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Final Report
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"A Study of the Decomposition Mechanism of Ammonium Perchlorate"

Prepared by: Departments of Chemistry and
Chemical Engineering,
Auburn University

For the period: 22 Feb. 1964 - 30 May 1965

Contract No. DA-01-009-ORD-1023(Z), Part I,
Birmingham Procurement District, U.S. Army.
Administered by The Auburn Research Foundation

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~~Final Report~~ on:

"A Study of the Decomposition Mechanism of Ammonium Perchlorate."

Prepared by: Departments of Chemistry and Chemical Engineering, Auburn University, and submitted by:

James E. Land,
Project Supervisor

~~For the Period: 22 Feb. 1961 - 30 May 1965~~

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1. Abstract

Using differential thermal analysis technique peak temperatures for the crystal transformation and chemical decomposition of ammonium perchlorate of various particle sizes have been determined at heating rates of approximately 2, 4 and 10° C./minute. It was found that peak temperatures varied with the heating rate and such variation permitted the calculation of activation energies for the particular changes occuring at the respective peak temperatures. The influence of the nature and pressure of the atmosphere over the ammonium perchlorate during heating was investigated.

Various materials function as catalysts on the decomposition of ammonium perchlorate and activation energies were measured with various additives present. The conclusion was reached that the lowering of peak temperature for the decomposition exotherm by the catalyst was a better criterion of its effectiveness than the change in activation energy.

An attempt was made to account for the mechanism of catalyst operation in order to explain the observed trends.

2. Contract Aims and Objectives

This project was undertaken for the purpose of studying the chemical reactions which occur when ammonium perchlorate (hereinafter abbreviated AP) undergoes decomposition as the result of the application of heat. It was reasoned that a formulation of the steps and mechanism involved in this decomposition could be attempted from a knowledge of the activation energy which accompanies each step. The determination of such activation energies was to be made by taking advantage of the measured shift with heating rate changes of the exo- and endothermic peak temperatures as obtained from differential thermal analysis plots.

In addition the effect of catalytic agents on the activation energies of the decomposition steps was to be investigated.

It was felt that, if a better understanding of the rate controlling step in this decomposition process could be realized, then a more judicious selection of catalysts could be made so as to achieve maximum oxidation potential from this chemical change.

3. Theory of Differential Thermal Analysis.

Differential thermal analysis (DTA) was used to obtain the data necessary for the evaluation of reaction orders, activation energies and the influence of catalysts.

DTA involves the heat effects associated with chemical changes that occur when a substance is subjected to a uniform increase in temperature. This heat effect, which occurs during a chemical change, is measured by a differential method. A sample holder, containing two symmetrically located and identical chambers, is placed in a furnace controlled by a programer which causes the temperature to increase at a constant and prescribed rate. Each chamber contains an identical temperature detection device so connected electrically that the difference in temperature of the chambers is recorded on the Y axis of a recording plotter, which at the same time, records time on the X axis, i.e. sample holder temperature since the rate of heating is constant. The sample being studied is placed in one chamber and a thermally inert substance, or reference, in the other chamber. If the sample becomes cooler or hotter than the reference due to a chemical or physical change, a peak in a downward and upward direction respectively will be produced on the plot.

Since the area under the peaks is proportional to the heat change involved, then knowing the sample weight, a

quantitative measure of the heat of the reaction is possible.

This total heat of reaction ΔH can be expressed in the form of an equation (Ref. 1 & 2)

$$\Delta H = (gk/M)\int_a^c \Delta T dt \qquad (1)$$

where g = geometrical shape constant for the furnace, k = thermal conductivity of the sample, M = mass of the reactive sample, ΔT = difference of temperature at center of sample and reference at some particular time, dt = differential of time and a and c represent points on the graphical plot where the thermograph peak starts and stops.

The use of this expression is predicated upon certain assumptions. Terms g and k are constants, since they depend upon the furnace used. Temperature gradients within the sample are neglected and too the area under the curve is considered to be independent of the specific heat.

To use DTA to obtain information concerning the kinetics and reaction order of a simple decomposition reaction such as, solid → solid + gas, one may describe such a reaction by the following differential equation (Ref. 3)

$$dx/dt = A(e^{-E/RT})\ (1 - x)^n \qquad (2)$$

where dx/dt is the rate of the reaction, x is the fraction reacted, n is the emperical order of the reaction, A is the frequence factor, R is the gas constant and T is

temperature in degrees Kelvin. This expression holds true for any value of T, whether constant or variable, so long as x and T are measured at the same instant.

For immediate purposes of simplification let us consider the order n to be unity.

When the reaction rate is a maximum, i.e. at the peak temperature, T_m, of the thermograph, the derivative with respect to time is zero, so solving the above equation (2) for d/dt(dx/dt):

$$d/dt(dx/dt) = dx/dt([E/RT^2][dT/dt] - Ae^{-E/RT}) \qquad (3)$$

and setting the left hand side equal to zero, we get at temperature, T_m,

$$Ae^{-E/RT_m} = (E/RT_m^2)dT/dt \qquad (4)$$

From this equation (4) the following expression is obtained (Ref. 4)

$$d(\ln[\phi/T_m^2])/d(1/T_m) = (-)\ E/R \qquad (5)$$

where $\phi = dT/dt$, the heating rate, must be constant in a given experiment.

Although the above equation (5) was derived for a first order reaction it is now known to hold regardless of the reaction order (Ref. 4).

In DTA work T_m for a given value of ϕ is determined by both A and E. If ϕ, which depends only on E is changed, T_m is changed. To find the variation of T_m as ϕ is altered

then a plot of $\ln[\phi/T_m^2]$ vs. $1/T_m$ should give a straight line of slope (-) E/R. With E found then A can also be calculated using equation (4).

The order of the reaction, n, can be found from the shape of the DTA curve peak. As n is decreased the peak becomes more asymmetric. Kissinger (Ref. 4) has developed a "shape index" defined as the absolute value of the ratio of the slopes of the tangents to the curve at the inflection points of S = a/b.

The order of the reaction is given by:

$$n = 1.26(S)^{1/2}$$

In our experiments known masses of AP were heated at various, constant heating rates and the DTA curves measured. From these curves the values ϕ, T_m, a and b were obtained so the E, A and n could be calculated. The repeat of these determinations with variation in such things as the atmosphere and pressure on the sample, the presence of catalytic agents and particle size gave us an indication as to how these variables influence the activation energy and/or the order of the AP decomposition.

4. Background Information

(a) Introduction. The thermal decomposition of AP is unusual in several respects, for even though it usually follows the course of a solid changing into all gaseous products, it may under certain experimental conditions give solid as well as gaseous products. AP also decomposes without melting and undergoes a crystal transformation from orthorhombic to cubic at 240° C. which is below the normal decomposition temperature.

It is evident that as AP is heated from ambient to 450° C. at least four different physical and chemical changes may occur and in some cases these may take place concurrently. The four changes are designated crystal change, sublimation, low temperature decomposition and high temperature decomposition.

Quite a number of factors also seem to have a bearing on the rate and nature of decomposition. These parameters are the nature and pressure of the atmosphere above the AP, particle size of the AP, the presence of impurities and the previous history of the AP sample.

(b) The Crystal Transformation. Bircumshaw and Newman (Ref. 5) concluded that the occurrence of the crystal transformation at 240° C. does complicate the kinetic results but does not alter the general picture of the

electron transfer mechanism. The more stable nature of the cubic form somewhat counterbalances the increased thermal rotation of the ions present. It has been observed (Ref. 6) that the maximum rate of decomposition in vacuo decreases at 240° C. where this crystal change occurs and continues to decrease to 250° C. then starts to rise again. It is possible that the maximum stability of the cubic crystal occurs at the latter temperature, however, it could be that the transition is slow and is not complete until that temperature is attained.

The heat of transition at 240° C. (Ref. 7) has been reported to be 2.3 ± 0.2 kcal/mole. The computed density (Ref. 7) of the cubic form is 1.76 g/cc as compared to 1.95 g/cc for the rhombic form. This means that as the temperature is raised through this transformation there will take place enough of a volume increase to cause strains and distortions to occur in the solid AP. This is contrary to Bircumshaw and Newman (Ref. 5) who report that the lattice distances are reduced when the cubic form is realized.

(c) The Sublimation Process. It is the opinion of Inami *et al.* (Ref. 8) that the dissociation pressure of AP is an important parameter in the analysis of the combustion machanism of solid propellants based upon this oxidizer. They measured the dissociation pressure of AP

in the temperature range of 247-347° C. by a transpiration method. Their data indicated that AP sublimes by the process of

$$NH_4ClO_4(s) = NH_3(g) + HClO_4(g).$$

The heat of dissociation was found to be 58 ± 2 kcal/mole in this temperature range. Bircumshaw and Phillips (Ref.35) report the energy of activation for sublimation to be 21.5 ± 2.78 kcal/mole.

It was observed that both low temperature decomposition and sublimation occur simultaneously, however, no evidence of any effect of the thermal decomposition on the sublimation was seen. Such confirms the report of Bircumshaw and Newman (Ref. 6) that sublimation depends only upon temperature and to a certain extent on pressure.

Some NH_4Cl was found in the sublimate. This must arise from the reaction of Cl_2 formed in the thermal decomposition with the NH_3. If sublimation is tried in an atmosphere of NH_3, only NH_4Cl is collected as no AP will sublime, since the NH_3 suppresses the perchloric acid vapor pressure to nearly zero.

Because of this tendency to sublime then it is obvious that the nature of and the type of atmosphere in contact with AP will indeed have a bearing on its decomposition process.

(d) The Low Temperature Thermal Decomposition. Below 350° C. (Ref. 6 and 9) the products of the thermal decomposition can be accounted for by the reaction

$$2NH_4ClO_4 \rightarrow Cl_2 + 3/2\ O_2 + 4\ H_2O + N_2O.$$

Bircumshaw and Newman (Ref. 6) demonstrated that this low temperature reaction always ceases after about 30% decomposition, leaving a residue of NH_4ClO_4 which is identical, chemically and physically, with the undecomposed product except in one respect (Ref. 9). The residue had a surface area corresponding to blocks of material of a size of the same order as that of mosaic blocks in crystals. Apparently the low temperature reaction involves only decomposition of strained materials in the intermosaic grain boundaries. Visual observations of whole crystals (Ref. 6) at various stages of the reaction show that nuclei are formed on the surface and these grow three-dimensionally until a coherent interface is built up which then penetrates the crystal. An analysis of random nucleation at potential nucleus forming sites, followed by three dimensional growth, leads to a kinetic equation which contains two constants, one of which depends upon the energy of nucleation and the other on the energy of linear growth. These energies reported by Galwey and Jacobs (Ref. 9) are as follows:

	Energy of formation of nuclei		Energy of Growth	
whole crystal----	31.7	kcal./mole--	16.9	kcal./mole
powder----------	31.7	"	-- 22	"
pellet----------	31.7	"	-- 30.1	"

The increase in the activation energy for nucleus growth in the sequence crystal: powder: pellet, is a most striking feature of the reaction.

The nature of the residue indicated that the low temperature reaction is confined to intergranular material. The low temperature reaction will occur only when the gaseous products formed are able to escape and in strained material where the activation energy for the rate determining step is less than in a perfect crystal. This means the reaction starts at the junction of mosaic blocks (nucleus formation) and spreads through intergranular material (growth) until this is all consumed leaving a mass of loosely attached mosaic blocks which are unreactive unless disturbed or exposed to water vapor for certain periods of time.

The increase in energy of growth in the series crystal: powder: pellet may be ascribed to differences in physical nature of the materials. A whole crystal consists of coarse mosaic blocks, separated by comparatively large-angled grain boundaries with less missfit. The powder is

intermediate between crystal and pellet.

Above the transition point (240° C.) the changes in activation energy are much smaller (25.3, 24.6, 29.9 kcal./mole for crystal, powder and pellets respectively). Apparently the phase change involves a reorganization of the mosaic structure which gives a much finer subgrain net work. Nucleation is followed by propogation of the reaction down this net work in what is essentially one-dimensional growth.

Galwey and Jacobs (Ref. 9) consider the decomposition to involve first the formation of the molecular complex, NH_4ClO_4, i.e. an electron is transferred from the ClO_4^- ion to the NH_4^+ ion. The reaction must start on the surface where there is an imperfection which will allow this electron and its corresponding positive hole to be trapped long enough for the molecular complex to decompose. From the complex NH_4ClO_4 two molecules of water are removed thereby leaving a nitrogen atom and a molecule of ClO_2. This is followed by the formation of N_2, Cl_2 and [O]. N_2 and [O] then can react to form N_2O.

(e) The High Temperature Decomposition. (Ref. 5, 6 and 10). To study the decomposition of AP above 350° it is necessary to introduce an inert gas under pressure over the sample, in order to minimize sublimation. Between 380-450° C. the AP decomposition obeys the power law

$$p = kt^n$$

where p = pressure evolved in a constant volume system in time t, and k and n are constants. n though was noted to vary somewhat irregularly with temperature between the values of 0.5 and 1.0. The reaction was deceleratory throughout and, in contrast to the low-temperature decomposition, resulted in complete decomposition of the salt. It is noted that the products also differ from the low temperature reaction in that NO instead of N_2O was produced. The following equation is representative:

$$2NH_4ClO_4 \rightarrow 4H_2O + Cl_2 + O_2 + 2NO.$$

Because the two different reactions are occuring in the temperature range 300-380° C. results are difficult to reproduce.

Decomposition in this high temperature zone probably takes place by (1) the transfer of a proton from the ammonium ion to the perchlorate ion, thereby forming free ammonia and perchloric acid, then (2) the perchloric acid decomposes quickly to form water and Cl_2O_7. (3) Next the Cl_2O_7 yields Cl_2 and oxygen, which, (4) oxidizes the ammonia to NO and water.

The energy of activation for this reaction has been evaluated at 40 kcal./mole.

J. Powling and Smith (Ref. 11) studying the surface

temperature of burning AP have concluded that the surface temperature of the AP is only of incidental importance at moderate pressures and that the gas phase reaction between the ammonia and perchloric acid control the rate of consumption of the oxidizer.

(f) The Thermal Explosion of Ammonium Perchlorate. Above 440° C. the reaction is too fast to be followed by the same experimental techniques used for the other temperature ranges. Here only the induction period could be measured (Ref. 12). After this induction period there is a sudden large pressure change which is often accompanied by a flash of light.

Results indicate that the low temperature process, despite its lower activation energy, still occurs more rapidly than the higher temperature process in this case, being 99% complete in less time than required for the explosion, so that it cannot account for the explosion. Explosion times show that the explosion occurs when the residue from the intergranular (low-temperature) reaction is about 1/3 decomposed. The activation energy measured to be about 41.5 kcal./mole and as such supports this conclusion.

(g) The Influence of Catalysts on the Ammonium Perchlorate Decomposition. Many materials have been tried

as positive catalysts to speed up the rate of thermal decomposition of AP. The following is a partial list of compounds, which have been used with perchlorate salts.*

Substance Used	Reference
MgO	(26)
CuO	(13) & (14)
Cu_2O	(15)
Cu salts	(16)
CrO_3	(13) & (17)
CrO_2Cl_2	(17)
ZnO	(18) & (19)
CdO	(33)
NiO	(34)
Ni_2O_3	(17)
Fe_2O_3	(20) & (21) & (6)
MgO	(17)
Co_2O_3	(17)
Co_3O_4	(17)
MnO_2 & other Mn oxides	(17) & (16) & (23) & (27) & (28) & (6)
$KMnO_4$	(16) & (22)
Rhenium compounds	(22)
Carbon	(24)
Al_2O_3	(23) & (6)
CaO	(6)

* Note-References 29, 30, 31 and 32 deal with catalysts used with $KClO_3$ decomposition. Some 75 catalyst systems are listed in these four references.

The most extensive effort seems to have been directed toward the use of MnO_2, and the work of Galwey and Jacobs (Ref. 23) seems to represent one of the most complete and authorative studies on this phase of the problem.

Using mixtures of 10% MnO_2 and 90% AP their time-pressure measurements clearly pointed up the fact that in the temperature range of 200-220° C. the reaction occurs in two distinct stages. There is an initial fast reaction which is followed by a much slower reaction that is decelerator throughout. Both by analysis of the graphical plots and the collection of the products it was evident that the second reaction is independent of the MnO_2.

All observations tended to indicate that the catalytic activity is the result of physical contact between the MnO_2 and the AP. The degree of compression of the sample always produced an effect on the kinetic results. The first reaction stops then when the particles no longer present a salt/oxide interface.

Those compounds which have been observed to give any positive catalytic effect contain metals that can demonstrate variable valence or oxidation states. Not only different oxidation states, but these states must be of about equal tendency to form. This was most clearly demonstrated in the work (Ref. 22) of Brown and Woods

comparing manganese and rhenium compounds as catalytic agents in the AP decomposition. Whereas manganese compounds were always found in mixed valence states at the conclusion of a reaction regardless of the starting valence condition, the rhenium always ended up in the very stable perrhennate state. Low valence rhenium compounds showed initial catalytic activity but this ceased as soon as the stable perrhennate condition prevailed. Manganese on the other hand showed continuing catalytic activity.

Galwey and Jacobs (Ref. 23) found little change in the activation energy of AP decomposition on adding the catalyst. This is apparently due to the fact that the catalyst has nothing to do with the initial and largest energy consuming step which is the transfer of the electron from the perchlorate ion to the ammonium ion and the formation of a positive hole. The role of the catalyst is to increase the life of the molecular complex thereby diminishing its tendency to revert to the ions. The presence of the Mn(IV) must do this by helping to delocalize the molecular electron orbital.

The mechanism proposed can be represented as:

$$NH_4^+ + ClO_4^- + Mn^{4+} \longrightarrow NH_4^+ + Mn^{3+} + ClO_4$$

$$Mn^{3+} + NH_4^+ \longrightarrow Mn^{4+} + NH_4$$

$$NH_4 + ClO_4 \longrightarrow 1/2\ N_2 + ClO_2 + 2H_2O$$

In the uncatalyzed reaction much more O_2 is noted to be set free as compared to the catalyzed one. Such O_2 must originate from the decomposition of the ClO_2. In the catalyzed reaction the reaction temperature being lower might account for less decomposition of the ClO_2.

Jacobs et al. (Ref. 15) in studying the effect of Cu_2O on the AP decomposition still noted the same activation energy value, and proposed a similar mechanism as noted before but in this case felt that the Cu_2O taking on oxygen might account for part of the effect.

One of the most interesting cases of a metal oxide that is quite effective in promoting the thermal decomposition of AP and which involves a non-variable valence metal is ZnO (Ref. 18). In some cases the reaction was so fast that explosion resulted. From the fact that small amounts of Al_2O_3 increased the effectiveness of the ZnO, while Li_2O decreased its effect, the authors concluded that the role played by the ZnO is one of an electron connector.

One case of a negative catalyst for a similar reaction has been reported (Ref. 25). Lithium perchlorate decomposition is slowed down by adding silver nitrate in 5-15% amounts. The authors advanced the idea that the retardation was due to the silver ions removing chloride ions as insoluble silver chloride. This idea was based upon the rate decrease

being function of the silver ion concentration and also that the effect tended to disappear when the temperature reached the melting point of the silver chloride.

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6. Apparatus and Instrumentation

(a) Apparatus. Figure 1 is a block diagram showing the components of the DTA equipment used and their relationships. The apparatus consisted of a furnace, heating block, thermocouple probe, sample and reference holder, S.R. recorder, x-y recorder, D.C. amplifier and temperature programer.

The electric furnace is detailed in Figure 2.

The heating block made of aluminum is outlined in Figure 3 and was constructed in our own shops as was the furnace.

Into the block are inserted two pyrex glass sample holders as pictured in Figure 4. These hold the AP (sample cell) and aluminum oxide (reference cell). After the sample and reference materials are placed into the respective holders and tamped into place, the thermocouple probe, containing the Chromel-Constantan thermocouple, is then pushed through the center of the material. These thermocouples transmit signals to the y-axis of the recorder. Another thermocouple in the block transmits a signal to the x-axis. A correction term, experimentally determined, must be algebraically added to this to obtain the temperature in the center of reference. It was found that the recorder would not function properly if an attempt was made to

record the signal from the reference thermocouple on the x-axis simultaneously with the signal from the voltage difference being recorded on the y-axis.

The side arm on the sample holder (Figure 4) allows the sample, while being heated, to be subjected to vacuum, normal atmospheric pressure or increased pressure of an unreactive gas such as nitrogen.

(b) Instrumentation. The accuracy of the DTA depends to a great extent on the precision with which a uniform heating rate can be maintained. The instrument used for the heating control was an F & M Model 240M Proportional Power Proportioning Temperature Programer.

The amplification system consisted of an Electro Instrument Model A-12 D.C. Amplifier, and was used only to magnify the voltage difference between the thermocouples in the reference and sample tubes.

The differential signal from the D.C. amplifier was fed into the y-input of a Moseley Model 2 x-y recorder. Into the x-input of this instrument was fed the signal from the thermocouple which recorded block temperature. The use of the Sargent SR recorder was to follow the heating rate so that it could be known with certainty at each peak temperature on the DTA plot. Such was necessary as experience demonstrated that the setting on the temperature programer was only approximate.

7. Materials

(a) The ammonium perchlorate used in this study was obtained from the G. Fredrick Smith Chemical Company of Columbus 22, Ohio and is item number 3 in their catalog. It is classified as reagent grade. When used from the stock bottle without further treatment it will be listed as stock material. The material was stored in a desiccator over P_4O_{10} to insure minimum moisture being absorbed. In an effort to obtain particles of AP of different sizes the stock material was screened through two stainless steel wire mesh sieves. That retained by U.S. 40 mesh was called coarse, that retained by U.S. 60 mesh was designated medium, while all passing through the 60 mesh was termed fine.

(b) All materials used as catalysts were either ACS grade or were prepared in our laboratory by standard literature reported procedures.

(c) During the course of this work, we began mixing very fine glass beads with the AP material. By using a smaller sample, the heat changes of the sample reaction do not influence the results as markedly and hence allow the temperature measuring devices to more accurately indicate the true temperature being experienced by the sample.

Glass beads were selected for the diluting of the

material since they are non-conductors for electrons and show no catalytic influence on the AP decomposition. In all cases we mixed the AP and glass beads in a 1:3 weight ratio.

The glass beads were Sign Beads, type 831A, Size B, wide angle and manufactured by Flex-O-Lite Manufacturing Company of St. Louis, Missouri.

Before being used the glass beads were washed with three molar hydrochloric acid solution, rinsed with distilled water and oven dried at 105° C.

A DTA run on the glass beads alone vs. the alundum reference indicated that they underwent no changes over the 25 to 450° C. temperature range that could produce exo- or endo-thermic peaks on the DTA plot.

(d) Commercial tank nitrogen, dried by bubbling through wash bottles of concentrated sulfuric acid, was used to create an inert atmosphere at pressure in excess of one atmosphere over the decomposing AP sample.

(f) The special samples of AP furnished by Mr. Huskins of the AMC Propulsion Laboratory, Redstone Arsenal, Huntsville, Alabama and disignated H-1 through H-6 had the following specifications:

H-1: 400 micron, rounded AP, 99.2% minimum AP, conditioned with tricalcium phosphate (TCP), lot no. 4080.

H-2: 45 micron, rounded AP, 99.2% minimum AP, conditioned

with TCP, lot no. 1030-194-1.

H-3: 17 micron, ground AP, conditioned with TCP, lot no. 2153.

H-4: 180 micron, unground AP, conditioned with TCP, lot no. 2153.

H-5: 8 micron, ground AP, conditioned with TCP.

H-6: 90 micron, rounded AP, conditioned with TCP, 99.2% minimum AP, lot no. 1075-38-11.

8. Results

Before commencing DTA runs with AP the performance of the equipment was checked by determining decomposition plots for samples of ammonium nitrate, benzoic acid, sodium nitrate and silver nitrate. The temperature values taken from these plots agreed within what was considered reasonable experimental variation to those given in the literature.

In Figure 5, curve (A) shows a typical DTA plot for AP when heated vs. air; curve (B) represents AP vs. a partial vacuum. On curve (A) reading from left to right four peaks are noted, and in the tables values quoted for T_1, T_2, etc. are for these so numbered peak temperatures. Peak number 3, an exothermic peak, is noted to be absent when medium and fine material was heated. Curve (C) on Figure 5 illustrates the run for sample 2-22-3 which was typical of this.

In Tables Number 1, 2, 3, and 4 are summarized the peak temperatures for the heating of AP of four different particle sizes vs. air. In addition the heating rate at each peak is recorded.

These values of heating rates and peak temperatures allowed us to make a plot of $\ln[\phi/T_m^2]$ vs. $1/T_m$, ϕ being the heating rate and T_m the peak temperature. The slope of

the straight line drawn through the points on such a plot permitted the computation of the activation energy since the latter is the product of this slope and R, the gas constant, in units of cal./deg./mole.

For purposes of illustration Figure 6 shows a typical plot of $\ln[\phi/T_m^2]$ vs. $1/T_m$, this particular one being for the data given in Table No. 1 for Stock AP, peak no. 4. The slope of the best straight line constructed through the plotted points equals $(-)25.8 \times 10^3$, which when multiplied by 1.98 cal./deg./mole gives 51.3 kcal./mole as the activation energy. This latter value along with all the other activation energies computed from the values in Tables 1 - 4 are given in Table No. 6.

Table No. 5 summarizes the peak temperatures taken from DTA plots for Stock AP heated vs. a partial vacuum. A typical plot of one of these runs is shown as Curve (B) in Figure 5. Activation energies computed from the values listed in Table No. 5 are given in Table No. 6.

In Table No. 2 no T_4 values are given for samples 2-5-1 and 2-5-2 because the experiment was purposely stopped at T_2. Sample 2-8-1 was a case where we had a malfunction of the thermocouple.

In Table No. 1 for samples 1-94-1 through 1-98-2, it is difficult to be certain whether the values recorded

for T_2 should be so classified or whether they should be called T_3. These plots were very difficult to interpret and the results are quite uncertain. T_4 values for 1-98-1, 1-98-2 and 1-97-1 are not given because the sample exploded and no peak temperature could be recorded. For samples 2-2-1 and 2-2-2 the missing T_4 values are the result of stopping the experiment at the end of T_3 so that we could determine the weight loss of the sample at this point. Such loss amounted to 40%.

In order to minimize the tendency of the AP sample to sublime from the hot to the cooler portion of the sample tube, DTA determinations were conducted under a nitrogen atmosphere where the pressure was maintained at approximately 82 cm. of Hg.

The DTA plots showed three peaks. Peak 1 is the enotherm associated with the change in crystal structure. Peaks 2 and 4 (we use 4 instead of 3 for designating this peak so as to indicate that it is the same peak so numbered on the DTA plots run against air pressure and shown as Curve (A) in Figure 5.) are the low and high temperature exotherms.

In Tables No. 7, 8, 9 and 10 are recorded the results of these runs and the last table summarizes the slope of the curves plotted from these data as well as the calculated activation energies.

In order to determine the influence of such things as particle size, shape of particle and added conditioners upon activation energies associated with the decomposition of AP, we were furnished certain samples by Mr. Huskins of the AMC Propulsion Laboratory, Redstone Arsenal, Huntsville, Alabama. The composition of these samples is given on page 26. In Table No. 11 we have listed the peak temperatures measured for these samples and Table No. 12 summarizes the activation energies calculated for such results.

Two materials, finely powdered aluminum oxide and iron (III) oxide, were studied for their catalytic effect on the AP decomposition reactions.

In all cases 0.01 g. of AP was mixed with the glass beads in a 3:1 weight ratio and then 5% by weight of the AP equalled the weight of the added catalytic agent. All of these were physically stirred together for a length of time deemed adequate to achieve uniform distribution of catalyst throughout the mixture.

The Tables No. 13 and 14 give the measured values for the DTA runs and summarize the computed activation energies of the reactions.

Similar studies on other catalysts are given in Table No. 15. No activation energies were computed for these. Curve (D) in Figure 5 shows a typical plot for one

of these catalyzed reactions. This particular one (Sample No. 3-94-1) is for Medium AP mixed with zinchexammine perchlorate and heated at 4° C./minute.

9. Conclusions

As a result of these several hundred runs we are convinced that particle size, additives and heating rates materially influence the DTA plot obtained when AP is heated from ambient temperature to about 450° C. Reproducibility is not all that one would desire. Here are some typical values:

Change (AP)	Activation energy (kcal./mole)				
	Fine	Medium	Coarse	Stock	Lit.
Crystal modification	90	95	24	74	25-30
Low T. decomp.	25	31	30	30	32
High T. decomp.	30	30	65-139	51	40

Agreement with literature values are not too good in all cases. However, it must be born in mind that the literature values were measured under isothermal conditions.

Here are typical activation energies when certain catalysts were present:

	Activation energy	
	Cryst. change	Decomposition
Iron (III) oxide		
AP (Fine)	179	22
AP (Medium)	15	28
Aluminum oxide		
AP (Fine)	267	27
AP (Medium)	25	27

Galwey and Jacobs (Ref. 23) report little change in activation energy of AP decomposition by adding a catalyst. Our results would seem to indicate a small lowering for these two cases, but it is not absolutely certain. Attempts to correlate activation energies from DTA data with the role of the catalyst have not been too fruitful. The better approach we think is the measure of the peak temperature of the decomposition isotherm. It is to be noted that some catalysts produce only one exothermic peak following the crystal transformation, while others produce several. We have reasoned that the best catalyst should be the one which produces complete decomposition of AP in one single step and at as low a temperature as possible.

Figure 7 shows a plot of the peak temperature of the AP decomposition exotherm vs. the atomic number of the metals in the catalyst for those we have measured. These results show that for certain metals from aluminum to cadmium in the periodic table there is a lowering of the temperature to a minimum at zinc. These catalysts were all oxides except Fe which was used as iron (III) oxide, ferrocene, butyl ferrocene and iron (II) hexammine perchlorate.

It was the main purpose of this study to try to find an answer to the question regarding the nature of the role

of the positive catalyst in AP decomposition.

Galwey and Jacobs in their work on the use of MnO_2 considered that physical contact between the catalyst and the AP was the important thing. Since most of the catalysts used have been compounds of the transition metals, the idea that the catalyst had to facilitate electron transfer has been prominent. Brown and Woods (Ref. 22) compared the effect of Mn and Re compounds and concluded that the stability of the high oxidation state of the latter accounted for its poor showing.

The most quoted mechanism for the low temperature decomposition is that proposed by Galwey and Jacobs and it involves an electron transfer from the perchlorate ion to the ammonium ion to give what they called a molecular complex. This is followed by interaction of the two free radicals to give the products. They concluded that the catalyst did not change activation energy because it was not involved in the largest energy consuming step, i.e., the electron transfer. They considered that the catalyst only stabilized the molecular complex.

We tend to disagree with this contention and would like to suggest a modification. First let us examine some known facts. From our work here, if we take the lowering of the peak temperature as a measure of the effectiveness

of the catalyst, we have this order: Zn > Cu > Cd > Fe > Mn > Al. Hermoni and Salmon (Ref. 17) used the time needed to produce a given fraction of decomposition of AP as a measure of effectiveness. They gave the following order: (Co_2O_3/Co_3O_4) > Ni_2O_3 > MnO_2 > Cr_2O_3 (the latter two reverse after a time lapse). $CuCrO_2$ is known also to be very effective as a catalyst. Gas products from the uncatalyzed reaction show more free oxygen than the catalyzed change. Up to a certain point increase in pressure increases the burning rate.

The very pronounced effect of zinc and cadmium would seem to indicate that the ability of the metal to exist in more than one oxidation state is not the controlling factor.

What really happens during this chemical change? First, we know that AP tends to sublime when heated. To do this a proton must be transferred from the ammonium ion to the perchlorate ion and the two gases vaporized. The perchlorate ion is a stable balanced structure. In ionic salts 480° C. or higher temperatures are required for its decomposition. The perchlorate ion has only a low attraction for protons. The charge on an oxygen of this ion is calculated to be about -0.21 units. But when a proton returns to the perchlorate ion the Cl-O bonds weaken and perchloric acid is known to decompose at 92° C. It is logical to assume that decomposition at low temperature must start with

perchloric acid. However, if this action is to be complete and to continue, there must be energy available to maintain the burning. Here is where the ammonia comes into the picture. The free OH radical from the decomposing perchloric acid extracts hydrogen from the ammonia to form water, ultimately leaving the two nitrogens to dimerize into molecular nitrogen. Both of these reactions are highly exothermic.

Something must prevent the collision of the ammonia and perchloric acid long enough to let the acid start to split out OH's, or when the ammonia and perchloric acid do collide something must interfere with the proton return process. Suppose in this brief period the ammonia has found it possible to make a nucleophillic attack on a site more desireable than a proton, then the perchloric acid would not be able to give up the proton, but rather would live long enough to start decomposing.

What is this particle which traps and holds the ammonia? It is the coordination of this ammine ligand with the metal part of the catalyst, i.e., a metal ammine complex species is formed. Now there is no data available by means of which we can judge the stability* of the metal ammine complexes at temperatures of 300-400 deg. C. There are,

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* Note (added in proof). Simpkin and Block have reported that $Zn(NH_3)Cl_2$ when heated to 200° C. for 200 hours showed a loss of weight of only 0.3% [J. Inorg. and Nucl. Chem., 24, 371 (1962)].

however, available formation constants for ammine complexes in water solution. It would be reasoned that since the same forces are involved in forming these complexes that the same relative ratio should exist between their stabilities at the higher temperature. Here are the logarithm of the first formation constants for a few metal ammine complexes:

Al(III)	0	Cd(II)	2.6
Fe(III)	0	Cu(II)	4.1
Fe(II)	1.4	Mn(II)	0.8
Co(II)	-0.3		
Co(III)	7.3		
Ni(II)	2.8		
Zn(II)	2.6		

According to this list Co(III) should be the best. It is noted, that as we move from transition to B family metal, ammine complexing tendency increases. The trend is toward greater stability as we move toward Zn and Cd, which is what Figure 7 illustrates.

It is known that a pressure increase, up to a point, enhances the AP decomposition when catalyzed. Such would help to keep the ammonia within reach of the oxidizing power of the perchloric acid vapor. Further increase in pressure prevents sublimation and as such cuts down on the acid vapor formation.

The fact that more free oxygen comes from the uncatalyzed reactions would seem to indicate that less contact is made between the ammonia and perchloric acid vapors formed during sublimation.

When using Zn, Cd and Cu our results seem to indicate complete decomposition while others have reported with MnO_2 that the reaction stopped when contact was lost between the catalyst and AP. On the basis of our contention, the material as a vapor goes to the catalyst and hence the ammonia holding power is the measure of success rather than physical contact.

The complexing power of the catalyst toward the ammonia has been stressed and is probably the controlling factor. However, it is known that when working in non-aqueous conditions certain metals can form rather stable complexes with the chlorate ion as the ligand. It may be that Fe, although not a good complexing metal toward ammonia, can hold the perchloric acid. Zinc's amphoteric nature may mean that such structures as $NH_3 \rightarrow Zn{=}O$---$H{-}O{-}ClO_3$ could form. This bridging is important because it could serve as a path for electron transfer from the nitrogen to the chlorine. The most efficient nature of mixed catalysts such as Cr_2O_3/Co_3O_4 or $CuCrO_2$ may be the result that one metal or oxidation state is the preferred site for the ammonia complexing while the other is preferred by the perchloric acid and the oxygen bridge between the metals provides the electron transfer path.

The proving or disproving of these theories can come

only from the synthesizing of specific catalyst compounds where the complexing sites are controlled and studying the effect they have on this AP decomposition. Such is the aim of our subsequent and continuing research program on this study of the mechanism of AP decomposition.

.'.BLES

List of abbreviations used in the following tables:

Sno = Sample number

Swt = Sample weight in grams

T_1 = Endotherm peak temperature (crystal transformation)

T_2, T_3, and T_4 = Peak exotherm temperatures in order of increasing temperature from left to right on the plot

HR_1, HR_2, HR_3, and HR_4 = Heating rates in deg. C./min. at temperatures of same number

FAP = Fine AP (less than 60 mesh)

MAP = Medium AP (between 40 and 60 mesh)

CAP = Coarse AP (greater than 40 mesh)

Abbreviations for Table #15 are given with that table.

Table 1. Summary of peak temperatures taken from DTA plots for stock AP heated vs. air at indicated rates.

Sno	Swt	HR_1	T_1	HR_2	T_2	HR_3	T_3	HR_4	T_4
1-70-1	0.5006	9.60	263.2	9.60	320.0	--	--	10.15	449.5
1-70-2	0.5000	4.41	252.9	3.70	291.8	--	--	3.48	426.8
1-71-1	0.4996	2.11	240.0	2.00	271.0	2.11	332.7	2.16	428.0
1-84-1	0.4994	10.03	248.9	8.86	306.0	8.44	357.4	7.78	439.2
1-84-2	0.4935	4.51	243.4	3.60	278.3	3.80	340.0	3.33	422.9
1-84-3	0.4974	2.22	240.3	2.13	263.4	2.14	331.0	2.03	409.0
1-87-1	0.5067	10.40	256.1	8.70	313.7	8.50	371.8	721.1	447.9
1-93-1	0.5046	4.70	248.9	3.40	287.1	4.20	349.1	3.80	435.5
1-94-1	0.5027	16.70	262.6	14.70	326.3	--	--	13.90	459.0
1-94-2	0.5023	15.90	262.6	11.70	322.5	--	--	8.70	454.6
1-96-1	0.4996	2.40	245.0	2.30	336.5	--	--	2.30	419.4
1-97-1	0.5028	10.30	258.7	9.80	316.4	--	--	--	--
1-98-1	0.5067	13.00	241.1	7.60	304.1	--	--	--	--
1-98-2	0.5039	10.70	256.8	10.70	314.9	--	--	--	--
2-2-1	0.5004	2.40	243.4	2.10	266.5	2.50	336.6	--	--
2-10-1	0.2489	1.89	243.0	--	--	--	--	1.87	431.8
2-11-1	0.2513	4.45	247.0	--	--	--	--	4.46	441.0
2-11-2	0.2508	1.98	243.0	--	--	--	--	1.98	428.4
2-11-3	0.2532	12.26	251.7	8.68	312.9	--	--	11.72	450.5
2-13-1	0.2514	2.23	241.8	--	--	--	--	2.13	427.3
2-13-2	0.2527	4.47	246.2	--	--	--	--	3.75	439.3
2-13-3	0.2518	11.66	252.1	--	--	--	--	11.85	452.3
2-2-2	0.5041	3.90	--	3.90	284.0	4.20	354.4	--	--

Table #2. Summary of peak temperatures taken from DTA plots for Coarse AP heated vs. air at indicated heating rates.

Sno	Swt	HR_1	T_1	HR_2	T_2	HR_4	T_4
2-5-1	0.5007	4.10	307.2	4.10	307.2	--	--
2-5-2	0.5052	2.10	243.8	2.00	297.6	--	--
2-8-1	0.5032	2.11	235.9	--	--	--	--
2-7-1	0.5002	2.05	245.0	1.90	290.0	--	--
*2-7-2	0.5023	4.44	250.9	4.26	298.7	4.22	448.6
*2-21-1	0.2019	9.40	262.5	--	--	9.10	469.1
2-21-2	0.2021	1.90	251.0	--	--	2.25	443.0
2-21-3	0.2027	4.16	268.4	--	--	4.32	465.3
2-23-1	0.2007	2.34	252.6	--	--	2.09	465.3
2-23-2	0.2063	4.16	252.1	--	--	4.32	457.9
2-23-3	0.2254	8.64	257.3	8.64	303.2	8.64	454.6

*Note T_3 = 399.3 for HR_3 of 4.12. These two runs were made vs. vacuum and the T numbers correspond to the peak numbers of curve B; Figure #5.

Table #3. Summary of peak temperatures taken from DTA peak for medium AP heated vs. air at indicated heating rates.

Sno	Swt	HR_1	T_1	HR_2	T_2	HR_4	T_4
2-22-1	0.1992	2.21	251.7	--	--	2.25	444.7
2-22-2	0.2017	4.30	250.1	4.15	297.6	4.01	461.3
2-22-3	0.1995	10.40	254.3	10.4	325.6	10.40	440.6
2-24-1	0.2005	2.15	245.8	--	--	1.97	473.4
2-24-2	0.2010	3.90	249.0	--	--	4.44	444.5
2-24-3	0.2010	--	--	10.50	303.3	10.50	457.9
2-29-1	0.1975	2.11	248.9	--	--	2.13	439.3
2-29-2	0.2011	4.16	255.1	--	--	3.83	459.9
2-30-2	0.2034	10.30	256.8	--	--	8.64	462.2
2-31-3	0.2006	10.13	254.0	--	--	10.00	453.5
2-32-1	0.1989	9.87	258.7	9.36	318.7	8.15	458.0
2-33-1	0.1968	2.11	246.2	--	--	2.25	443.0
2-31-2	0.2006	--	--	9.63	311.0	--	--

Table #4. Summary of peak temperatures taken from DTA plots for fine AP heated vs. air at indicated heating rates.

Sno	Swt	HR_1	T_1	HR_2	T_2	HR_4	T_4
2-25-1	0.2013	2.11	246.5	--	--	2.00	415.0
2-25-2	0.2021	4.29	249.0	4.21	304.5	4.13	441.5
2-25-3	0.2020	10.39	254.8	--	--	9.00	448.6
2-26-1	0.1993	2.20	245.0	--	--	1.98	425.4
2-26-2	0.2048	4.15	246.2	--	--	4.00	441.1
2-27-1	0.2014	10.25	254.8	9.63	312.9	8.65	454.2
2-30-1	0.2017	2.13	242.4	--	--	--	--
2-31-1	0.2005	4.47	248.9	--	--	--	--
2-31-2	0.2014	9.87	267.7	8.99	327.1	--	--

Table #5. Summary of peak temperatures taken from DTA plots for stock AP heated vs. vacuum.

Sno	Swt	HR_1	T_1	HR_2	T_2	HR_4	T_4
1-87-3	0.5084	11.80	260.3	8.10	304.5	8.00	413.9
1-88-2	0.5020	1.97	244.2	2.20	258.3	2.10	394.6
1-88-1	0.5010	4.30	248.2	3.60	275.1	3.60	390.3

Table #6. Calculated activation energies from DTA data for the crystal and chemical changes of AP when heated vs. air.

Sample	Atmosphere	Peak No.	Slope x 10^{-3}	Activation energy in kcal./mole
Stock AP	air	1	-37.0	73.6
Stock AP	air	2	- 9.7	18.2
Stock AP	air	3	-15.0	29.8
Stock AP	air	4	-25.8	51.3
Coarse AP	air	1	-11.9	23.7
Coarse AP	air	2	-40.0	79.6
Coarse AP	air	3	-*-	-*-
Coarse AP	air	4	-70.0	139.3
Medium AP	air	1	-54.3	108.0
Medium AP	air	2	-15.86	31.6
Medium AP	air	4	-84.6	168.4
Fine AP	air	1	-45.0	89.6
Fine AP	air	2	-15.84	30.46
Fine AP	air	4	-18.3	36.4
Stock AP	vacuum	1	-60.0	119.4
Stock AP	vacuum	2	- 7.7	15.3
Stock AP	vacuum	3	-20.0	39.8

-*- Insufficient data from which to make the calculation.

Table #7. Summary of peak temperatures taken from DTA plots of fine AP heated vs. nitrogen at p. = 82 cm. of Hg.

Sno	Swt	HR_1	T_1	HR_2	T_2	HR_4	T_4
2-40-2	0.2010	4.47	247.8	4.43	298.7	4.37	443.0
2-41-1	0.2014	2.34	246.6	--	--	2.13	430.2
2-41-2	0.2034	10.10	267.7	8.80	330.9	8.40	479.0
2-61-1	0.1989	2.10	244.2	2.00	310.0	2.10	420.6
2-62-1	0.2006	9.20	257.2	9.60	310.8	11.00	459.8
2-62-2	0.2003	4.20	250.5	--	--	4.20	449.8

Table #8. Summary of peak temperatures taken from DTA plots of medium AP heated vs. nitrogen at p. = 82 cm. of Hg.

Sno	Swt	HR_1	T_1	HR_2	T_2	HR_4	T_4
2-42-1	0.2002	2.23	241.4	--	--	2.13	424.4
2-42-2	0.2004	4.21	245.8	4.11	293.0	3.95	441.1
2-42-3	0.2015	11.70	258.7	8.72	318.0	10.48	456.8
2-60-3	0.2024	4.00	253.3	4.10	310.1	4.10	458.6
2-61-2	0.2047	2.20	252.1	2.00	315.2	2.20	439.3
2-63-1	0.2005	10.00	250.5	9.40	313.0	8.70	446.8

Table #9. Summary of peak temperatures taken from DTA plots of coarse AP heated vs. nitrogen at p. = 82 cm. of Hg.

Sno	Swt	HR_1	T_1	HR_2	T_2	HR_4	T_4
2-44-1	0.2023	2.20	248.9	--	--	2.12	439.3
2-45-1	0.2003	3.95	263.4	4.04	329.8	4.07	472.7
2-45-2	0.2007	10.50	254.3	9.00	317.2	9.13	451.2
2-59-3	0.2006	4.30	250.1	4.10	296.8	4.10	458.0
2-60-1	0.2031	2.20	248.2	2.10	303.8	1.90	435.5
2-60-2	0.2013	10.50	254.4	8.90	314.8	9.20	447.5

Table #10. Calculated activation energies from DTA data for the crystal and chemical charges of AP when heated vs. nitrogen under 82 cm. of Hg. pressure.

Sample	Peak No.	Slope x 10^{-3}	Act. Energy (kcal./mole)
Fine AP	1	-29.7	59.09
Fine AP	2	-12.8	25.45
Fine AP	4	- 9.9	19.67
Medium AP	1	-33.5	66.55
Medium AP	2	- 6.5	129.2
Medium AP	4	-42.0	83.45
Coarse AP	1	-36.0	71.55
Coarse AP	2	-13.5	26.82
Coarse AP	4	-32.6	64.78

Table #11. Summary of peak temperatures from DTA plots of the samples H-1 through H-6 (cf page 26).

Sno	Swt	HR_1	T_1	HR_2	T_2	HR_4	T_4
H-1(2-45-3)	0.2004	4.48	248.6	4.11	290.7	4.50	445.0
H-1(2-46-1)	0.1997	10.39	254.9	9.12	305.0	10.36	448.6
H-1(2-54-1)	0.2033	2.20	251.3	2.10	284.9	2.10	434.8
H-1(2-72-1)	0.1943	2.37	243.4	1.95	278.2	--	--
H-2(2-46-2)	0.2013	4.47	241.9	4.16	287.2	3.87	427.4
H-2(2-48-2)	0.2002	9.89	259.0	8.98	316.9	8.77	449.8
H-2(2-56-3)	0.2029	2.20	245.0	2.30	279.8	2.10	429.4
H-3(2-50-1)	0.2002	4.30	248.6	4.30	299.5	4.30	428.8
H-3(2-50-2)	0.2028	2.20	247.7	2.10	291.8	2.00	424.4
H-3(2-50-3)	0.2002	10.40	255.7	9.20	325.7	10.88	446.0
H-4(2-49-2)	0.2055	4.50	247.8	4.10	294.9	4.38	446.8
H-4(2-53-1)	0.2010	2.50	244.2	2.10	268.8	2.10	439.3
H-4(2-56-1)	0.2003	9.90	264.6	9.10	319.5	11.00	471.5
H-5(2-54-2)	0.2003	4.30	251.3	--*	--*	4.10	427.5
H-5(2-58-1)	0.2000	2.00	242.2	--*	--*	1.90	402.6
H-5(2-58-2)	0.2008	9.70	260.7	--*	--*	10.20	453.1
H-6(2-56-2)	0.2000	4.40	253.0	4.20	322.6	4.20	463.5
H-6(2-58-3)	0.2012	2.20	245.0	2.10	293.3	2.40	434.4
H-6(2-59-1)	0.2004	10.70	257.6	9.00	345.3	8.80	465.4

* Note - in these runs no distinct peak was present for the low temperature decomposition. Instead the plot showed a gradual rise that tended to become a part of peak T_4.

Table #12. Summary of activation energies calculated for samples supplied by Propulsion Laboratory.

Sample	Peak No.	Slope x 10^{-3}	Act. Energy (kcal./mole)
H1	1	-29.7	59.0
H1	2	-16.6	33.0
H1	4	-62.0	123.3
H2	1	-20.2	40.1
H2	2	- 9.8	19.4
H2	4	-28.0	55.6
H3	1	-56.0	111.2
H3	2	-11.0	21.8
H3	4	-37.5	74.5
H4	1	-17.6	35.0
H4	2	- 7.2	14.3
H4	4	-23.6	46.9
H5	1	-22.8	45.3
H5	4	-15.4	30.6
H6	1	-35.0	69.5
H6	2	- 9.1	18.1
H6	4	-30.0	59.6

Table #13. Summary of peak temperature from DTA plots for AP of designated size containing indicated additive.

Sno	AP Size	Additive	HR_1	T_1	HR_4	T_4	Atmosphere
2-85-1	FAP	Fe_2O_3	2.10	247.0	2.00	352.9	Air
2-85-2	"	"	14.80	248.9	7.90	396.2	"
2-84-2	"	"	4.20	251.3	4.00	369.1	"
2-86-1	"	"	12.20	250.0	8.00	397.4	N_2 at 82 cm.
2-91-1	"	"	2.20	248.2	2.00	357.8	"
2-91-2	"	"	4.10	248.9	3.80	380.0	"
2-79-1	MAP	"	13.70	250.1	9.13	401.9	Air
2-82-3	"	"	4.30	252.9	4.13	400.0	"
2-82-2	"	"	2.20	250.9	2.13	372.9	"
2-81-1	"	"	2.20	250.1	2.13	372.5	"
2-82-1	"	"	13.50	252.5	8.38	419.1	N_2 at 82 cm.
2-83-2	"	"	4.31	251.7	4.13	395.1	"
2-83-1	"	"	2.11	251.3	2.13	373.6	"
2-79-2	FAP	Al_2O_3	4.34	249.7	4.00	396.3	Air
2-80-2	"	"	13.80	252.1	8.00	418.0	"
2-81-2	"	"	2.47	252.5	2.25	377.8	"
2-78-2	"	"	4.16	255.6	4.13	388.7	N_2 at 82 cm.
2-78-3	"	"	11.45	251.3	9.75	419.1	"
2-80-1	"	"	2.37	253.6	2.00	375.9	"
2-76-1	MAP	"	4.34	247.8	3.88	404.9	Air
2-76-2	"	"	12.70	251.7	10.38	433.6	"
2-77-2	"	"	1.97	248.5	2.25	386.1	"
2-76-3	"	"	4.34	252.1	4.00	397.0	N_2 at 82 cm.
2-77-1	"	"	13.03	252.5	8.00	435.9	"
2-78-1	"	"	2.08	252.1	2.13	371.4	"

Table #14. Summary of activation energies calculated for AP of various sizes with added catalysts.

Sample	Atmosphere	Peak	Slope x 10^{-3}	Act. Energy (kcal./mole)
Fine AP/Fe_2O_3	Air	1	-90.0	178.8
"	Air	4	-11.2	22.05
"	N_2	1	-260	517.0
"	N_2	4	-15.1	30.0
Medium AP/ Fe_2O_3	Air	1	- 7.7	15.3
"	Air	4	-13.8	27.5
"	N_2	1	-421	836.0
"	N_2	4	-12.2	24.0
Fine AP/Al_2O_3	Air	1	-134.5	267.0
"	Air	4	-12.9	25.7
"	N_2	1	-92	182.8
"	N_2	4	-14.8	29.5
Medium AP/ Al_2O_3	Air	1	-12.5	24.8
"	Air	4	-13.6	26.9
"	N_2	1	-83.9	166.7
"	N_2	4	- 9.0	17.9

Table #15. Summary of peak temperatures for various particle size AP samples containing different catalysts.

The following abbreviations have been employed in the following listing:

Size of AP material, F = fine, M = medium and C = coarse.

Catalysts: Iron (III) oxide = (1)

Aluminum oxide = (2)

Colloidal iron oxide, organosol, (Diamond Chemical Co.) = (3)

Manganese dioxide = (4)

Copper (II) oxide = (5)

Zinc oxide = (6)

Cadmium oxide = (7)

Ferrocene = (8)

Butylferrocene = (9)

Hexammine iron (II) perchlorate = (10)

Catalyst & its % of mixture	Size of AP	Rate of heating °C./min.	In degrees Centigrade T_1	T_2	T_3	T_4
(1) 5%	C	2	247.0	363.1		
		4	247.0	388.4		
		10	247.4	417.6		
(2) 5%	C	2	249.8	395.5		
		4	250.5	436.6		
		10	249.8	447.1		

(Continued)

(Continued)

Catalyst &its % of mixture	Size of AP	Rate of heating °C./min.	In degrees Centigrade T_1	T_2	T_3	T_4
(3) 5%	F	2	250.5	281.3	303.3	342.3
		4	248.8	289.1	310.3	348.3
		10	247.4	293.1	383.1	
	M	2	251.0	294.4	307.2	355.2
		4	247.8	302.6	360.9	
		10	225.9	235.5	268.4	364.3
	C	2	246.6	329.4	340.4	
		4	245.0	300.3	306.7	374.4
		10	245.0	257.9	325.2	450.5
	F	7	254.0	264.9	316.0	379.0
		5	252.5	296.0	314.5	353.7
	M	2	250.9	292.6	307.2	343.8
		4	250.1	307.2	362.4	
		10	248.2	258.3	311.0	366.1
(4) 5%	M	2	250.1	398.5		
		4	246.1	332.1	429.1	
		10	248.5	308.3	385.7	
	C	2	250.5	376.7		
		4	254.4	333.9		
		10	247.8	348.0		
(5) 5%	M	2	248.8	354.4		
		4	250.1	354.4		
		10	254.1	365.4		
(6) 5%	F	2	247.8	285.2	297.9	
		4	250.5	332.4		
		10	249.7	353.7		
	M	2	250.9	296.8	307.6	
		4	250.9	312.2	324.4	
		10	252.1	349.9		
		10	251.3	346.2		

(Continued)

(Continued)

Catalyst & its % of mixture	Size of AP	Rate of heating °C./min.	In degrees Centigrade T_1	T_2	T_3	T_4
	C	2	242.6	303.3		
		4	245.0	310.3		
		10	247.0	344.9		
		10	245.8	306.1		
(8) 5%	M	2	243.0	286.0	373.3	
		4	246.2	304.1	400.8	
		10	245.8	325.2	353.2	
		10	243.4	318.7	427.0	
(9) 5%	M	2	243.8	265.3	297.6	309.5
		4	244.2	307.2	376.6	
(9) 33%	M	2	241.8	310.6	376.3	
		2	243.2	288.3	344.0	
(10) 5%	F	2	239.2	300.6	357.5	
		4	240.0	311.4	365.4	
		10	241.1	321.8	384.6	
	M	2	240.3	286.8	368.8	
		4	239.9	316.0	379.3	
		10	241.4	322.2	398.5	
	C	2	240.0	307.2	360.9	
		4	241.1	321.8	385.4	
		10	244.2	331.3	410.9	
(9) 50%	M	2	243.8	352.2		
		4	242.6	279.9	306.0	375.9
		10	243.8	314.1	425.1	
		10	242.2	287.8	312.2	369.1
(9) 5%	M	2	243.3	379.4		
		4	246.2	298.3	421.8	
		10	244.6	312.9	449.5	
(7) 5%	F	2	243.4	344.9	372.9	
		4	245.0	362.4	394.4	
		10	245.4	377.8	406.8	

FIG. 1

CIRCUIT DIAGRAM

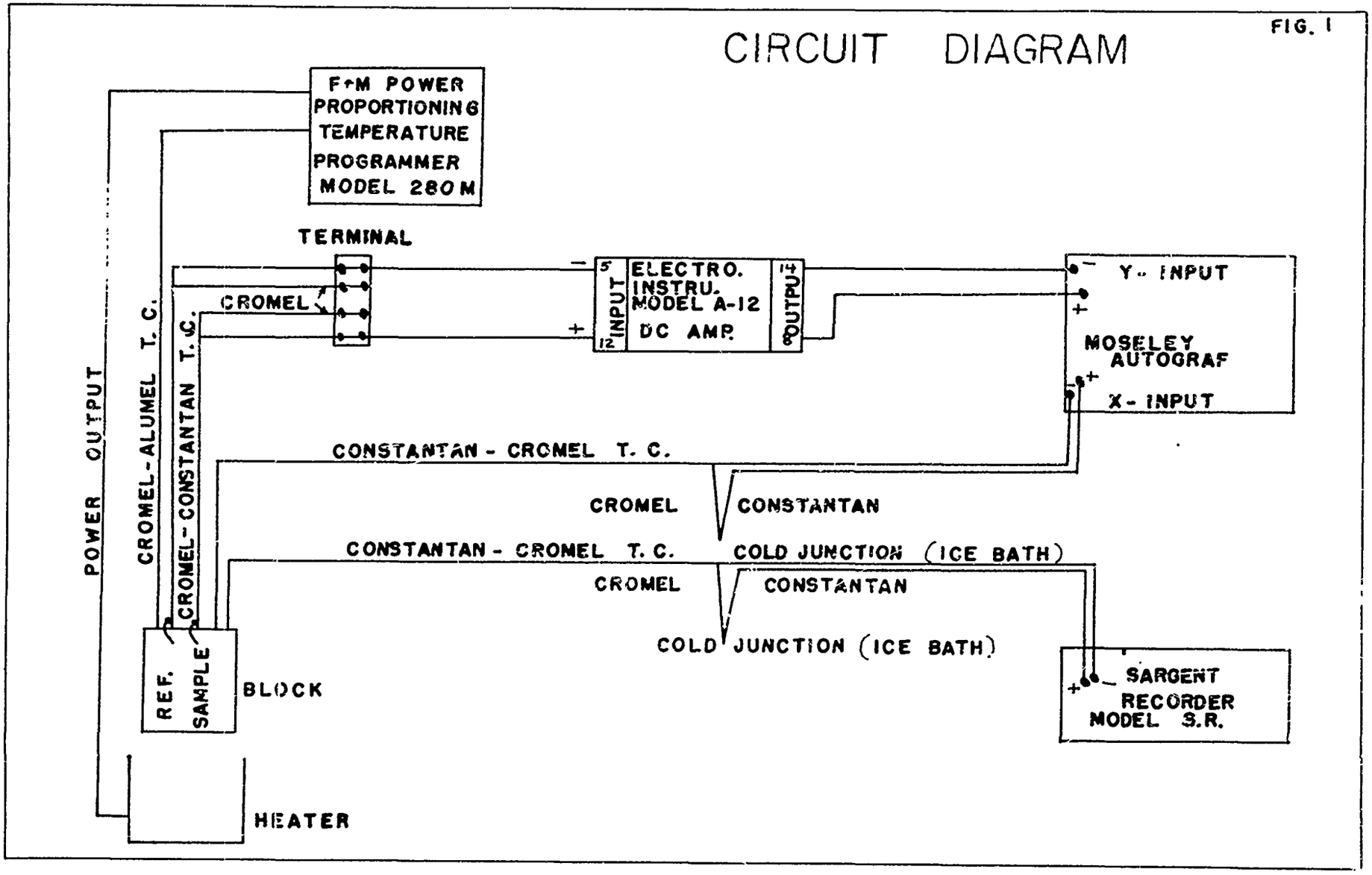
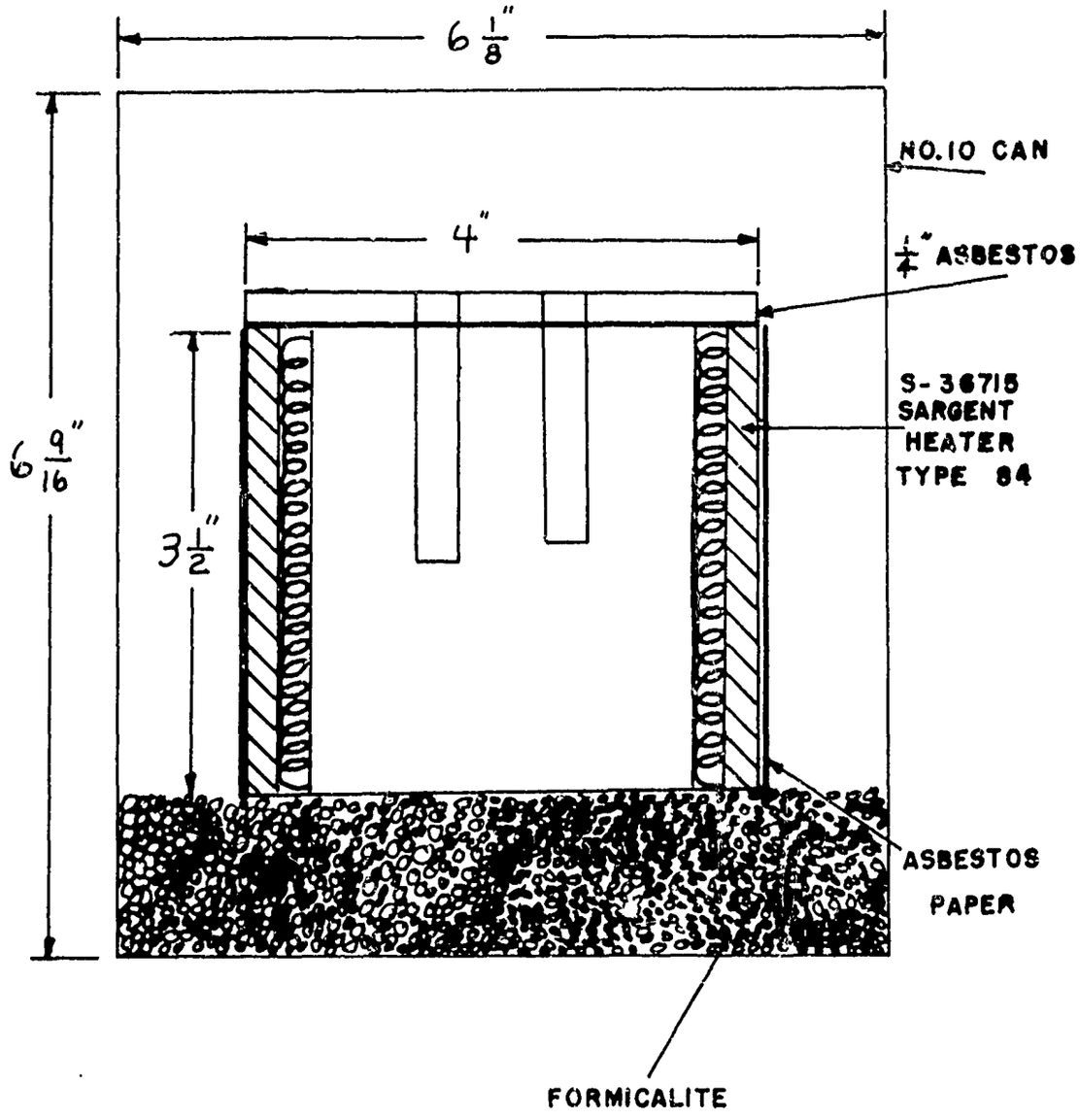


FIG. 2

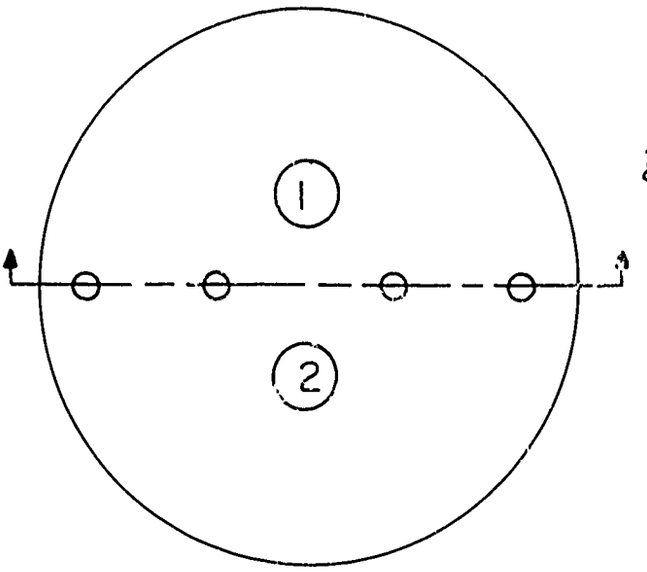
HEATER & BLOCK



3/4 SCALE

FIG. 3

ALUMINUM BLOCK



HOLE #1 – REFERENCE
$\frac{3}{8}''$ DIA $1\frac{3}{4}''$ DEEP

HOLE #2 – SAMPLE
$\frac{3}{8}''$ DIA. $1\frac{5}{8}''$ DEEP

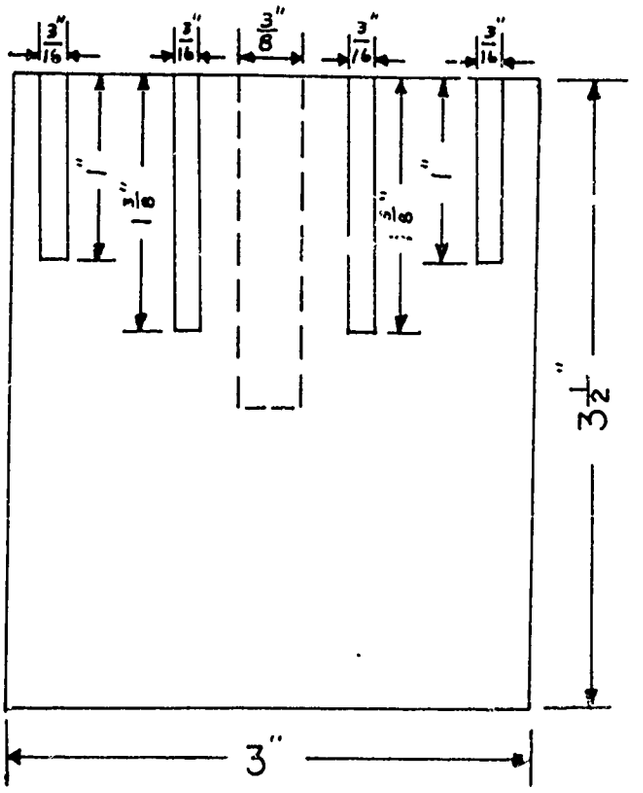
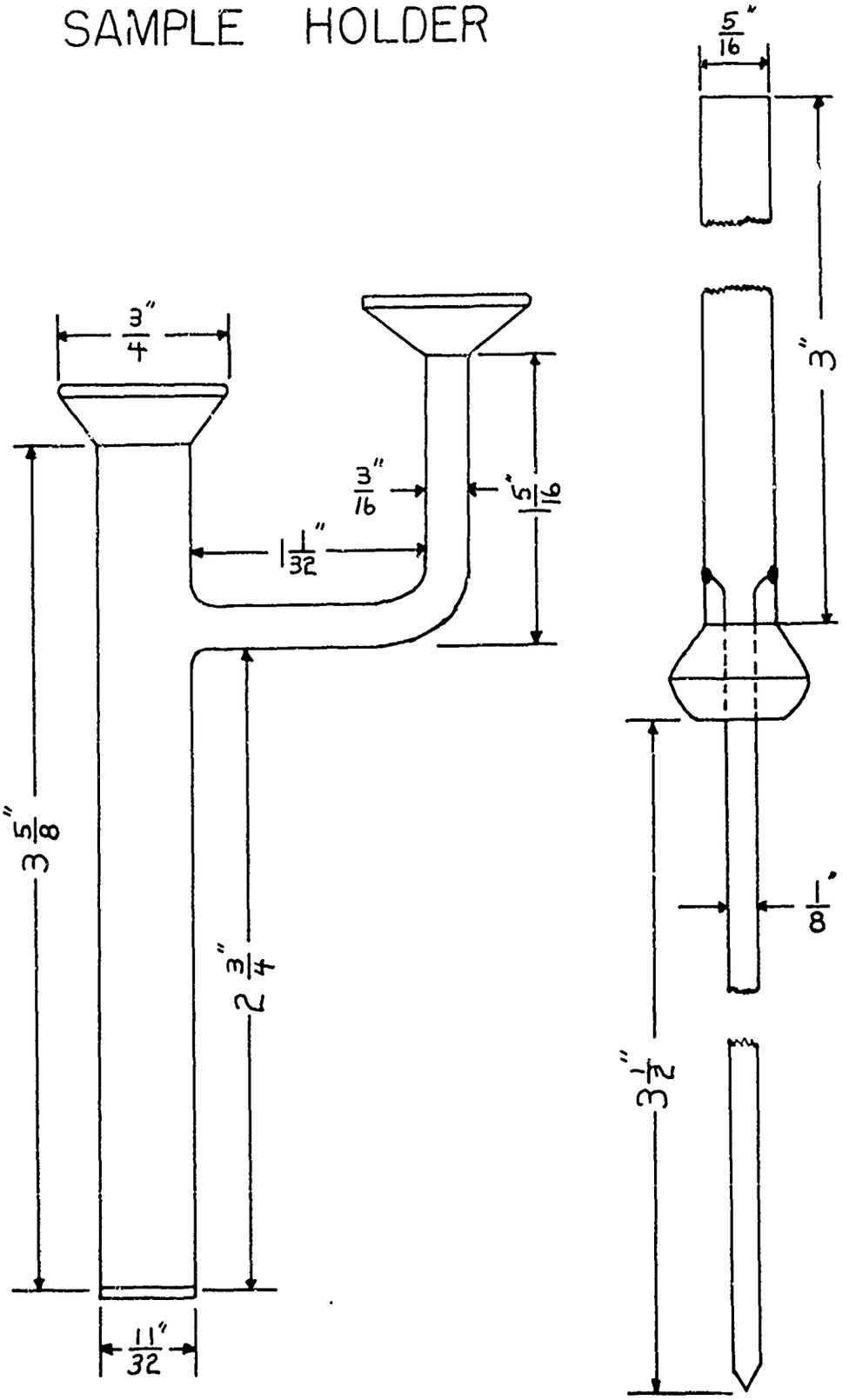


FIG. 4

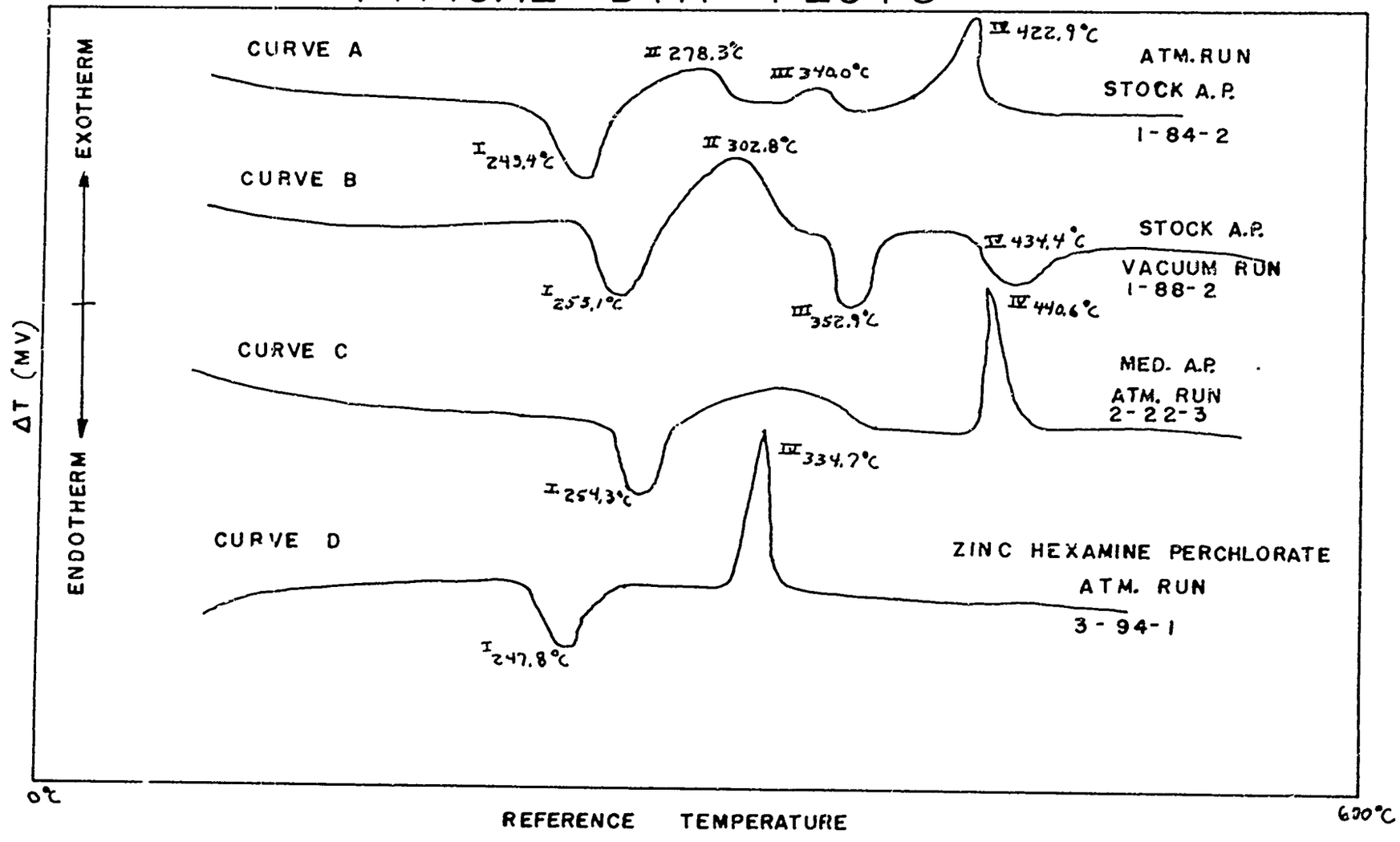
SAMPLE HOLDER



1½ SCALE

FIG. 5

TYPICAL DTA PLOTS



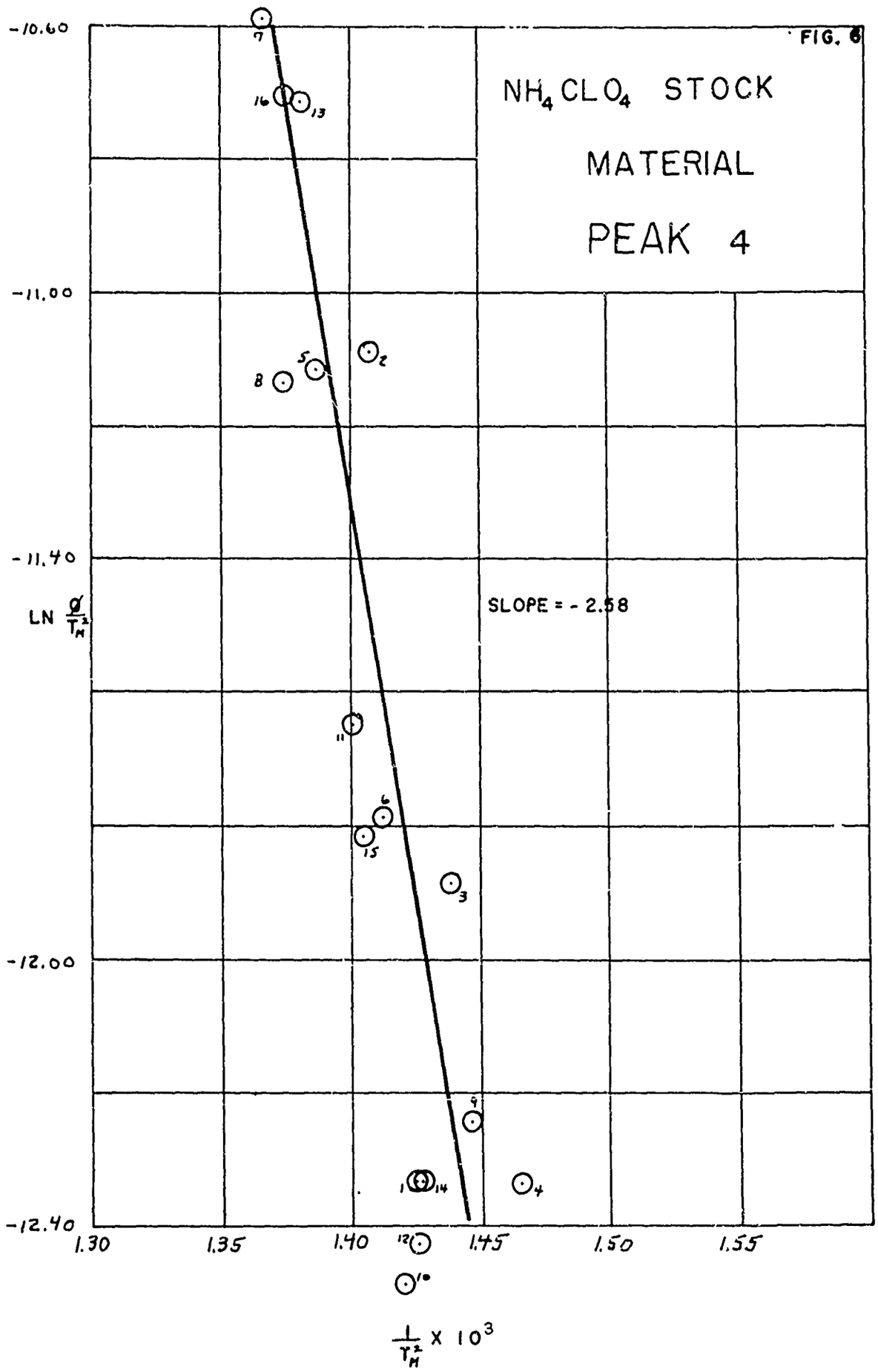
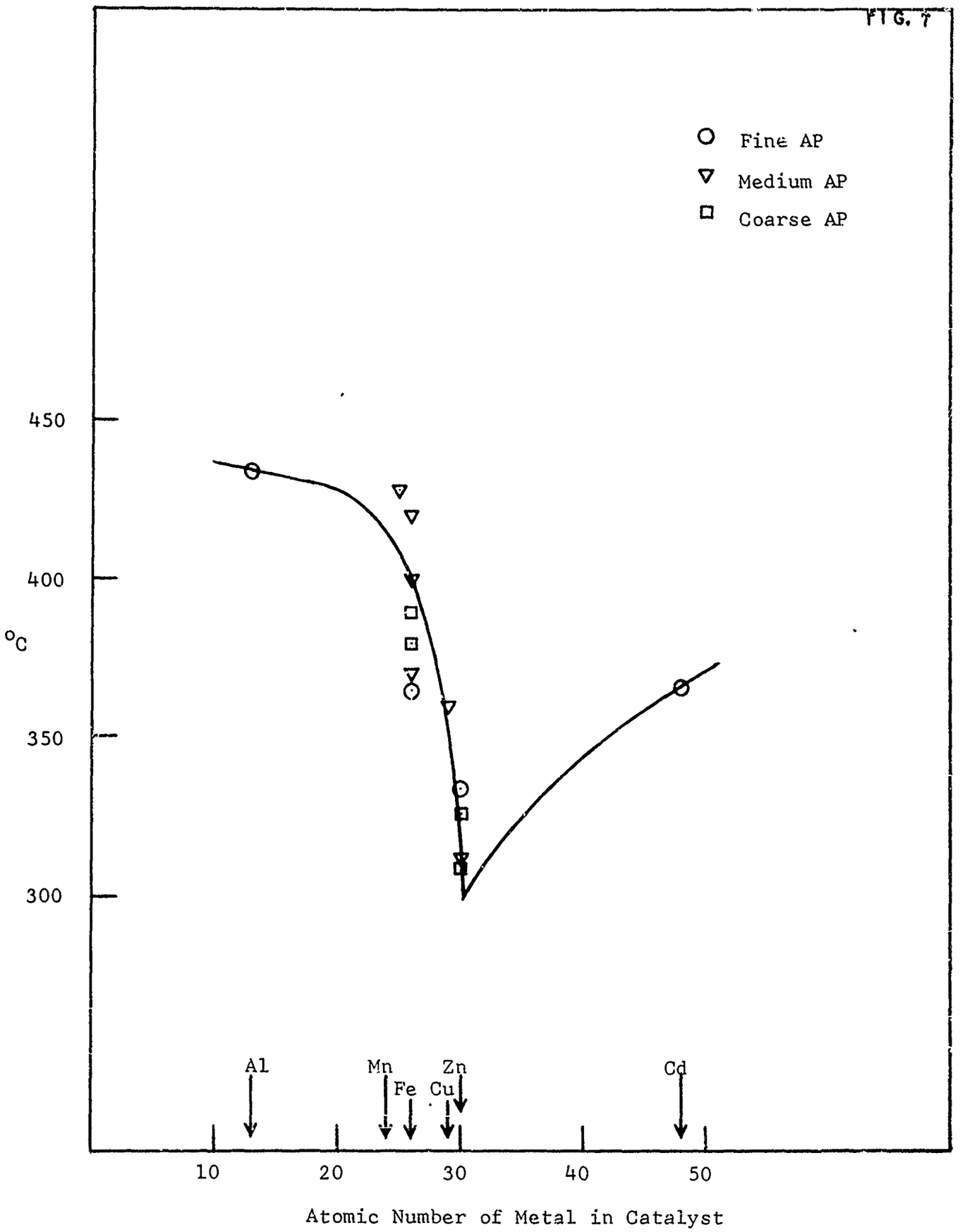


FIG. 6
NH4 CLO4 STOCK
MATERIAL
PEAK 4
SLOPE = - 2.58
-10.60
-11.00
-11.40
-12.00
-12.40
LN Ø/T_M^2
1.30
1.35
1.40
1.45
1.50
1.55
1/T_M^2 X 10^3

FIG. 7


Fine AP
Medium AP
Coarse AP
450
400
350
300
°C
Al
Mn
Fe
Cu
Zn
Cd
10
20
30
40
50
Atomic Number of Metal in Catalyst