THERMOGRAVIMETRIC AND DISTILLATION STUDIES
ON
MERCURY, ANTIMONY AND ARSENIC SULFIDES

M.I.R.L. Report No. 33

Mineral Industry Research Laboratory
University of Alaska
Fairbanks, Alaska 99701

Joseph W. Town and P. Dharma Rao

December 1975

ABSTRACT

Thermogravimetric studies were made on naturally occurring sulfides of mercury, antimony and arsenic to determine activation energies and Arrhenius rates of reaction in vacuum and in atmospheres of air and nitrogen. Of the three sulfides only antimony showed an appreciable change in rate of reaction for the different test conditions. Distillation results on three flotation concentrates from Alaska mining operations showed that cinnabar (mercury sulfide) could be distilled in a closed system, with over 99 percent recovery of the mercury as metal when the sulfur was reacted with iron. Over 98 percent mercury recovery was obtained from a cinnabar-stibnite (antimony sulfide) concentrate, with less than 1 percent of the antimony distilled from the furnace charge. Cinnabar-realgar-orpiment (arsenic sulfides) could not be separated by distillation and large quantities of soot (condenser residue) formed with the metallic mercury in the condenser.

ACKNOWLEDGEMENTS

The senior author wishes to express his appreciation to Dr. Donald J. Cook, Department of Mineral Engineering, for his technical assistance and advice as chairman of his thesis advisory committee for the Master of Science Degree.

Thanks are also extended to those individuals responsible for making the samples and equipment available: Bob Lyman for the White Mountain concentrate; Al Hubbard for the Cinnabar Creek concentrate; Haruo Kato of the U.S. Bureau of Mines for the Red Devil cinnabar and stibnite concentrates and for the loan of the tube furnace and controller; and Dr. G. D. Sharma, Associate Professor of Marine Science for the use of the thermogravimetric (TGA) equipment.

Thanks is also extended to Dr. E. N. Wolff, Associate Director, Mineral Industry Research Laboratory, for his help in making the graduate assistantship available for conducting this research investigation and to Jim Russell of the U.S. Bureau of Mines for assistance in the mathematical evaluation of the thermogravimetric studies.

CONTENTS

Page

ABSTRACT ii

ACKNOWLEDGEMENTS iii

ILLUSTRATIONS v

TABLES vi

SUMMARY viii

INTRODUCTION 1

  Previous Studies 2

  Scope of Study 3

ANALYTICAL METHODS AND METERIALS 4

  Methods of Analysis 4

  Test Materials 5

THERMOGRAVIMETRIC STUDIES 8

  TGA Testing Procedure 9

  Mercury Studies 10

  Antimony Studies 22

  Arsenic Studies 31

  Comparison of Arrhenius Data in Air and Nitrogen 31

DISTILLATION STUDIES 40

  Testing Procedure 40

  Mercury Concentrate Tests 43

  Mercury - Antimony Concentrate Tests 47

  Mercury - Arsenic Concentrate Tests 50

DISCUSSION 53

APPENDIX A - Analytical Procedure 54

APPENDIX B - Thermogravimetric Data 58

APPENDIX C - Computer Programs 68

APPENDIX D - Distillation Data 83

APPENDIX E - Statistical Evaluation 92

BIBLIOGRAPHY 94

ILLUSTRATIONS

Figure		Page
1.	Photographic View of TGA Unit	11
2.	Plot of TGA Analysis of Calcium Carbonate in Air	12
3.	Reproduction of TGA Chart for Mercury Sulfide in Air	13
4.	Reproduction of TGA Chart for Mercury Sulfide in Air	14
5.	Plot of TGA Analysis of Mercury Sulfide in Air	16
6.	Plot of TGA Analysis of Mercury Sulfide in Vacuum	18
7.	Plot of TGA Analysis of Mercury Sulfide in Vacuum	19
8.	Plot of TGA Analysis of Mercury Sulfide in Nitrogen	20
9.	Arrhenius Plot of Reaction Rates for Mercury Samples	21
10.	Reproduction of TGA Chart for Antimony Sulfide in Air	23
11.	Reproduction of TGA Chart for Antimony Sulfide in Nitrogen	25
12.	Plot of TGA Analysis of Antimony Sulfide in Air	26
13.	Plot of TGA Analysis of Antimony Sulfide in Vacuum	27
14.	Plot of TGA Analysis of Antimony Sulfide in Nitrogen	28
15.	Plot of TGA Analysis of Antimony Sulfide in Nitrogen	29
16.	Arrhenius Plot of Reaction Rates for Antimony Samples	30
17.	Reproduction of TGA Chart for Arsenic Sulfide in Nitrogen	32
18.	Plot of TGA Analysis of Arsenic Sulfide in Air	33
19.	Plot of TGA Analysis of Arsenic Sulfide in Nitrogen	34
20.	Plot of TGA Analysis of Arsenic Trioxide in Air	35
21	Arrhenius Plot of Reaction Rates for Arsenic Samples	36
22.	Arrhenius Plot of Reaction Rates for Three Sulfides in Air	37
23.	Arrhenius Plot of Reaction Rates for Three Sulfides in Nitrogen	38
24.	Pictorial and Photographic Views of Distillation Unit	41
25.	Effect of Significant Variables on Metallic Mercury Recovery	44
26.	Metallic Mercury Recovered from White Mountain Concentrates	46
27.	Effect of Four Variables on Metallic Mercury Recovery	48
28.	Metallic Mercury Recovered from Red Devil Concentrate	49
29.	Metallic Mercury Recovered from Cinnabar Creek Concentrate	51
30.	Metallic Mercury Recovered from Samples with Arsenic Sulfide	52

TABLES

Table		Page
1.	Analytical and Purity Evaluation of Test Samples	6
A-1.	Operating Conditions for Model 303 Atomic Absorption Unit	55
B-1.	TGA Data for Calcium Oxalate in Air	59
B-2.	TGA Data for Calcium Carbonate in Air	59
B-3.	TGA Data for Mercury Sulfide Conc. in Air	59
B-4.	TGA Data for Mercury Sulfide Conc. in Air	59
B-5.	TGA Data for Mercury Sulfide Conc. in Vacuum	60
B-6.	TGA Data for Mercury Sulfide Conc. in Air	60
B-7.	TGA Data for Mercury Sulfide in Air	60
B-8.	TGA Data for Mercury Sulfide in Air	60
B-9.	TGA Data for Mercury Sulfide in Air	61
B-10.	TGA Data for Mercury Sulfide in Vacuum	61
B-11.	TGA Data for Mercury Sulfide in Air	61
B-12.	TGA Data for Mercury Sulfide Conc. in Air	61
B-13.	TGA Data for Mercury Sulfide Conc. in Air	62
B-14.	TGA Data for Mercury Sulfide Conc. in Vacuum	62
B-15.	TGA Data for Mercury Sulfide Conc. in Nitrogen	62
B-16.	TGA Data for Mercury Sulfide Conc. in Air	62
B-17.	TGA Data for Mercury Sulfide Conc. in Nitrogen	63
B-18.	TGA Data for Antimony Sulfide Conc. in Air	63
B-19.	TGA Data for Antimony Sulfide Conc. in Air	63
B-20.	TGA Data for Antimony Trisulfide in Air	63
B-21.	TGA Data for Antimony Sulfide Conc. in Air	64
B-22.	TGA Data for Antimony Sulfide Conc. in Air	64
B-23.	TGA Data for Antimony Sulfide Conc. in Vacuum	64
B-24.	TGA Data for Antimony Sulfide Conc. in Nitrogen	65
B-25.	TGA Data for Arsenic Sulfide Conc. in Air	65
B-26.	TGA Data for Arsenic Trioxide in Air	66
B-27.	TGA Data for Arsenic Sulfide Conc. in Air	66
B-28.	TGA Data for Arsenic Sulfide Conc. in Vacuum	66
B-29.	TGA Data for Arsenic Sulfide Conc. in Nitrogen	66

TABLES (Continued)

Table		Page
B-30.	TGA Data for Arsenic Sulfide Conc. in Nitrogen	67
C-1.	Regression Analysis of TGA Data for Mercury Activation Energies	76
C-2.	Regression Analysis of TGA Data for Antimony and Arsenic Activation Energies	77
D-1.	Effects of Iron, Lime, Time and Temperature on Mercury Recovery (Series I)	84
D-2.	Effects of Iron, Lime, Time and Temperature on Mercury Recovery (Series II)	85
D-3.	Effect of Temperature on Mercury Recovery from White Mountain Concentrate	86
D-4.	Effect of Temperature on Mercury Recovery from White Mountain Concentrate (charge covered with iron)	87
D-5.	Effects of Antimony Sulfide, Iron, Time and Temperature on Mercury Recovery (Series III)	88
D-6.	Effect of Temperature on Mercury Recovery from Red Devil Concentrate	89
D-7.	Effect of Temperature on Mercury Recovery from Red Devil Concentrate (charge covered with iron)	90
D-8.	Effect of Temperature on Two Samples Containing Arsenic (Cinnabar Creek Concentrate and a Laboratory Prepared Sample)	91
E-1.	Method Used in Determining Mean Levels for Statistically Planned Test Series (Series II Data)	93

SUMMARY

Thermogravimetric (TGA) studies were made to determine the activation energies and rates of reaction for pure mineral fractions of cinnabar (mercury sulfide), stibnite (antimony sulfide) and realgar-orpiment (arsenic sulfides) in vacuum and in atmospheres of air and nitrogen. Activation energies for cinnabar were found to be about 25 Kcal per mole in nitrogen, 30 Kcal per mole in air and 37 Kcal per mole in vacuum, with little shift in the rate of reaction with respect to temperature under the three different atmospheres. Stibnite showed about the same activation energies in air and vacuum (15 to 18 Kcal per mole), while in nitrogen the activation energy required increased to 48 Kcal per mole. For equivalent rate of reaction the temperature required in nitrogen was from 250 to 300 degrees centigrade higher than in air or vacuum. The realgar-orpiment samples showed nearly identical activation energies in vacuum and nitrogen (15 and 16 Kcal per mole, respectively) while the results in air were about 20 Kcal per mole. The rates of reaction for arsenic sulfide with respect to temperature changed very little for the three atmospheric conditions. (A computer program was developed for calculating and plotting the final Arrhenius figures from the original TGA graphic data).

Distillation results on the three Alaskan flotation concentrates showed that for temperatures above 430 to 440 degrees centigrade, one hour was sufficient to allow over 99 percent recovery of the mercury as metal from the White Mountain (Alaska) cinnabar concentrate in the closed distillation unit. To complex the sulfur one equivalent of iron per equivalent mercury sulfide was mixed with the charge and an additional one-half equivalent was spread as a cover over the charge. Results on the cinnabar-stibnite concentrate from Red Devil, Alaska showed that over 98 percent of the mercury could be recovered as metal with less than 1 percent of the stibnite distilling into the condenser under similar conditions to those reported for the White Mountain concentrate. Studies on the Cinnabar Creek (cinnabar-realgar) concentrate and on a laboratory prepared cinnabar-realgar-orpiment sample showed that the arsenic distilled over with the mercury, forming considerable soot (arsenic oxides), reducing metallic mercury recovery to about 70 percent on the concentrate and 40 percent on the prepared sample.

INTRODUCTION

The need in Alaska for an improved retorting method for mercury was considered of sufficient importance to the state to justify a graduate research program, since the overall processing of mercury has changed very little in the past 500 years. Factors to be considered during the study were the requirements to reduce sulfur dioxide pollution, improve the recovery of mercury from complex products (cinnabar-stibnite), simplify the retorting process for the small mine operator and demonstrate a method of processing that would reduce health hazards from mercury poisoning.

A review of the history of mercury mining in Alaska shows that it has been one of intermittent operation, with the mines opening and closing as the price of mercury rose and fell. All operations have been of relatively small scale as compared with current mining operations and usually under financed. Mining is further inhibited by poor operating conditions in the Kuskokwim area, the main mercury producing region in Alaska, which include severe winter weather and lack of transportation, communication and supply facilities in the area. The discontinuous and erratic nature of the ore shoots thus far found has resulted in increased exploration, development and mining costs, thus limiting the operations to relatively small scale ones which has prevented the development of any large proven ore reserves or continuous operations.

To improve the Alaska mercury mining situation a more versatile treatment method must be used, one which will reduce man-power requirements per ton of ore treated and require less skilled labor. This can be done by treating lower grade ores by flotation to produce concentrates for retorting. Fifty tons of ore containing 10 to 20 pounds of mercury per ton can be treated by flotation to recover usually over 95 percent of the mercury in a product weighing less than one ton. This small amount of concentrate can then be treated at the mine or shipped to an area where fuel costs are lower for retorting. Batch type retorts can be used on these high grade concentrates because of the high mercury content per ton.

Estimates of inferred mercury ore reserves for Alaska as discussed by K. Malone[6] take into account past production, the wide spread area in the Kuskokwim region over which mercury mineralization occurs, and the cinnabar float noted by both gold and mercury prospectors. With a favorable mercury price these factors indicate a large inferred reserve for the region and an appreciable future contribution to the nation's mercury needs. Malone further states that no information for estimating measured reserves is available because of the erratic nature of the known lode deposits and the limited amount of development work performed by the current mining operations. This has been caused by the high exploration and development costs in the area and will likely preclude any large scale accumulation of such reserves under the present market conditions.

Previous Studies

A literature search showed that the reaction of powdered iron with cinnabar has been known for over 200 years. The reaction is as follows:

$$HgS + Fe \longrightarrow FeS + Hg.$$

A good summary of the chemistry and general retorting process is given by J. W. Mellor in Volume IV of his works, 'A Comprehensive Treatise on Inorganic Theoretical Chemistry'.[7] Mellor's summary reveals that in every case the reaction, whether with air (O_2), lime (CaO) or iron (Fe) takes place at a temperature that exceeds the boiling point of metallic mercury, so that the condensation of mercury is part of the process. He also quotes on page 955 that, 'according to G. F. Hildebrandt cinnabar is desulphurized when heated with iron, copper, tin, lead, silver, bismuth or antimony; forming a sulfide while mercury (vapor) distills over'. These results indicated that operation of a closed retort for the recovery of metallic mercury would be feasible if all the sulfur were reacted with iron.

Information on the separation of mercury from cinnabar-stibnite ores or condentrates is limited mostly to current research being done in Russia. S. D. Levina states that mercury can be driven off without the antimony sulfide decomposing at 425 to 525 degrees centigrade under 20 to 100 mm (millimeters) partial pressure of mercury in an unlined iron apparatus.[5] V. K. Mikhailov in a later article reports that the activation energy for mercury sulfide in an oxidizing medium was 25.8 Kcal per mole and in neutral (vacuum) 25.9 Kcal per mole.[9] He states that the distillation of mercury from ore is limited by the diffusion of the mercury vapor through the quartz gangue. A report by S. M. Mel'nikov suggests that at low pressures the retorting temperature could be considerably reduced. For example at 0.1 mm mercury partial pressure the temperature could be dropped by 250 to 300 degrees centigrade, and at pressures around 100 mm mercury the temperature could be reduced by 90 to 100 degrees.[8] A figure in this report also shows that to obtain the same vapor pressure antimony sulfide must be heated to nearly 500 degrees centigrade higher than mercury sulfide. The rate of oxidation of antimony sulfide, however, is reported to start at a lower temperature than mercury sulfide, be equal at about 65 percent oxidation and then proceed slightly slower.

Information on the behavior of stibnite, published by H. O. Hofman and J. B. Blatchford in 1917, shows clearly the problems encountered in the treatment of antimony bearing materials.[4] Stibnite begins to melt at about 550 degrees centigrade and oxidation (in air) starts at about 290-340 degrees centigrade depending on particle size, and kermesite $(Sb_2S_3)_2 \cdot Sb_2O_3$ forms at 517 degrees centigrade. R. F. Lyman reports in U.S. Bureau of Mines Inf. Cir. 8131 by K. Malone that the antimony in the Red Devil, Alaska mercury ore greatly increased the furnacing problems because antimony sulfide passed through the liquid state, and the time and temperature required to release the mercury from the plus 2-mesh material resulted in nearly complete oxidation of the minus 2-mesh stibnite.[6] Lyman further states that the temperature in the four lower hearths of the six-hearth Herreshoff furnace was sufficient to fuse the antimony oxide. Such large quantities (approximately one ton per day) of soot (condenser dust) were formed at Red Devil that no visible mercury was obtained from the condenser launders, and despite considerable treatment the soot residue had to be returned to the furnace for recovery of entrapped mercury.

Scope of Study

The possibility of preventing sulfur dioxide pollution during the production of metallic mercury by the distillation of mercury sulfide is of sufficient importance to Alaska to warrant consideration as one of the two objectives of this research. The second objective was the possibility of separating cinnabar from stibnite or realgar-orpiment by preventing the oxidation of the latter two sulfides during distillation of mercury from the mercury sulfide. This would prevent the formation of large amounts of soot, reduce the total air pollution and improve the recovery of metallic mercury.

It seemed appropriate with the limited information on the decomposition of cinnabar, stibnite and realgar-orpiment to divide the work into two phases; the first being a more theoretical approach to the rates of decomposition of the three sulfides by TGA (thermogravimetric analysis) methods and the second phase, the decomposition of the three sulfides in a small atmosphere-controlled distillation unit to confirm the TGA results. The TGA studies were made with essentially pure mineral fractions of the three minerals while the distillation studies were done on three cinnabar flotation concentrates that had been produced by Alaska mining operations.

ANALYTICAL METHODS AND MATERIALS

In initiating any research project the results are only as reliable as the analytical methods and materials used. Considerable time was therefore spent checking three possible methods for mercury analysis, distillation, atomic absorption and x-ray fluorescence, to determine which method would yield the best accuracy and most reproducible results. In considering the methods available, two additional criteria of importance were considered: 1) the time required to do the analysis and, 2) the possibility of doing antimony and arsenic analyses on the same aliquot from which the mercury analysis was made.

The flotation concentrates used in this study were dried at low temperature (100 degrees centigrade), mixed, split by riffling into approximately 500-gram samples and stored in plastic bags.

Methods of Analysis

Since the mercury analysis was of major concern the initial studies were made to determine the accuracy and reproducibility on samples of varying mercury content. Of the three methods tested atomic absorption yielded the best accuracy, on an average within 3.38 percent of the correct value on prepared samples of known mercury content. Mercury levels on the twelve prepared samples ranged from 0.05 to 60 percent mercury. The atomic absorption method showed very high accuracy on samples of less than 0.1 percent mercury. Accuracy by the distillation method averaged 7.93 percent of the true value, usually on the low side. The effect of particle size on mercury content could not be resolved for x-ray fluorescence; therefore the method was dropped from consideration. In determining the reproducibility of the two methods, the twelve prepared samples, plus four flotation concentrates and two ore samples were used. Results showed that the distillation method gave the best reproducibility, 6.22 percent variation. The reproducibility of the atomic absorption results were very nearly the same (6.67 percent).

The above information indicated that the atomic absorption method would be the most satisfactory for mercury analysis. By using this method the possibility of doing antimony and arsenic analyses from the same sample aliquot could be considered. Additional literature search indicated that since the antimony and arsenic sulfides of concern were low temperature, non-complex sulfides (stibnite, realgar and orpiment), they could be digested at low temperature (60 degrees centigrade) with the mercury sulfide when the acid addition for the mercury method was reversed and the nitric acid added before the hydrochloric acid. It was also necessary in diluting the antimony and arsenic containing samples to use a 1 percent tartaric - 10 percent nitric acid solution to prevent the precipitation of the two elements during dilution.

The detailed digestion procedure, dilution requirements, equipment set-up, and standard solution concentrations are given in Appendix A. Additional information is also available with the atomic absorption units on the details of individual units.

During the research, metallurgical balances were made on each run and the standard deviations calculated for each test series to determine the reproducibility of the results and to check that no errors were occurring in the results from sample loss, analytical error, or operator technique. Results showed that for a calculated metallurgical balance of 20.0 grams mercury the data had a standard deviation of from 1.12 to 0.35 for sample sizes of from 10 to 16 tests. Thus the reproducibility of a test series, using one standard deviation, was within 5 percent of the mean, an adequate figure for the study.

Two test series were also evaluated for the reproducibility of the antimony metallurgical balance. The calculations showed that on samples analyzing 14.9 and 10.1 percent antimony one standard deviation equaled 0.70 and 0.18, respectively. Results were again adequate for the study. Insufficient arsenic results were obtained at a given concentration to determine the reproducibility; however, the results were definitely inferior to those of mercury and antimony, because of the low wavelength of the analytical arsenic line used.

Test Materials

Three cinnabar flotation concentrates, products of Alaska mining operations, were obtained for testing because they represented distinct ore types and would show the effects of mercury, antimony and arsenic sulfides in the closed-circuit distillation unit. The three cinnabar samples were all finely ground flotation concentrates which had been concentrated for retorting. Results in the upper half of Table 1 show the levels of mercury, antimony and arsenic in each sample. The Red Devil Hg and Sb concentrates were obtained from the U.S. Bureau of Mines in Albany, Oregon, products of research reported in R.I. 6569, a study of the selective flotation of cinnabar from stibnite by J. W. Town and others.[12] For the distillation studies the two Red Devil concentrates were recombined. Bob Lyman supplied White Mountain concentrate from his 1971 flotation production at White Mountain, Alaska. Al Hubbard supplied the low-grade flotation concentrate from Cinnabar Creek, a reject concentrate obtained during start-up of the flotation plant in 1971.

Table 1. Analytical and Purity Evaluation of Test Samples

Sample	Analyses, Percent			X-ray Analyses, Compounds Detected
	Hg	Sb	As	
Red Devil Hg. Conc.	66.4	6.5	<0.01	
Red Devil Sb. Conc.	3.84	42.0	0.79	
White Mountain Conc.	75.3	0.012	<0.01	
Cinnabar Creek Conc.	16.2	0.50	0.90	
TGA Mercury Sulfide Conc.[1]	----[4]	<0.01	<0.01	Cinnabar
TGA Antimony Sulfide Conc.[2]	0.02	----	0.08[5]	Stibnite, with trace of Quartz
TGA Arsenic Sulfide Conc.[3]	0.10	0.28	----	Realgar, Orpiment, with trace of Quartz

[1] White Mountain Conc. ground 5 minutes and cleaned three times by flotation.

[2] Stampede antimony jig-bed ground 10 minutes and cleaned four times by flotation.

[3] Sample of massive arsenic sulfide (Realgar and Orpiment) ground and cleaned by flotation.

[4] Weight Loss by TGA indicated 99.3 percent of the conc. was volatile.

[5] Weight Loss by TGA indicated 97.1 percent of the conc. was volatile.

To obtain results that would be comparable from the TGA and distillation studies, high purity mineral concentrates were considered as more representative than chemically prepared samples for the TGA studies. As shown in the lower part of Table 1, essentially pure mineral samples were obtained by regrinding the concentrates or grinding the massive sulfide and cleaning by flotation. The mercury sulfide concentrate indicated by TGA analysis over 99.3 percent volatile material, with less than 0.01 percent antimony or arsenic. Both the antimony sulfide and arsenic sulfide concentrates showed a trace of quartz by x-ray diffraction after the repeated cleaning by flotation, but both were considered satisfactory for TGA use.

THERMOGRAVIMETRIC STUDIES

To obtain information on the decomposition rates of the three sulfides at corresponding temperatures and in different atmospheric environments the TGA method is considered the most applicable. No literature references were found for the decomposition of cinnabar, stibnite, or realgar-orpiment mineral concentrates by thermogravimetric methods. Considerable information and debate is presented in the literature on which is the most appropriate mathematical method for evaluating TGA data.[10,11,1] Personal correspondence with Jim Russell of the U.S. Bureau of Mines resulted in the selection of the following method, which is based on the works of Coats and Redfern.[1]

In a reaction that can be expressed as:

$$aA_{(s)} \longrightarrow bB_{(s)} + cC_{(g)}$$

or

$$aA_{(s)} \longrightarrow bB_{(g)} + cC_{(g)}$$

the rate of disappearance of A can be expressed as:

$$da/dt = k(1-a)^n$$

where a equals the fraction of A decomposed at time t, n equals the order of reaction, and k the rate constant given by the expression:

$$k = A \exp(-E/RT)$$

where A equals a frequency factor, R the gas constant, T the temperature in degrees Kelvin, and E the activation energy of the reaction in Kcal per mole. The equation can then be written as:

$$da/dt = A\,(1-a)^n \exp(-E/RT)$$

or rewritten as follows for solution by regression analysis:

$$\ln(da/dt) = \ln A + n \ln(1-a) + (-E/RT)$$

To obtain da/dt (the differential weight loss with respect to time) from the TGA graphic data a computer program written by M. Noofin of Union Carbide Corp., which used a five point approximation, was modified to calculate da/dt, tabulate additional information, and punch the computer cards for the subsequent calculations.[13] These data (computer punched cards) were then analyzed by linear regression analysis to obtain the corrected differential weight loss and the line of best fit. The regression analysis used was 'BMDO2R' published in 'The Biomedical Computer Programs' by the University of California.[3] A plot program for the IBM-1620 computer-plotter was written for plotting the measured differential weight loss, corrected differential weight loss and the line of best fit, all with respect to reciprocal temperature (degrees Kelvin). Reference is made to Appendix C for a listing of the three programs, detailed instructions on their use, data preparation and data printout. These programs have been written so that a wide range of TGA data can be used.

TGA Testing Procedure

A brief description of the operating procedure is given below and the tabulated data for each TGA run listed in Tables B-1 to B-30 of Appendix B. Close adherence to the operating manual is necessary in conducting tests with the TGA unit to ensure that consistent results are obtained.

On start up the chart recorder and furnace programer were turned on for a 10-minute warmup, with the furnace set at 200 degrees centigrade, while the hangdown tube was being removed for cleaning and a new sample pan placed on the balance hangdown wire.

The tube assembly for flowing gas operation was used. This consists of a concentric flow tube hung inside the hangdown tube to allow gas flow downward through the flow tube and back upward between the two tubes. On heating from room temperature to 600 degrees centigrade the increased gas flow resulting from gas expansion was found to cause a weighing error of about 0.08 mg when the flow rate equaled 0.06 liters per minute. This was considered excessive for the small samples used. When the flow rate was reduced to 0.02 liters per minute the weighing error was less than 0.02 mg for the 600 degree centigrade temperature change. This was considered within an acceptable range.

A zero check was made on the thermocouple in the hangdown tube at least once a week with an ice bath to check the zero degree calibration of the recorder. The hangdown tube was then repositioned and the electrobalance zero adjusted with a 0.02 liter per minute flow rate. The recorder and balance were calibrated for a given weight range, with rezeroing of the balance and recalibration of the recorder repeated until the recorder pen remained at zero without readjustment. Removal of the hangdown tube was then required so that an approximated amount of material could be loaded on the balance pan. The hangdown tube was then reconnected and the sample weight determined in a flowing gas stream. The preheated furnace was slowly raised into position and the hangdown assembly allowed to come to temperature. Just before the furnace was raised the chart drive was turned on to observe any changes in sample weight as the hangdown tube preheated. When the temperature recording pen indicated that the furnace was at approximately 200 degrees centigrade, the temperature programer was activated for the desired heating rate. Weight and temperature recordings were observed, with the mass dial and temperature suppression adjusted to keep both chart pens on scale. When a constant weight was displayed by the weight recording pen or when a temperature of about 900 degrees centigrade was recorded, the run was terminated. Figure 1 shows the TGA unit (recorder, temperature programer, balance electronics, electrobalance, and furnace) used, with the furnace in the down position.

To ensure that the TGA unit was operating satisfactorily after calibration two runs were made, one with calcium oxalate and the other with calcium carbonate (marbleized $CaC0_3$), for comparing the results with those reported by other investigators. Tabulated results are shown in Table C-1 of Appendix C and the plot of the TGA analysis of calcium carbonate shown in Figure 2. Results in Figure 2 show that the line of best fit approximates the corrected weight loss data points very closely, resulting in an activation energy (slope) equaling 60.5 Kcal per mole. Sharp and Wentworth[11] report an activation energy for calcium carbonate (powder) of 43 to 47 Kcal per mole, but do not state whether their sample was marble or chemically prepared. A comparison of the 54.9 Kcal per mole activation energy obtained from the decomposition of calcium carbonate to calcium oxide from a starting material of calcium oxalate, with the 51.7 Kcal per mole reported by Coats and Redfern[1], indicated that the data obtained were indeed very close to those reported by other investigators. As the results showed reasonable agreement with published results, tests were initiated on the sulfide samples.

In Figure 2 the 'x' symbols represent the measured rate (weight loss per unit time (da/dt)) with respect to reciprocal temperature (degrees Kelvin), while the 'o' symbols represent the corrected rate (weight loss per unit time) with respect to reciprocal temperature (degrees Kelvin). The corrected rate represents adjustment of the weight loss data for the reduced amount of material on the balance pan as the reaction proceeds. A line of best fit is then calculated by regression analysis from the corrected rate, the slope of this line representing the activation energy in Kcal per mole.

Mercury Studies

To show the uniformity of the weight loss curves for the mercury sulfide concentrate and the flexibility of the TGA unit, Figures 3 and 4 are shown. Results in Figure 3 show a very

FIGURE I. PHOTOGRAPHIC VIEW OF TGA UNIT

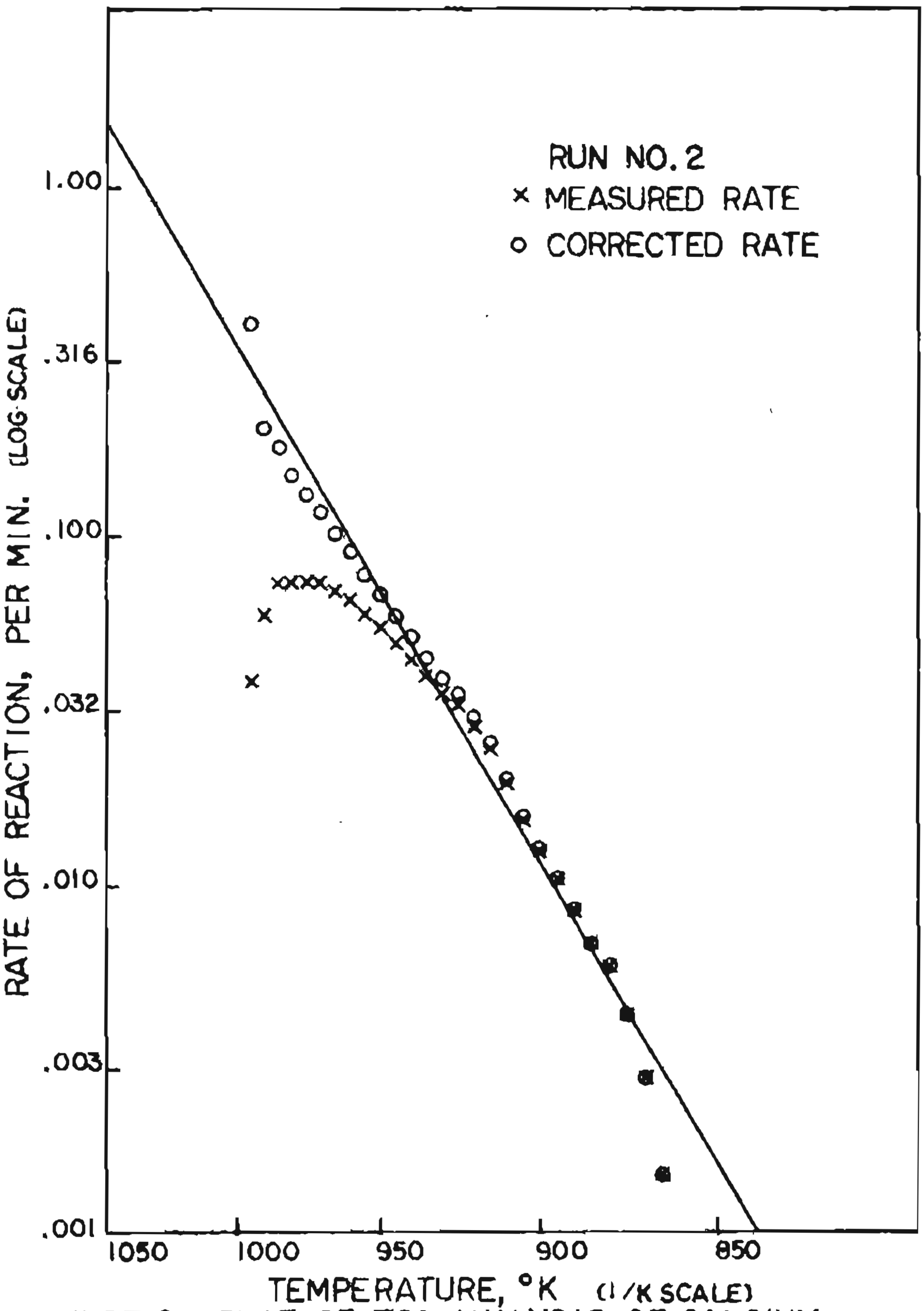

FIGURE 2. PLOT OF TGA ANALYSIS OF CALCIUM CARBONATE IN AIR

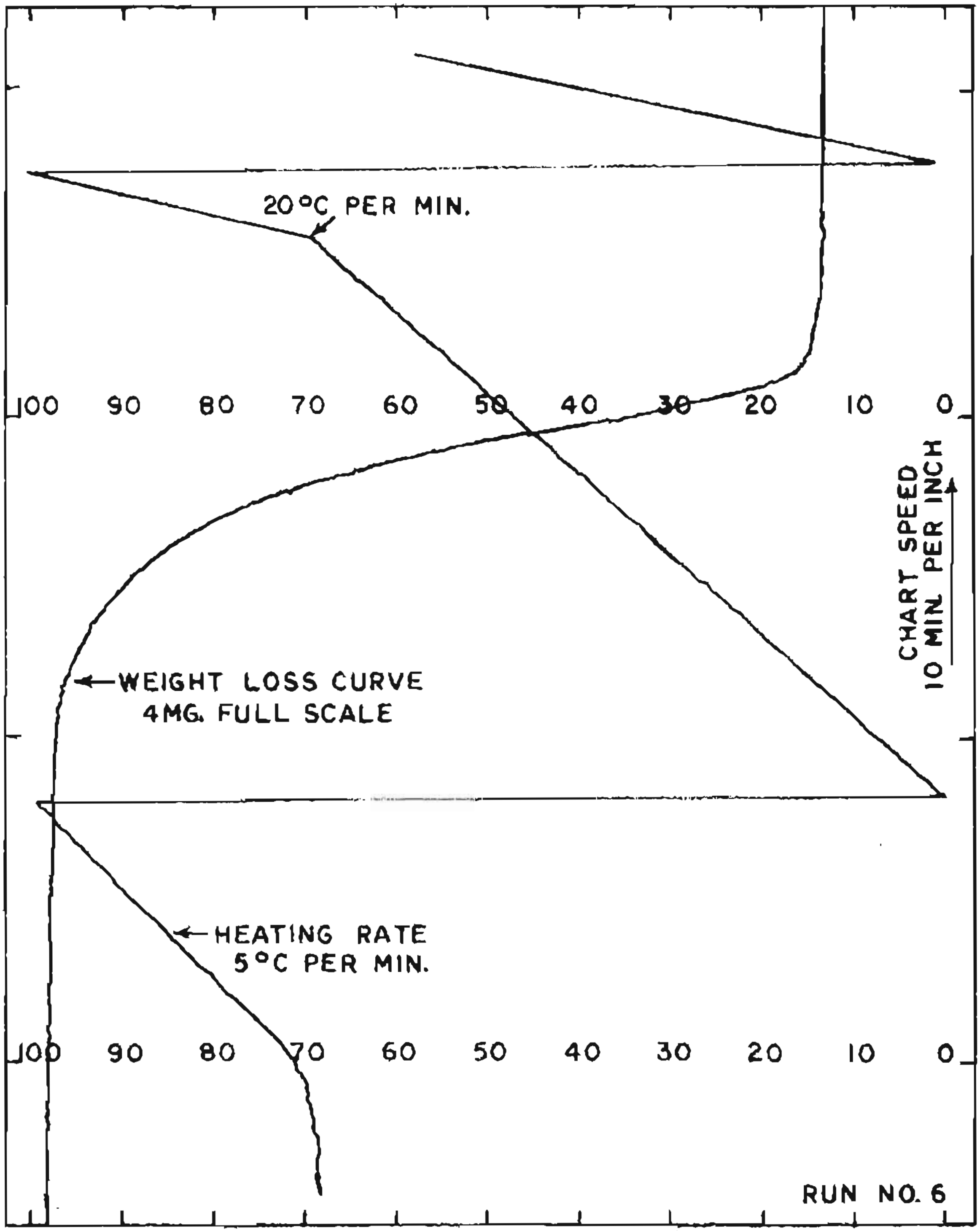

FIGURE 3. REPRODUCTION OF TGA CHART FOR MERCURY SULFIDE IN AIR

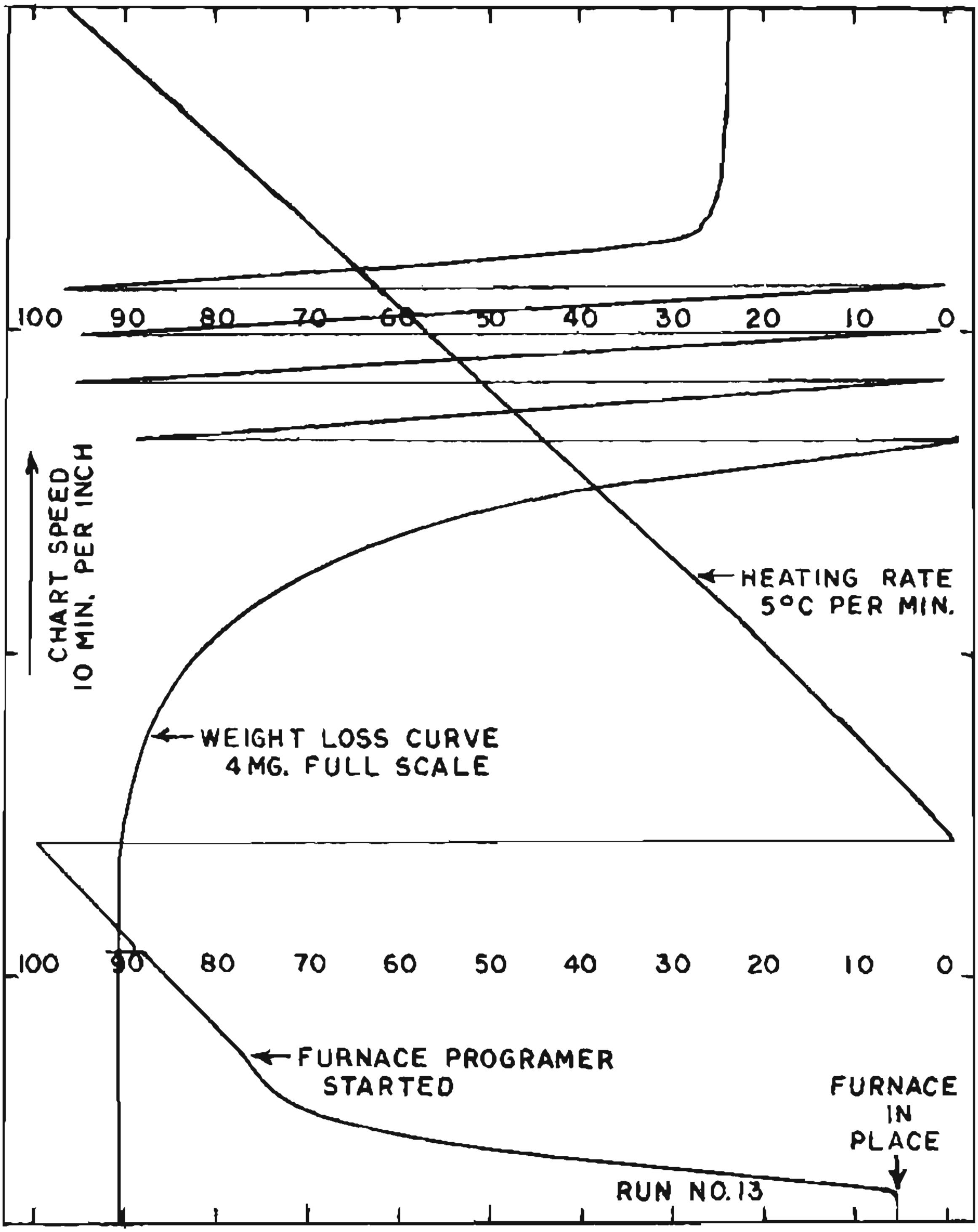

FIGURE 4. REPRODUCTION OF TGA CHART FOR MERCURY SULFIDE IN AIR

uniform weight loss curve for a sample of less than 4 mg of cinnabar indicating that only one reaction is taking place during the run. The heating rate was switched from 5 degrees centigrade per minute to 20 degrees per minute after the sample indicated no additional weight loss to reduce the time to check at higher temperatures. The full-scale step of the temperature recording pen to keep the pen on scale was accomplished by switching a one millivolt suppression into the circuit when the pen reached 100 on the chart. Figure 4 shows the weight loss for a large sample (18,800 mg), which required the adjustment of the mass dial for every 4 mg of weight loss to keep the weight recording pen on scale. Again the uniformity of the weight loss curve should be noted. In evaluating the TGA weight loss curve, points on the curve were read for each one- or five-minute interval. These data points were then tabulated as shown in Appendix B for all runs, and computer cards prepared for computer evaluation and plotting, as stated earlier. Run numbers have been placed on all figures and used in the tables to allow for cross referencing the data.

To evaluate or compare the TGA data for a given sulfide under different atmospheric conditions the data had to be evaluated on an equivalent basis, since starting weights and decomposition temperatures varied for each run. A common method for comparing such data is by Arrhenius plots (rate of reaction versus reciprocal temperature in degrees Kelvin), as mentioned previously. The computer plot of the measured differential rate, corrected differential rate, and the regression analysis line of best fit were plotted to determine if the corrected rate was linear and if the line of best fit was representative of the corrected rate data points. The results in Figure 5 show that the mercury sulfide started to decompose, with a rate of reaction of 0.001 per minute (0.1 percent of the sample per minute) at about 547 degrees Kelvin (276 degrees centigrade) and reached a rate of 1 per minute at 730 degrees Kelvin, with the line of best fit following the corrected rate data points very closely.

A comparison of the activation energies of runs 8 and 11 in Table C-1 for chemically pure mercury sulfide, with those of the mercury sulfide concentrate in runs 12 and 13 showed nearly identical results; 29.5, 32.0, 30.1, and 29.9 Kcal per mole, respectively. Air flow was 0.02 liters per minute. The initial runs listed in Table C-1 show higher activation energies, because of the increased weight loss indicated by the air flow rate of 0.06 liters per minute. It should be noted that the high purity mercury sulfide mineral concentrate showed nearly identical results to those of the chemically pure precipitated sulfide.

Tests were conducted in vacuum and in an inert atmosphere (nitrogen) to determine whether the rate of reaction for each had increased or decreased when compared to the rate

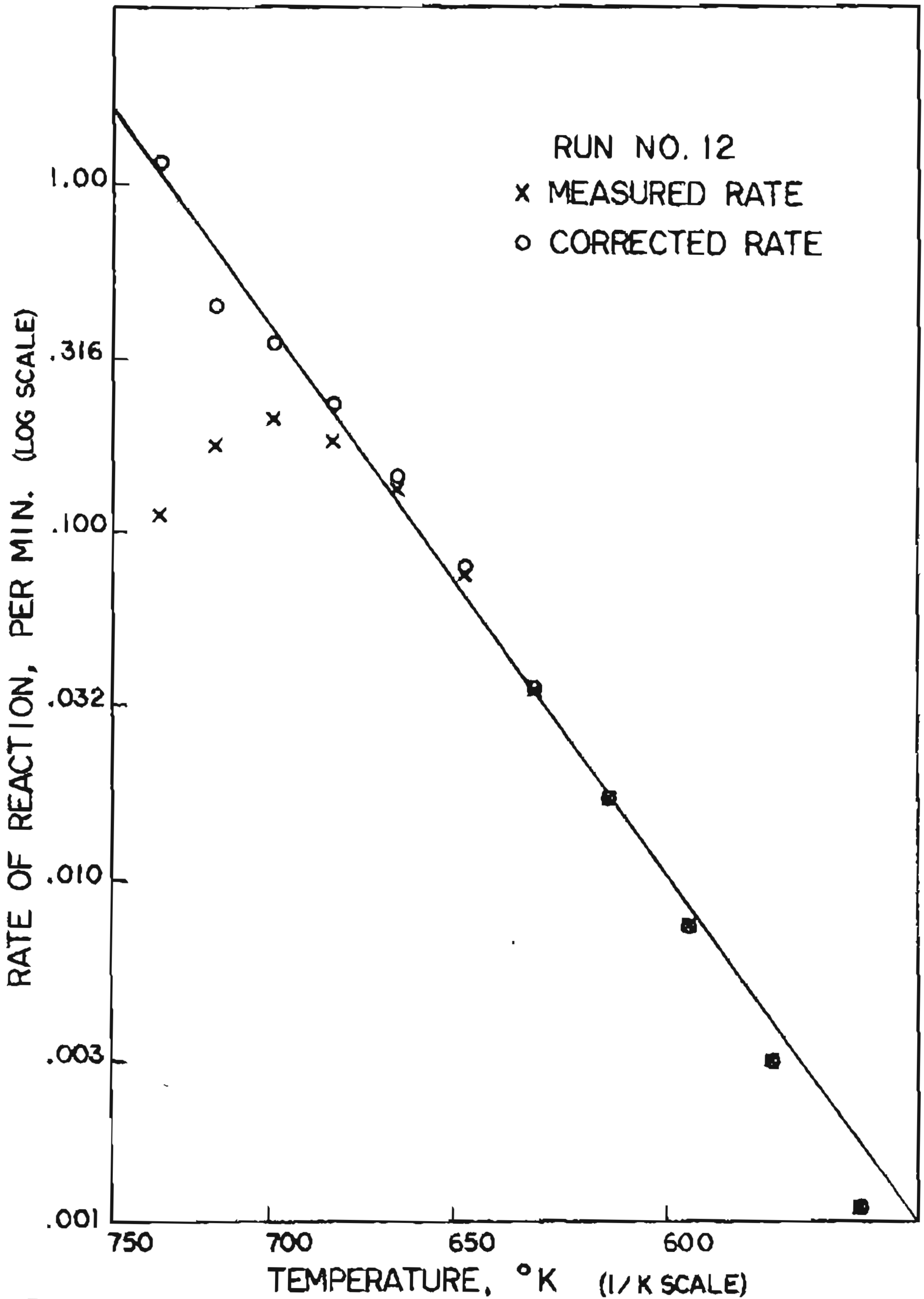

FIGURE 5. PLOT OF TGA ANALYSIS OF MERCURY SULFIDE IN AIR

in air. Figure 6 shows for the mercury sulfide concentrate in vacuum that the line of best fit follows the corrected data very closely, except for a slight rise between 0.010 and 0.032 per minute. In Figure 7 where chemically pure mercury sulfide was treated, no deviation between the line of best fit and corrected data points was noted. It was proved by later results that this slight rise in Figure 6 as compared to Figure 7 was a result of the greater particle size range in the mineral concentrates.

The run in nitrogen, shown in Figure 8, resulted in a lower activation energy, 25 Kcal per mole, indicating that the rate was more temperature dependent. A very good fit of the corrected data was obtained by regression analysis. The slight rise in the corrected data points is still present, only at a slightly higher temperature. The line of best fit could have been improved by dropping two starting data points. This lack of fit will be shown in clearer fashion later on an antimony run. When the very low rates at the start of decomposition are used, the slope of the line is reduced, thus showing a poor fit with the corrected data points.

To compare the data on mercury sulfide, having verified the calculations with the preceding four figures, the rates of reaction for the three atmospheric test conditions were plotted versus reciprocal temperature (Arrhenius plot) in Figure 9. Results reveal that little temperature spread is obtained at the very low rates of reaction (0.001 per minute), while at the high rates (1.00 per minute) the temperature required in an inert atmosphere nitrogen is about 50 degrees centigrade higher than in air, while in vacuum the temperature is reduced about 75 degrees centigrade. These results show a smaller temperature effect in vacuum than reported by S. M. Mel'Nikov who found a 90 degree centigrade temperature reduction in vacuum.[8]

In evaluating and comparing the TGA results to those of the small scale distillation unit, a TGA rate of reaction of about 0.10 per minute was used. This rate of reaction can be shown to compare favorably with the time and temperature required to obtain 99 percent distillation of the mercury in the distillation unit. A 0.10 per minute rate can be expressed as 10 percent decomposition (distillation) of the amount remaining per unit time. Using a half-life equation for a first order reaction, the time required to obtain 99 percent decomposition can be calculated as follows:

$$t_{\frac{1}{2}} = (0.693/k)$$

or

$$t_T = (0.693/k) \quad \text{(Number of half-lives);}$$

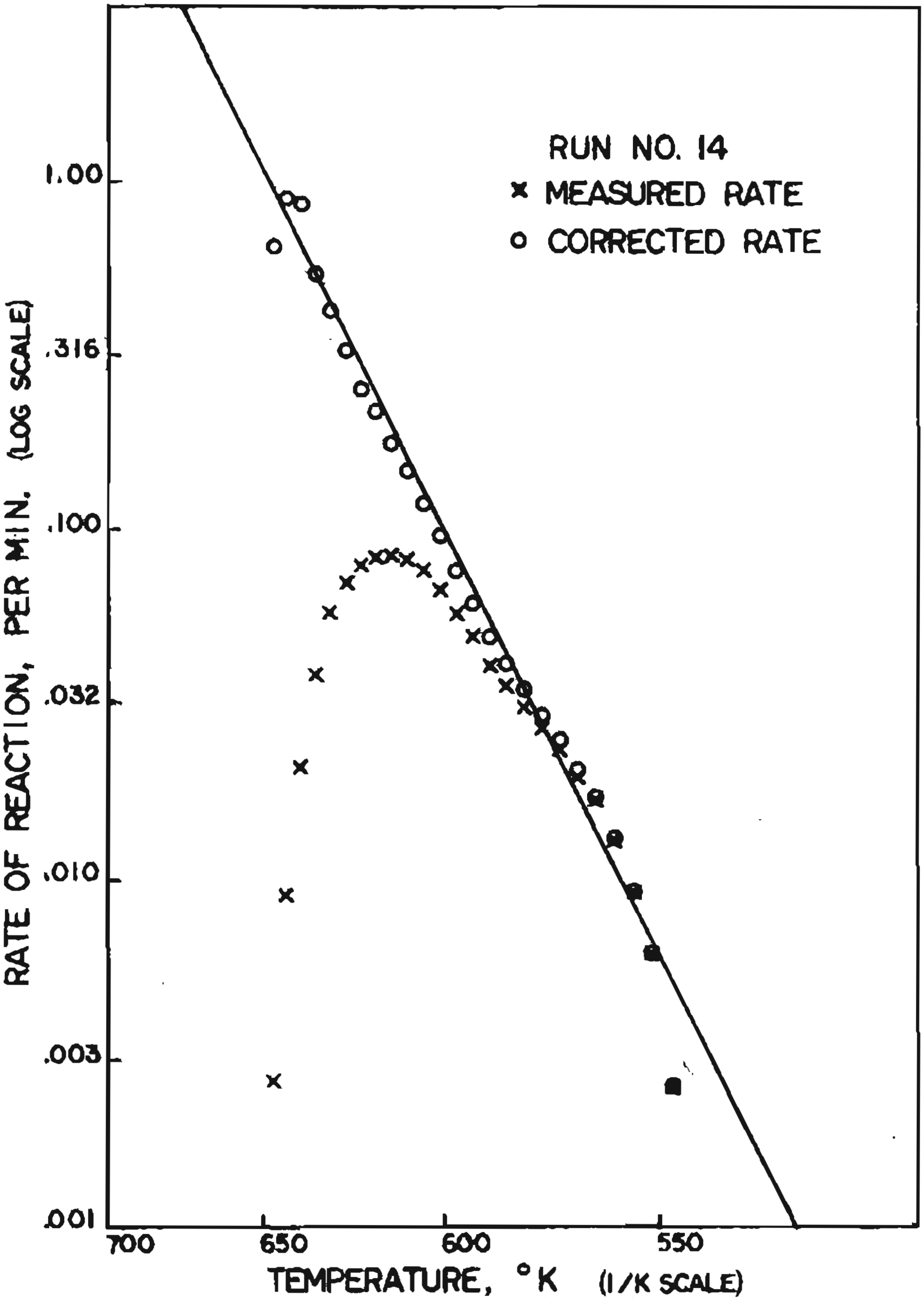

FIGURE 6. PLOT OF TGA ANALYSIS OF MERCURY SULFIDE IN VACUUM

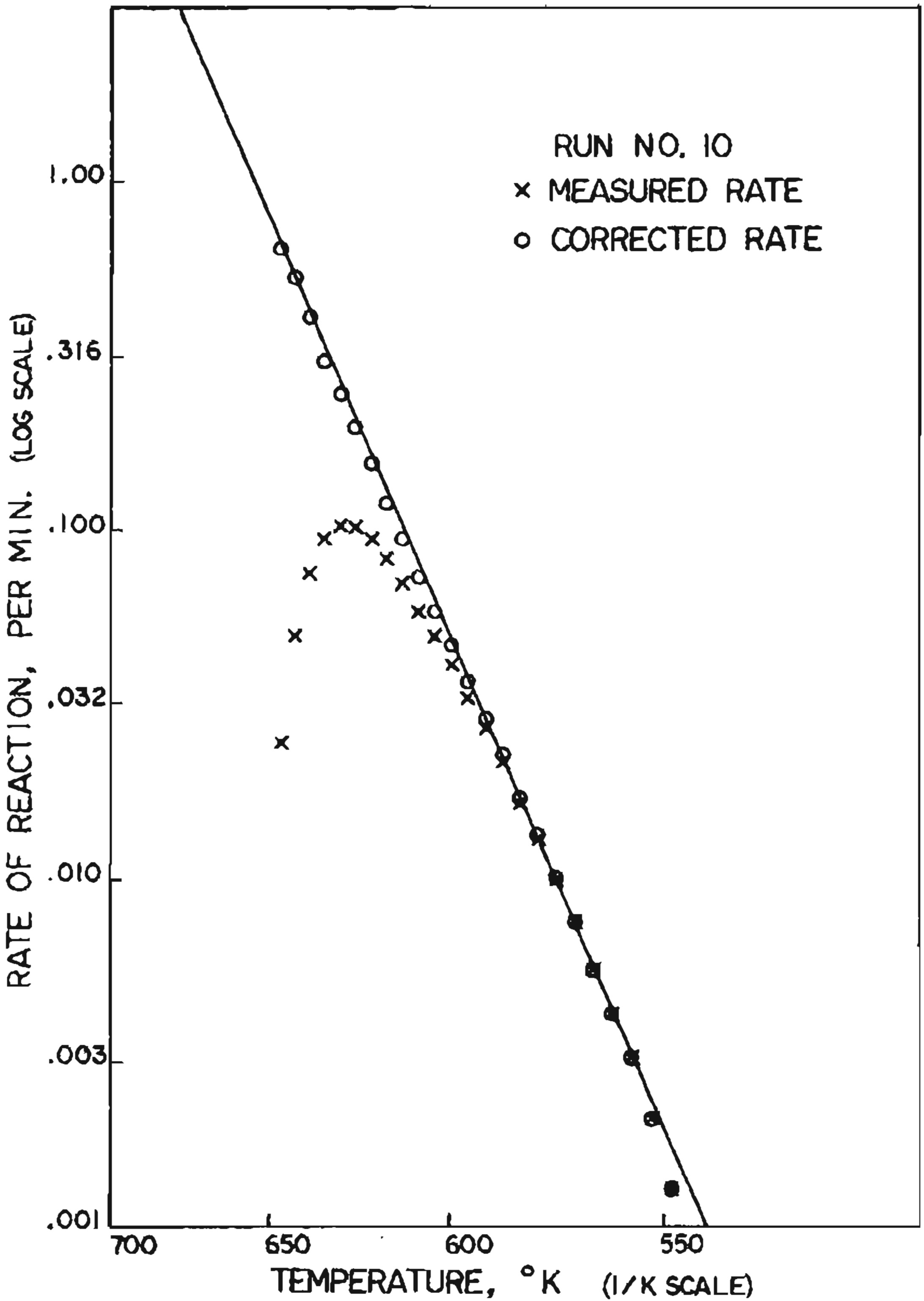

FIGURE 7. PLOT OF TGA ANALYSIS OF MERCURY SULFIDE IN VACUUM

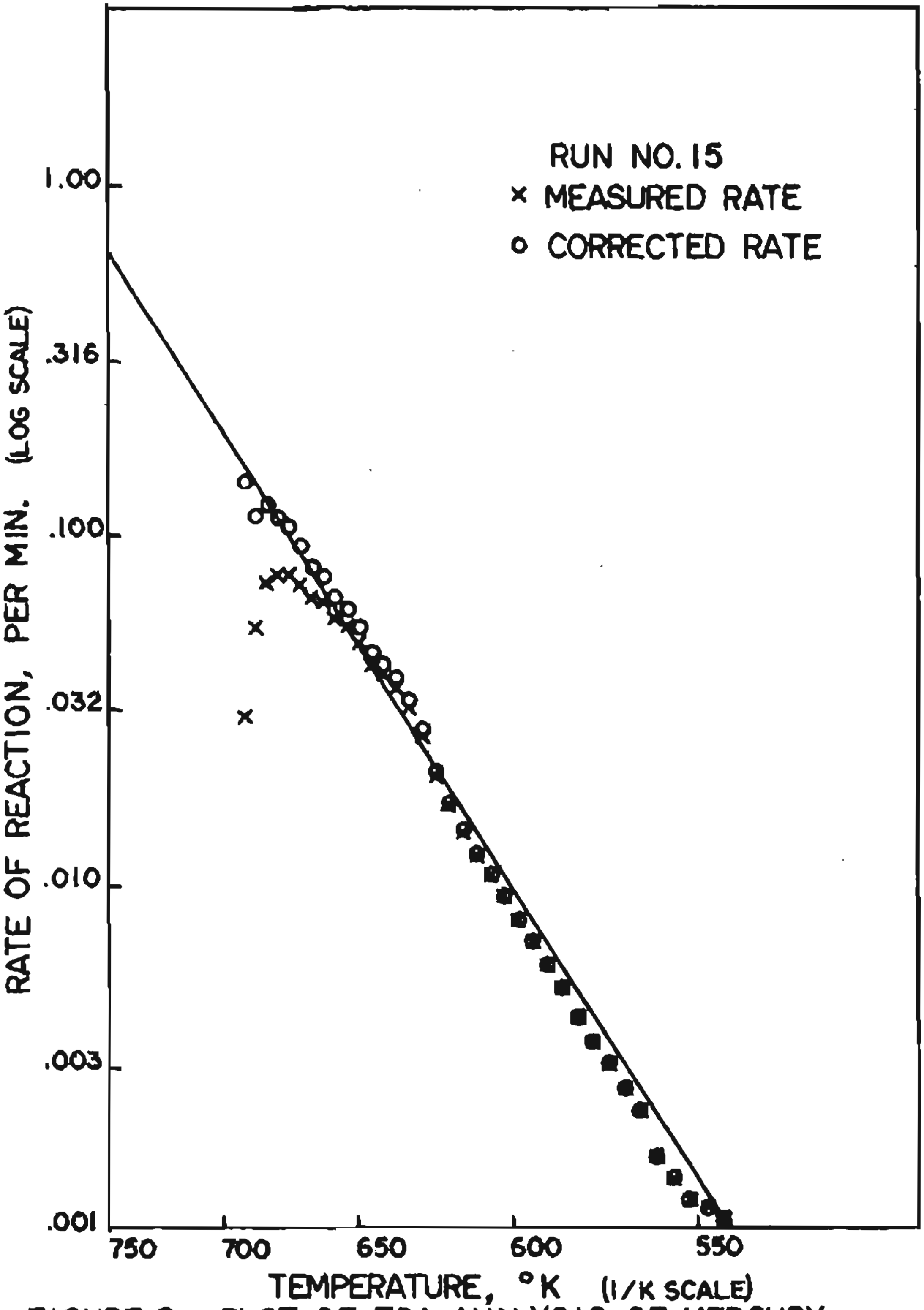

FIGURE 8. PLOT OF TGA ANALYSIS OF MERCURY SULFIDE IN NITROGEN

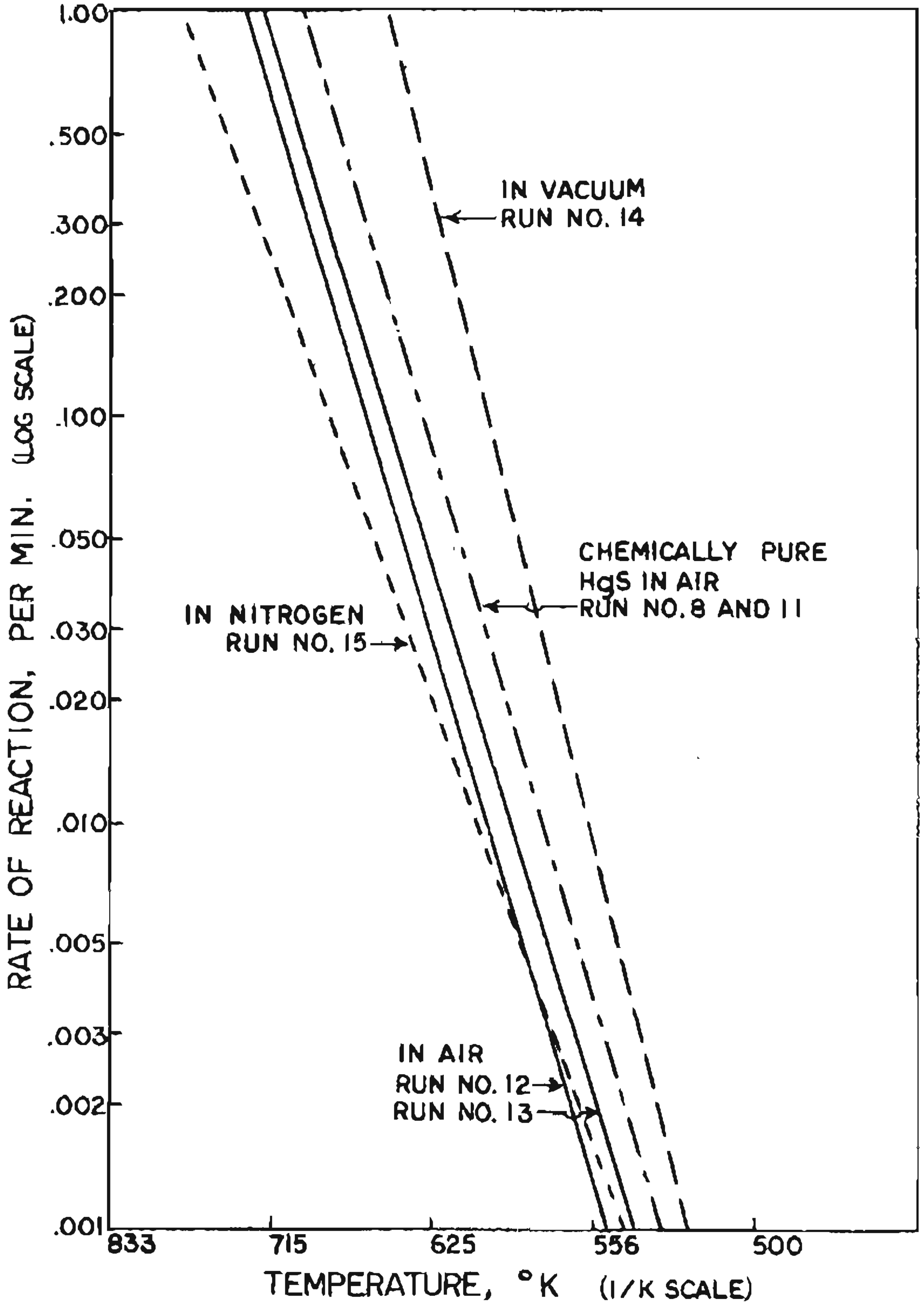

FIGURE 9. ARRHENIUS PLOT OF REACTION RATES FOR MERCURY SAMPLES

where $t_{\frac{1}{2}}$ equals the half-life, t_T the total time and k the rate of reaction. Thus for a rate of 0.10 per minute $t_{\frac{1}{2}}$ equals 6.93 minutes and for seven half-lives (which equals plus 99 percent decomposition) t_T would equal 48.5 minutes. To obtain from Figure 9 a rate of 0.10 per minute in an inert atmosphere a temperature of 680 degrees Kelvin (407 degrees centigrade) would be required (as compared to the 430 degree centigrade temperature used for one hour in the final distillation studies). This represents about a 25 degree centigrade temperature difference between the TGA and distillation results. When the effects of mercury vapor pressure, temperature lag and mass effect of the charge in the distillation unit are considered, the results for the two testing methods can be considered comparable at this rate of reaction. This rate (0.10 per minute) or temperature (680 degrees Kelvin) will be used for all further comparisons in the TGA studies.

Antimony Studies

In conducting the TGA studies on the antimony sulfide concentrate four conditions must be considered: 1) the vaporization of antimony sulfide with respect to temperature, 2) the conversion of Sb_2S_3 to Sb_2O_3 or Sb_2O_4, 3) the vaporization of antimony oxides, and 4) the melting points of the different compounds, which would change the surface area of the sample.

Figure 10 shows a typical weight loss curve for the antimony sulfide concentrate. Points A, B and C on the weight loss curve were used as stopping points on later runs to obtain samples for x-ray diffraction for evaluation of compounds present. X-ray diffraction results showed that at point A both Sb_2S_3 and Sb_2O_3 existed, while at point B only Sb_2O_3 was present. Further heating to point C resulted in continued oxidation of the Sb_2O_3 to Sb_2O_4. If the weight loss for the conversion of Sb_2S_3 to Sb_2O_3 (starting weight to point B) is calculated the observed weight loss is within 5 percent of that calculated from the equation:

$$2Sb_2S_3 + 9\,O_2 \rightarrow 2Sb_2O_3 + 6SO_2 \quad .$$

However, there should have been a weight gain in going from point B to point C as the Sb_2O_3 oxidized to Sb_2O_4. Thus the weight gain during oxidation on this part of the curve was counteracted by the vaporization of Sb_2O_3. Calculations indicate that about 8 percent of the Sb_2O_3 was vaporized. Heating was continued past point C for another 200 degrees centigrade with no additional weight loss, indicating that Sb_2O_4 has a much lower vapor pressure than Sb_2O_3. Additional runs 21 and 22 (Table C-2 of Appendix C) show that when

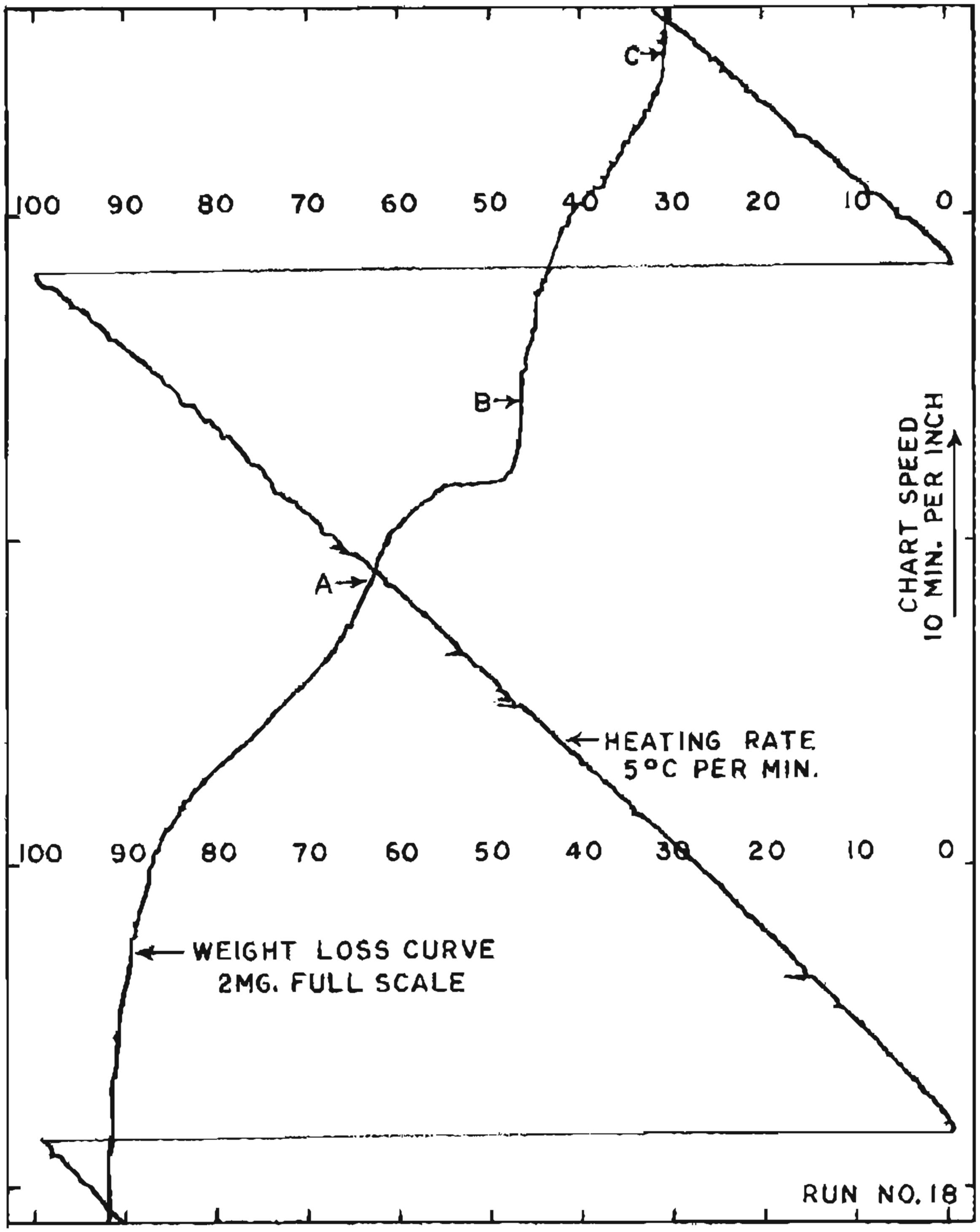

FIGURE 10. REPRODUCTION OF TGA CHART FOR ANTIMONY SULFIDE IN AIR

the sample was reduced to a finer size or additional material was used the time between initial weight loss and point B was shortened, with the very rapid weight loss accounting for more of the total weight loss. Results showed that the conversion of Sb_2S_3 to Sb_2O_3 could be reduced to a temperature range of from 260 to 400 degrees centigrade.

Figure 11 was included to show that in a nitrogen atmosphere the weight loss curve is more uniform since there is no oxidation of the sulfide and that a higher temperature is required before an appreciable weight loss rate is observed. The results do show that the antimony sulfide (stibnite) will vaporize at an appreciable rate above 720 degrees centigrade.

For the antimony sulfide concentrate in an air atmosphere the activation energy (the temperature for a rate of reaction of 0.10 per minute) or the rate of reaction at 407 degrees centigrade (temperature selected for a rate of 0.10 per minute for mercury sulfide) was much more difficult to obtain, because the line of best fit was dependent on more than one reaction. As shown in Figure 12 the corrected rate data points indicate that a number of reactions with different activation energies are present during the decomposition of the antimony sulfide in air. A line of best fit that approximates the activation energy for the total weight loss curve, however, can be obtained by regression analysis. This approximated total reaction activation energy equals 18.3 Kcal per mole (run 22 of Table C-2 Appendix C).

Once the oxygen was removed from the system by vacuum the rate of reaction became one of only vaporization of antimony sulfide, which as shown in Figure 13 is much more uniform. The activation energy calculated for this run was 18.4 Kcal per mole, but at a considerably higher temperature for a corresponding rate of reaction than in air.

Evaluations of the vaporization rate of antimony sulfide in nitrogen are presented in Figures 14 and 15 for run 24 and show a problem that occurred in evaluating the data. Usinf the total weight loss curve in Figure 11 to calculate the rate of reaction the results in Figure 14 show that the initial rate points between about 740 to 820 degrees Kelvin are not representative of the reaction. By dropping the data between point A and point B in Figure 11 and re-evaluating the data as shown in Figure 15 the line of best fit more nearly represents the corrected rate data points over the major part of the curve. The correct activation energy for the vaporization of antimony sulfide equaled 47.9 Kcal per mole, whereas the incorrect value (Figure 14) was 22.2 Kcal per mole.

The rates for the two evaluations in nitrogen are also shown in Figure 16 with those for air and vacuum. A comparison of the lines of slope shows that the difference is not as great as Indicated from Figures 14 and 15. The shift in temperature at the rate of 0.10 per minute shows

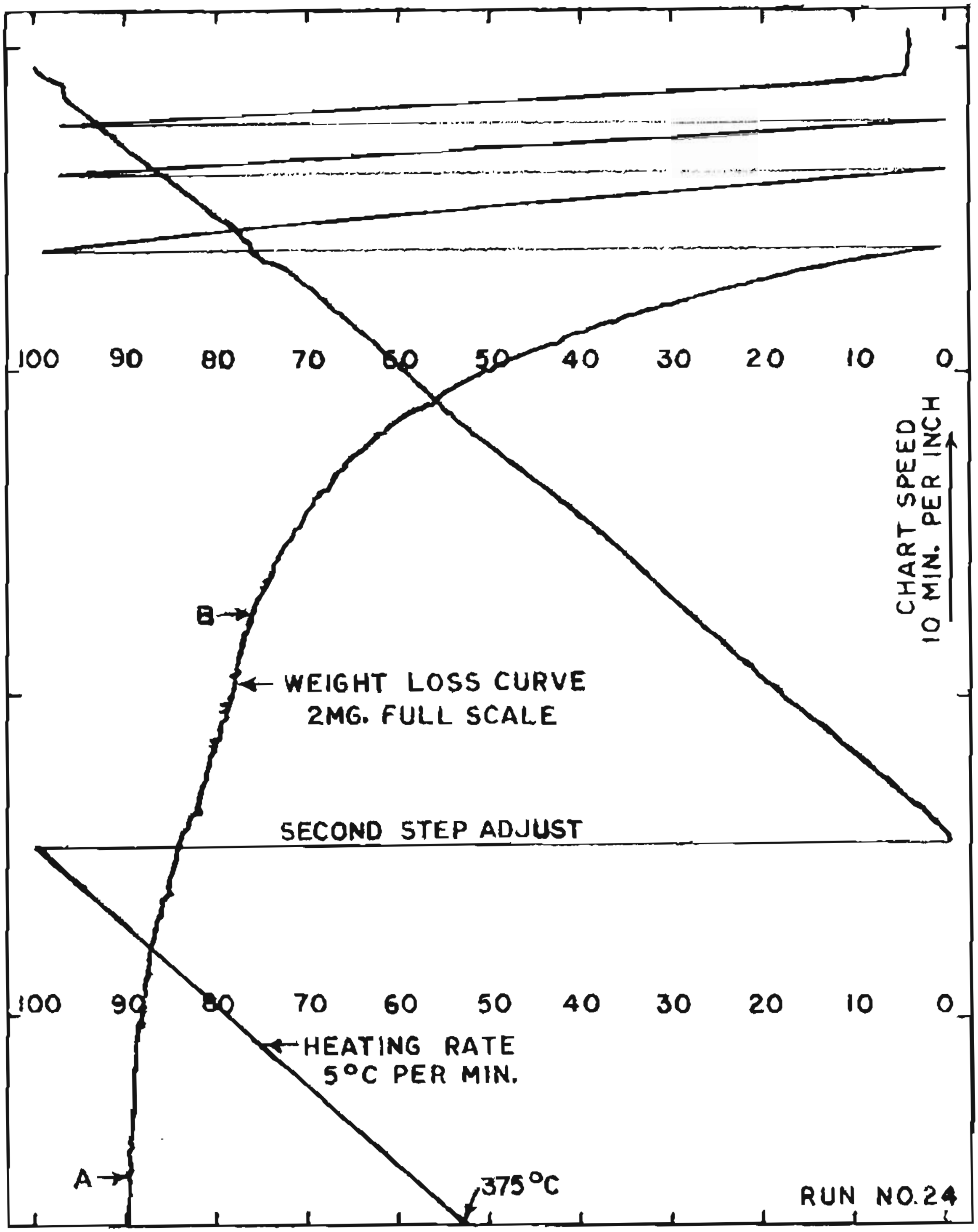

FIGURE 11. REPRODUCTION OF TGA CHART FOR ANTIMONY SULFIDE IN NITROGEN

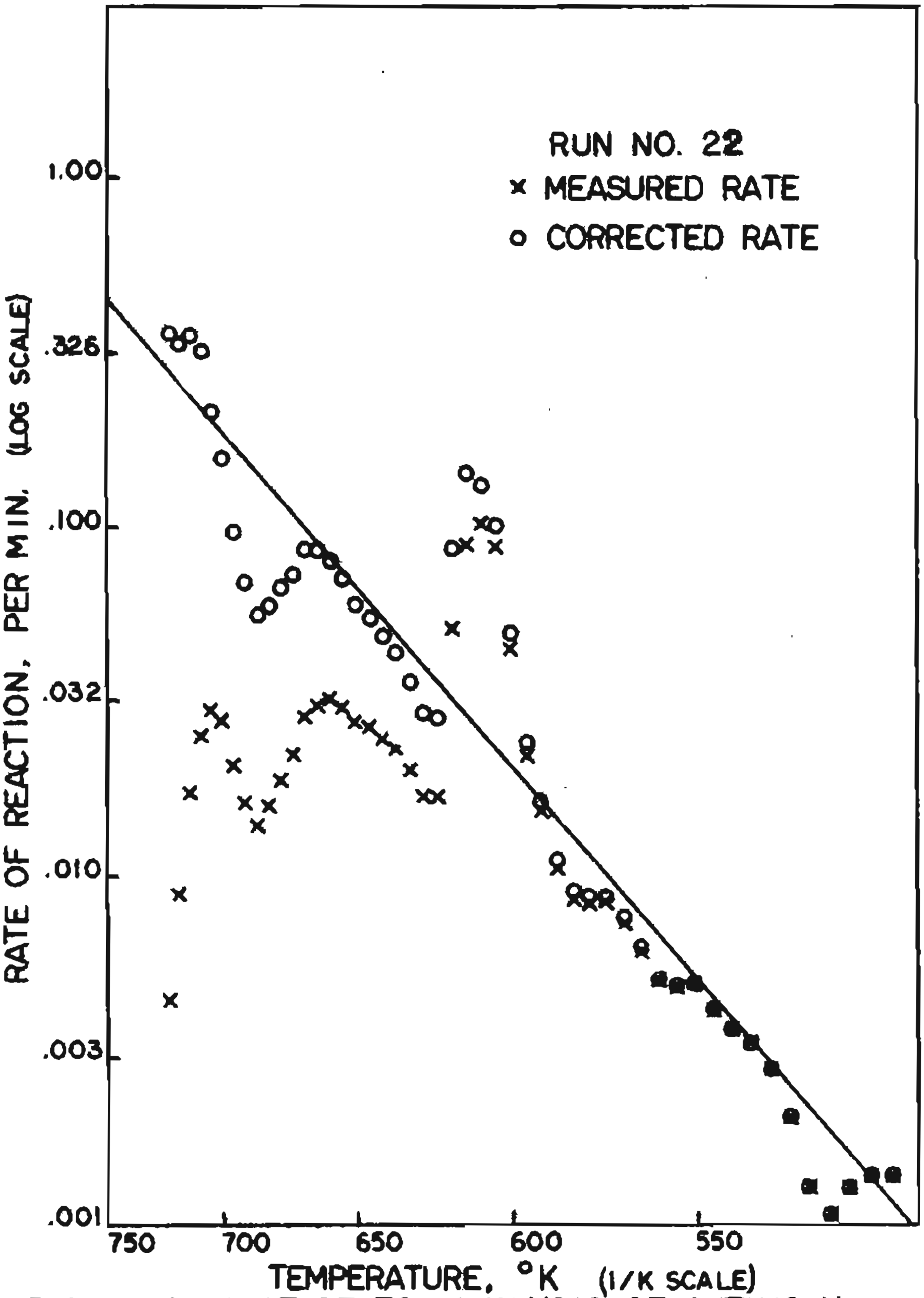

FIGURE 12. PLOT OF TGA ANALYSIS OF ANTIMONY SULFIDE IN AIR

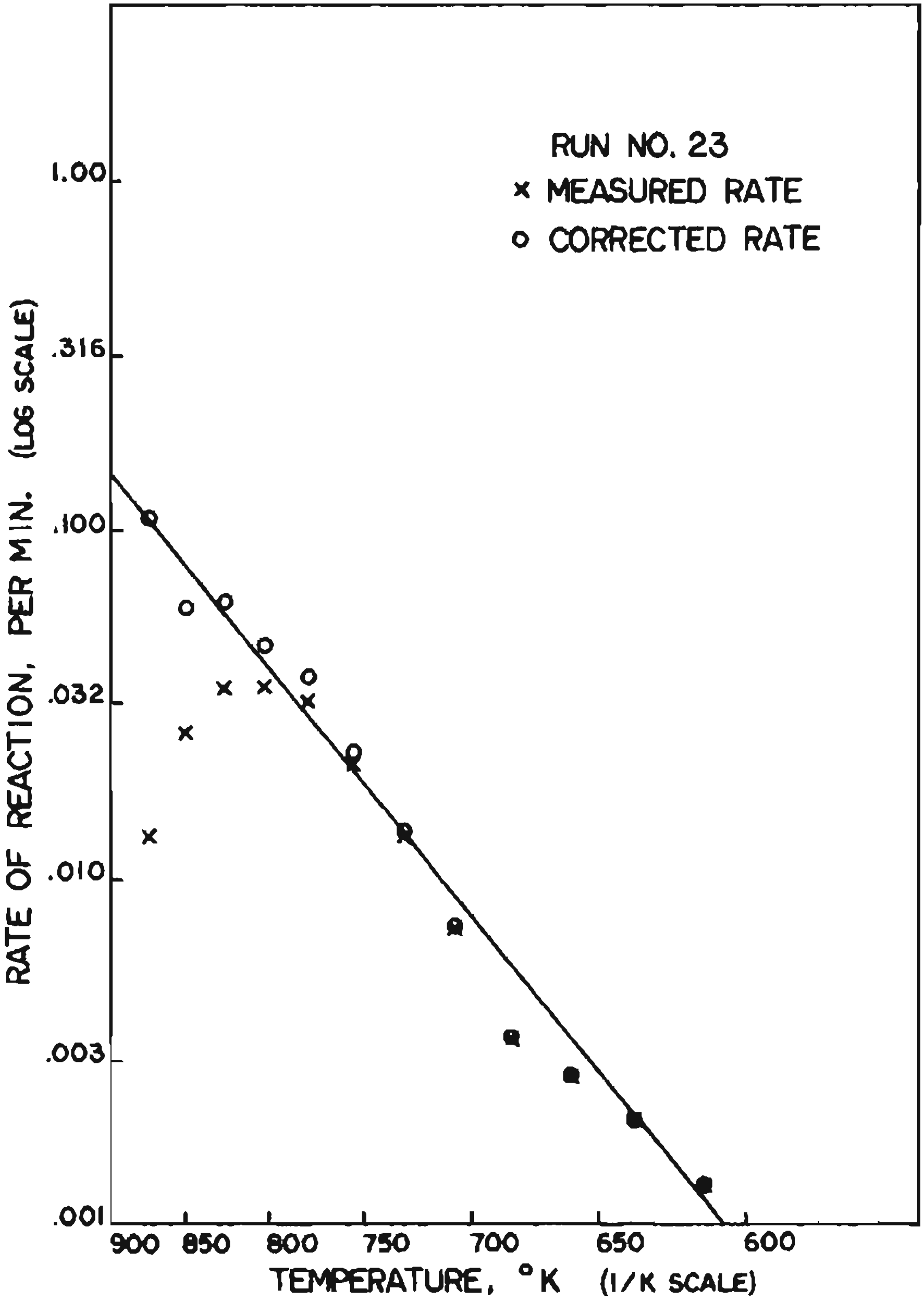

FIGURE 13. PLOT OF TGA ANALYSIS OF ANTIMONY SULFIDE IN VACUUM

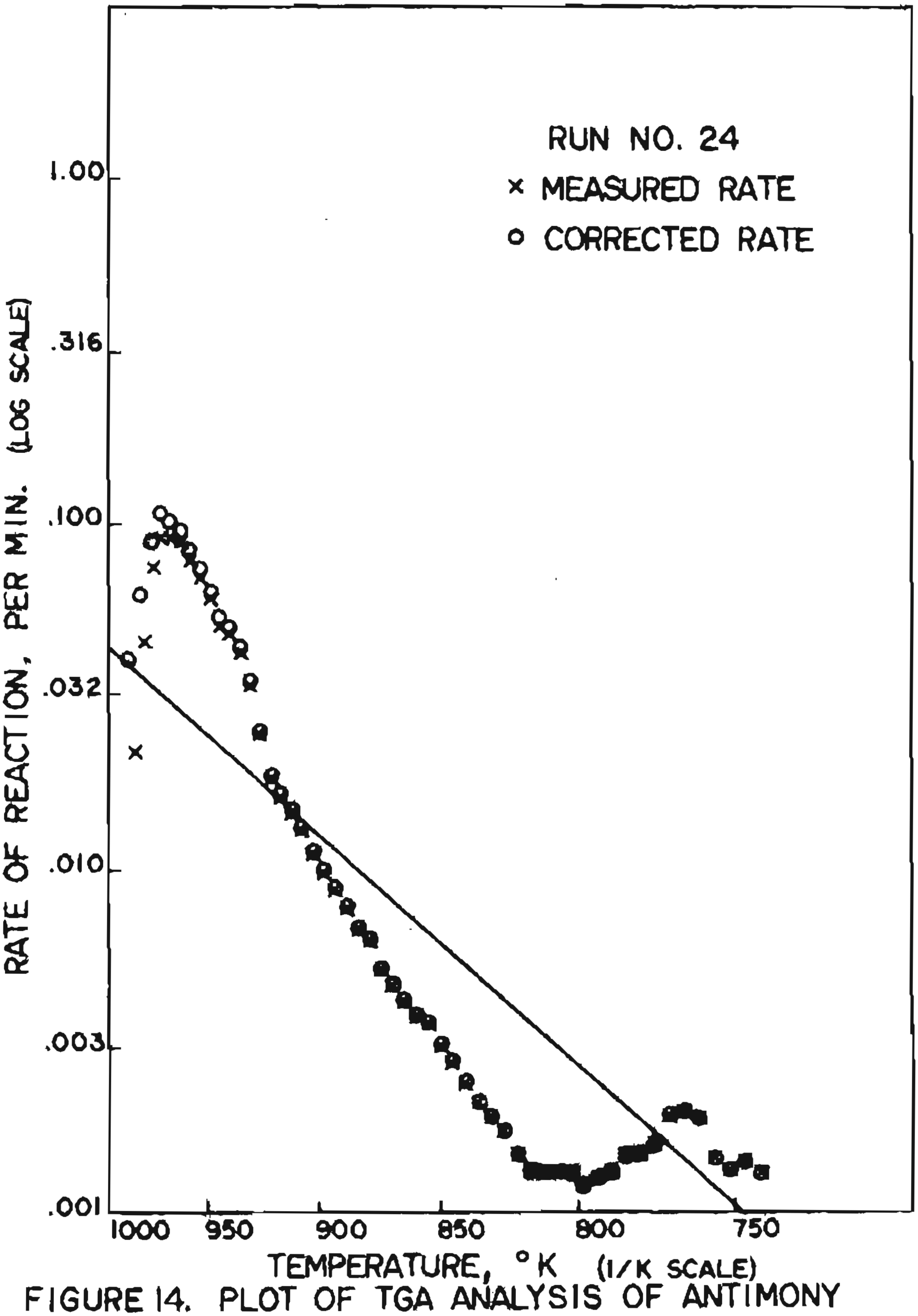

FIGURE 14. PLOT OF TGA ANALYSIS OF ANTIMONY SULFIDE IN NITROGEN

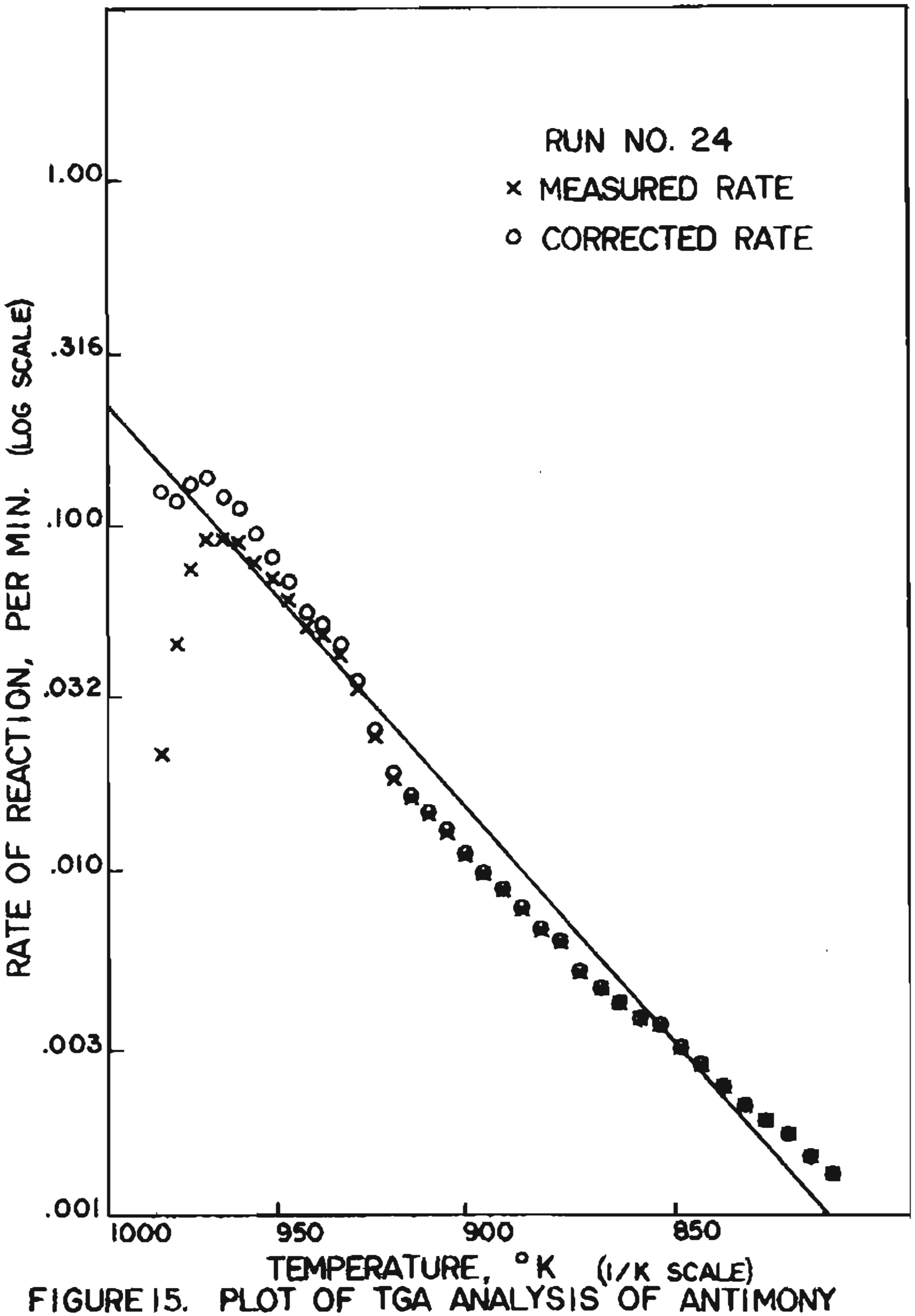

FIGURE 15. PLOT OF TGA ANALYSIS OF ANTIMONY SULFIDE IN NITROGEN

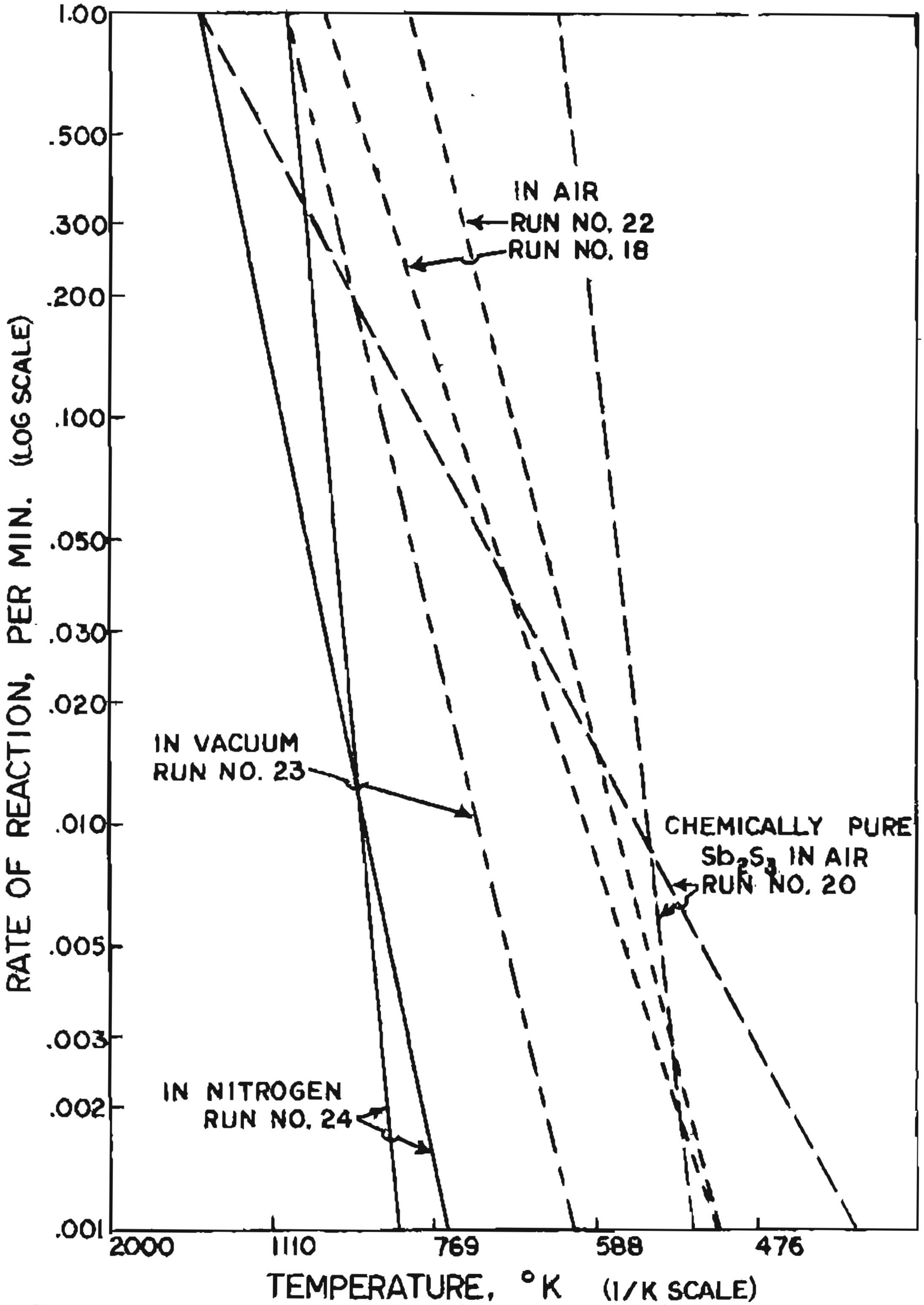

FIGURE 16. ARRHENIUS PLOT OF REACTION RATES FOR ANTIMONY SAMPLES

that the line representing the higher activation energy occurs at a lower temperature than the low activation line. Results show that for both vacuum and nitrogen the 0.10 per minute rate is at a higher temperature than that obtained for the two runs shown in air. Two activation energy lines are also shown for chemically pure antimony sulfide in air. The line of least slope represents the total weight loss curve and its just calculated activation energy was 8.5 Kcal per mole. When just the rapid weight loss part of the TGA curve (oxidation of Sb_2S_3 to Sb_2O_3) was used the activation energy equaled 38.5 Kcal per mole (the steeper line).

Arsenic Studies

The TGA graph for the vaporization and decomposition of arsenic sulfide in a nitrogen atmosphere is shown in Figure 17. The results show a fairly uniform weight loss except for the slight break at B. Similar graphs were obtained for the sulfide in air and vacuum except for a more pronounced break at B. The line from A to B represents the decomposition of As_2S_3 to As_2S_2, plus some vaporization of the arsenic compounds present. The line from B to the end of the run shows conversion of As_2S_2 to As_2O_3 and the vaporization of the different compounds present. If Figures 18 and 19 are compared the measured rate data points show that the dip around 600 degrees Kelvin is more pronounced in Figure 18 for the run in air compared to Figure 19 for the run in nitrogen. This greater dip is a result of the loss of one sulfur atom plus the sulfide converting to the oxide. The line of best fit for both curves, however, does represent the corrected rate data points fairly well. A sample of chemically pure As_2O_3 was run in air to determine the true decomposition rate for the trioxide. Results in Figure 20 show that the vaporization of the trioxide was very uniform and the line of best fit follows the corrected rate data very closely. Activation energies for the arsenic sulfide and trioxide samples in air were nearly identical showing 20.0 and 22.3 Kcal per mole, respectively. However, for the same rate of reaction the trioxide temperature was 80 degrees below that of the sulfide.

Results in Figure 21 show the Arrhenius plots for arsenic sulfide in vacuum and in atmospheres of air and nitrogen and for arsenic trioxide in air. Little change in either the activation energy or rate of reaction at a given temperature was noted for the sulfide in air, vacuum, or nitrogen. The arsenic trioxide line has bout the same slope as the arsenic sulfide line in air, but for a rate of reaction of 0.10 per minute the temperature is about 80 degrees lower.

Comparison of Arrhenius Data in Air and Nitrogen

For comparison of the activation energies and rates of reaction at given temperatures the three sulfides were plotted for air and nitrogen. The results in Figure 22 for the air atmosphere

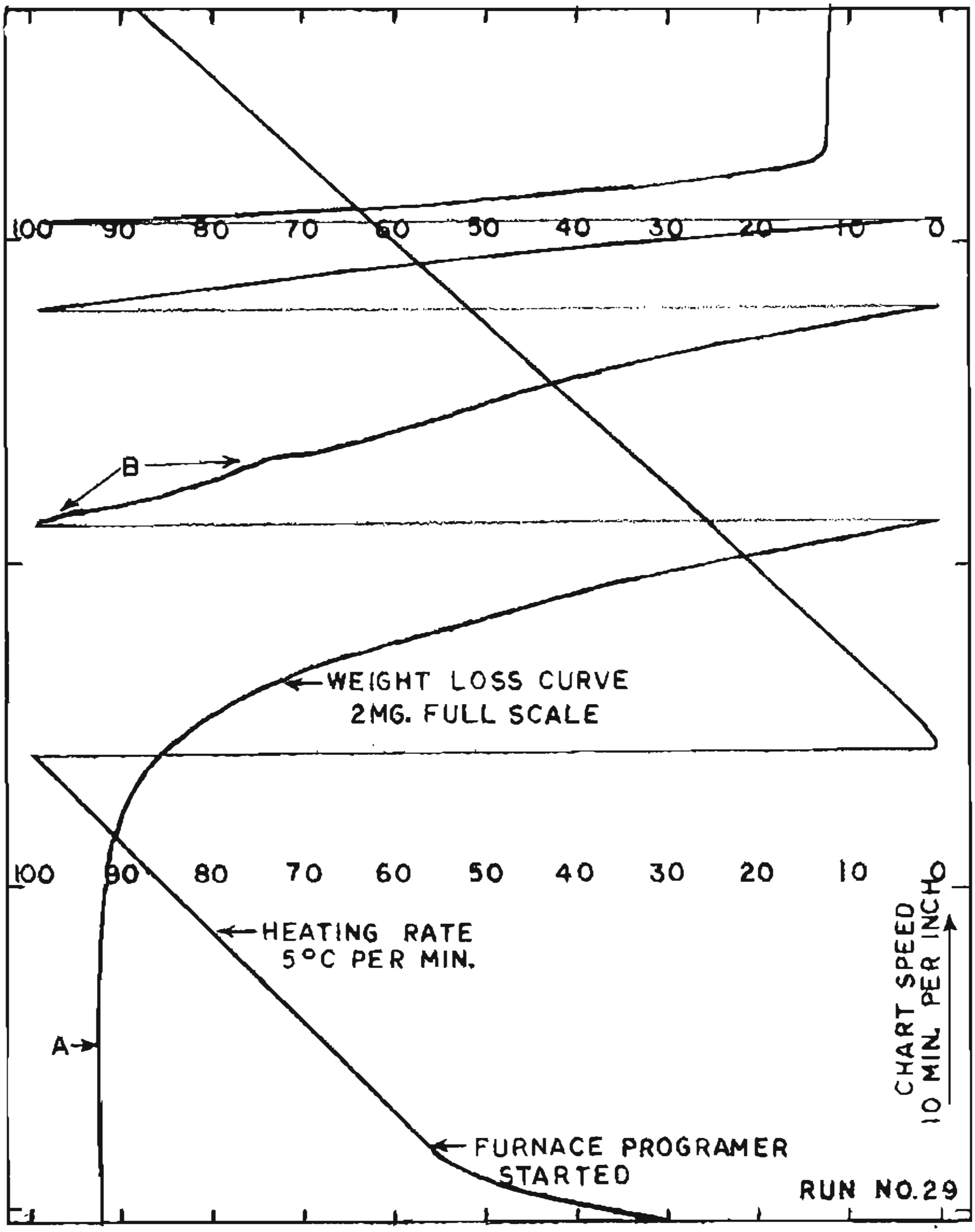

FIGURE 17. REPRODUCTION OF TGA CHART FOR ARSENIC SULFIDE IN NITROGEN

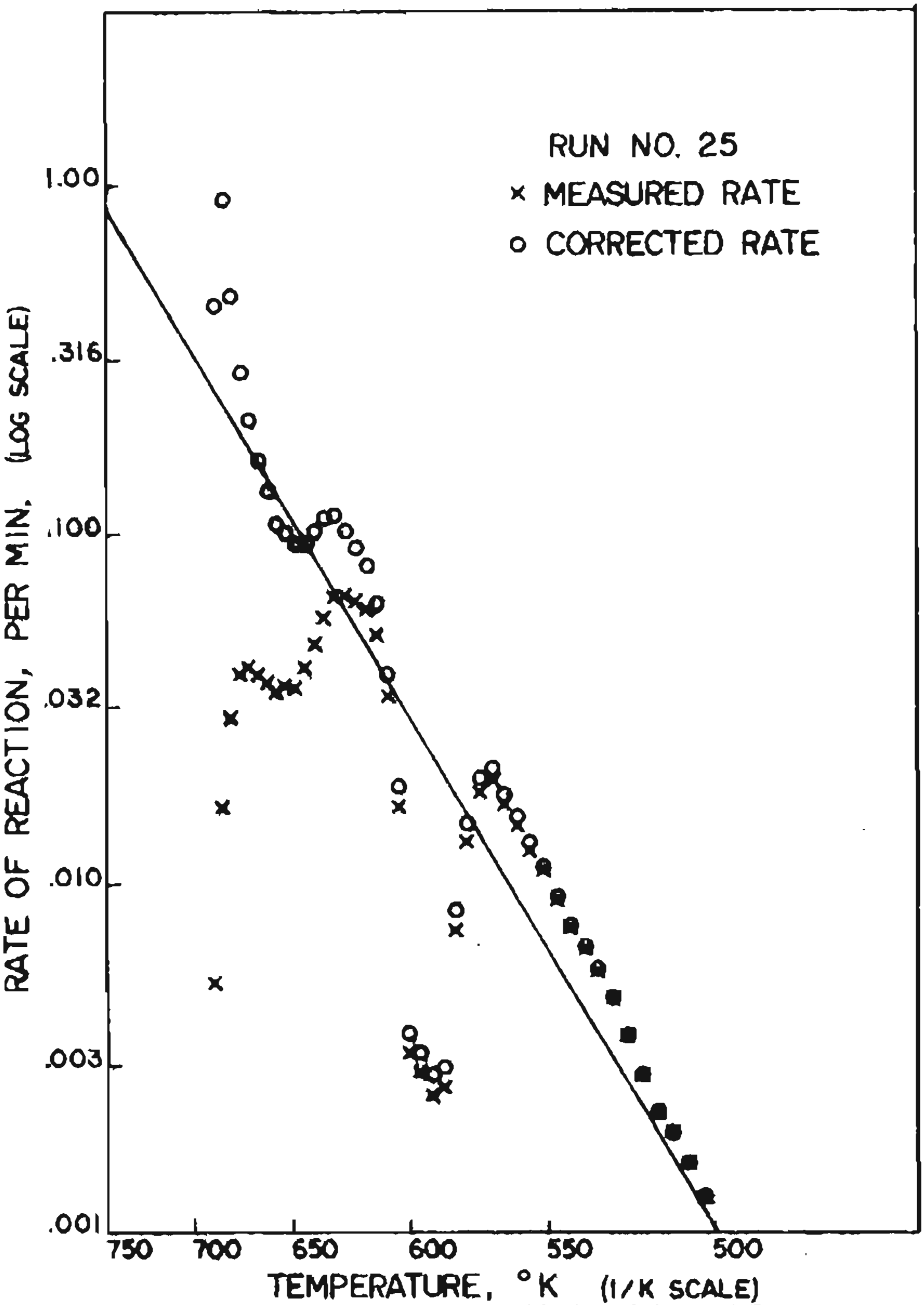

FIGURE 18. PLOT OF TGA ANALYSIS OF ARSENIC SULFIDE IN AIR

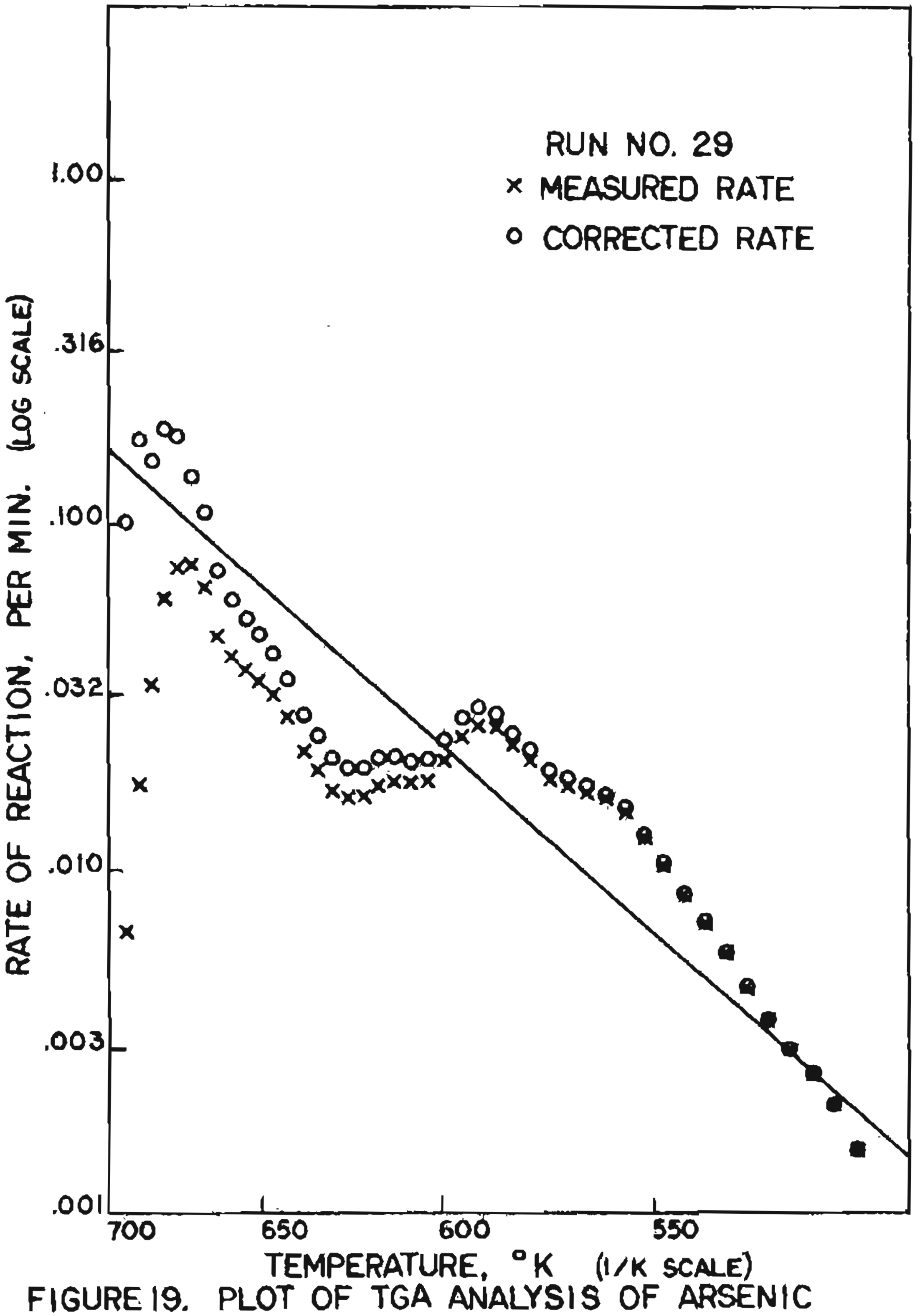

FIGURE 19. PLOT OF TGA ANALYSIS OF ARSENIC SULFIDE IN NITROGEN

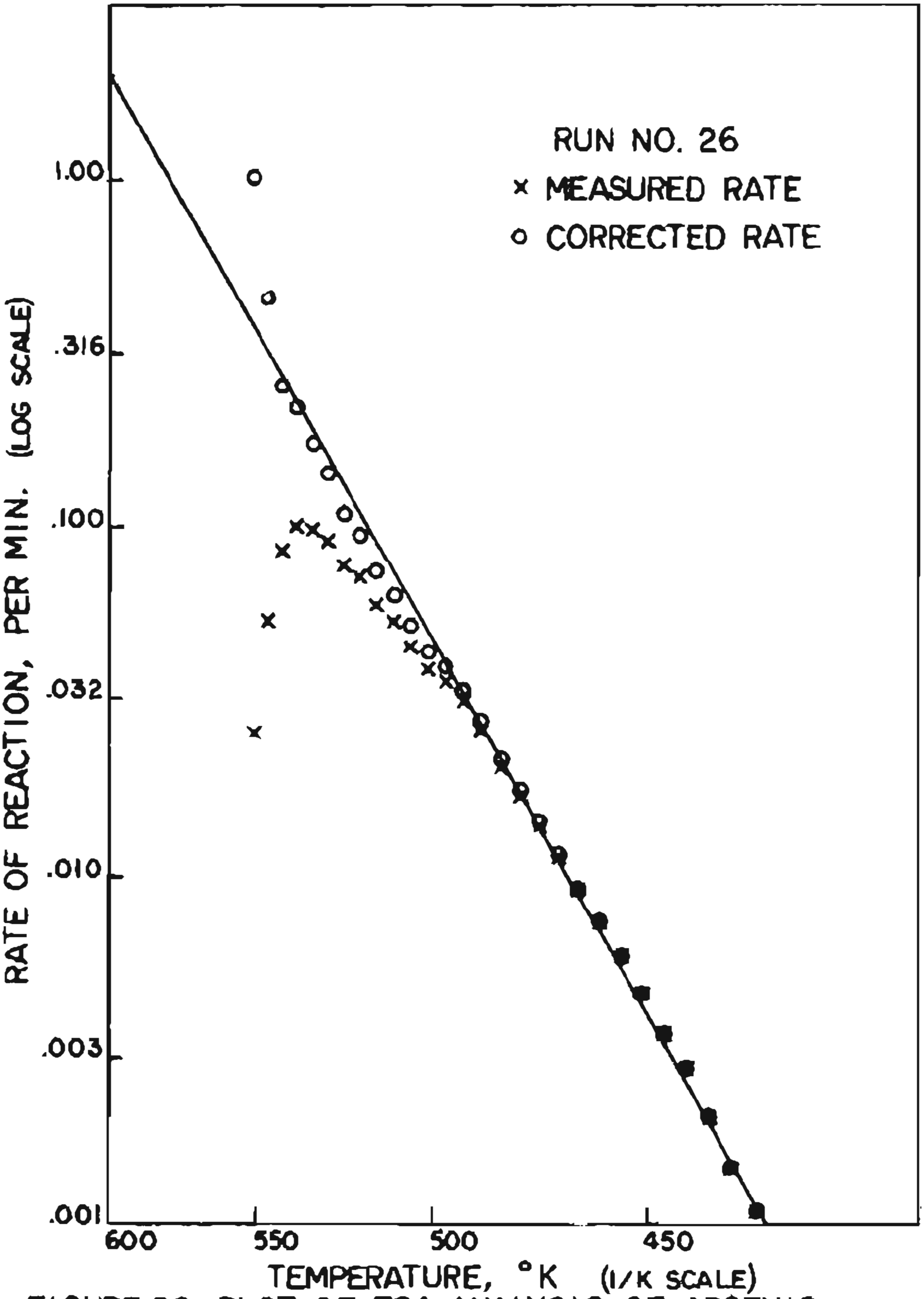

FIGURE 20. PLOT OF TGA ANALYSIS OF ARSENIC TRIOXIDE IN AIR

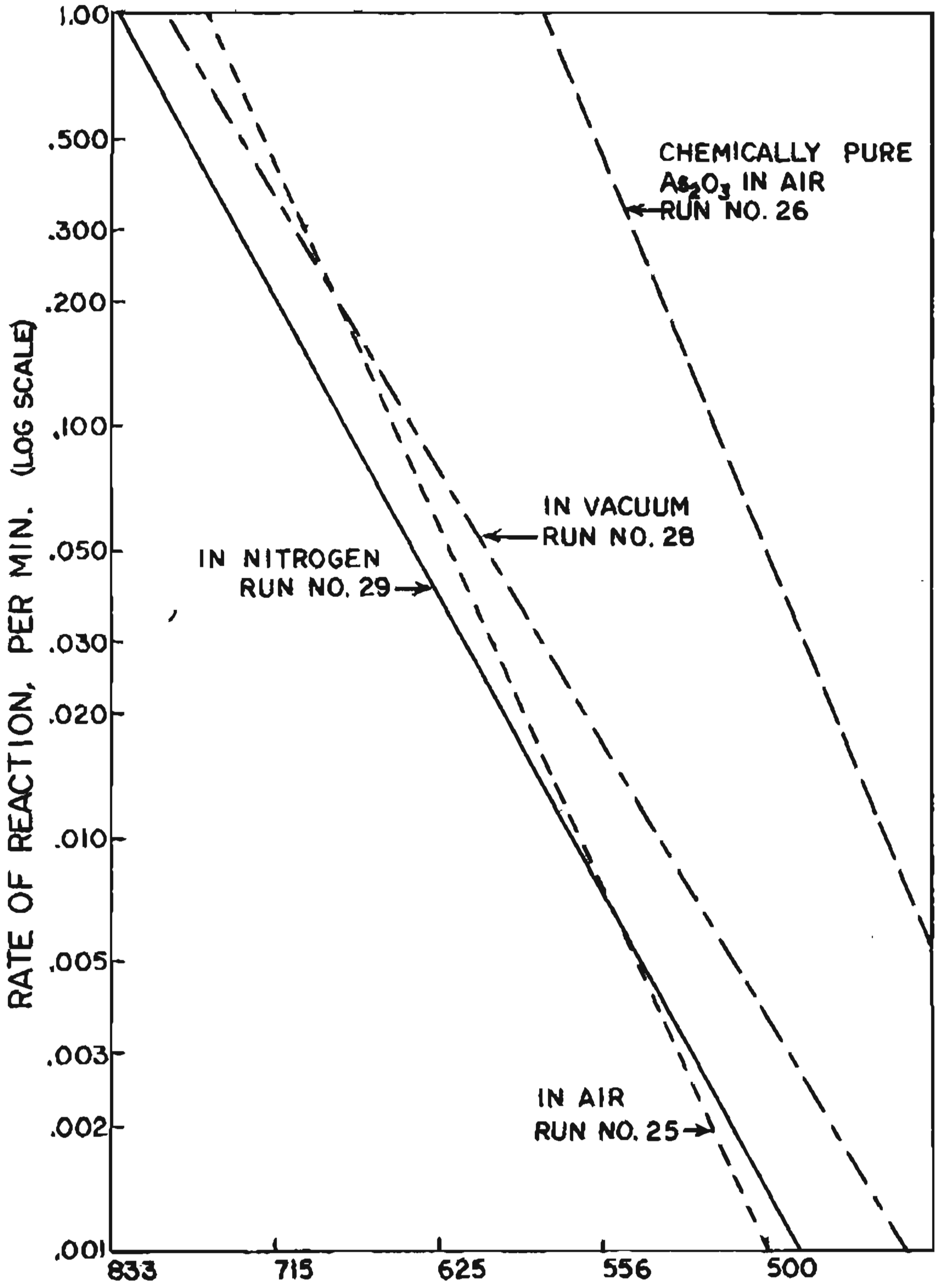

FIGURE 21. ARRHENIUS PLOT OF REACTION RATES FOR ARSENIC SAMPLES

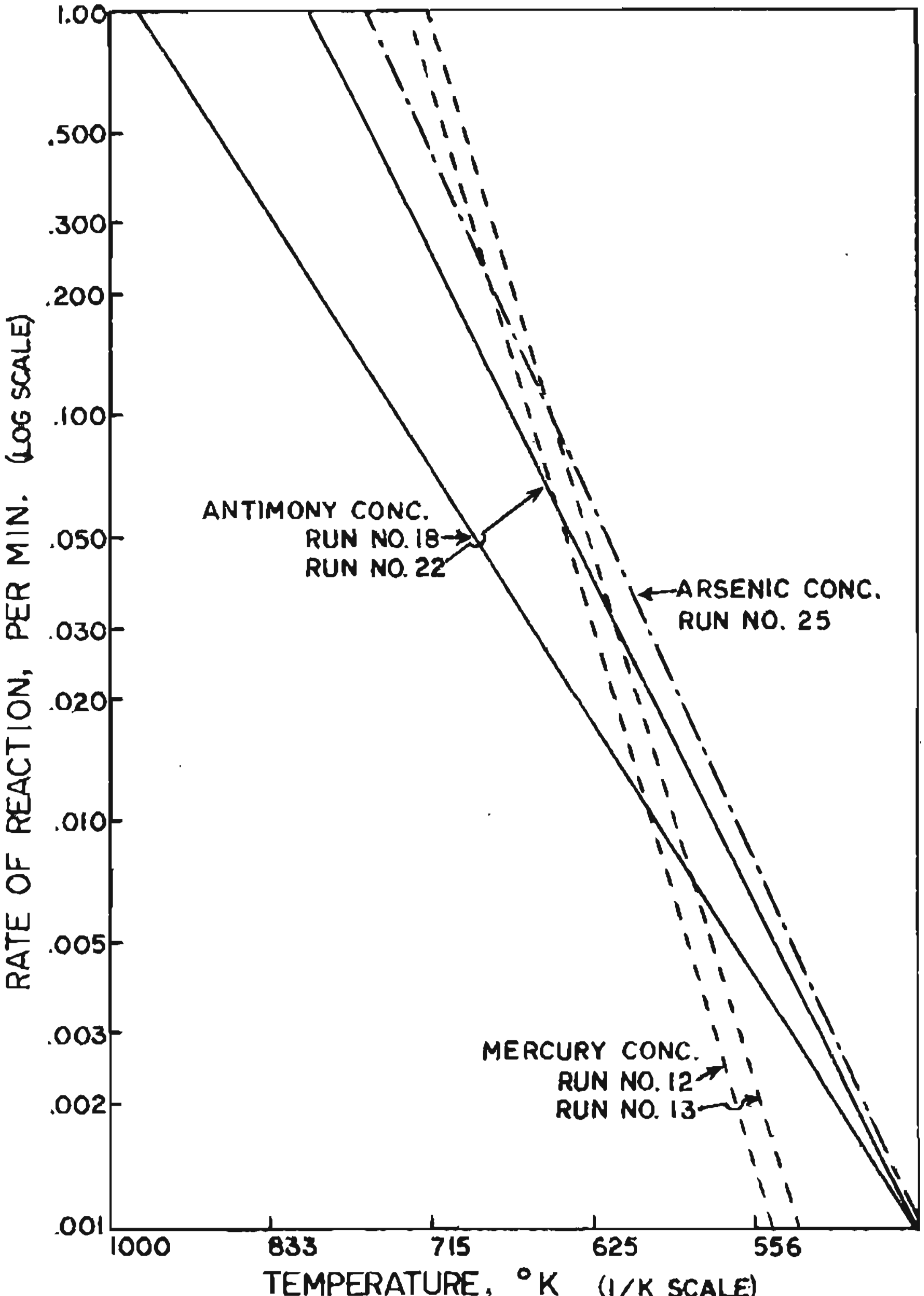

FIGURE 22. ARRHENIUS PLOT OF REACTION RATES FOR THREE SULFIDES IN AIR

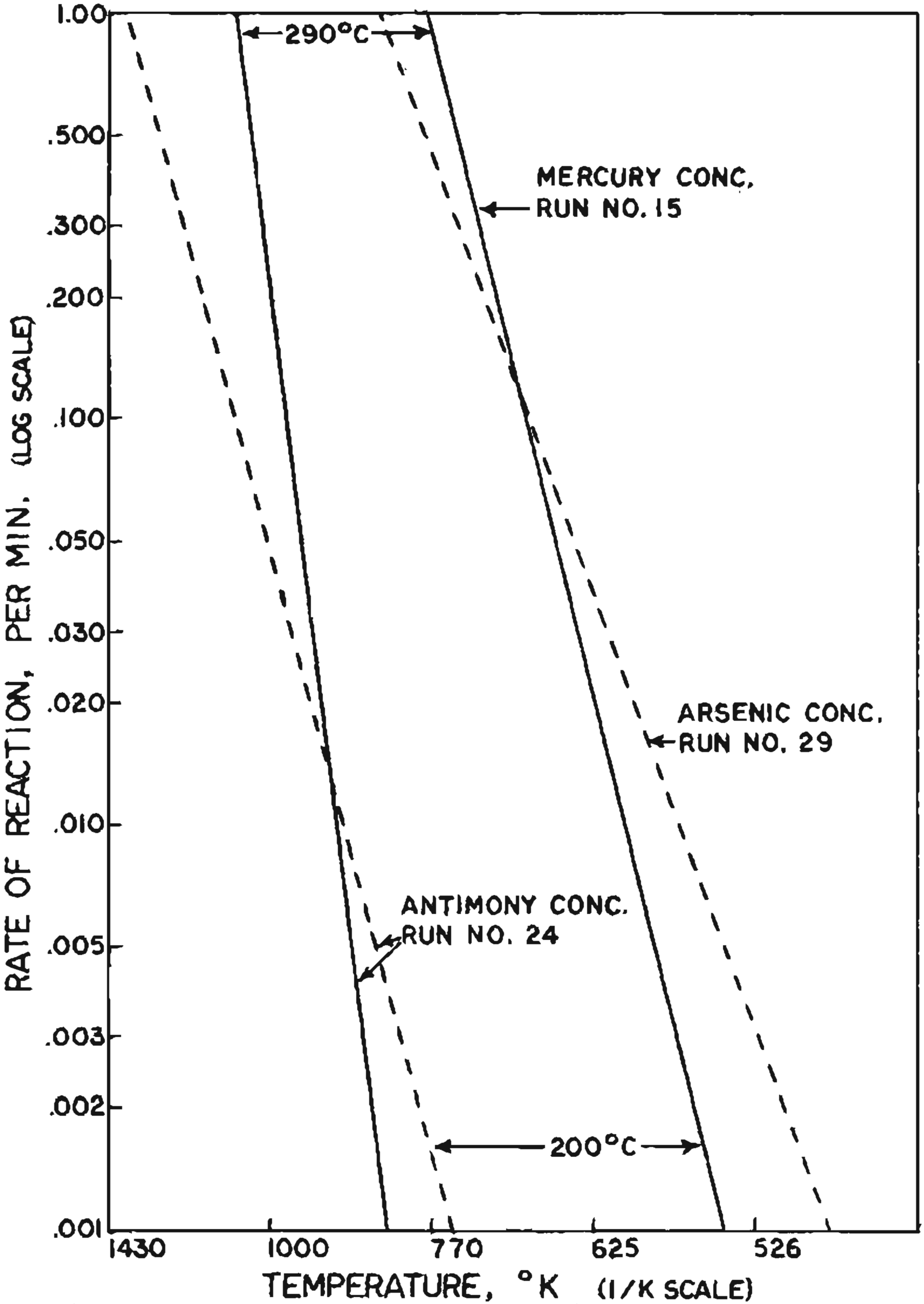

FIGURE 23. ARRHENIUS PLOT OF REACTION RATES FOR THREE SULFIDES IN NITROGEN

show that all three sulfides tend to start reacting between 500 and 550 degrees Kelvin.

Both the antimony and arsenic sulfides started to react at lower temperature than the mercury sulfide and crossed the mercury line between the 0.01 to 0.10 per minute rates. Decomposition of the antimony sulfide proceeded at a higher rate than the mercury sulfide at low temperatures, was nearly equal between 0.01 and 0.05 per minute (600 to 640 degrees Kelvin), and higher for antimony above 0.10 per minute. These results agreed with the data cited earlier by Mel'nikov.[8] The possibility of obtaining any selective separation of the three sulfides in an oxidizing atmosphere is essentially precluded by this data.

A possible method of separating mercury from antimony sulfide is shown in Figure 23 because of the wide temperature difference obtained on the two sulfides when treated in an inert atmosphere (nitrogen). If a comparison is made at the projected mercury sulfide decomposition rate of 0.10 per minute or 680 degrees Kelvin (407 degrees centigrade) the comparable result for antimony sulfide at this temperature is a rate of reaction of 0.0002 per minute (500 times slower than for mercury sulfide). The temperature for a comparable rate (0.10 perminute) for antimony sulfide would be 295 degrees higher than that of the mercury sulfide. A comparison of the mercury and arsenic sulfide data shows that at the rate of reaction (0.10 per minute) considered for the mercury sulfide decomposition, the arsenic sulfide rate is essentially identical, thus making it essentially impossible to obtain a separation of these two sulfides.

DISTILLATION STUDIES

With the information from the literature search and the results from the TGA studies indicating the possibility of separating mercury and antimony sulfides in a distillation unit studies were initiated to evaluate the closed circuit system. The four samples selected for test were a cinnabar concentrate, a cinnabar-stibnite concentrate, a low grade cinnabar-realgar-orpiment concentrate and a prepared cinnabar-realgar product. The results of these studies follow the description of the operating procedure in this chapter.

Testing Procedure

Considerable planning was given to the possible methods of constructing a small scale distillation unit. Of major concern was the recovery of the condensed mercury metal, collection and separation of the liquid mercury and soot (solid residue) for weighing, observation of the system during a run, cleaning the system between runs and cooling at the end of a run. The only major problem that occurred after the first unit was assembled was the condensation of mercury in the end of the reactor tube that projected beyond the end of the furnace (Figure 24). This was solved by installing a small tubing pump to circulate the furnace atmosphere (gases). After the pump was installed the unit was operated for over 100 runs with no problem. The rubber stopper that sealed the end of the reactor tube would blow (pop-out) whenever the condenser plugged, thus preventing any breakage.

Figure 24 shows both a pictorial and a photographic view of the distillation unit as assembled for operation. The split hinged electric tube furnace was designed for a two-inch diameter tube, with a thermocouple situated half way between the furnace ends at the edge of the two hinged sections. To observe the inside of the reactor during operation and withstand the moderate temperature required, Vycor glass ware was selected for construction of the reactor tube, condenser tube, and sample boat. An additional advantage of the glass was that no side reactions were probable at the temperatures being used. The sample boat was of sufficient size to hold about 120 grams of low-grade concentrate or 200 grams of high-grade concentrate. The small tubing pump gave sufficient circulation of the gases (about 400 ml per minute) to ensure that all mercury vapor flowed into the condenser before condensing. Very little vapor or soot was noted in the condenser-dust trap (a 500 milliliter filter flask). Excess pressure caused by expansion of the gases in the reactor during heating was compensated by displacement of water from the first of the two 2000 milliliter acid bottles. The volume of the reactor tube was approximately 700 milliliters; thus a 300 degree centigrade

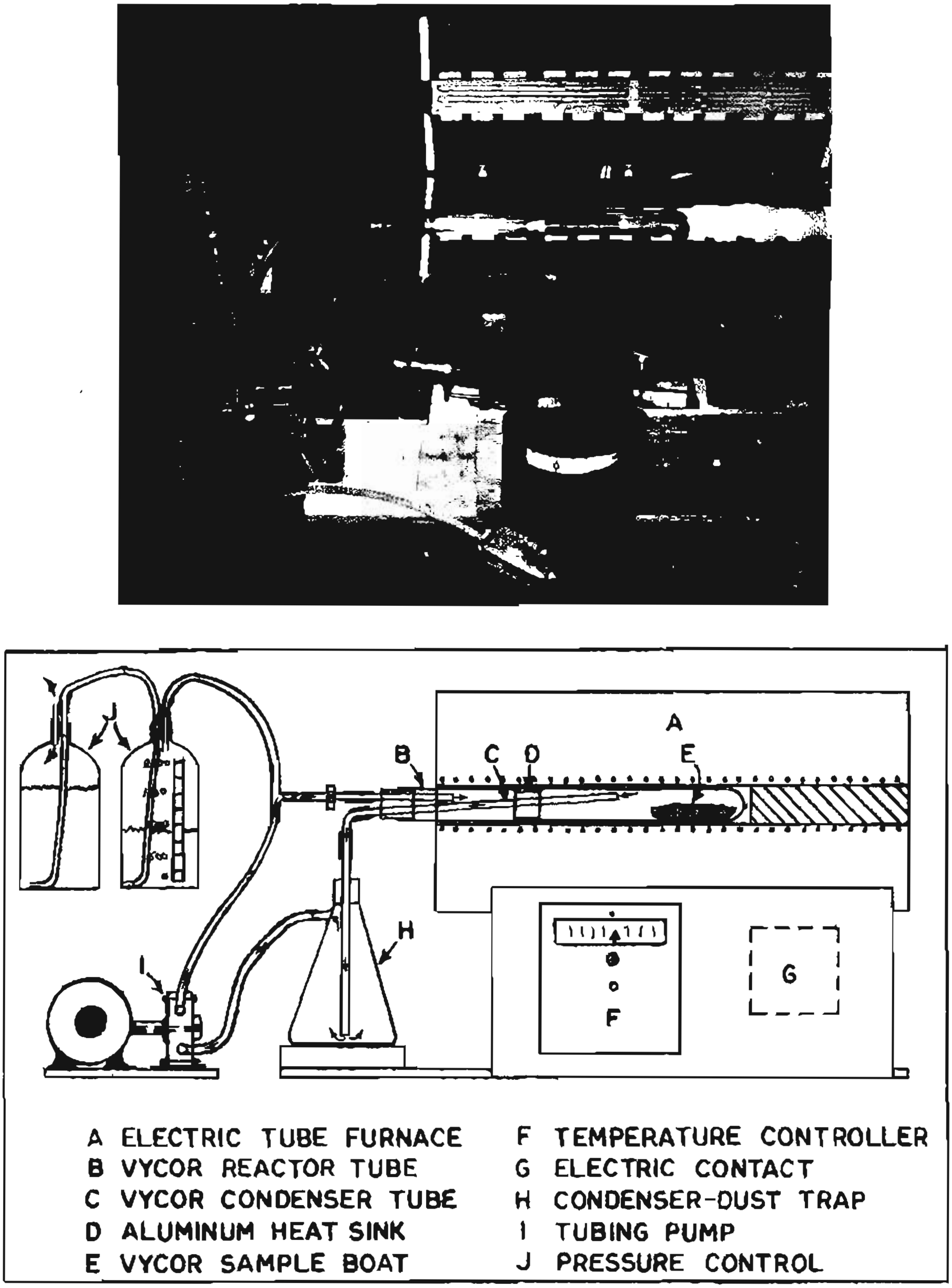

FIGURE 24. PICTORIAL AND PHOTOGRAPHIC VIEWS OF DISTILLATION UNIT

temperature rise resulted in about a 700 milliliter increase in gas volume or water displacement. For temperature calibration a thermocouple was placed in the center of the reactor tube and the furnace temperature control adjusted to indicate the same temperature as measured in the reactor. After adjustment, the furnace controller maintained the temperature within 5 degrees of that set on the controller.

The operating procedure used in preparing the samples and running the distillation unit consisted of first planning the objective of a test series and the number of runs required to complete each series. Materials for each run were then weighed out (all samples were calculated to contain 20 grams of mercury) placed in glass vials, and mixed on a small Pitchford vibrator for one to three minutes to ensure uniformity of sample. Because of the temperature rise during vibrating the mixing time was held to a minimum. Minus 40-mesh degreased iron filings and 80 percent minus 100-mesh lime were used as sulfur complexing agents. After the samples had been prepared the furnacing equipment was placed in a large laboratory hood to insure removal of any mercury vapor leaked during operation. A mixed sample was placed in the Vycor sample boat and the boat slid into the furnace. The condenser tube and heat sink were inserted into the reactor tube and the condenser-dust trap and pump connected. When the furnace was turned on the time and water level in the first pressure control bottle were recorded. The circulating tubing pump was turned on when the furnace controller indicated 200 degrees centigrade to ensure that all mercury vapors and soot were swept into the condenser. When the furnace reached temperature both the time and water level were again recorded. Distillation time was considered from the time the furnace reached temperature and, depending on the temperature, the preheat time ranged from 10 to 25 minutes. This introduced some error into the time factor effect; however, it was considered more factual to consider only the time at temperature. At the completion of the run the furnace was opened and the complete reactor assembly removed and placed on a retainer beside the furnace for cooling. Removing the reactor from the furnace reduced the cooling time thus helping keep the time at temperature closer to that planned in the test series. The circulating pump was turned off after the reactor had cooled for about 10 minutes and the entire unit was allowed to cool until it could be handled without asbestos gloves. It was then dis-assembled, the mercury and soot were collected, the mercury separated from the soot by squeezing through tissue paper and the three products, metallic mercury, soot, and furnace residue, weighed. The soot and residue were then individually mixed on the Pitchford vibrator and one gram samples were taken for analysis. After the analyses were completed a metallurgical balance was calculated for each run in the test series so that total mercury content could be used to check the accuracy and reproducibility of the series. After a few preliminary tests the following test series were conducted to determine the effects of the different variables on mercury distillation and recovery.

Mercury Concentrate Tests

In initiating a research study where more than one or two variables are to be considered simultaneously the number of runs becomes too large to complete in a reasonable time; it then becomes appropriate to select a test design that will reduce the total number of runs and still allow for the evaluation of the desired variables. Since four variables were considered of importance in the distillation studies, iron, lime, time and temperature, a factorial designed test series as described in 'Experimental Designs' by Cochren and Cox was used.[2] The specific test design was a one-fourth replica of four variables at four levels, which required only sixteen tests to complete the series, instead of the total 256 tests. A more detailed description of the statistical arrangement is listed in Appendix E.

The initial studies were made on the high-grade White Mountain concentrate to ensure that no uncontrolled variables from impurities would be affecting the results. A summary of the results for the first test series is shown in the lower half of Figure 25 and the tabulated test plan and analytical results in Table D-I of Appendix D. Regression analysis for the linear and quadratic effects showed that only the linear effects of iron and temperature were significant above the 80 percent level. Both show a 98 percent level of significance. The plotted results in Figure 25 were calculated at the mean levels of the other three variables, these data points therefore represent an average of four runs. Appendix E explains the method of averaging used in more detail and Table E-I the data used to calculate the results for the four iron points (levels) for series II.

The results show that with increased temperature the percent metallic mercury recovered increased rapidly and that higher temperatures would be required to obtain additional recovery. Also, the effect of iron was tending to reach a maximum around 8.4 grams (1.5 equivalents Fe to HgS) and increased time had a slight positive effect (not significant by regression analysis). The effect of lime was very inconsistent and showed no trend (also not significant). It therefore was not plotted. Visual observation of the condenser residue showed that a considerable amount of mercury sulfide was reforming, indicating

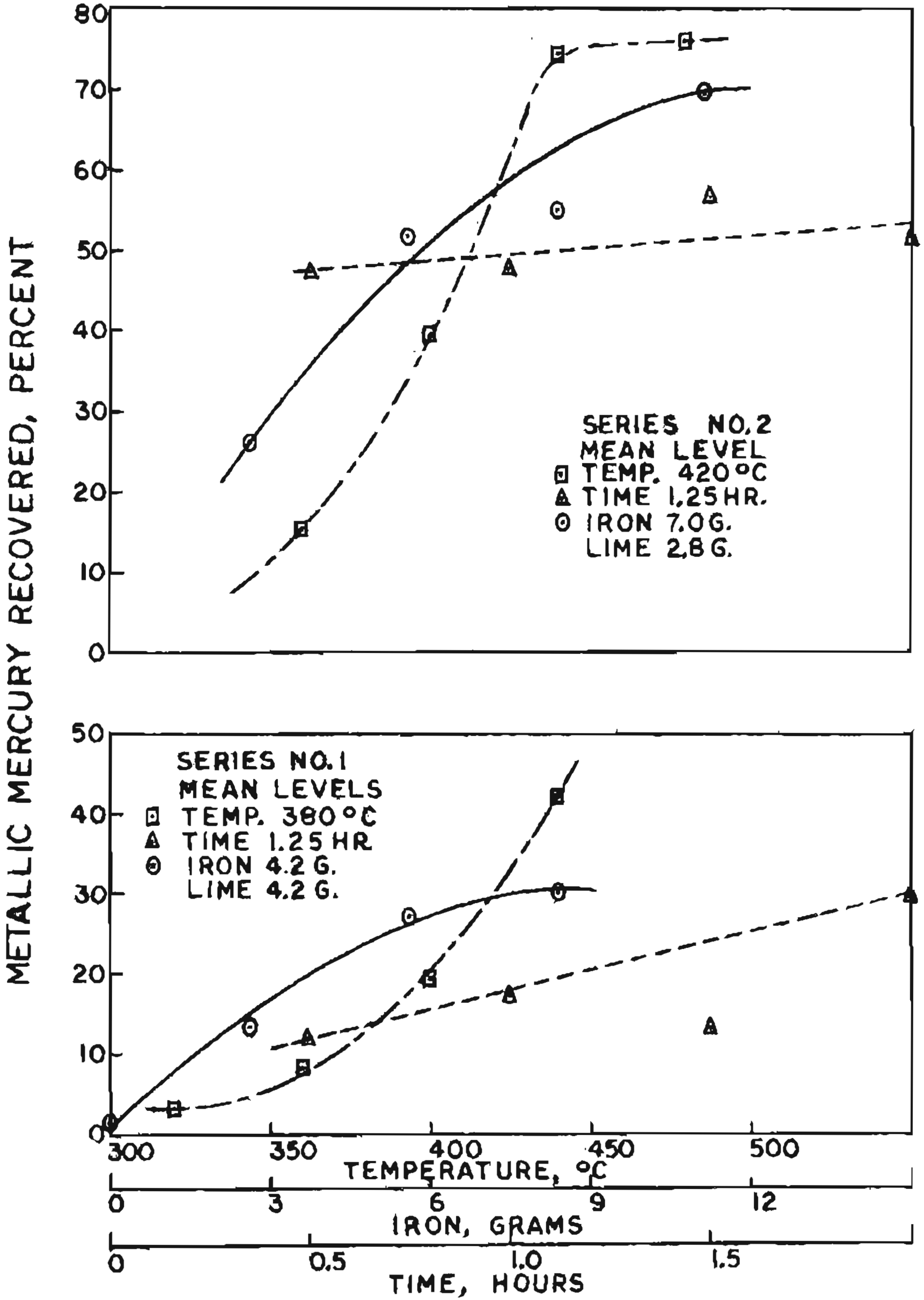

FIGURE 25. EFFECT OF SIGNIFICANT VARIABLES ON METALLIC MERCURY RECOVERY

that not all the sulfur released by the cinnabar was reacting with the iron or lime. This resulted in much lower metallic mercury recoveries than expected.

A second test series was planned to attempt to improve recovery by increasing the mean levels of temperature by 40 degrees centigrade and iron by 2.8 grams (0.5 equivalent Fe to HgS). Time was maintained at the same levels and lime reduced to a mean level of 2.8 grams (0.5 equivalent CaO to HgS) to try to obtain a significant effect.

Results in the upper half of Figure 25 show that the percent metallic mercury recovered was nearly double that of the first test series, 80 percent as compared to 40 percent. Both the temperature and iron data indicate maximums at about 80 percent recovery. However, the tabulated data from this test series, Table D-2, show that on six of the runs less than 0.1 percent of the mercury remained in the residue. Results again showed that recovery was low because of the formation of mercury sulfide in the condenser and indicated that additional iron was needed to react with the sulfur. It is evident from the plotted results that additional iron was having essentially no effect. Regression analysis showed iron and temperature to have a linear effect, significant at the 98 percent level and lime to have a negative effect, significant at the 80 percent level. Lime was therefore dropped from further consideration.

With the information that one-hour contact at about 440 degrees centigrade would essentially remove all the mercury from the charge an additional test series with two levels of iron was planned at a number of temperatures to try to obtain higher metallic mercury recovery. The results in Figure 26 and Table D-3 show that low mercury recoveries were again obtained. The additional iron showed only about 10 percent higher recovery. At the higher temperatures the amount of soot increased (observed as mostly mercury sulfide) and lower recoveries were obtained.

After considerable thought it was decided that at the higher temperatures the sulfur was being released so rapidly that it was escaping from the charge before it had time to react with the iron. An additional test series was then conducted with the same amount of iron, only the excess 2.8 grams (0.50 equivalent) was spread over the top of the charge. These results are also shown in Figure 26 and listed in Table D-4. These data confirmed that the problem was one of the released sulfur having insufficient contact with the iron. Test results demonstrated that over 99 percent of the mercury could be recovered as metal and that a closed mercury distillation unit could be operated satisfactorily.

Six additional tests were then conducted under similar conditions except that air was

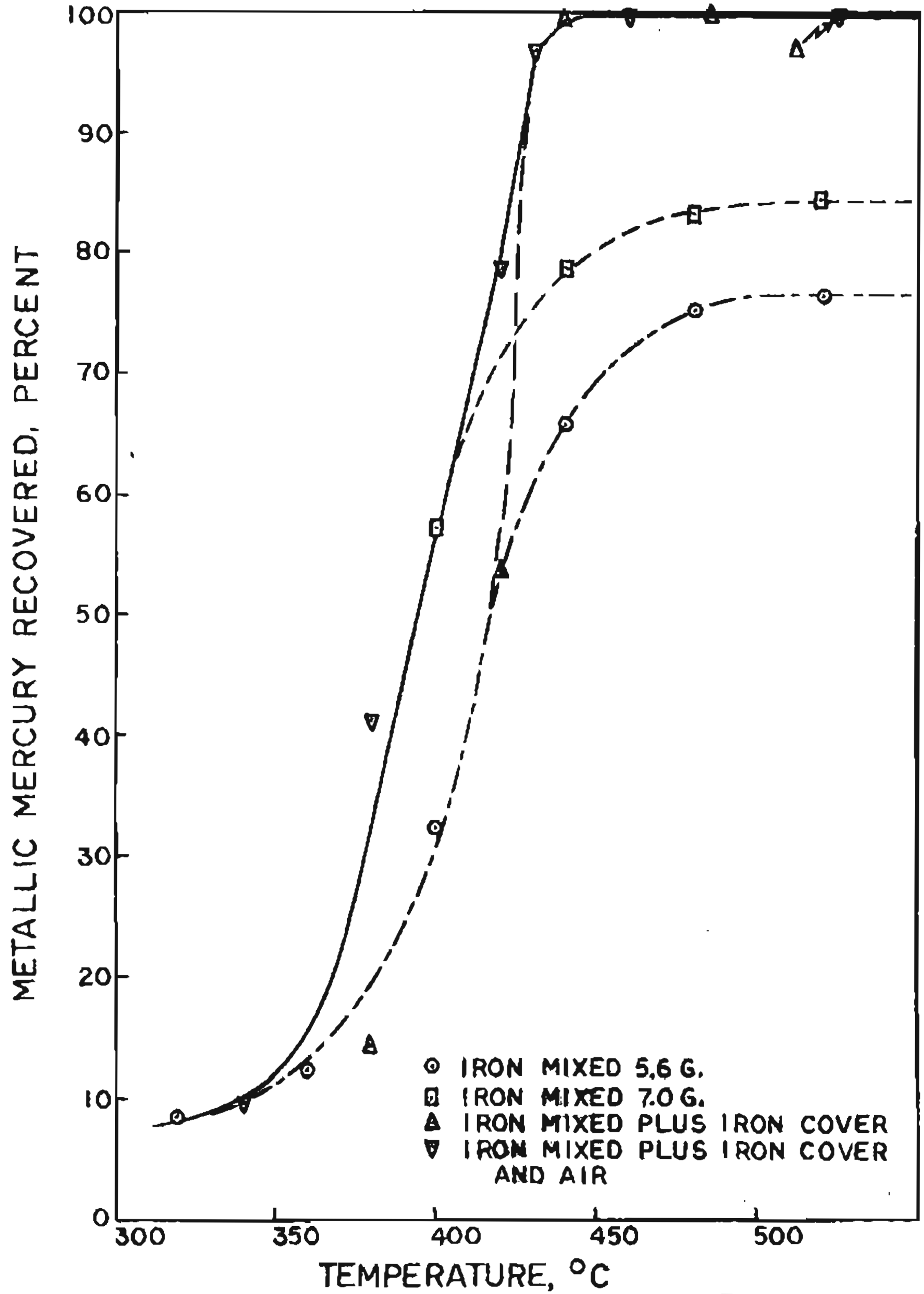

FIGURE 26. METALLIC MERCURY RECOVERED FROM WHITE MOUNTAIN CONCENTRATE

circulated through the reactor. Results in Figure 26 and Table D-4 show that the mercury tended to distill off at a slightly lower temperature (in agreement with the TGA results), while high mercury metal recoveries were obtained.

Mercury - Antimony Concentrate Tests

The first test series on the combined Red Devil cinnabar-stibnite concentrates was completed before the idea of covering the charge with iron had been considered; therefore the results show lower metallic mercury recoveries than desired. A test series similar to that conducted on the White Mountain concentrate was planned, with antimony (stibnite) being used in place of lime as one of the variables. Time was held at the same levels, while both the iron and temperature levels were increased. Different amounts of stibnite were added (0 to 30 grams) to the charge to see if there would be an effect from its presence in the charge. Results in Figure 27 and Table D-5 show that nearly 100 percent recovery of the mercury was obtained with 8.4 grams of iron (1.5 equivalents Fe to HgS) at a temperature of about 440 degrees centigrade. Antimony distribution in the soot amounted to less than 1.0 percent of the antimony in the furnace charge; thus indicating that a separation of mercury from a cinnabar-stibnite concentrate was feasible under these test conditions. Regression analysis showed that both the linear and quadratic effects of temperature, the quadratic effect of iron and the linear effects of time and antimony were significant at an 80 percent or higher level. The significant effect of antimony may have been a result of the 3.64 percent mercury contained in the antimony concentrate, as shown in Table 1.

Twenty-seven additional tests were then conducted to determine the optimum conditions for mercury recovery from two prepared cinnabar-stibnite concentrates, using a standard distillation time of one hour at different temperatures. The amount of iron mixed in the charge was held at 5.6 grams (1.0 equivalent Fe to HgS); however, an iron cover of 2.8 grams (0.50 equivalent) was used on some runs and air was admitted to others. Results are shown in Figure 28 and listed in Tables D-6 and D-7 of Appendix D. With the iron cover on the charge the recovery of metallic mercury above 440 degrees centigrade remained over 98 percent as the temperature was increased, while without the iron cover the mercury recovery tended to drop at the higher temperatures and additional mercury sulfide formed as soot in the condenser. When air was admitted to the distillation unit a steady cloud of white smoke was observed flowing through the dust trap and coming out the tube connection on the flask. This fine white powder coated the mercury droplets, thus preventing them from combining (running together). Several passes through tissue paper were required to remove

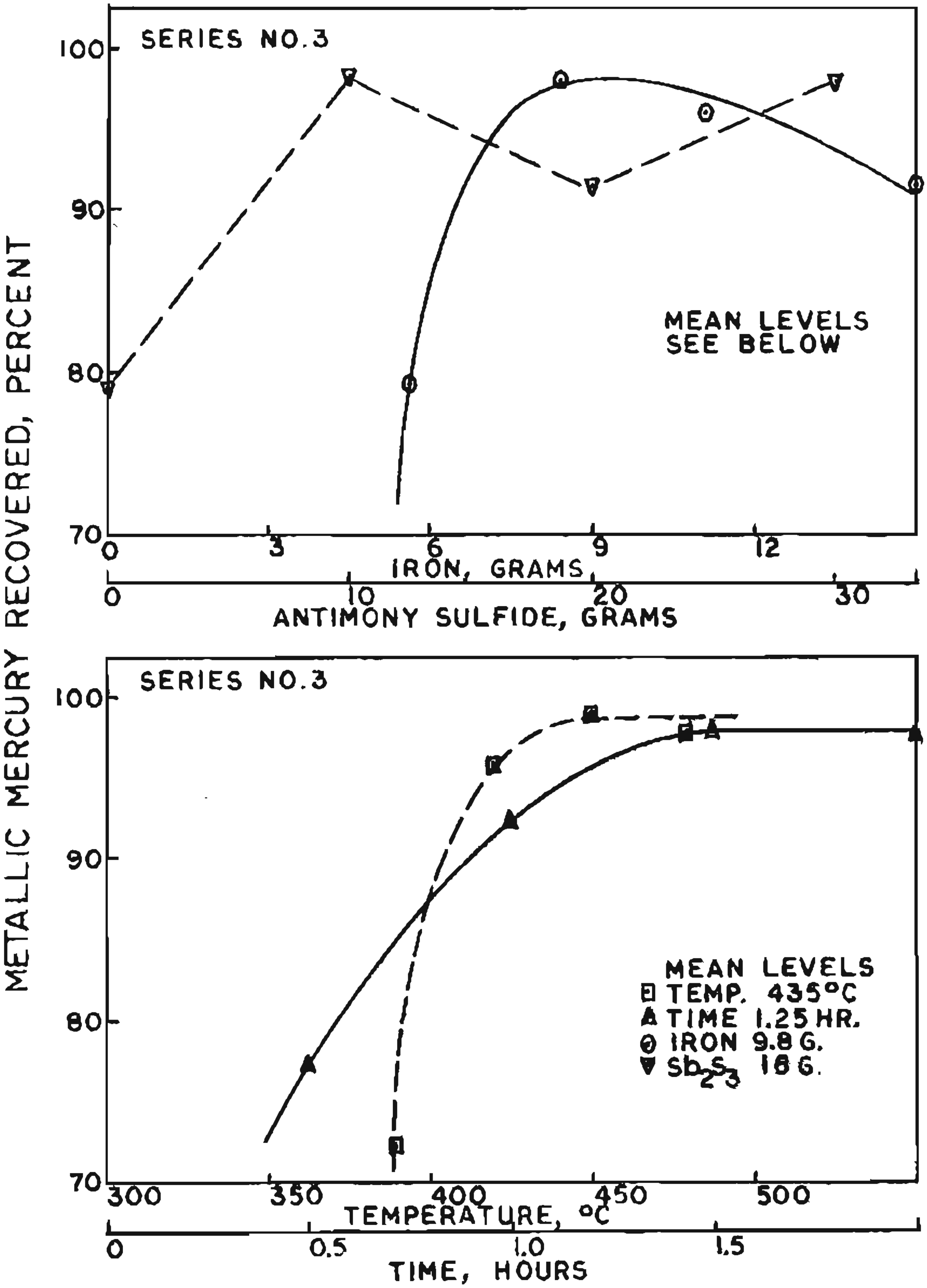

FIGURE 27. EFFECT OF FOUR VARIABLES ON METALLIC MERCURY RECOVERY

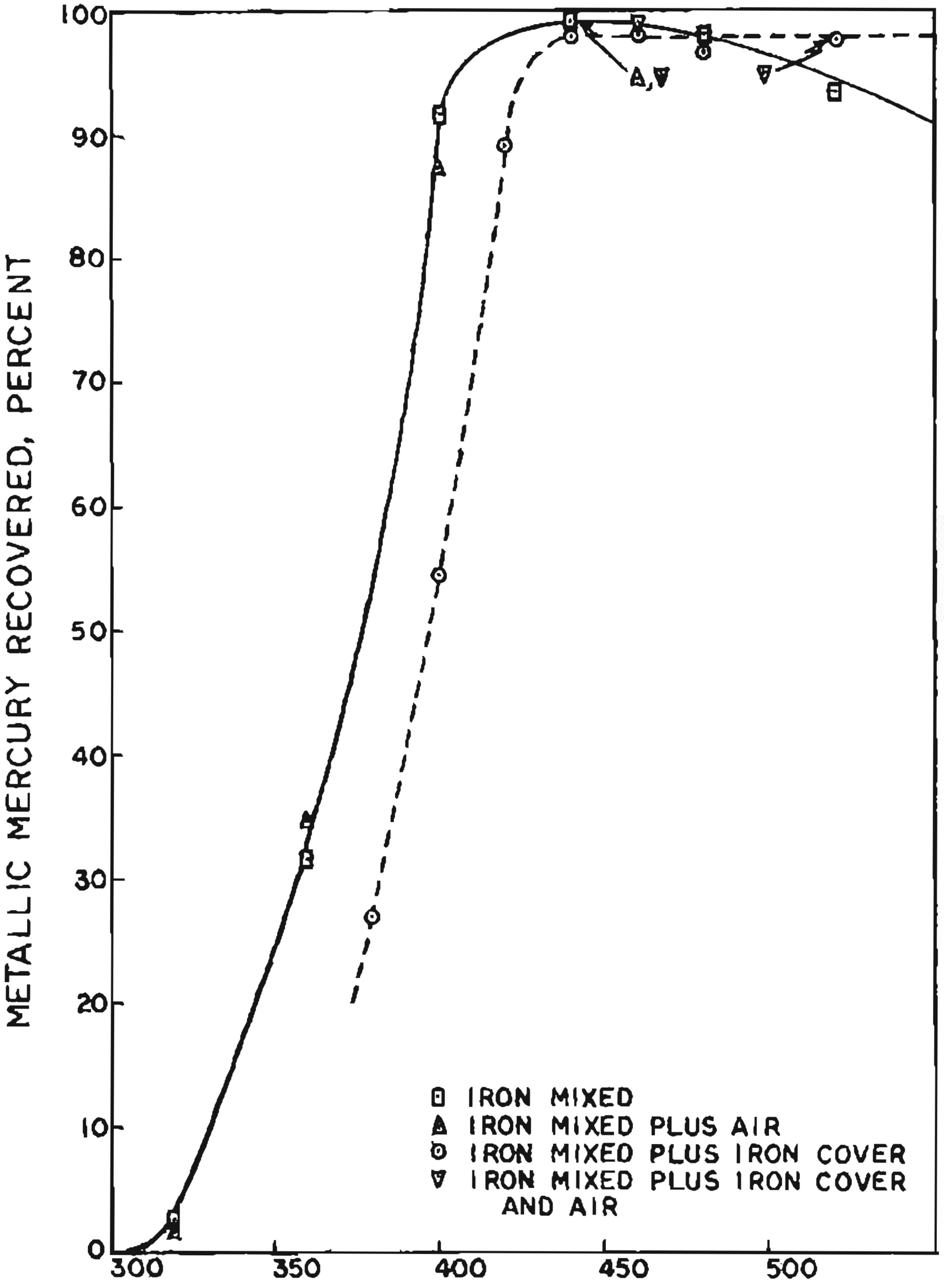

FIGURE 28. METALLIC MERCURY RECOVERED FROM RED DEVIL CONCENTRATE

enough of the powder so that the mercury droplets would combine. Results show that high metallic mercury recoveries can be obtained from cinnabar-stibnite concentrates in a closed system, without the stibnite distilling over into the condenser.

Mercury - Arsenic Concentrate Tests

With the results from the TGA studies showing that either arsenic sulfide or trioxide would distill at a lower temperature than mercury sulfide two test series were conducted on two cinnabar-realgar-orpiment samples to demonstrate the effects on mercury distillation. The first four tests were made on the Cinnabar Creek low-grade concentrate which contained 16.2 percent mercury and 0.90 percent arsenic. The furnace charge consisted of 120 grams of concentrate, which contained only 1.42 grams of As_2S_3. Test results in Figure 29 and Table D-8 show that all the mercury was distilled from the charge in one hour at 440 degrees centigrade. However, because of the mercury entrapped in the soot, only about 70 percent of the mercury was recovered as metal. Even with this low arsenic content considerable soot was formed which tended to plug the condenser and entrap the mercury.

To obtain additional information five samples were prepared with the high-grade concentrate from White Mountain and the realgar-orpiment concentrate used in the TGA studies. Each sample contained 27 grams of White Mountain concentrate and 10 grams of the realgar-orpiment concentrate. Results in Figure 30 and Table D-8 show that with the increased arsenic content even less mercury was recovered and the soot at the higher temperatures equaled 50 percent of the total weight. The condenser tube plugged a number of times and had to be opened with a rod each time. Nearly all the mercury was distilled from the charge at 420 degrees centigrade in one hour; however, less than 40 percent of it was recovered as metal. These results show that some means other than distillation need to be developed to recover mercury from cinnabar-realgar-orpiment samples.

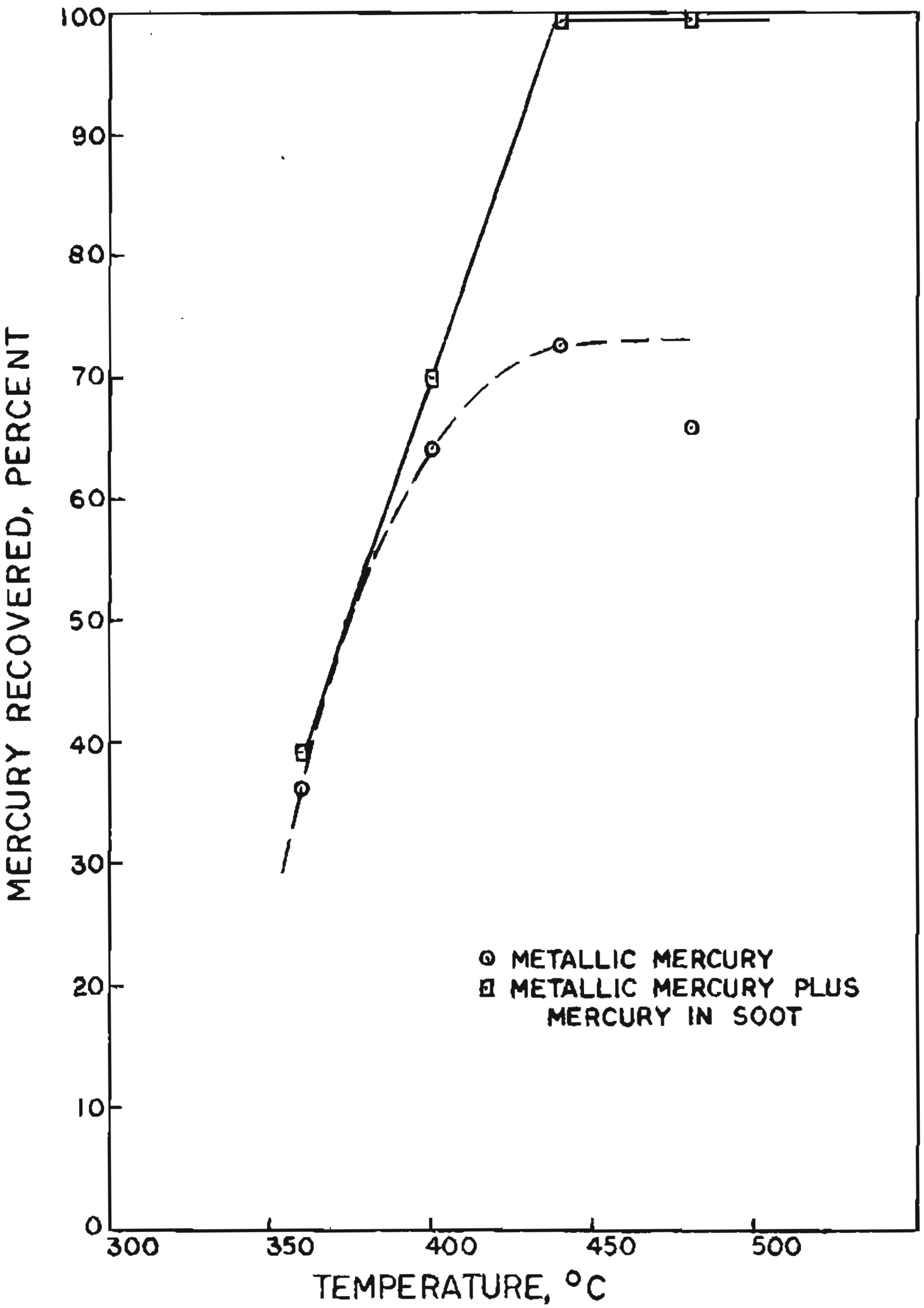

FIGURE 29. METALLIC MERCURY RECOVERED FROM CINNABAR CREEK CONCENTRATE

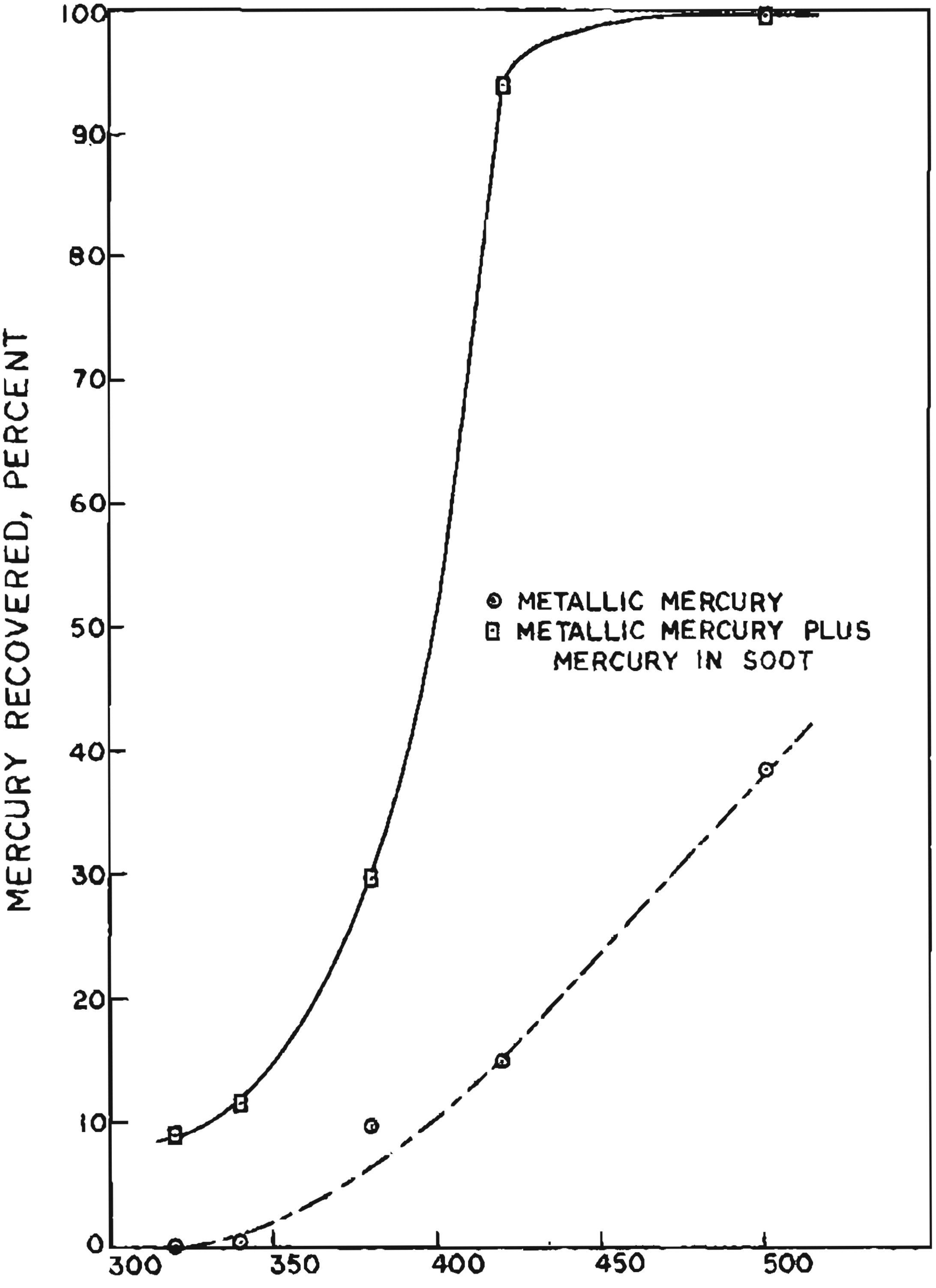

FIGURE 30. METALLIC MERCURY RECOVERED FROM SAMPLES WITH ARSENIC SULFIDE

DISCUSSION

TGA (thermogravimetric analysis) tests have proved that stibnite in an inert atmosphere (nitrogen) requires a temperature about 295 degrees centigrade higher than mercury to obtain a rate of reaction of 0.10 per minute; whereas in an oxidizing atmosphere (air) the two sulfides require about the same temperature to obtain the 0.10 per minute rate. Arsenic sulfides (realgar-orpiment) and trioxide were shown by TGA to have either the same or lower temperature requirements than mercury sulfide at the 0.10 per minute rate selected for the distillation of cinnabar.

The results of the distillation studies demonstrated that either cinnabar or cinnabar-stibnite concentrates could be treated in a closed distillation unit for recovery of over 98 percent of the mercury as metal, when the sulfur was reacted with iron and oxidation of the stibnite was prevented. Separation of mercury from cinnabar-realgar-orpiment concentrates by distillation was unsuccessful because of the large amount of soot formed. Either a flotation or a leaching method should be considered for separating these two sulfides, because small amounts of arsenic tend to cause condenser problems and prevent the coalescence of mercury. A complexing agent could also be studies to attempt to form arsenates with the arsenic sulfides or oxides.

Additional retort tests should be made with a larger scale unit to demonstrate the applicability of the process for commercial use. This would also allow for preparation of enough retort residue for studying the possibilities of upgrading the stibnite from the residue by flotation.

The commercial use of a closed retort for mercury sulfide distillation would eliminate the need for filing air pollution reports with the EPA (Environmental Protection Agency), allow for the distillation of mercury in populated areas and make possible the recovery of antimony from cinnabar-stibnite concentrates.

APPENDIX A

- Analytical Procedure -

This appendix lists in a step-wise sequence the analytical procedures used for testing both mercury and complex mercury-antimony-arsenic sulfide products. The equipment settings for the Perkin-Elmer Model 303 AA used are listed with the concentrations and average percent absorption results obtained on the standard solutions.

Table A-1. Operating Conditions for Model 303 Atomic Absorption Unit

Conditions	Mercury		Antimony		Arsenic	
	Test, Conditions	Absorption, Percent	Test, Conditions	Absorption, Percent	Test, Conditions	Absorption, Percent
Burner, 3 inch	3-slot		1-slot		1-slot	
Air flow, ml/min.	12.0		6.5		4.0	
Fuel flow, ml/min.	5.0[1]		7.5[1]		6.0[2]	
Wavelength, Angstroms	2536		2176		1937	
Lamp current, ma.	10		20		16	
Slit setting	4		3		3	
Scale expansion	1		1		1	
Meter response	1		1		1	
	ppm		ppm		ppm	
Standard Solutions	50	15-20	25	30-35	10	12-15
Standard Solutions	100	25-30	50	45-50	20	20-23
Standard Solutions	200	45-50	100	60-67	30	24-27
Standard Solutions	300	55-65	150	69-73	50	28-33
Standard Solutions	400	60-70	200	73-77	100	30-35

[1] Acetylene

[2] Hydrogen

Standard Analytical Procedure for

Mercury Sulfide Samples

1) Weigh out 1.0000 gram of sample.
2) Place in 50 milliliter culture tube:
   a) Add 1 milliliter of water
   b) Add 4 milliliter of concentrated nitric acid and heat at 60°C for 5 minutes.
   c) Cool and add 4 milliliters of concentrated hydrochloric acid.
3) Heat below boiling for 60 minutes in a water bath (about 60°C), while stirring with magnetic stirrers.
4) Cool and bring to about 20 milliliters or dilute to 100 milliliters and take required aliquot.
5) Make neutral with ammonium hydroxide and add 5 milliliters in excess (10 ml total).
6) Add 1 milliliter potassium iodide.
7) Add exactly 10.0 milliliters methyl isobutyl ketone (MIBK).
8) Mix for about 1 minute and then centrifuge.
9) Analyze on AA-303 for mercury.

Dilution Requirements

Percent, mercury	Sample, gram	Dilution Factor
20 to 80	1.0000	5000
5 to 20	1.0000	1000
1 to 5	1.0000	200
0.25 to 1	1.0000	100
less than 0.25	1.0000	10

Standard Analytical Procedure for Complex Samples

This procedure is satisfactory for antimony, mercury-antimony, mercury-antimony-arsenic, mercury-arsenic, or antimony-arsenic sulfide samples.

1) Weigh out 1.0000 gram of sample.

2) Place in 50 milliliter culture tube:

   a) Add 1 milliliter of water.
   b) Add 4 milliliters of concentrated nitric acid and heat at 60°C for 5 minutes.
   c) Cool and add 4 milliliters of concentrated hydrochloric acid.

3) Heat below boiling for 60 minutes in a water bath (about 60°C), while stirring with magnetic stirrers.

4) Cool and transfer to 100 milliliter graduate, with a solution of 1 percent tartaric acid and 10 percent nitric acid.

5) Take required aliquot for mercury analysis.

6) Use remainder for antimony and/or arsenic analysis by taking aliquot and diluting with tartaric-nitric solution (1 percent tartaric acid, 10 percent nitric acid) as required.

7) Analyze on AA-303 for required elements.

Dilution Requirements

Percent, antimony or arsenic	Sample, gram	Dilution Factor
10 to 80	1.0000	10,000
1 to 10	1.0000	1,000
less than 1	1.0000	100

APPENDIX B

- Thermogravimetric Data -

The tabulated data listed in this appendix represent the chart readings as interpreted from the TGA recorder graphs and punched on IBM cards for use in determining the differential weight loss with respect to time and temperature. The data from the thermogravimetric weight loss graph times the chart span gives the sample weight in milligrams for each time interval. All tests conducted with vacuum were obtained from an air atmosphere.

```
TABLE B-1.    TGA DATA FOR CALCIUM OXALATE IN AIR
              HEATING RATE = 20 DEGRESS PER MINUTE
              AIR FLOW RATE = 0.07 LITER PER MINUTE


DATA   INTER     CHART    INITIAL    FINAL
POINTS -VAL.     SPAN.    TEMP..     TEMP..
       MIN.       MG.       C          C
 8     1.0       4.00     700.00     839.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
           FOR EACH TIME INTERVAL
     0.678      0.670      0.628      0.570
     0.490      0.405      0.377      0.375
```

```
TABLE B-2.    TGA DATA FOR CALCIUM CARBONATE IN AIR
              HEATING RATE = 5 DEGRESS PER MINUTE
              AIR FLOW RATE = 0.02 LITER PER MINUTE


DATA   INTER     CHART    INITIAL    FINAL
POINTS -VAL.     SPAN.    TEMP..     TEMP..
       MIN.       MG.       C          C
32     1.0       4.00     580.00     740.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
           FOR EACH TIME INTERVAL
    0.935      0.935      0.935      0.935
    0.930      0.928      0.924      0.918
    0.912      0.905      0.895      0.884
    0.870      0.851      0.828      0.808
    0.780      0.754      0.720      0.687
    0.645      0.605      0.558      0.508
    0.458      0.408      0.358      0.308
    0.260      0.255      0.255      0.255
```

```
TABLE B-3.    TGA DATA FOR MERCURY SULFIDE CONC. IN AIR
              HEATING RATE = 20 DEGRESS PER MINUTE
              AIR FLOW RATE = 0.07 LITER PER MINUTE


DATA   INTER     CHART    INITIAL    FINAL
POINTS -VAL.     SPAN.    TEMP..     TEMP..
       MIN.       MG.       C          C
16     1.0       20.00    286.00     529.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
           FOR EACH TIME INTERVAL
     0.955      0.955      0.954      0.952
     0.945      0.933      0.890      0.794
     0.595      0.420      0.250      0.070
     0.020      0.019      0.017      0.016
```

```
TABLE B-4.    TGA DATA FOR MERCURY SULFIDE CONC. IN AIR
              HEATING RATE = 5 DEGRESS PER MINUTE
              AIR FLOW RATE = 0.07 LITER PER MINUTE


DATA   INTER     CHART    INITIAL    FINAL
POINTS -VAL.     SPAN.    TEMP..     TEMP..
       MIN.       MG.       C          C
36     1.0       4.00     254.00     403.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
           FOR EACH TIME INTERVAL
     0.988      0.988      0.987      0.986
     0.984      0.982      0.980      0.976
     0.971      0.965      0.960      0.954
     0.945      0.933      0.926      0.910
     0.890      0.870      0.847      0.819
     0.785      0.736      0.680      0.616
     0.530      0.444      0.350      0.263
     0.194      0.148      0.134      0.133
     0.132      0.131      0.130      0.130
```

```
TABLE B-5.    TGA DATA FOR MERCURY SULFIDE CONC. IN VACUUM
              HEATING RATE = 5 DEGRESS PER MINUTE
              VACUUM = 300 TORR


DATA   INTER     CHART    INITIAL   FINAL
POINTS -VAL,     SPAN,    TEMP.,    TEMP.,
        MIN.      MG.       C         C
40     1.0       4.00     260.00    426.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
            FOR EACH TIME INTERVAL
      0.876      0.876      0.875      0.874
      0.872      0.870      0.866      0.862
      0.858      0.850      0.843      0.835
      0.825      0.815      0.799      0.781
      0.762      0.741      0.708      0.675
      0.630      0.580      0.522      0.460
      0.388      0.315      0.250      0.200
      0.167      0.158      0.150      0.146
      0.140      0.138      0.136      0.135
      0.134      0.132      0.130      0.129
```

```
TABLE B-6.    TGA DATA FOR MERCURY SULFIDE CONC. IN AIR
              HEATING RATE = 5 DEGRESS PER MINUTE
              AIR FLOW RATE = 0.06 LITER PER MINUTE


DATA   INTER     CHART    INITIAL   FINAL
POINTS -VAL,     SPAN.    TEMP.,    TEMP.,
        MIN.      MG.       C         C
32     1.0       4.00     275.00    425.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
            FOR EACH TIME INTEPVAL
      0.975      0.973      0.970      0.965
      0.960      0.954      0.946      0.936
      0.922      0.912      0.894      0.874
      0.850      0.820      0.785      0.747
      0.685      0.620      0.540      0.440
      0.340      0.250      0.190      0.160
      0.150      0.145      0.141      0.140
      0.138      0.137      0.136      0.135
```

```
TABLE B-7.    TGA DATA FOR MERCURY SULFIDE IN AIR
              HEATING RATE = 5 DEGRESS PER MINUTE
              AIR FLOW RATE = 0.06 LITER PER MINUTE


DATA   INTER     CHART    INITIAL   FINAL
POINTS -VAL.     SPAN,    TEMP.,    TEMP.,
        MIN.      MG.       C         C
36     1.00      4.00     260.00    403.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
            FOR EACH TIME INTERVAL
      0.972      0.971      0.970      0.968
      0.967      0.966      0.965      0.962
      0.958      0.953      0.944      0.938
      0.929      0.915      0.902      0.886
      0.863      0.839      0.812      0.772
      0.724      0.655      0.608      0.530
      0.440      0.367      0.290      0.230
      0.186      0.164      0.150      0.133
      0.128      0.123      0.121      0.120
```

```
TABLE B-8.    TGA DATA FOR MERCURY SULFIDE IN AIR
              HEATING RATE = 5 DEGRESS PER MINUTE
              AIR FLOW RATE = 0.02 LITER PER MINUTE


DATA   INTER     CHART    INITIAL   FINAL
POINTS -VAL,     SPAN,    TEMP.,    TEMP.,
        MIN.      MG.       C         C
10     5.00      4.00     250.00    476.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
            FOR EACH TIME INTERVAL
      0.960      0.954      0.939      0.888
      0.756      0.430      0.170      0.121
      0.115      0.113
```

TABLE B-9. TGA DATA FOR MERCURY SULFIDE IN AIR
HEATING RATE = 5 DEGRESS PER MINUTE
AIR FLOW RATE NONE

DATA POINTS	INTER -VAL. MIN.	CHART SPAN. MG.	INITIAL TEMP., C	FINAL TEMP., C
32	1.00	4.00	282.00	416.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
FOR EACH TIME INTERVAL

0.970	0.969	0.966	0.962
0.960	0.957	0.951	0.942
0.938	0.925	0.914	0.898
0.886	0.863	0.835	0.775
0.731	0.690	0.638	0.580
0.533	0.510	0.467	0.416
0.360	0.300	0.255	0.225
0.212	0.211	0.210	0.210

TABLE B-10. TGA DATA FOR MERCURY SULFIDE IN VACUUM
HEATING RATE = 5 DEGRESS PER MINUTE
VACUUM = 240 TORR

DATA POINTS	INTER -VAL. MIN.	CHART SPAN. MG.	INITIAL TEMP., C	FINAL TEMP., C
28	1.00	4.00	265.50	383.80

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
FOR EACH TIME INTERVAL

0.933	0.933	0.933	0.931
0.929	0.927	0.923	0.918
0.912	0.903	0.892	0.877
0.861	0.834	0.808	0.773
0.730	0.679	0.628	0.550
0.470	0.390	0.310	0.230
0.183	0.160	0.150	0.150

TABLE B-11. TGA DATA FOR MERCURY SULFIDE IN AIR
HEATING RATE = 5 DEGRESS PER MINUTE
AIR FLOW RATE = 0.02 LITER PER MINUTE

DATA POINTS	INTER -VAL. MIN.	CHART SPAN. MG.	INITIAL TEMP., C	FINAL TEMP., C
36	1.00	4.00	257.00	405.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
FOR EACH TIME INTERVAL

0.985	0.983	0.981	0.979
0.977	0.974	0.972	0.969
0.963	0.959	0.952	0.945
0.938	0.928	0.915	0.900
0.885	0.864	0.842	0.814
0.782	0.732	0.680	0.610
0.522	0.421	0.322	0.210
0.120	0.060	0.024	0.015
0.010	0.009	0.007	0.005

TABLE B-12. TGA DATA FOR MERCURY SULFIDE CONC. IN AIR
HEATING RATE = 20 DEGRESS PER MINUTE
AIR FLOW RATE = 0.02 LITER PER MINUTE

DATA POINTS	INTER -VAL. MIN.	CHART SPAN. MG.	INITIAL TEMP., C	FINAL TEMP., C
16	1.00	4.00	234.00	494.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
FOR EACH TIME INTERVAL

5.000	4.998	4.996	4.994
4.986	4.976	4.933	4.844
4.640	4.280	3.400	2.315
1.260	0.305	0.195	0.193

TABLE B-13. TGA DATA FOR MERCURY SULFIDE CONC. IN AIR
HEATING RATE = 5 DEGRESS PER MINUTE
AIR FLOW RATE = 0.02 LITER PER MINUTE

DATA POINTS	INTER -VAL. MIN.	CHART SPAN. MG.	INITIAL TEMP.. C	FINAL TEMP.. C
12	5.00	4.00	244.00	450.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
FOR EACH TIME INTERVAL

4.905	4.895	4.875	4.820
4.705	4.425	3.540	2.040
0.430	0.245	0.240	0.238

TABLE B-14. TGA DATA FOR MERCURY SULFIDE CONC. IN VACUUM
HEATING RATE = 5 DEGRESS PER MINUTE
VACUUM = 40 TORR

DATA POINTS	INTER -VAL. MIN.	CHART SPAN. MG.	INITIAL TEMP.. C	FINAL TEMP.. C
28	1.00	4.00	269.00	381.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
FOR EACH TIME INTERVAL

0.970	0.969	0.966	0.960
0.950	0.940	0.924	0.905
0.888	0.863	0.836	0.805
0.772	0.730	0.675	0.622
0.555	0.482	0.410	0.352
0.281	0.227	0.187	0.164
0.158	0.156	0.155	0.155

TABLE B-15. TGA DATA FOR MERCURY SULFIDE CONC. IN NITROGEN
HEATING RATE = 5 DEGRESS PER MINUTE
NITROGEN FLOW RATE = 0.02 LITER PER MINUTE

DATA POINTS	INTER -VAL. MIN.	CHART SPAN. MG.	INITIAL TEMP.. C	FINAL TEMP.. C
52	1.00	2.00	210.00	425.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
FOR EACH TIME INTERVAL

4.917	4.917	4.916	4.915
4.914	4.912	4.911	4.910
4.909	4.908	4.907	4.906
4.901	4.899	4.891	4.888
4.880	4.876	4.867	4.860
4.848	4.831	4.819	4.800
4.778	4.750	4.721	4.687
4.643	4.598	4.540	4.480
4.408	4.320	4.210	4.080
3.880	3.700	3.508	3.290
3.050	2.720	2.456	2.180
1.762	1.450	1.072	0.650
0.300	0.054	0.048	0.045

TABLE B-16. TGA DATA FOR MERCURY SULFIDE CONC. IN AIR
HEATING RATE = 5 DEGRESS PER MINUTE
AIR FLOW RATE NONE

DATA POINTS	INTER -VAL. MIN.	CHART SPAN. MG.	INITIAL TEMP.. C	FINAL TEMP.. C
36	1.00	2.00	271.00	427.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
FOR EACH TIME INTERVAL

5.890	5.888	5.885	5.882
5.879	5.876	5.872	5.865
5.860	5.850	5.838	5.825
5.810	5.783	5.760	5.725
5.683	5.630	5.560	5.470
5.340	5.180	4.930	4.670
4.410	4.130	3.700	3.370
3.020	2.500	2.100	1.580
1.250	0.910	0.908	0.905

TABLE B-17. TGA DATA FOR MERCURY SULFIDE CONC. IN NITROGEN
HEATING RATE = 5 DEGRESS PER MINUTE
NITROGEN FLOW RATE = 0.02 LITER PER MINUTE
ONE EQUIVILENT OF IRON MIXED IN CHARGE

DATA POINTS	INTER-VAL, MIN.	CHART SPAN, MG.	INITIAL TEMP., C	FINAL TEMP., C
36	1.00	2.00	243.00	397.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
FOR EACH TIME INTERVAL

2.910	2.908	2.907	2.905
2.900	2.895	2.885	2.874
2.858	2.840	2.820	2.796
2.767	2.736	2.696	2.659
2.610	2.563	2.510	2.454
2.390	2.310	2.230	2.130
2.020	1.850	1.690	1.524
1.330	1.130	0.850	0.640
0.403	0.180	0.060	0.058

TABLE B-18. TGA DATA FOR ANTIMONY SULFIDE CONC. IN AIR
HEATING RATE = 5 DEGRESS PER MINUTE
AIR FLOW RATE = 0.02 LITER PER MINUTE

DATA POINTS	INTER-VAL, MIN.	CHART SPAN, MG.	INITIAL TEMP., C	FINAL TEMP., C
15	5.00	2.00	243.20	538.30

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
FOR EACH TIME INTERVAL

0.920	0.916	0.910	0.895
0.874	0.818	0.726	0.652
0.613	0.471	0.462	0.448
0.410	0.343	0.306	

TABLE B-19. TGA DATA FOR ANTIMONY SULFIDE CONC. IN AIR
HEATING RATE = 5 DEGRESS PER MINUTE
AIR FLOW RATE NONE

DATA POINTS	INTER-VAL, MIN.	CHART SPAN, MG.	INITIAL TEMP., C	FINAL TEMP., C
66	1.00	2.00	278.00	575.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
FOR EACH TIME INTERVAL

0.980	0.976	0.970	0.965
0.954	0.948	0.942	0.937
0.930	0.920	0.911	0.900
0.883	0.877	0.848	0.827
0.803	0.778	0.750	0.720
0.694	0.666	0.640	0.616
0.593	0.575	0.556	0.540
0.530	0.518	0.510	0.504
0.470	0.320	0.293	0.288
0.282	0.281	0.280	0.280
0.280	0.280	0.280	0.280
0.280	0.280	0.280	0.280
0.270	0.258	0.244	0.230
0.215	0.200	0.188	0.170
0.150	0.133	0.111	0.090
0.070	0.050	0.030	0.010
-0.012	-0.022		

TABLE B-20. TGA DATA FOR ANTIMONY TRISULFIDE IN AIR
HEATING RATE = 5 DEGRESS PER MINUTE
AIR FLOW RATE = 0.02 LITER PER MINUTE

DATA POINTS	INTER-VAL, MIN.	CHART SPAN, MG.	INITIAL TEMP., C	FINAL TEMP., C
16	5.00	2.00	226.50	565.30

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
FOR EACH TIME INTERVAL

0.977	0.960	0.955	0.940
0.911	0.822	0.512	0.458
0.425	0.400	0.391	0.377
0.354	0.309	0.290	0.280

```
TABLE B-21.  TGA DATA FOR ANTIMONY SULFIDE CONC. IN AIR
             HEATING RATE = 5 DEGRESS PER MINUTE
             AIR FLOW RATE = 0.02 LITER PER MINUTE
             SAMPLE GROUND TO A FINER SIZE


DATA   INTER     CHART   INITIAL    FINAL
POINTS -VAL,     SPAN,   TEMP.,     TEMP.,
        MIN.      MG.      C          C
88     1.00      2.00    243.00     381.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
           FOR EACH TIME INTERVAL
     0.950     0.950     0.950     0.949
     0.949     0.948     0.948     0.947
     0.946     0.945     0.943     0.941
     0.939     0.937     0.934     0.931
     0.928     0.925     0.921     0.916
     0.911     0.907     0.901     0.894
     0.890     0.886     0.878     0.873
     0.865     0.857     0.851     0.830
     0.802     0.580     0.572     0.568
     0.562     0.555     0.550     0.547
     0.541     0.534     0.528     0.525
     0.521     0.518     0.512     0.509
     0.508     0.506     0.502     0.498
     0.496     0.495     0.494     0.493
     0.491     0.489     0.488     0.486
     0.482     0.481     0.480     0.478
     0.475     0.469     0.464     0.462
     0.455     0.445     0.441     0.434
     0.430     0.418     0.410     0.400
     0.392     0.383     0.377     0.370
     0.368     0.367     0.366     0.366
     0.366     0.366
```

```
TABLE B-22.  TGA DATA FOR ANTIMONY SULFIDE CONC. IN AIR
             HEATING RATE = 5 DEGRESS PER MINUTE
             AIR FLOW RATE = 0.02 LITER PER MINUTE

DATA   INTER     CHART   INITIAL    FINAL
POINTS -VAL,     SPAN,   TEMP.,     TEMP.,
        MIN.      MG.      C          C
52     1.00      2.00    222.00     452.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
           FOR EACH TIME INTERVAL
     1.000     0.999     0.998     0.996
     0.995     0.994     0.993     0.992
     0.990     0.986     0.983     0.980
     0.976     0.970     0.965     0.963
     0.956     0.946     0.939     0.932
     0.924     0.913     0.899     0.872
     0.840     0.730     0.556     0.530
     0.519     0.506     0.489     0.465
     0.444     0.418     0.394     0.363
     0.340     0.300     0.272     0.250
     0.230     0.215     0.200     0.190
     0.177     0.150     0.122     0.084
     0.068     0.058     0.053     0.050
```

```
TABLE B-23.  TGA DATA FOR ANTIMONY SULFIDE CONC. IN VACUUM
             HEATING RATE = 5 DEGRESS PER MINUTE
             VACUUM = 30 TORR

DATA   INTER     CHART   INITIAL    FINAL
POINTS -VAL,     SPAN,   TEMP.,     TEMP.,
        MIN.      MG.      C          C
16     5.00      2.00    268.00     621.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
           FOR EACH TIME INTERVAL
     6.360     6.352     6.341     6.322
     6.273     6.202     6.120     6.020
     5.880     5.310     4.620     3.650
     2.160     1.510     0.730     0.685
```

TABLE 8-24. TGA DATA FOR ANTIMONY SULFIDE CONC. IN NITROGEN
HEATING RATE = 5 DEGRESS PER MINUTE
NITROGEN FLOW RATE = 0.02 LITER PER MINUTE

DATA POINTS	INTER -VAL, MIN.	CHART SPAN, MG.	INITIAL TEMP., C	FINAL TEMP., C
72	1.00	2.00	388.00	719.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
FOR EACH TIME INTERVAL

3.898	3.897	3.896	3.895
3.894	3.892	3.891	3.889
3.888	3.887	3.884	3.880
3.877	3.874	3.871	3.868
3.865	3.861	3.853	3.849
3.844	3.840	3.830	3.820
3.817	3.810	3.805	3.798
3.795	3.790	3.785	3.780
3.775	3.770	3.765	3.760
3.752	3.744	3.737	3.728
3.715	3.703	3.691	3.672
3.660	3.640	3.620	3.595
3.564	3.540	3.500	3.460
3.418	3.370	3.300	3.242
3.175	3.080	2.910	2.730
2.540	2.340	2.126	1.770
1.480	1.173	0.725	0.415
0.118	0.042	0.040	0.039

TABLE 8-25. TGA DATA FOR ARSENIC SULFIDE CONC. IN AIR
HEATING RATE = 5 DEGRESS PER MINUTE
AIR FLOW RATE = 0.02 LITER PER MINUTE

DATA POINTS	INTER -VAL, MIN.	CHART SPAN, MG.	INITIAL TEMP., C	FINAL TEMP., C
56	1.00	2.00	193.00	436.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
FOR EACH TIME INTERVAL

4.195	4.194	4.193	4.192
4.191	4.190	4.188	4.185
4.181	4.175	4.168	4.160
4.150	4.140	4.122	4.101
4.076	4.050	4.017	3.980
3.930	3.875	3.820	3.740
3.660	3.560	3.545	3.535
3.525	3.518	3.504	3.488
3.475	3.200	2.955	2.720
2.480	2.141	1.900	1.680
1.538	1.345	1.230	1.100
0.925	0.787	0.630	0.450
0.260	0.175	0.165	0.163
0.161	0.159	0.155	0.153

```
TABLE B-26.  TGA DATA FOR ARSENIC TRIOXIDE IN AIR
             HEATING RATE = 5 DEGRESS PER MINUTE
             AIR FLOW RATE = 0.02 LITER PER MINUTE


DATA   INTER    CHART   INITIAL   FINAL
POINTS -VAL,    SPAN,   TEMP..    TEMP..
       MIN.     MG.       C         C
36     1.00     2.00    136.50    299.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
          FOR EACH TIME INTERVAL
     5.600     5.598     5.595     5.590
     5.585     5.580     5.570     5.558
     5.540     5.518     5.494     5.455
     5.410     5.356     5.290     5.200
     5.100     4.980     4.830     4.612
     4.406     4.192     3.960     3.580
     3.230     2.891     2.310     1.880
     1.210     0.700     0.120     0.040
     0.039     0.038     0.037     0.036

TABLE B-27.  TGA DATA FOR ARSENIC SULFIDE CONC. IN AIR
             HEATING RATE = 5 DEGRESS PER MINUTE
             AIR FLOW RATE NONE


DATA   INTER    CHART   INITIAL   FINAL
POINTS -VAL.    SPAN,   TEMP.,    TEMP.,
       MIN.     MG.       C         C
68     1.00     2.00    190.00    485.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
          FOR EACH TIME INTERVAL
     6.328     6.326     6.324     6.322
     6.320     6.319     6.318     6.316
     6.312     6.308     6.300     6.290
     6.280     6.267     6.258     6.225
     6.198     6.165     6.122     6.080
     6.025     5.965     5.893     5.806
     5.722     5.626     5.560     5.510
     5.488     5.476     5.468     5.460
     5.453     5.449     5.440     5.434
     5.425     5.418     5.409     5.397
     5.384     5.357     5.320     5.293
     5.262     5.180     5.094     5.050
     4.990     4.920     4.800     4.676
     4.540     4.327     4.105     3.848
     3.480     2.940     2.460     1.828
     1.200     0.755     0.350     0.268
     0.266     0.265     0.264     0.263
```

```
TABLE B-28.  TGA DATA FOR ARSENIC SULFIDE CONC. IN VACUUM
             HEATING RATE = 5 DEGRESS PER MINUTE
             VACUUM = 55 TORR


DATA   INTER    CHART   INITIAL   FINAL
POINTS -VAL.    SPAN,   TEMP.,    TEMP..
       MIN.     MG.       C         C
50     1.00     2.00    181.00    401.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
          FOR EACH TIME INTERVAL
     4.980     4.979     4.977     4.975
     4.971     4.968     4.962     4.954
     4.946     4.935     4.918     4.898
     4.874     4.845     4.806     4.758
     4.695     4.624     4.533     4.440
     4.304     4.170     3.930     3.733
     3.480     3.222     2.860     2.630
     2.570     2.540     2.516     2.490
     2.465     2.435     2.400     2.360
     2.308     2.240     2.160     1.350
     1.020     0.680     0.570     0.470
     0.360     0.270     0.200     0.188
     0.180     0.179       .         .

TABLE B-29.  TGA DATA FOR ARSENIC SULFIDE CONC. IN NITROGEN
             HEATING RATE = 5 DEGRESS PER MINUTE
             NITROGEN FLOW RATE = 0.02 LITER PER MINUTE


DATA   INTER    CHART   INITIAL   FINAL
POINTS -VAL.    SPAN.   TEMP.,    TEMP..
       MIN.     MG.       C         C
52     1.00     2.00    218.00    436.00

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
          FOR EACH TIME INTERVAL
     3.920     3.918     3.916     3.913
     3.910     3.902     3.893     3.883
     3.872     3.857     3.838     3.815
     3.786     3.752     3.710     3.660
     3.600     3.532     3.475     3.410
     3.335     3.260     3.160     3.070
     2.950     2.870     2.803     2.754
     2.670     2.603     2.540     2.490
     2.420     2.360     2.287     2.190
     2.090     1.940     1.810     1.673
     1.510     1.310     1.090     0.640
     0.400     0.240     0.140     0.128
     0.124     0.123     0.122     0.121
```

```
TABLE B-30.  TGA DATA FOR ARSENIC SULFIDE CONC. IN NITROGEN
             HEATING RATE = 5 DEGRESS PER MINUTE
             NITROGEN FLOW RATE = 0.02 LITER PER MINUTE
             ONE EQUIVILENT OF IRON MIXED IN CHARGE


DATA    INTER     CHART   INITIAL   FINAL
POINTS -VAL.      SPAN,   TEMP.,    TEMP.,
        MIN.      MG.       C         C
32     1.00       2.00    203.30    331.50

DATA FROM THERMOGRAVIMETRIC WEIGHT LOSS GRAPH
           FOR EACH TIME INTERVAL
     3.909     3.908     3.906     3.903
     3.901     3.898     3.894     3.890
     3.880     3.865     3.850     3.826
     3.800     3.770     3.736     3.700
     3.650     3.600     3.540     3.470
     3.398     3.320     3.245     3.160
     3.050     2.850     2.675     2.440
     2.160     1.700     1.620     1.619
```

APPENDIX C

Computer Programs

The three programs listed in this appendix are in the order used. Instructions necessary for preparing the control and data cards for each of these programs are listed before the main- and sub-programs of each. A listing of the main- and sub-programs is then shown, followed by the printout of the input and output data. Each program has been prepared so that a wide range of TGA data can be used.

The figure shown for the TGA3 program is as plotted by the IBM 1620 computer-plotter. All TGA plot figures shown in the text were traced from similar computer plots. These have the same style of lettering and additional information could be added.

Tables C-1 and C-2 contain the tabulated data for the TGA runs and the regression analyses results from the TGA2 printout. Activation energies for all runs are listed in the extreme right of the two tables.

PART ONE

TGA1 INSTRUCTIONS

PART ONE OF THIS PROGRAM CALCULATES DA/DT FROM A FIVE POINT APPROXIMATION AND PREPARES THE DATA CARDS FOR THE OTHER TWO PROGRAMS. THIS PROGRAM CAN BE RUN UNDER BUFF40 OR FORTRAN.

```
  COLUMN '1'   '7'             COMMENTS ARE INCLOSED IN BRACKETS,(ETC.)
          // JOB NAME,ACCONT  (NAME MAY BE UP TO 8 LETTERS LONG)
                              (ACCOUNT INDICATES WHO TO CHARGE 6 LETTERS)
          // EXEC BUFF40
          $COMPILE
                DO 5 I=1,N    (N EQUALS NUMBER OF SETS OF DATA USED)
              5 CALL TGA1
                STOP
                END
  SUBROUTINE TGA1 GOES HERE IF NOT IN COMPUTER LIBRARY
          $EXECUTE
          DATA                (ENTER DATA HERE SO AS TO EXECUTE TGA1)
          $COMPILEX
          /+
```

DATA CARDS REQUIRED ARE AS FOLLOWS, THEY MUST BE IN THE CORRECT ORDER AND EXACT NUMBER.

```
  COLUMN '1'
CARD 1    NN                  (I2, NN EQUALS NUMBER OF DATA POINTS)
C    1      ZZZZZ.ZZ          (2X,F8.2, TIME INTERVAL IN MINUTES)
C    1              ZZZZZZZ.ZZ(10X,F10.2, MILLIGRAMS FULL SCALE ON CHART)
C    1                         ZZZZZZ.ZZ
                              (20X,F10.2, TEMP. OF FIRST DATA POINT)
C    1                                  ZZZZZZZ.ZZ
                              (30X,F10.2, TEMP. OF LAST DATA POINT)
CARD 2    WWWWWW.WWWZZZZZZ.ZZZXXXXXX.XXXVVVVVV.VVV
CARD 2+N  WWWWWW.WWWZZZZZZ.ZZZXXXXXX.XXXVVVVVV.VVV
                              (4F10.3, FOUR BITS OF DATA ON EACH CARD)
```

TGA1 PROGRAM LISTING

```
      DO 5 I=1,12
    5 CALL TGA1
      STOP
      END
      SUBROUTINE TGA1
      DIMENSION F(99),CHART(99),TEMP(99),WEIGHT(99),TIME(99),CWTPER(99),
     1DADT(99),WTCHAN(99)
      READ(1,2)N,TIMINT,SCALE,TEMP1,TEMPN
    2 FORMAT(I2,F8.2,F10.2,F10.2,F10.2)
      WRITE(3,1)
    1 FORMAT('1',T20,'A SUMMARY OF THE DATA READ',/)
      WRITE(3,92)N,TIMINT,SCALE,TEMP1,TEMPN
   92 FORMAT(10X,I2,F8.2,F10.2,F10.2,F10.2)
      READ(1,3)(CHART(I),I=1,N)
    3 FORMAT(4F10.3)
      WRITE(3,93)(CHART(I),I=1,N)
   93 FORMAT(10X,4F10.3)
      H=TIMINT
      XN=N-1
      TEMINT=(TEMPN-TEMP1)/XN
      TEM=TEMP1-TEMINT
      TIM=0.0
      DO 5 I=1,N
      TIM=TIM+TIMINT
      TIME(I)=TIM
      TEM=TEM+TEMINT
      TEMP(I)=TEM
      TWTLOS=(CHART(1)-CHART(N))*SCALE
      F(I)=(SCALE*(CHART(I)-CHART(N)))/TWTLOS
      IF (I.EQ.1) GO TO 4
      WTCHAN(I)=(CHART(I)-CHART(I-1))*SCALE
    4 WTCHAN(1)=0.000
      CWTPER(I)=F(1)-F(I)
    5 WEIGHT(I)=CHART(I)*SCALE
      DO 100 I=1,N
      IF (I.LE.2) GO TO 10
      IF (I.GE.(N-1)) GO TO 10
      DERIV1=(-2.*F(I-2)-F(I-1)+F(I+1)+2.*F(I+2))/(10.*H)
      GO TO 50
   10 IF (I.EQ.1) GO TO 30
      IF (I.EQ.N) GO TO 30
      IF (I.EQ.2) GO TO 20
      DERIV1=-(-11.*F(N)+3.*F(N-1)+7.*F(N-2)+F(N-3))/(20.*H)
      GO TO 50
   20 DERIV1=(-11.*F(1)+3.*F(2)+7.*F(3)+F(4))/(20.*H)
      GO TO 50
   30 IF (I.EQ.1) GO TO 40
      DERIV1=-(-21.*F(N)+13.*F(N-1)+17.*F(N-2)-9.*F(N-3))/(20.*H)
      GO TO 50
   40 DERIV1=(-21.*F(1)+13.*F(2)+17.*F(3)-9.*F(4))/(20.*H)
   50 CONTINUE
      DADT(I)=DERIV1
      WRITE(2,51)DADT(I),CWTPER(I),TEMP(I),TIME(I)
   51 FORMAT(4F15.7)
  100 CONTINUE
      WRITE(3,52)
   52 FORMAT('1',T2,'NO.',T7,'TIME',T13,' CHART ',T22,'WEIGHT',T30,'WEIG
     1HT',T38,'  DA/DT   ',T49,'  F    ',T57,'CWTPER',T65,'TEMP. ',/,T7,'M

     2IN.',T13,'READING',T22,'  MG.',T30,' LOSS',T38,'PER MIN.',T49,'UNI
     3TLES',T57,'UNITLES',T65,' C',/,T30,'  MG ',T57,'ALPHA')
       WRITE(3,53)(I,TIME(I),CHART(I),WEIGHT(I),WTCHAN(I),DADT(I),F(I),
     1CWTPER(I),TEMP(I),I=1,N)
   53 FORMAT(T2,I2,T7,F4.0,T13,F7.3,T22,F6.3,T30,F6.3,T38,F9.5,T49,F6.3,
     1T57,F6.3,T65,F6.1)
   55 CONTINUE
      WRITE(3,54)
   54 FORMAT('1')
      RETURN
      END
```

```
               A  SUMMARY  OF  THE  DATA  READ

 16      1.00          4.00       234.00       494.00
        5.000         4.999        4.996        4.994
        4.986         4.976        4.933        4.844
        4.640         4.280        3.400        2.315
        1.260         0.305        0.195        0.193
```

TGA1 DATA PRINT OUT

```
 NO.   TIME    CHART    WEIGHT   WEIGHT     DA/DT        F     CWTPER   TEMP.
       MIN.   READING    MG.      LOSS    PER MIN.   UNITLES UNITLES    C
                                   MG                         ALPHA
  1      1.     5.000   20.000   0.0      -0.00042    1.000   0.0       234.0
  2      2.     4.999   19.992  -0.008    -0.00042    1.000   0.000     251.3
  3      3.     4.996   19.984  -0.008    -0.00067    0.999   0.001     268.7
  4      4.     4.994   19.976  -0.008    -0.00112    0.999   0.001     286.0
  5      5.     4.986   19.944  -0.032    -0.00300    0.997   0.003     303.3
  6      6.     4.976   19.904  -0.040    -0.00734    0.995   0.005     320.7
  7      7.     4.933   19.732  -0.172    -0.01714    0.986   0.014     338.0
  8      8.     4.844   19.376  -0.356    -0.03505    0.968   0.032     355.3
  9      9.     4.640   18.560  -0.816    -0.07551    0.925   0.075     372.7
 10     10.     4.280   17.120  -1.440    -0.13102    0.850   0.150     390.0
 11     11.     3.400   13.600  -3.520    -0.13151    0.667   0.333     407.3
 12     12.     2.315    9.260  -4.340    -0.20990    0.441   0.559     424.7
 13     13.     1.260    5.040  -4.220    -0.17516    0.222   0.778     442.0
 14     14.     0.305    1.220  -3.820    -0.11044    0.023   0.977     459.3
 15     15.     0.195    0.780  -0.440    -0.01932    0.000   1.000     476.7
 16     16.     0.193    0.772  -0.008     0.07981    0.0     1.000     494.0
```

PART TWO

TGA2 INSTRUCTIONS

PART TWO OF THIS PROGRAM CALCULATES THE BEST FIT FOR THE FOLLOWING EQUATION, LN(DADT)=LN(A)+N*(LN(1.-ALPHA))+(E/R)*(1./T) OR DA/DT=A*(1.-ALPHA)**N*EXP((E/R)*(1./T)). IN THE EQUATION (1.-ALPHA)**N REPRESENTS THE CORRECTION FACTOR FOR THE WEIGHT LOSS AS THE REACTION PROCEEDS, DA/DT THE PERCENT WEIGHT LOSS PER UNIT TIME, 'A' THE CONSTANT, 'N' DIVIDED BY'R' THE SLOPE, AND '1' DIVIDED BY 'T' THE RECIPROCAL OF TEMP. IN DEGREES K.

```
A SIMPLIFIED FORM OF THE EQUATION WOULD BE, Y=M*X+B
     WHERE,    Y=LN(DADT/Z)    B=CONSTANT LNA
               M=(-E/R)        Z=(1.-ALPHA)**N
               X=1./T
```

DATA CARD VALUES

CARDS MUST BE CHECKED TO SEE THAT NO ZERO VALUES FOR DADT OR 1.00000 VALUES OF ALPHA ARE USED. BECAUSE NATURAL LOG OF ZERO IS IMPOSSIBLE, NEGATIVE VALUES HAVE BEEN CORRECTED IN BOTH TGA2 AND TGA3 PROGRAMS. CHECK TGA1 PRINT OUT, PULL ZERO AND ONE CARDS AND CORRECT FOR NO. OF DATA CARDS USED IN TGA2 AND TGA3. THE FOLLOWING CARDS ARE REQUIRED FOR USING PROGRAM BMD02R

```
  COLUMN '1'
CARD 1     // JOB NAME,ACCONT  (NAME MAY BE UP TO 8 LETTERS LONG)
                               (ACCOUNT INDICATES WHO TO CHARGE 6 LETTERS)
CARD 2     // EXEC BMD02R
CARD 3     PROBLM              (COLUMNS  1 TO 6)
C     3    TGA2                (COLUMNS 10 TO 15)
C     3    NN                  (COLUMNS 19 AND 20, NO. OF DATA CARDS)
C     3    03                  (COLUMNS 24 AND 25, NO. OF VARIABLES)
C     3    07                  (COLUMNS 29 AND 30, NO. OF TRNGEN CARDS)
C     3    00                  (COLUMNS 34 AND 35, NO. OF VARIABLES ADDED)
C     3    01                  (COLUMNS 44 AND 45, NO. OF SOLUTIONS)
C     3    03                  (COLUMNS 48 AND 49. TOTAL VARIABLES IN PROB.)
C     3    YES                 (COLUMNS 51 TO 53, CONTROL-DELETE CARD)
C     3    YES                 (COLUMNS 59 TO 61, SUMMARY TABLE PRINT)
CARD 4     TRNGEN00109001-1.000     (REQUIRED TO PUT DATA IN PROPER FORMAT)
CARD 5     TRNGEN00117001000000     (REQUIRED TO PUT DATA IN PROPER FORMAT)
CARD 6     TRNGEN00209002-1.000     (REQUIRED TO PUT DATA IN PROPER FORMAT)
CARD 7     TRNGEN002080021.0000     (REQUIRED TO PUT DATA IN PROPER FORMAT)
CARD 8     TRNGEN00217002000000     (REQUIRED TO PUT DATA IN PROPER FORMAT)
CARD 9     TRNGEN00308003273.20     (REQUIRED TO PUT DATA IN PROPER FORMAT)
CARD10     TRNGEN00307003000000     (REQUIRED TO PUT DATA IN PROPER FORMAT)
CARD11     LABELS0001DADTLN    (NAMES 'Y' VARIABLE)
CARD12     LABELS0002SMALLN    (NAMES SMALL 'N')
CARD13     LABELS0003SLOPE     (NAMES SLOPE VARIABLE)
CARD14     (3F15.7)            (DATA FORMAT, PUNCHED BY TGA1 PROGRAM)
C       N                      (DATA CARDS GO HERE AND SHOULD EQUAL
                                NUMBER ON CARD 3)
CARD14+N   SUBPRO              (COL. 1 TO 6, CONTROLS PRINT OUT)
C    14+N  01                  (COL. 9 AND 10, NO. DEPENTENT VARIABLES)
C    14+N  02                  (COL. 49 AND 50, VARIABLES ON INDEX PLOT)
C    14+N  YES                 (COL. 53 TO 55, DELETE CARDS INCLUDED)
C    14+N  YES                 (COL. 58 TO 60, PRINT LIST OF RESIDUALS)
C    14+N  YES                 (COL. 63 TO 65, PRINT SUMMARY TABLE)
CARD15+N   CONDEL12            (SEQUENCE FOR SOLVING EQUATION)
CARD16+N   IDXPLT0203          (PLOT PRINT OUT)
CARD17+N   FINISH
CARD18+N   /*
CARD19+N   /+
```

TGA2 DATA PRINT OUT

```
BMD02R - STEPWISE REGRESSION - REVISED JULY 18, 1968
HEALTH SCIENCES COMPUTING FACILITY, UCLA

PROBLEM CODE                     TGA2
NUMBER OF CASES                    13
NUMBER OF ORIGINAL VARIABLES        3
NUMBER OF VARIABLES ADDED           0
TOTAL NUMBER OF VARIABLES           3
NUMBER OF SUB-PROBLEMS              1
THE VARIABLE FORMAT IS      (F15.7,F15.7,F15.7)




  VARIABLE          MEAN        STANDARD DEVIATION
 DADTLN   1       -3.38927            2.29217
 SMALLN   2       -0.52189            1.06941
 SLOPE    3        0.00161            0.00017


CORRELATION MATRIX

VARIABLE       1          2          3
 NUMBER

    1        1.000     -0.457     -0.970
    2                   1.000      0.646
    3                              1.000


SUB-PROBLEM      1
 DEPENDENT VARIABLE             1
 MAXIMUM NUMBER OF STEPS        6
 F-LEVEL FOR INCLUSION     0.010000
 F-LEVEL FOR DELETION      0.005000
 TOLERANCE LEVEL           0.001000
```

```
   STEP NUMBER    1
   VARIABLE ENTERED    3

   MULTIPLE R                 0.9700
   STD. ERROR OF EST.         0.5821

   ANALYSIS OF VARIANCE
                          DF    SUM OF SQUARES    MEAN SQUARE    F RATIO
           REGRESSION      1           59.321          59.321    175.068
           RESIDUAL       11            3.727           0.339 .

                    VARIABLES IN EQUATION                   .                  VARIABLES NOT IN EQUATION
                                                            .
     VARIABLE       COEFFICIENT  STD. ERROR  F TO REMOVE    .     VARIABLE    PARTIAL CORR.     TOLERANCE    F TO ENTER
                                                            .
                                                            .
     (CONSTANT         16.45111 )                           .
    SLOPE   3     -12709.51172   960.56030    175.0687 (2)  .    SMALLN  2        0.91363         0.5830       50.5030 (2)


   STEP NUMBER    2
   VARIABLE ENTERED    2

   MULTIPLE R                 0.9951
   STD. ERROR OF EST.         0.2482

   ANALYSIS OF VARIANCE
                          DF    SUM OF SQUARES    MEAN SQUARE    F RATIO
           REGRESSION      2           62.433          31.216    506.713
           RESIDUAL       10            0.616           0.062

                    VARIABLES IN EQUATION                   .                  VARIABLES NOT IN EQUATION
                                                            .
     VARIABLE       COEFFICIENT  STD. ERROR  F TO REMOVE    .     VARIABLE    PARTIAL CORR.     TOLERANCE    F TO ENTER
                                                            .
                                                            .
     (CONSTANT         20.73543 )                           .
    SMALLN  2          0.62358     0.08775     50.5030 (2)  .
    SLOPE   3     -15171.07813   536.40552    799.9197 (2)  .

F-LEVEL OR TOLERANCE INSUFFICIENT FOR FURTHER COMPUTATION
```

```
SUMMARY TABLE

  STEP             VARIABLE                  MULTIPLE                    INCREASE  .      F VALUE TO     NUMBER OF INDEPENDENT
 NUMBER        ENTERED  REMOVED          R               RSQ              IN RSQ        ENTER OR REMOVE    VARIABLES INCLUDED
        .

    1          SLOPE    3              0.9700          0.9409            0.9409           175.0687                1
    2          SMALLN   2              0.9951          0.9902            0.0493            50.5030                2


  LIST OF RESIDUALS

  CASE          Y                Y
 NUMBER       X( 1)           COMPUTED         RESIDUAL          X( 3)          X( 2)

    1        -7.7841          -8.1878           0.4037           0.0019        -0.0004
    2        -7.3145          -7.2629          -0.0516           0.0018        -0.0008
    3        -6.7915          -6.3953          -0.3962           0.0018        -0.0012
    4        -5.8106          -5.5807          -0.2299           0.0017        -0.0029
    5        -4.9139          -4.8140          -0.1000           0.0017        -0.0050
    6        -4.0663          -4.0951           0.0289           0.0016        -0.0140
    7        -3.3509          -3.4224           0.0715           0.0016        -0.0330
    8        -2.5834          -2.8026           0.2192           0.0015        -0.0778
    9        -2.0324          -2.2413           0.2089           0.0015        -0.1623
   10        -1.7065          -1.8099           0.1034           0.0015        -0.4047
   11        -1.5611          -1.5137          -0.0474           0.0014        -0.8177
   12        -1.7421          -1.4156          -0.3265           0.0014        -1.5052
   13        -2.2033          -2.3193           0.1160           0.0014        -3.7593
```

Table C-1. Regression Analysis of TGA Data for Mercury Activation Energies

Run No.	Sample Description	Test Conditions				Data Points, No.	Interval, min.	Regression Analysis			Activation Energy, Kcal/mole
		Atm.	Flow Rate, L/min.	Heating Rate, °C/min.	Sample Size, mg.			Slope	Small n	Ln A	
1	Calcium Oxalate ($CaCO_3 \rightarrow CaO$)	Air	0.07	20	3.800	8	1.0	-27,627	0.61	25.4	54.9
2	Calcium Carbonate ($CaCO_3 \rightarrow CaO$)	Air	0.02	5	6.160	32	1.0	-30,439	0.48	29.4	60.5
3	Mercury Sulfide Conc.	Air	0.07	20	18.780	16	1.0	-20,939	1.14	29.3	41.6
4	Mercury Sulfide Conc.	Air	0.07	5	3.520	36	1.0	-18,543	0.90	27.7	36.8
5	Mercury Sulfide Conc.	Vac.	300[1]	5	3.040	40	1.0	-19,746	1.32	29.8	39.2
6	Mercury Sulfide Conc.	Air	0.06	5	3.528	32	1.0	-19,809	1.19	29.8	39.3
7	HgS Chemically Pure	Air	0.06	5	3.508	36	1.0	-19,835	0.99	29.8	39.4
8	HgS Chemically Pure	Air	0.02	5	3.448	10	5.0	-14,844	1.09	21.3	29.5
9	HgS Chemically Pure	Air	None	5	3.472	32	1.0	-17,738	0.71	25.6	35.2
10	HgS Chemically Pure	Vac.	240[1]	5	3.296	28	1.9	-21,659	0.75	33.2	43.0
11	HgS Chemically Pure	Air	0.02	5	3.960	36	1.0	-16,110	0.84	23.4	32.0
12	Mercury Sulfide Conc.	Air	0.02	20	19.400	16	1.0	-15,171	0.62	20.7	30.1
13	Mercury Sulfide Conc.	Air	0.02	5	18.800	12	5.0	-15,051	0.49	20.9	29.9
14	Mercury Sulfide Conc.	Vac.	40[1]	5	3.880	28	1.0	-18,517	0.82	28.6	36.8
15	Mercury Sulfide Conc.	N_2	0.02	5	9.820	52	1.0	-12,591	0.25	16.4	25.0
16	Mercury Sulfide Conc.	Air	None	5	13.190	36	1.0	-17,609	0.32	24.1	34.9
17	Mercury Sulfide Conc. + Iron	N_2	0.02	5	7.830	36	1.0	-12,555	0.34	17.3	24.9

[1] Torr

Table C-2. Regression Analysis of TGA Data for Antimony and Arsenic Activation Energies

Run No.	Sample Description	Test Conditions				Data Points, No.	Inter-val, min.	Regression Analysis			Activation Energy, Kcal/mole
		Atm.	Flow Rate, L/min	Heating Rate °C/min.	Sample Size mg.			Slope	Small n	Ln A	
18	Antimony Sulfide Conc.	Air	0.02	5	7.240	15	5.0	-7,164	1.13	7.45	14.2
19	Antimony Sulfide Conc.	Air	None	5	10.500	66	1.0	-4,085	0.53	2.46	8.1
20	Sb_2S_3 Chemically Pure	Air	0.02	5	10.020	16	5.0	-4,282	0.88	3.11	8.5
--	Sample No.20, Less Data	Air	0.02	5	------	18	1.0	-19,261	0.49	29.32	38.5
21	Antimony Sulfide Conc.[1]	Air	0.02	5	8.380	88	1.0	-8,278	0.30	10.56	16.4
22	Antimony Sulfide Conc.[2]	Air	0.02	5	15.100	52	1.0	-9,229	0.76	11.51	18.3
23	Antimony Sulfide Conc.	Vac.	30[3]	5	12.760	16	5.0	-9,279	0.44	8.39	18.4
24	Antimony Sulfide Conc.	N_2	0.02	5	7.810	72	1.0	-11,215	0.08	8.09	22.2
--	Sample No.24, Less Data[4]	N_2	0.02	5	------	37	1.0	-24,121	0.25	22.63	47.9
25	Arsenic Sulfide Conc.	Air	0.02	5	8.380	56	1.0	-10,068	0.77	13.26	20.0
26	As_2O_3 Chemically Pure	Air	0.02	5	11.200	36	1.0	-11,235	0.51	19.44	22.3
27	Arsenic Sulfide Conc.	Air	None	5	12.640	68	1.0	-5,340	0.11	3.78	10.6
28	Arsenic Sulfide Conc.	Vac.	55[3]	5	9.960	50	1.0	-7,626	0.57	9.67	15.1
29	Arsenic Sulfide Conc.	N_2	0.02	5	7.840	52	1.0	-8,320	0.43	10.10	16.5
30	Arsenic Sulfide Conc. + Iron	N_2	0.02	5	7.780	32	1.0	-14,116	0.27	22.09	28.0

[1] Sample ground in a mortar to a finer size.

[2] Run stopped at "B" in figure 10.

[3] Torr

[4] Data taken from point "B"in figure 11.

PART THREE

TGA3 INSTRUCTIONS

PART THREE OF THIS PROGRAM IS TO CALCULATE AND PREPARE THE CARDS FOR PLOTTING ON THE 1620. THE PROGRAM IS RUN UNDER FORTRAN AND THE FOLLOWING CARDS ARE REQUIRED.

DATA CARD VALUES

CARDS MUST BE CHECKED TO SEE THAT NO ZERO VALUES FOR DADT OR 1.00000 VALUES OF ALPHA ARE USED. BECAUSE NATURAL LOG OF ZERO IS IMPOSSIBLE, NEGATIVE VALUES HAVE BEEN CORRECTED IN BOTH TGA2 AND TGA3 PROGRAMS. CHECK TGA1 PRINT OUT, PULL ZERO AND ONE CARDS AND CORRECT FOR NO. OF DATA CARDS USED IN TGA2 AND TGA3.

```
COLUMN '1'   '7'               COMMENTS ARE INCLOSED IN BRACKETS.
        // JOB NAME,ACCOUNT (NAME MAY BE UP TO 8 LETTERS LONG.)
                            (ACCOUNT INDICATES WHO TO CHARGE 6 LETTERS)
        // OPTION LINK
        // EXEC FORTRAN
              CALL TGA3     ( MAIN PROGRAM ONLY CALLS SUBROUTINE)
              STOP
              END
SUBROUTINE TGA3 GOES HERE IF NOT IN COMPUTER LIBRARY
        /*
        // EXEC
      DATA                  (ENTER DATA HERE SO AS TO EXECUTE TGA3)
        /*                  (LEFT JUSTIFY ALL 'A' FORMAT DATA)
        /&
```

```
C COLUMN '1'
CARD 1    + MEASURED RATE     (4A4 FORMAT,CAN BE CHANGED,MAX. 16 SPACES)
CARD 2    O CORRECTED RATE    (4A4 FORMAT,CAN BE CHANGED,MAX. 16 SPACES)
CARD 3    FIGURE (ETC)        (11A4, WRITES FIRST PART OF FIGURE TITLE)
CARD 4    FIGURE TITLE CONT.  (8A4, SECOND LINE OF FIG.,PUT BLANK CARD
                               IF NOT USED, MAX. 32 SPACES)
CARD 5    TEMPERATURE,  K     (4A4, X AXES TITLE, MAX. 16 SPACES)
CARD 6    (1/T SCALE)         (3A4, X AXES SCALE, MAX. 12 SPACES)
CARD 7    RATE OF REACTION,ETC(7A4, Y AXES TITLE, MAX.28 SPACES)
CARD 8    (LOG SCALE)         (3A4, Y AXES SCALE, MAX. 12 SPACES)
CARD 9                        (5I2, TWO SPACES FOR EACH COUNTER)
C    9    ZZ                  (NO. OF DATA VALUES USED,COL. 1&2)
C    9      ZZ                (NO. OF DIVISIONS ON X AXES, MAX. 10)
C    9        ZZ              (NO. OF DIVISIONS ON Y AXES, MAX. 10)
C    9          ZZ            (NO. OF SPACES USED ON CARD 3, MAX. 44)
C    9            ZZ          (NO. OF SPACES USED ON CARD 4, MAX. 32)
CARD10    TEMP VALUES         (10A4, TEMP SCALE'A'FORMAT, LEFT JUSTIFIED
CARD11    RATE VALUES         (10A4, RATE SCALE'A'FORMAT, LEFT JUSTIFIED
CARD12    TEMP SCALE          (10F5.0, VALUES TO CAL. SCALE, RIGHT JUST.
CARD13    RATE SCALE          (10F7.3, VALUES TO CAL. SCALE, RIGHT JUST.
CARD14    +OO                 (3A1, SYMBOLS FOR PLOTTING)
CARD15    ZZ.ZZWW.WW          (2F5.2, LENGTH, INCHES X-AXES AND Y-AXES
CARD16    XXXXXXX.XXXXXXXZZZZZZZ.ZZZZZZZWWWWWWW.WWWWWWW
                              (3F15.7, FROM TGA2,SLOPE,SMALLN,AND CONSTA)
CARD17    DATA AS PUNCHED     (4F15.7, DATA TGA1, FOUR SETS OF NUMBERS
CARD17+N                       DA/DT,SMALLA,TEMP(DEGREES C ), NUMBER(N)
                               N SHOULD EQUAL FIRST VALUE ON CARD 9)
```

TGA3 PROGRAM LISTING

```
      CALL TGA3
      STOP
      END
      SUBROUTINE TGA3
      DIMENSION RATEM(4),RATEC(4),TITLE1(11),T1CONT(8),TITLE2(4),STITL2(
     13),TITLE3(7),STITL3(4),XSC(10),YSC(10),XCAL(10),YCAL(10),FDATA(99,
     23),CLDADT(99)
      WRITE(3,1)
    1 FORMAT('1',///,T20,'A SUMMARY OF THE DATA AS READ',//)
      READ(1,2)RATEM,RATEC,TITLE1,T1CONT,TITLE2,STITL2,TITLE3,STITL3
    2 FORMAT(4A4,/,4A4,/,11A4,/,8A4,/,4A4,/,3A4,/,7A4,/,4A4)
      WRITE(3,92)RATEM,RATEC,TITLE1,T1CONT,TITLE2,STITL2,TITLE3,STITL3
   92 FORMAT(10X,4A4,/,10X,4A4,/,10X,11A4,/,10X,8A4,/,10X,4A4,/,10X,3A4,
     1/,10X,7A4,/,10X,4A4)
      READ(1,3)N,NX,NY,NOTIT1,NOT1CO
    3 FORMAT(5I2)
      WRITE(3,93)N,NX,NY,NOTIT1,NOT1CO
   93 FORMAT(10X,5I2)
      READ(1,4)XSC,YSC
    4 FORMAT(10A4,/,10A4)
      WRITE(3,94)XSC,YSC
   94 FORMAT(10X,10A4,/,10X,10A4)
      READ(1,5)XCAL,YCAL
    5 FORMAT(10F5.0,/,10F7.3)
      WRITE(3,95)XCAL,YCAL
   95 FORMAT(10X,10F5.0,/,10X,10F7.3)
      READ(1,6)A,B,C
    6 FORMAT(3A1)
      WRITE(3,96)A,B,C
   96 FORMAT(10X,3A1)
      READ(1,8)XINCH,YINCH
    8 FORMAT(2F5.2)
      WRITE(3,98)XINCH,YINCH
   98 FORMAT(10X,2F5.2)
      READ(1,9)SLOPE,SMALLN,CONSTA
    9 FORMAT(3F15.7)
      WRITE(3,99)SLOPE,SMALLN,CONSTA
   99 FORMAT(10X,3F15.7)
      READ(1,7)((FDATA(I,J),J=1,3),I=1,N)
    7 FORMAT(3F15.7)
      WRITE(3,97)((FDATA(I,J),J=1,3),I=1,N)
   97 FORMAT(10X,3F15.7)
      CALL PLOTDK
C
C DRAW AXES AND INCLOSE
C     ALSO DRAW PAGE SIZE
      CALL PLOT(-1.0,-1.0,3)
      CALL PLOT(-1.0,7.5,2)
      CALL PLOT(5.00,7.5,2)
      CALL PLOT(5.0,-1.0,2)
      CALL PLOT(-1.0,-1.0,2)
      CALL PLOT(5.0,0.0,3)
      CALL PLOT(0.0,0.0,2)
      CALL PLOT(0.0,7.5,2)
      CALL PLOT(-2.5,-2.0,3)
      CALL PLOT(-2.5,9.0,2)
      CALL PLOT(-2.5,9.0,3)
      CALL PLOT(6.0,9.0,3)
      CALL PLOT(6.0,-2.0,2)
      CALL PLOT(2.5,6.3,3)
C
C DRAW TITLES AND SCALE
C         ALSO TICK MARKS
      CALL SYMBOL(2.5,6.3,.14,RATEM,0.,15)
      CALL SYMBOL(2.5,6.0,.14,RATEC,0.,16)
      CALL SYMBOL(-0.5,-0.6,.14,TITLE1,0.,NOTIT1)
      CALL SYMBOL(1.0,-0.8,.14,T1CONT,0.,NOT1CO)
      CALL SYMBOL(1.0,-0.4,.14,TITLE2,0.,15)
      CALL SYMBOL(3.0,-0.4,.10,STITL2,0.,11)
      CALL SYMBOL(2.55,-0.3,.07,C,0.,1)
      CALL SYMBOL(-0.5,1.5,.14,TITLE3,90.,25)
      CALL SYMBOL(-0.5,4.7,.10,STITL3,90.,11)
      CALL PLOT(-0.5,4.7,3)
      CALL PLOT(0.,0.,3)
```

```
C
C SCALE X=1.0/TEMP AND Y=NATURAL LOG. OF DA/DT.
C
      XFACT=XINCH/(1000./XCAL(1)-1000./XCAL(NX))
      K=NX-1
      DO 10 I=1,K
      IF(I.EQ.1) GO TO 11
      X=(1000./XCAL(1)-1000./XCAL(I))*XFACT
      GO TO 12
   11 X=0.0
   12 CALL SYMBOL(X,-0.15,.10,XSC(I),0.,4)
      CALL PLOT(X,0.0,3)
      CALL PLOT(X,0.1,2)
      CALL PLOT(X,0.1,3)
   10 CONTINUE
      YFACT=YINCH/(ALOG(YCAL(1))-ALOG(YCAL(NY)))
      K=NY-1
      DO 20 I=1,K
      IF(I.EQ.1) GO TO 21
      Y=(ALOG(YCAL(1))-ALOG(YCAL(I)))*YFACT
      GO TO 22
   21 Y=0.0
   22 CALL SYMBOL(-0.4,Y,.10,YSC(I),0.,4)
      CALL PLOT(0.0,Y,3)
      CALL PLOT(0.1,Y,2)
      CALL PLOT(0.1,Y,3)
   20 CONTINUE
      DO 30 I=1,N
      DADT=ABS(FDATA(I,1))
      Y=YFACT*(ALOG(YCAL(1))-ALOG(DADT))-0.07
      TEMP=FDATA(I,3)+273.2
      X=XFACT*(1000./XCAL(1)-1000./TEMP)-0.07
      CALL PLOT(X,Y,3)
      CALL SYMBOL(X,Y,.14,4,0.,1)
   30 CONTINUE
      DO 40 I=1,N
      CLDADT(I)=ABS(FDATA(I,1))/((1.0-FDATA(I,2))**SMALLN)
      Y=(ALOG(YCAL(1))-ALOG(CLDADT(I)))*YFACT-0.03
      X=(1000./XCAL(1)-1000./(FDATA(I,3)+273.2))*XFACT-0.05
      CALL PLOT(X,Y,3)
      CALL SYMBOL(X,Y,.07,8,0.,2)
   40 CONTINUE
      Y=0.0
      TEMP=SLOPE/(ALOG(YCAL(1))-CONSTA)
      X=(1000./XCAL(1)-1000./TEMP)*XFACT
      IF(X.LT.(XFACT*(1000./XCAL(1)-1000./XCAL(NX)))) GO TO 50
      X=XFACT*(1000./XCAL(1)-1000./XCAL(NX))
      DADTLN=CONSTA+SLOPE/XCAL(NX)
      Y=YFACT*(ALOG(YCAL(1))-DADTLN)
   50 CALL PLOT(X,Y,3)
      X=0.0
      DADTLN=CONSTA+SLOPE/XCAL(1)
      Y=YFACT*(ALOG(YCAL(1))-DADTLN)
      IF(Y.LT.(YFACT*(ALOG(YCAL(1))-ALOG(YCAL(NY))))) GO TO 51
      Y=YFACT*(ALOG(YCAL(1))-ALOG(YCAL(NY)))
      TEMP=SLOPE/(ALOG(YCAL(NY))-CONSTA)
      X=XFACT*(1000./XCAL(1)-1000./TEMP)
   51 CALL PLOT(X,Y,2)
      CALL PLOT(X,Y,3)
      CALL PLOT(X,Y,100)
      RETURN
      END
```

```
          A SUMMARY OF THE DATA AS READ


+ MEASURED RATE
0 CORRECTED RATE
FIGURF  . PLOT OF TGA ANALYSIS OF MERCURY
SULFIDE IN AIR
TFMPFRATURF,  K
(1/T SCALE)
RATE OF REACTION, PER MIN.
(LOG SCALF)
13 5 84114
 700 650 600 550 500
.001.003.010.032.100.3161.003.16
 700. 650. 600. 550. 500.   0.    0.    0.    0.    0.
  0.001  0.003  0.010  0.032  0.100  0.316  1.000  3.161  0.0    0.0
+00
 5.00 7.50
 -15171.0781250      0.6235800      20.7354279
     -0.0004163      0.0004166     251.3333130
     -0.0006658      0.0008325     268.6662598
     -0.0011233      0.0012483     285.9997559
     -0.0029956      0.0029132     303.3327637
     -0.0073435      0.0049932     320.6662598
     -0.0171414      0.0139383     337.9992676
     -0.0350529      0.0324531     355.3327637
     -0.0755147      0.0748910     372.6657715
     -0.1310170      0.1497819     389.9992676
     -0.1815060      0.3328481     407.3322754
     -0.2099020      0.5585607     424.6657715
     -0.1751609      0.7780324     441.9987793
     -0.1104429      0.9767007     459.3322754
```

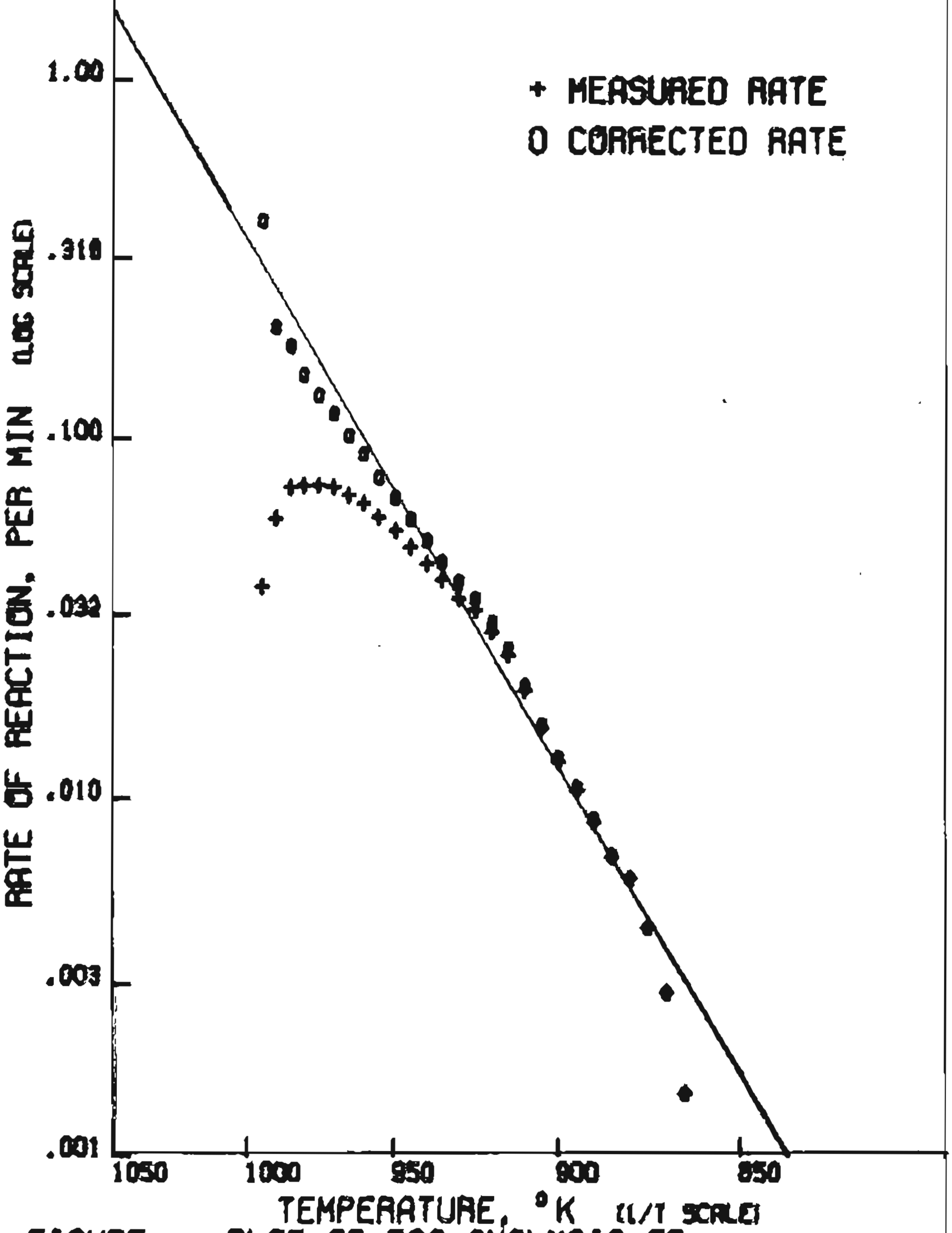

FIGURE . PLOT OF TGA ANALYSIS OF CALCIUM CARBONATE

APPENDIX D

- Distillation Data -

This appendix contains all the data used in preparing the figures for the distillation section of this report. The tabulated data are presented so that the test set-up, recorded data, analytical results and metallurgical calculations can be used to verify the results presented in the distillation figures. Additional data are also shown in some tables to conform some of the conclusions drawn that are not readily apparent from the figures.

Table D-1. Effects of Iron, Lime, Time and Temperature on Mercury Recovery (Series I)

Metallurgical Data

Run No.	Variables				Time to Temp., min.	Products, Weight Percent			Analyses, Percent Mercury		Distribution, Percent Mercury		
	Iron, grams	Lime, grams	Time, hours	Temp., °C		Metal	Soot	Residue	Soot	Residue	Metal	Soot	Residue
1	0.0	8.4	1.0	400	17	0.0	23.3	76.7	94.0	54.0	0.0	34.6	65.4
2	5.6	2.8	2.0	320	10	3.2	0.3	96.5	86.0	63.5	4.9	0.4	94.7
3	8.4	0.0	1.5	360	11	8.3	0.9	90.8	86.4	58.5	13.3	1.3	85.4
4	2.8	5.6	0.5	440	19	14.5	26.4	59.1	73.5	38.0	25.6	34.5	39.9
5	0.0	2.8	1.5	440	16	0.0	61.5	38.5	89.3	49.0	0.0	74.4	25.6
6	5.6	8.4	0.5	360	10	3.4	0.4	96.2	86.4	53.0	6.3	0.6	93.1
7	8.4	5.6	1.0	320	8	1.8	0.1	98.1	86.4	53.5	3.3	0.1	96.6
8	2.8	0.0	2.0	400	22	17.1	22.7	60.2	92.5	53.0	24.4	30.0	45.6
9	0.0	0.0	0.5	320	8	1.3	0.1	98.6	86.4	83.0	1.6	0.1	98.3
10	8.4	8.4	2.0	440	13	42.7	4.7	52.6	92.5	<.1	90.6	9.3	0.1
11	2.8	2.8	1.0	360	8	4.6	.4	95.0	86.4	71.0	6.4	0.4	93.2
12	5.6	5.6	1.5	400	22	22.1	8.1	69.8	92.5	38.5	39.1	13.3	47.6
13	0.0	5.6	2.0	360	11	3.8	1.9	94.3	99.0	71.0	5.2	2.6	92.2
14	2.8	8.4	1.5	320	7	1.5	0.1	98.4	86.4	56.5	2.6	0.1	97.3
15	5.6	0.0	1.0	440	15	39.8	13.7	46.5	95.0	29.0	60.0	19.6	20.4
16	8.4	2.8	0.5	400	11	10.0	1.2	88.8	96.5	54.0	16.9	1.9	81.2

Operating Conditions

Charge --- 27 grams White Mountain Concentrate (75.3 percent Hg)
0 to 8.4 grams (0 to 2 equivalents) minus 40-mesh iron mixed in charge
0 to 8.4 grams (0 to 2 equivalents) 80 percent minus 100-mesh lime mixed in charge

Table D-2. Effects of Iron, Lime, Time and Temperature on Mercury Recovery (Series II)

Metallurgical Data													
Run No.	Variables				Time to temp., min.	Products, Weight Percent			Analyses, Percent Mercury		Distribution, Percent Mercury		
	Iron, grams	Lime, grams	Time, hours	Temp., °C		Metal	Soot	Residue	Soot	Residue	Metal	Soot	Residue
1	2.8	5.6	1.0	440	20	23.2	34.8	42.0	84.5	12.2	40.2	51.0	8.8
2	8.4	1.9	2.0	360	14	10.7	2.3	87.0	91.0	51.5	18.6	3.6	77.8
3	11.2	0.0	1.5	400	18	42.9	2.2	54.9	85.5	17.9	78.5	3.5	18.0
4	5.6	3.9	0.5	480	17	43.7	14.9	41.4	84.5	0.11	77.6	22.3	0.1
5	2.8	1.9	1.5	480	16	27.4	43.5	29.1	88.8	0.09	41.5	58.4	0.1
6	8.4	5.6	0.5	400	10	9.8	0.6	89.6	93.5	45.5	19.2	1.0	79.8
7	11.2	3.9	1.0	360	15	10.1	1.0	88.9	94.0	45.5	19.7	1.8	78.5
8	5.6	0.0	2.0	440	14	46.7	19.0	34.3	86.5	0.13	73.9	26.0	0.1
9	2.8	0.0	0.5	360	10	5.4	0.3	94.3	94.3	67.5	7.8	0.5	91.7
10	11.2	5.6	2.0	480	18	45.6	2.2	52.2	92.5	0.01	95.7	4.3	<0.1
11	5.6	1.9	1.0	400	17	26.3	6.4	67.3	90.2	45.0	42.2	9.3	48.5
12	8.4	3.9	1.5	440	14	48.6	5.0	46.4	82.1	0.02	92.2	7.8	<0.1
13	2.8	3.9	2.0	400	12	10.6	10.7	78.7	88.3	50.5	17.7	15.7	66.6
14	5.6	5.6	1.5	360	15	8.2	3.0	88.8	93.5	51.5	14.5	5.0	80.5
15	8.4	0.0	1.0	480	20	52.0	7.1	40.9	88.7	0.01	89.2	10.8	<0.1
16	11.2	1.9	0.5	440	13	44.4	2.0	53.6	87.5	10.6	85.7	3.3	11.0

Operating Conditions

Charge --- 27 grams White Mountain Concentrate (75.3 percent Hg)
2.8 to 11.2 grams (0.5 to 2.0 equivalents) minus 40-mesh iron mixed in charge
0 to 5.6 grams (0.0 to 0.67 equivalent) 80 percent minus 100-mesh lime mixed in charge

Table D-3. Effect of Temperature on Mercury Recovery from White Mountain Concentrate

Metallurgical Data

Run No.	Iron mixed, grams	Temp., °C	Time to temp., min.	Products, Weight Percent			Analyses, Percent Mercury		Distribution, Percent Mercury		
				Metal	Soot	Residue	Soot	Residue	Metal	Soot	Residue
1	5.6	320	14	5.4	0.2	94.4	85.5	61.0	8.6	0.3	91.1
2	5.6	360	12	7.8	0.8	91.4	93.8	60.3	12.3	1.1	86.6
3	5.6	400	15	20.7	4.3	75.0	94.2	51.7	32.5	6.4	61.1
4	5.6	440	14	40.7	17.2	42.1	94.0	11.3	66.0	26.3	7.7
5	5.6	480	24	50.9	14.4	34.7	90.5	9.5	75.7	19.4	4.9
6	5.6	520	19	49.3	16.4	34.3	90.0	4.0	75.4	22.5	2.1
7	5.6	560	20	50.2	15.5	34.3	94.0	3.0	76.3	22.2	1.5
8	5.6	600	24	49.3	16.3	34.4	90.5	5.2	74.9	22.4	2.7
9	7.0	400	18	35.1	6.0	58.9	90.5	35.0	57.3	8.9	33.8
10	7.0	440	15	52.4	9.9	37.7	87.7	14.5	78.8	13.0	8.2
11	7.0	480	14	51.8	9.6	38.5	93.7	3.0	83.6	14.6	1.8

Operating Conditions

Charge --- 27.0 grams White Mountain Concentrate (75.3 percent Hg)
5.6 or 7.0 grams (1.0 or 1.25 equivalents) minus 40-mesh iron mixed in charge
Furnace at temperature --- 1.0 hour

Table D-4. Effect of Temperature on Mercury Recovery from White Mountain Concentrate (charge covered with iron)

Metallurgical Data

Run No.	Temp., °C	Time to temp., min.	Products, Weight Percent			Analyses, Percent Mercury	Distribution, Percent Mercury	
			Metal	Soot[1]	Residue	Residue	Metal	Residue
1	380	13	9.0	0.3	90.7	58.5	14.4	85.6
2	420	12	32.5	0.3	67.2	41.0	53.9	46.1
3	440	21	58.9	0.1	41.0	0.17	99.8	0.2
4	460	15	59.1	0.1	40.8	0.06	99.9	0.1
5	500	24	59.5	0.1	40.4	0.06	99.9	0.1
6[2]	340	9	5.1	<0.1	94.9	53.5	9.2	90.8
7[2]	380	9	25.7	0.1	74.2	47.5	42.1	57.9
8[2]	420	11	47.3	0.1	52.6	23.0	79.6	20.4
9[2]	430	27	57.0	0.2	42.8	3.30	97.3	2.7
10[2]	460	12	59.2	0.1	40.7	0.03	99.9	0.1
11[2]	500	15	58.9	0.1	41.0	0.02	99.9	0.1

Operating Conditions

Charge --- 27.0 grams White Mountain Concentrate (75.3 percent Hg)
5.6 grams (1.0 equivalent) minus 40-mesh iron mixed in charge
2.8 grams (0.5 equivalent) minus 40-mesh iron spread on top of charge

Furnace at temperature --- 1.0 hour

---

[1] Insufficient sample for analysis.

[2] Air circulated through furnace.

Table D-5. Effects of Antimony Sulfide, Iron, Time and Temperature on Mercury Recovery (Series III)

Metallurgical Data

	Variables				Products, Weight Percent			Analyses, Percent				Distribution, Percent				
								Mercury		Antimony		Mercury			Antimony	
Run No.	Iron, grams	Sb_2S_3, grams	Time, hours	Temp., °C	Metal	Soot	Residue	Soot	Residue	Soot	Residue	Metal	Soot	Residue	Soot	Residue
1	5.6	30	1.0	450	31.9	0.7	67.4	59.3	<0.01	6.4	32.5	98.7	1.3	<0.1	0.2	99.8
2	11.2	10	2.0	390	38.7	1.0	60.3	63.3	0.97	4.7	18.5	96.9	1.6	1.5	0.4	99.6
3	14.0	0	1.5	420	45.4	0.2	54.4	52.8	<0.01	5.5	7.0	99.8	0.2	<0.1	0.2	99.8
4	8.4	20	0.5	480	34.6	1.4	64.0	72.9	<0.01	5.2	26.0	97.1	2.9	<0.1	0.4	99.6
5	5.6	10	1.5	480	44.3	1.3	54.4	73.0	<0.01	6.0	23.5	98.0	2.0	<0.1	0.6	99.4
6	11.2	30	0.5	420	26.1	0.4	73.5	62.7	3.08	2.5	27.0	91.2	0.9	7.9	0.1	99.9
7	14.0	20	1.0	390	22.6	0.4	77.0	70.3	10.5	3.6	18.5	73.0	0.9	26.1	0.1	99.9
8	8.4	0	2.0	450	51.9	0.3	47.8	66.6	<0.01	7.5	7.7	99.6	0.4	<0.1	0.6	99.4
9	5.6	0	0.5	390	13.3	0.4	86.3	73.5	53.5	4.6	7.6	22.2	0.5	77.3	0.3	99.7
10	14.0	30	2.0	480	27.3	1.7	71.0	53.8	0.01	9.6	23.5	96.7	3.3	<0.1	1.0	99.0
11	8.4	10	1.0	420	33.3	0.6	66.1	66.7	<0.01	5.0	20.0	98.8	1.2	<0.1	0.2	99.8
12	11.2	20	1.5	450	33.2	1.5	65.3	66.4	<0.01	4.3	22.5	97.1	2.9	<0.1	0.4	99.6
13	5.6	20	2.0	420	36.1	2.0	61.9	57.8	<0.01	4.4	30.0	96.9	3.1	<0.1	0.5	99.5
14	8.4	30	1.5	390	29.4	1.1	69.5	66.6	<0.01	4.4	30.0	97.5	2.5	<0.1	0.2	99.8
15	11.2	0	1.0	480	48.6	0.3	51.1	64.9	<0.01	10.7	8.0	99.6	0.4	<0.1	0.8	99.2
16	14.0	10	0.5	450	37.5	0.5	62.0	60.7	<0.01	10.4	17.0	99.2	0.8	<0.1	0.5	99.5

Operating Conditions

Charge --- 30 grams Red Devil Hg Concentrate (66.4 percent Hg, 6.5 percent Sb)
0 to 30 grams Red Devil Sb Concentrate (3.84 percent Hg, 42 percent Sb)
5.6 to 14.0 grams (1.0 to 2.5 equivalents)minus 40-mesh iron mixed in charge

Table D-6. Effect of Temperature on Mercury Recovery from Red Devil Concentrate

Metallurgical Data

Run No.	Temp., °C	Time to temp., min.	Products, Weight Percent			Analyses, Percent				Distribution, Percent				
						Mercury		Antimony		Mercury			Antimony	
			Metal	Soot	Residue	Soot	Residue	Soot	Residue	Metal	Soot	Residue	Soot	Residue
1	320	7	0.5	<0.1	99.5	75.8	29.3	2.8	21.8	2.3	0.2	95.5	<0.1	100.0
2	360	11	9.1	0.4	90.5	54.1	21.5	3.6	24.8	31.7	0.8	67.5	0.1	99.9
3	400	14	28.8	0.6	70.6	40.2	3.55	3.9	32.7	91.2	0.9	7.9	0.1	99.9
4	440	22	31.6	0.4	68.0	64.0	0.01	5.3	36.4	99.2	0.8	<0.1	0.1	99.9
5	480	18	31.3	1.0	67.7	55.4	0.04	25.3	36.4	98.1	1.8	0.1	1.1	98.9
6	520	24	30.1	3.3	66.6	64.0	0.02	0.74	36.4	93.2	6.8	<0.1	0.1	99.9
7	560	28	29.2	4.6	66.2	63.2	0.03	1.1	36.4	90.9	9.1	<0.1	0.2	99.8
8	600	36	27.9	6.6	65.5	43.0	0.02	10.9	35.7	90.7	9.3	<0.1	3.0	97.0
9[1]	320	8	0.6	<0.1	99.3	----	35.2	---	21.2	1.7	0.0	98.3	---	100.0[3]
10[1]	360	9	10.5	0.3	89.2	79.5	21.5	---	25.4	35.0	0.9	64.1	---	100.0[3]
11[1,2]	400	10	28.4	0.8	70.8	59.9	5.0	15.3	31.5	87.6	1.4	11.0	0.5	99.5[3]
12[1,2]	440	12	32.3	0.6	67.1	57.7	0.02	18.3	33.8	99.0	1.0	0.1	0.5	99.5[3]

Operating Conditions

Charge --- 30.0 grams Red Devil Mercury Concentrate (66.4 percent Hg, 6.5 percent Sb)
30.0 grams Red Devil Antimony Concentrate (3.84 percent Hg, 42.0 percent Sb)
5.6 grams (1.0 equivalent) minus 40-mesh iron mixed in charge

Furnace at temperature --- 1.0 hour

---

[1] Air circulated through retort.

[2] Considerable white smoke.

[3] Based on antimony remaining in system.

Table D-7. Effect of Temperature on Mercury Recovery from Red Devil Concentrate (charge covered with iron)

Metallurgical Data

Run No.	Temp., °C	Time to Temp., min.	Products, Weight Percent			Analyses, Percent				Distribution, Percent				
						Mercury		Antimony		Mercury			Antimony	
			Metal	Soot	Residue	Soot	Residue	Soot	Residue	Metal	Soot	Residue	Soot	Residue
1	380	9	9.5	0.2	90.3	71.2	28.25	4.6	19.0	27.0	0.4	72.6	<0.1	100.0
2	400	10	18.8	0.2	81.0	67.9	18.75	3.4	21.0	55.1	0.4	44.5	<0.1	100.0
3	420	10	30.1	0.2	67.7	65.8	4.85	8.3	25.0	89.6	0.3	10.1	0.1	99.9
4	440	14	34.9	1.1	64.0	51.2	0.04	7.9	26.0	98.3	1.6	0.1	0.5	99.5
5	460	26	34.4	1.2	64.4	55.8	0.04	8.9	27.5	98.0	1.9	0.1	0.6	99.4
6	480	24	34.1	2.1	63.8	49.5	0.04	10.1	27.5	96.9	3.0	0.1	1.2	98.8
7	520	26	34.6	1.6	63.8	40.8	0.10	13.6	27.5	97.9	1.9	0.2	1.2	98.8
8	560	21	34.3	2.2	63.5	60.5	0.01	11.8	27.5	96.3	3.7	<0.1	0.2	99.8
9	600	25	34.3	2.0	63.7	18.0	0.02	11.0	27.5	98.9	1.1	<0.1	1.3	98.7
10	640	29	33.8	2.5	63.7	36.5	0.01	14.0	27.8	97.4	1.0	1.6	2.0	98.0
11[1]	440	23	35.2	0.7	64.1	51.0	0.03	19.3	27.5	99.0	0.9	0.1	0.7	99.3[2]
12[1]	480	16	35.4	0.7	63.9	58.4	0.04	21.2	27.5	98.8	1.1	0.1	0.8	99.2[2]
13[1]	520	20	34.8	1.5	63.7	53.0	0.12	15.0	27.5	97.6	2.2	0.2	1.2	98.8[2]
14[1]	560	17	34.8	1.8	63.4	43.5	0.06	15.8	27.5	97.7	2.2	0.1	1.6	98.4[2]
15[1]	600	22	35.1	1.9	63.0	30.5	0.08	27.8	27.5	98.2	1.6	0.2	3.0	97.0[2]

Operating Conditions

Charge --- 30.0 grams Red Devil Mercury Concentrate (66.4 percent Hg, 6.5 percent Sb)
20.0 grams Red Devil Antimony Concentrate (3.84 percent Hg, 42.0 percent Sb)
5.6 grams (1.0 equivalent) minus 40-mesh iron mixed in charge
2.8 grams (0.5 equivalent) minus 40-mesh iron spread on top of charge

Furnace at temperature --- 1.0 hour

---

[1] Air circulated through retort, with considerable white smoke discharged.

[2] Based on antimony remaining in system.

Table D-8. Effect of Temperature on Two Samples Containing Arsenic (Cinnabar Creek Concentrate and a Laboratory Prepared Sample)

Metallurgical Data

Run No.	Temp., °C	Time to temp., min.	Products, Weight Percent			Analyses, Percent				Distribution, Percent				
						Mercury		Arsenic		Mercury			Arsenic	
			Metal	Soot	Residue	Soot	Residue	Soot	Residue	Metal	Soot	Residue	Soot	Residue
1	360	17	6.0	1.1	92.9	37.0	10.7	41.0	0.83	36.5	2.6	60.9	36.8	63.2
2	400	15	8.7	2.2	89.1	35.5	4.60	46.5	0.68	64.2	5.7	30.1	26.1	78.9
3	440	23	11.1	7.1	81.8	56.3	0.10	32.1	0.35	73.0	26.5	0.5	44.4	55.6
4	480	--	9.4	7.8	82.8	61.5	0.10	28.2	0.17	66.1	33.3	0.6	60.8	39.2
5	320	9	0.0	6.8	93.2	56.5	41.5	10.3	3.0	0.0	9.0	91.0	19.9	80.1
6	340	4	0.0	8.8	91.2	62.0	46.5	10.2	3.0	0.0	11.4	88.6	24.7	75.3
7	380	6	4.2	13.6	82.2	62.0	36.0	9.2	2.7	9.9	20.0	70.1	36.1	63.9
8	420	13	4.5	52.8	42.7	45.0	4.20	9.8	3.0	15.1	78.9	6.0	80.1	19.9
9	500	18	18.1	50.9	31.0	56.5	0.22	9.9	1.2	38.6	61.2	0.2	93.2	6.8

Operating Conditions

Charge --- For runs 1, 2, 3, and 4
120.0 grams Cinnabar Creek Concentrate (16.2 percent Hg, 0.90 percent As)
5.6 grams (1.0 equivalent) minus 40-mesh iron mixed in charge
2.8 grams (0.5 equivalent) minus 40-mesh iron spread on top of charge
Charge --- For runs 5,6,7,8, and 9
27.0 grams White Mountain Concentrate (75.3 percent Hg)
10.0 grams High Purity Realgar Orpiment Concentrate (58.5 percent As)
5.6 grams (1.0 equivalent) minus 40-mesh iron mixed in charge
2.8 grams (0.5 equivalent) minus 40-mesh iron spread on top of charge

Furnace at temperature --- 1.0 hour

APPENDIX E

Statistical Evaluation

To initiate a research study wherein four variables are of concern and interaction of the variables may have significance, the number of tests required becomes very large. To eliminate enough tests so that the research can be completed in a reasonable period of time requires that a partial replicate be considered. A one-sixteenth replicate using a lattice design of four variables at four levels was chosen, thus reducing the number of tests required from 256 to 16 for each test series.

In preparing the results from a one-sixteenth replicate of a four by four test design for graphic presentation, each variable is calculated for its four levels at the mean level of the other three variables. The calculations shown in Table E-1 are for the four levels of iron used. Note that the mean level for iron changes, while those for the other three variables do not. The data were then rearranged for calculating the effects of CaO, time and temperature on mercury recovery in a similar manner. These values are then plotted to show the effect of each variable at the mean levels of the others on mercury recovery. This information can then be compared to the linear regression analysis for further evaluation of the results.

Table E-1. Method Used in Determining Mean Levels for Statistically, Planned Test Series (Series II Data)

Test No.		Coded Values				Mean Levels				Yield	
		Fe	CaO	Time	Temp.	Fe, grams	CaO, grams	Time, hours	Temp., C	Metal, grams	Dist., Percent
1		-3	+3	-1	+1	2.8	5.6	1.0	440	8.00	40.2
5		-3	-1	+1	+3	2.8	1.9	1.5	480	8.44	41.5
9		-3	-3	-3	-3	2.8	0.0	0.5	360	1.60	7.8
13		-3	+1	+3	-1	2.8	3.9	2.0	400	3.47	17.7
	Totals	-12	0	0	0	11.2	11.4	5.0	1680	21.51	107.2
	Means	-3	0	0	0	2.8	2.8	1.25	420	5.38	26.8
4		-1	+1	-3	+3	5.6	3.9	0.5	480	15.77	77.6
8		-1	-3	+3	+1	5.6	0.0	2.0	440	15.13	73.9
11		-1	-1	-1	-1	5.6	1.9	1.0	400	8.87	42.2
14		-1	+3	+1	-3	5.6	5.6	1.5	360	3.10	14.5
	Totals	-4	0	0	0	22.4	11.4	5.0	1680	42.87	208.2
	Means	-1	0	0	0	5.6	2.8	1.25	420	10.72	52.1
2		+1	-1	+3	-3	8.4	1.9	2.0	360	3.93	18.6
6		+1	+3	-3	-1	8.4	5.6	0.5	400	3.97	19.2
12		+1	+1	+1	+1	8.4	3.9	1.5	440	19.17	92.2
15		+1	-3	-1	+3	8.4	0.0	1.0	480	18.50	89.2
	Totals	+4	0	0	0	33.6	11.4	5.0	1680	45.57	219.2
	Means	+1	0	0	0	8.4	2.8	1.25	420	11.39	54.8
3		+3	-3	+1	-1	11.2	0.0	1.5	400	16.26	78.5
7		+3	+1	-1	-3	11.2	3.9	1.0	360	4.22	19.7
10		+3	+3	+3	+3	11.2	5.6	2.0	480	19.90	95.7
16		+3	-1	-3	+1	11.2	1.9	0.5	440	17.83	85.7
	Totals	+12	0	0	0	44.8	11.4	5.0	1680	58.21	279.6
	Means	+3	0	0	0	11.2	2.8	1.25	420	14.55	69.9

BIBLIOGRAPHY

1. Coats, A. W., and J. P. Redfern, 'Kinetic Parameters from TGA Data', Nature, 201(4914), p. 68-9 (1964).

2. Cochran, W. G., and G. M. Cox, 'Experimental Designs', 2d, John Wiley, New York, N. Y., 1957.

3. Dixon, J. J., 'The Biomedical Computer Programs', Univerisity of California Press, Berkeley, 1970.

4. Hofman, H. O., and John Blatchford, 'The Behavior of Stibnite in an Oxidizing Roast', Trans. A.I.M.E. Vol. 54, p. 671, 1917.

5. Levina, S. D., and K. A. Gal'bert, 'Separation of Mercury from Antimony-Mercury Ores', U.S.S.R. Patent 67,130, Sept. 30, 1946.

6. Malone, Kevin, 'Mercury Occurrences in Alaska', U. S. Bureau of Mines Inf. Cir. 8131, 1962, 57 pp.

7. Mellor, J. W., 'A Comprehensive Treatise on Inorganic Theoretical Chemistry', Vol. 4, Longmans Green and Co., New York, N. Y., 1946.

8. Mel'nikov, S. M., and R. A. Isakova, 'Technological Improvement in Processing of Mercury-Bearing Raw Material', Tsvet, Metal., 49(9), p. 61-4, 1967.

9. Mikhailov, V. K., and M. I. Kochegarova, 'Kinetics of Roasting Mercury Ore', Byul. Nauchno-Tekhn. Inform. Tsentr. Nauch-Issled. Inst. Olva. Sur'mg I Rtuti: p. 28-39, 1961.

10. Satava, V., and F. Skvara, 'Mechanism and Kinetics of the Decomposition of Solids by a Thermogravimetric Method', (Cesk. Aked. Ved. Prague, Czech.), J. American Ceramic Soc., Vol. 52 (11), p. 591-5, 1969.

11. Sharp, J. H., and S. A. Wentworth, 'Kinetics Analysis of TGA Data', Anal. Chem., Vol. 41 (14), p. 2060-2, 1969.

12. Town, J. W., and W. A. Stickney, 'Beneficiation of Hydrometallurgical Treatment of Complex Mercury Sulfide Products', U. S. Bureau of Mines Rept. of Inv. 6569, 1964, 35 pp.

13. Westley, G. W., and J. A. Watts, 'The Computing Technology Center Numerical Analysis Library', Union Carbide Corporation, Nuclear Division, Computing Technology Center, Oak Ridge, Tennessee, Oct. 1970.