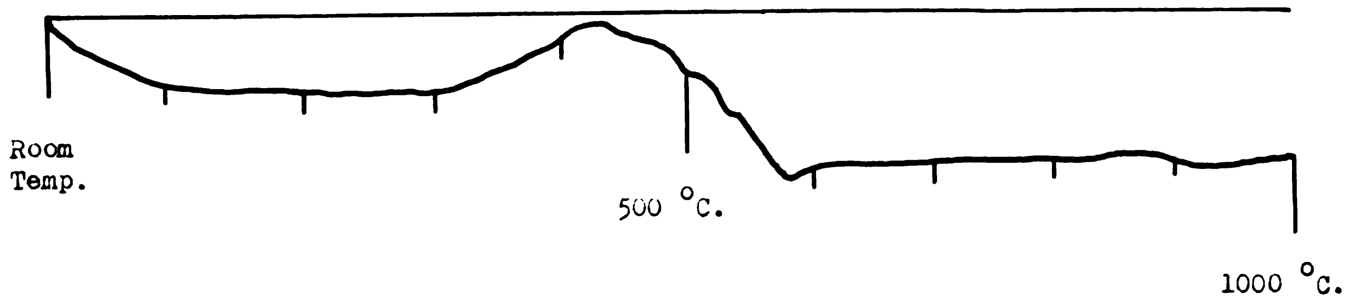
Heating Rate: 13.8 °C./min.



Experiment 3

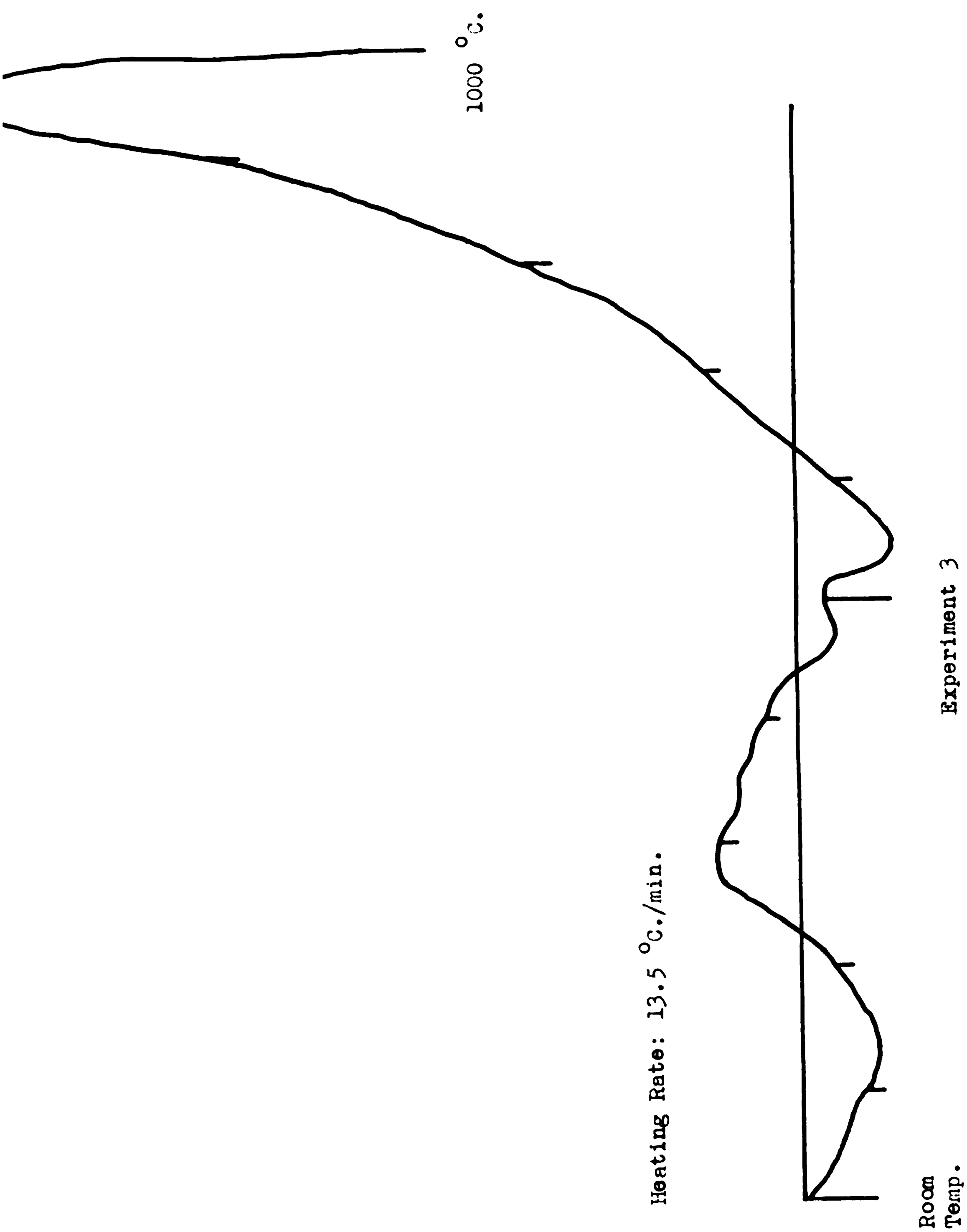
Part B   Trial 2

Heating Rate: 15.3 °C./min.



Experiment 3

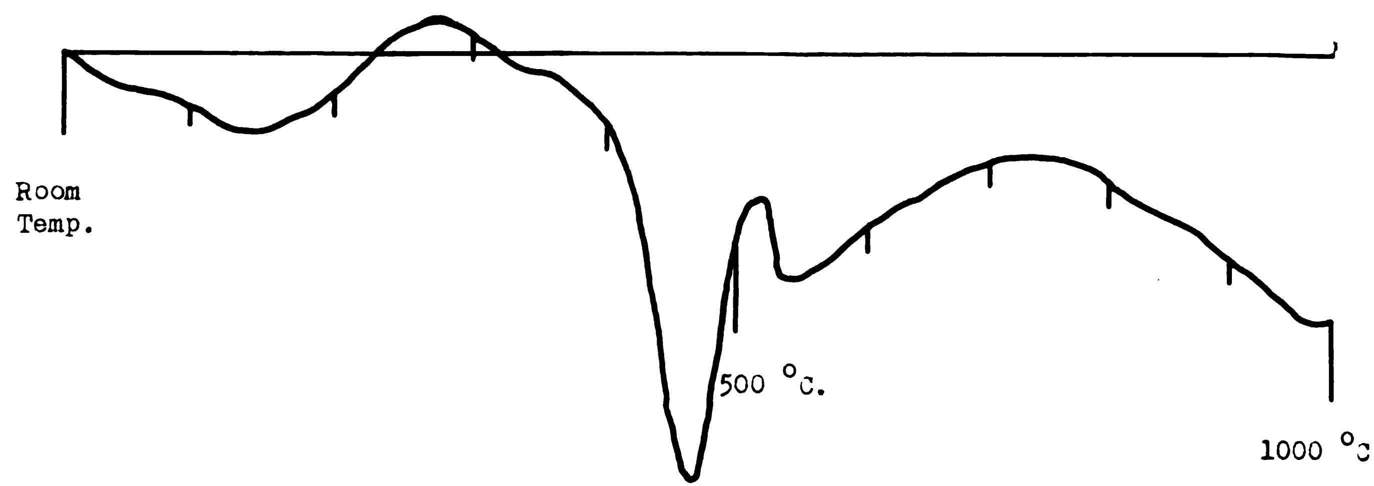
Part B Trial 3



Experiment 3

Part C Trial 1

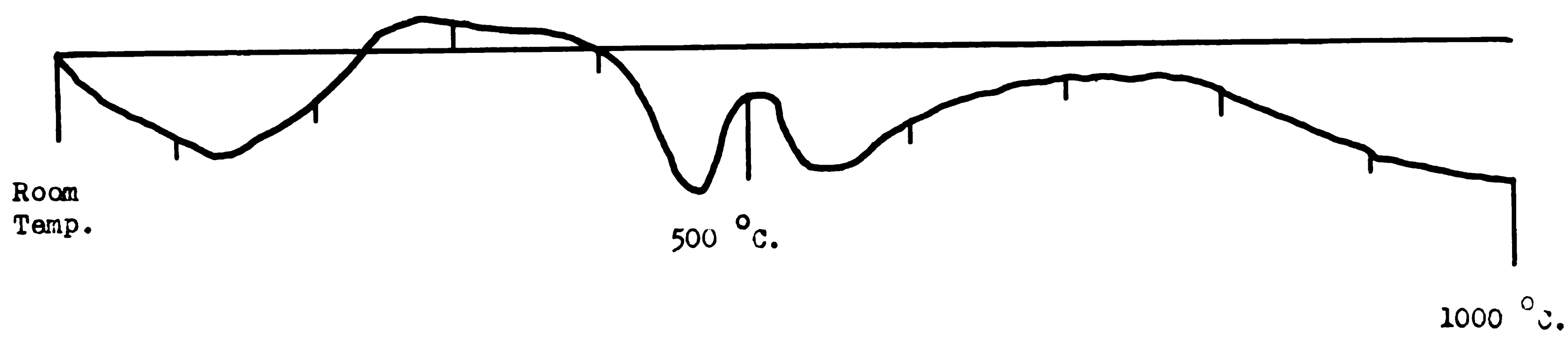
Heating Rate: 14.8 °C./min.



Experiment 3

Part C   Trial 2

Heating Rate: 13.3 °C./min.



Experiment 3

Part C   Trial 3

Experiment 4

Purpose

The purpose of this experiment is to see if identical thermal curves of a shale may be obtained as a result of holding contant the weight of material and degree of packing.

Discussion

The experiment is divided into three parts--A, B, and C--each representing a different shale. Each part is also divided into two trials. All trials are identical in procedure.

The same material was used as in Experiment 3, which is shown in Table 1.

Procedure

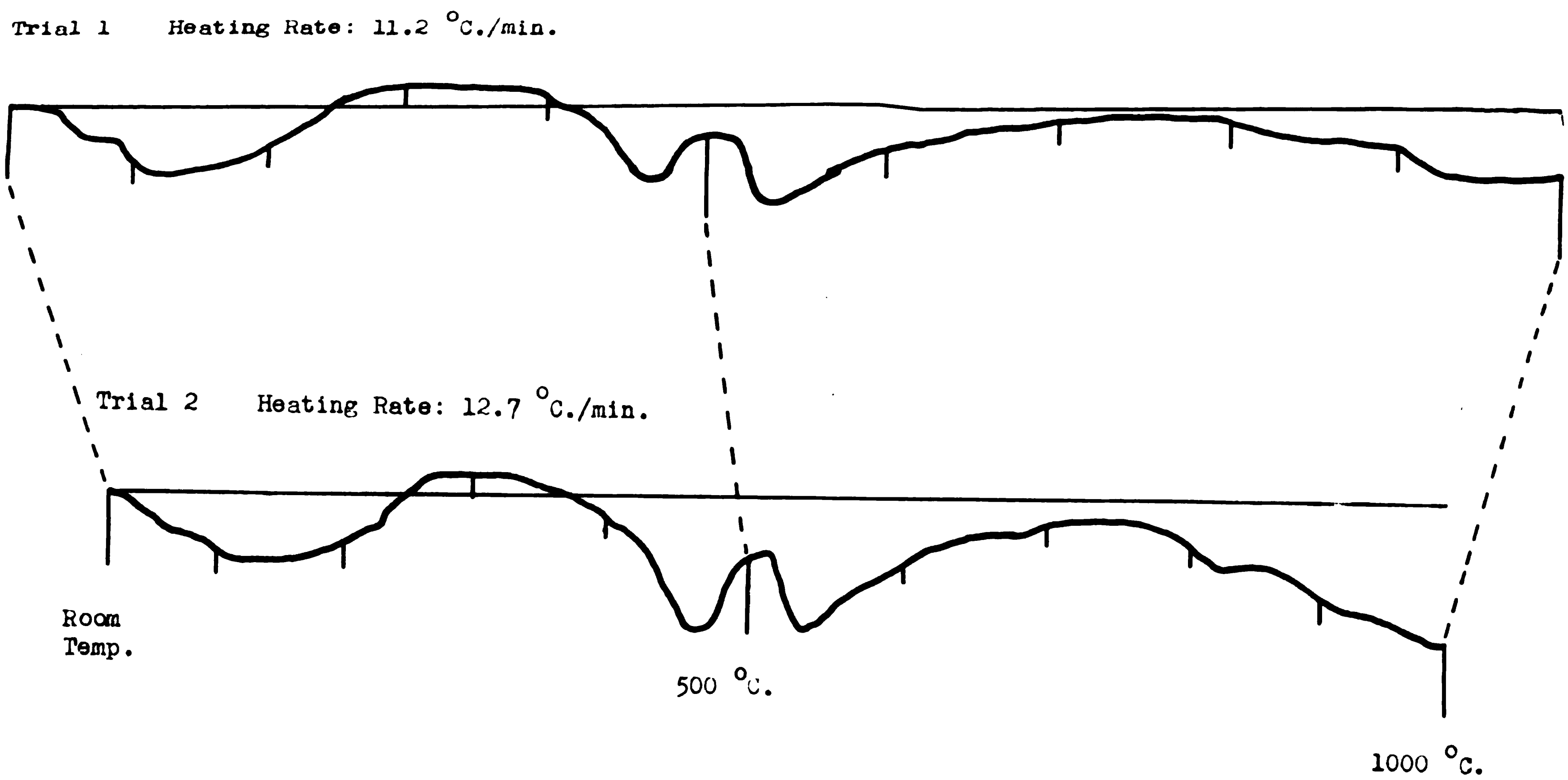
Iron was removed from two 0.3000-gm. samples of each shale, which were then crushed, ground, and placed in separate bottles. The standard packing procedure was applied in order to obtain identical packing for each trial.

Conclusion

Parts A and C--black cherty carbonaceous Antrim shales. Comparison of each pair of curves shows that they are similar but not identical.

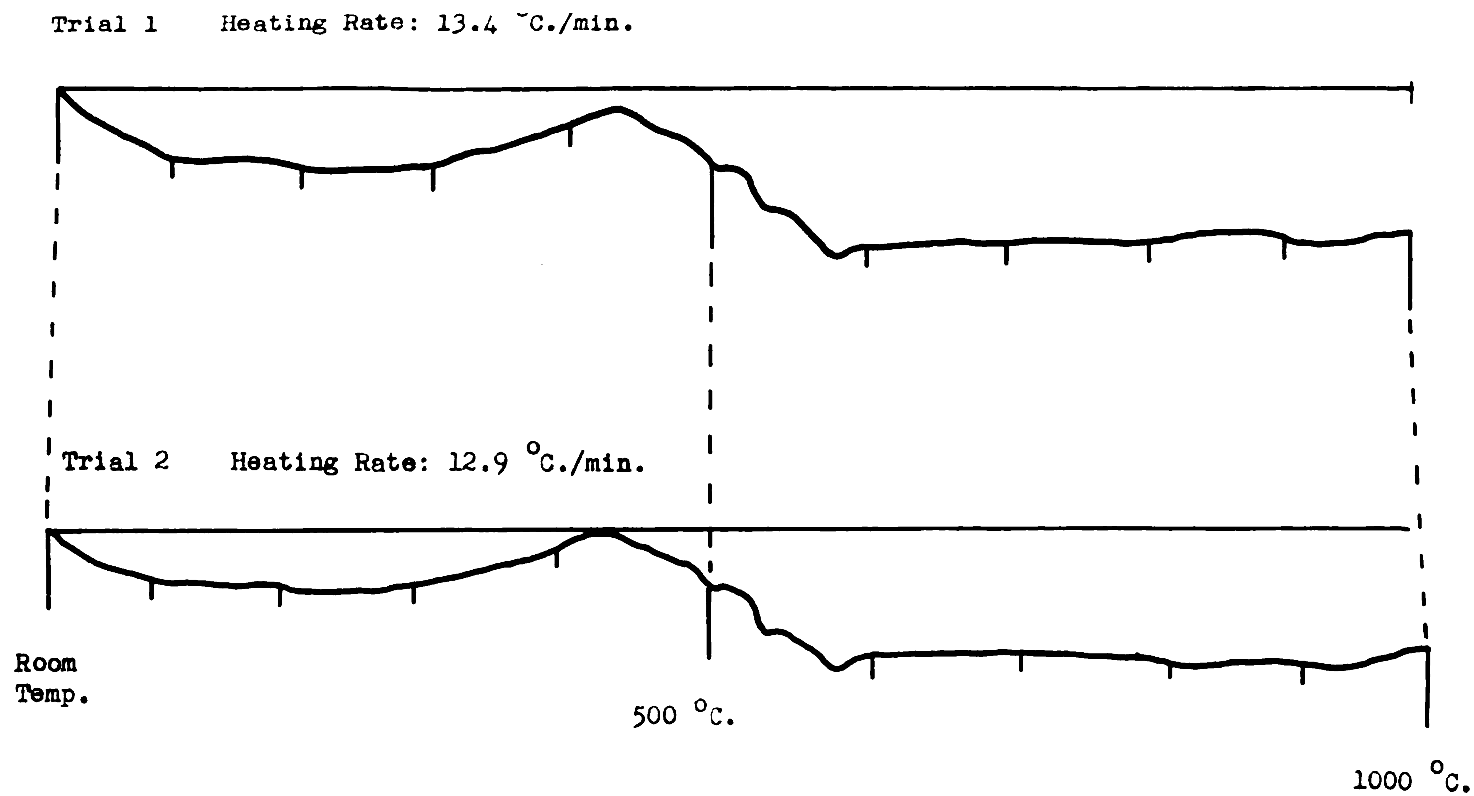
Part B--gray cherty noncarbonaceous Bedford-Berea shale. Comparison of this pair of curves shows that they are very nearly identical.

By holding the amount of material used and degree of packing constant, consistent results were obtained from the gray shale, but not from either of the black shales. This inconsistency may be due to carbonaceous material.



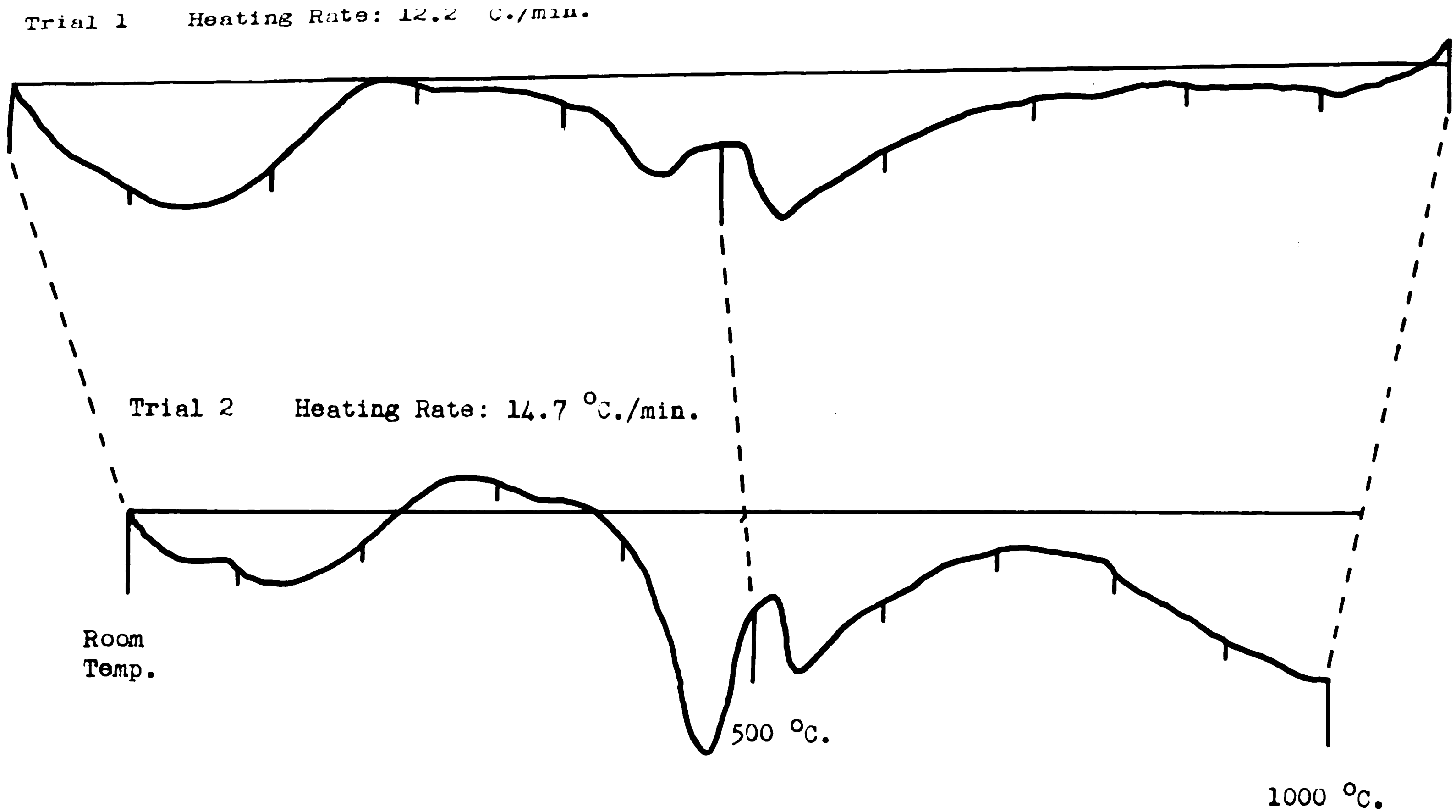
Experiment 4

Part A



Experiment 4

Part B



Experiment 4

Part C

DISCUSSION OF EXPERIMENTS 5 THROUGH 9

Experiments 1 through 4 showed that consistent thermal curves for the gray shale could be obtained by holding constant the weight of material and degree of packing. These controls, however, were not sufficient to produce consistent results for the black shales. Experiments 5 through 9 were therefore designed to study some variables that may be influencing the erratic behavior of the thermal curves of black shale.

Iron was removed from material taken from a depth of 390 ft.-470 ft. in well #1276. The shale was then ground and passed through the complete set of sieves. Material resting on each sieve and in the pan was placed in separate labeled bottles. It should be noted at this point that the 200^{-} mesh material was lighter in color than the coarser material, which may indicate a difference of composition. In addition, particles of the coarser material lay within definite size limits, in contrast to the particles of the 200^{-} mesh material which theoretically had no lower limit as to size.

THERMAL CURVES AND GRAPHS

In order to interpret the results of experiments 5 through 9, two measurements were made on each of three peaks, labeled X, Y, and Z, which were common to all of the thermal curves. The height of reaction was the vertical distance in cm. on the original thermal curve measured from the horizontal base line to the highest point of the peak. The furnace temperature at which this point occurred was called the peak temperature. These measurements are indicated in the tables of the experiments. Since experiments 5 through 9 were related, their results were analyzed as a unit under ''Analysis of Results.'' A series of graphs designed to facilitate visualization of the relationship of several variables was included in this section.

Experiment 5

Purpose

The purpose of this experiment was to find the differences in the thermal curves of the various sieve sizes by holding constant the weight of material and degree of packing.

Procedure

The experiment was divided into six trials, each representing a different sieve size. The procedure was identical for each trial.

TABLE 4

MATERIAL USED FOR EACH TRIAL

Trial	Sieve Size
1	60-80
2	80-100
3	100-120
4	120-150
5	150-200
6	200^-

Three-tenths gm. of sample was used in each trial, and uniform packing was obtained by applying the standard packing procedure.

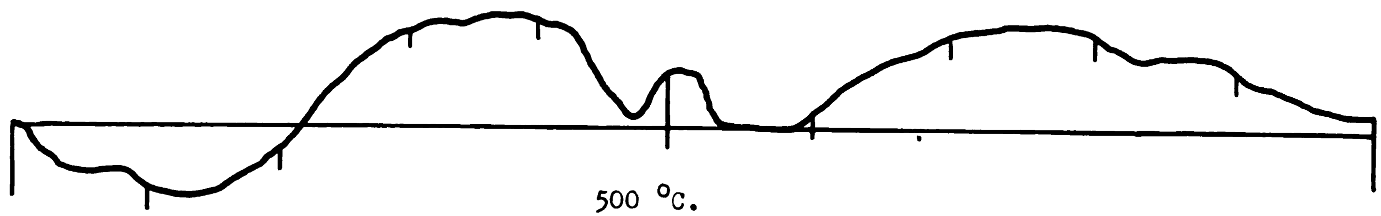
Results

TABLE 5

HEIGHT AND TEMPERATURE OF PEAKS X, Y, AND Z

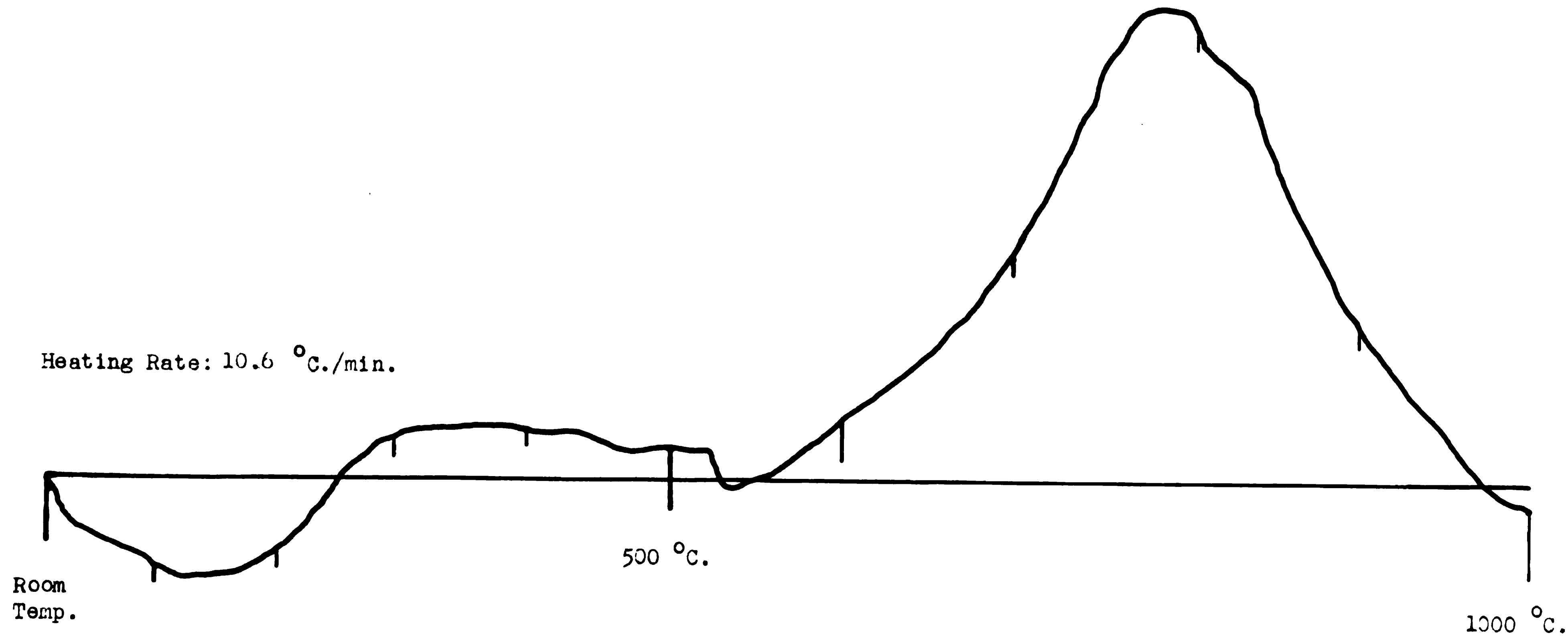
Sieve Size	Peak X		Peak Y		Peak Z	
	Temp. (°C.)	Height (cm.)	Temp. (°C.)	Height (cm.)	Temp. (°C.)	Height (cm.)
60-80	125	-0.9	380	1.5	750	1.4
80-100	140	-1.6	380	0.8	780	7.5
100-120	130	-1.9	380	1.0	770	8.5
120-150	130	-1.4	380	1.3	770	9.1
150-200	130	-1.4	360	1.3	820	9.9
200⁻	150	-1.6	410	-0.5	910	7.6

Heating Rate: 13.7 °C./min.



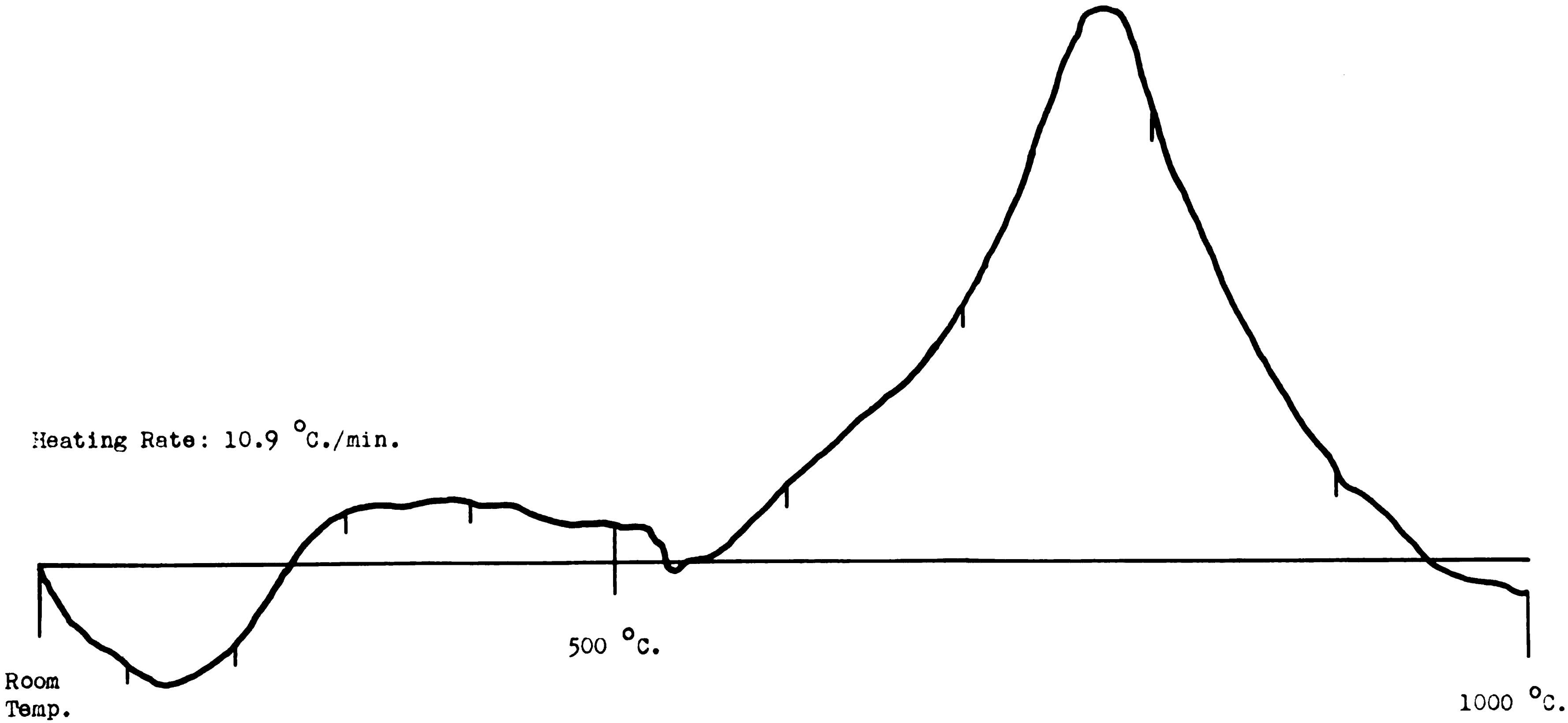
Experiment 5

Trial 1



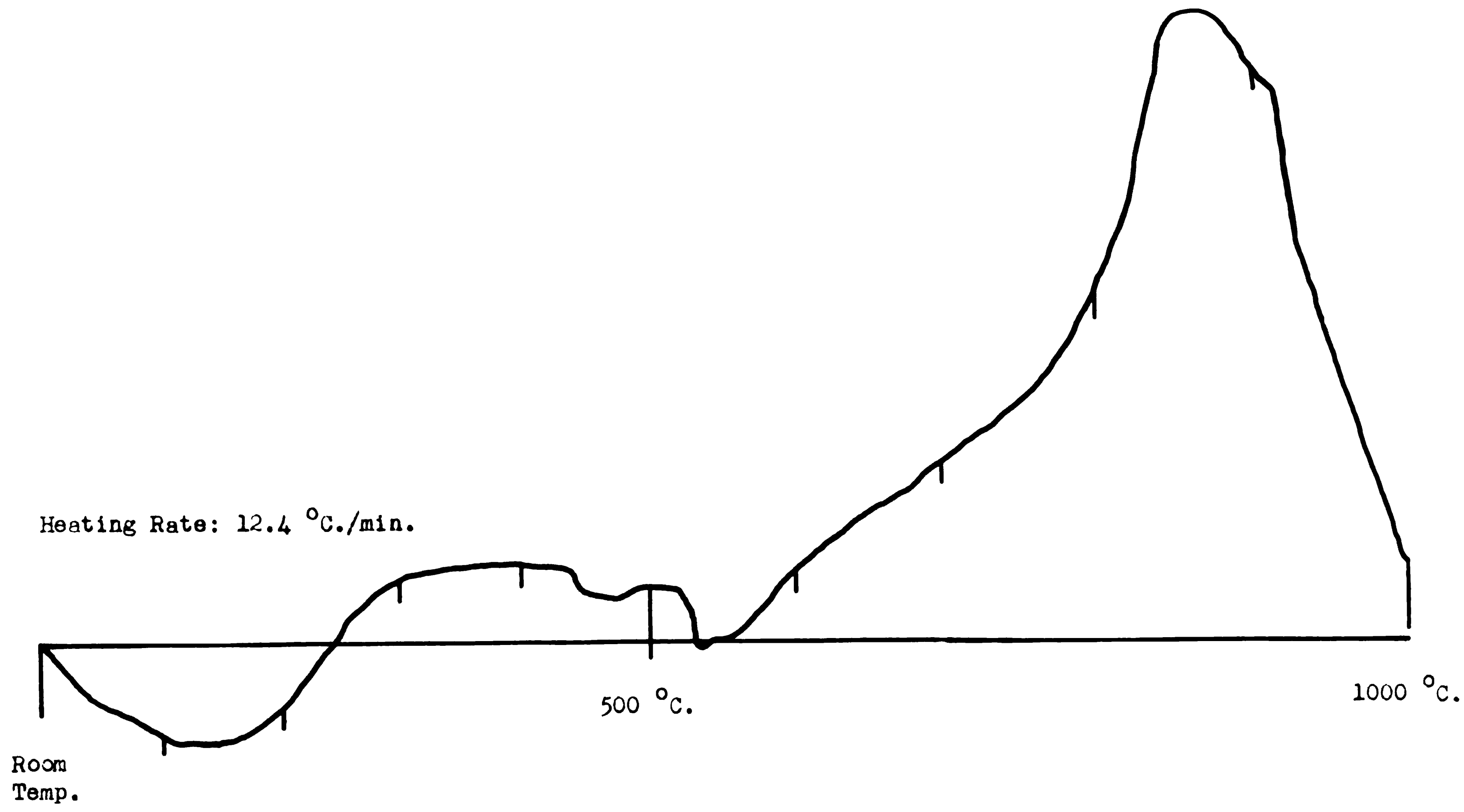
Experiment 5

Trial 2



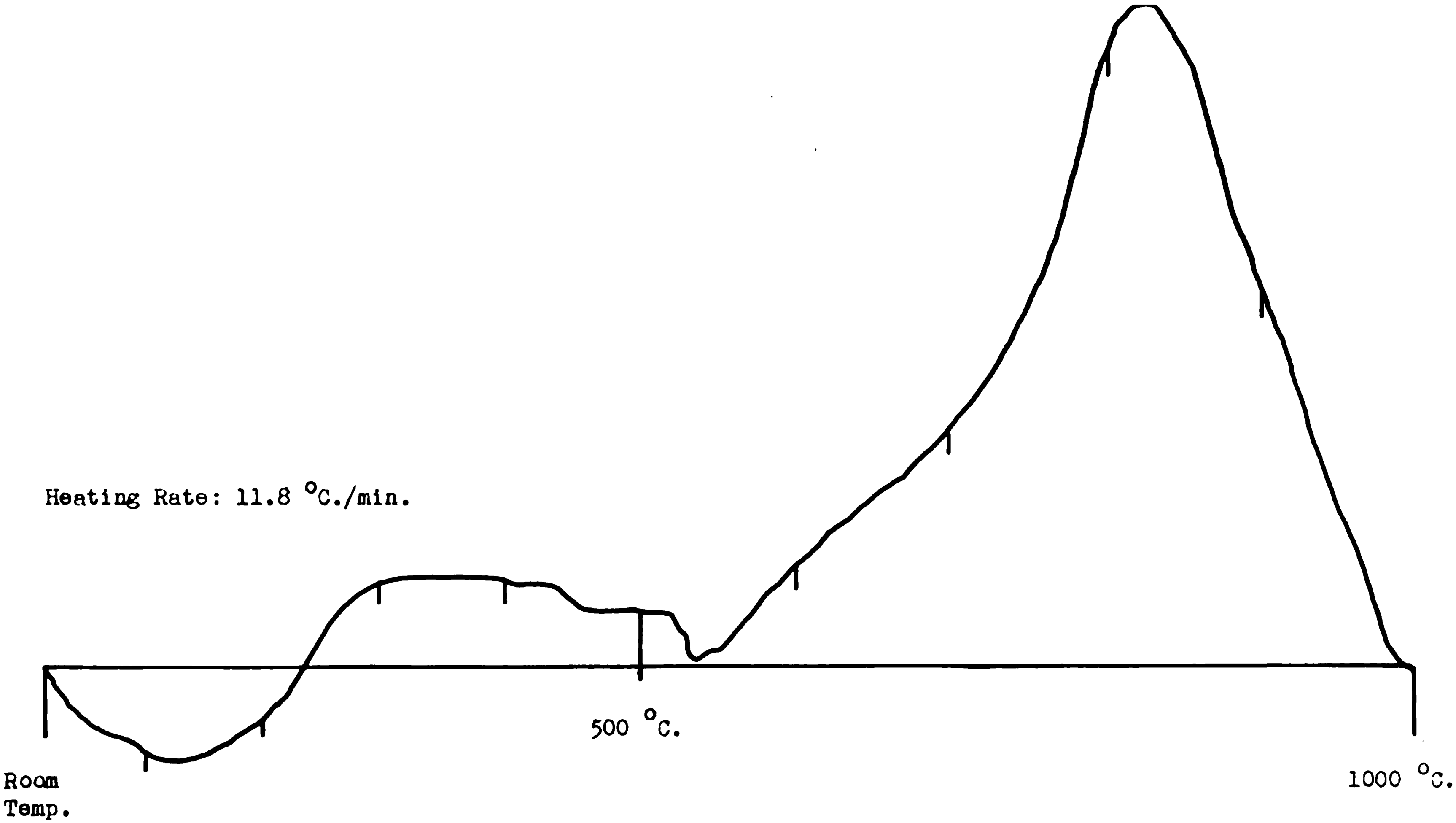
Experiment 5

Trial 3



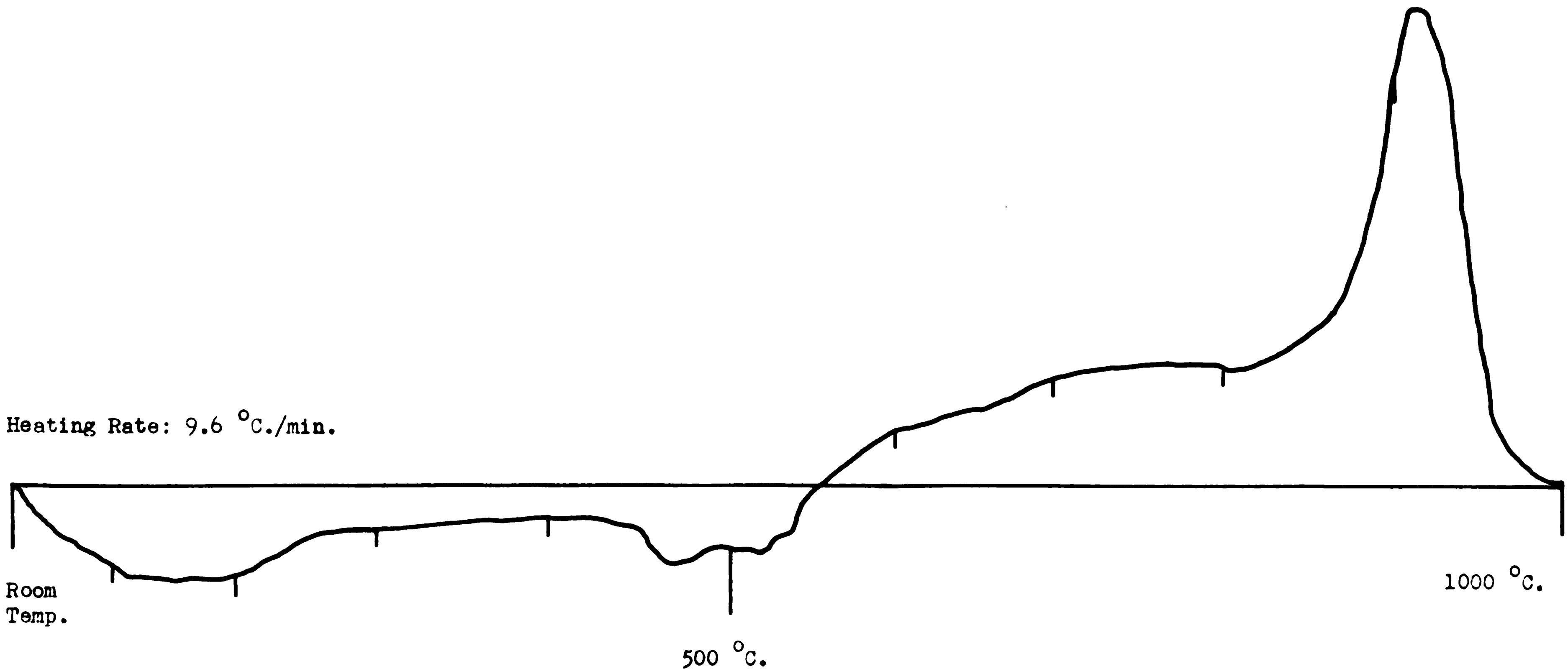
Experiment 5

Trial 4



Experiment 5

Trial 5



Experiment 5

Trial 6

Experiment 6

Purpose

The purpose of this experiment was to find how variations in amount of material and degree of packing affect the thermal curve of a particular sieve size when volume is held constant.

Procedure

Since greater variation of packing was possible with the finest material, the 200^{-} sieve size was used.

The experiment was divided into five trials, each differing from the next by 0.0300 gm. Except for Trial 1, each sample was packed by tapping the side of the holder several times with a metal rod and then smoothing the sample flush with the top of the holder with a knife blade. The sample in Trial 1 required but one tap with the metal rod to bring the material flush with the top of the sample-holder. Table 1 shows the weight of material used in each trial.

TABLE 6

WEIGHT OF MATERIAL USED FOR EACH TRIAL

Trial	Weight (gm.)
1	0.1400[a]
2	0.1700
3	0.2000
4	0.2300
5	0.2600

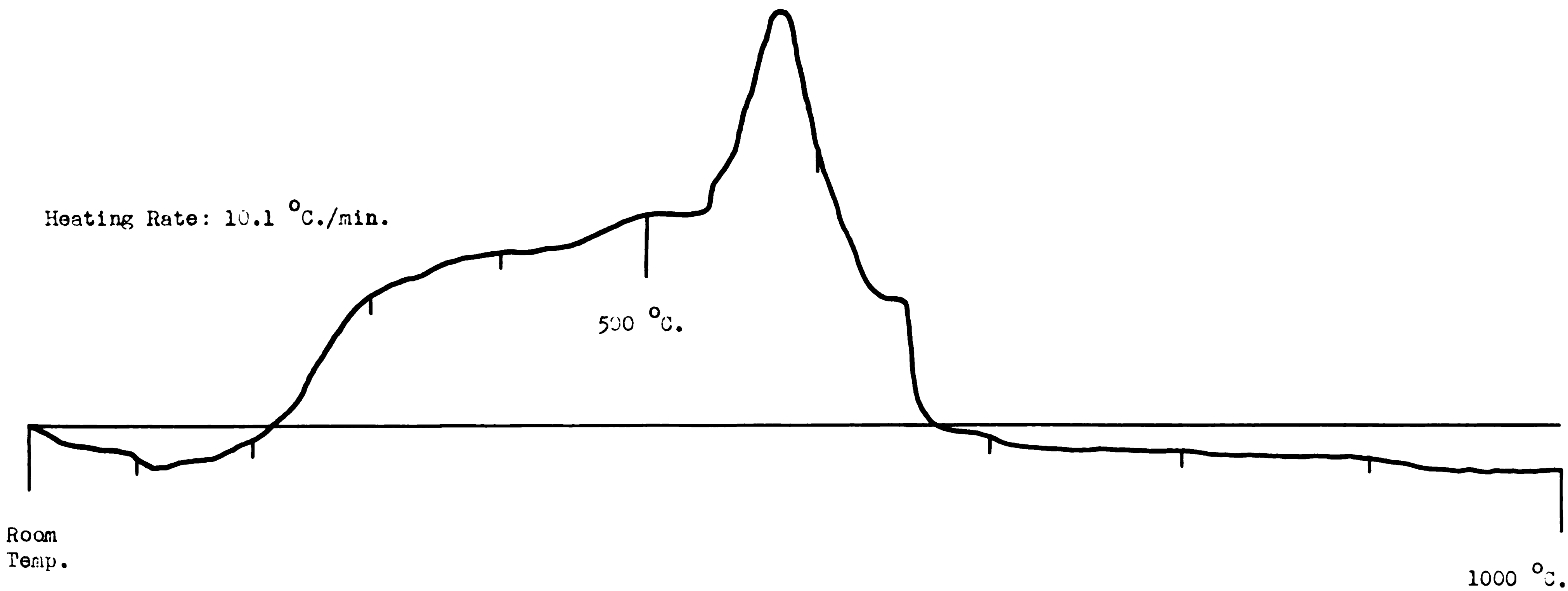
[a]Tapped once with metal rod.

Results

TABLE 7

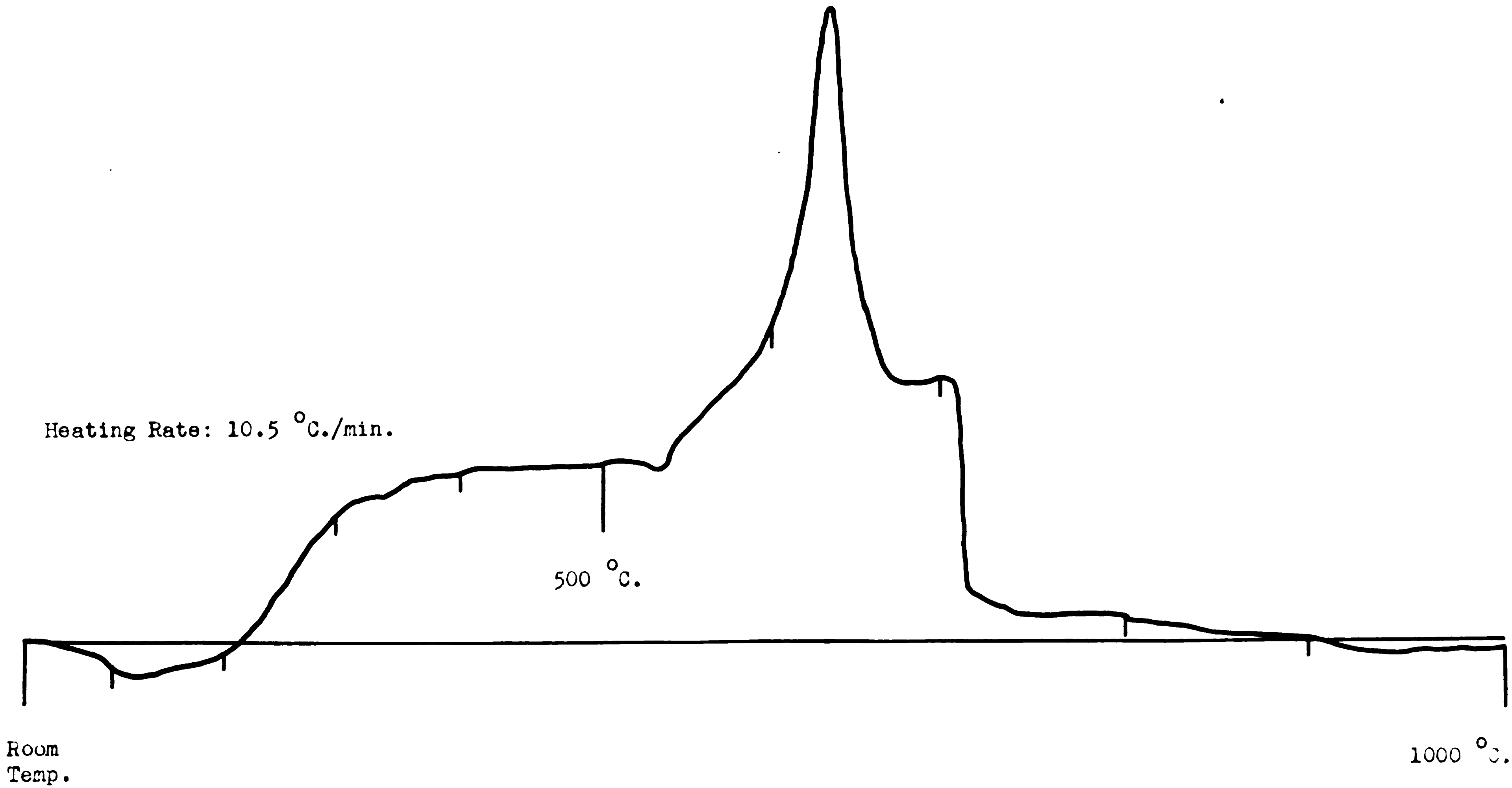
HEIGHT AND TEMPERATURE OF PEAKS X, Y, AND Z

Weight (gm.)	Peak X		Peak Y		Peak Z	
	Temp. (°C.)	Height (cm.)	Temp. (°C.)	Height (cm.)	Temp. (°C.)	Height (cm.)
0.1400	120	-0.6	440	3.0	580	6.9
0.1700	110	-0.6	480	2.9	630	10.5
0.2000	120	-0.9	440	2.5	690	10.3
0.2300	120	-0.8	460	2.3	750	8.4
0.2600	120	-0.8	440	2.2	805	11.5



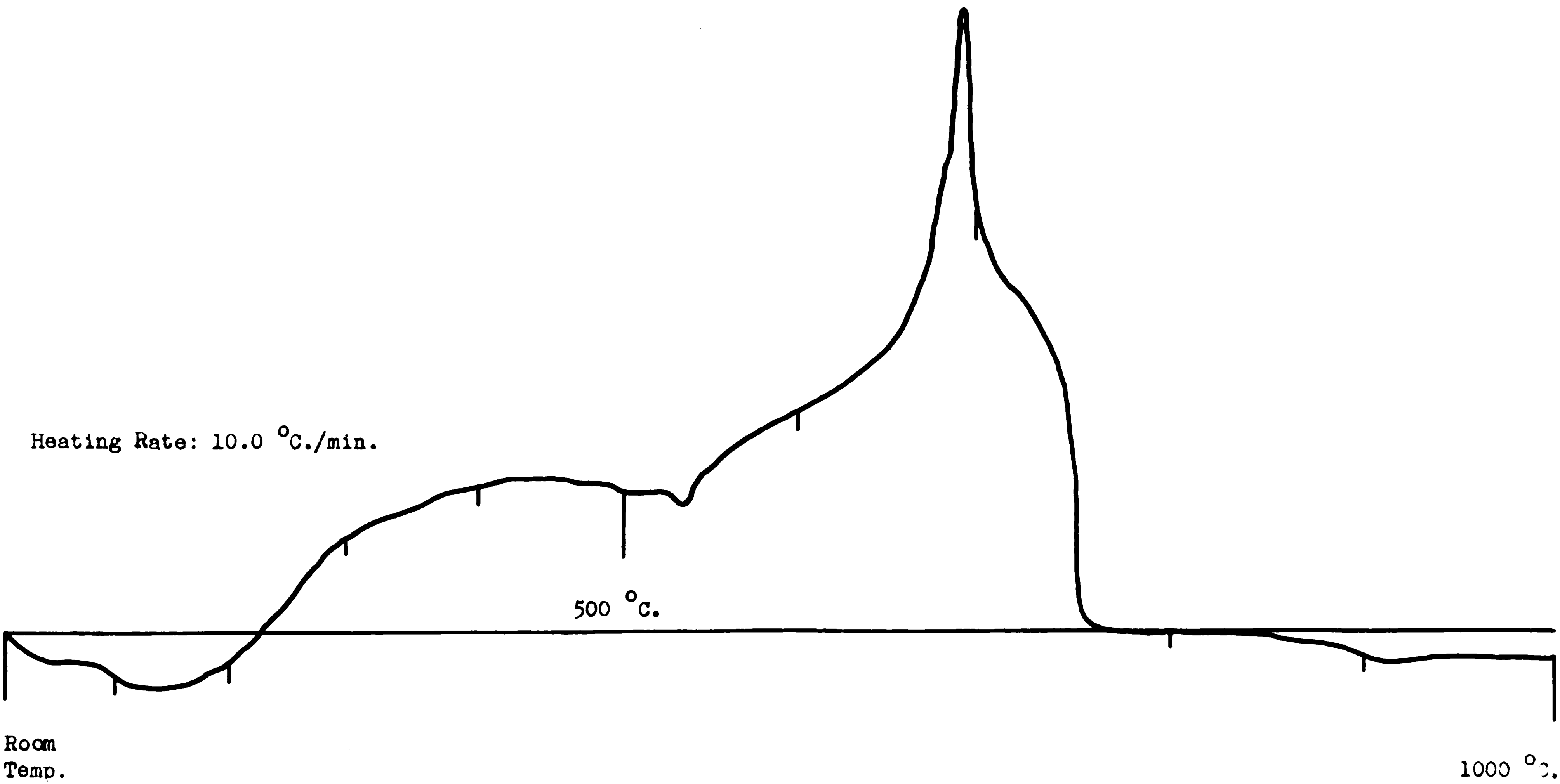
Experiment 6

Trial 1



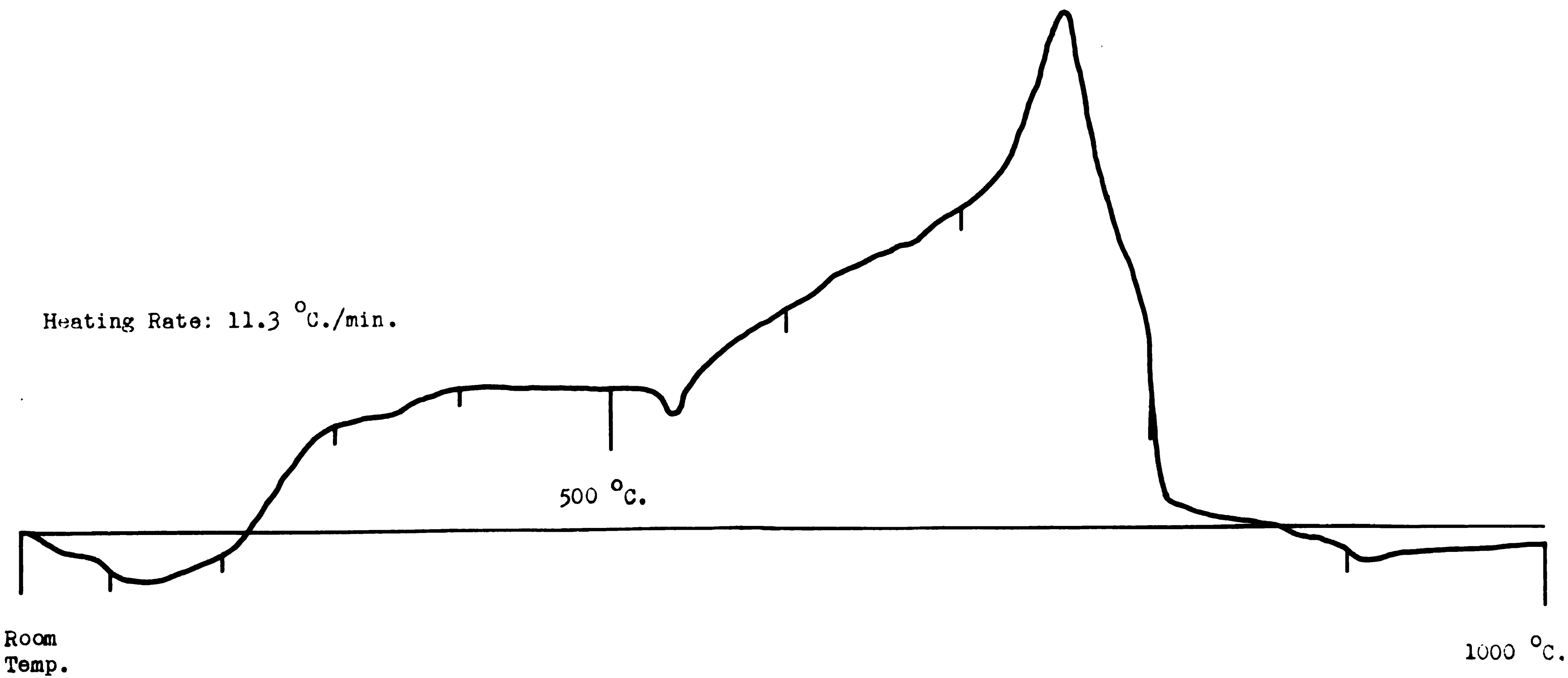
Experiment 6

Trial 2



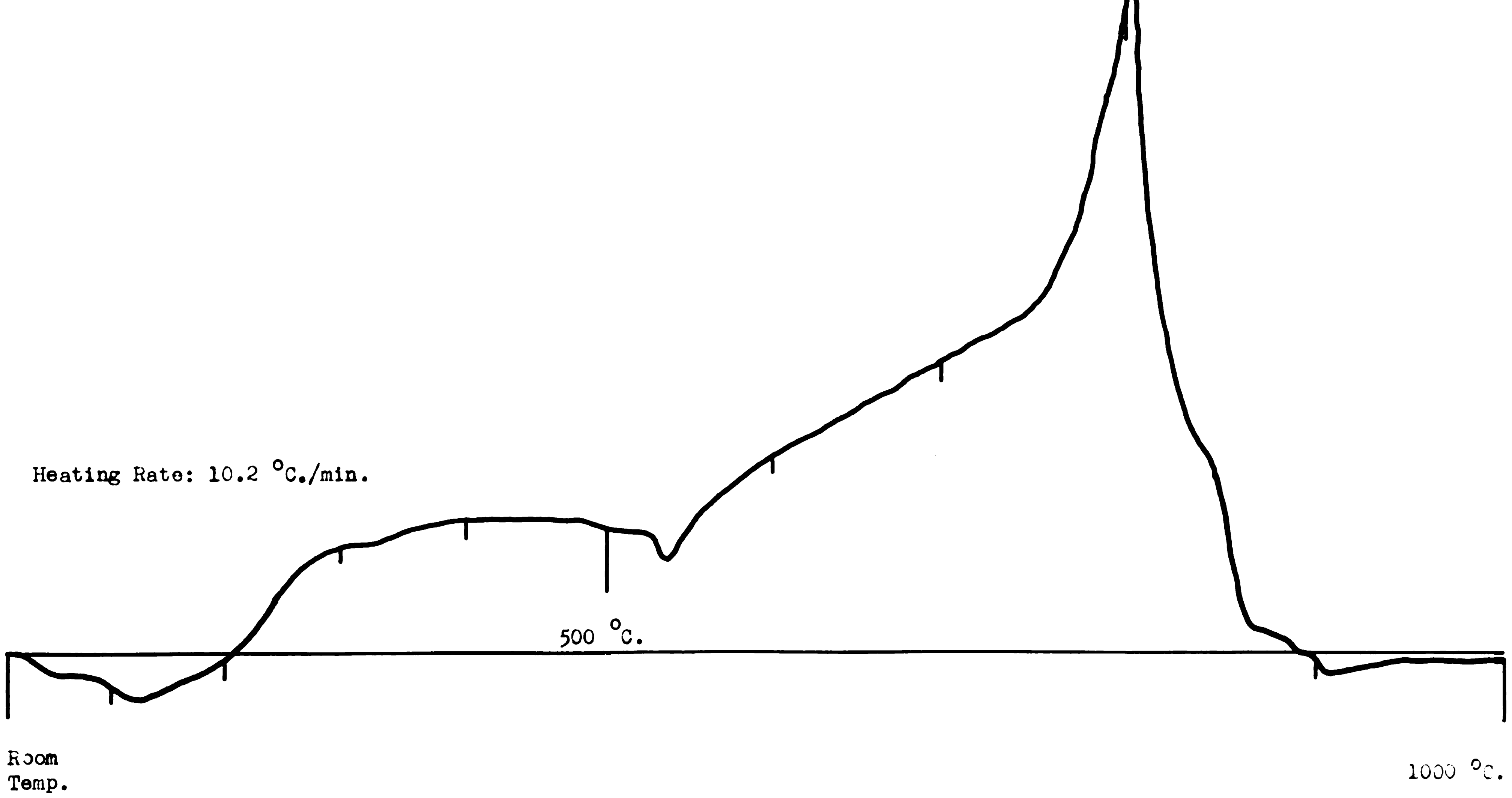
Experiment 6

Trial 3



Experiment 6

Trial 4



Experiment 6

Trial 5

Experiment 7

Purpose

The purpose of this experiment was to find how changes in volume and weight affect the thermal curves of two particular sieve sizes when the degree of packing is held constant.

Discussion

The experiment was divided into two parts, A and B, each representing a different sieve size. Each part was divided into three trials which differed only by the weight of material used. The procedure was identical for each trial.

Procedure

Table 8 shows the weights of sample used in each trial.

TABLE 8

WEIGHT OF MATERIAL IN EACH TRIAL

Part	Sieve Size	Trial	Weight (gm.)
A	150-200	1	0.2400
		2	0.2600
		3	0.2800
B	200⁻	4	0.1400
		5	0.1600
		6	0.1800

Uniform packing was obtained by applying the standard packing procedure to each trial.

TABLE 9

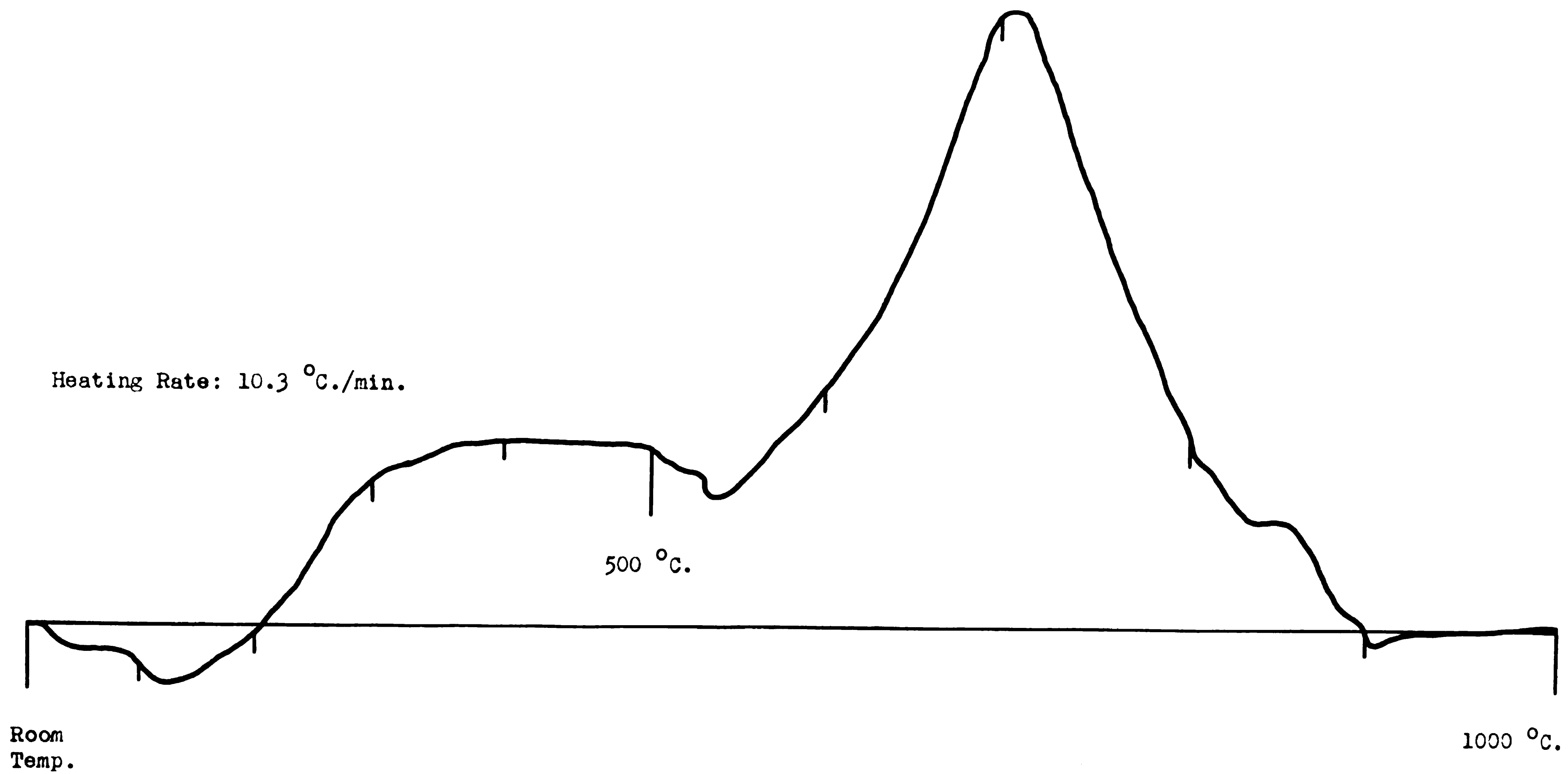
HEIGHT AND TEMPERATURE OF PEAKS X, Y, AND Z FOR PART A

Weight (gm.)	Peak X		Peak Y		Peak Z	
	Temp. (°C.)	Height (cm.)	Temp. (°C.)	Height (cm.)	Temp. (°C.)	Height (cm.)
0.2400	120	-0.9	430	3.0	710	10.2
0.2600	120	-0.8	440	2.3	730	11.1
0.2800	120	-0.8	430	2.4	780	11.4

TABLE 10

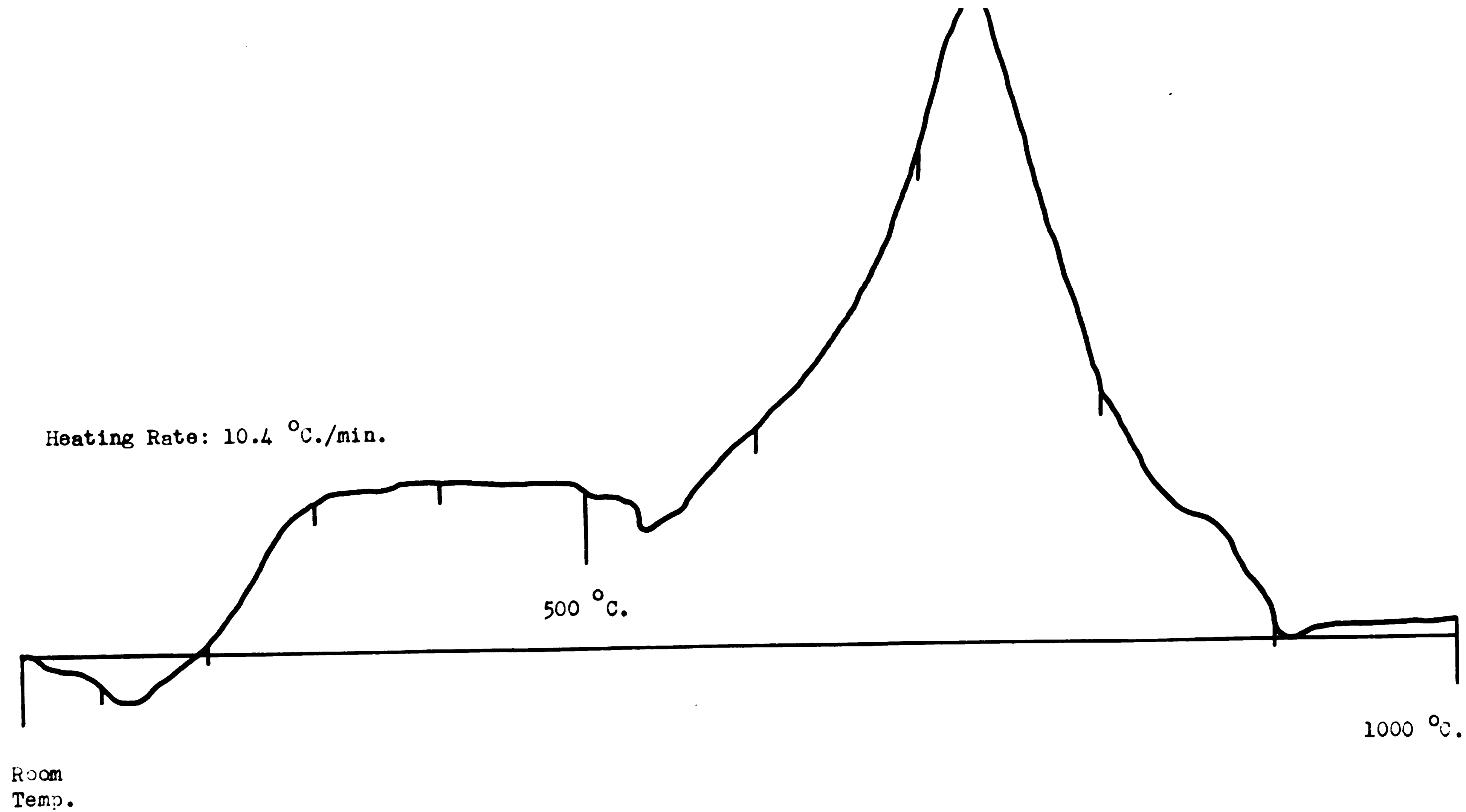
HEIGHT AND TEMPERATURE OF PEAKS X, Y, AND Z FOR PART B

Weight (gm.)	Peak X		Peak Y		Peak Z	
	Temp. (°C.)	Height (cm.)	Temp. (°C.)	Height (cm.)	Temp. (°C.)	Height (cm.)
0.1400	100	-0.4	430	5.1	550	8.3
0.1600	110	-0.8	460	3.4	590	9.5
0.1800	110	-1.2	450	3.4	660	13.0



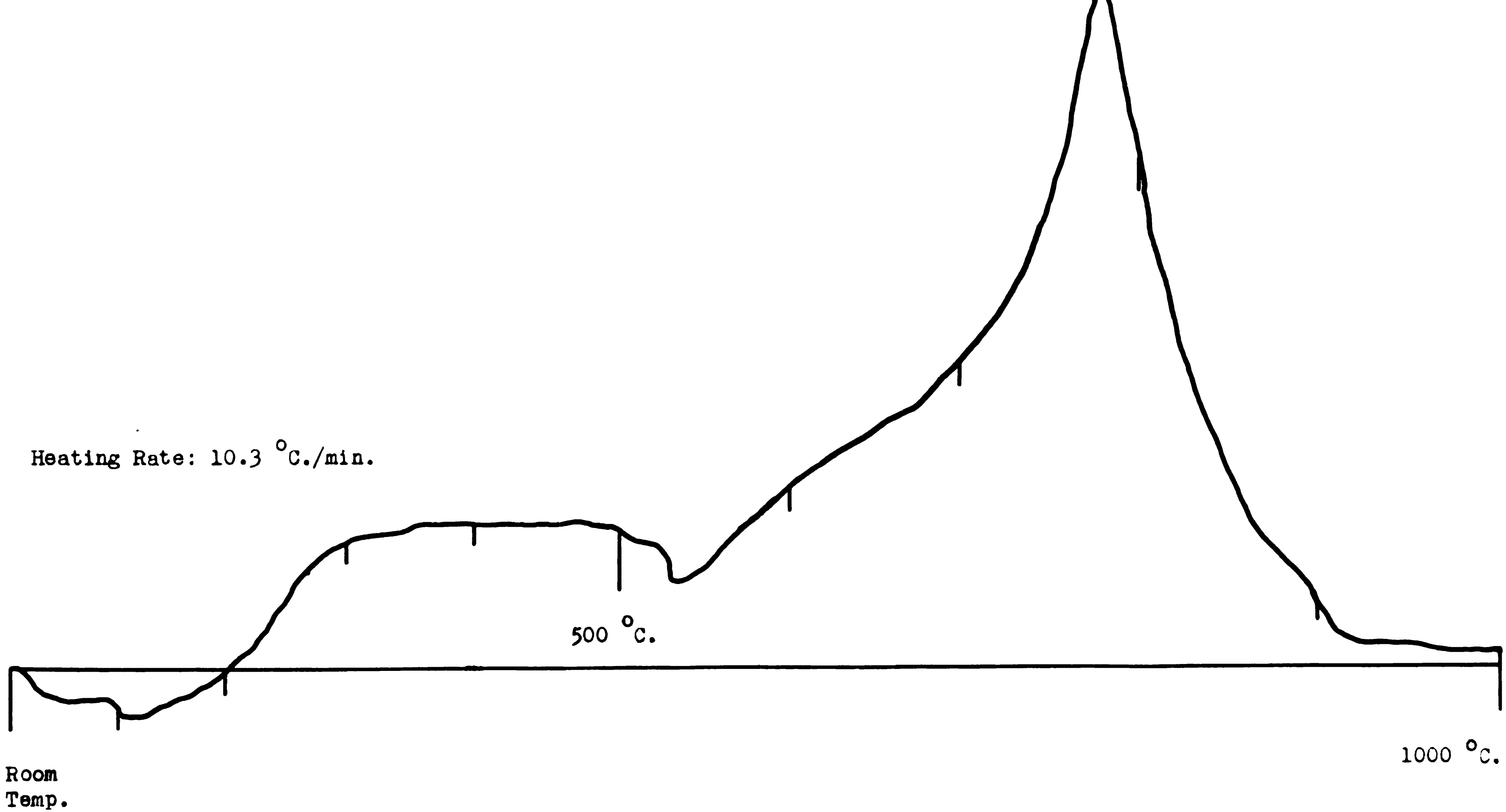
Experiment 7

Part A Trial 1



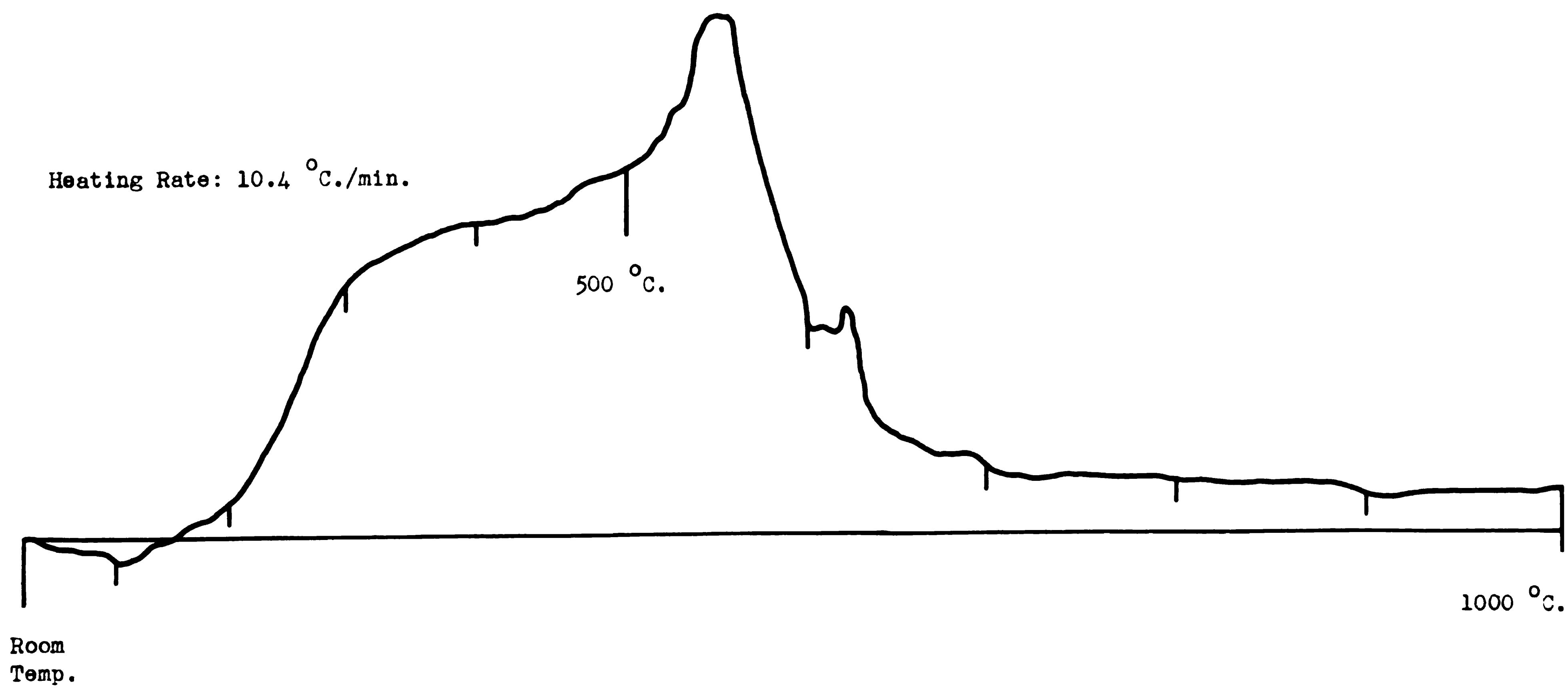
Experiment 7

Part A Trial 2



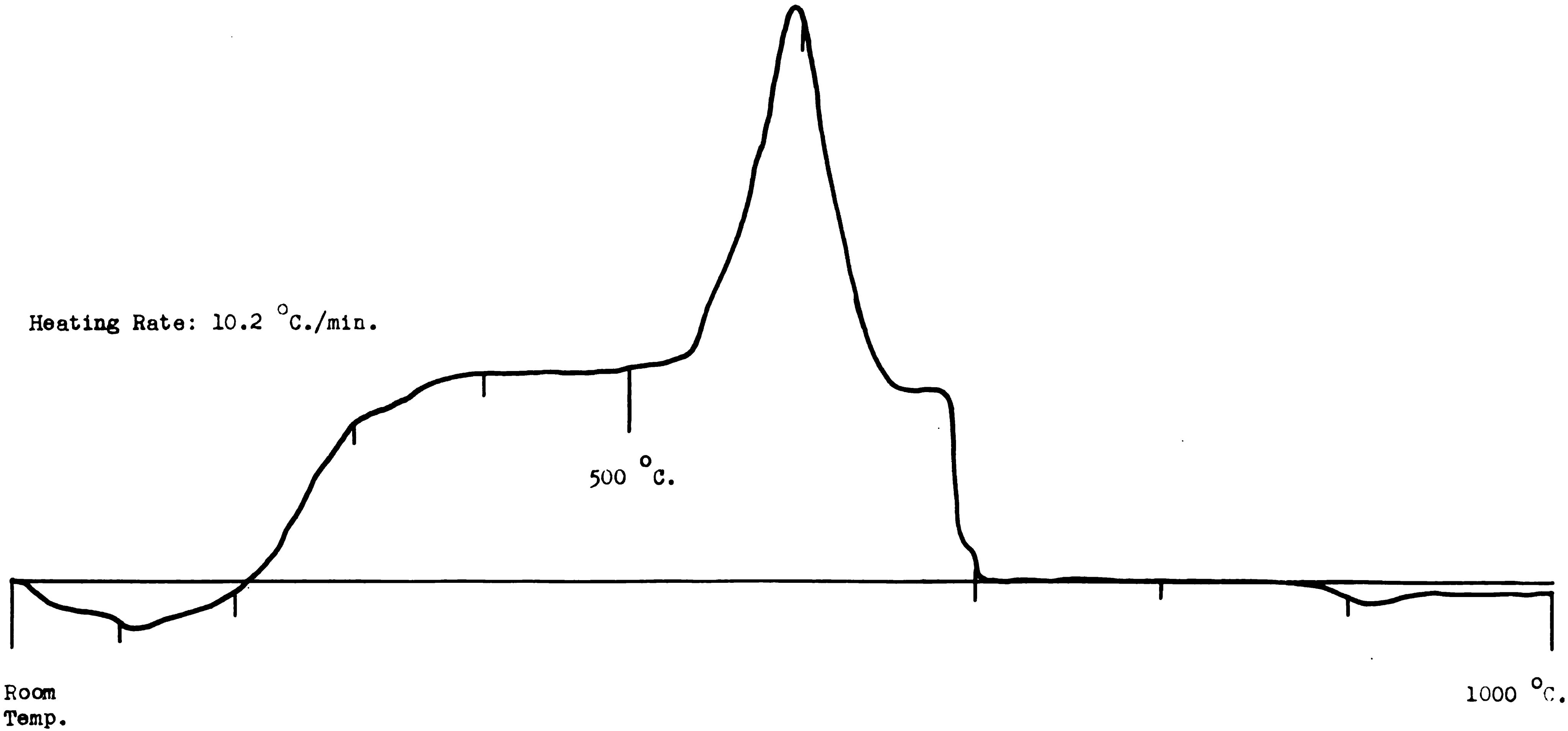
Experiment 7

Part A Trial 3



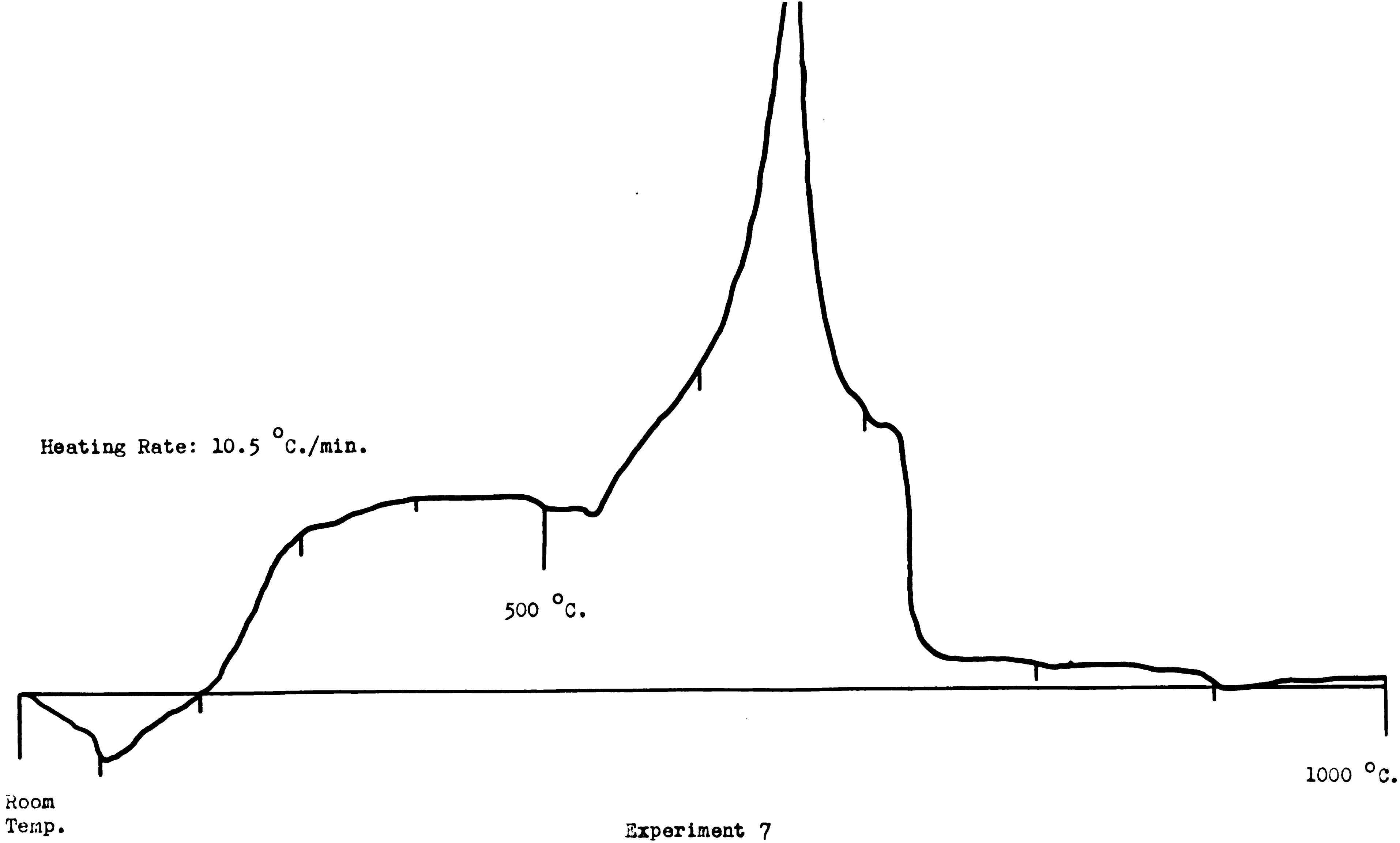
Experiment 7

Part B   Trial 4



Experiment 7

Part B   Trial 5



Experiment 7

Part B Trial 6

Experiment 8

Purpose

The purpose of this experiment was to find how variations of volume and packing affect the thermal curve of a particular sieve size when the weight of material is held constant.

Procedure

A 0.14-gm. sample of the 200^- mesh material was poured into the sample-holder and subjected to the degree of packing for each trial indicated in Table 11. Trial 1 was taken from the first trial of Experiment 6.

TABLE 11

DEGREE OF PACKING USED IN EACH TRIAL

Trial	Degree of Packing
1	1 tap with metal rod
2	15 taps
3	30 taps
4	30 taps + weight of glass rod

Results

TABLE 12

HEIGHT AND TEMPERATURES OF PEAKS X, Y, AND Z DUE TO PACKING

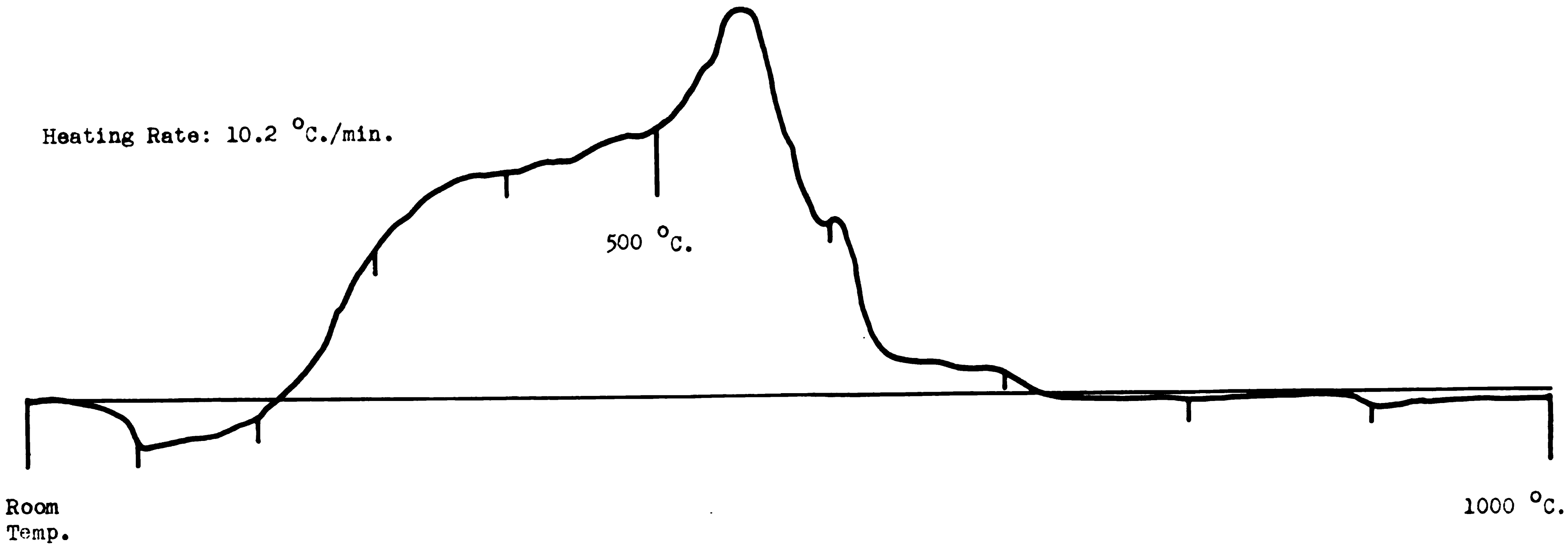
Packing	Peak X		Peak Y		Peak Z	
	Temp. (°C.)	Height (cm.)	Temp. (°C.)	Height (cm.)	Temp. (°C.)	Height (cm.)
1 tap	120	-0.6	440	3.0	580	6.9
15 taps	110	-0.8	440	3.8	550	6.9
30 taps	110	-0.7	440	3.8	550	6.3
30 taps + glass rod	110	-0.7	410	4.4	560	8.6

Experiment 8

Trial 1

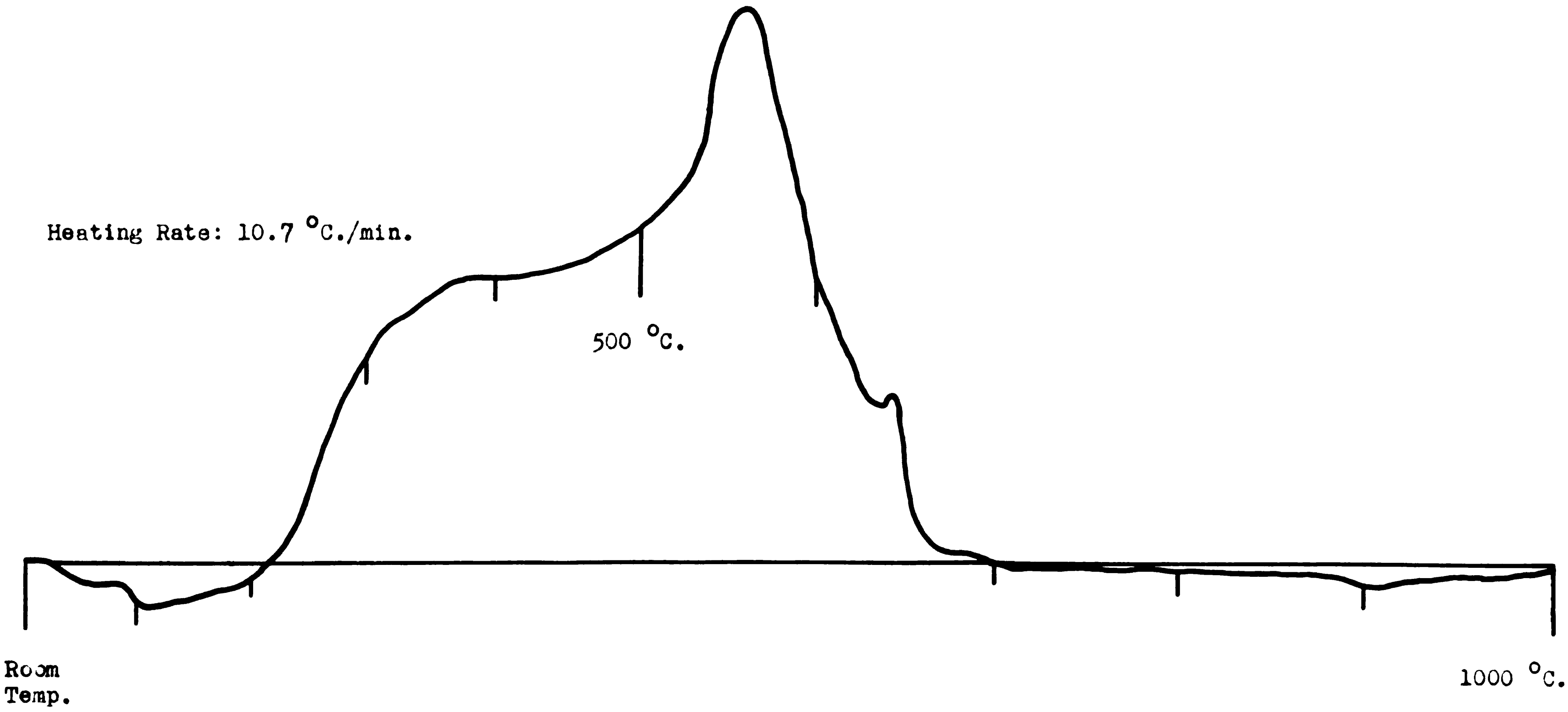
Experiment 8

Trial 2



Experiment 8

Trial 3



Experiment 8

Trial 4

Experiment 9

Purpose

The purpose of this experiment was to find how various furnace atmospheres affect the thermal curve of a particular sieve size when weight, volume, and degree of packing are held constant.

Procedure

The experiment was divided into four trials, each representing a different furnace atmosphere. A 0.28-gm. sample of the 150-200 mesh material was packed according to the standard procedure.

Trial 1. Air at 0.36 atmospheres of pressure was applied to the furnace. This was essentially a vacuum.

Trial 2. Air at ordinary atmospheric pressure was applied to the furnace. Information for this trial was taken from Trial 3 of Experiment 7.

Trial 3. Air at 5.14 atmospheres of pressure was applied to the furnace.

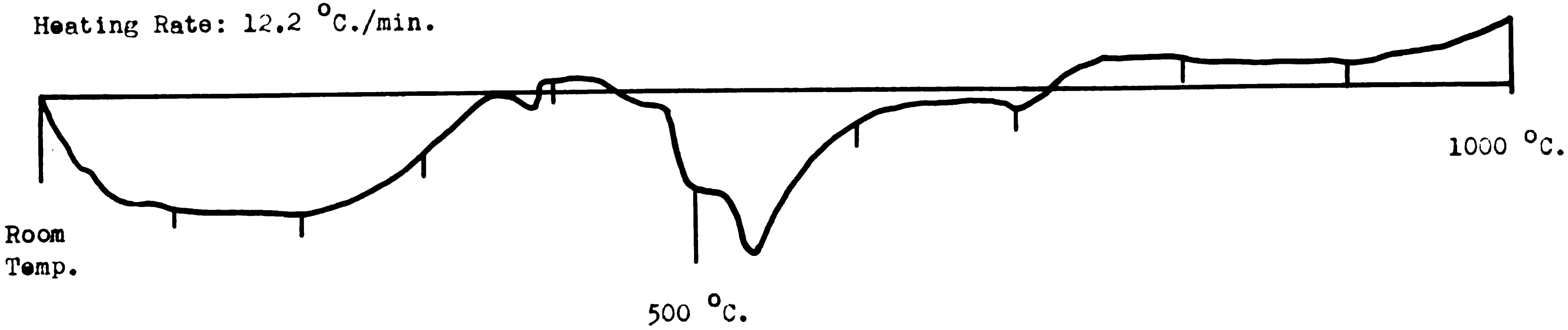
Trial 4. An inert atmosphere of nitrogen under pressure was used. To accomplish this, 5.14 atmospheres of air pressure were applied to the furnace. Nitrogen was then forced through a porous plug at the bottom of the sample to counterbalance this pressure.

Results

TABLE 13

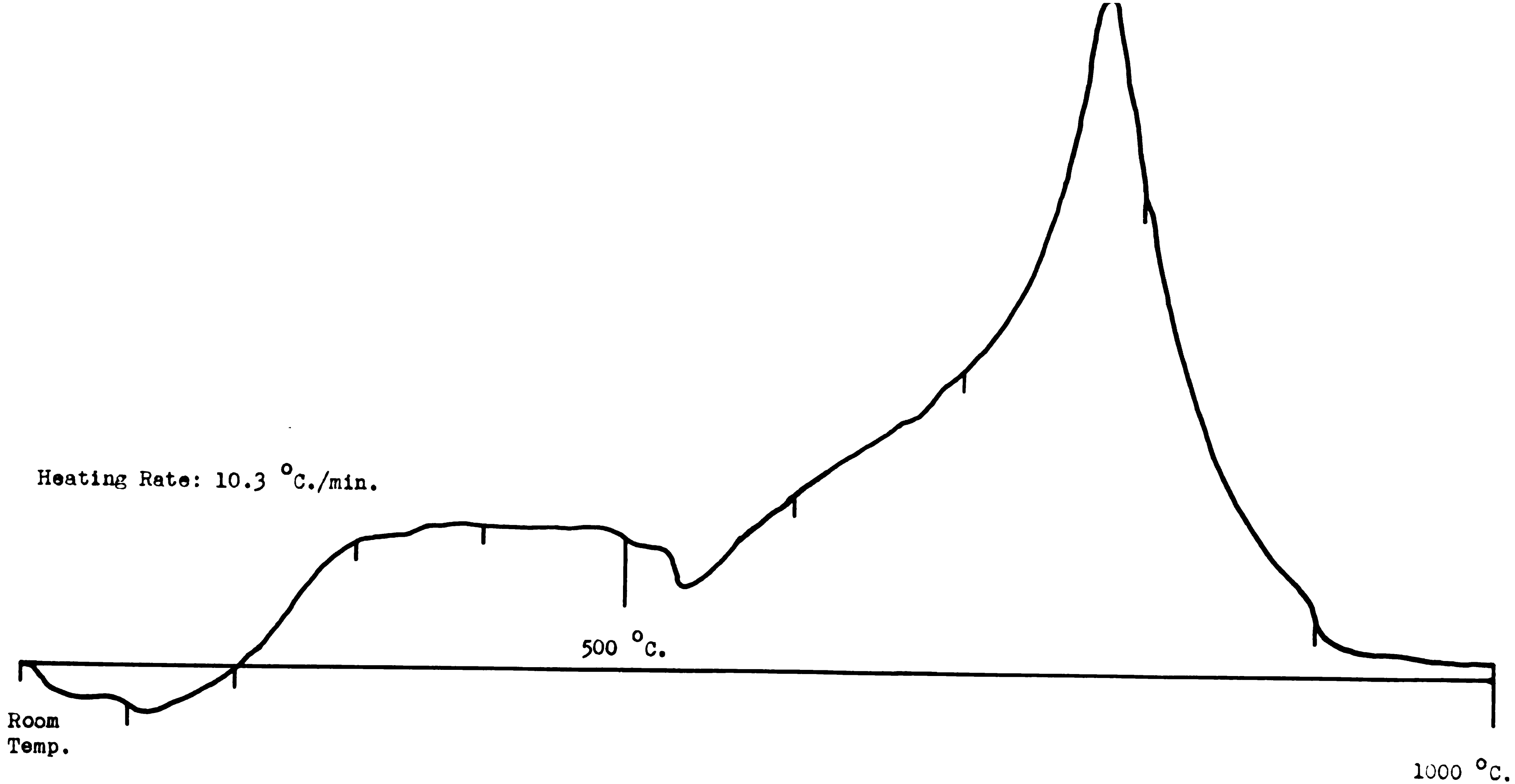
HEIGHT AND TEMPERATURE OF PEAKS X, Y, AND Z DUE TO FURNACE ATMOSPHERE

Atmosphere	Pressure in Atmospheres	Peak X		Peak Y		Peak Z	
		Temp. (°C.)	Height (cm.)	Temp. (°C.)	Height (cm.)	Temp. (°C.)	Height (cm.)
Air	0.36	150	-1.7	410	0.2	770	0.4
Air	1.0	120	-0.8	430	2.4	780	11.4
Air	5.14	140	-0.5	520	2.6	710	10.8
Nitrogen	5.14	110	-0.9	380	-0.2	720	-0.6



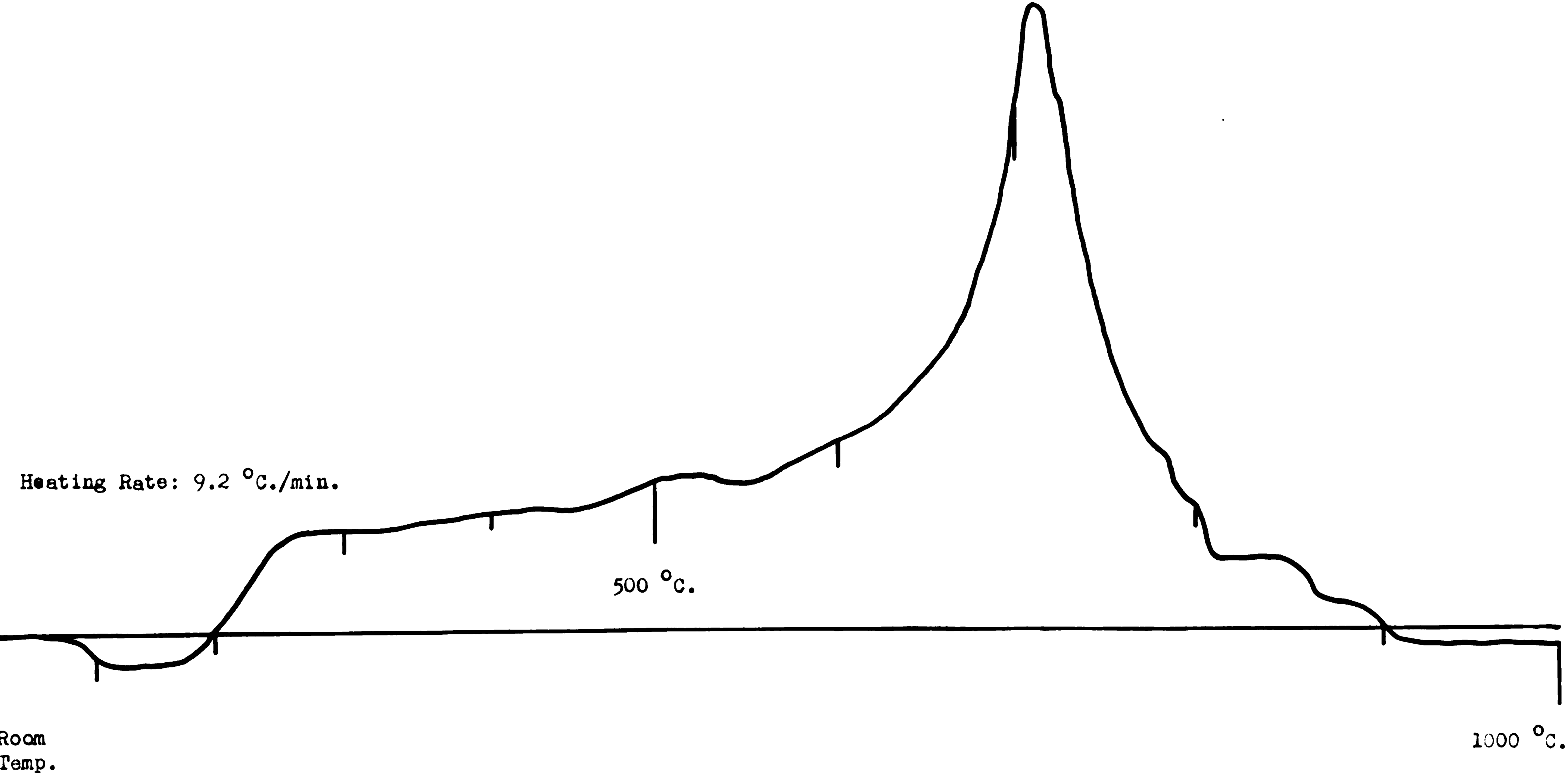
Experiment 9

Trial 1



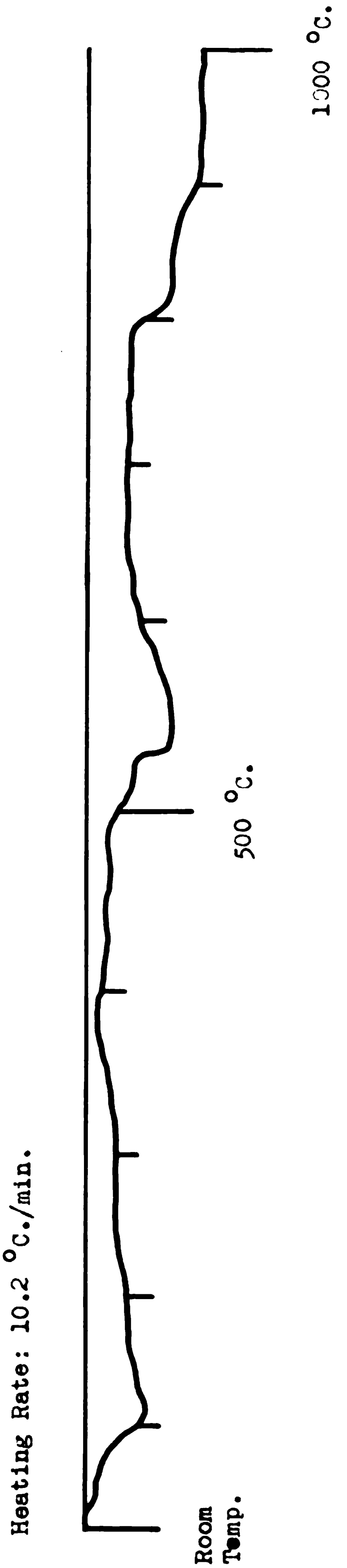
Experiment 9

Trial 2



Experiment 9

Trial 3



Experiment 9

Trial 4

ANALYSIS OF RESULTS

In order to interpret easily the results, graphs of the position and size of the peaks on the thermal curves versus the variables were drawn and are shown at the end of this section.

Probable Causes of Peaks

Peak X has the same character and position throughout all of the experiments. Because this peak is at a temperature of 110°-140°C. and because it is endothermic in nature, it is concluded that this reaction is probably caused by dehydration.

Peaks Y and Z are present on all thermal curves to greater or lesser extent. These exothermic peaks may be caused by devolatilization of organic matter, phase changes, chemical reactions between components, or oxidation. By comparing the thermal curves of air under pressure and nitrogen under the same pressure in Experiment 9, and also Graphs 7 and 13, of peak height against atmosphere, it is concluded that the reactions were not due to devolatilization of organic material because this should not depend upon the nature of the atmosphere, but upon variations of pressure. Phase changes and reactions between components should not depend upon the nature of the furnace atmospheres or pressures used in Experiment 9, unless gases be involved in the reaction. But the reactions increase in intensity as pressure is increased; therefore, these possibilities may be eliminated.

The thermal curves and Graphs 7 and 13 of peak height against atmosphere do fit the oxidation possibility for Peaks Y and Z. As the availability of oxygen increases, the reactions increase; and when nitrogen, an inert atmosphere, is introduced, the reactions do not take place. The tentative conclusion may therefore be made that Peaks Y and Z were caused by oxidation reactions.

Using these tentative conclusions, it should be possible to predict the effects of the variables tested in Experiments 5 through 9.

Peak X--Possible Dehydration

1. A decrease of particle size should make dehydration easier; therefore, the peak should increase in height in the negative direction.

2. An increase of weight should give more material to dehydrate, and the peak should increase in height in the negative direction.

3. An increase of packing should hinder the escape of water vapor, and the peak should decrease in height.

4. An increase in volume, being related directly to weight and inversely to packing, should produce indeterminate effects depending on relative importance of mass.

Peaks Y and Z--Possible Oxidation Reactions

1. A decrease of particle size should make oxidation easier; therefore, these peaks should increase in height.

2. An increase of weight gives more material to oxidize, and therefore, should increase the height of these peaks.

3. An increase of packing should hinder oxygen from gaining access to the material, and the peaks should decrease in height.

4. As described above, an increase of volume should produce indeterminate effects on the thermal curves.

Discussion of Peaks

Peak X

In Graph 4 the peak increases in magnitude (in the negative direction) as mass and volume increase, which indicates that mass, volume, or both may contribute to this effect. Graph 2 shows that increase of mass and packing cause only a slight increase of peak height. Furthermore, when packing increases and volume decreases, as shown in Graph 5, the height of the peak remains essentially constant. These facts may be resolved into the following relationships for the 200^- mesh material:

1. An increase of mass increases the height of the peak in the negative direction.

2. An increase of packing slightly decreases the height of the peak but not enough to mask the effects of mass.

3. An increase of volume increases slightly the height of the peak.

An anomalous result appears in Graph 3, which shows a slight decrease of peak height when mass and volume are increased. It should be recalled, however, that the 200^- mesh material was of a decidedly different color than the coarser material. Changes in mass and volume, therefore, have little effect on the height of Peak X for the coarser material.

Graph 6 indicates that a decrease in particle size and a corresponding increase of volume have a variable effect, but tend to increase the peak height. Since volume has little effect on this peak, the cause may be attributed to a change in particle size.

Peak Y

In Graph 10 the peak decreases in height as mass and volume increase, which indicates that either or both of these variables may contribute to this effect. Graph 8, however, shows an increase of mass and packing decrease the height of the peak to a lesser amount than in Graph 10. Furthermore, an increase of packing and decrease of volume, shown in Graph 11, increases the height of the peak. These facts lead to the following conclusions:

1. An increase of mass decreases the height of the peak.

2. An increase of packing increases the height of the peak to the extent that it overcomes the effect of mass increase.

3. A volume increase may or may not increase the height of reaction.

Anomalous conclusions 1 and 2 may be explained as experimental error or the superposition of two reactions which are differently dependent on the variables.

From Graph 12 it can be seen that, except for the coarsest and finest material, a decrease of particle size increases the height of reaction.

Peak Z

Graph 16 shows that an increase of mass and volume causes an increase of peak height. The same effect is produced when mass and packing are increased, as shown in Graph 14. Graph 17 shows that an increase of packing with a corresponding decrease of volume slightly increases the height of Peak Z. These facts lead to the following conclusions:

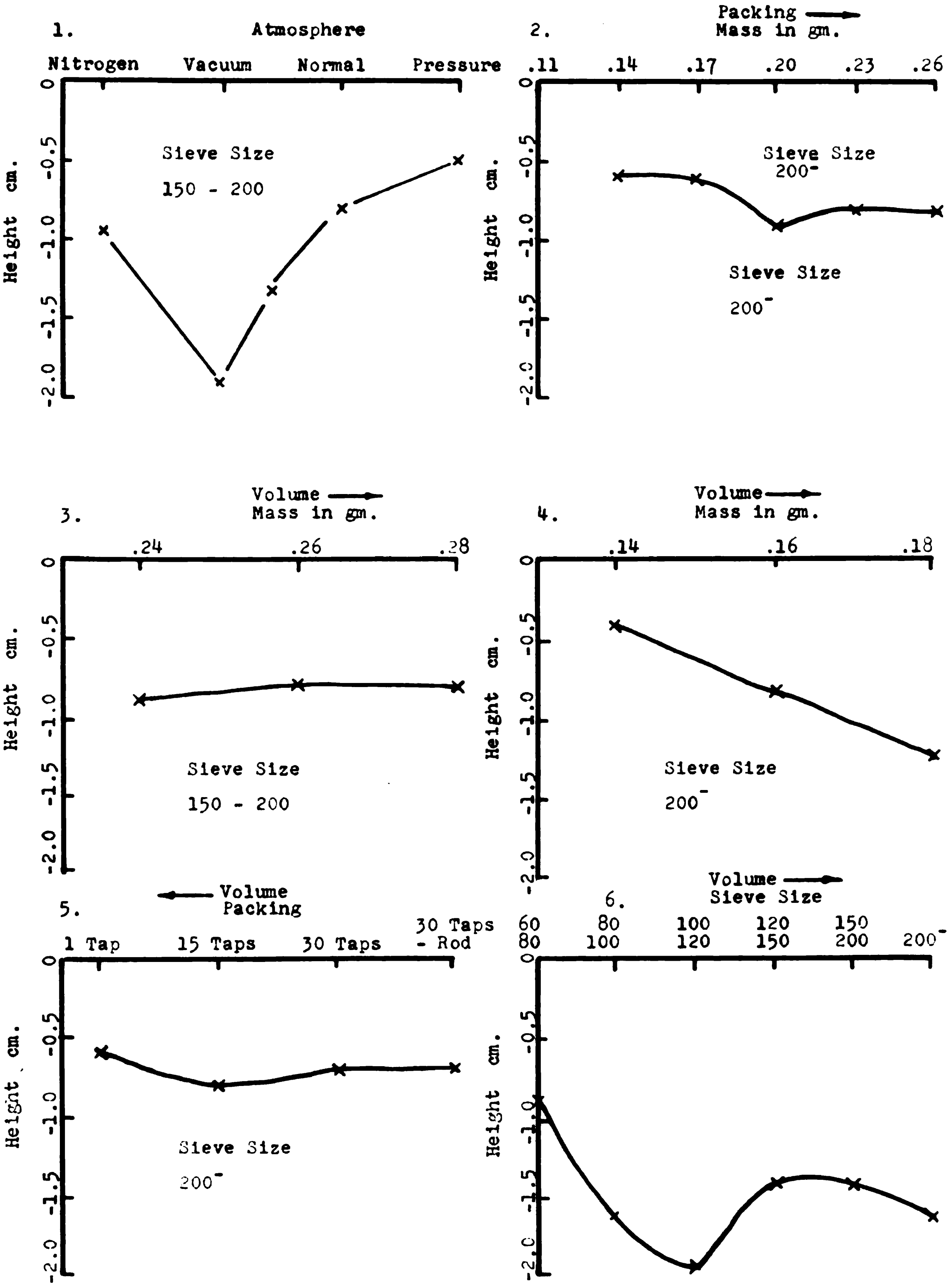
1. An increase of mass increases the height of Peak Z.

2. An increase of packing slightly increases the height of Peak Z.

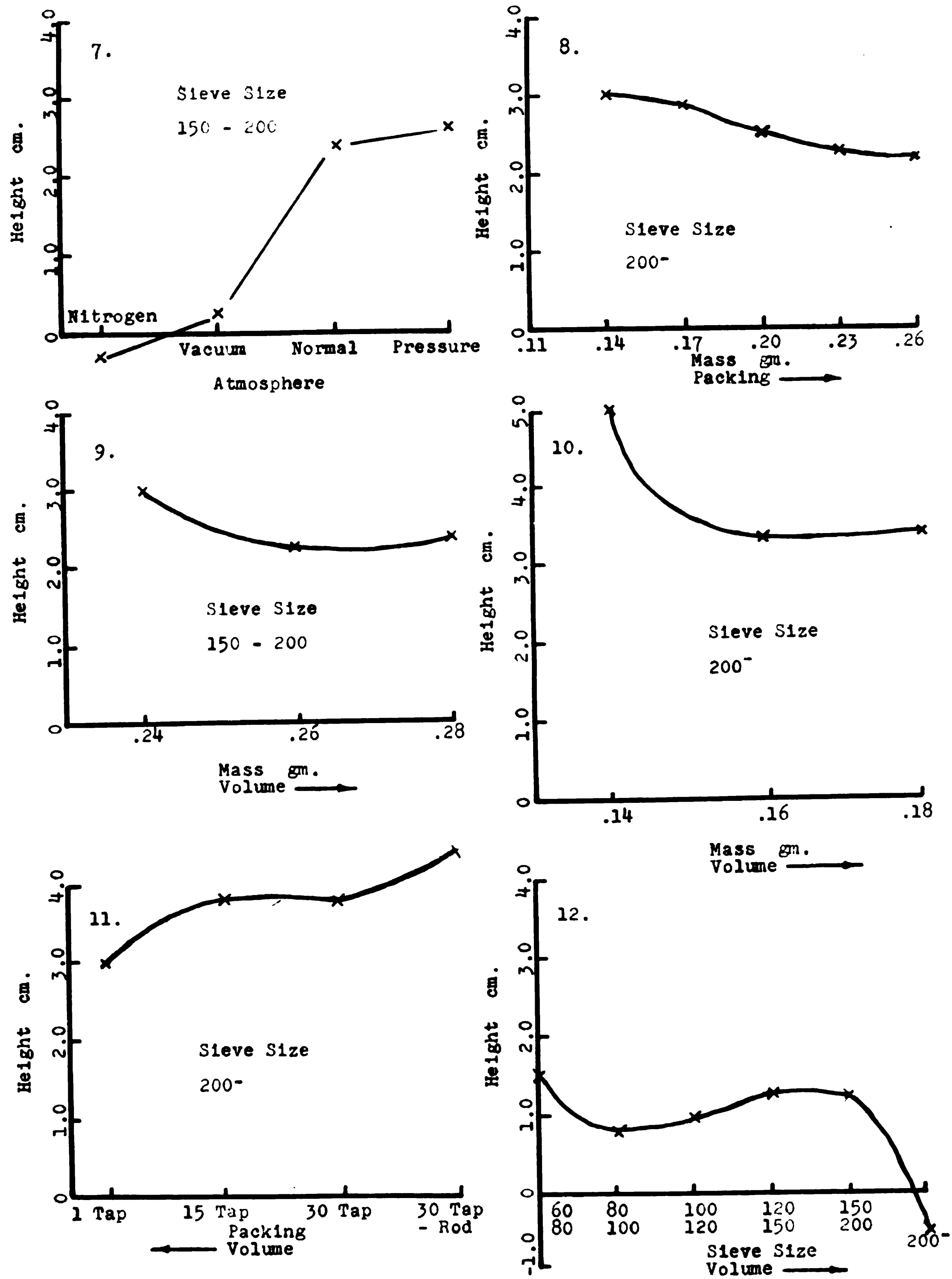
3. An increase of volume probably has little effect on the height of this peak.

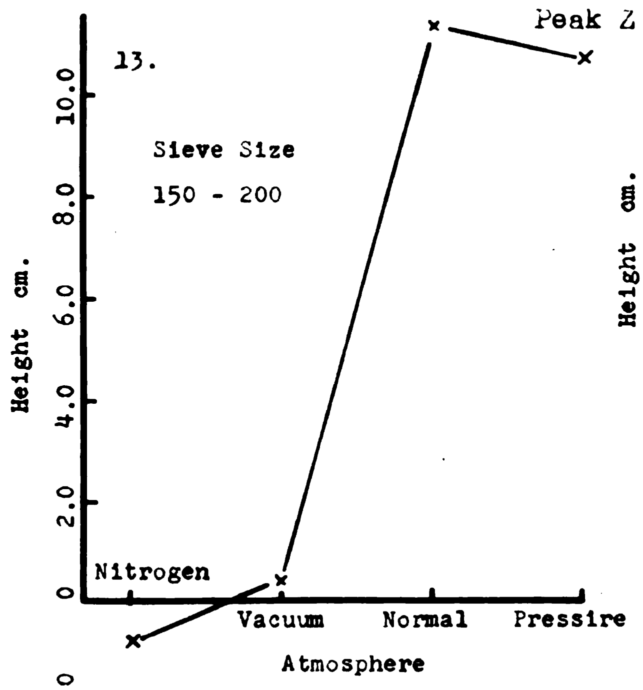
Graphs 19, 20, 21, and 22 show that a decrease of particle size and increase in mass, volume, and packing all shift the peak temperature to the right, with packing the predominate factor.

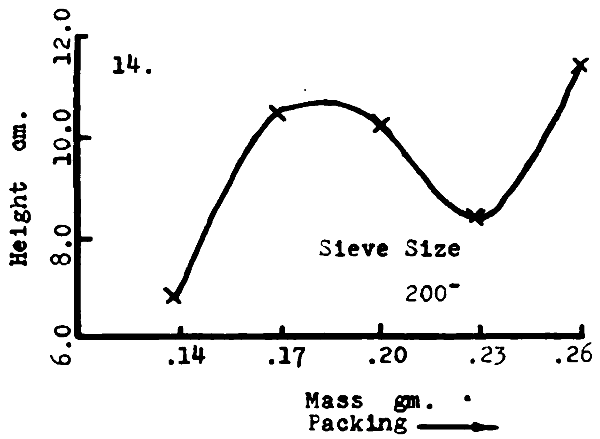
Peak X

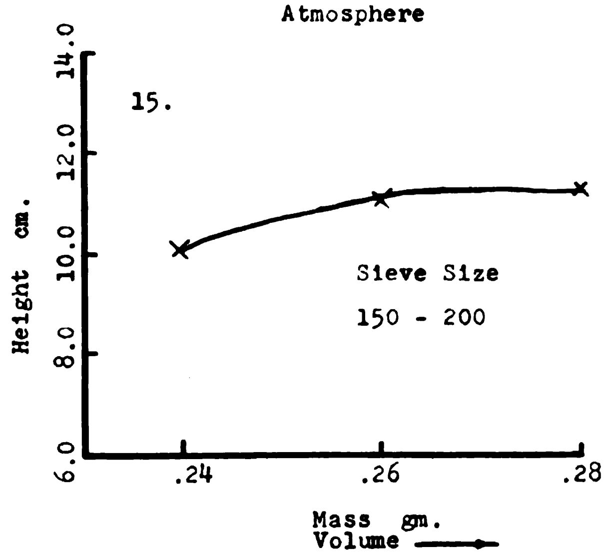

1.
Atmosphere
Nitrogen
Vacuum
Normal
Pressure
Height cm.
Sieve Size
150 - 200
2.
Packing
Mass in gm.
.11
.14
.17
.20
.23
.26
Sieve Size
200⁻
3.
Volume
Mass in gm.
.24
.26
.28
Sieve Size
150 - 200
4.
Volume
Mass in gm.
.14
.16
.18
Sieve Size
200⁻
5.
Volume
Packing
1 Tap
15 Taps
30 Taps
30 Taps - Rod
Sieve Size
200⁻
6.
Volume
Sieve Size
60 80
80 100
100 120
120 150
150 200
200⁻
0
-0.5
-1.0
-1.5
-2.0

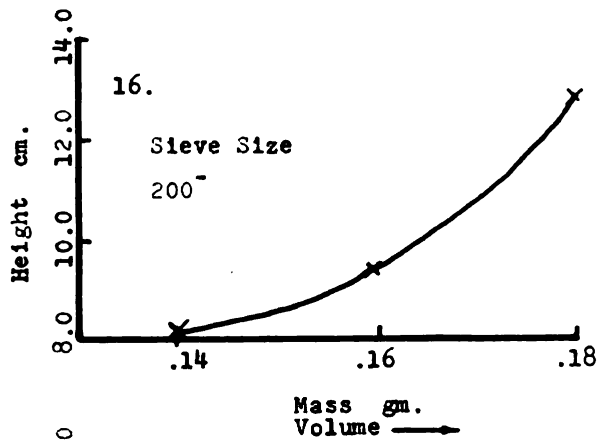
Peak Y

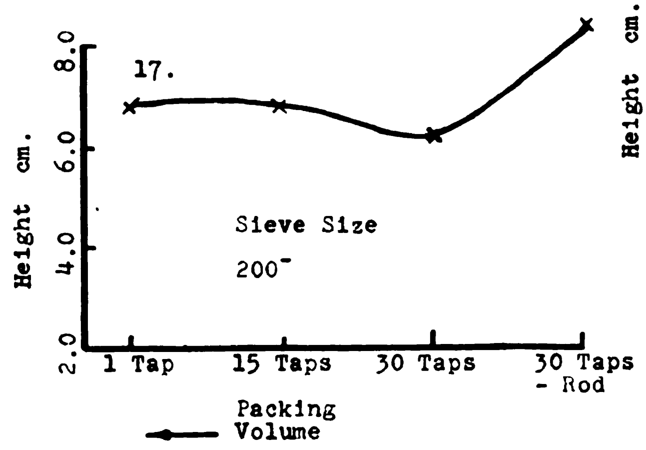

7.
Sieve Size
150 - 200
Height cm.
0
1.0
2.0
3.0
4.0
Nitrogen
Vacuum
Normal
Pressure
Atmosphere
8.
Sieve Size
200⁻
Height cm.
.11
.14
.17
.20
.23
.26
Mass gm.
Packing
9.
Sieve Size
150 - 200
Height cm.
.24
.26
.28
Mass gm.
Volume
10.
Sieve Size
200⁻
Height cm.
5.0
.14
.16
.18
Mass gm.
Volume
11.
Sieve Size
200-
Height cm.
1 Tap
15 Tap
30 Tap
30 Tap - Rod
Packing
Volume
12.
Height cm.
-1.0
60 80
80 100
100 120
120 150
150 200
200-
Sieve Size
Volume

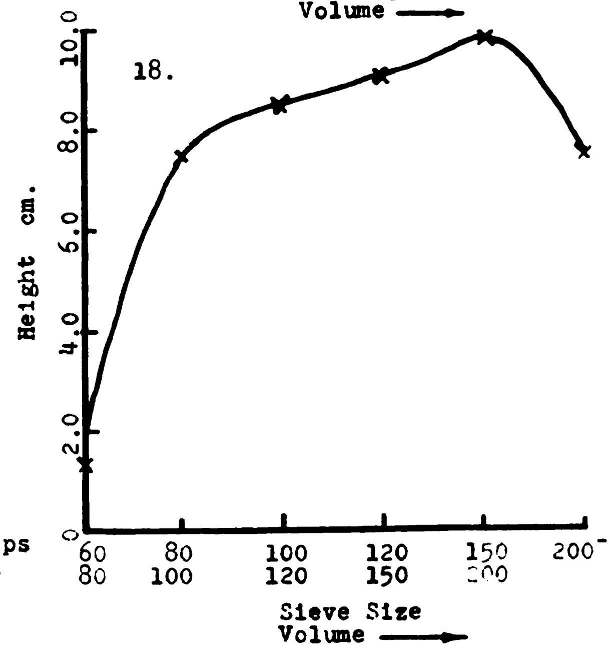

Peak Z
13.
Sieve Size
150 - 200
Height cm.
0
2.0
4.0
6.0
8.0
10.0
Nitrogen
Vacuum
Normal
Pressire
Atmosphere


14.
Sieve Size
200⁻
Height cm.
6.0
8.0
10.0
12.0
.14
.17
.20
.23
.26
Mass gm.
Packing

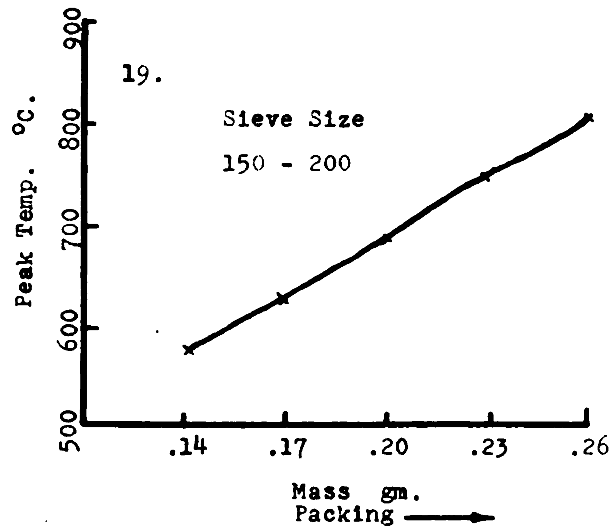

15.
Sieve Size
150 - 200
Height cm.
6.0
8.0
10.0
12.0
14.0
.24
.26
.28
Mass gm.
Volume

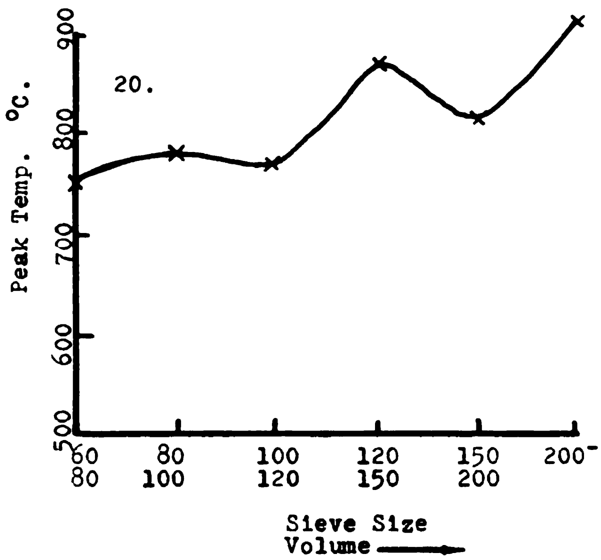

16.
Sieve Size
200⁻
Height cm.
8.0
10.0
12.0
14.0
.14
.16
.18
Mass gm.
Volume

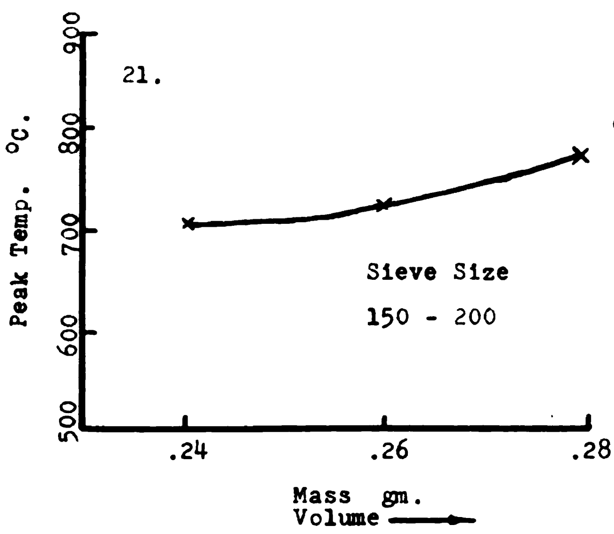

17.
Sieve Size
200⁻
Height cm.
2.0
4.0
6.0
8.0
1 Tap
15 Taps
30 Taps
30 Taps - Rod
Packing
Volume

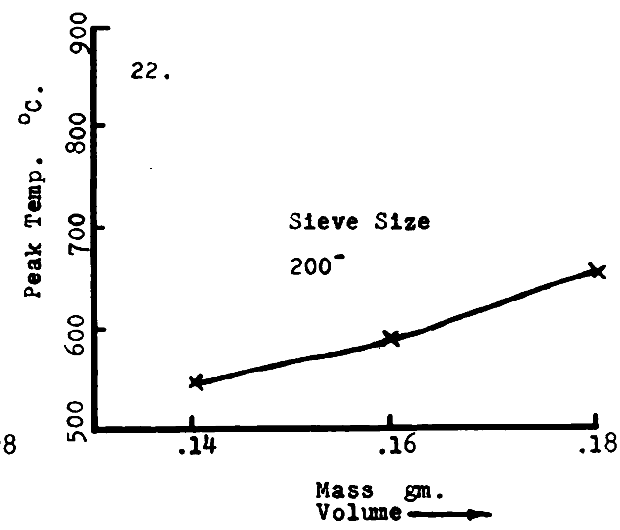

18.
Height cm.
0
2.0
4.0
6.0
8.0
10.0
60 80
80 100
100 120
120 150
150 200
200⁻
Sieve Size
Volume

Peak Z


19.
Sieve Size
150 - 200
Peak Temp. °C.
500
600
700
800
900
.14
.17
.20
.23
.26
Mass gm.
Packing


20.
Peak Temp. °C.
500
600
700
800
900
60 80
80 100
100 120
120 150
150 200
200⁻
Sieve Size
Volume


21.
Sieve Size
150 - 200
Peak Temp. °C.
500
600
700
800
900
.24
.26
.28
Mass gm.
Volume


22.
Sieve Size
200⁻
Peak Temp. °C.
500
600
700
800
900
.14
.16
.18
Mass gm.
Volume

CONCLUSION

The conclusions drawn from this research may best be considered in two parts, A and B. Part A, involving Experiments 1 through 4, deals with both gray and black shales. Part B, involving Experiments 5 through 9, deals with the black Antrim shale.

Part A

1. A simple procedure is not sufficient to product consistent results using the same sample.

2. Changes in quantity of material and degree of packing have little effect on the thermal curves of the gray noncarbonaceous shale, but do have a pronounced effect on the thermal curves of the black carbonaceous shale. Changes in degree of packing have the greater effect.

3. Consistent results may be obtained from the gray but not the black shale used in these experiments by holding constant the mass and degree of packing.

Part B

4. An increase of mass causes:

   a) Peak X to increase in height, in the negative direction, with the fine material, but has little effect on the coarser grain sizes.

   b) Peak Y to decrease in height.

   c) Peak Z to increase in height and shift to the right.

5. An increase of packing causes:

   a) Peak X to decrease in height, but not enough to overcome the effects of mass increase.

   b) Peak Y to increase in height to a greater extent than increase of mass.

   c) Peak Z to slightly decrease in height and shift to the right.

6. A decrease of particle size causes:

   a) Variations in Peak X with a tendency toward increase of height.

   b) Peak Y to increase in height except in the coarsest and finest material.

   c) Peak Z to shift to the right and, except in the finest material, to increase in height.

7. An increase of volume causes Peak Z to shift to the right. Changes in volume introduce yet another variable: the relative position of the thermocouple in the sample. The significance of this factor has not been determined.

8. An increase of air pressure causes all three peaks to increase in magnitude.

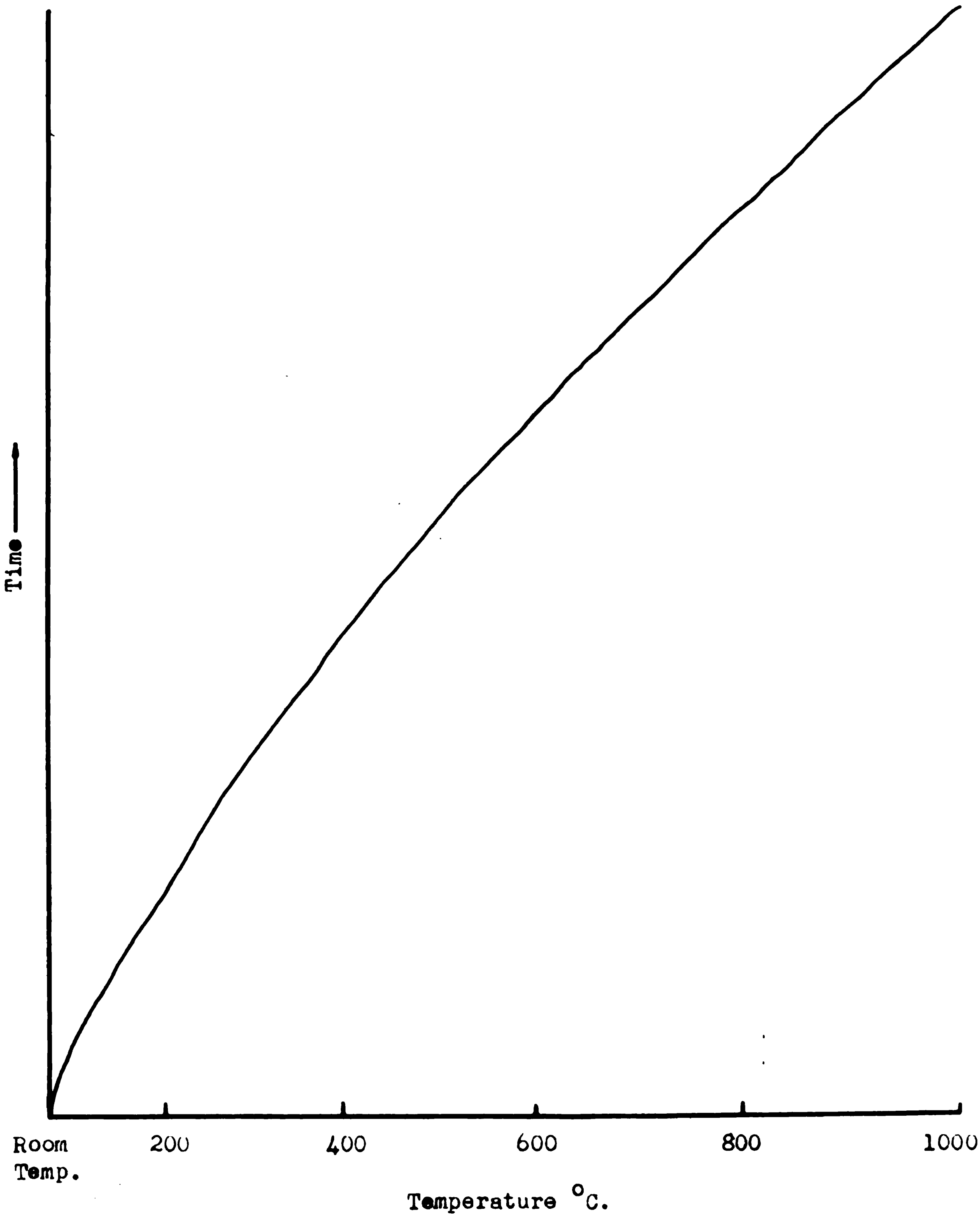
9. Nitrogen under pressure produces a relatively flat thermal curve which indicates that a gas present in air, other than nitrogen, is required to produce the exothermic reactions Y and Z.

10. Peaks X and Z were probably caused by dehydration and oxidation reactions, respectively, since the predictions have been substantiated for the most part. Peak Y however does not behave as predicted and therefore may not be an oxidation reaction. It is not possible at this point to determine the cause of Peak Y.

SUGGESTIONS FOR IMPROVEMENT OF EQUIPMENT

By comparing the furnace heating rates indicated on the thermal curves, it may be seen that there was considerable variance. Even within the same trial the heating rate varied, which is shown by a typical furnace temperature curve on the following page. The slope of the curve at any point gives the instantaneous heating rate at that point. The deviation from a straight line indicates that the rate was not constant throughout the trial. This fact is also shown by the unequal distances between the fiducial marks on the thermal curves. It has been found that the best heating rate lies between 10° and 15°C./min. When this rate is much faster than 15°C/min. the thermal reactions overlap. It is the opinion of the writer that any heat rate within this range is adequate, but any variance in the heating rate should not be tolerated. Therefore, the program controller should be designed to give a constant furnace heating rate somewhere between 10° and 15°C./min.

As described previously, the thermocouples pass through holes in the side of the sample-holder into the spaces for the inert material and the sample. This arrangement prohibits the removal of the sample-holder for cleaning or replacement without disturbing the



Typical furnace temperature curve.

thermocouples. Consequently, a sample block should be designed that would permit removal without disturbing the thermocouples.

The process of obtaining a thermal curve at its best is slow. An hour and a half was required to obtain a thermal curve, with an additional four hours required for the furnace to cool sufficiently to insert another sample. Since it would not be feasible to increase the furnace heating rate, it is further suggested that some method be devised to increase the cooling rate of the furnace.

SUGGESTIONS FOR FURTHER STUDY

It would appear that the only way consistent results could be obtained on black shale would be to hold constant sieve size, mass, packing, and volume. Probably the best approach would be first to break the shale down to a constant sieve size. A possible way to do this would be to use the ultrasonic method of breakdown to 200^- mesh. Then with sieve size, mass, and packing held constant, it would necessarily follow that volume would be constant.

If consistent results were obtained, it would be necessary to develop a standard procedure of sample preparation and insertion into the sample-holder. In addition it would be imperative that a standard method of quantitative measurement be devised. Three possible measurements would be peak temperature, peak height, and area under the peak. The latter two in themselves would introduce interesting problems such as the proper establishment of a base line and the exact determination of the beginning and end of any reaction.

It may be possible, eventually, to apply differential thermal analysis to the correlation of shales. This, however, may not be the most fruitful line of investigation.

The clay minerals, comprising the whole or part of a shale, that have been transported and deposited in a body of water are the products of weathering of one or more adjacent land masses. There is a possibility that one or more of the clay minerals may be the product of a specific climatic, depositional, or lithologic environment. If this is so, then a detailed study of the assemblage of clay minerals present in a shale should lead to accurate knowledge of the environmental conditions that produced that shale. It should be stressed at this point that differential thermal analysis is of limited value when used alone, but as a supplement to chemical and X-ray analyses it is a valuable aid in the determination of the clay minerals. It is therefore suggested that a detailed investigation be made of the clay minerals resulting from known environments using chemical, X-ray, and differential analyses. These data could then be used to determine accurately the environmental conditions that produced a particular shale, provided the original minerals were not affected by diagenetic processes.

Date Due
