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Equilibria in the Oxide Systems of Praseodymium and Americium

L. B. Asprey

April 26, 1949

Berkeley, California

DECLASSIFIED

To be declassified as a thesis.

Equilibria in the Oxide Systems of Praseodymium and Americium

DECLASSIFIED

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ABSTRACT

The thermal decomposition of the higher oxides of praseodymium and americium have been investigated. The decomposition of $PrO_{1.833}(Pr_6O_{11})$ to $PrO_{1.5}(Pr_2O_3)$ was accomplished and a value of 47 ± 5 kcals. for the heat of the reaction obtained. The reaction proved to be very complex. The decomposition of AmO_2 was carried out only to $AmO_{1.35}$ due to the greater stability of AmO_2. It was impossible to extend the value of 21 kcals. obtained for the partial heat of the reaction to obtain a value for the decomposition to $AmO_{1.5}$. The composition of the higher oxide was shown to be $AmO_{1.98 \pm 0.02}$.

The work described in this report was done under the auspices of the Atomic Energy Commission.

DECLASSIFIED

Equilibria in the Oxide Systems of Praseodymium and Americium

L. B. Asprey
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University of California, Berkeley, California

April 26, 1949

I. Introduction

An investigation of the thermal decomposition of the higher oxides of praseodymium and americium was undertaken with the following objectives in mind:

a) Equilibrium data would permit an evaluation of ΔF, ΔH and ΔS for the reactions

$$PrO_2 \longrightarrow 1/2\ Pr_2O_3 + 1/4\ O_2$$

$$AmO_2 \longrightarrow 1/2\ Am_2O_3 + 1/4\ O_2$$

Such data would furnish a basis for estimating the free energies for the aqueous reactions

$$Pr^{+3}(aq) + H^+ = Pr^{+4}(aq) + 1/2\ H_2$$

$$Am^{+3}(aq) + H^+ = Am^{+4}(aq) + 1/2\ H_2$$

b) In the case of americium this would constitute the first oxidation-reduction equilibrium studies for this element, and would be of value in estimating the thermodynamic stability of other compounds (AmF_4, for example).

c) The thermal stability and exact composition of the compound "AmO_2" would be directly determined and the oxygen pressure measured as a function of temperature. This would constitute a check on the validity of the assumption that the composition AmO_2 results from the direct ignition of the nitrate in air at 800° C -- an assumption made in calculating the half-life of the isotope Am^{241} from specific activity measurements based on weighing the higher oxide[1].

It should be mentioned that although the americium oxide equilibria were of primary interest, practical considerations required that most of the initial work

on this problem be carried out with a "stand-in" element. Because of the extremely limited availability and high toxicity of americium, the apparatus and techniques employed were developed using praseodymium as the most suitable "stand in" for americium.

Not all of the objectives mentioned previously were attained in this investigation. As will be made evident subsequently, the principle difficulty encountered arose from the (unanticipated) highly complex nature of the thermal decomposition of the higher praseodymium oxides. Because of the unique complexity of this reaction it was investigated in some detail. Another difficulty was the stability of AmO_2 which proved to be much greater than previously believed. It was impossible to carry out the thermal decomposition of AmO_2 beyond $AmO_{1.85}$ at the temperatures available with the apparatus used.

Of the experimental methods which have been used to study equilibria between solids and gases, two were investigated as best fulfilling the requirements as to sample size and reduction of the hazard associated with handling the highly radioactive dry americium oxide.

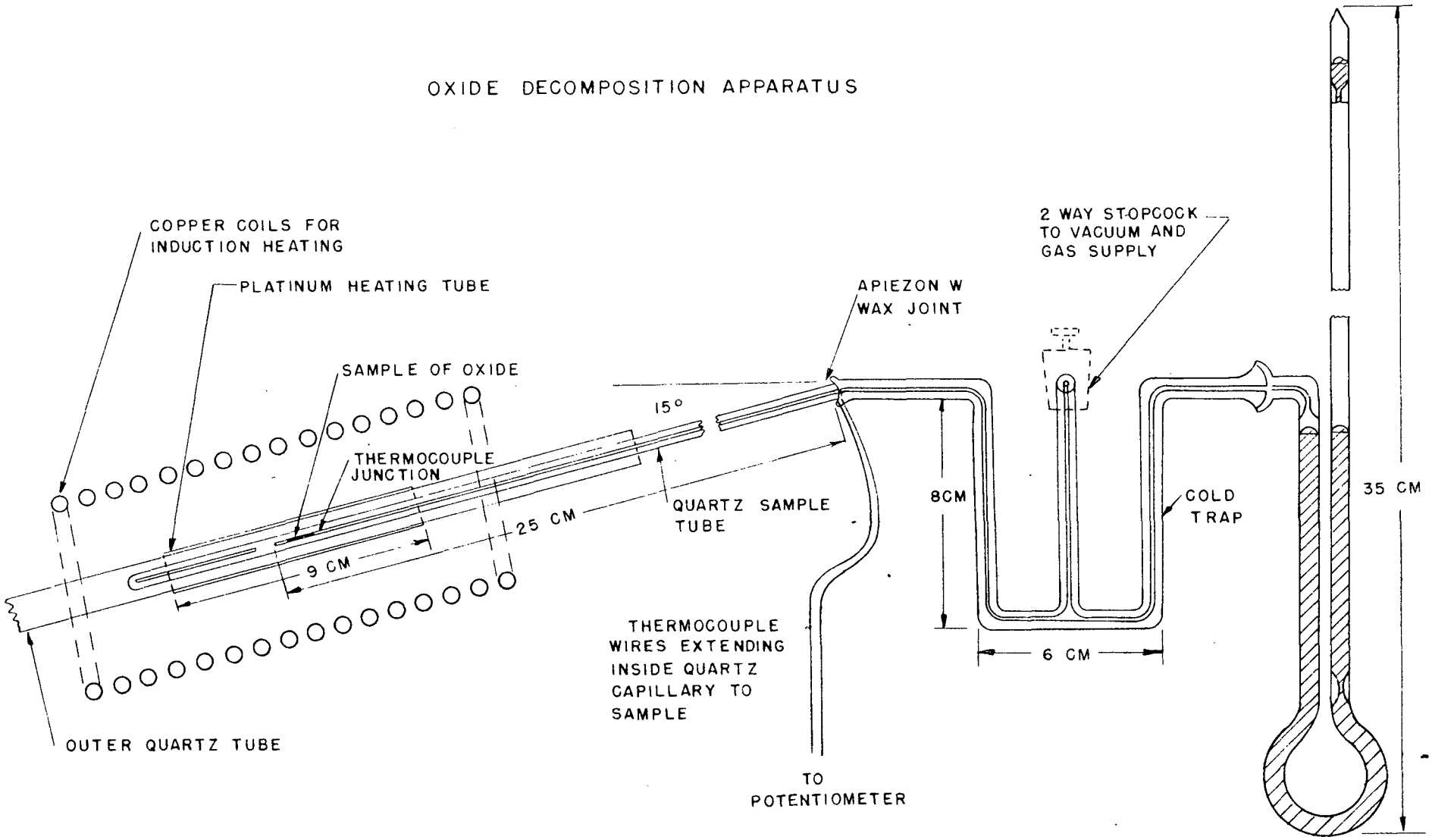
In the first method, the course of the decomposition was followed with a simple quartz fiber cantilever balance inside a closed system by measuring the weight of the oxide under various pressures of oxygen. Suitable reaction rates could be attained only at elevated temperatures. At those temperatures thermal currents prevented any measurement of the weight of the oxide. Hence after a preliminary qualitative investigation on praseodymium, the method was abandoned.

The second and more useful method consisted of following the course of the reaction by measurement of the pressure of oxygen in equilibrium with the solid in a system of known volume and temperature. Such investigations are ordinarily carried out with much larger samples than those used here, so that a relatively large change in oxygen pressure causes a very small change in composition of the

oxide. Particularly for the americium system but also for the praseodymium, since the amount of material available was limited to very small amounts, severe difficulties were placed in the way of accurate measurements. A system had to be designed so that the degradation of the oxide all the way to the sesquioxide would occur at readily measurable pressures, et. seq. the volume of the system had to be small, of the order of one to two milliliters of PrO_x. Since the total weight of oxygen evolved during the transition to $PrO_{1.5}$ was of the order of 100-200 micrograms, it was necessary to prevent the reaction of this oxygen with any other material in the system such as mercury vapor or stopcock grease or large errors in the calculation of the composition of the solid phase would result. As the vapor pressure of mercury at room temperature is 10^{-3} mm and since a mercury manometer was used to measure pressures, it was obvious that this vapor must be kept from contact with the hot oxide. A cold trap maintained at the temperature of sublimation of solid CO_2 was built into the system, separating both the stop-cocks and the manometer from the part of the system undergoing heating. Due to volume considerations, small bore tubing was used for the manometer, introducing large corrections for the capillary depression of Hg. Since the weight of oxygen in the system was calculated from the known volume, pressure and density of the gas, it was necessary to correct for the effect of the cold trap and the heated section of the system. Further errors resulted from absorption of oxygen on the oxide itself and on the walls of the tubing of which the system was constructed. Since it was impossible to outgas the sample tube itself without subjecting the oxide to prolonged heating at high temperatures which would tend to decrease the reactivity of the sample, a further error entered due to the gases desorbed from the fused silica tube.

In the case of americium it was necessary to reduce still further the volume of the system due to the much smaller amount of americium available.

OXIDE DECOMPOSITION APPARATUS



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II. Apparatus - for praseodymium oxide decompositions

The system consisted of a manometer, a cold trap with a 3-way stopcock connecting to gas and vacuum lines, and a quartz capillary tube containing the oxide whose vapor pressure was to be measured. A thermocouple and potentiometer were used for measuring the temperature of the oxide, and a platinum tube was placed around the sample end of the quartz tube and was surrounded in turn by a copper coil used for induction heating. Differences in Hg level were measured by means of an cathetometer equipped with a telescope.

The mercury manometer was constructed of 3.6 mm I. D. precision bore tubing. It was of the closed type and could measure pressures up to 200 mm of mercury. The closed end contained a section of capillary to remove desorbed gases[2]. The open end of the manometer was sealed onto a short piece of 1 mm capillary, bent at right angles, to which was attached a capillary socket joint designated as S 12/1.

To this manometer, a cold trap made out of 1/2 mm capillary tubing was connected by an S 12/1 ball joint as shown in the diagram. The purpose of the trap was to keep mercury vapor from the hot end of the system and to remove any condensable gases. The middle leg of the trap was connected to a 3-way stopcock which in turn connected to gas and vacuum lines. By this means, any easily condensable gases were removed from oxygen added to the system. The end of the trap opposite to the manometer was blown out and then partially melted to make a flared joint to which the quartz tube could be fastened by Apiezon wax. The trap was cooled to -78.5° C by a mixture of crushed "dry ice" and ethyl alcohol.

A thick walled quartz tube, 23-25 cm. long and about 1 mm I. D. and 1.25 mm wall thickness was used to contain the sample. The end of the tube was sealed off and then an eight cm. piece of the same tubing welded on to reduce temperature

end effects when the tubing was heated. The end of the tube to be fastened to the cold trap was rounded by grinding on emery paper.

The oxide was heated by means of a 3 KVA oscillator, feeding into a copper coil. The sample tube was surrounded by a 12 mm. O. D. quartz tube over which was slipped a platinum tube 9 cm. in length. The water cooled induction coil consisted of a 6.0 cm. diameter coil, 16 cm. long, containing 16 turns, of 1/4" O. D. copper tubing, connected to the oscillator. The coil was placed so that the oxide sample and the outer platinum tube were centered in the copper coil. Test showed that the temperature was constant to within $\pm 1^{\circ}$ C over the length of tube occupied by the sample.

Earlier experiments had employed a nickel block 5" long and 1-1/4" in diameter containing 2 holes, one for the sample tube and another for the thermocouple. The Ni block was surrounded by an asbestos insulated tube furnace of the ordinary type. The temperature gradient was too large and the time consumed in coming to an equilibrium temperature was too great so the change was made to induction heating.

Attempts to measure the temperature of the oxide sample by means of an exterior thermocouple gave variable results so an interior thermocouple was used. Five mil Pt, Pt-10% Rh wire was inserted down the length of the quartz sample tube. At the lower end of the thermocouple one wire was insulated from contact with the other by means of fine quartz capillary, and near the waxed joint by a coat of glyptal varnish. The hot junction was buried in the oxide or was within 2 mm of it for all runs. A cold junction was maintained at 0° C by means of an ice and water bath. The effect of the inductive field on the thermocouple was small and it was felt that the thermal conductivity between the junction and sample was sufficiently great so no appreciable error in the measurement of the temperature would result.

The potential developed was measured by a Rubicon Portable Precision Potentiometer of more than adequate sensitivity, since measurements were made only to the nearest degree Centigrade.

The difference in the level of the 2 Hg arms of the manometer was measured by means of a Gaertner cathetometer, equipped with a telescope and a vernier so that readings could be made accurately to the nearest 0.05 mm and estimated still more closely.

Since it was necessary to know the total volume at any pressure in order to calculate the composition, all parts of the system were calibrated by filling with mercury which was then removed and weighed. A reference mark was scratched on the precision bore section of the manometer near the open end. The volume of the manometer up to this point was measured before the manometer was filled with mercury. Changes in the volume of the system due to pressure changes could then easily be calculated. An assumption was made that the menisci were spherical segments and their volume calculated on this basis. The volume of the quartz insulation on the thermocouple wire was calculated from a measurement of its diameter and length. The overall uncertainty in the volume of the system at any pressure was estimated to be $\pm$ 2 μl. which varies from $\pm$0.4% to $\pm$ 0.2% depending on the pressure in the system. The volume of the quartz sample tube was approximately 1/4 ml and the cold trap and manometer to the reference point another 1/4 ml. At a pressure of approximately 100 mm. the total volume of the system was equal to 1 ml.

The capillary depression of mercury in tubes of 3.6 mm diameter is a large effect which must be corrected for. The system was pumped to $< 10^{-3}$ mm and the mercury levels of the manometer read, including the height of the menisci. A series of readings at zero pressure with different menisci heights were obtained and the correction to be applied determined from these. It is estimated that

the pressure read from the manometer should be accurate to $\pm$ 0.2 mm for all cases and nearer $\pm$ 0.1 mm for most.

The weight of oxygen in the system was calculated from the pressure at some known temperature, the density of oxygen at this temperature, and the volume of the system at this pressure. Since a cold trap was added to the system, cooling only a fraction of it, and the part containing the sample was heated to different temperatures, it was necessary to determine the extent of these two effects. This was done empirically by first filling the system with a known pressure of oxygen, then adding the cold trap and measuring the decrease in pressure. This was done over the range of pressures that would be worked with and the results plotted as % correction versus pressure in mm of Hg, giving a straight line. Calculations of the corrections were in close agreement with the measured values. The corrections for the increase in pressure due to heating the sample were determined in the same way. A certain pressure of O_2 was admitted to the system with the cold trap in place, and then the temperature raised over the desired range. This was done for a series of pressures. A series of straight lines were obtained by plotting T vs. % correction, one line for each pressure measured. The correction for the measured pressure could be obtained from this plot by interpolation. The over-all accuracy of these corrections probably falls within $\pm$ 0.5%.

The decomposition, $2\ CuO = Cu_2O + 1/2\ O_2$, was carried out in an apparatus of this type. The ΔH value obtained by plotting 1/T versus log P agreed with the value found by other workers[3] to within 0.2%, indicating that the system is capable of giving good results with samples of the order of a few milligrams.

When used for the decomposition of americium oxide, the system was surrounded by a box made from plywood and lucite, fitted with sliding doors on the front and connected to the exhaust system of the room so that air was constantly being drawn through the box. The system used in this case was similar but of much smaller volume.

III. Preparation of Sample

The praseodymium used in this investigation was obtained from Johnson-Matthey and Co., Ltd. of London, and was of their best quality. Spectroscopic analysis showed several percent of sodium and potassium and less than 1% of other rare earths. This material was further purified by R. C. Lilly and D. C. Stewart of this laboratory by means of ion exchange methods, yielding a praseodymium oxide that was pure within the sensitivity of the spectroscopic method.

Table I

Spectrographic Analysis of Praseodymium
reported as micrograms per fifty micrograms of sample
(ND = not detected)

Al - ND	Gd - ND $<$ 0.1	Ta - ND $<$ 0.5
Ba - ND	Ho - ND $<$ 0.1	Tb - ND $<$ 0.1
Be - ND $<$ 0.005	K - ND $<$ 0.1	Yb - ND $<$ 0.1
Ca - $<$ 0.01	La - ND $<$ 0.1	Y - ND $<$ 0.1
Ce - ND $<$ 0.1	Lu - ND $<$ 0.1	
Dy - ND $<$ 0.1	Na - ND $<$ 0.01	
Er - ND $<$ 0.1	Nd - ND $<$ 0.01	
Eu - ND $<$ 0.1	Sm - ND $<$ 0.1	
Fe - ND $<$ 0.1	Sr - ND $<$ 0.01	

The americium was purified by various chemical procedures to give a spectroscopically pure material.

In the case of praseodymium, the uncertainty in the composition of the compound usually designated as "Pr_6O_{11}", made it desirable to use Pr_2O_3 as the primary standard for weighing. The sesquioxide was obtained by hydrogen reduction of the higher oxide at 500° C. This was weighed in an air-tight platinum capsule.

In one case, the loose salt was removed in a dry N_2 atmosphere and its weight obtained by difference. This weight was known to $\pm$ 20 μg for an 8 mg sample of Pr_2O_3. This salt was added by means of a platinum funnel to the quartz sample tube of the apparatus. This tube was then vigorously tapped until all the oxide appeared to drop to the bottom of the tube. Due to the uncertainty as to whether all the salt had fallen to the bottom of the tube and due to the interaction of metal salts and SiO_2 at high temperatures, another procedure was adopted for a second sample. A small platinum tube about 1.5 cm long and about 1 mm O.D. was fabricated from 1/2 mil platinum foil. This tube was placed inside the larger platinum weighing vessel and subjected to the treatment to be used for the H_2 reduction, then capped and weighed. It was opened and the small inner tube removed, then recapped and weighed again, giving the weight of the tube by difference. After constant weight was obtained for the tube, it was filled with previously prepared Pr_2O_3, treated with H_2 at 500° C, and the weight of the salt found by difference. This procedure was repeated until constant weight was obtained. The weight of about 5 mg of Pr_2O_3 was known to $\pm$ 6 μg. The small tube was placed in the quartz sample tube and allowed to fall down to the bottom. In this case all of the oxide was in the zone that was to be heated.

Due to health hazards involved in the manipulations necessary to carry out the reduction, it was decided to weigh the americium oxide as AmO_2. The composition of this compound seems well established. No change in lattice constants for the oxide were detected after treatment of the compound under 50 atmospheres of O_2 at 200° C[4].

A small platinum tube was weighed repeatedly on a microgram balance after being treated in the same manner as was to be used for the weighing of the americium oxide. After constant weight was obtained, the tube was filled with

the americium oxide, heated to 700° C and cooled slowly to 250° C where it was held for 15 min. to allow maximum absorption of O_2. It was then put in the weighing capsule and capped. After checking by the health group for outside contamination, it was weighed. The vessel was opened, the inner tube removed and transferred to the quartz sample tube. The empty outer vessel was again weighed and the weight of AmO_2 determined by difference.

All weighings of praseodymium oxide were made on the Ainsworth F D J micro-balance, with the exception of the second praseodymium oxide sample called Sample 2 of Series 1 which was weighed on the American Balance Corp. semi-micro-balance sensitive to 10 μg. The americium oxide was weighed on a sensitive quartz balance.

IV. Experimental Results

The oxide decomposition data obtained from these studies is presented as a series of plots of the log of the pressure in mm of mercury versus the reciprocal of the absolute temperature. (Figs. I through IX, XIII, XIV).

The various samples and apparati used were as follows:

Pr Oxide Decomposition

Series 1 -- Preliminary apparatus - approximate calibration.

Sample 1 -- 8.037 ± 0.020 mg weighed as Pr_2O_3 directly into the quartz tube in the form of pellets. (Fig. I).

Sample 2 -- 8.11 ± 0.30 mg weighed as Pr_6O_{11} directly into the quartz tube as a powder. (Fig. II).

Series 2 -- Improved apparatus as shown in drawing - Accurately calibrated within the limits given in Section II.

Sample 1 -- 8.76 ± .020 mg weighed as Pr_2O_3, added directly to quartz sample tube (Figs. III, IV, V, VI).

Sample 2 -- 5.145 ± 0.006 mg weighed as Pr_2O_3 in small Pt tube which was then placed in the sample tube (Figs. VII, VIII, IX).

Am Oxide Decomposition

[A micro-modification of the apparatus used in Series 2 above]

Sample 1 -- Weighed as AmO_2 in small Pt tube which was then placed in the sample tube. (Figs. XIII and XIV).

Since the volume of the system was known at any pressure of O_2, the composition of the oxide could be calculated. Due to the fact that in some cases oxygen appeared to react with substances within the system and also due to outgassing of the absorbed gases in the fused silica tube, the composition of the oxide is not known with high accuracy particularly at temperatures above 1,000° C. The compositions given on Fig. XI represent the best values obtained from the average of several different runs. Compositions from a decomposition run which did not agree with any other runs were not considered in this compilation. Compositions given to only two decimal places are from only one or two separate runs and the degree of error is quite uncertain.

The x-ray data were obtained only for the praseodymium oxide decomposition. One set of samples was taken at $PrO_{1.66}$ and another at $PrO_{1.73}$. These data along with lattice constants of Pr_6O_{11}, PrO_2, and Pr_2O_3(C form) from measurements[5] made in these laboratories are presented in Fig. XII. The lattice constants given for the body-centered cubic structures are actually one-half of the true lattice constant. Another sample was taken at what corresponded to $PrO_{1.58}$ but was inhomogeneous yielding hexagonal Pr_2O_3 and a fluorite structure with the same lattice constant as that of $PrO_{1.73}$. This sample was cooled very rapidly which probably explains the inhomogeneity.

The composition of the higher oxide of americium was determined as follows: The higher oxide was reduced with H_2 at 550° C to Am_2O_3. Oxygen was then admitted to the system but in the first instance reaction occurred so rapidly that the

pressure of oxygen could not be accurately measured and only an approximation of the pressure could be obtained. This observation gave a minimum O : Am ratio of 1.95 to 1.0. A second experiment where the reduction was carried out at 750° C followed by heating one hour under high vacuum at 990° C, gave a reduction product which did not react rapidly with oxygen at room temperature. This allowed a more accurate measurement to be made. The result of this second measurement gave an oxygen to americium ratio of 1.98 ± 0.02 to 1.

The ΔH of the decomposition

Slopes of the various curves were measured by visually drawing the best straight line through the points of the log p vs. 1/T plots and those curves were used which had the best defined slopes. By plotting the points at which points of inflection at the beginning of curves F and H of Fig. XI first appeared for all runs at many different pressures, two straight lines were obtained on which most of the points fell. (Fig. X) The slopes of these two curves were calculated from this collected data. The lines of lesser slope (Curves A, B, C, D and E. Fig. XI) contributed only small amounts to the ΔH value and thus small inaccuracies in measurement of the slope were unimportant in the ΔH for the total reaction. The slopes of the curves beyond H were obtained from runs where only relatively small amounts of oxygen were present in the system and the decomposition could be effected at lower temperatures. Slight inaccuracies in these curves would cause large errors in the ΔH value as would errors in the composition at these points of inflection. The value of ΔH calculated using these slopes and compositions gave 47 ± 5 kcals. as the ΔH for the decomposition of Pr_6O_{11} to Pr_2O_3 over a temperature range of 400° to 1200° C. The ΔH obtained from heats of solution given in Bichowsky and Rossini[6] is 48 kcals. A further check on these values was the measurement of the heat of solution of Pr_2O_3 by L. Eyring[4], which agreed with the previous value. The conclusion is drawn that for much of the decomposition, at least, equilibrium pressures were measured.

Table III

ΔH Values for the Decomposition of Pr_6O_{11}
Letters refer to Fig. XI

Phase	Fraction of Total Reaction	$\log P_1/P_2$	$1/T_2 - 1/T_1$	$-\Delta H$(kcal) for fraction decomposed
A	0.021	0.439	0.30	0.157
B	0.039	0.368	0.20	0.775
C + D*	0.093	0.439	0.30	0.624
F	0.201	0.512	0.15	3.142
H	0.171	0.924	0.06	12.050
I	0.144	0.494	0.20	1.628
J	0.210	0.323	0.03	26.376
K	0.120	1.2505	0.30	2.292
Total	0.999	- - -	- - -	47.05

* Inclusion of the slope of curve E causes an increase of 0.3 kcal in the total ΔH.

V. Discussion

One original objective of this study was to obtain a ΔH value for the thermal decomposition of americium dioxide to americium sesquioxide. By assuming that there is the same difference between the heats of formation of AmO_2 and $Am^{+4}(aq)$ and 1/2 Am_2O_3 and $Am^{+3}(aq)$ as there is for the corresponding plutonium compounds and ions and that the ΔS values are the same, a value for the potential of the III-IV couple could be estimated.

Although the praseodymium-oxide system proved very complex and there was a lack of rapid, reversible equilibrium pressures over certain portions of the system, a reasonably accurate approximation of the ΔH for the decomposition of Pr_6O_{11} to Pr_2O_3 was obtainable. It was significant that a ΔH based on an idealized picture of the system agreed with the ΔH obtained from heats of solution to within the experimental error.

Unfortunately the thermal decomposition of AmO_2 could be carried out only to $AmO_{1.85}$ at the temperatures possible with this apparatus. Within the range of decomposition investigated ($AmO_2 \longrightarrow AmO_{1.85}$), ΔH for the total reaction assuming the ΔH of the partial reaction amounts to 21 kcals. This may be compared with 49 kcals from estimations based on the heat of solution of AmO_2[4].

The data presented in preceding sections show conclusively that the course of the thermal decomposition

$$Pr_6O_{11} = 3Pr_2O_3 + O_2$$

is highly complex. The most interesting feature of this reaction is that it suggests that it is possible to have immiscibility of oxides of very similar crystal structure and composition. In support of this hypothesis the data of McCullough showing immiscibility of Pr_6O_{11} and PrO_2 may be presented.[5]

Although no final interpretation of the data can be made until the system is examined by means of a high temperature x-ray camera, a tentative explanation based on meagre x-ray data taken at room temperature may be advanced. From the fact that both $PrO_{1.833}(Pr_6O_{11})$ and $PrO_{1.73}$ have fluorite structures, it would appear that all intermediate compositions have the same fluorite type structure.

The regions between $PrO_{1.833}$ and $PrO_{1.782}$ on the one hand and $PrO_{1.715}$ and $PrO_{1.51}$ on the other would appear to be regions of continuous solid solution formation, although if this is the case the P-T relationships are of an unusual nature. There is a certain inertia in the system in the area C, the upper curve being obtained by continually raising the temperature until the curve D is reached. Upon cooling from the point of intersection of C and D, the absorption of oxygen follows the lower dotted line which has the same slope as D and is reversible in that region. Again, as decomposition proceeds further, the curves C and D are followed up to the point of inflection between D and F, which apparently represents a limit of solid solution formation decomposition. The curve E was obtained in only two of the many decompositions effected and may represent another possible path for the decomposition. The loss of oxygen atoms as the decomposition proceeds eventually results in the formation of a new phase with a decomposition slope H. The actual experimental curve F shows a considerable curvature as it approaches curve G which may be an indication of solid solution formation. However, x-ray evidence shows only one prominent phase at $PrO_{1.73}$ which is near the composition $PrO_{1.715}$ at which the horizontal curve G intersects curve F.

The structure obtained at $PrO_{1.73}$ is the fluorite type with a coordination number of eight for the metal ion, while the structure at $PrO_{1.66}$ is of the C type with a coordination number of 6 for the metal ion. The pressure of oxygen

over the new phase represented by the decomposition curve H seems to be less than 1 mm of Hg at about 650° C. This was shown by the data presented in Fig. I, Runs A and B, where the oxygen pressure was lowered to zero by evacuation of the system at a temperature just high enough to have decomposed all of the previous phase, i.e. to the right of curve G. The pressure of oxygen then increased along the curve obtained in run B, Fig. I, which could be extrapolated to intersect the point of inflection between G and H and which had the same slope as curve H of Fig. XI.

Since the C type structure occurs at $PrO_{1.66}$, and a C type structure is known for $PrO_{1.5}(Pr_2O_3)$ it is probable that intermediate compositions also have the C type lattice. At high temperatures, the final product, $PrO_{1.5}$, has the A type structure (hexagonal) and presumably a transition to this lattice type must occur. From the data avilable, it is impossible to tell where this transition does take place. There are three points of inflection between phase H and the final phase Pr_2O_3, all having different slopes. As the temperature is increased, the same sort of decomposition takes place as for the fluorite structures.

The fact that the compositions of oxide existing at the intersections of the various straight lines conform to no simple stoichiometric ratios of Pr_2O_3 to PrO_2 seems analogous to the situation which has been demonstrated for many different oxides such as those of Ti, V, Mo, W, Mn, Cr, Ni, and Pb oxides[7].

VI. Acknowledgements

Appreciation is expressed to William Ruehle and J. R. Lawson of the Health Chemistry Group for their assistance during the studies on americium, to Mrs. W. B. Heppler who carried out the necessary weighings, to J. G. Conway who performed the spectrographic analyses; to Dr. D. H. Templeton, Carol Dauben, and Lee Jackson of the x-ray crystallography group who made all the crystal measurements; and to Miss Betty Summers who aided in the preparation of the figures.

Particular thanks are offered to Professor B. B. Cunningham under whose direction this work was carried out for his thoughtful advice and encouragement.

This work was performed uner the auspices of the Atomic Energy Commission.

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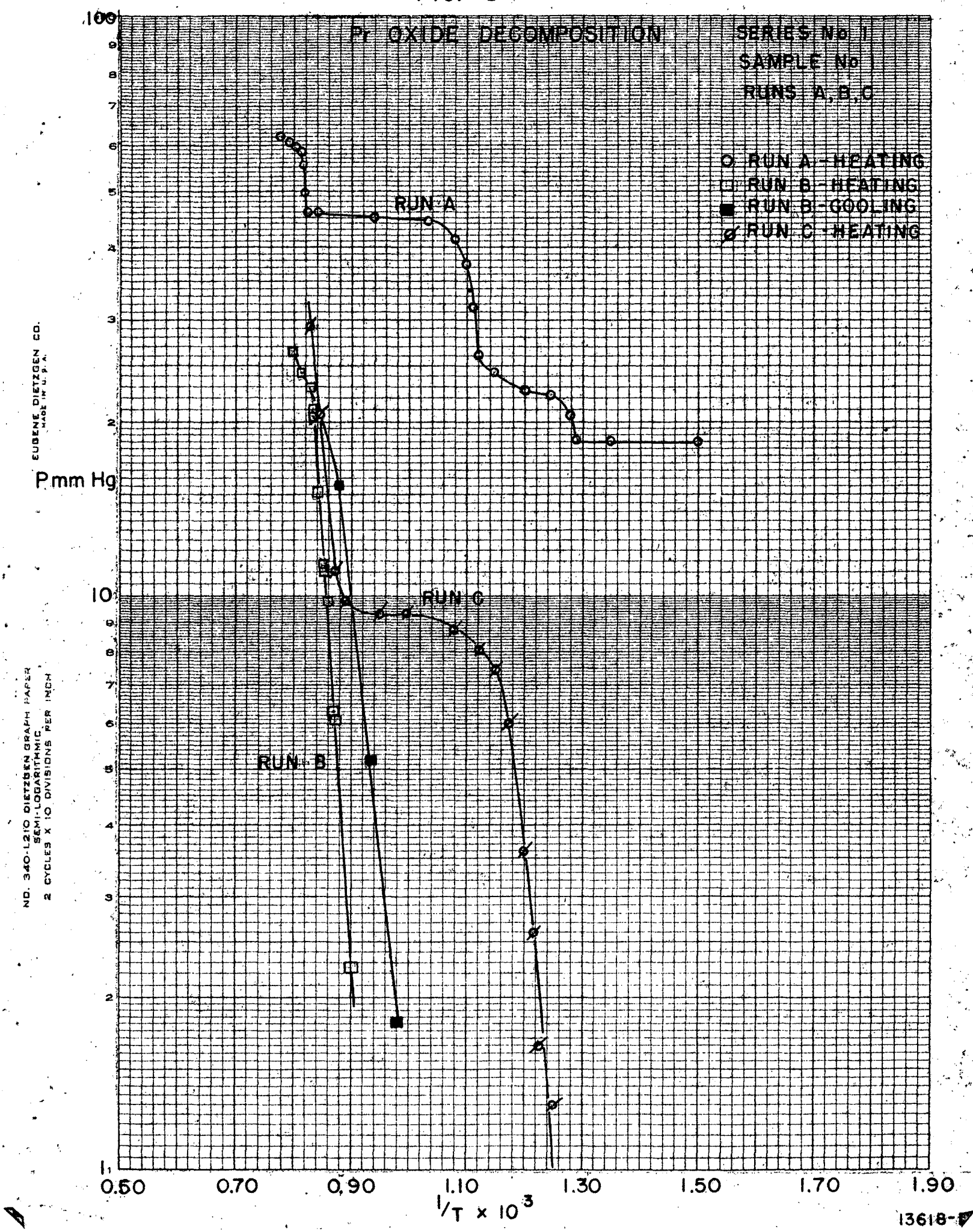
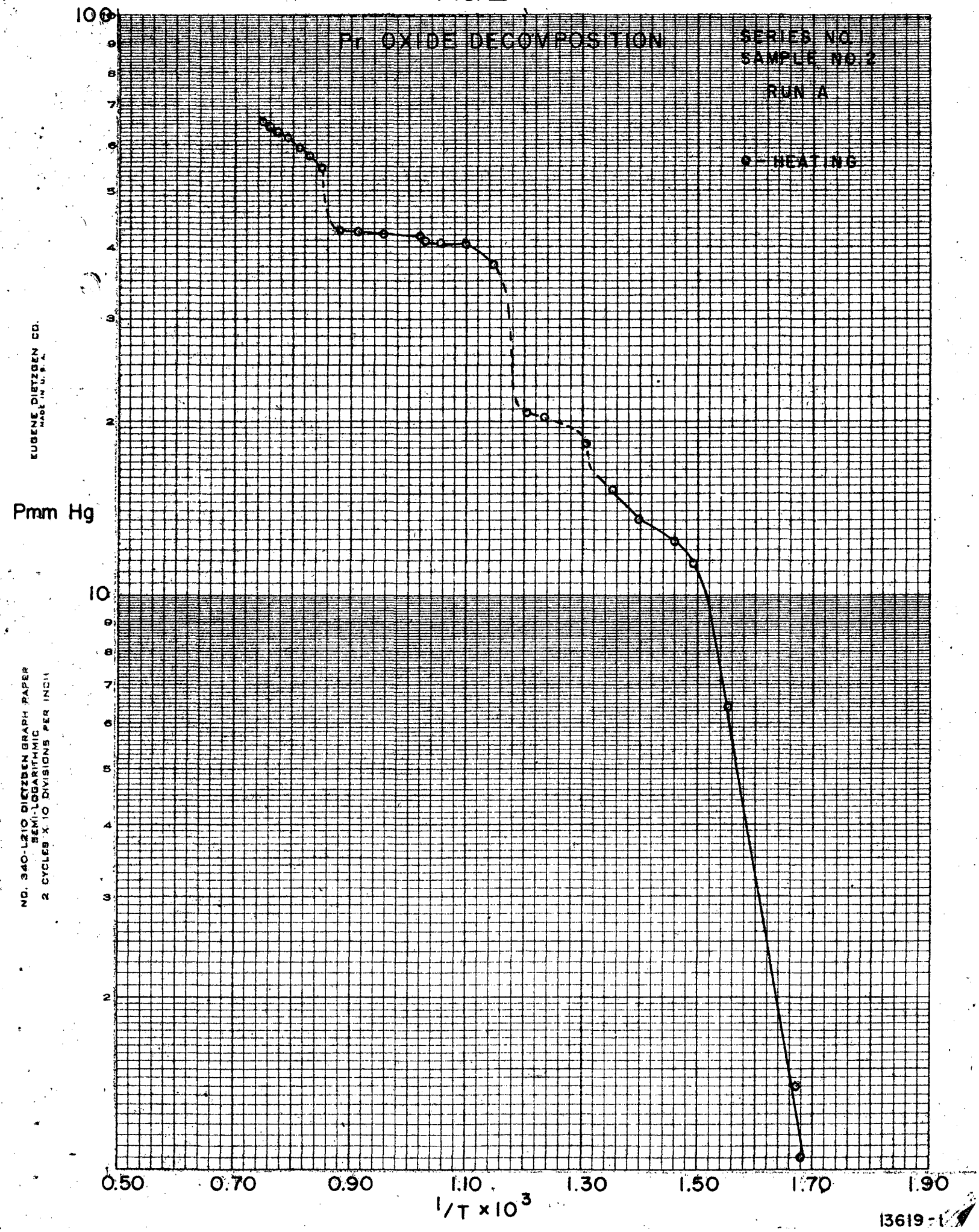
FIG. I


Pr OXIDE DECOMPOSITION
SERIES No. I
SAMPLE No. I
RUNS A, B, C
RUN A - HEATING
RUN B - HEATING
RUN B - COOLING
RUN C - HEATING
RUN A
RUN B
RUN C
P mm Hg
100
10
1
0.50
0.70
0.90
1.10
1.30
1.50
1.70
1.90
1/T x 10^3
EUGENE DIETZGEN CO.
MADE IN U.S.A.
NO. 340-L210 DIETZGEN GRAPH PAPER
SEMI-LOGARITHMIC
2 CYCLES X 10 DIVISIONS PER INCH

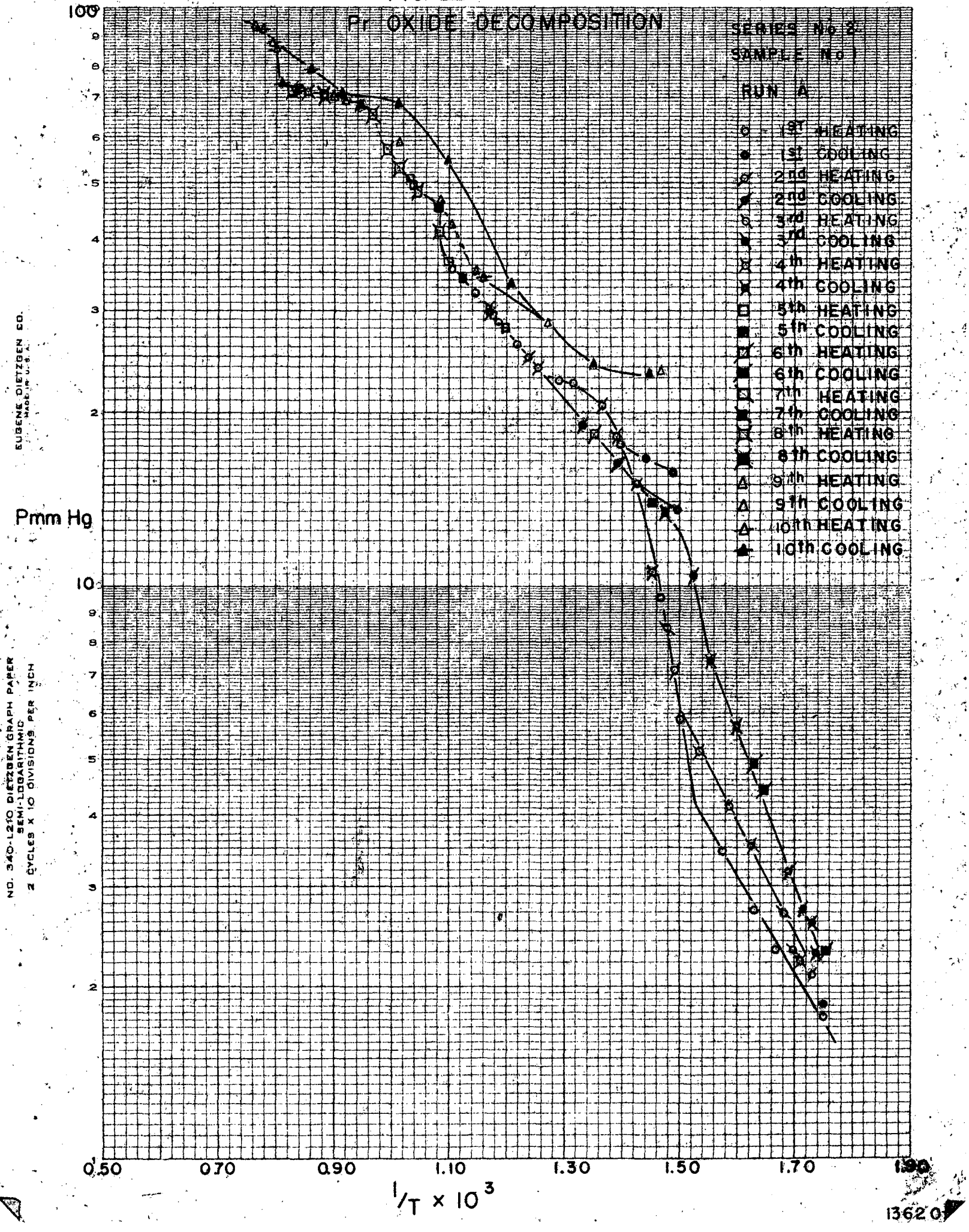
13618-

FIG. II



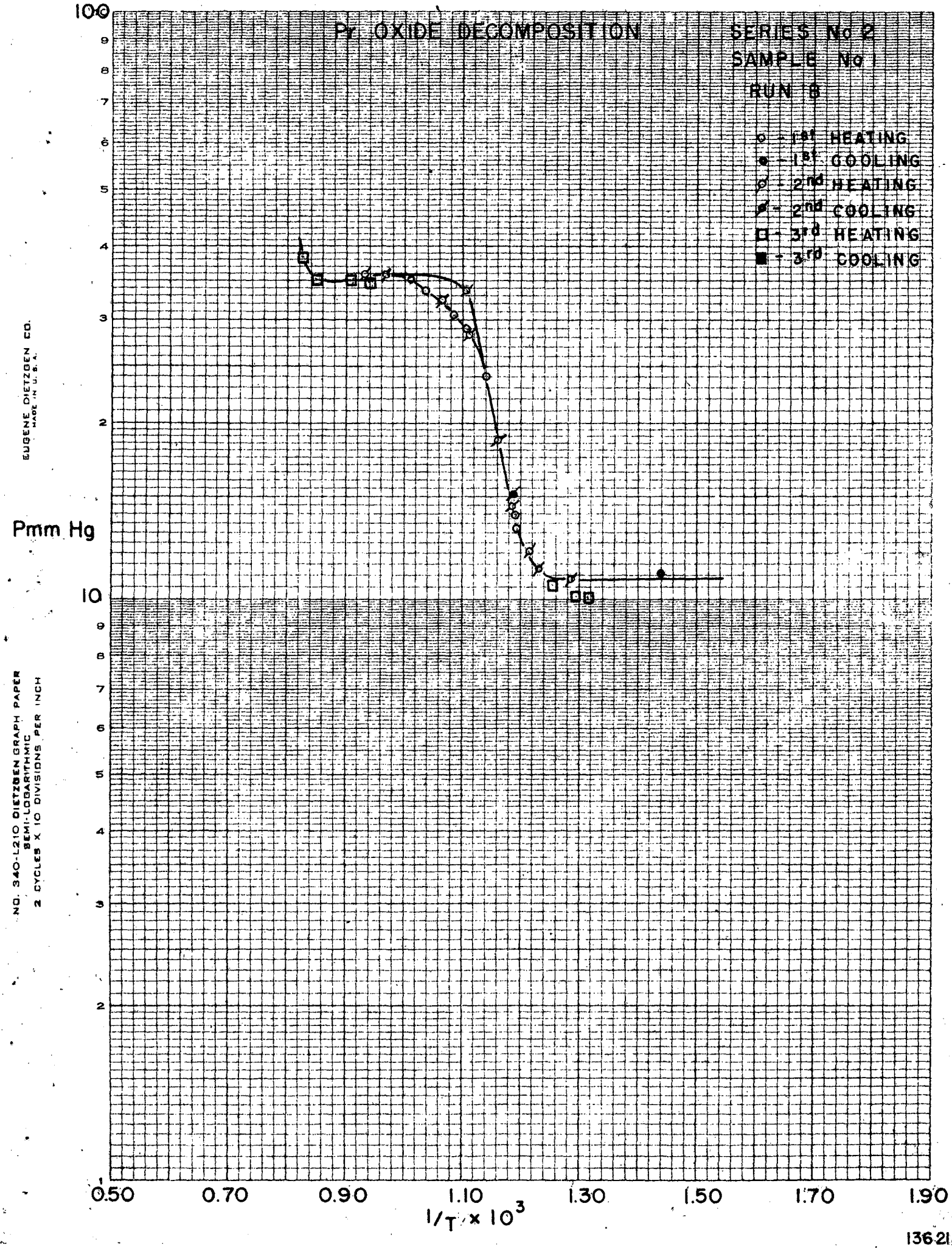
13619-1

FIG. III



13620

FIG. IV


Pr. OXIDE DECOMPOSITION
SERIES No 2
SAMPLE No 1
RUN 8
1st HEATING
1st COOLING
2nd HEATING
2nd COOLING
3rd HEATING
3rd COOLING
Pmm Hg
100
10
1
0.50
0.70
0.90
1.10
1.30
1.50
1.70
1.90
1/T x 10^3
EUGENE DIETZGEN CO.
MADE IN U.S.A.
NO. 340-L210 DIETZGEN GRAPH PAPER
SEMI-LOGARITHMIC
2 CYCLES X 10 DIVISIONS PER INCH

13621

FIG. V

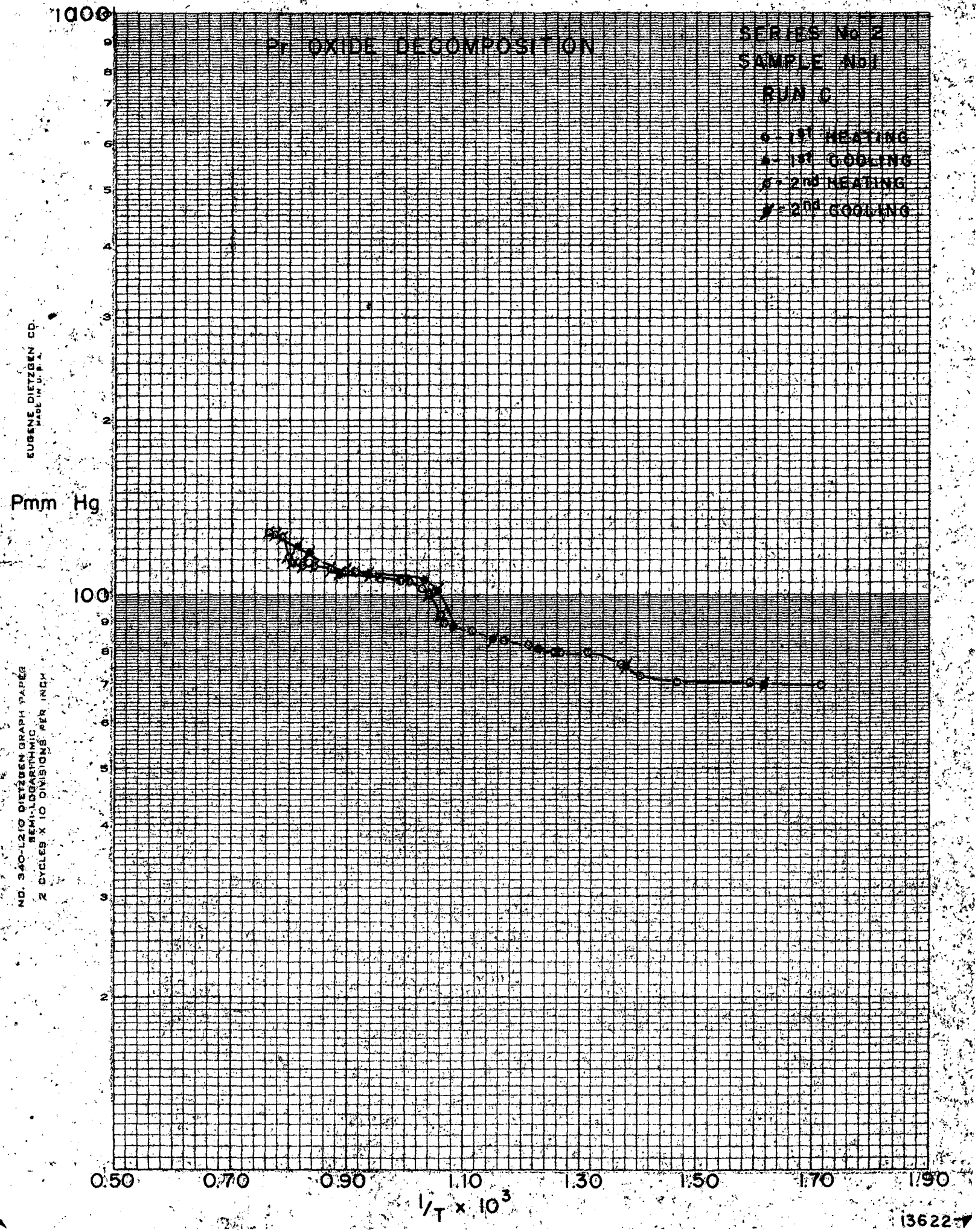
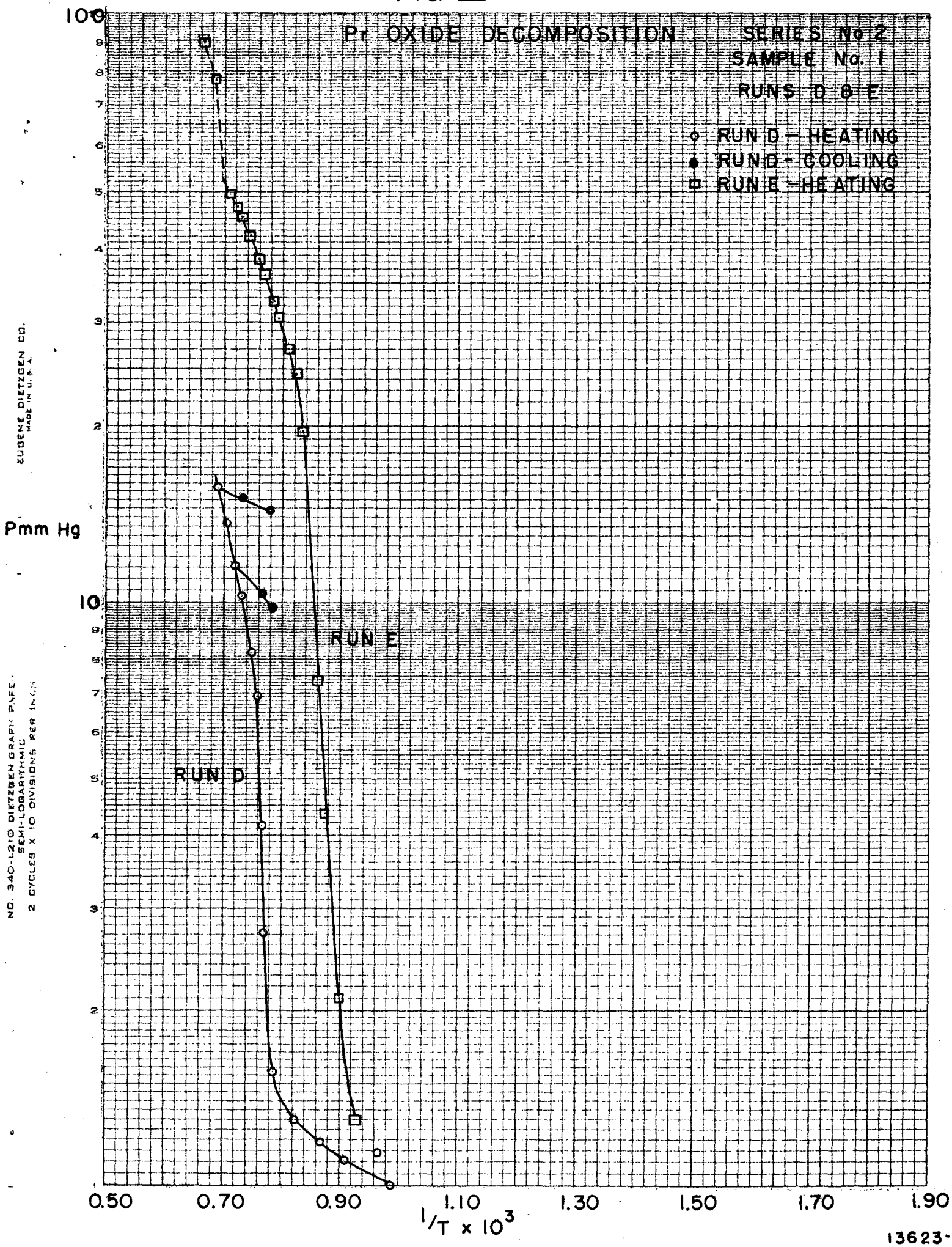
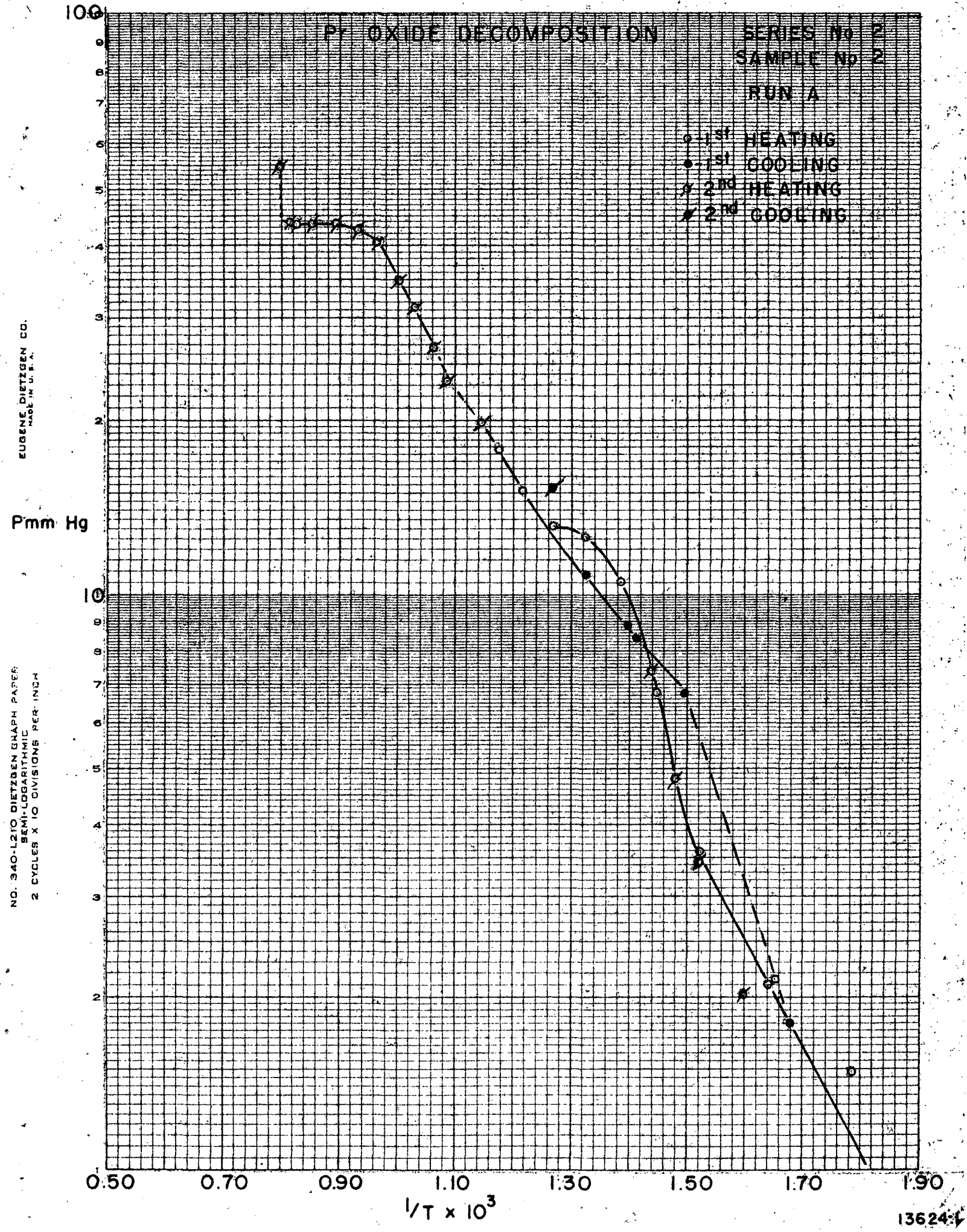

Pr OXIDE DECOMPOSITION
SERIES No 2
SAMPLE No 1
RUN C
o - 1st HEATING
▲ - 1st COOLING
ø - 2nd HEATING
✗ - 2nd COOLING
Pmm Hg
1000
100
0.50
0.70
0.90
1.10
1.30
1.50
1.70
1.90
1/T x 10^3
EUGENE DIETZGEN CO.
MADE IN U.S.A.
NO. 340-L210 DIETZGEN GRAPH PAPER
SEMI-LOGARITHMIC
2 CYCLES X 10 DIVISIONS PER INCH
13622

FIG. VI



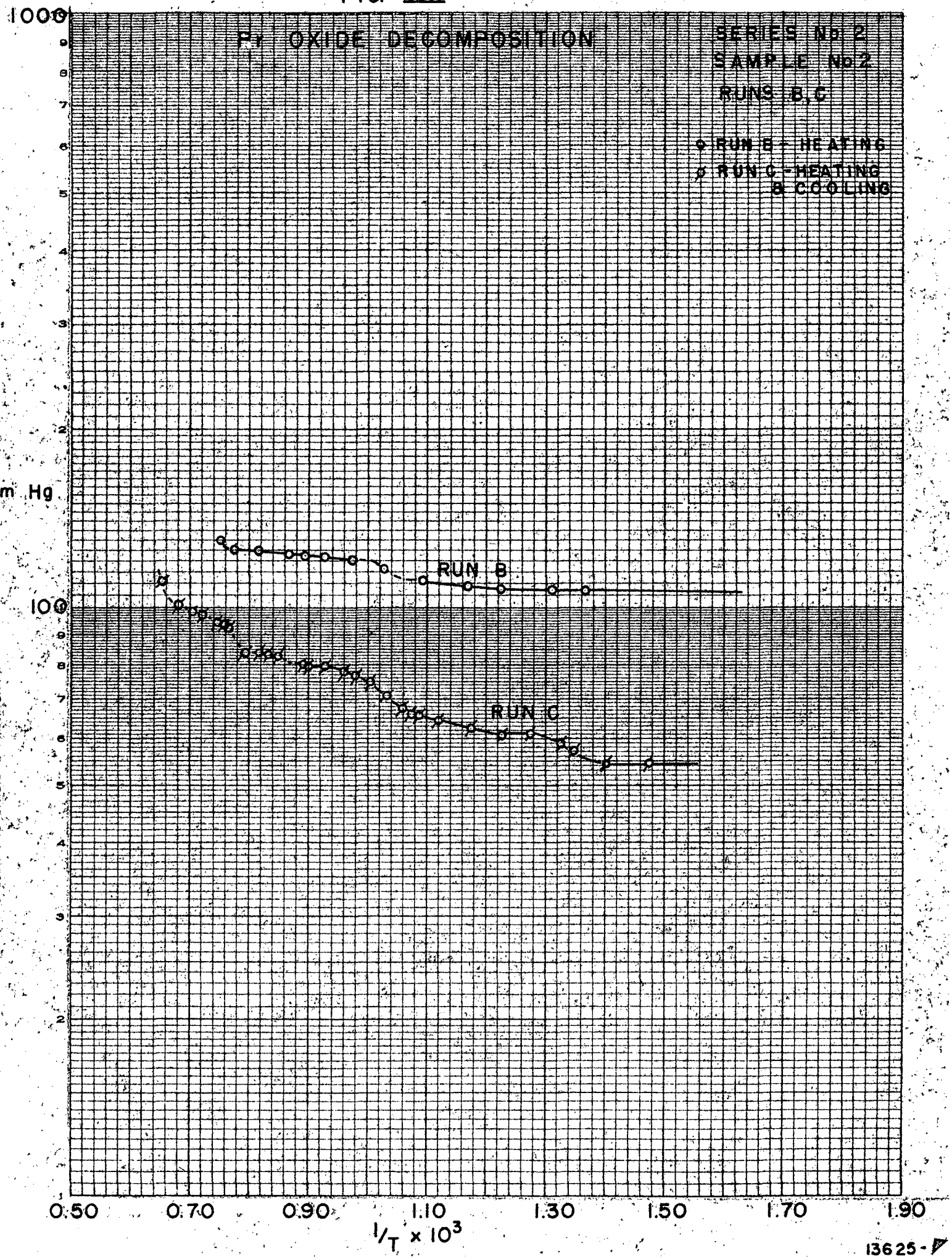
13623-1

FIG. VII



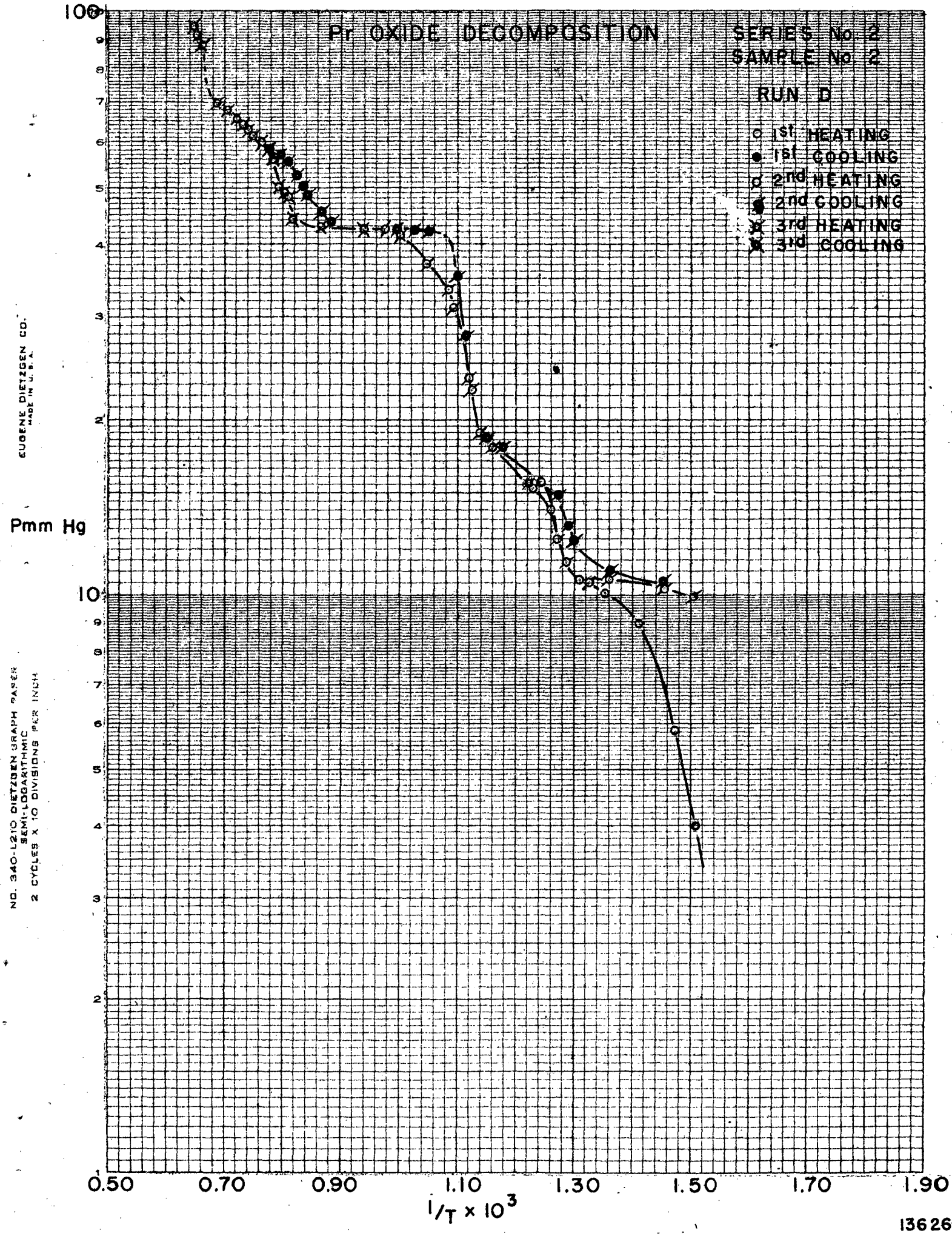
13624-1

FIG. VIII



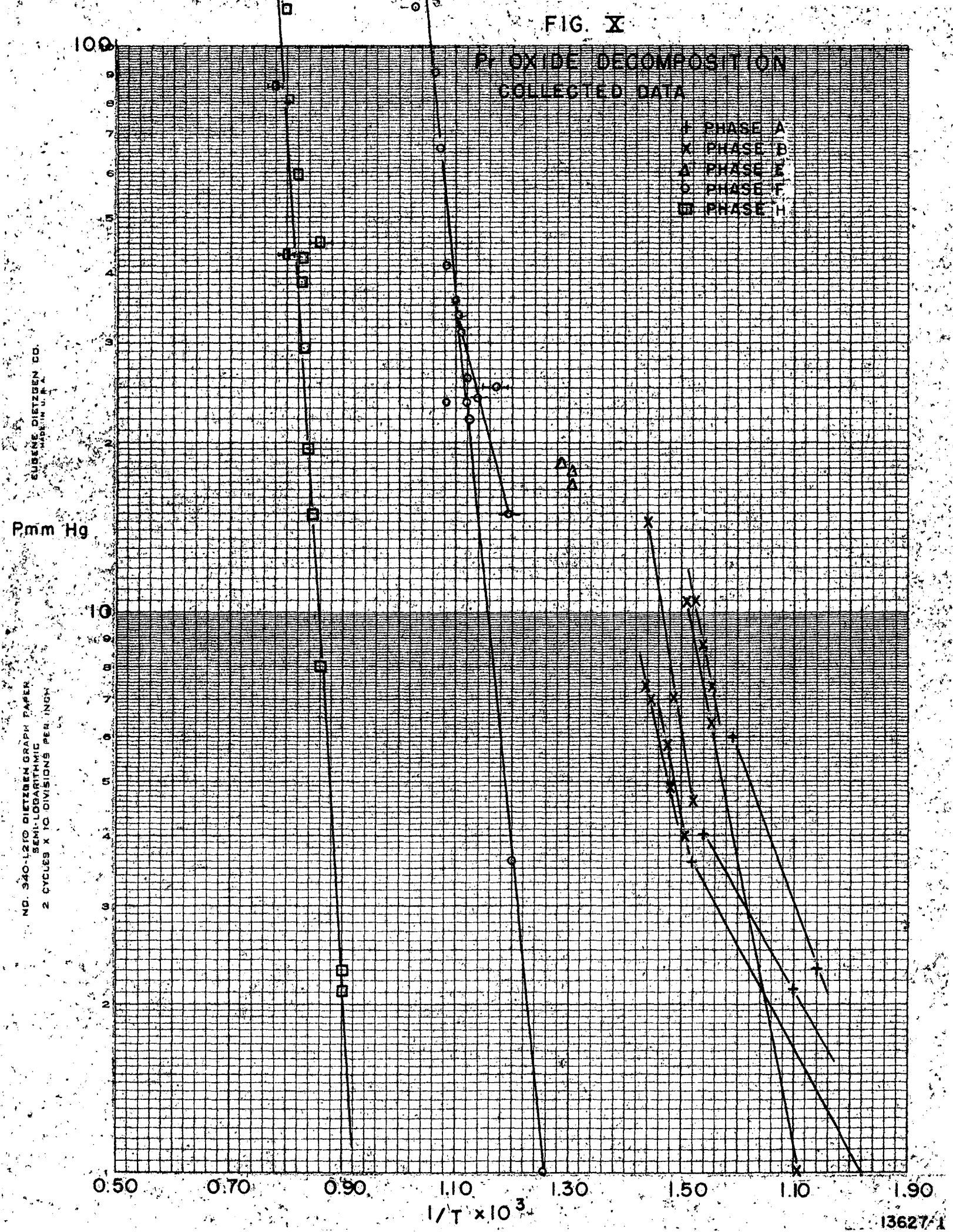
13625-

FIG. IX


Pr OXIDE DECOMPOSITION
SERIES No. 2
SAMPLE No. 2
RUN D
1st HEATING
1st COOLING
2nd HEATING
2nd COOLING
3rd HEATING
3rd COOLING
Pmm Hg
100
10
1
0.50
0.70
0.90
1.10
1.30
1.50
1.70
1.90
1/T x 10^3
EUGENE DIETZGEN CO.
MADE IN U.S.A.
NO. 340-L210 DIETZGEN GRAPH PAPER
SEMI-LOGARITHMIC
2 CYCLES X 10 DIVISIONS PER INCH

13626-

FIG. X


Pr OXIDE DECOMPOSITION
COLLECTED DATA
+ PHASE A
X PHASE B
Δ PHASE E
O PHASE F
□ PHASE H
Pmm Hg
100
10
0.50
0.70
0.90
1.10
1.30
1.50
1.10
1.90
1/T x 10^3
EUGENE DIETZGEN CO.
MADE IN U.S.A.
NO. 340-L210 DIETZGEN GRAPH PAPER
SEMI-LOGARITHMIC
2 CYCLES X 10 DIVISIONS PER INCH

13627-1

FIG. XI

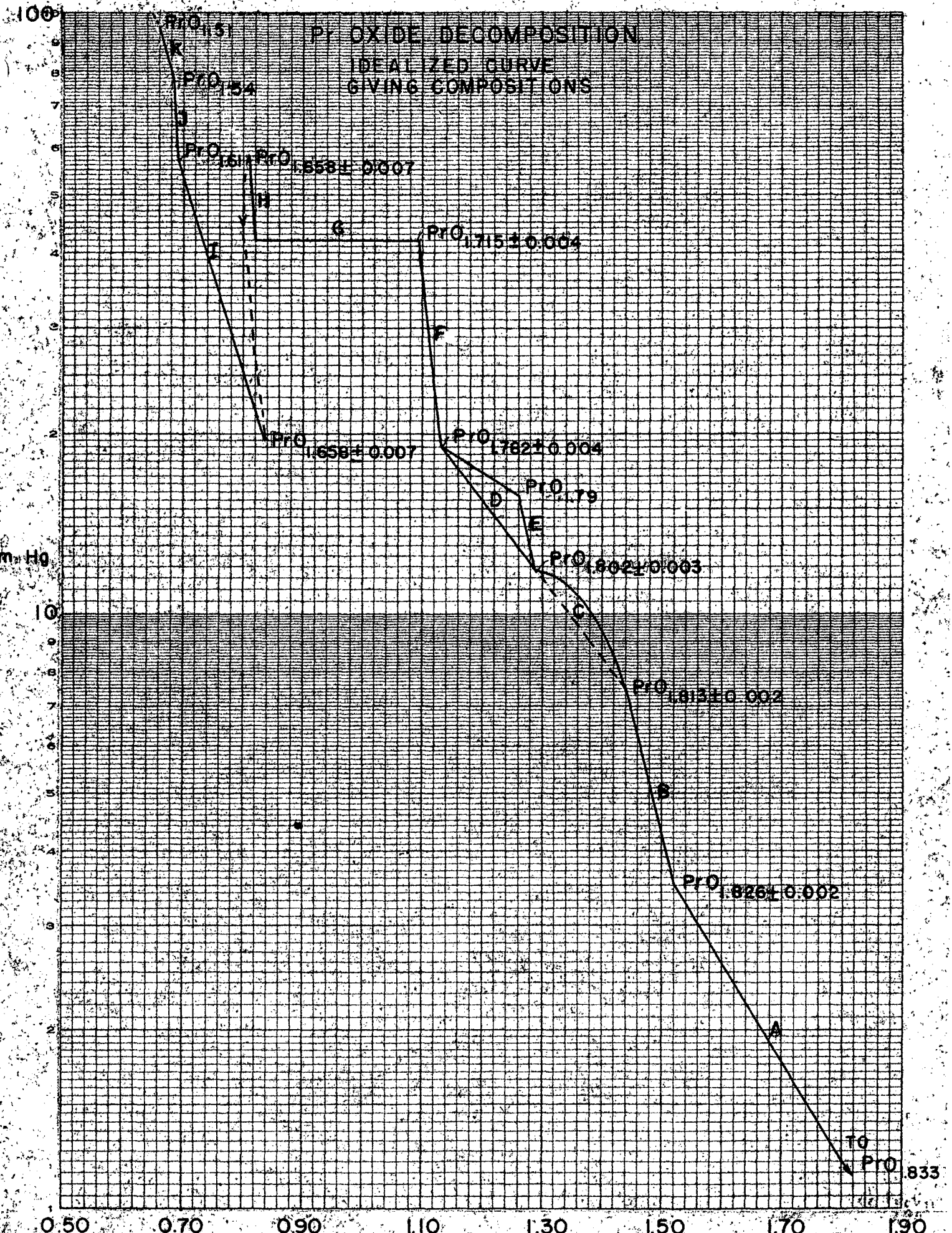
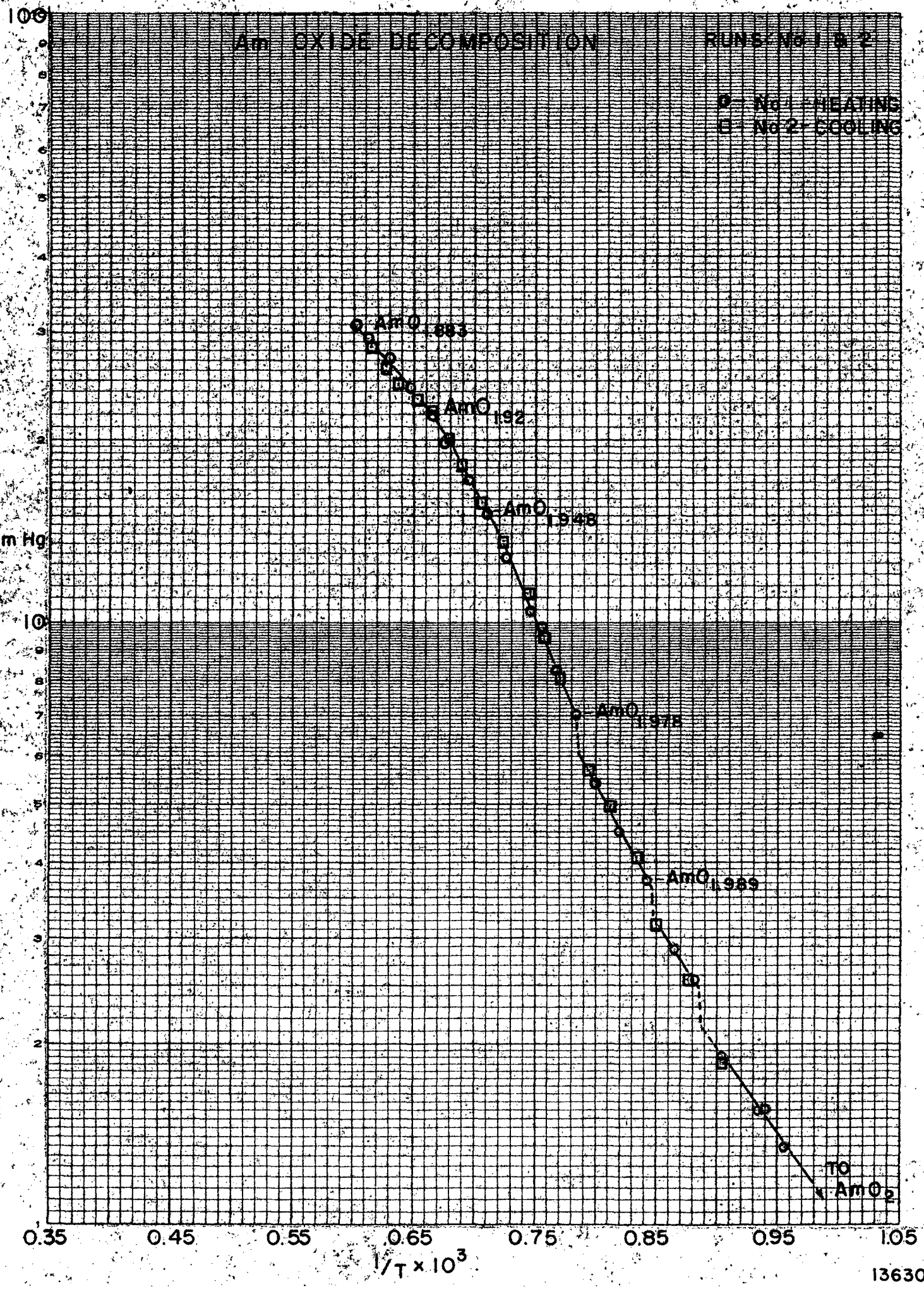
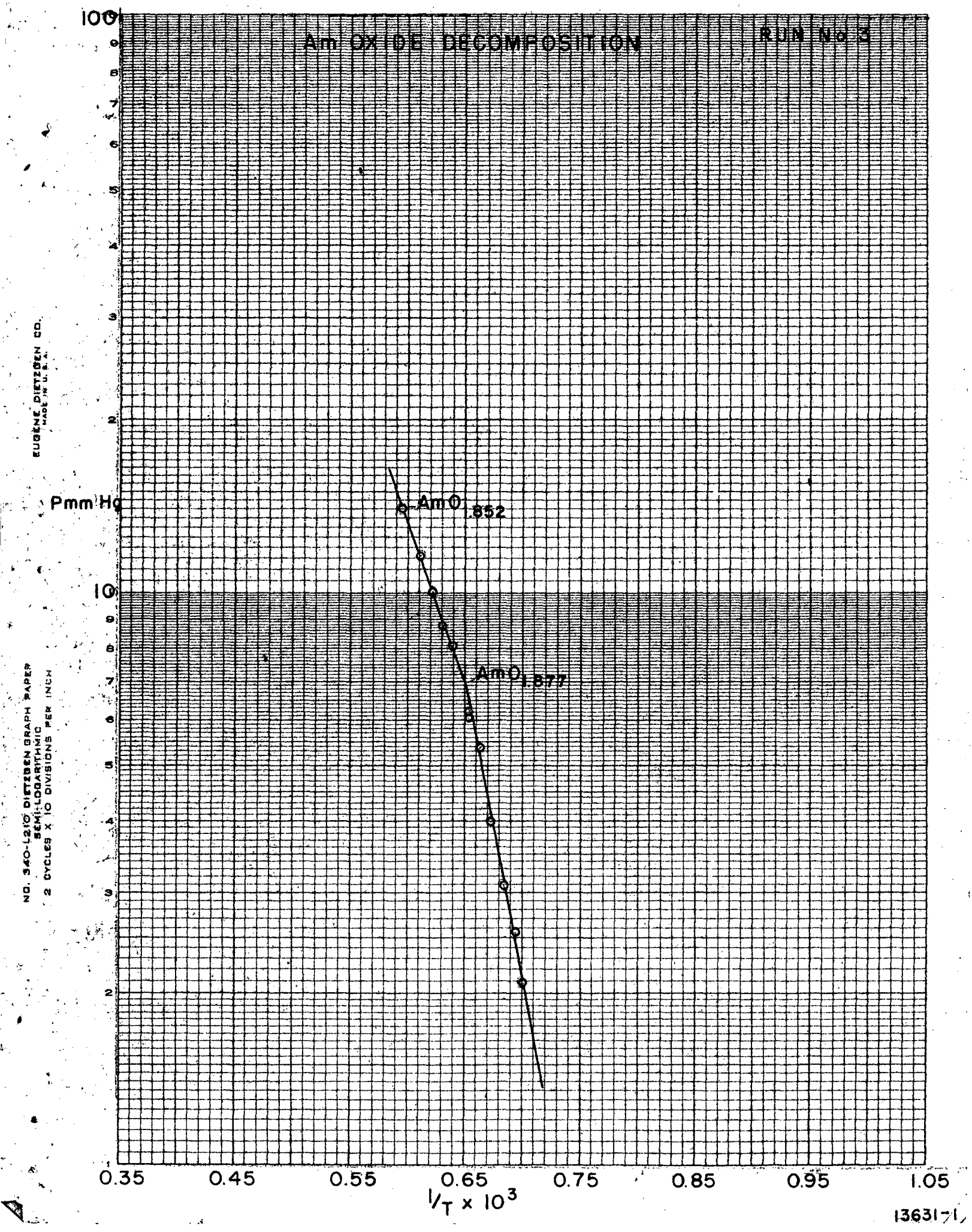

Pr OXIDE DECOMPOSITION
IDEALIZED CURVE
GIVING COMPOSITIONS
PrO1.151
K
PrO1.154
J
PrO1.611
PrO1.558±0.007
H
Y
G
PrO1.715±0.004
I
F
PrO1.658±0.007
PrO1.782±0.004
PrO1.79
D
E
PrO1.802±0.003
C
PrO1.813±0.002
B
PrO1.826±0.002
A
TO
PrO1.833
Pmm. Hg
100
10
1
0.50
0.70
0.90
1.10
1.30
1.50
1.70
1.90
1/T x 10^3
EUGENE DIETZGEN CO.
MADE IN U.S.A.
NO. 340-L210 DIETZGEN GRAPH PAPER
SEMI-LOGARITHMIC
2 CYCLES X 10 DIVISIONS PER INCH
13628-1

FIG. XIII



13630-1

FIG. XIV


Am OXIDE DECOMPOSITION
RUN No 3
Pmm Hg
100
10
1
AmO1.852
AmO1.877
0.35
0.45
0.55
0.65
0.75
0.85
0.95
1.05
1/T x 10^3
EUGENE DIETZGEN CO.
MADE IN U.S.A.
NO. 340-L210 DIETZGEN GRAPH PAPER
SEMI-LOGARITHMIC
2 CYCLES X 10 DIVISIONS PER INCH
13631-1

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