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BUREAU OF SHIPS

DIFFERENTIAL THERMAL ANALYSIS AS APPLIED
to
THERMAL ENDURANCE OF DIELECTRICS

Lab. Project 6406, Progress Report 1
SR 007-04-01, Task 1050

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SUMMARY

The Problem

To develop a rapid and inexpensive means for the temperature classification of dielectrics.

Findings

An oxygen injection differential thermal analysis method was developed which provided for the obtaining of life-temperature plots in a much shorter time than existing thermal endurance methods. The new method is applicable to materials whose deterioration at elevated temperatures is caused by a reaction with atmospheric oxygen. Results of the new method correlate well with those of existing thermal endurance method for materials investigated.

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ADMINISTRATIVE INFORMATION

1. In accordance with Bureau of Ships letter R 007-04-01 Ser 634C4-458 of 16 May 1962, the U.S. Naval Applied Science Laboratory is conducting an investigation directed toward the development of a rapid and inexpensive means for the temperature classification of dielectric materials. The work reported herein involved the development of a new oxygen injection DTA method for the rapid establishment of slopes of life lines analogous to those previously obtained by existing long term methods. This project is being accomplished in the Plastics and Elastomers Branch, Mr. C.K. Chatten, Head, under the technical direction of Mr. H.K. Graves, Senior Task Leader. The Bureau of Ships Program Manager is Mr. E. A. Bukzin, Code 342A and the Cognizant Engineer is Mr. W. B. Shetterly, Code 634C4.

OBJECT

2. The object of the investigation is the development of a rapid means by which polymeric dielectric materials can be investigated accurately and inexpensively as to their long term operating characteristics with particular reference to heat aging.

INTRODUCTION

3. Deterioration of insulating materials in Naval applications has always constituted a serious problem for design engineers. The practical solution to the problem rests in the availability of materials with improved deterioration resistance. Since 1940, material development has increased at such a rapid rate that now design engineers have a large and varied inventory of materials from which to choose. However, in the absence of in-service experience with these new materials, their use involves considerable risk on the part of the design engineer. To some extent this situation impedes the improvement of equipment. Thus, it has been recognized by the Laboratory that a considerable advantage would be gained if a rapid means could be found for the estimation of a new material's deterioration resistance. A great deal of effort has been directed toward the achievement of this objective and some success has been realized. However, the methods presently in use have the disadvantage of requiring long testing programs, in many cases lasting one year or longer, resulting in a delay in the application of new dielectrics. The purpose of this report is to describe a new method which will, in many instances, considerably shorten the time required to estimate a new material's deterioration resistance, particularly at elevated temperatures (thermal endurance).

4. In service, dielectrics are subjected simultaneously to many different deteriorating factors including oxidative atmospheres, moisture, radiation, corona discharges and elevated temperatures. All of these factors are known to contribute to changes in one or more properties of the dielectric. Since the individual application would determine, in large measure, the relevancy of any of these, no general order of importance can be readily established.

5. Dakin [1,2] has shown that, in many instances, deterioration is primarily the result of chemical reactions occurring in the material which are temperature accelerated. (Table 1 lists pertinent references) There was developed a means of interpreting data dealing with the change of physical properties with time at various temperatures. This approach is based upon

the assumption that a physical property is a function of the concentration of some important chemical constituent of the material. Further, that there is another function of this concentration which varies with time at a rate determined by temperature. Thus, there is a function of the physical property which varies with time at the same rate, i.e.

$$F(P) = Kt \tag{1}$$

where:

P = physical property
K = rate constant
t = time

See Table 2 for list of symbols used throughout entire report. Now, if the level of the physical property is fixed, the time to reach this level is a function of K alone, i.e.

$$t_e = \frac{F(P_e)}{K} \tag{2}$$

where:

P_e = a particular value of physical property P
t_e = time required to attain P_e

The Arrhenius equation gives K as a function of temperature, i.e.

$$K = Ae^{-\Delta H^*/RT} \tag{3}$$

where:

A = constant
ΔH^* = activation energy, cal $mole^{-1}$
R = ideal gas constant, 1.987 cal deg C^{-1} $mole^{-1}$
T = temperature (°K)

Therefore, by combining equations 2 and 3, t_e, time to reach P_e, may be expressed as a function of temperature alone, i.e.

$$t_e = \frac{F(P_e)}{Ae^{-\Delta H^*/RT}} \tag{4}$$

Taking logarithms of both sides of equation 4 we get,

$$\log_e t_e = \log_e F(P_e) - \log_e A + \frac{\Delta H^*}{RT} \tag{5}$$

Combining constants:

$$\log_e t_e = B + \frac{\Delta H^*}{RT} \tag{6}$$

where:

$$B = \log_e F(P_e) - \log_e A$$

Therefore, a graphical plot of $\log_e t_e$ vs. $1/T$ would yield a straight line whose slope is $\Delta H^*/R$.

6. It is to be noted that the values of t_e for a given temperature are dependent upon an arbitrarily chosen end point, P_e, and thus are arbitrary to this extent. However, regardless of the choice of end point, assuming a single rate determining reaction over a temperature range, the slope of the $\log_e t_e$ vs. $1/T$ plot is constant and equal to $\Delta H^*/R$ over this temperature range. (See Figure 1). This follows since $\Delta H^*/R$ is a measure of the activation energy which is essentially constant for a given reaction over a wide temperature range. Therefore, the existing thermal stability methods, based upon Dakin's work, essentially constitute a means of establishing the $\Delta H^*/R$ constant for the chemical reaction underlying deterioration of some physical property.

NEW METHOD

7. There is another approach by which $\Delta H^*/R$ may be established. It follows from equation 3 that

$$CK = CAe^{-\Delta H^*/RT} \qquad (7)$$

where:

C = arbitrary constant

Then, by taking the logarithms of both sides of equation 7,

$$\log_e CK = \log_e CA - \frac{\Delta H^*}{RT} \qquad (8)$$

Plotting $\log_e CK$ vs. $1/T$, as in Figure 2, yields a straight line with slope equal to $-\Delta H^*/R$. Once the value of $\Delta H^*/R$ is determined from a plot similar to that in Figure 2, a plot equivalent to that in Figure 1 may be obtained using only one value of t_e determined at a single temperature. The main advantage of this method over the existing methods is that only one value of t_e instead of a minimum of three is determined experimentally. Since this value may be taken as the one requiring the least time, a saving of thousands of hours often results. The essence of this method, developed by the Laboratory and described below, involves the obtaining of the $\Delta H^*/R$ value from a plot such as in Figure 2. It is comparatively rapid and requires only a minimum of sample and effort.

8. The basis for this new method is that, during the course of a chemical reaction, there exists a difference between the average energy level of reactant molecules compared with product molecules. Thus during a reaction, energy, in the form of heat, may be evolved (a reaction where the energy level of product molecules is less than that of reactant molecules) or absorbed (a reaction where the energy level of product molecules is greater than that of reactant molecules). Since this heat effect is a function of K, and what we must measure is related to K, it appeared appropriate to choose a technique that would sense this heat effect. Differential thermal analysis (hereafter referred to as DTA) was considered to be such a technique.

9. In conventional DTA a sample of unknown material and an inert reference material, contained in separate cavities of a special holder, are heated at a constant rate of temperature rise. The thermal diffusivities of the cavities are matched as closely as possible. A differential thermocouple is connected to provide for recording of temperature differences between

sample and inert materials. Thus, heat effects (exothermic or endothermic) occurring in the sample, due to the initiation of chemical or physical changes, are monitored vs. time or temperature, these two being linearly related since rate of temperature rise is constant. The resulting recording (thermogram) would resemble Figure 3, representing a plot of difference in temperature between sample and inert material (ΔT) vs. time (temperature).

10. Methods have been developed by Borchardt and Daniels[4] for obtaining K from the conventional DTA thermograms. These methods were developed primarily for reactions in the liquid state although their use with solids is not excluded. The reaction under study must be carried out over a sufficiently wide temperature range to include both the inception and disappearance of ΔT indication. In developing formulas for the calculation of K values it is assumed that a single reaction is taking place over the above temperature range. Further, a high degree of reliability is required in the determination of the base line from which ΔT is measured. If the two above conditions cannot be met, treatment of the conventional DTA results by these methods is not valid. This was the case in the present investigation. It was found from preliminary work that the materials studied exhibit both internal chemical changes and a reaction with the air atmosphere. Also, the reliability with which the base line could be determined was extremely poor at the high equipment sensitivity required to detect the small heat effects involved. Thus, a different method was required which could be applied to these materials avoiding the shortcomings of the conventional DTA method.

11. If the reaction occurring between the materials and air is the deterioration rate determining reaction, then, of necessity, the heat effects of this reaction alone should be measured. It was assumed that such was the case. In other words, oxidation was assumed to be the rate determining reaction in existing thermal endurance studies on these materials. Therefore, by limiting the work to the measurement of oxidation alone, a DTA method could be developed which avoided the obstacles which rendered the conventional DTA method inappropriate. There is some evidence to bear out the above assumption. However, in the final analysis, the assumption must be verified by the experimental data. This point will be dealt with further in paragraph 24 below.

12. Utilizing Dynamic Gas equipment wherein provision is made for the passage of known gases through the sample and inert materials while being heated, it is possible to initiate and terminate the oxidation reaction at will by alternating the gas flowing through the materials between pure oxygen and some other inert gas (e.g. nitrogen). This approach was suggested by work of Stone[5]. Employing a slow heating rate (1°C. / min.) and with nitrogen gas flowing through the materials, at various temperatures, oxygen is rapidly substituted for nitrogen for a short period of time. Immediately afterwards, nitrogen is reintroduced into the materials. The result is an increase in ΔT indication over the nitrogen base line while oxygen is flowing, which indication, ΔT_0, returns to the nitrogen base line upon reinjection of nitrogen gas. Since ΔT_0 (Figure 4) is measured from the nitrogen base line from a point coincident with the injection of oxygen, it is a function of the oxidation reaction alone. Therefore, effects of base line drift are eliminated. This allows for the use of the higher amplification of ΔT signal necessary to measure the small heat effects involved. Also should physical transitions or parallel internal chemical changes which do not share the reactants be occurring simultaneously with oxidation, their effects on ΔT are eliminated, since only ΔT due to oxidation is measured. Finally, by sampling for short

intervals of time, the amount of material reacted can be made negligible over a sufficiently large temperature range. This method allows for the occurrence of simultaneous reactions. However, there must be no interaction resulting in changes in the concentration of the active mass of material undergoing oxidation. It is important to note that this method does not require that the reaction go to completion. In fact, the determination is concluded when there are indications that the concentration of the active mass of material has been appreciably decreased. Therefore, conditions of test need be met only over a comparatively small temperature range.

13. Consideration must now be given to the problem of relating the results of the new DTA method to the required $\Delta H^*/R$ factor. In this respect, reference is made to heat conduction theory in DTA measurements. It has been shown by Spiel et al[6] and Vold[7] that the following is true:

$$\frac{\Delta H}{C_s}\frac{df}{dt} = \frac{d\Delta T}{dt} + A'\Delta T \tag{11}$$

where:

ΔH = total heat of reaction
C_s = total heat capacity of sample holder plus contents
f = fraction of active material's concentration transformed
t = time
ΔT = differential temperature of DTA thermogram
A' = constant

In deriving equation 11 , it is assumed that the heat of reaction per mole is constant over the temperature interval used. This makes possible the establishment of the above relation between the time rate of change of the concentration of the active material and ΔT through ΔH, the total heat of reaction. The following is also true:

$$f = 1 - \frac{n}{n_o} \tag{12}$$

where:

n = no. of moles of active material remaining at time t
n_o = no. of moles of active material present at time $t = 0$

Differentiating both sides of equation 12:

$$\frac{df}{dt} = -\frac{1}{n_o}\frac{dn}{dt} \tag{13}$$

Now, from chemical kinetics[8]:

$$-\frac{dn}{dt} = Kn^x \tag{14}$$

where:

x = order of reaction
K = reaction rate constant

Therefore, substituting for dn/dt in equation 13 its equivalent from equation 14:

$$\frac{df}{dt} = \frac{Kn^x}{n_o} \tag{15}$$

Now substituting for df/dt in equation 11 its equivalent from equation 15:

$$\frac{\Delta H}{C_s} \frac{Kn^x}{n_o} = \frac{d\Delta T}{dt} + A'\Delta T \qquad (16)$$

In describing the method it was pointed out that the concentration of active material, n, may be considered essentially constant and that the investigation stops when results indicate that this concentration is effectively decreasing. Since x is, in all probability, less than 3, the factor n^x is considered to be also essentially constant. More will be said about this in paragraphs 22 and 23. Moreover, since the heating rate is slow, $d\Delta T/dt$ may be neglected for sufficiently large ΔT. Therefore, equation 16 can be simplified to:

$$\Delta T = CK \qquad (17)$$

where:
C = constant

Thus we have a technique which provides a measure of a quantity which is proportional to K at various temperatures. This makes possible the obtaining of a plot as in Figure 2 and thereby the value of $\Delta H^*/R$.

14. In summary, Dakin's application of chemical kinetic theory to the study of insulation deterioration is valid if the assumptions and conditions made are met. The present work is a natural extension of Dakin's work, made possible by the introduction of DTA techniques. In developing a DTA technique for studying the specific materials employed in the present work, it was found that an additional assumption had to be made. This assumption is that oxidation is the deterioration rate determining reaction over the temperature range of interest. The experimental work below was directed mainly toward the verification of this assumption. Verification was believed to rest in the degree of correlation between available data and results utilizing the new method.

15. As mentioned previously, existing thermal endurance methods involve the measurement of time to reach a certain value of a physical property at various temperatures. In these methods it is not necessary to specify a chemical reaction. However, implicit in the theoretical considerations is the assumption that a deterioration rate determining chemical reaction exists. Therefore, the result of this work is what amounts to an activation energy plot for this reaction. Now, if an activation energy plot is obtained using the new DTA method, which plot is in good agreement with that obtained using an existing thermal endurance method, then there is evidence to show that oxidation is the above deterioration rate determining reaction. It should be noted that the assumption is not valid for all materials and physical properties thereof. However, it is believed that it will hold for a wide spectrum of materials and for important functional properties.

EXPERIMENTAL

16. The materials selected for study in the present work were four modified polyester electrical insulating varnishes. Table 3 codes and identifies the materials. These materials were applied to 6"x12"x0.003" glass cloth panels by dipping and were heat cured according to individual manufacturer's instructions. Using the thermal endurance method of ASTM D-1932-61T and the

above panels as specimens, the materials were previously investigated by the U.S. Naval Applied Science Laboratory making plots available, as in Figure 1, of t_e (life) vs. 1/T. In brief, these plots were arrived at by the measurement of time to failure after aging at three or more temperatures. Failure criterion was the occurrence of appreciable damage of the insulation upon subjection of the panels to a 2% maximum elongation, induced by bending over a mandrel. Failure was detected by measuring the voltage required to "break down" the panels while bent, 300 volts per mil being considered indicative of the occurrence of failure.

Apparatus

17. The present experimental work was performed using a R.L. Stone Co. Model DTA-12BC2 Controlled Pressure and Controlled Atmosphere Differential Thermal Analysis Apparatus. An overall view of the equipment is shown in Figure 5. Essentially, the apparatus consists of three basic components, namely, a temperature controller-recorder, a differential temperature recorder and a sample holder and furnace platform assembly. The third component embodies an important feature of this equipment in regard to the present work, consisting of provisions for conducting Dynamic Gas DTA studies. This involves the use of a special sample holder so constructed as to allow for the passage of gas through the volume of both sample and inert materials and also for the rapid substitution of one gas for another. Thus the atmosphere surrounding each particle of sample and reference material is continually under control and can be varied at will. A schematic diagram of the sample holder and furnace platform assembly is shown in Figure 6.

Sample Preparation

18. Samples employed for DTA studies were obtained from the above described panels of impregnated glass cloth. Based on prior experience, it was decided to reduce the panels to a powdered form. This was accomplished by end milling using a Dremel Moto-Tool Model No. 1 with a HS-415 Cutter. The resulting powder was passed through a series of sieves, the fraction measuring less than 200 mesh being selected for use. The reference material employed was calcined alumina having particle sizes between 100 and 200 mesh and stored, prior to use, at 0% relative humidity.

Procedure

19. The inert and sample cavities of the sample holder were completely filled with calcined alumina and sample, respectively. This was accomplished by gently tapping the sample block and subsequently applying a 45 gram weight to the cavity contents. The above was believed to give a sufficiently uniform and reproducible loading of both cavities. Nitrogen gas was flowing through the cavities throughout the loading process.

20. The work was conducted in two phases. The first involving conventional Dynamic Gas studies and, subsequently, oxygen injection studies. Differential recorder sensitivities were 10 or 20 microvolts full scale for conventional Dynamic Gas method and 5 microvolts full scale for oxygen injection method. Temperature rates of rise employed for conventional Dynamic Gas and oxygen injection methods were 10 and 1°C. / min., respectively. Rate of gas flow employed for both phases of work was 30 to 50 cc./ min. The purpose of the conventional Dynamic Gas studies was to provide qualitative information

regarding the presence of internal chemical changes occurring on heating. It was believed that the materials were only partially cured after completion of the recommended cure schedule. In order to ascertain whether curing would take place when the temperature was raised above the original cure temperature, conventional Dynamic Gas studies employing nitrogen were made. Exothermic reactions were in evidence on all materials above 200°C. These results were believed to confirm the assumption that curing was continuing at these temperatures. The occurrence of this curing during measurements to obtain an activation energy plot by the oxygen injection method would invalidate the results. The reason for this is that the curing, in effect, causes a variation in the factor A of equation 3 which negates the assumption that A is constant during the obtaining of data for the plot of Figure 2. It was decided to further age the materials for 24 hours at 250°C. which was believed would produce the desired effect of maintaining the factor A constant during the obtaining of an activation energy plot. Although it was realized that aging would change the value of A, this in no way would effect the validity of the activation energy plots, since this value may be considered an arbitrary constant for these plots. In order to ascertain the effect of aging, conventional Dynamic Gas DTA studies using nitrogen gas were repeated on the aged materials. Results of this work for unaged and aged samples are shown in Figure 7. and may be considered typical of all four materials studied. It can be seen that the thermogram for aged material covers a smaller area above the base line between 100 and 300°C, the temperature range of interest, than that of the unaged. Thus, assuming the same reaction is occurring in both cases, this shows that the aged material underwent appreciably less curing between 100 and 300°C. than the unaged material. Since it was considered desirable to limit the aging of the materials to the necessary minimum,it was decided to conduct the second phase of the work, namely, the oxygen injection DTA studies, on samples aged 24 hours at 250°C. The ultimate justification for this decision will rest in the degree with which the activation energy plot so obtained approximates a single straight line over the temperature range of interest. Figure 7 also shows a typical conventional Dynamic Gas DTA thermogram run on aged material with oxygen as the Dynamic Gas. This work was conducted to obtain a qualitative comparison between oxidation and internal reactions occurring in nitrogen. It is apparent that the oxidation reaction predominates between 100 and 300°C as evidenced by a much larger area above the base line.

21. The oxygen injection DTA studies were then conducted on all four materials. The procedure employed involved heating the loaded sample holder at a rate of 1°C./min. with nitrogen as the Dynamic Gas. However, starting at approximately 100°C., oxygen was rapidly substituted for nitrogen for a period of one minute, after which period nitrogen was reintroduced into the cavities. One minute was found to be sufficient time to obtain thermal equilibrium in the sample cavity. This procedure was repeated at approximately 10°C. intervals until two successive readings showed equal or decreasing ΔT_0 value, at which time the determination was concluded.

RESULTS

22. Results of oxygen injection DTA studies on all four materials are shown in Figures 8 through 11 which consist of plots of ΔT_0 vs. temperature on a log ΔT_0 vs. reciprocal absolute temperature scale. The quantity ΔT_0 is the increase in ΔT resulting from the injection of oxygen for a one minute period, as shown in Figure 4. In this context, the dimensions of ΔT_0 are arbitrary, therefore, for convenience, the unit of measure

chosen was inch X 10^{-2}. Temperatures corresponding to individual values of ΔT_0 are taken immediately after the termination of the one minute oxidation periods. It should be noted that at the extremes of temperature the plotted points tend to deviate from a straight line. The lower temperature ΔT_0 values are small in magnitude and thus, to a large extent, are subject to experimental errors. Also equation 17 is not accurate for small values of ΔT_0, as indicated in the derivation. At the upper temperatures, deviations from a straight line are believed to be due to changes occurring in the concentration of active mass of materials. As mentioned in connection with the derivation of equation 17, relating ΔT to K, the relationship holds only under the assumption that the concentration of the active mass remains essentially constant. The temperature at which the plotted points first deviate from a straight line is considered the temperature above which this assumption no longer holds. Therefore, these points were neglected in drawing the lines shown. The slopes of the lines representing the best fit to the remaining points are equal to $- \Delta H^*/R$ as can be seen from equation 17 and Figure 2, where ΔT in equation 17 is taken as ΔT_0.

23. Figures 12 through 15 show comparisons between lines having slopes equal to $\Delta H^*/R$ arrived at by the existing thermal stability method, described above, and the new oxygen injection DTA method. The points plotted represent t_e (life) values analogous to those in Figure 1. The best straight line is drawn through these points. The other lines are simply reproductions of those shown in Figures 8 through 11 and analogous to that in Figure 2, where the negative slope is shown. It is important to note that the only parameter determined by the new method is the slope of the line and, thus, its location on Figures 8 through 15 is arbitrary. Also Table 4 shows a comparison between $\frac{\Delta H^*}{R}$ values as obtained by the new oxygen injection DTA method and the existing thermal endurance method.

DISCUSSION

24. It is apparent from Figures 12 through 15 and Table 4 that there is good agreement between the values of $\Delta H^*/R$ as arrived at by both the existing thermal endurance method and the new oxygen injection DTA method. It can thus be concluded that the assumption underlying the new method, namely, that oxidation is the deterioration rate determining reaction in the existing thermal endurance method, is valid. This is true, since the slope of the line based on the DTA method represents the activation energy of the oxidation reaction; while, on the other hand, the slope of the line as determined by the existing thermal endurance method represents the activation energy of the chemical reaction controlling the rate of deterioration of a physical property. Since these two activation energies agree so well, it can be concluded that oxidation is the chemical reaction controlling the rate of deterioration of the physical property investigated.

Significance

25. A comparison may be drawn between the existing thermal endurance methods and the new oxygen injection DTA method. Simultaneously, the practical significance of the new method will be shown.

26. Using the existing thermal endurance methods, at first it must be assumed that failure or termination of useful life can be defined in terms of some measurable physical property. The degree of certainty involved in

the making of this assumption will vary with individual circumstances. Secondly, it must be assumed that there is a chemical reaction underlying the deterioration of the physical property. Then the level of the physical property must be selected which would be considered to constitute failure of the dielectric. A test must then be devised which would provide for the determination of times to reach this level of physical property after being subjected to aging at three or more suitable temperatures. The resulting failure times would be plotted versus temperature as log time versus reciprocal absolute temperature. The best straight line is drawn through the plotted points and extrapolated to a desired life value. The corresponding temperature is thus determined.

27. Employing the new oxygen injection DTA method, it is necessary to make the two assumptions mentioned above. In addition, it must be assumed that oxidation is the chemical reaction in question. Then, as above, a level of the physical property is selected which is considered to constitute failure of the dielectric. A test is devised which provides for the determination of time to reach this level of physical property after being subjected to aging at only one temperature. The temperature selected should, for convenience, correspond to a short failure time. The slope of the line analogous to that determined by an existing thermal endurance method would be obtained by use of the new oxygen injection DTA method. The resulting failure time and slope make possible the obtaining of a plot of life versus temperature which is equivalent to that arrived at using the existing thermal endurance method. The significant advantage of the new method is that the plot of life versus temperature can be determined in a very short time since only one aging temperature is required, which can correspond to a short life value.

28. It would at first seem that the assumption that oxidation is the chemical reaction controlling deterioration is too restrictive, since other modes of deterioration are known to exist. However, in light of the results of the present work and in view of work done by others in determining causes of deterioration[9], it seems that the assumption will prove to be valid in many instances.

CONCLUSIONS

29. It can be concluded, that the new oxygen injection DTA technique described above, is tentatively acceptable as a rapid means of estimating life-temperature characteristics of insulating varnish materials of the phenolic modified polyester type.

FUTURE WORK

30. The Laboratory intends to further develop the oxygen injection DTA method described herein by extending its application to a broader range of dielectrics. In this respect, future studies will be made on additional varnish materials, including silicone types, and also magnet wire insulations of at least two chemical classes.

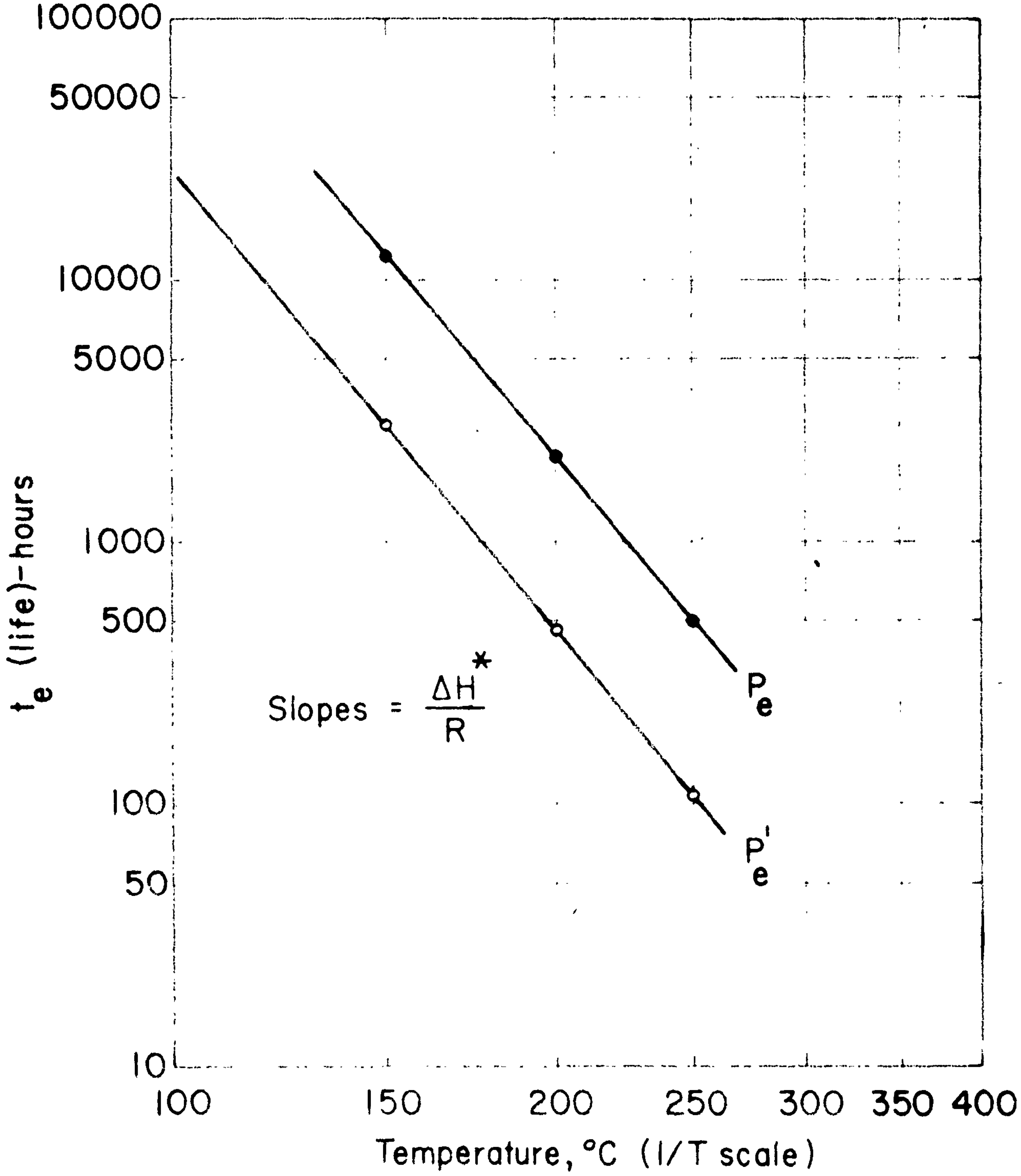

Fig. 1. Typical life-temperature plots as obtained by use of existing thermal endurance methods for two values of P_e.

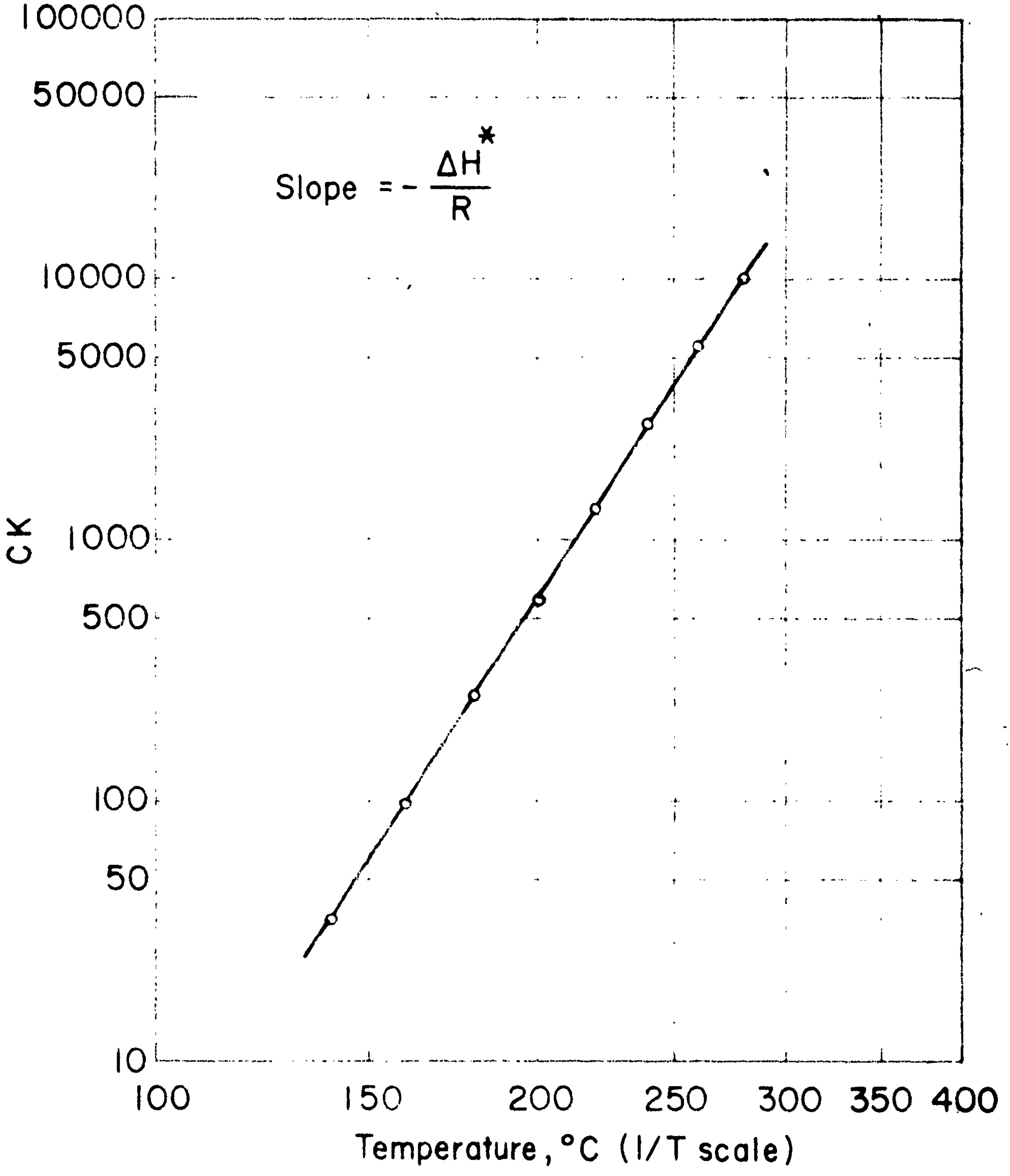

Fig. 2. Typical activation energy plot of equation 8.

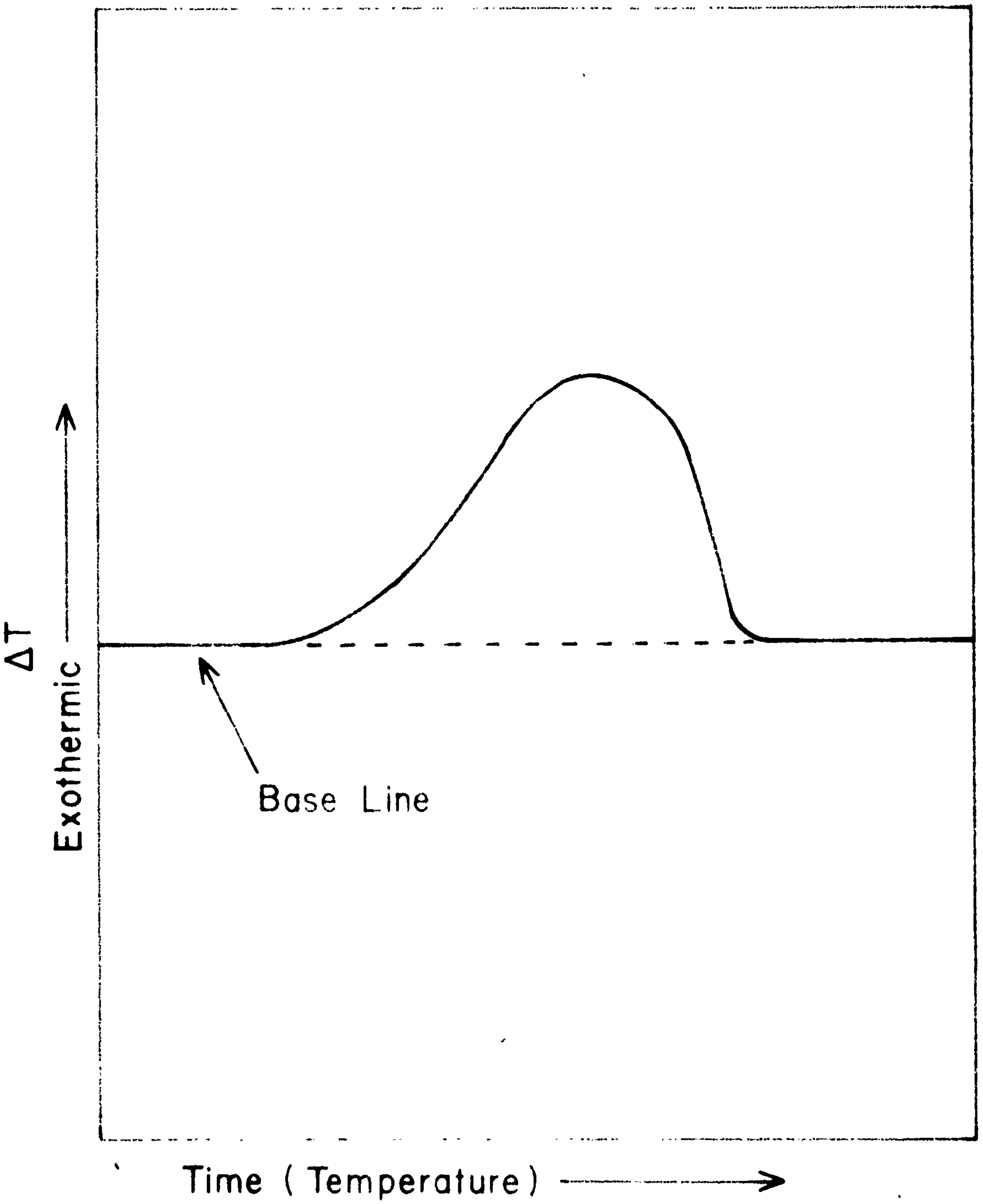

Fig. 3. Typical conventional DTA thermogram.

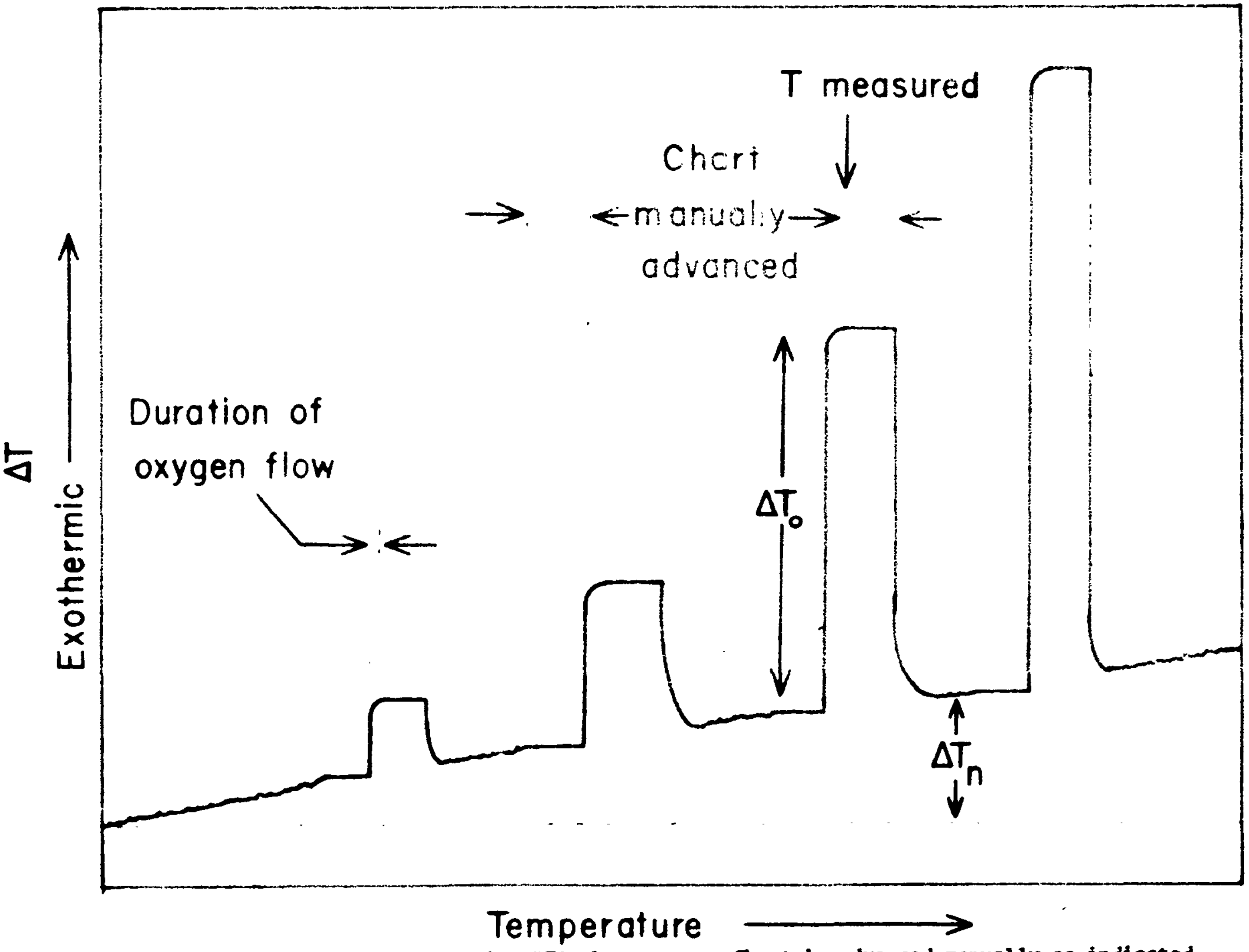

Fig. 4. Typical oxygen injection DTA thermogram. Chart is advanced manually as indicated to facilitate measurement of ΔT_o.

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Figure 5 - Overall view of R. L. Stone Co. Model DTA-12BC2 Controlled Pressure and Controlled Atmosphere DTA Apparatus. Furnace and sample molder platform is at extreme left. Furnace has been removed and placed at the right of the platform to show heating chamber.

PHOTO L-19591-1

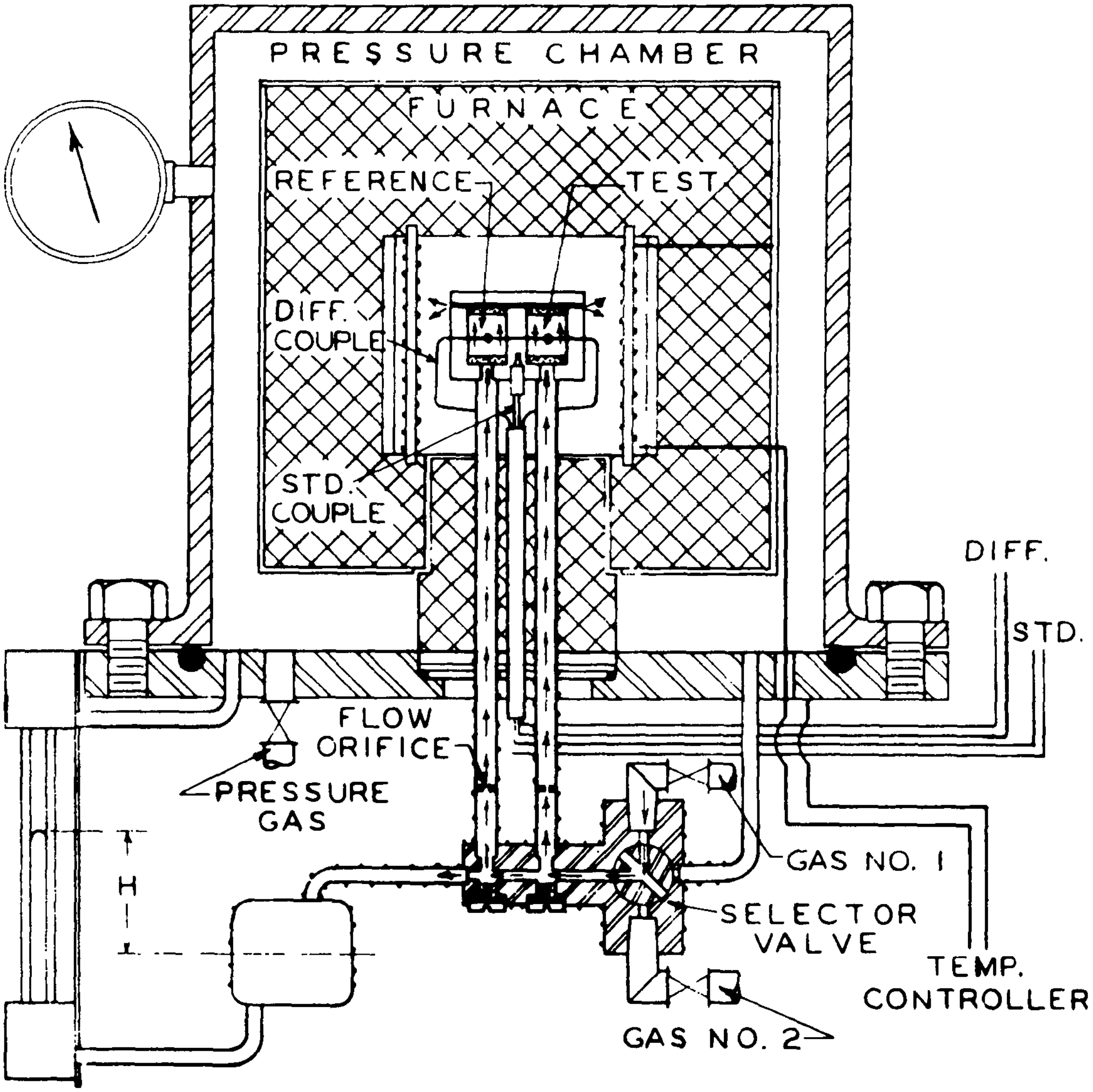

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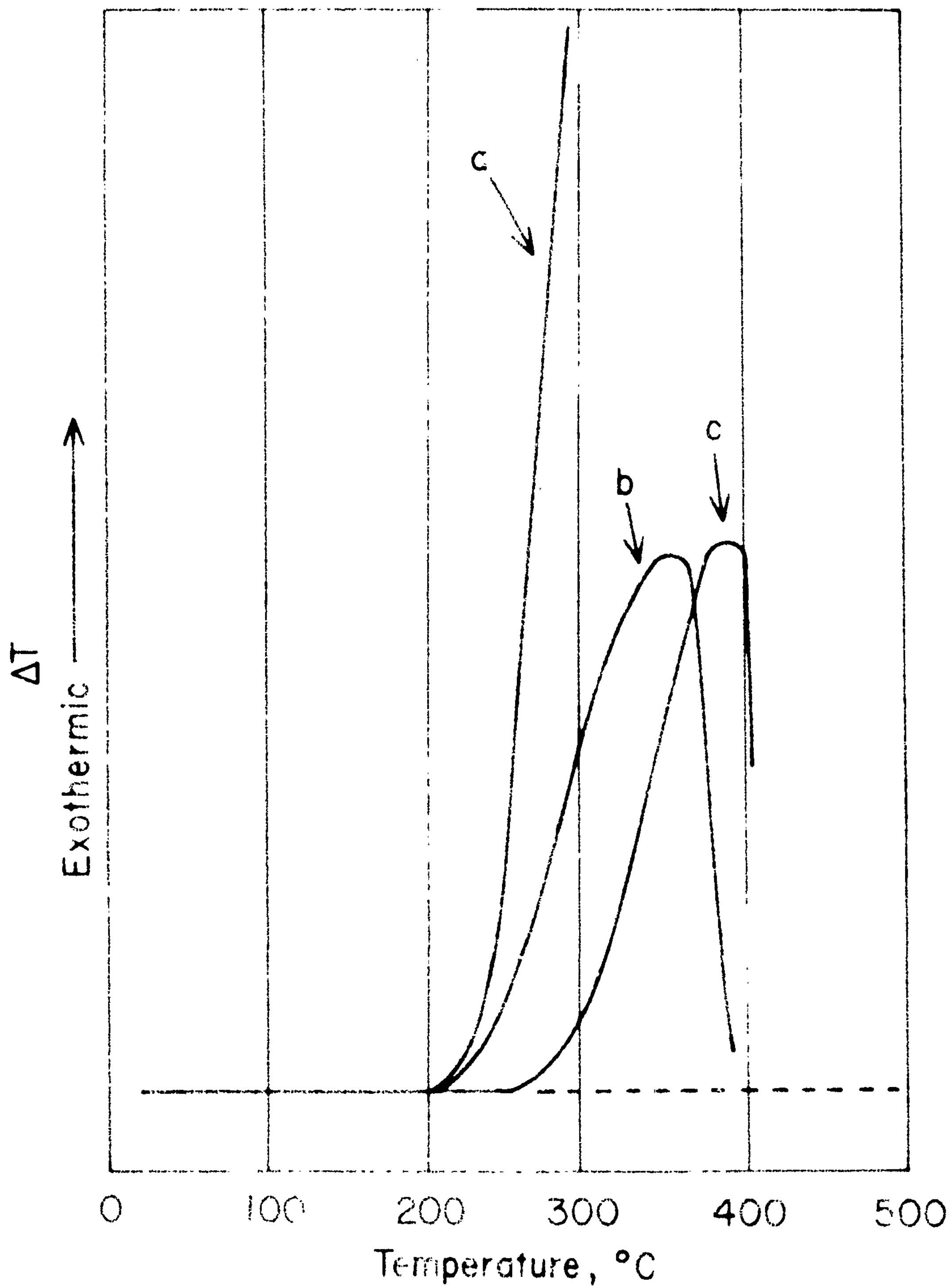
Figure 6 - Schematic diagram of the sample holder and furnace platform assembly of the R. L. Stone Co. DTA apparatus.

PHOTO L-19591-2

Fig. 7. Conventional Dynamic Gas DTA thermograms conducted on samples of materials C having different preparative histories and in different atmospheres:

a. Sample aged 24 hours at 250°C. DTA run in oxygen.
b. Sample unaged. DTA run in nitrogen.
c. Sample aged 24 hours at 250°C. DTA run in nitrogen.



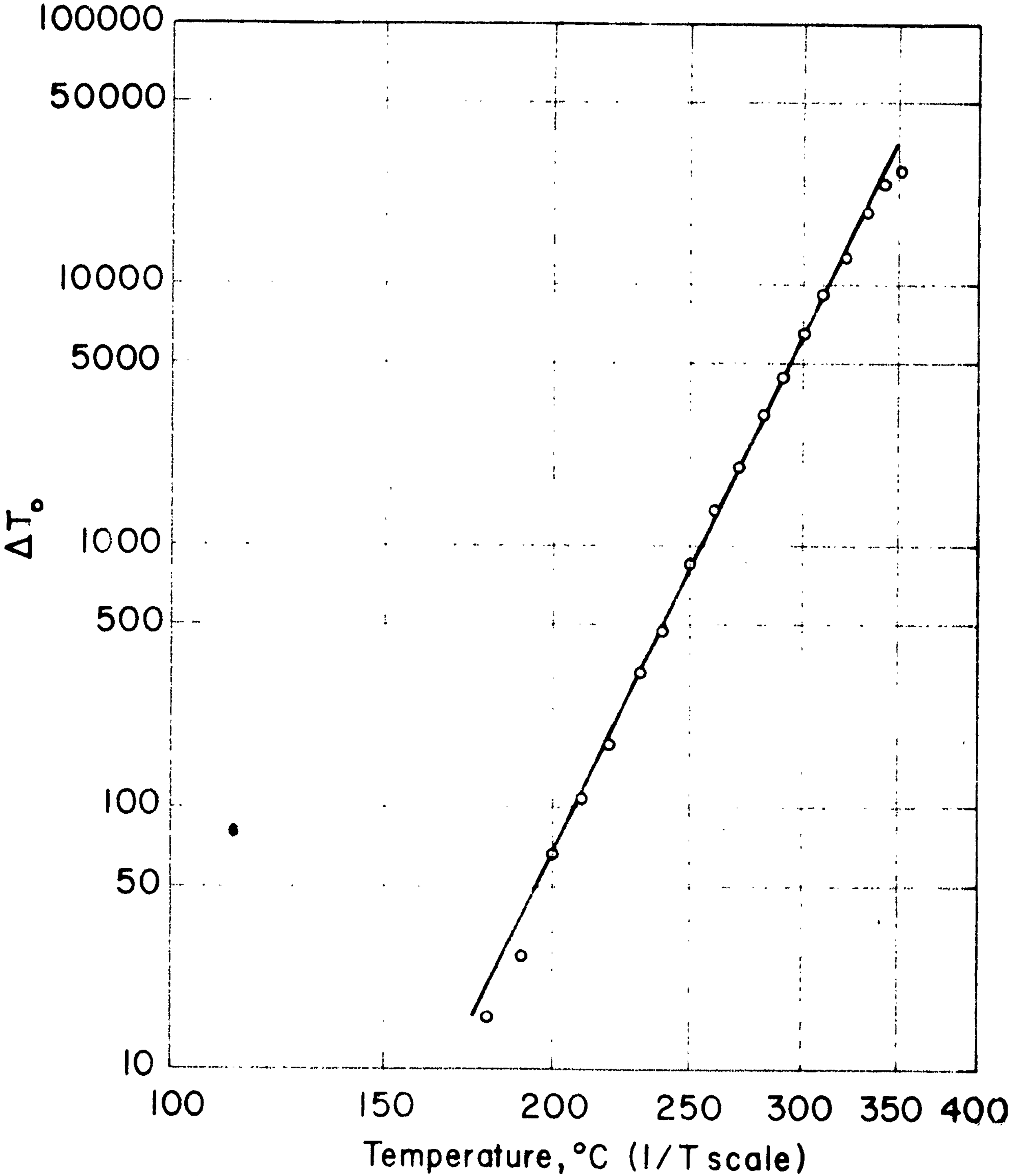


Fig. 8. Plot of results of oxygen injection DTA method obtained on material A. Slope of line equals $-\frac{\Delta H^*}{R}$.

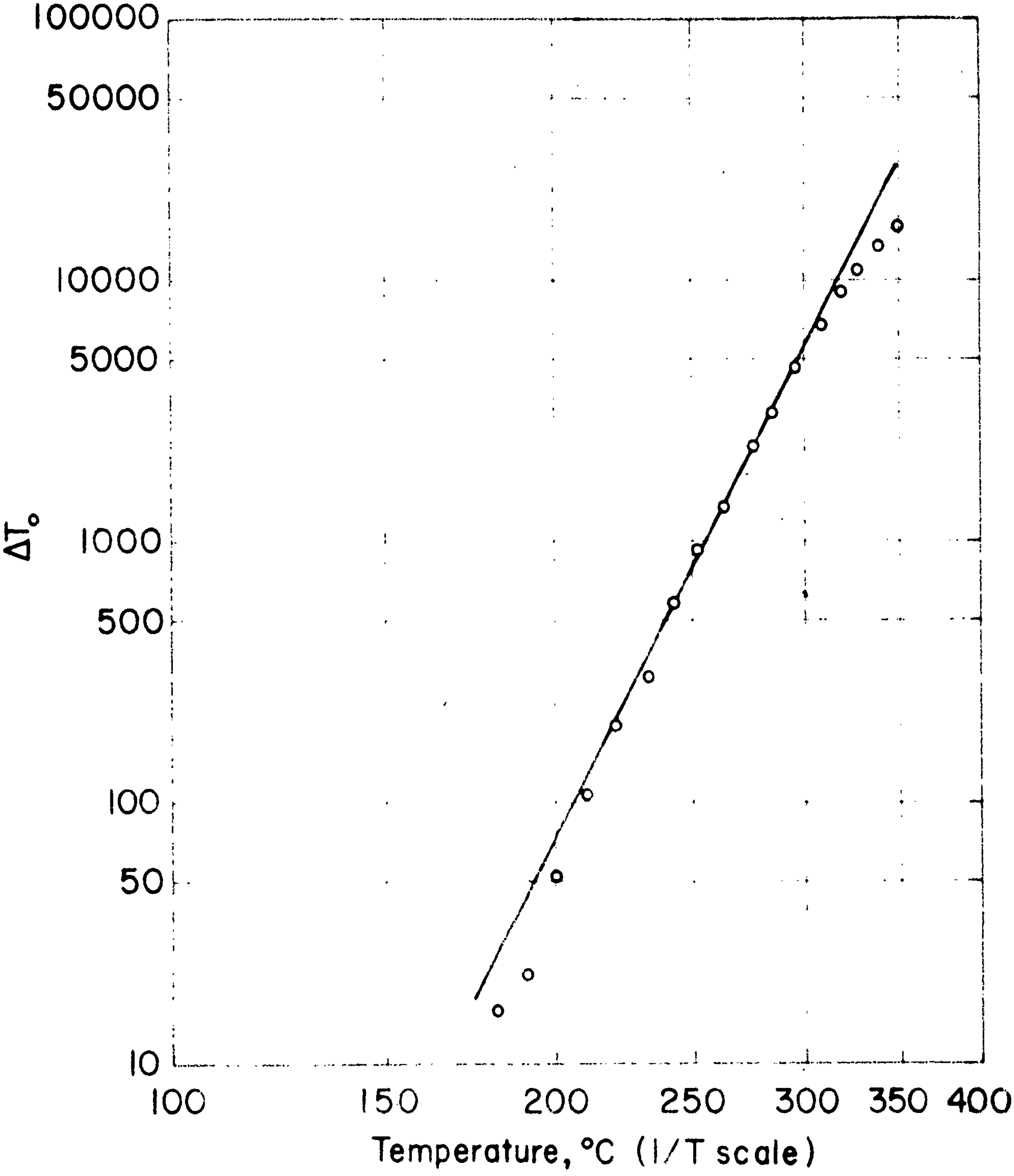


Fig. 9. Plot of results of oxygen injection DTA method obtained on material B. Slope of line equals $-\frac{\Delta H^*}{R}$.

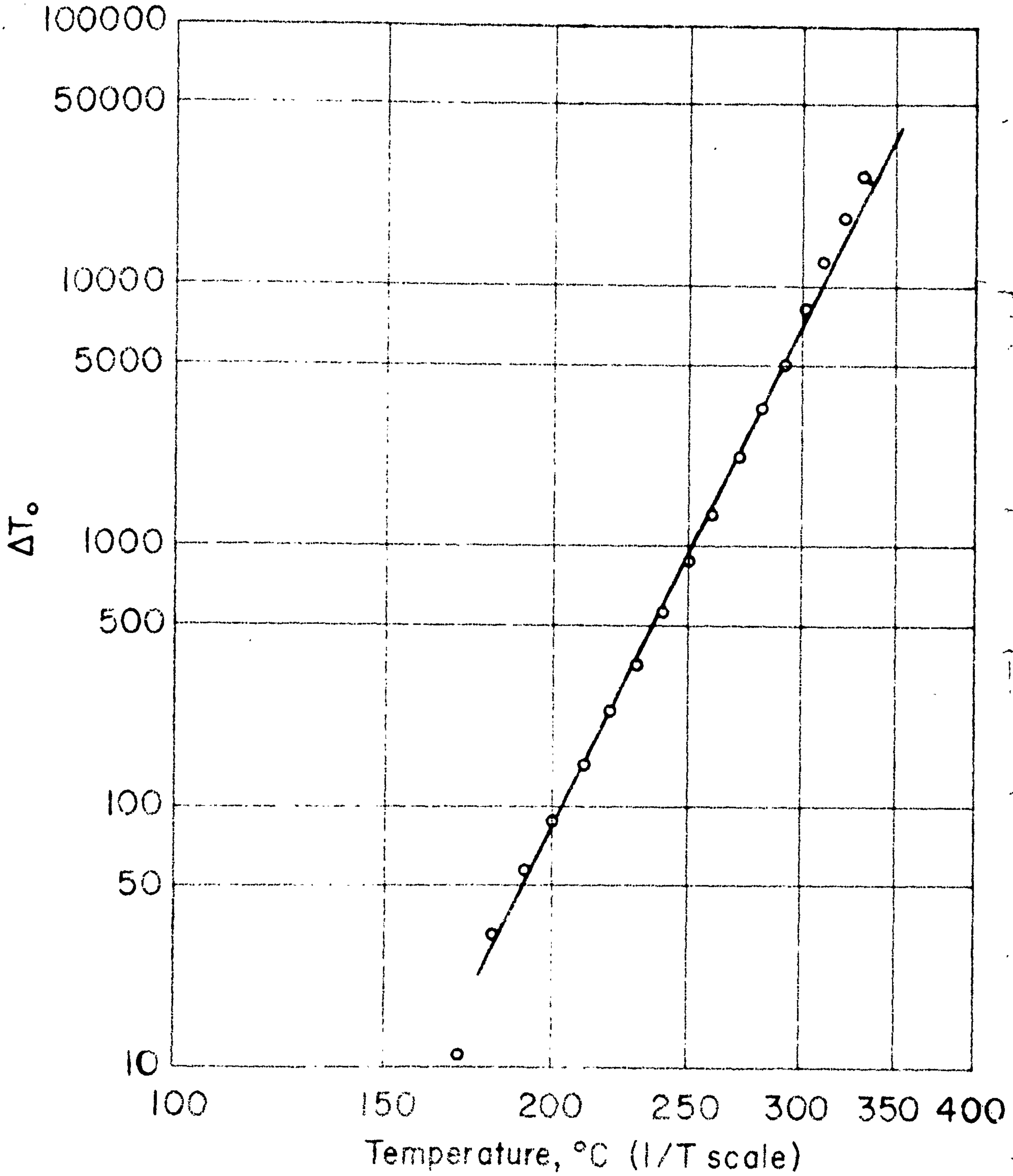


Fig. 10. Plot of results of oxygen injection DTA method obtained on on material C. Slope of line equals $-\frac{\Delta H^*}{R}$.

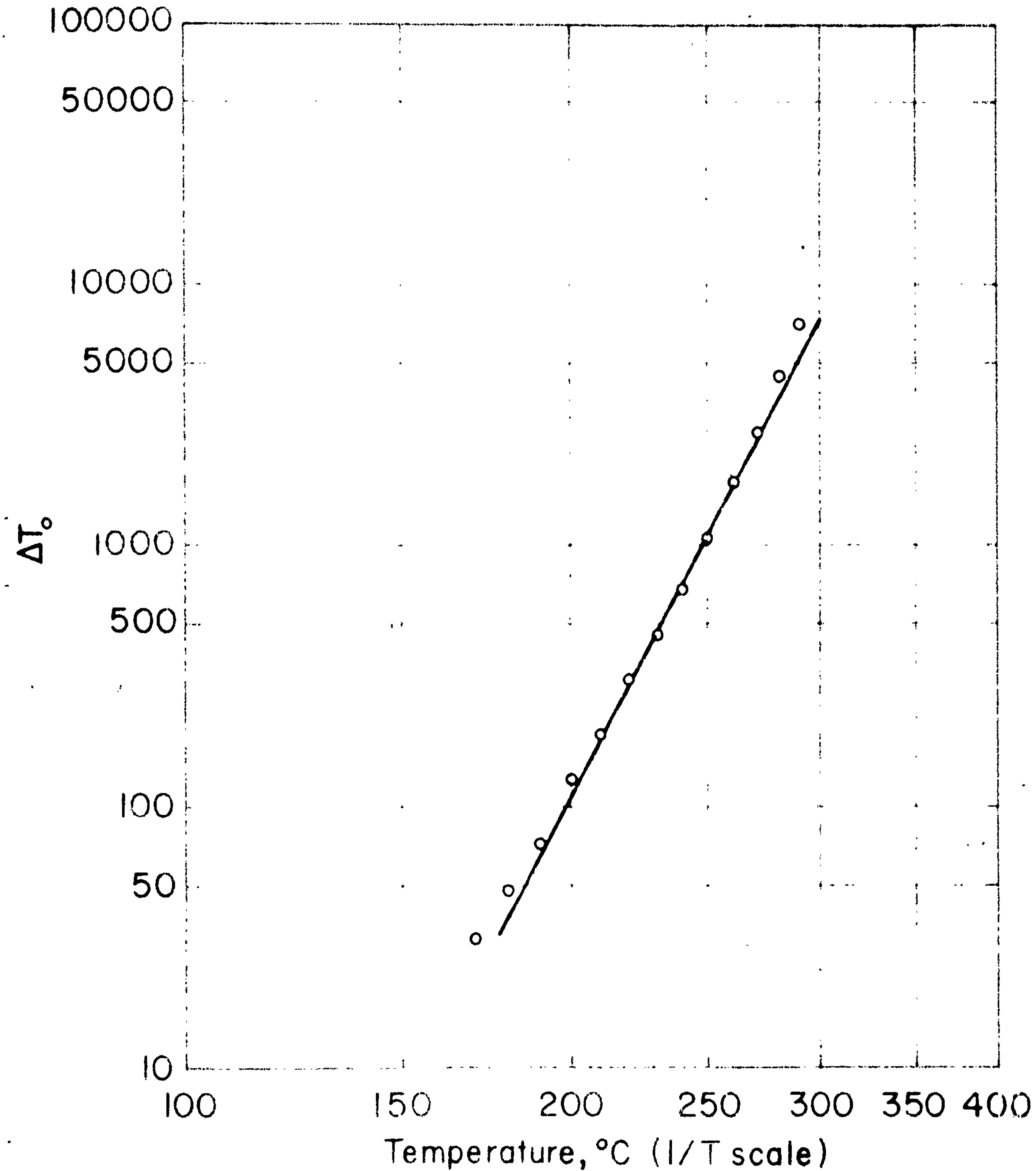


Fig. 11. Plot of results of oxygen injection DTA method obtained on material D. Slope of line equals $-\frac{\Delta H^*}{R}$.

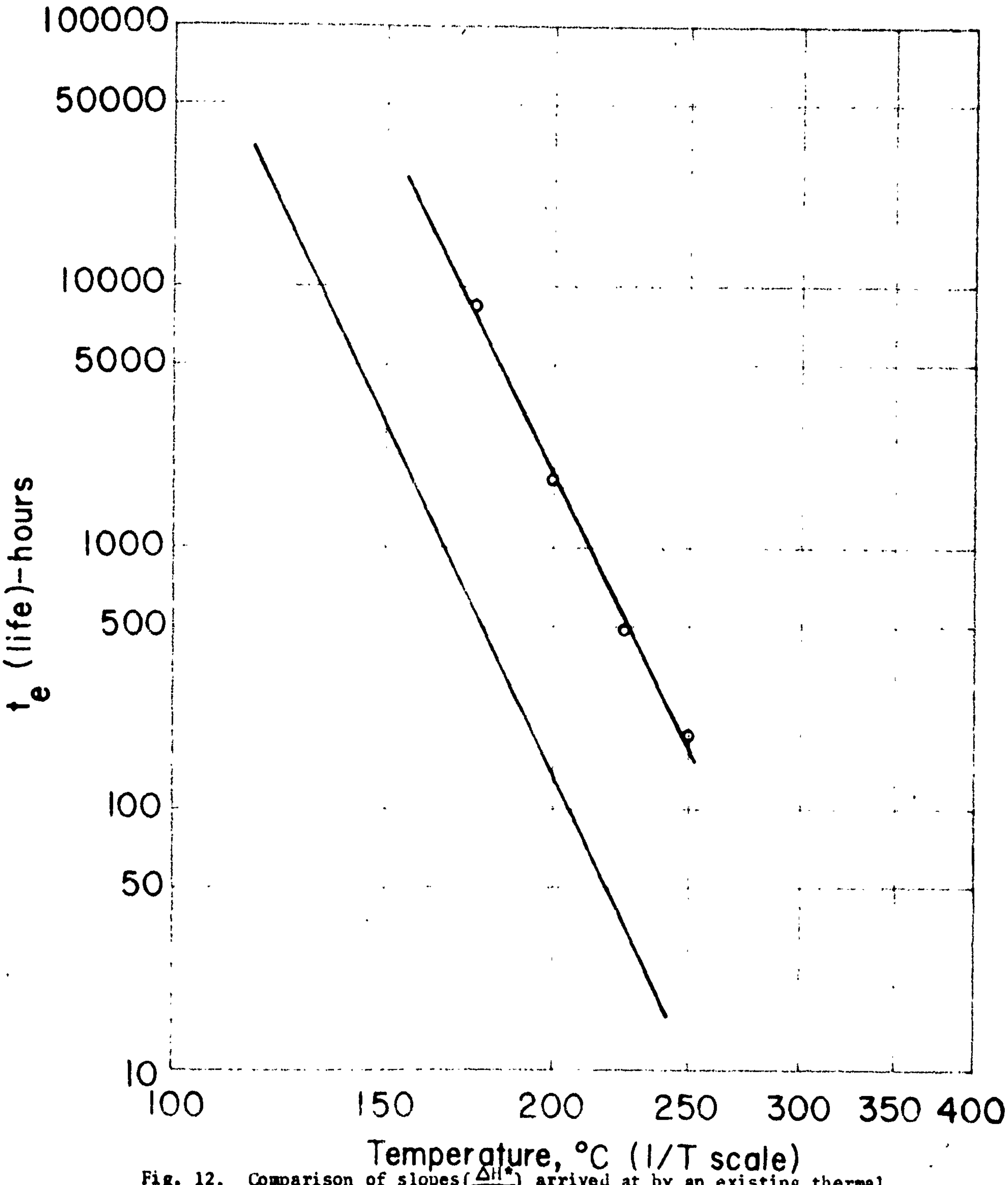


Fig. 12. Comparison of slopes($\frac{\Delta H^*}{R}$) arrived at by an existing thermal endurance method and the new oxygen injection DTA method for material A. Line drawn through points is that obtained by the existing thermal endurance methods.

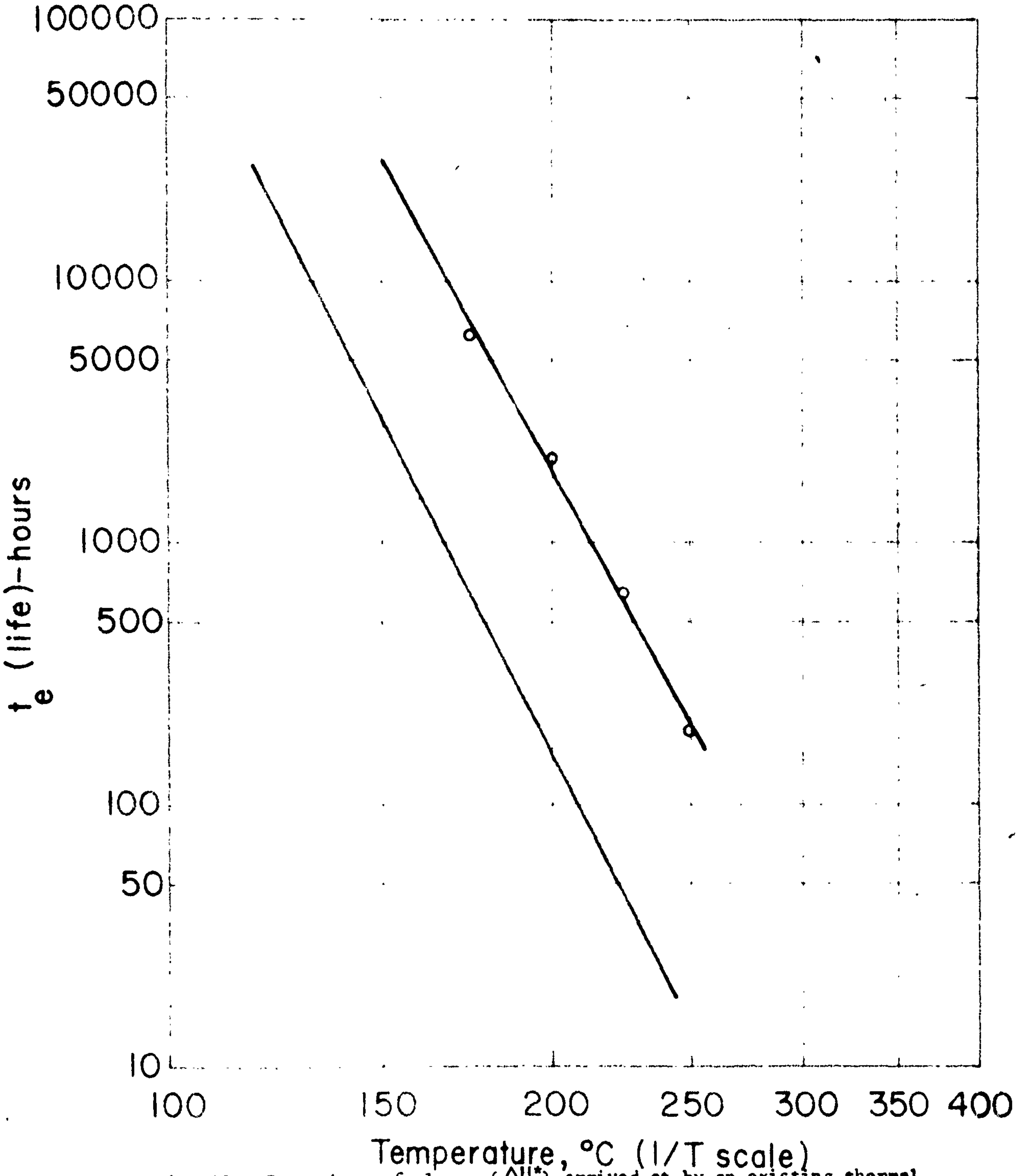


Fig. 13. Comparison of slopes $(\frac{\Delta H^*}{R})$ arrived at by an existing thermal endurance method and the new oxygen injection DTA method for material B. Line drawn through points is that obtained by the existing thermal endurance method.

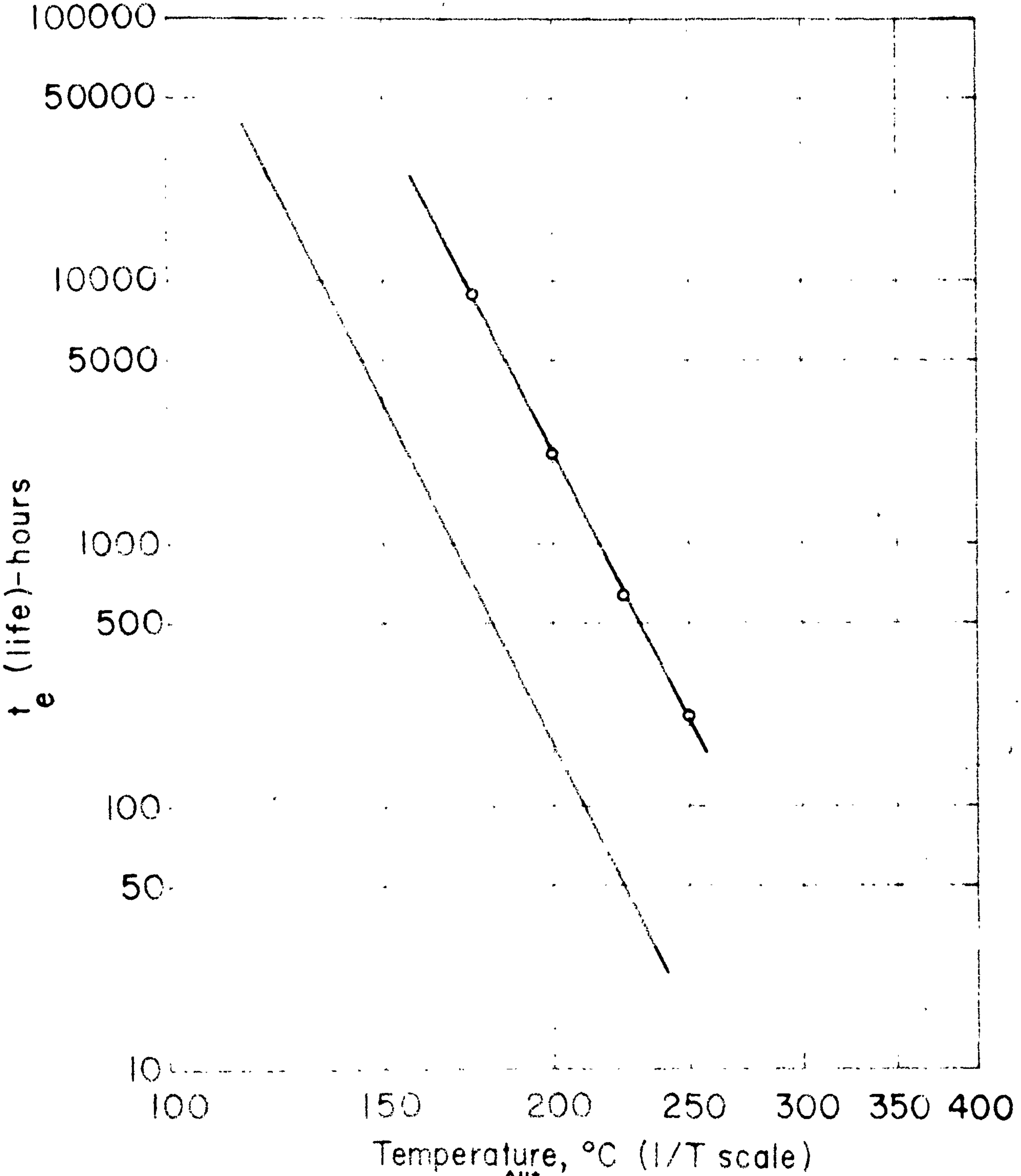


Fig. 14. Comparison of slopes($\frac{\Delta H^*}{R}$) arrived at by an existing thermal endurance method and the new oxygen injection DTA method for material C. Line drawn through points is that obtained by the existing thermal endurance method.

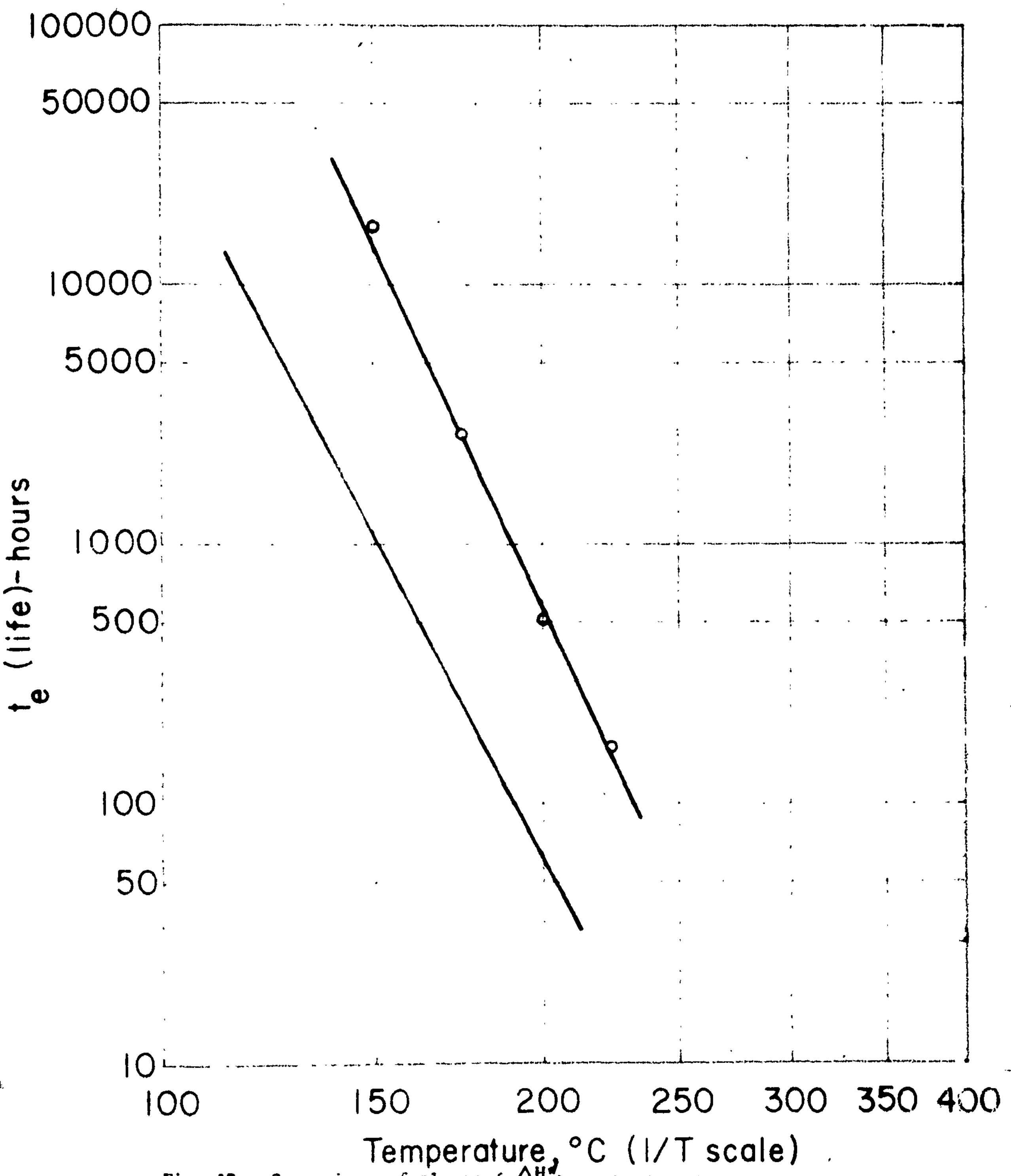


Fig. 15. Comparison of slopes $\left(\frac{\Delta H}{R}\right)$ arrived at by an existing thermal endurance method and the new oxygen injection DTA method for material D. Line drawn through points is that obtained by the existing thermal endurance method.

TABLE 1

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TABLE 2

TABLE OF SYMBOLS

P = physical property
P_e = particular value of physical property P
K = rate constant
t = time
t_e = time required to attain P_e
A = constant
A' = constant
ΔH^* = activation energy
R = ideal gas constant
T = absolute temperature
C = constant
ΔH = heat of reaction
C_s = heat capacity
f = fraction of active material's concentration transformed
ΔT = differential temperature
n = no. of moles of active material remaining at time t
n_o = no. of moles of active material present at time $t = 0$
x = order of reaction

TABLE 4

COMPARISON OF $\frac{\Delta H^*}{R}$ VALUES AS OBTAINED BY THE NEW DTA METHOD AND EXISTING THERMAL ENDURANCE METHOD

Material	New DTA Method $\frac{\Delta H^*}{R} \times 10^3$, °C	Existing Thermal Endurance Method $\frac{\Delta H^*}{R} \times 10^3$, °C
A	12.3	12.0
B	11.8	11.0
C	12.0	11.7
D	11.4	12.8

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