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# THE THERMAL DECOMPOSITION OF PYRITE

A. W. COATS & NORMAN F. H. BRIGHT

DEPARTMENT OF MINES AND  
TECHNICAL SURVEYS, OTTAWA

MINERAL SCIENCES DIVISION

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THE THERMAL DECOMPOSITION OF PYRITE

by

A. W. Coats\* and Norman F. H. Bright\*\*

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ABSTRACT

A study has been made of the kinetics of the thermal decomposition of pyrite to pyrrhotite and sulphur in a dynamic argon atmosphere. The reaction was followed (a) by the rate of loss of weight as indicated by the extension of a quartz spring and (b) by the rate of progression of the pyrite/pyrrhotite interface into a polycrystalline compressed pellet. The temperature coefficient of the reaction was found to be  $69.5 \pm 5.9$ ,  $64.7 \pm 3.3$  and  $66.9 \pm 5.1$  kcal. mole<sup>-1</sup> when the results were processed in three different ways. The pyrite/pyrrhotite interface was found to progress at a linear rate into the pellet, and equations were derived to express the variation of reaction rate with temperature. Attempts to study the early nucleation stage of the decomposition, using mineral crystals, proved abortive.

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Direction des mines

Rapport de recherches R 173

## DÉCOMPOSITION THERMIQUE DE LA PYRITE

par

A. W. Coats\* et Norman F. H. Bright\*\*

### RÉSUMÉ

Les auteurs ont étudié la cinétique de la décomposition thermique de la pyrite en pyrrhotine et en soufre dans une atmosphère dynamique d'argon. La réaction a été suivie a) par le taux de perte de poids indiqué par un ressort à quartz et b) par le taux de progression de l'interface pyrite/pyrrhotine en une pastille polycristalline comprimée. Lorsque les résultats sont interprétés de trois façons différentes le coefficient de température de la réaction est de  $69.5 \pm 5.9$ ,  $64.7 \pm 3.3$  et  $66.9 \pm 5.1$  Kcal. moléc.  $^{-1}$ . L'interface pyrite/pyrrhotine progresse à un taux linéaire dans la pastille et les auteurs ont dérivé des équations pour exprimer la variation de la vitesse de réaction selon la température. Ils ont essayé d'étudier les premières étapes de la nucléation de la décomposition en utilisant des cristaux minéraux mais ils n'ont pas réussi.

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## INTRODUCTION

The thermal decomposition of the mineral pyrite into pyrrhotite and sulphur, under vacuum or in an inert atmosphere, has been investigated by a number of workers and this work has recently been reviewed by Kullerud and Yoder (1). Most studies have been made using sulphur pressure measurements ( $p_S$ ) under equilibrium conditions, whence, from the slope of a plot of  $\log p_S$  against  $\frac{1}{T^\circ K}$ , the enthalpy of the reaction ( $\Delta H$ ) has been determined. The values of  $\Delta H$  obtained by previous workers are given in Table 1.

TABLE 1

Values of  $\Delta H$  for the Decomposition of Pyrite,  
Obtained by Previous Workers

Ref. No.	Authors	$\Delta H$ (kcal. mole <sup>-1</sup> )
2	Allen and Lombard (1917)	80.3
3	Kamura (1921)	39.0
4	Raeder (1929)	82.9
5	D'Or (1931)	65.9
6	Juza, Biltz and Meisel (1932)	81.7
7	Rudder (1936)	82.6
8	Rosenqvist (1954)	86.9
9	Bog and Rosenqvist (1959)	72.0
10	Dickson, Shields and Kennedy (1962)	104

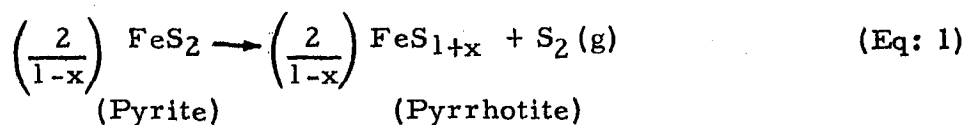
Various methods of measuring the sulphur vapour pressure were employed. The dew-point method was used by Allen and Lombard (2), by Rosenqvist (8), and by Dickson et al. (10). Kamura (3) used a mercury manometer but, in view of the fact that sulphur vapour reacts with mercury, his results are generally discounted. Raeder (4) and Rudder (7) used a DTA approach in which the pyrite was heated under a known pressure at a constant rate of heating, the equilibrium temperature for this particular pressure being taken as that temperature at which the heating curve started to depart from its linear rate of increase. D'Or (5) and Juza et al. (6) employed a Bodenstein hollow quartz spiral as a pressure gauge. A high-temperature manometer was used by Bog and Rosenqvist (9) for sulphur pressures in the range  $10^{-2}$  to  $10^{-5}$  atm. Toulmin and Barton (11)

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(1) For references, see pages 18 and 19.

determined the fugacity of sulphur over the temperature range 325° to 743°C by employing the electrom-tarnish method. All of these workers studied the reaction at pressures below one atmosphere. Kullerud and Yoder (1), however, studied the reaction at higher pressures. The only workers who have studied the pyrite decomposition under dynamic conditions, e.g., a steady flow of inert gas, appear to be Udintseva and Chufarov (12), who used polycrystalline cubes and single crystals of pyrite.

One of the main problems in studying the decomposition of pyrite is the variability of composition of the resultant pyrrhotite. Another problem is the molecular composition of the sulphur vapour, since Wunderlich (13) has shown that S<sub>2</sub>, S<sub>6</sub> and S<sub>8</sub> molecules can exist at the temperatures usually employed in the study of this reaction. Bog and Rosenqvist (9) expressed the reaction by the equation:



for temperatures of 500° to 550° C. They state that x varies with temperature. Also, since higher pressures and lower temperatures would favour association of S<sub>2</sub> molecules into S<sub>6</sub> and S<sub>8</sub>, it is clear that the reaction is complex in its stoichiometry.

Thus, it can be seen that, in general, the previous work done on the pyrite decomposition has involved equilibrium conditions. In the present work, however, a study of the reaction has been made under constant gas flow conditions similar to those that might exist in the industrial manufacture of sulphur from pyrite, namely, the evolved sulphur is swept away by a stream of inert gas and condensed. The aim of this work was to determine kinetic parameters for the reaction of small cylindrical pellets of pyrite that would approximate in size the pieces of ore that would be used in the industrial process. Polycrystalline pellets were used also to see whether the approach adopted by McKewan (14) for the reduction of iron oxide pellets in hydrogen was applicable to the pyrite decomposition.

The results of a preliminary investigation of the initial or nucleation stage of the decomposition reaction are given as an Appendix to this report. (See page 20.)



### EXPERIMENTAL TECHNIQUES

The pyrite used in this work was obtained from Eastman, Quebec, and was treated as follows. The material was crushed and washed with dilute hydrochloric acid to remove any pyrrhotite and then thoroughly washed with distilled water to remove the acid. The dried powder (-40 + 100 mesh, U.S. standard) was analysed by X-ray and spectroscopic methods and found to contain an appreciable amount of quartz. This impurity was removed by a heavy-liquid separation in tetrabromoethane (sp. gr. = 2.96), when the quartz (sp. gr. = 2.66) floated while the pyrite (sp. gr. = 5.00) sank. The pyrite was washed with alcohol to remove the organic material, dried at 100°C, and then crushed to a particle size of -200 mesh. A portion of this powder was subjected to chemical and spectroscopic analyses. The results of the former correspond to the formula  $FeS_{1.99}$ ; the results of the latter are shown in Table 2.

TABLE 2

Semi-Quantitative Spectrographic  
Analysis of Purified Crushed Pyrite Sample

Principal constituent		--- Fe.	
Element	% by Weight	Element	% by Weight
Si	0.30	Zr	0.01
Mn	0.02	Cu	0.12
Mg	0.08	Ti	0.006
Pb	0.01	Ni	0.10
Cr	0.005	Co	0.01
Al	0.10	V	0.003

Notes: 1. These results were taken from Mineral Sciences Division Internal Report MS-AC-65-738, August 26, 1965, by Douglas P. Palombo, Technician, Spectrographic Laboratory, Analytical Chemistry Sub-division, Mineral Sciences Division, Mines Branch, Ottawa.

2. It will be observed that these results indicate that the only significant impurity is the 0.30% Si, presumably present as a small amount of residual, unliberated quartz.

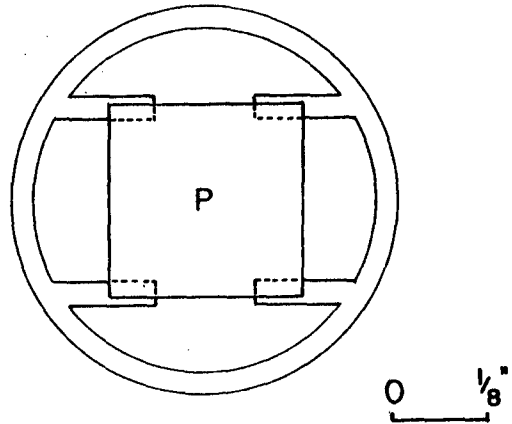
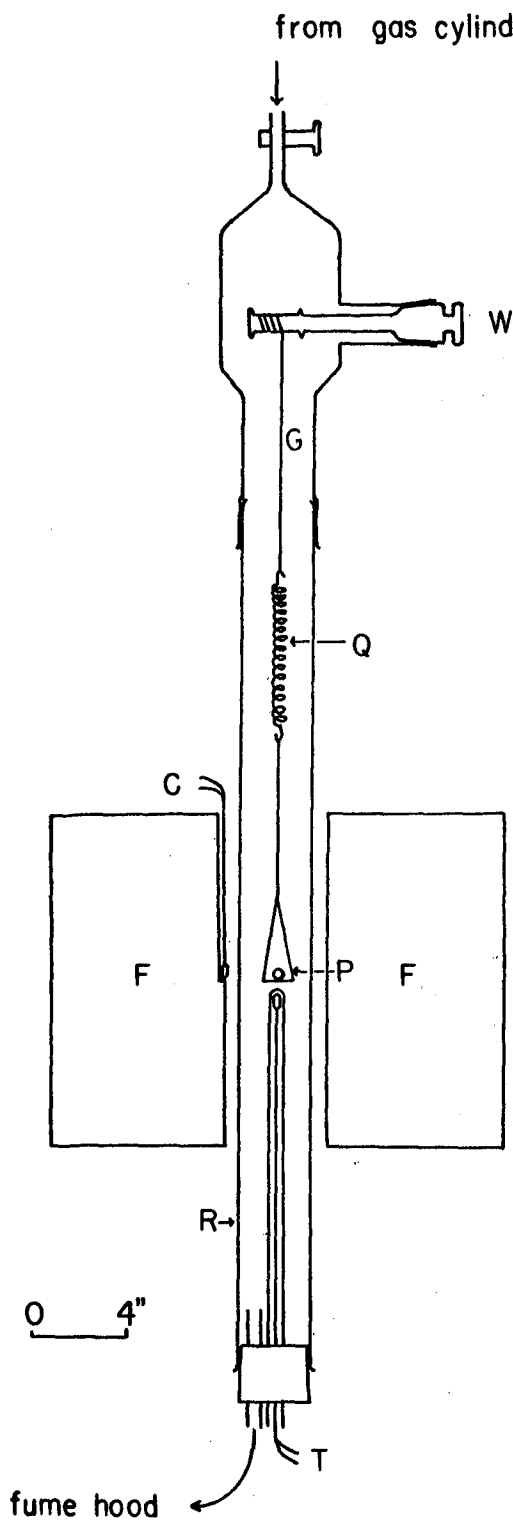
This material was pressed into cylindrical pellets of 0.25 in. diameter and height at a pressure of 160,000 lb. in.<sup>-2</sup> Each pellet weighed approximately 0.86 g and had a density of approximately 4.10 g.cm<sup>-3</sup>. This size of pellet was chosen since, in larger pellets, the endothermic heat of reaction would cause a significant discrepancy between the furnace temperature and the internal pellet temperature.

The apparatus used for the study is shown in Figure 1. The reaction tube, the thermocouple sheath, and the pellet holder were made of fused quartz.

The control chromel-alumel thermocouple was placed outside the reaction tube, close to the furnace wall, where the response would be rapid. The temperature of the furnace was maintained constant to within  $\pm 0.5^\circ\text{C}$ . The temperature of the pellet was measured with a Pt vs Pt: 10% Rh thermocouple located directly beneath the sample. The hot zone of the furnace was located by varying the position of the inner thermocouple along the axis of the reaction tube and recording the temperature after it had obtained a steady value at a given position. The thermocouple sheath, which was necessary since sulphur vapour attacks platinum, was located 0.25 in. below the pellet. The pellet holder, shown in Figure 1, was constructed in such a way that argon could flow completely around the pellet.

The quartz spring was calibrated in argon at atmospheric pressure and the sensitivity was found to be 5.39 cm. g<sup>-1</sup>. The flow meter was calibrated for argon flows of up to 220 ml.min<sup>-1</sup> by timing the collection of a known volume of argon. A flow rate of 180 ml.min<sup>-1</sup> was normally used. The rate of gas flow was shown not to affect the amount of decomposition for gas flows greater than 90 ml.min<sup>-1</sup>, up to the above maximum figure.

The mode of operation in a typical experimental run was as follows. A weighed and measured pellet was placed on the holder and lowered into the cool portion of the reaction tube, the hot zone of which had been adjusted to the desired steady temperature. The gas flow was continued through the reaction tube for 10 minutes to sweep out all the air before the pellet holder was lowered into the hot zone. Every pellet was lowered to the same position by observation through a cathetometer. Readings of the length of the quartz spring and of the temperature were taken at 5-minute intervals until the end of the required time of heating, when the pellet was taken out of the furnace and allowed to cool for 15 minutes in the argon stream. The pellet was then removed, weighed, measured, cut in half laterally, and the diameter of the unreacted pyrite measured.



Plan of pellet carrier

FIGURE 1

Diagram of apparatus.

- C - Control T/C
- F - Furnace
- G - Gold chain
- P - Pellet
- Q - Quartz spring
- R - Reaction tube
- T - Temp. measuring T/C
- W - Winch



The appearance of a partly decomposed pellet of pyrite is shown in Figure 2.

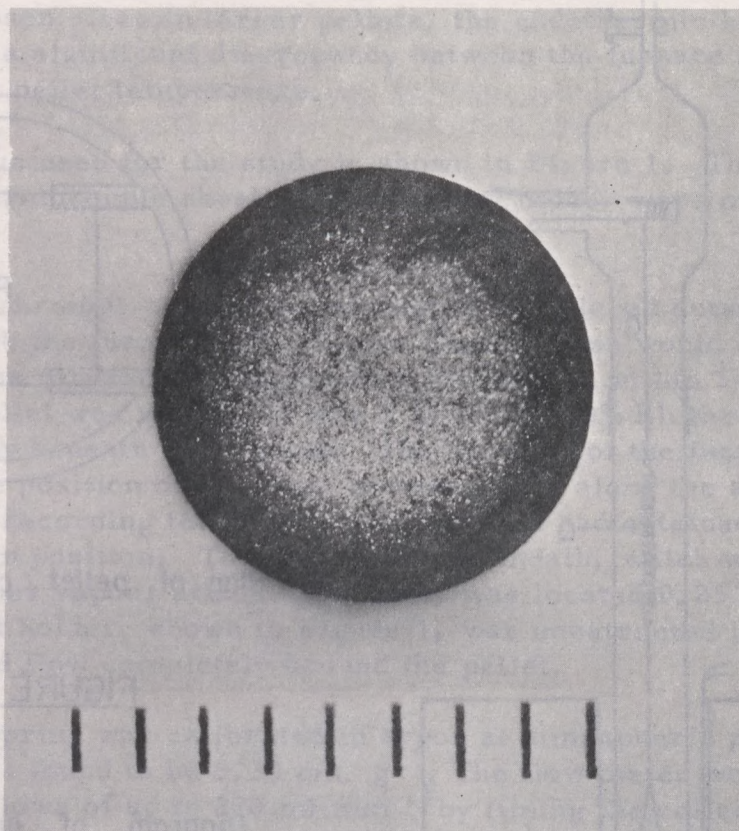


Figure 2 - Lateral Section of Partly Decomposed Pellet of Pyrite.

N. B. The scale shown below the pellet is in millimetres.

Observation of the section under a low-power microscope showed that the line of demarcation between the undecomposed pyrite and the pyrrhotite product was much sharper than it appeared from this photograph and was readily measurable. The average of two diameters, measured at right angles to each other on each half of the pellet, gave a mean of four figures for each experimental observation.

## EXPERIMENTAL RESULTS

The kinetic parameters of the reaction were calculated by two methods:

(a) From direct measurement of the diameter of the unreacted pyrite

Plots of the diameter of the unreacted pyrite against time were constructed (see Figure 3), yielding straight lines, the slopes of which were taken as the rate constant or velocity of the interface,  $k_0$  (units are  $\text{cm}\cdot\text{min}^{-1}$ ). An Arrhenius plot of  $\log_{10} k_0$  against  $\frac{1}{T^\circ\text{K}}$  for six different temperatures was also constructed (see Figure 4). The equation of the best straight line through the points, obtained by the method of least squares, was:

$$\log_{10} k_0 = 14.3 - \frac{15.18 \times 10^3}{T} \quad (\text{Eq 2})$$

(b) From the equations used by McKewan (14)

McKewan assumed Equation 3 (below) and, from it, derived Equation 4 for spherical pellets and for cylindrical pellets with equal height and diameter:

$$\frac{dw}{dt} = k_1 A \quad (\text{Eq 3})$$

$$r_0 d_0 \left[ 1 - (1 - R)^{1/3} \right] = k_2 T \quad (\text{Eq 4})$$

where  $\frac{dw}{dt}$  = rate of weight loss,

$A$  = interfacial area between reactant and product,

$r_0$  = initial radius of pellet,

$d_0$  = initial density of pellet,

$k_1$  and  $k_2$  = rate constants,

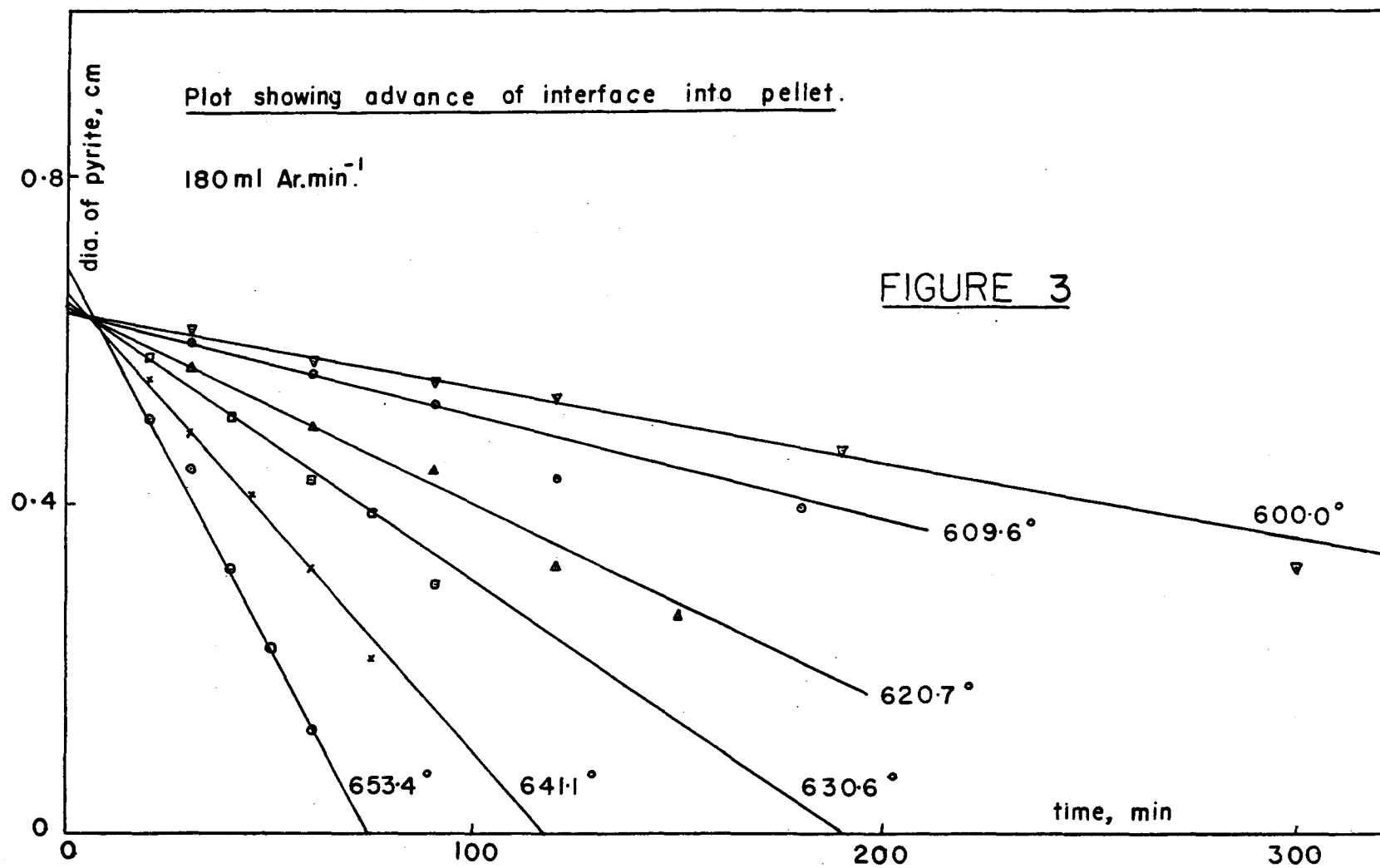
$t$  = time,

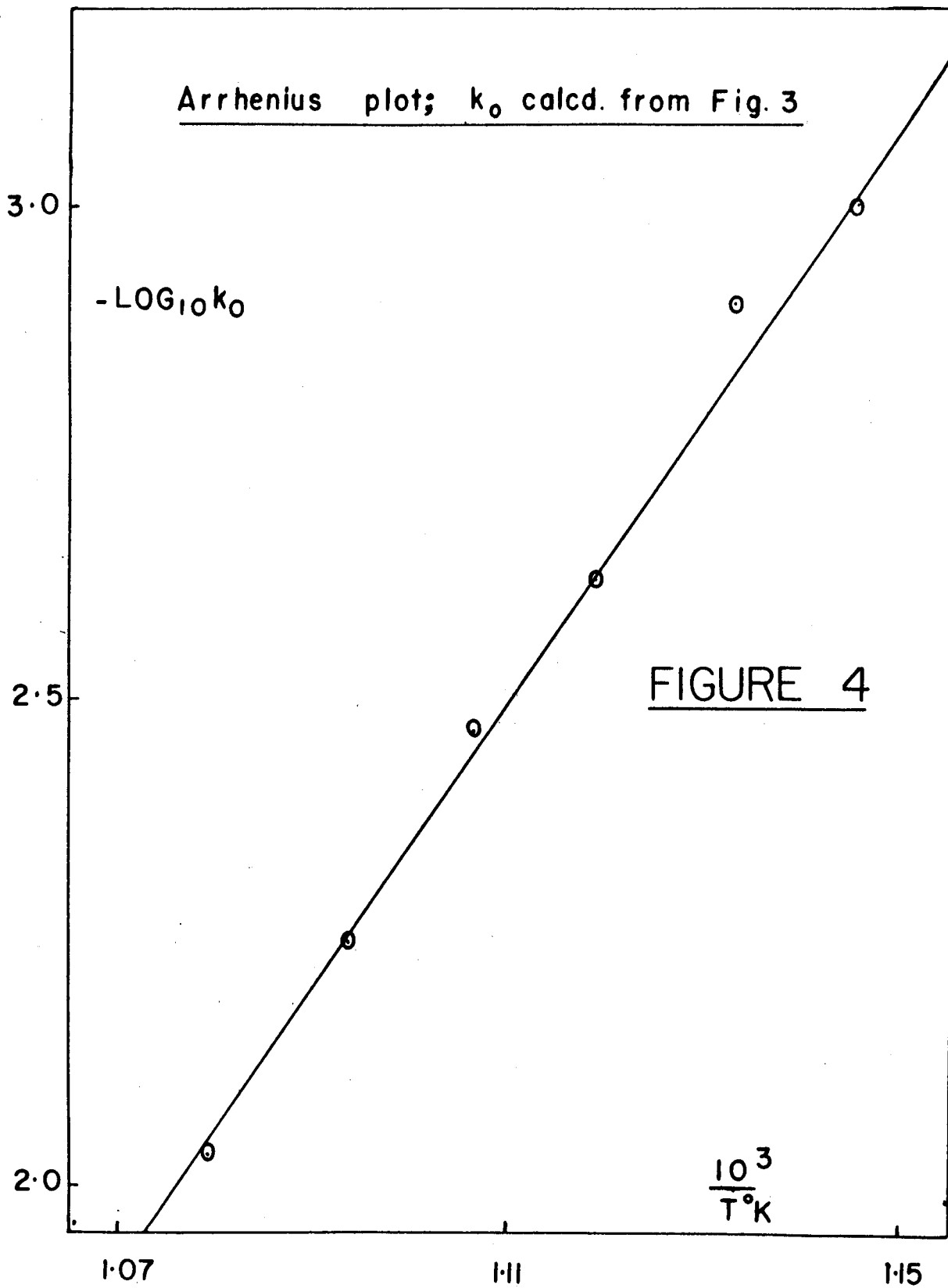
and  $R$  = fraction of reactant decomposed at time  $t$ .

$R$  can be defined as  $\frac{\% \text{ wt lost at time } t}{\% \text{ wt lost at end of reaction}}$

$R$  lies between 0 and 1.

In the present work, results were available to test the validity of Equations 3 and 4.



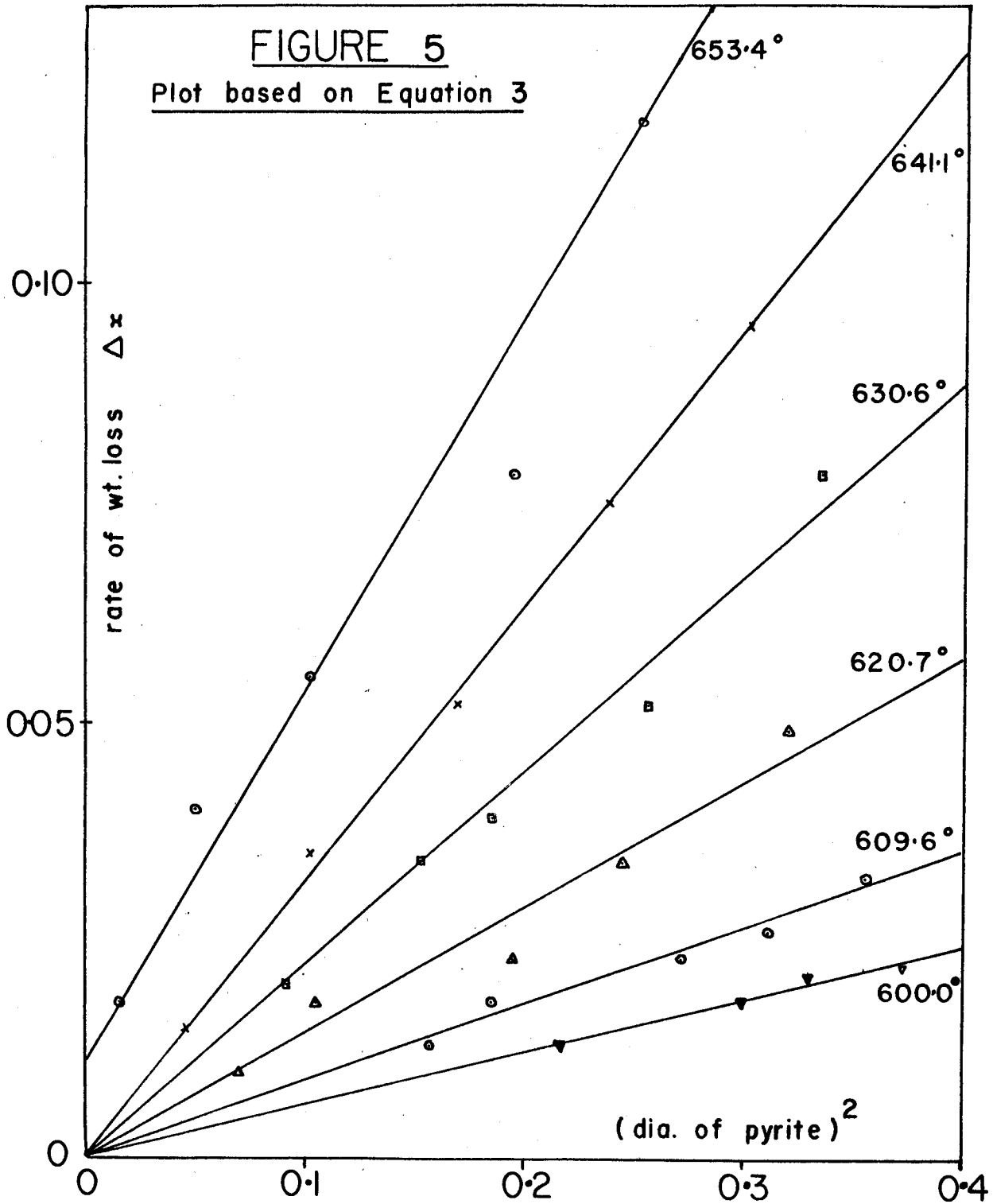


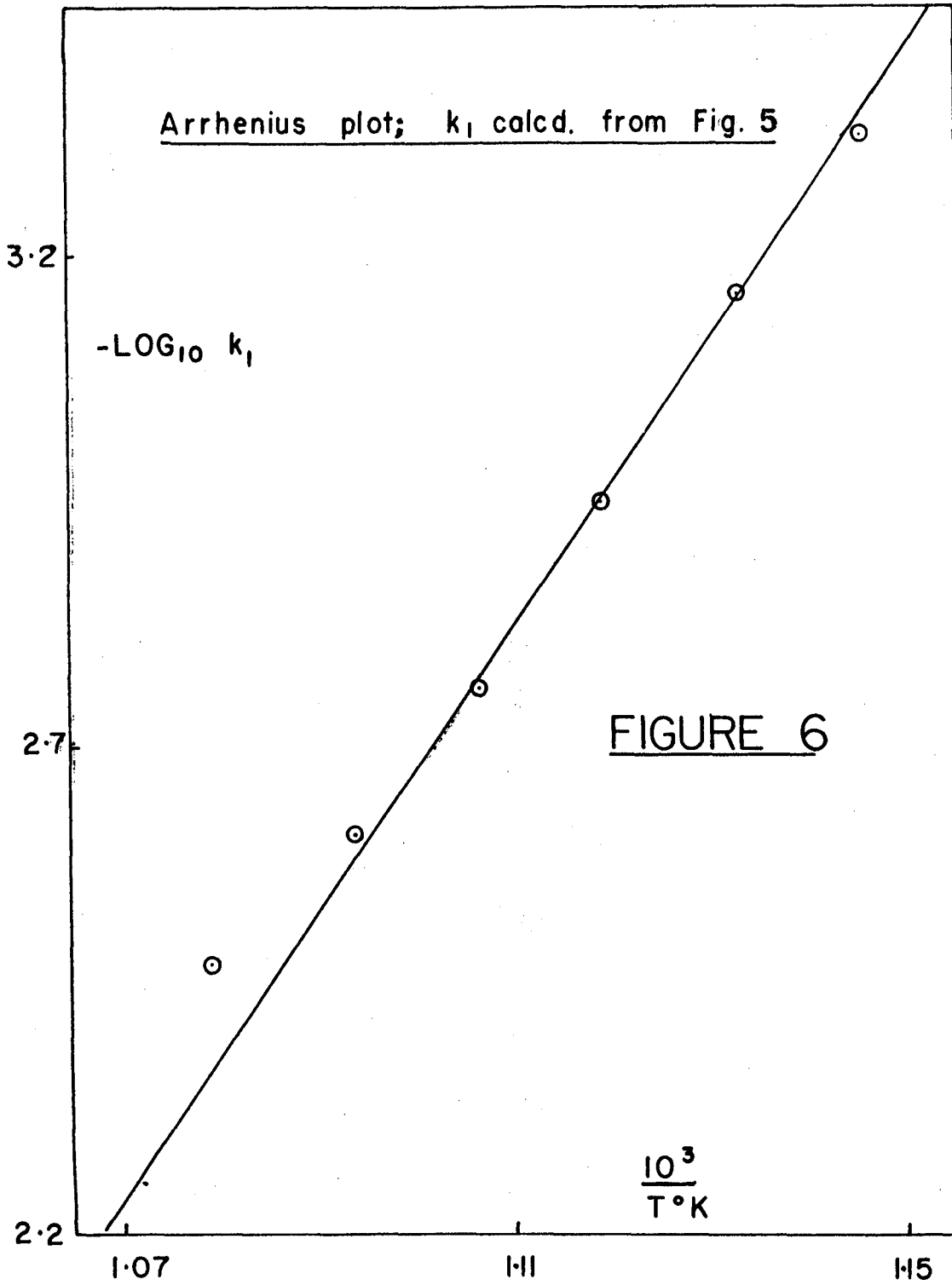
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In Equation 3,  $\frac{dw}{dt}$  is directly proportional to the difference in successive cathetometer readings ( $\Delta x$ ), which were taken at 5-minute intervals;  $A$ , the area of the interface between the pyrite and the pyrrhotite, is directly proportional to the square of the diameter of the unreacted pyrite ( $d^2$ ). Thus, a plot of  $\Delta x$  against  $d^2$  should be a straight line and, from the slope,  $k_1$  can be determined (see Figure 5). The Arrhenius plot of  $\log_{10} k_1$  against  $\frac{1}{T^\circ K}$  (see Figure 6) can be fitted by the method of least squares to give the line:

$$\log_{10} k_1 = 12.8 - \frac{14.14 \times 10^3}{T} \quad (\text{Eq 5})$$



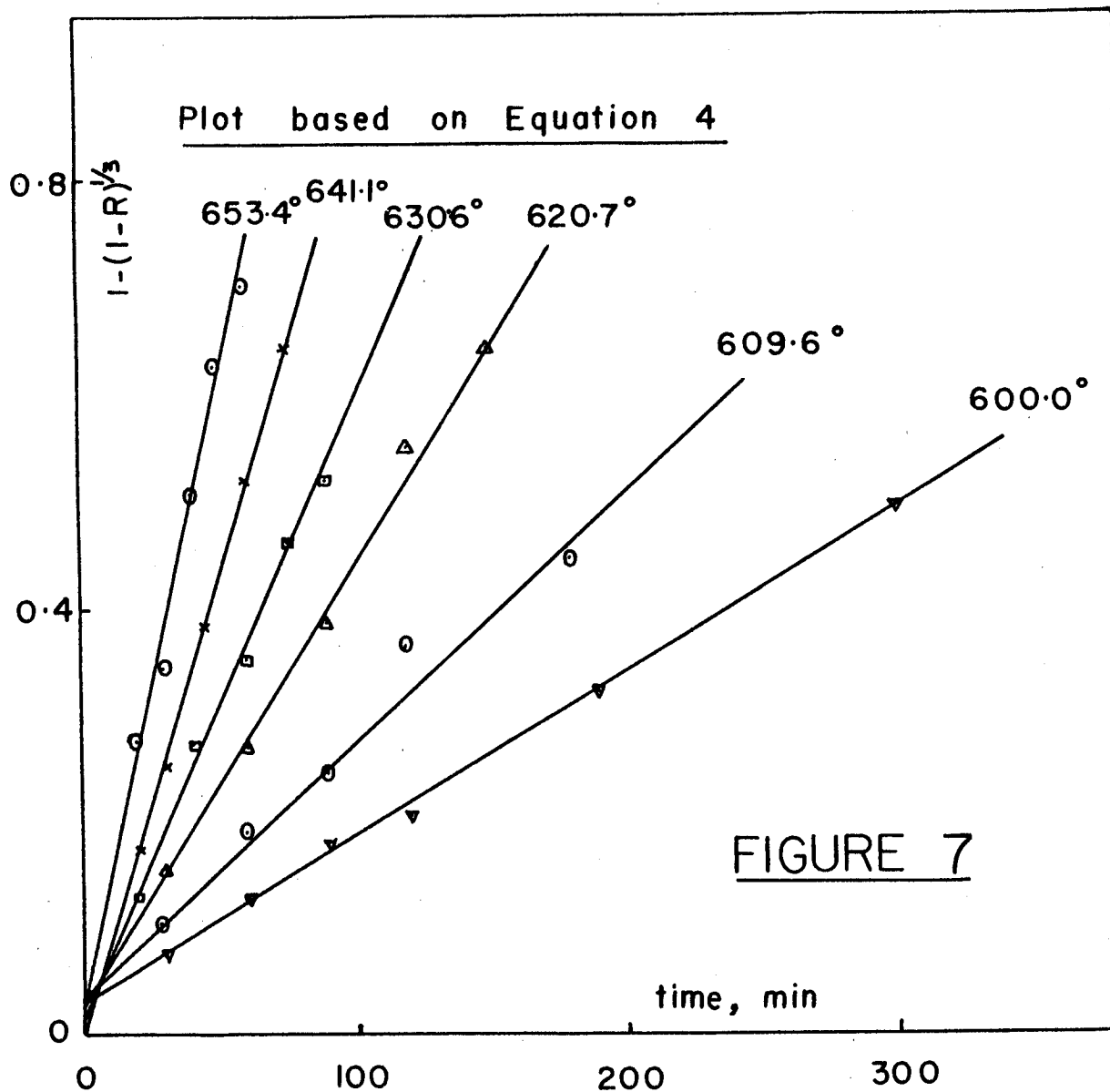


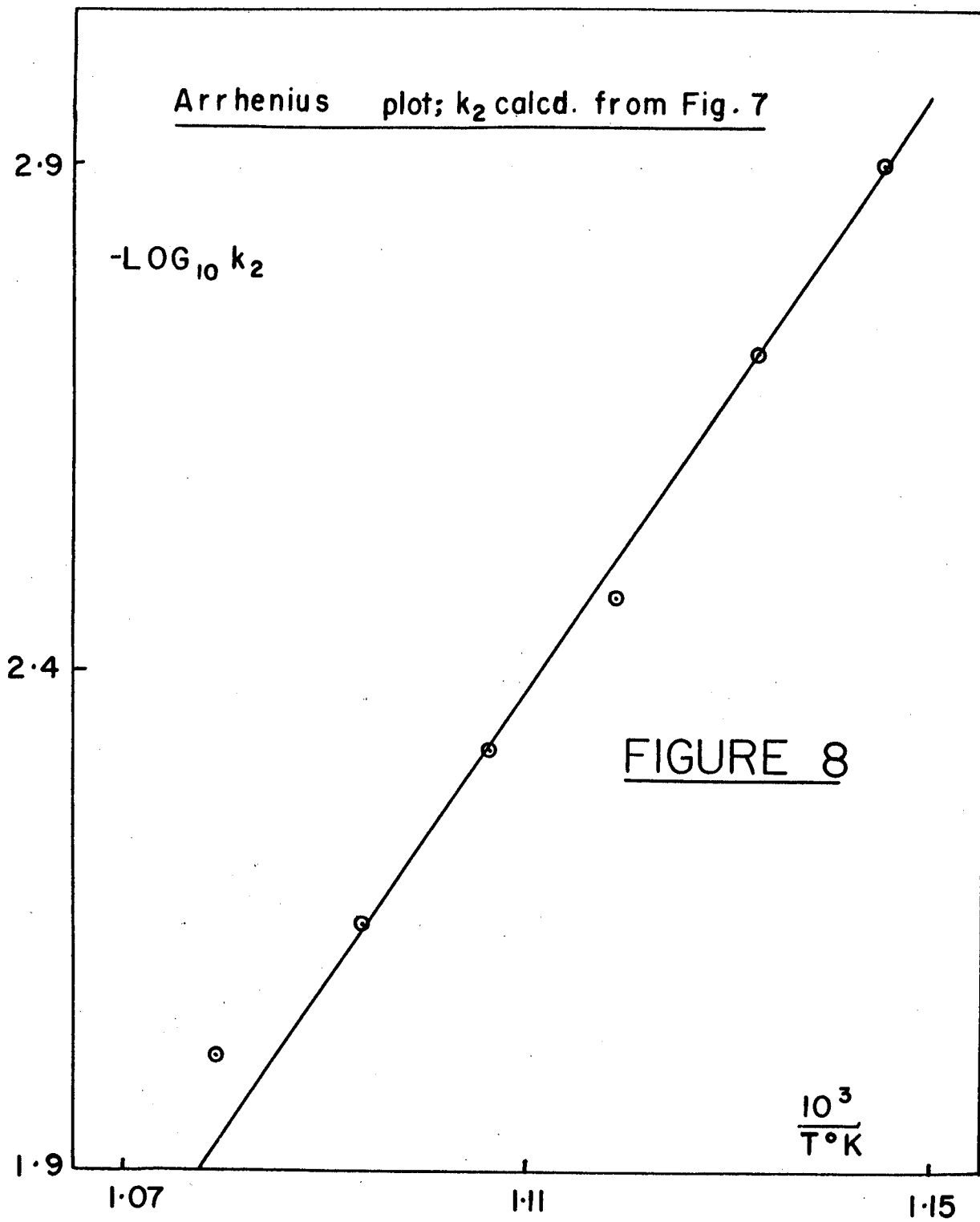


In Equation 4, values of R can be calculated from the weight of the pellet at a known time. The weight of the pellet can be obtained either by direct weighing after a known reaction time, or by computation from the cathetometer readings. In this work, the former method was employed. Plots of  $\left[1 - (1-R)^{1/3}\right]$  against t were constructed and, from the slope of the straight lines drawn through the points, values of  $k_2$  were calculated (see Figure 7). The Arrhenius plot of  $\log_{10} k_2$  against  $\frac{1}{T^{\circ}\text{K}}$  (see Figure 8) was fitted by the method of least squares to give the line:

$$\log_{10} k_2 = 14.0 - \frac{14.63 \times 10^3}{T} \quad (\text{Eq 6})$$

In the calculation of R, a value of 23.0% was taken as the total percentage weight loss in the reaction. The reason for taking this particular figure is discussed later (see page 17).





DISCUSSION

The temperature coefficient of the pyrite decomposition reaction or, as it has been called, the activation energy of the reaction, is the E term of the Arrhenius expression,  $k = Ae^{-E/RT}$ . Values of E were obtained from the slopes of the three Arrhenius plots (Figures 4, 6 and 8) and are shown in Table 3.

TABLE 3  
Temperature Coefficients of the Pyrite  
Decomposition

Method	Slope	E (kcal. mole <sup>-1</sup> )
(a) From diameter - time plots (Fig. 3, 4)	15.18 <sup>±</sup> 1.28	69.5 <sup>±</sup> 5.9
(b) From Equation 3 (Fig. 5, 6)	14.14 <sup>±</sup> 0.73	64.7 <sup>±</sup> 3.3
(b) From Equation 4 (Fig. 7, 8)	14.62 <sup>±</sup> 1.12	66.9 <sup>±</sup> 5.1

The <sup>±</sup> values in the slope and E columns were calculated for 90% confidence limits (15). From these results, it would appear that there is no significant difference in the value of E obtained from the three different plots.

In terms of absolute rate theory, where the rate constant, k<sub>3</sub>, is given by the equation

$$k_3 = \frac{kT}{h} e^{\Delta S/R} e^{-\Delta H/RT} \quad (\text{Eq. 7})$$

the value of E should be equivalent to ΔH. It can be seen from Table 1 that the values of Bog and Rosenqvist (9) and D'Or (5) for the ΔH of the reaction fall within the 90% confidence limits obtained in this work.

Of the two methods used to determine the kinetic parameters of the reaction, method (a), based on direct measurement of the diameter of the unreacted material, appears to be simple to perform and involve no assumptions. The method shows whether the interface is advancing at a linear rate but it also requires a large number of experimental runs. Method (b), based on the work of Mc.Kewan, on the other hand, can be evaluated from far fewer experiments, since the weight can be obtained from the extension of the quartz

spring or some other similar method. However, method (b) does incorporate a number of assumptions, e. g., that the rate is proportional to the interfacial area (Equation 3), and that the stoichiometry of the reaction is known. A complete verification of Equation 3 would require practically the same amount of results as would be used in method (a), but if Equation 4 was found to hold, this would constitute a verification of Equation 3. In this particular reaction, the exact stoichiometry is not known, since the composition of pyrrhotite is a function of temperature; in this work, the value of 23.0% decomposition, which was taken as the end point of the reaction, had to be an approximation. This approximation was based on Figure 4, which shows that the reaction was completed after 75 minutes and corresponded to the 23.0% weight loss. This value of 23.0% would imply the formula  $\text{Fe}_7\text{S}_8$  for the reaction product, pyrrhotite.

### CONCLUSIONS

(a) This study has shown that the temperature coefficient of the decomposition of pyrite, in a dynamic argon atmosphere, is  $69.5 \pm 5.9$ ,  $64.7 \pm 3.3$  and  $66.9 \pm 5.1$  kcal.mole<sup>-1</sup>, when the results are processed in three different ways.

(b) The latter two values, obtained from the equations used by McKewan, show that these equations can be used to represent the decomposition reaction.

(c) It was shown that the interface advances at a linear rate into the pyrite pellet; equations were derived expressing the variation of reaction rate with temperature.

### ACKNOWLEDGEMENT

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## APPENDIX

### Preliminary Investigation of the Nucleated Decomposition of Natural Pyrite Crystals

This study was conducted on small natural pyrite crystals (approx. 0.25-in. cubes) with the aim of observing the formation and growth of nuclei of the decomposition product on the crystal faces. The crystals were heated in a vacuum and observed with a low-powered microscope. No individual nuclei could be observed up to a temperature of 550°C, but, on removal of the crystal from the vacuum enclosure, it was obvious that some decomposition had taken place since the crystal was then black in contrast to its original brass colour. Illumination of the crystal with coloured light also failed to reveal the formation of nuclei on heating.

On close examination, blue-grey areas were observed which appeared at first to increase and then to decrease in size. This effect could possibly be due to interference colours caused by a very thin film of pyrrhotite over the surface of the crystal, the appearance and disappearance of the colours being associated with the varying film thickness.

Other problems encountered using the natural pyrite crystals were: inhomogeneity of the interior of the crystal, presence of impurities, and the variation of weight, size and composition from crystal to crystal. These problems could be eliminated by using polycrystalline, pelletized material, and, as no nuclei had been observed, the aim of the work was thereafter directed towards studying the kinetics of the post-nucleation reaction. It had originally been hoped that it might have been possible to correlate the rates of nucleus formation and growth with the kinetics of the post-nucleation reaction, in a similar way to that found possible by one of the authors (16) for the dehydration of salt hydrates. This preliminary work did, however, imply that the surface of a crystal was quickly covered by a thin film of product and that growth of individual nuclei was unlikely to be the rate-controlling step, but, rather, the gradual movement of the pyrite/pyrrhotite interface into the crystal.