Some Studies on Solid Propellants
Part I. Kinetics of Thermal Decomposition of Ammonium Perchlorate

By
Kenji Kuratani

Summary. For the purpose of finding the factors which influence the burning rate of propellant composed of ammonium perchlorate, the catalytic effects of the various catalysts on the thermal decomposition rate of ammonium perchlorate are mainly studied in this paper. The mild decomposition kinetics of the pure AP (ammonium perchlorate) and of the AP containing 1 per cent of CuO and MnO₂ respectively are represented with appropriate kinetics formulae and from these equations the critical temperatures where reaction transfers from mild decomposition to explosion are calculated and their results are compared with the observed values. For the other catalysts critical temperatures are observed as the measures to represent the catalytic effect of these catalysts.

In the observed values of induction periods of explosion reactions, a warming up period to heat a sample from room temperature to reaction temperature is included, therefore these values should be corrected to the true induction periods, and from the temperature variation of these values activation energies for the explosion reaction are obtained and compared with the values derived from the mild thermal decomposition. These two values are almost the same and it is concluded that there is no significant difference between the reaction mechanisms of the mild decomposition and the explosion.

The catalytic effects on the thermal decomposition of AP are divided into CuO type and MnO₂ type, and each of which shows its characteristic features. The effectiveness of CuO type catalysts may be related to the fact that these catalysts belong to the p-type semiconductors.

Ammonium perchlorate (AP) is powerful oxidizer and its mixture with polymer fuels is used as the best composite propellant at present. Recently, the multiple and specialized properties are required for the individual solid propellant according to its use, for example, it is required that for the inside burning grain, propellant must be consumed with a quite low burning rate, and on the other hand for the cigarette burning grain, propellant must have the extraordinarily high burning rate. These unique requirements should be satisfied without any loss of specific impulse, that is, the thrust level of the propellant must keep its usual value. Therefore it is not suitable to change the burning rate of propellant with the variation of the mixture ratio of oxidizer to fuel, since mixture ratio greatly affects the value of specific impulse. It is also not suitable to use the other inorganic oxidizer for the same reason. Then the remaining means to solve this problem seem to be limited to the several cases*. The one of these probable

* For the propellant of same composition, the burning rate can be changed within fairly wide range by the choice of suitable oxidizer particle size [1].
means is the suitable choice of the polymer fuel, that is, when AP is mixed with
the appropriate fuel, propellant having high specific impulse and the desirable
burning rate will be realized. Among these probable means, to vary the burning
rate of propellant with the addition of a small amount of additives also seems to
be favourable. Then we have made the studies on the thermal decomposition of
ammonium perchlorate (AP) and tried to find the relation between the pyrolysis
of AP and the burning rate of propellant composed of AP.

Bircumshaw and Newman [2] studied in detail the rate of thermal decomposi-
tion of pure AP in the temperature range 280 to 450°C, and they also found the
catalytic effects of a few metal oxides in the low temperature pyrolysis of AP.
Galwey and Jacobs [3, 4, 5] also studied the thermal decomposition of AP in the
wide temperature range, and the pyrolysis of mixture of AP and manganese
dioxide [6] over the temperature range 137 to 212°C. But these authors did not
make the experiments on the catalytic action of the various metal oxide additives
on the thermal decomposition of AP in the higher temperature range. Therefore,
in this paper discussion on these subjects are presented, since for the fundamental
research to elucidate the factors which influence the burning rate of solid prop-
ellants, it seems to be useful to change the burning rate of propellant and the
thermal decomposition of AP simultaneously by adding a small amount of vari-
ous additives and to investigate the relation between the results of these two ex-
periments.

**EXPERIMENTAL**

To find the catalytic action of the additives on the pyrolysis of AP, rate of de-
composition at one atmosphere was measured in the temperature range 260 to
500°C.

A simple apparatus shown in Figure I-1 was used to observe the slow reaction
rate of pyrolysis at one atmosphere. To maintain the temperature of the hot zone
of the reaction vessel uniform, aluminum sheet fitted to the outer size of a glass
tube A covers the central portion of the tube, and heating wire was wound over
the aluminum sheet, which is insulated from the electric wire with the thin layer
of glass tape. The decomposition process was observed through the rise of the

![Figure I-1. Apparatus used for the low temperature pyrolysis.](image-url)
product gas pressure measured by an aqueous manometer M, and a trap B was used to keep the whole system near the atmospheric pressure. The sample disk S was pushed into the center of the hot zone of the tube from the left-hand side by a glass rod, and at that moment measurement of time was started. The temperature just above the sample disk was measured by a chromel-alumel thermocouple inserted in the thin glass tube which was sealed to the tube A.

For the rapid reaction in the higher temperature range, the pressure-time curves were measured by a vertical reaction vessel of Figure I-2. The sample disk S was laid on a small iron chair C, which hung from a glass hook. When the electromagnetic switch D was turned on, an iron chair was attracted to outside and the disk dropped into the hot zone. At the same moment, the ink writing oscillograph was driven and the amplified output from the strain gage pick-up P was recorded automatically.

![Diagram of the experimental setup](image)

**Figure I-2.** Apparatus used for the high temperature pyrolysis.

Ammonium perchlorate was three times recrystallized from water and refined AP was ground and to avoid the effect due to the difference in particle size of perchlorate, the ground powders were sifted and from 200 to 270 mesh of powders were used*.

To the fine powders of these particle size a few per cent of additive powders of less than 200 mesh were mixed by a magnetic stirrer and compressed into disks of 12 mm diameter and 100 mg. weight by a small die. To obtain the reproducible results and to avoid the difference of the warming up period caused by the sample size, 100 mg. of mixed powders of perchlorate and additives were weighed and formed into a disk under the pressure of 6 tons/cm². For the additives, oxides of lighter metals (lighter than zinc) such as MgO, Al₂O₃, TiO₂, V₂O₅, Cr₂O₃, MnO₂, Fe₂O₃, Co₃O₄, NiO, CuO, Cu₂O and ZnO were mainly used. But the oxides of rare metals such as Be and Sc were not obtained and CaO was also omitted because of its hygroscopic properties. No attempt was made to try to produce catalyst of particular high efficiency, and the metal oxides of guaranteed quality were used in their respective original forms supplied. But copper chromite was synthesized by the ordinary method as described in literature [7].

Details on quantitative analysis of gaseous products and on the measurement of the burning rate will be described in the succeeding papers.

* Bircumshaw and Newman pointed out the effect of particle size on the pyrolysis rate [2].
RESULTS AND ANALYSES

1. Thermal Decomposition of Pure Ammonium Perchlorate (without Additives)

The thermal decompositions of AP are quite unique, and show their characteristic features according to the temperature at which reaction proceeds. Accordingly, we can divide the thermal decompositions of AP into three groups. That is, i) in the low temperature range below 350°C, the decomposition of AP ceases only approximately 30 per cent of its initial weight decomposes and residues remain. This type of decomposition is named tentatively as the "low temperature reaction", and the rate of this process is relatively faster than that of the following "high temperature reaction" at the same temperature. The reaction rate of the "low temperature reaction" changes abruptly at 240°C, since at that temperature crystal structure of AP is transformed.

In contrast to this, ii) at above 350°C mild decomposition continues and goes to completion, but the temperature of the reaction system is raised and exceeds the critical value, the reaction becomes faster and at last an AP disk explodes. Then the reaction in the temperature range from 350°C to the critical temperature is named as the "high temperature reaction". And iii) beyond the critical temperature, reaction rate becomes so fast that an AP disk finally explodes or ignites. This "explosion reaction" or deflagration occurs after a short induction period.

Each of these three reactions is already discussed by the previous authors, [2 ~5] and here only the experimental results on the "high temperature reaction" and the "explosion reaction" will be discussed. Since our ultimate aim is to find the relation between the thermal decomposition of AP and the burning rate of AP propellant, and the reaction kinetics at the higher temperature range seems to be more important for our purposes. With reference to this, purity of AP should be noticed. We found in our preliminary experiments, that the critical temperature was greatly reduced by the impurity, and thereafter three times recrystallized AP was used, because further recrystallization did not bring about any improvement of the results and no appreciable effect on the rise of the critical tempera-

![Figure I-3. Pressure-time curves of pure AP.](image-url)
ture value was observed.

In the first place, the experimental results on the "high temperature reaction" of pure AP are illustrated in Figure I-3, in which the results obtained in the temperature range from 380 to 440°C are plotted. These curves always have initial sharp pressure rises and the decelerating periods follow them. The first sharp rises are probably due to the relatively fast "low temperature reaction" at that temperatures. And the whole process is so complicated that it is very difficult to express the whole pressure-time curve from beginning to the last with one analytical formula of reaction kinetics, and following to Galwey and Jacobs [4], we express only the deceleratory period using the fractional decomposition \( \alpha = p/p_{\infty} \), as

\[
1 - \sqrt{1 - \alpha} = kt.
\]

(1)

This equation is of a good approximation and represents accurately the experimental values over the wide time interval as shown in Figure I-4. Using equation (1), the values of rate constant \( k \) at various temperatures are obtained, and the value of activation energy is also obtained applying these values of rate constant to the Arrhenius equation. This calculation is carried out for the decomposition kinetics of pure AP in the temperature range 350 to 440°C, and the rate constant was obtained for the deceleratory period as

\[
k = 10^{11.28} \exp \left(-44800/RT\right).
\]

This rate constant is similar to that reported by Galwey and Jacobs [4].

Secondly, critical temperature can be obtained as an arithmetic mean of the maximum temperature of reaction system under which reaction proceeds gradually and the minimum temperature under which explosion occurs. And to obtain the more accurate value of critical temperature, it is desirable to make the temperature interval between the two extreme cases as narrow as possible. The value
of critical temperature is a very useful parameter for the purpose of discussing the thermal decomposition process, and therefore the observed value and the literature values are compared in Table I–1. The observed value is lower than any of those mentioned in the previous reports, but our result is not improved by the further purification. In Table I–1 the induction periods before the explosions are also illustrated as a second useful means of comparison. This value is also shorter than any of those of the literature values. These facts show that AP which we used contains some impurity which cannot be removed by recrystallization, but other purifications of AP besides recrystallization are not made.

2. Simple Comparison of the Catalytic Effect of the Various Additives

Next problem is related to the effect of the various additives on the thermal decomposition of AP, and for this purpose kinetics at definite temperatures are measured with AP disks containing various additives.

In the first place, to find the relative effectiveness of the various additives on the thermal decomposition of AP, the reaction processes at 330°C and 380°C were measured respectively with AP disks of 100 mg. weight containing 1 per cent of additives. For example, the experimental results obtained at 330°C show the remarkable differences among the various additives, and from these experiments additives are divided into three groups.

i) With the addition of Cu₂O, CuO, CuCl and ZnO catalysts, AP disks explode after short induction periods even at 330°C. The induction period and the equilibrium pressure after the completion of reaction are not same in each case, and in Figure I–5 only the pressure time history of AP containing ZnO is represented as an example. This fact indicates the pronounced catalytic effect of these additives on the decomposition of AP, since at 330°C pure AP undergoes only about 30 per cent decomposition and does not go to completion. In these cases, pressure rises suddenly to the maximum value after the various length of induction period and then it gradually falls to the equilibrium value. This descending slope of pressure-time curve is due in part to the condensation of product gases since the gases are once heated to the quite high temperature by the heat of explosion, and in part to the volume contraction because of the occurrence of the secondary reaction between the first reaction products such as

$$2\text{NO} + \text{Cl}_2 = 2\text{NOCl}.$$  

In the presence of MgO catalysts, decomposition reaction proceeds also explosively,
but the effect of MgO differs from the other catalysts referred in this group, since the induction period before the explosion is extraordinarily long and it takes about twelve minutes at 330°C. And the pressure-time curve is so complex that the several different reaction steps may be deduced from this single curve. So MgO is treated as an exceptional case of this group.

ii) Catalytic effects of MnO₂ and copper chromite are less pronounced than those of Cu₃O group and do not proceed explosively at 330°C, but in these cases the thermal decompositions of AP do not stop at 30 per cent decomposition and go to completion gradually. NiO and Cr₂O₃ also show similar effect and the amount of decomposition reaches 60 per cent during ten minutes' decomposition at 330°C. But in these four additives, reaction proceeds explosively at a higher temperature, for example at 380°C.

iii) TiO₂, Fe₂O₃ and V₂O₅ do not show any catalytic effect, but in the presence of Al₂O₃, a slightly greater amount of AP decomposes than when pure AP decomposes.

These reaction processes are illustrated in Figure I-5, but only some representative results are shown for clarity. In Table I-2, the values of induction periods at 330 and 380°C are summarized for the benefit of numerical comparison of the
TABLE I-2. Induction periods of AP containing various additives at 330 and 380°C

<table>
<thead>
<tr>
<th>Additives</th>
<th>$\tau_{330}$</th>
<th>$\tau_{380}$</th>
<th>Additives</th>
<th>$\tau_{330}$</th>
<th>$\tau_{380}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>39 sec.</td>
<td>16 sec.</td>
<td>MnO$_2$</td>
<td>—</td>
<td>28 sec.</td>
</tr>
<tr>
<td>CuCl</td>
<td>43</td>
<td>17</td>
<td>NiO</td>
<td>—</td>
<td>28</td>
</tr>
<tr>
<td>ZnO</td>
<td>46</td>
<td>22</td>
<td>Cr$_2$O$_3$</td>
<td>—</td>
<td>26</td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>48</td>
<td>16</td>
<td>Cu-chromite</td>
<td>—</td>
<td>29</td>
</tr>
<tr>
<td>MgO</td>
<td>690</td>
<td>54</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

relative effectiveness of these additives.

3. Effect of Additives on the Reaction Kinetics in the Mild Reaction Range

In the preceding section, it was described that thermal decomposition of AP is greatly modified by the addition of some catalysts and their relative activities at a certain temperature are compared. And in section 1 reaction kinetics of mild decomposition of pure AP has been discussed and the reaction processes are expressed with the contracting-cube type formulae. Then in this section we further describe the effects of the some representative catalysts on the mild decomposition process at various temperatures more in detail. But the kinetics of individual cases are different in each case, and single universal reaction kinetics formula cannot be applied to all cases. Therefore the comparison of rate constants of various catalysts which based on the different equations has no significant meaning, and only a few representative cases are discussed in detail, and the remaining cases are only briefly mentioned.

i) With the addition of Cu$_2$O, CuO, CuCl and ZnO, the critical temperature which corresponds to the dividing line between the mild reaction and the explosion reaction shifts to the far lower temperature range. And below the critical temperature, reaction proceeds acceleratedly after the long induction period, and then its rate falls. This process is apparently quite similar to the “low temperature reaction” of the pure AP, but it differs from the case of absence of catalyst, since the decomposition in the presence of these catalysts does not stop at 30 per cent decomposition and reaction further continues. This last behaviour is the characteristic of the “high temperature reaction”, therefore it is concluded that below the critical temperature the whole process is more alike to the combination of both types of reaction. That is, it is difficult to decide whether these catalysts affect the “low temperature reaction” or the “high temperature reaction”. The catalysts may promote both types of reaction. These reaction processes are illustrated in Figure I–6, and the type of reaction seems to transfer at relatively low temperature from this combination reaction scheme to the “explosion reaction”.

In Figure I–6 the pressure-time curves of AP decomposition in the presence of a Cu$_2$O catalyst are plotted. Mild reaction processes are approximated by the several simple kinetics formulae, and acceleratory periods of these processes are approximated with the simple exponential formula,

$$\log p = kt + C.$$
This approximation does not seem to show the best coincidence with the observed values, but the other equations such as Prout-Tompkins equation and Avrami-Erofeyov's equation [3, 4] show also similar adaptability and any significant difference between these equations are not found, and therefore the simplest formula is used here. Arrhenius plots are also made as usual and rate constant using equation (2) is found to be

\[ k = 10^{12.54} \exp (-36000/RT). \]

ii) In the presence of an NiO catalyst, the mild decomposition processes are rather different from those aforementioned cases. It is found from the pressure-time curves in Figure I-7 that, the "low temperature reaction" range transfers
to the "explosion reaction" range via the quite narrow "high temperature reaction" range. That is, at a lower temperature than 336°C, the pressures converge on the saturated value and show an essential feature of the "low temperature reaction" but only about 10°C higher than 336°C, the reaction goes to explosion. The initial remarkable but not so high peaks which are observed between 330 and 340°C correspond to the initial slope change in Figure I–3. The fact that this catalyst obviously promotes the "low temperature reaction" of AP is confirmed by the comparison of the kinetics at low temperature with or without NiO*.

iii) MnO₂ and copper chromite belong to the other typical group of additives. The pressure-time curves are very similar to the case of no catalyst, and below the critical temperature they show the initial sharp pressure rises and the deceleratory periods follow them. It has been already pointed out that the "low temperature reaction" is faster than the "high temperature reaction" in the same temperature range, and therefore these pressure increases at the initial period may be attributed to the occurrence of the "low temperature reaction" before the slow "high temperature reaction" commences. The presence of an MnO₂ catalyst affects slightly the rate of the "low temperature reaction" as shown in Figure I–5, but it promotes greatly the rate of the "high temperature reaction". In the presence of copper chromite similar effects are observed.

![Figure I-8. Pressure-time curves of AP in the presence of 1 per cent MnO₂.](image)

The effect of the MnO₂ catalyst is illustrated in Figure I–8, and the pressure-time histories are nicely represented by the same equation as applied to the case of pure AP, that is,

\[ 1 - \frac{3}{2} \sqrt{1 - \alpha} = kt. \]

And from the Arrhenius plot of rate constants at various temperatures, rate constant is expressed by

---

* Catalyst CuCl is seemed to be an intermediate of the Cu₂O-class and the NiO-class, and Cr₂O₃ seems to belong to the NiO-class.
iv) Noneffective catalysts such as TiO₂, Fe₂O₃, Al₂O₃ and V₂O₅ are not studied further, but V₂O₅ will be discussed in the succeeding papers from the other point of view.

MgO is a quite singular catalyst, the pressure-time curves of decomposition is very complicated, and its treatment with the appropriate kinetics formula is very difficult and the details of this case are not mentioned here. But it is clear that MgO inhibits the "low temperature reaction" of AP remarkably.

4. Critical Temperature and its Derivation from the Mild Decomposition Kinetics at the Temperature lower than Critical Value

When an AP disk is thrown into the reaction cell at temperature $T₀ °C$, the temperature of a disk raises with the heat transfer from the reaction cell, and simultaneously AP begins to decompose at that temperature. Owing to this decomposition, the heat of decomposition is released and the sample disk itself is heated. But when a disk is superheated over the temperature of reaction cell $T₀$ by this heat of reaction, then the disk will be cooled by the heat transfer from the disk to surrounding medium. Therefore when rate of thermal decomposition of AP is slow and self-heating rate by the heat of reaction is less than the cooling rate by the heat transfer, the reaction does not go to explosion, but when the rate of decomposition is faster and self-heating rate exceeds the cooling rate, the temperature of the disk continues to rise and the decomposition of AP is accelerated and finally develops into explosion. These phenomena are clearly observed in Figures 1-6~8, and the critical temperature of reaction system which distinguishes the reaction process from explosion to mild decomposition is defined.

For the approximated treatment of these problems, we assume the heat transfer term to be $-hS(T-T₀)$ and then time dependence of disk temperature $T$ is represented as,

$$C_p a \cdot dT/dt = -hS(T-T₀) + q \cdot dx/dt,$$  \hspace{1cm} (3)

where $a$, $C_p$ and $S$ are the weight, the heat capacity and the surface area of that disk respectively, $h$ is the heat transfer coefficient between the disk and the surrounding medium, $q$ is the heat of decomposition, and $dx/dt$ is the rate of decomposition. The critical condition is obtained by putting $dT/dt=0$, and it is represented as,

$$hS(T-T₀)=q \cdot dx/dt.$$  \hspace{1cm} (4)

When the rate of decomposition reaction is expressed as an $n$-order reaction, then equation (4) modified to the following equation by the similar approximation carried out by Semenov [9], Gray and Harper [10],

$$q a^n \cdot A \exp (-E/RT) = hS/e,$$  \hspace{1cm} (5)

where $A$ is the frequency factor of the rate constant and $e$ is the base of natural
logarithm. Then when we obtain the appropriate reaction rate expression, we can derive the critical condition with the same manner, and some cases where we have already found the rate formulae are treated as follows:

i) Pure AP

Galway and Jacobs [5] discussed the critical condition of AP with first order reaction kinetics, but the correct rate equation is given by contracting-cube equation as described in section 1. Then the reaction rate is obtained by differentiating equation (2),

\[ \frac{dx}{dt} = 3a \cdot k(1 - \alpha)^{2/3}. \]  

This equation represents the deceleratory period, and when we apply the critical condition to the reaction rate at \( \alpha = 0.3 \) namely at the point where the "low temperature reaction" finishes,

\[ \frac{E}{RT^2} \cdot q \cdot 3a(1 - \alpha)^{2/3} A \exp \left( -\frac{E}{RT} \right) = hS/e, \]

and where

\[ k = A \exp \left( -\frac{E}{RT} \right) = 10^{11.28} \exp \left( -\frac{44800}{RT} \right), \]
\[ q = 340 \text{ cal/g}, \quad a = 0.1 \text{ g}, \]
\[ \alpha = 0.3, \quad hS = 0.0051 \text{ cal/deg. sec}. \]

Here we use the heat transfer coefficient \( h \) which is derived from the discussion in section 6. The calculated value of the critical temperature from equation (7) is 392°C and differs appreciably from the observed value of 430°C.

ii) \( \text{MnO}_2 \)

In this case similar equation for the reaction kinetics is used as discussed in section 3, and the rate constant is given as,

\[ k = 10^{7.76} \exp \left( -\frac{31000}{RT} \right). \]

Then applying this rate constant to equation (7), the critical value is calculated as 337°C and the agreement with the observed value of 336°C is very excellent. Equation (7) also suggests that the critical value may decrease with the increase of the sample weight and this presumption is confirmed by the following experimental results,

| sample weight | 50, 100, 150 mg |
| critical temperature observed | 360±5, 336±5, 325±5°C |

* The fact that the observed length of the apparent induction period is not affected whether the surrounding medium is air or nitrogen, shows that the main reaction which determines the rate of explosion is the thermal decomposition of AP itself and the oxidation reaction between AP and oxygen in air seems to act minor role. Therefore as the value of \( q \), the heat of decomposition is adopted.
iii) Cu₂O

As discussed in section 3, the reaction process is approximated by the exponential formula, and reaction rate is obtained by differentiating equation (2),

\[
\frac{dx}{dt} = k \cdot \alpha,
\]

then the critical condition is expressed as,

\[
\frac{E}{RT^*_\alpha} q \cdot a \alpha A \exp \left(-\frac{E}{RT}\right) = h S/e,
\]

where rate constant

\[
k = 10^{12.54} \exp \left(-\frac{36000}{RT}\right).
\]

The calculated value of the critical temperature is 250°C and the agreement with the observed value of 263°C is fair. The dependence of \( T_{cr} \) (critical temperature) on the sample weight is also found as follows;

<table>
<thead>
<tr>
<th>Sample weight</th>
<th>50, 100, 150 mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical temp.</td>
<td>285 ± 3, 268 ± 2, 248 ± 3°C</td>
</tr>
</tbody>
</table>

Theoretical calculation of the critical temperature is limited to these three cases, since reaction processes for the other cases are not analysed in detail. In Table I–3 the experimental values of the critical temperature \( T_{cr} \) for the other cases are shown.

<table>
<thead>
<tr>
<th>Table I–3. Critical temperature ( T_{cr} ) of AP containing various catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalysts</td>
</tr>
<tr>
<td>none</td>
</tr>
<tr>
<td>Al₂O₃</td>
</tr>
<tr>
<td>V₂O₅</td>
</tr>
<tr>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>TiO₂</td>
</tr>
</tbody>
</table>

5. Explosion Reaction

When the temperature of reaction system rises beyond the critical value, explosion or deflagration occurs after an induction period of certain length. The kinetics of these explosion reaction is very important to the elucidation of the relation between the burning rate of the propellant and the rate of thermal decomposition of AP, for it is predicted that the propellant may burn at relatively higher temperature. And therefore in this section, explosion reaction kinetics will be discussed on the basis of the experimental results on the induction period at various temperature. But the observed induction period \( \tau_0 \), which is defined here as the time interval required for the occurrence of the initial sharp pressure peak from the start of the sample insertion and it involves the warming up period to
heat the sample disk from room temperature to the reaction cell temperature. Accordingly, it is necessary to reduce the warming up period from the apparent induction period. This procedure is made on the several simplifying assumptions.

When we assume that a sample disk of initial temperature \( T_i \) is thrown into the reaction cell of temperature \( T_0 \), and after \( t \) sec. a disk may attain temperature \( T \), then heat transfer to and from the disk may be approximated to

\[
\ln \frac{T_0 - T_i}{T_0 - T} = \frac{hS}{V C_p \rho} t,
\]

(9)

where \( S, V, C_p, \rho \) show area, volume, heat capacity, density of the disk respectively, and \( h \) shows the heat transfer coefficient between the disk and the surrounding reaction cell.

On the other hand, in the reaction cell a disk decomposes at a rate corresponding to that temperature \( T \) simultaneously to the warming up process. And there is no appropriate rate equation for the explosion process, we assume secondly that the induction period \( \tau \) at temperature \( T \) relates with the simple equation as,

\[
\log \tau = (E/RT) - B,
\]

(10)

where \( E \) and \( R \) denote the activation energy of this process and gas constant respectively.

Accordingly, the process which starts at the moment when a disk is thrown into the reaction cell and proceeds to explosion is expressed as follows:

i) Temperature of a sample disk attains to \( T^oK \) after \( t \) sec.

ii) At temperature \( T^oK \), a disk explodes after \( \tau \) sec.

Therefore the process is non-isothermal, and differs from the ordinary low temperature isothermal decomposition. But these hypothetical stepwise processes do not confine to the only one combination, but many sorts of combination of these two processes may be possible, but the process that actually occurs is assumed to be the one which consumes the shortest time interval.

From equation (10), a time constant of a warming up period is defined as

\[
\frac{1}{\tau_e} = \frac{hS}{V \cdot C_p \cdot \rho}
\]

(11)

and this value of \( \tau_e \) is determined when we know the value of heat transfer co-

<table>
<thead>
<tr>
<th>Weight of disk</th>
<th>Temperature of reaction cell ( T_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>279°C</td>
</tr>
<tr>
<td>50 mg.</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>175 sec.</td>
</tr>
<tr>
<td>150</td>
<td></td>
</tr>
</tbody>
</table>

* These values are obtained with AP disks containing 1 per cent of CuO.
FIGURE I-9. Correction for the apparent induction periods.

a) $\tau_e = 0.2, 0.1, 0.067$;  
b) $\tau_e = 0.3, 0.15, 0.1$;  
c) $\tau_e = 0.4, 0.2, 0.133$. 
efficient \( h \). (The other constants of equation (11) are already known, and heat capacity of AP is assumed to be 0.34 cal/g.). Then the determination of heat transfer coefficient is an important step to discuss the explosion process, and the following treatments are adopted.

When three samples of different weight such as 50, 100 and 150 mg. with same surface area are used, since heat transfer coefficient is invariant throughout these threes, so the time constants of these three disks differ from each other, being in a ratio of 2:1:2/3. Therefore the observed apparent induction period (see Table I-4) of explosion of these samples of different weight should be explained with the time constants of this proportion, and each set of apparent \( \tau_a \) data should be converged to the single true relation between the induction period \( \tau_o \) and temperature.

When we plot the values of \( \tau_a \) against the reciprocal of absolute temperature \( 1/T_0 \), there are three curves, corresponding to the different sample weight respectively. And when we assume the value of the time constant of the warming up process, the time \( t \) required to warm a disk from \( T_i \) to \( T \) is obtained from equation (9), and \( (\tau_a - t) \) will be plotted against reciprocal of temperature \( T \) (Notice that this temperature should be \( T \) not \( T_o \)). These plots of \( (\tau_a - t) \) vs. \( 1/T \) may be drawn with different values of \( h \) (that is, time constants \( \tau_e \)), and if we choose a proper value of \( h \), the three plots of \( (\tau_a - t) \) for the different sample

![Figure I-10. Apparent induction period as a function of temperature.](image-url)
weight may be coincident to or converged on the one point. Accordingly, when we apply these procedure to observed values at the different temperature, we can draw a straight line which is tangential to the converged values. In Figure I–9 one example is given, where a) a set of the values of time constant 0.2, 0.1 and 0.067 corresponding to the sample of 50, 100 and 150 mg. of weight is used, and b) a set of 0.3, 0.15, 0.1 and c) a set of 0.4, 0.2, 0.133 is used respectively. The best fit is obtained when we assume that the set of time constants is equal to 0.3, 0.15, 0.1 corresponding to the samples of 50, 100, 150 mg. of weight (that is to say \( kS \) is equal to 0.0052 cal/deg. sec.).

When the value of heat transfer coefficient is determined, the relation between the observed value of \( \tau_a \) at various temperatures of reaction cell \( T_0 \) can be corrected to the relation between the true induction period \( \tau_0 \) at temperature \( T \) with the same procedure as described here, and from this result activation energies are obtained.

In Figure I–10 the relation between the observed apparent induction period \( \tau_a \) vs. reciprocal temperature of reaction cell \( 1/T_0 \) is plotted and in Figure I–11 these plots are corrected by the aforementioned procedures and the relation between the true induction period \( \tau_0 \) to the reciprocal temperature \( 1/T \) is expressed. The final results on the activation energies for the “explosion reaction” are cal-

\[ \tau \text{ sec} \]

\[ \begin{array}{c}
\text{ZnO} \\
\text{Cu}_2\text{O} \\
\text{CuO} \\
\text{CuCl} \\
\text{MnO}_2 \\
\text{MgO}
\end{array} \]

**Figure I–II.** True induction period as a function of temperature.
TABLE I-5. Activation energies obtained from the true induction period τg of explosion reaction

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Activation energies for explosion reaction</th>
<th>Activation energies for mild decomposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>29.5 kcal./mole</td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>31.0</td>
<td></td>
</tr>
<tr>
<td>Cu₂O</td>
<td>38.1</td>
<td>36.0 kcal./mole</td>
</tr>
<tr>
<td>CuCl</td>
<td>36.0</td>
<td></td>
</tr>
<tr>
<td>MnO₂</td>
<td>33.5</td>
<td>31.0</td>
</tr>
<tr>
<td>MgO</td>
<td>43.5</td>
<td></td>
</tr>
<tr>
<td>none</td>
<td>(41.5)***</td>
<td>44.8</td>
</tr>
</tbody>
</table>

** Throughout this work, 1 weight % catalysts are added to AP, unless noticed otherwise.
*** Bircumshaw and Newman [2].

culated from Figure I–11* and represented in Table I–5.

In Table I–5, the activation energies for the “high temperature reaction”, that is, the activation energies obtained from the mild decomposition kinetics are also shown, and relatively good agreements between these values suggest the fact that the reaction mechanism for the “explosion reaction” and the “high temperature reaction” are not so greatly different.

6. **Effect of the Concentration Changes of Additives on the Pyrolysis of AP**

In the preceding sections, the catalytic actions of various additives are compared with the disks containing 1 per cent each of these additives. To find the further details of the catalytic effects of these additives, the change in the kinetics of the thermal decomposition of AP with the increase of the concentration of additives should be discussed. For example, the process of the thermal decomposition of AP containing 1 per cent each of TiO₂, V₂O₅, Fe₂O₃ and Al₂O₃ does not differ remarkably from that of the pure AP, so the amount of oxide is increased to 4 per cent to reveal the effects of these non-effective additives. However, even when the concentration of additives such as TiO₂, Fe₂O₃ and V₂O₅ is increased to 4 per cent, any appreciable change is not observed, and it is concluded that these three additives have very weak catalytic action.

In the case of Al₂O₃ catalyst, the degree of decomposition at 330°C is increased with the increase of this catalyst. Accordingly, Al₂O₃ may be considered as a weak catalyst, but stronger than V₂O₅ et al.

For the effective catalysts such as CuO and MnO₂, the effects of the concentration of catalysts differ from each other. For example, in Figure I–12, the critical temperatures are plotted against the concentration of additives, and this figure shows the quite remarkable difference between the additives. That is, in the presence of 0.1 to 4 per cent Cu₂O, no significant change of the critical tempera-

* Two corrected induction period vs. 1/T curves should cross at the same value of 1/T where the apparent induction period vs. 1/T curves for these two catalysts intersect. These correction procedures satisfy this requirement.
ture value is obtained, and in the cases of ZnO, CuO, CuCl, changes are revealed a little, but for the additives such as MnO₂, Cr₂O₃, NiO, the concentration of additives affects greatly the critical temperature of AP decomposition. This is a very important support for the opinion that the effects of additives may be classified into two groups, to one of which the additives such as Cu₂O, CuO, ZnO and CuCl belong, and to the other group MnO₂, Cu-chromite, Cr₂O₃ and NiO belong.

The effect of concentration on the apparent induction period at some definite temperature is similar to that on the critical temperature. And for the case of the first group such as Cu₂O changes of τₚ are observed quite a little, but the effect

\[
\tau_p (\text{sec})
\]

\[
\begin{array}{c|c|c|c|c|c}
\hline
\text{Cr}_2\text{O}_3 & \text{MnO}_2 & \text{CuCl} & \text{Cu}_2\text{O} & \text{CuO} \\
\hline
\text{1%} & \text{4%} & \text{1%} & \text{4%} & \text{1%} \\
\hline
\end{array}
\]

\[
\begin{array}{c|c|c|c|c}
\hline
0.0013 & 0.0015 & 0.0017 & 1/\tau & 0.0019 \\
\hline
\end{array}
\]
for the case of second group is very pronounced. For example, \( \tau_a \) vs. \( 1/T_0 \) curves are illustrated in Figure I–13 for the \( \text{Cr}_2\text{O}_3 \) catalyst. Contrary to these, MgO remains as a strange catalyst, and the effect of the concentration on the induction period shows the abnormal behavior and the apparent \( \tau_a \) increases with the increase of the concentration of MgO (see Fig. I–14).

In section 2 and 3, the remarkable differences between the various kinds of catalysts are described. And for convenience, the active additives are classified into two representative groups. The one is a \( \text{Cu}_2\text{O} \) type and it decreases greatly the critical temperature of AP, and moreover its effect is quite unique in comparison with that of the second group. The members of the second group are included in the \( \text{MnO}_2 \) type, since following observations clearly show the similarity among the members of the second group.

i) When \( \text{MnO}_2 \) type catalysts are added, the critical temperature of AP is greatly affected by the impurity which can be removed by the recrystallization process, but when \( \text{Cu}_2\text{O} \) type catalysts are present, there is no significant change of the critical temperature in the process of recrystallization.

ii) It is also pointed out that as described in this section, the effect of the concentration of additives on the critical temperature is less pronounced for the \( \text{Cu}_2\text{O} \) type. For example when \( \text{Cu}_2\text{O} \) concentration changes from 0.1 to 4 per cent, the critical temperature remains unchanged.

iii) When we make the similar sample disks from the propellant mixtures which composed of AP containing various additives and polymer fuel, and measure their critical temperature by the aforementioned procedures, it is concluded that the critical temperature of \( \text{Cu}_2\text{O} \) type catalysts is slightly affected by the presence of fuel, but for the \( \text{MnO}_2 \) type catalysts the reduction of the critical temperature by the mixing of fuel is quite remarkable. In this respect further detail will be discussed in the following papers.

iv) The results of the quantitative analysis of gaseous composition also show
the difference between these two groups. That is, the amount of NO (or its secondary reaction products such as NOCl, NO₂) is less for the Cu₂O type than for the MnO₂ type. This fact will be also treated in more detail in the following papers.

**DISCUSSIONS**

Before the critical temperature is reached, there are two kinds of reaction schemes relating to the thermal decomposition of pure AP. One of them is the “low temperature reaction” and the another is the “high temperature reaction”. However, when catalysts exist it is very difficult to assign the effects of the catalysts to the one of these two reactions. Actually both of these reactions are more or less affected by the presence of the catalysts, but from the experimental results illustrated in Figures I–5 to I–8 and the similar measurements at low temperature, it is considered to be distinguished roughly as follows:

i) Cu₂O, CuO, CuCl and ZnO promote both of “low temperature” and “high temperature” reactions,

ii) NiO and Cr₂O₃ promote mainly the “low temperature reaction”,*

iii) MnO₂ and Cu-chromite promote mainly the “high temperature reaction”,

iv) Al₂O₃, TiO₂, Fe₃O₄ and V₂O₅ are ineffective for the both types of reactions.

On the thermal decomposition of AP [2~5], electron transfer theory is proposed for the “low temperature reaction” and proton transfer model is used for the “high temperature reaction”. And for the former reaction scheme the catalysts which act as bridges of the electron transfer process become effective, so the catalysts which contain metals of variable valence promote this reaction and the catalysts which are composed of metals of fixed valence become ineffective. This presumption is confirmed by Glasner [8] in the catalytic action on the pyrolysis of guanidine perchlorate. But this contradicts our experimental results that transition metal oxides such as Ti, V, Al and Fe are almost ineffective on the pyrolysis of AP.

Therefore it is concluded that only p-type semiconductor of transition metal oxide is effective for the “low temperature reaction” of AP, and n-type semiconductor of transition metal oxide is ineffective, since Cu₂O, CuO and NiO belong to the p-type semiconductor and promote greatly the “low temperature reaction”, on the other hand ineffective catalysts such as Fe₂O₃, V₂O₅, TiO₂ and Al₂O₃ belong to the n-type. But ZnO is an exceptional catalyst which belongs to the n-type and yet has the highest catalytic activity to the AP pyrolysis. In Figure I–15, the values of the critical temperature for the various catalysts are plotted and compared with the similar experimental results on the nitrous oxide decomposition [11, 12]. This figure clearly shows the superiority of the p-type semiconductor, and it is consistent with our conclusion.

According to the proton transfer theory for the “high temperature reaction”, it is considered that the catalysts which promote the oxidation process of ammonia become effective. This presumption is confirmed by the fact that MnO₂ and Cr₂O₃

* MgO is an exceptional catalyst which inhibits the “low temperature reaction”.
promote the ammonia oxidation process most efficiently. This finding is made by Tsuda during the study of the catalytic oxidation of ammonia gas by air [13].

The order of the effectiveness of these catalysts on the thermal decomposition of AP is expressed in Figure I-15 in terms of the critical temperature values and this will be explained by the following considerations:

i) Cu₂O, CuO and CuCl reduce the critical value of AP atmost, since they belong to the p-type and also they promote the "high temperature reaction".

ii) Contrary to this, NiO and Cr₂O₃ promote mainly the "low temperature reaction" and MnO₂ and Cu-chromite only promote the "high temperature reaction", therefore these catalysts are less effective than those aforementioned catalysts for the lowering of the critical value.

iii) And the other n-type catalysts do not affect both of the "low temperature" and the "high temperature" reactions as already pointed out, therefore these catalysts scarcely reduce the critical values.

ACKNOWLEDGEMENT

The author wishes to express his thanks to the Late Mr. G. Onoue and Messrs. M. Ishikawa and T. Sakai for their helps during this study.
Some Studies on Solid Propellants. I.

Department of Propulsion
Aeronautical Research Institute
University of Tokyo, Tokyo
July 11, 1962.

REFERENCES