

THE MECHANISM OF THE ANTIMONY/POTASSIUM PERMANGANATE COMBUSTION REACTION

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(i)

DECLARATION

I hereby declare that the work embodied in this thesis is the result of my own independent investigation unless otherwise stated.

I also declare that this thesis has not been, or is not being concurrently submitted, in part or as a whole for any other degree.

.....A.z.. Moghaddam. (Candidate)

CERTIFICATE OF RESEARCH

This is to certify that, except where specific reference is made, the work in this thesis is the result of the investigation carried out by the candidate.

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A B S T R A C T

Results of a detailed thermoanalytical study of the reactions in the antimony/potassium permanganate system, which has been in use for many years as a delay composition, are presented.

The starting points for such a study were the investigation of the thermal decomposition of KMnO $_4$, and the oxidation characteristics of the antimony as well as the thermal analysis of the oxides of antimony.

Thermal decomposition of freshly prepared crystals and finely powdered $KMnO_4$ were studied utilising thermogravimetry, differential scanning calorimetry and hot stage microsocopy techniques, under atmospheres of air, nitrogen and argon. Data obtained from both TG and DSC analysis were used to measure the non-isothermal decomposition kinetics of $KMnO_4$. The activation energy was calculated applying a number of different methods, and the results were compared with the isothermal evaluation of activation energy.

The decomposition of single crystals of KMn04 was observed under a hot-stage microscope with a particular interest in the fragmentation process, and the mechanism of the decomposition reaction is discussed.

The gas-solid oxidation of antimony in air was carried out by both DSC and TG methods. The results revealed a two stage oxidation process corresponding to the surface and bulk oxidation of antimony particles.

The reactions of the Sb/KMnO $_4$ systems were investigated extensively in pelleted form as well as in powdered form by the thermoanalytical methods.

The ignition reactions of $Sb/KMnO_4$ mixtures were observed by a microscope as the temperature of the sample increased rapidly. The effect of atmosphere on the occurrence of the ignition reaction was tested. On the basis of the results obtained from thermal analysis and the studies of the mixtures in compacted form, conclusions on the mechanisms of the main propagation reaction were drawn.

CHAPTER ONE

INTRODUCTION

Pyrotechnics, is defined as the science of controlled exothermic chemical reactions which are used to create timing devices, sound effects, aerosol dispersions, high pressure gas, intense heat, electromagnetic radiation or a combination of these. High explosives are excluded, but initiators are included [1].

Basic components of pyrotechnic compositions are a reducing agent and an oxidising agent. The reducing agent, referred to as fuel, is usually a powdered metal, non-metal, lower metal oxide or an organic substance. Necessary oxygen for the fuel to ignite is provided by oxidiser in the mixture which enables the combustion to take place in isolation from atmospheric oxygen and to be self contained.

Patent literature in pyrotechnics is extensive, but only few papers dealing with the system from a more fundamental point of view have been published. Ellern in his book "Military and Civilian Pyrotechnics"

published in 1968, states that pyrotechnics is still an art rather than a science.[2]

One of the principal reasons for the slow progress of science and technology of pyrotechnics has been the lack of literature, which is the consequence of government and commercial restrictions.

Spice and Staveley [3,4], for the first time published two articles in the open chemical literature concerning propagation reactions of gasless delay compositions. They proved conclusively that the solid-solid self-propagating exothermic reaction proceeds through a pre-ignition stage that was truly a solid-solid reaction. The following is a summary of their findings.

(A) The maximum rate of propagation usually occurs at the higher weight percentage of reducing agent than that for maximum heat of evolution per gram sometimes at the same but never at the lower rate.

(B) When compressed mixtures of Fe/BaO_2 and $Fe/K_2Cr_2O_p$ are heated to temperatures somewhat below the ignition temperature, a pre-ignition reaction takes place at a measurable rate.

(C) Burning rate and sensitivity to ignition spark depended mainly on the nature of the oxidant.

(D) Stoichiometry could be obtained by plotting Q (the heat out-put per mole of oxidiser) versus the percent reductant fuel.

McLain [5] in his book "Pyrotechnics", referring to Spice and Staveley's work and the importance of the pre-ignition reaction, states that if one can control the temperature required to start the pre-ignition reaction as well as the slope of the rate versus the temperature curve, then one can control the reactivity of the system. Also if the pre-ignition reaction is a true solid-solid reaction then the reactivity control may be attained by a solid-state method. The theory of solid-state reactions (those which can be shown to have a pre-ignition reaction) is, therefore the theory of solid-state reactivity.

The next papers of importance to the theory of pyrotechnic delay compositions were by Hill and co-workers [6,7]. By developing a special thermocouple technique for measuring the temperature profile Hill's group were more successful than Spice and Staveley had been in finding agreement between delay performance and the Mallard Le-Chatelier theory of propagation. Their

combined mathematical and experimental approach yielded a clear physical model to obtain propagation rates and activation energies.

The development and advance of thermal methods of analysis provided a new scope for the study of the pyrotechnic reactions, under controlled conditions. Although, in general, the mechanism of the reactions under controlled conditions of thermal analysis might differ from those occurring during the propagation process. However, thermal analysis does provide a starting point for the unravelling of the complex stages involved and produces useful thermochemical information.

Considerable success in the study of the mechanisms of solid-solid pyrotechnic reactions has been achieved through the use of thermoanalytical techniques.[8]

The different steps involved in the ignition reaction of black powder were clearly separated when investigated by thermal analysis [9]. Thermal analysis traces for the ignition and non-ignition reactions have been introduced. [10] With the strictly solid-solid reactions repeatable DSC patterns corresponding to the surface and bulk reactions were obtained. [11] The present work relates to a detailed thermoanalytical study of Sb/KMn04 delay system and its individual constituents.

CHAPTER TWO

SUMMARY OF PREVIOUS WORK

Pyrotechnic fuel/oxidant delay systems are self-contained mixtures which on ignition can propagate in isolation from the oxygen of air. The necessary oxygen for the fuel to ignite is provided by the oxidiser in the mixture. In most fuel/oxidant systems, the oxidiser, at an early stage of the combustion reaction or during the combustion, undergoes a decomposition reaction(s) to give either gaseous oxygen or more reactive solid oxidiser to react with fuel. In this way, the mechanism and propagation rate of the overall ignition reaction of the system is related to the decomposition characteristics of the oxidant.

Prout and Tompkins [12] invesigated the isothermal decomposition of potassium permanganate at the temperature range 200° to 225°C. They found that the decomposition takes place in three stages, a period of slow reaction followed by one of rapid acceleration which in turn passes into a decay period. The first stage followed a linear relationship, $P=K_1$ t+C₁. The acceleratory and decay stages obeying the equation log $P/(P_f - P) = K_t+C$. (P = Pressure, $P_f = final pressure$, t = time K₁, K_t, C and C₁ = constants). The above

equations, which they suggested were derived theoretically on the premise that the formation of the product molecules induces strain in the crystal, which produces cracks and thus forms fresh surfaces in which decomposition can occur. These cracks spread in a branching manner into the crystal over the acceleratory period. The branching mechanism breaks down ultimately due to the interference of the branching planes and after the time of maximum velocity, the rate is controlled by the number of unreacted molecules remaining.

Prout [13] also studied the isothermal decomposition of rubidium permanganate to determine whether the kinetics were similar to those of KMnO₄ and CsMnO₄ In addition the knowledge of the kinetics of unirradiated RbMnO₄ was necessary for a systematic study of the effects of pre-irradiation by thermal neutrons and Co X-ray on the subsequent decomposition of the permanganates of the alkali metals. The results showed that the mechanism proposed for the decomposition of KMnO₄ is applicable for RbMnO₄.

Hill [14] suggested the diffusion chain theory of the decomposition of inorganic solids, for the first time taking into the consideration the mobility of the products formed. Theoretically and from the

investigation of the KMnO₄ decomposition results, he suggested that the chain mechanism, for the thermal decomposition proposed by other workers are in fact diffusion chains, consisting of a few ions of atoms from the products wandering through dislocation network of the reactant until they reach a nucleus forming site which they can fertilize and turn into a nucleus. He showed that this process can lead to an exponential rate of decomposition.

Hill and co-workers [15] investigated thermal decomposition of recrystallised and stored potassium permanganate in the temperature range of 110 to 230°C. KMn0 " freshly prepared crystals of With the decomposition rate accelerated exponentially, with detectable divergences varying from sample to sample. They showed that better control of crystallisation would give substantially perfect exponential behaviour. With crystals stored for several years in dark or in daylight for a few weeks, the acceleratory period became less rapid and less smooth and rate of decomposition with long storage time became non-acceleratory, replaced by a uniform reaction rate. Similar results were obtained with $KMnO_L$ mixed with end products . This change in the decomposition characteristics was explained by a slight chemical decomposition at the surface and grain boundaries during the storage time.

They also used the method of rapid temperature change from one constant value to another when a certain degree of decomposition occurred. Equation

$$E_{1} = \frac{4.6 \log(R_{1}/R_{2})}{1/T_{2} - 1/T_{1}}$$

was suggested for the calculation of the activation energy of the interface process, where R_1 is the rate of the reaction at T_1 and R_2 rate of the reaction at T_2 . The temperature change at the middle of acceleration stage gave $E_1 = 36.7$ kcal when the equation above contained acceleration constants K_1 and K_2 very close to the isothermal value 37 kcal. They applied the equations of diffusion chain theory to the decomposition and used them to calculate the activation energy for nucleation. They also used this theory with additional assumptions that nuclei grow equally in three dimensions, to calculate the number of nuclei present at any time during the acceleration period. They showed that for the isothermal reactions, the nucleation efficiency decreased from about 10⁻¹ at 220 $^{\circ}$ C to about 10⁻⁴ at 140 $^{\circ}$ C. From the results they deduced that exponential acceleration comes to an end largely because of ingestion of potential nuclei by growing nuclei. Experiments at low temperature provided further evidence for the diffusion chain mechanism. They obtained a low activation energy of 15 kcal which could be associated

with a diffusion process in the dislocation network.

Phillips and Taylor [16] studied the kinetics of the early stages of the isothermal decomposition of potassium permanganate - potassium perchlorate solid solution, at the temperature between 187 and 237 °C, where only the permanganate component decomposes. They found that reaction, in general, involved the successively a sigmoid constant rate and a t^2 power law stage, with finally a main acceleration stage, which may be either of the exponential or the power law type. The presence of the perchlorate retarded the first three stages more than the fourth. They determined activation energies for the stages and proposed mechanisms. They concluded that influence on activation energies of the heat of formation of the solid solutions from the solid components, first considered by Hinshelwood and Bowen, has been shown to be insufficient to account for the observed inhibition by perchlorate.

Oates and Todd [17] made a microscopic investigation of the thermal decomposition of silver and potassium permanganate. They described the microscopic study of the sectioned and partially decomposed crystals of both manganates suggesting that with both substances two-dimensional product chains are formed. In the case of branching it is localised, and usually takes place

along certain closely spaced crystallographic planes so that subsequent lateral growth of the plates, required for the complete transformation of the crystal, is slight. With KMnO_h however the internal decomposition which takes place is neither crystallographic nor localised, and hence subsequent growth is extensive. suggested that internal decomposition Thev is responsible for the mechanical disruption and concluded the products of decomposition for that both permanganates are single phase.

Boldyrev [18] applied the methods and conception of solid-state physics in the study of the mechanism of the thermal decomposition of potassium permanganate. He measured the change in the electrical conductivity of KMnO $_{L}$ in the course of its thermal and radiative decomposition. Similar experiments were carried out with pre-irradiated and pre-heated KMnO, and also with samples co-crystallised, and mixed with oxides which influence the decomposition rate of ${\tt KMn0}_{L}$. From the results he concluded that the elementary stages in the thermal decomposition of KMnO $_h$ are associated with electron transition from one site to another. Based on this. conclusion he explained the mechanism of the action of the catalytic additives, the influence of solid products formed in the course of the reaction, and the mechanism of the effect of preliminary irradiation on

the rate of subsequent thermal decomposition. Boldyrev Oblirantsev [19] studied the influence and of preliminary irradiation on the rate of thermal decomposition of lithium, potassium, rubidium and cerium permanganates. They showed that preliminary irradiation leads to an increase in the rate of subsequent thermal decomposition of the permanganates. the effect increasing in series from lithium to silver. They used the obtained data in a critical examination of Prout's theory, which explains the influence of preliminary irradiation on the thermal decomposition from the viewpoint of displacement effects. Their data contradicted Prout's theory and they attributed the irradiation effect on the decomposition rate to the production in the lattice of the solid substance, of radiolysis products which catalyse thermal decomposition. The quantity of the radiolysis products depending on the yield of the radiation - chemical decomposition of permanganate.

Herbstein and Weissman [20] studied thermal decomposition of $KMnO_{l_1}$ by a dynamic method in the temperature range 25 - 900°C in air and nitrogen, using thermogravimetric and differential thermal analysis, X-ray diffraction and chemical analysis. The decomposition equation at 25°C in air, they found to be

$$10 \text{ KMn0}_4 \longrightarrow 2.6 \text{ K}_2 \text{Mn0}_4 + 2.3 \text{ K}_2 0, 7.3 \text{ Mn0}_{2.05} + 60_2$$

Decomposition in air at high temperatures (up to 540 °C) or in nitrogen gave the same amount of K_2MnO_4 but larger amounts of O_2 owing to changes in composition of the $K_4Mn_7O_{16}$ phase.

They also studied decomposition of K_2Mn0_4 above 540 ^{o}C in air and in nitrogen using the same technique. The following chemical equation explained the decomposition.

$$10 \text{ K}_{2}\text{Mn0}_{4} \longrightarrow 5.7 \text{ K}_{3}\text{Mn0}_{4} + 0.5(2.9 \text{ K}_{2}^{0}, 8.6 \text{ Mn0}_{2.1}) + 3.40_{2}$$

This reaction was reversible in air, K_2MnO_4 reacting with atmospheric CO_2 to form unidentified phases at ca $400 \, ^{\rm OC}$ but giving the same products at higher temperatures as were obtained in a CO_2 free atmosphere. They found good agreement between their results and most of those of earlier workers, however a considerable difference in interpretation was made.

Herbstein and Wiessman [21] in a further investigation on the decomposition of KMnO_4 put the emphasis on the intermediate compounds formed during the thermal decomposition of KMnO_4 in air at 200°C. They

designated and built a special type of camera in which the diffraction pattern is registered continuously on moving film as the sample temperature is changed. In this way they prevented any changes on the intermediates, as could happen during cooling of the sample or transfer from the reaction vessel to the X-ray diffraction camera. From the results they concluded that, in contrast with Boldyrev's [22] suggestion, $K_3(MnO_4)_2$ is not an intermediate, but $K_2^{MnO_4}$ and $K_4^{Mn}7_{16}^{O}$ are formed directly as has been generally accepted. Similar conclusions held for the RbMnO_h system. Booth and co-workers [23] investigated thermal decomposition reactions of Group I permanganates using non-isothermal methods of thermogravimetry and differential thermal analysis, under oxygen, air and nitrogen atmosphere.

The DTA trace of KMnO $_4$ showed an exothermic peak at around 300 $^{\circ}$ C and an endothermic peak at around 600 $^{\circ}$ C corresponding to the decomposition of K_2 MnO $_4$. The thermogravimetric analysis of KMnO $_4$ showed that the weight loss is independent of atmosphere (11 to 12%).

Their results agreed with Herbstein's mechanism, however they did not rule out the possibility of both mechanisms, suggested by Boldyrev and Herbstein taking place simultaneously. Two stages were found to exist

in the thermal decomposition of $RbMn0_4$ and $CsMn0_4$. The reaction being analogous to that of $KMn0_4$ but the exact nature of the products is still uncertain.

The mechanisms of the reaction of potassium permanganate with iron and molybdenum have been investigated by Hill and co-workers [24,25]. They applied the temperature profile method [26] to study the self-propagation reaction of each system in compressed With the iron/potassium permanganate system it form. was found that, the reaction kinetics at low density (loose powder) are very different from those at high density (hard pellets), and that the difference can be explained on the hypothesis that at low density the reaction takes place by way of the gas phase, and at high density, where the contact between the particles are better, by diffusion across a solid-solid interface. The mobile species at low density being 0_p and at high density Fe²⁺.

From the thermal and X-ray data they suggested the following equation for the chemical reaction of $Fe/KMn0_4$ system.

2 KMn0₄ + 3.22 Fe
$$\rightarrow \frac{2.42}{3}$$
 Fe₃0₄ + K₂0 · 2 Mn0_{1.89}

With a large excess of iron at high temperature of

combustion possibly the FeO first being formed rather than $Fe_{3}O_{4}$.

2 KMnO₄ + 3.22 Fe
$$\rightarrow$$
 3.22 FeO + K₂O . 2 MnO_{1.89}

The study of the effect of addition of chemically inert substances such as sodium fluoride and calcium fluoride on the lightly pressed mixtures of the KMnO₄ system show that the initial rate of solid-gas-solid combustion reaction slows down by a factor of 10^4 . From the comparison of these initial reaction rates with the independently measured thermal decomposition rates of KMnO₄, it was concluded that, in combustion, decomposition of KMnO₄ is normally catalysed by contact with iron and that this effect is substantially inhibited by sodium fluoride.

With the molybdenum/potassium permanganate system, the temperature profile curves showed that the reaction takes place in two stages. The chemical kinetics of the first stage in the temperature range $25 - 110^{\circ}$ C have been derived by means of the thermal conduction theory of wave propagation, as in the case of the iron/potassium permanganate system. It was observed that the activation energy decreased with temperature, from which it was deduced that there was a single reaction path having several successive energy barriers.

It was suggested that the first stage of the reaction involved only those permanganate ions which were favourably placed at the boundaries of mosaic blocks, and that these were decomposed by molybdenum ions which had diffused through the dislocation network of the potassium permanganate. Hasegawa and co-workers [27] studied the solid state reaction between potassium permanganate and oxalic acid anhydrate by means of differential thermal analysis, thermogravimetry, X-ray diffraction and infra-red absorption methods. They found that when the mixture of the two reactants is heated it reacts violently at a certain temperature, which changes with the mixture ratio of the two reactants and with the particle size of the reactants. However violent reaction does not seem to occur at an arbitrary temperature. With excess oxalic acid anhydrate the reaction was found to occur at 147° C and this temperature does not change much with the particle size of KMnO $_{L}$. The main reaction products were found to be MnC_2O_4 , $KH_3(C_2O_4)_2$, CO_2 and H_2O and the reaction being initiated by the fusion of reactant mixture caused by $K_2C_2O_4$ and/or $KH_3(C_2O_4)_2$ and $H_2C_2O_4$.

Rees [28] investigated the mechanism of layer-to-layer combustion reactions in

ferro-titanium/barium peroxide, magnesium/cupric oxide magnesium/barium sulphate systems, with special and reference to the influence of reduced pressure and rotational motion on the combustion. The compositions that were investigated were of use in rocket propellant and related technology, and reduced pressure was used to simulate high altitude conditions. Similarly high speeds of rotation reproduce conditions of tracing compositions in bases of spinning projectiles. He showed that the reduced pressure decreases mean time of combustion, and the increased speed of rotation, up to a certain point, increased the velocity of propagation, after which further increase was small. The centrifugal force generated exerted a marked influence upon the combustion rate and also upon the shape of the final products. In other respects, the essential mode of propagation followed the mechanism of the Mallard-Le Chatelier theory.

Rees [29] also made a detailed investigation of the mechanism of the self-sustained reaction between powdered iron and potassium dichromate, as a simple system for the simulation of rocket propulsion reactions. The temperature profile method was applied and propagation velocities were calculated in accordance with the Mallard-Le Chatelier theory. The results agreed fairly well with the directly observed

velocities. It was concluded that the thermal theory is a good representation of the behaviour of the iron/potassium dichromate system. Clement and Beardell [30] have developed a differential thermal analysis apparatus in which the sample is heated under conditions complete volume confinement. of The sample and reference material are tightly confined to their original volume during the heating cycle. They applied the apparatus to study the effects of total volume confinement on solid state pyrotechnic reactions. From the comparison of the DTA thermograms for the reaction of 65% powdered zirconium, 25% ferric oxide and 10% silicon dioxide, it was found that the reaction at confined volume was enhanced, and the examination of products showed the following chemical equations :

Unconfined (non propagative)

$$Fe_30_4, Zr0_2$$

 $Fe_20_3 + Si0_2$
 $Fe_20_3 + Si0_2$
 $Confined (propagative)$
 $Fe_30_4, ZrSi0_4$
 $Fe_2Si0_4 + Si0_2 (\propto - quartz)$

Whereas the reaction of Sb/KMn04 mixture at the confined volume was found to be inhibited and the reaction becomes non-propagative



An example of a reaction that was little affected by the degree of confinement was that of 65% powdered tungsten, 15% potassium perchlorate and 20% barium chromate.

Rosenberg et al [31] analysed the kinetics of oxidation of antimony under isothermal conditions at the temperature range 265 to $285 \,^{\circ}$ C. The results showed that the reaction begins with a parabolic growth rate, which degenerates into a time-independent rate (stationary rate), controlled by the gaseous diffusion of $Sb_2 0_3$ from the surface region to the cold wall outside the sample furnace. The stationary rate decreases with increasing oxygen pressure and with increasing diffusion length. When the reaction was at the stationary rate, they evacuated the oxygen from the sample chamber and allowed $Sb_2 0_3$ to vapourize completely. When the oxygen was repeated as at the beginning of the experiment.

They suggested that the oxidation proceeds in two stages, the formation of an oxide film presumably controls the initial stage. The growth of the film, requiring the penetration of either antimony or oxygen, so that rate diminishes as the film thickens. While the reaction proceeds, Sb_2O_3 is slowly oxidized to non-volatile Sb_2O_5 which crystallized as a porous overgrowth on the Sb_2O_3 film. Its rate of formation is so small as to contribute only slightly to the overall rate of oxygen uptake. Thermal stability and phase transitions of the oxides of antimony have been the subject of detailed study by Golunski and co-workers [32].

The main thermoanalytical technique they used was DTA in conjunction with TG, thermodilatometry and measurement of electrical conductivity. From the results obtained they concluded that, orthorhombic Sb_2O_3 melts reversibly at 628 °C, when heated in flowing nitrogen, further heating leads only to volatilization of the melt.

Cubic Sb_2O_3 does not melt, but undergoes a solid phase transition at essentially the same temperature, (629 °C) to give solid orthorhombic Sb_2O_3 which immediately melts. On heating in flowing air or oxygen both crystal forms of Sb_2O_3 oxidise to orthorhombic Sb_2O_4 .

However oxidation of valentinite (orthorhombic) was first apparent at 463° C, while senurmonite (cubic) remains stable up to 575° C. Orthorhombic $\propto -$ Sb₂O₄ was found not to undergo any physical or chemical change on heating below 1000°C, either in air or nitrogen.

Cerventite Sb_20_5 behaves very similarly when heated in nitrogen or air. Oxygen is lost progressively from the crystal structure above 400° C leading eventually to a transition to orthorhombic Sb_20_4 . This is reflected in an irreversible exothermic DTA peak and a sudden fall in electrical conductivity with increasing temperature. Their data did not support the information cited in a standard reference book which states that Sb_20_5 loses one oxygenation at 380° C and second at 930° C.

Goodfield and Rees [33] applied the differential scanning calorimetry and bomb calorimetry to study the reaction between boron and lead monoxide. They obtained DSC traces for PbO/B compositions (80/20, 50/50, 97/3 Wt) and also for PbO/B₂O₃ (1:1) mixtures using heating rates of 5, 10 and 20^oC/min. From the results and infra red analysis of products, they concluded that the reaction between PbO and B, at the stoichiometric ratios under propagative conditions produces B₂O₃ and Pb, whilst in thermal analysis

equipment (DSC) the PbO/B $_{2}^{0}$ reaction also occurs, but is suppressed as the rate of heating is increased.

At fuel levels above the stoichiometric level, under propagative conditions, vapour-phase side-reactions also occur to produce boron suboxides, effectively increasing the heat output of the reaction. They also believed that the surface B_2O_3 on the boron particles plays an important part in increasing the rate of the PbO/B reaction, and that the onset temperature for the reaction is determined by the properties of the PbO lattice.

A detailed investigation on the solid-state reactions in the $MgO-Cr_2O_3$ and $ZnO-Cr_2O_3$ systems has been carried out by Ishii and co-workers [34] using DTA and isothermal techniques under an atmosphere of oxygen, air and nitrogen.

For the Mg0-Cr $_2$ O $_3$ system they considered that the reaction proceeds through the following steps:

(a) Initial reaction step corresponding to an exothermic peak at around $800 \, {}^{\circ}$ C. At this stage Cr_2O_3 reacts with atmospheric oxygen to form CrO_3 under the catalytic action of MgO. This is followed by the coverage of the MgO grains with CrO_3 formed, and

formation of a thin layer of spinel on the surface of the MgO grains.

 $Mg0 + 2 Cr0_3 \longrightarrow MgCr_{3}0_4 + 3/2 0_2$

(b) A second reaction step is represented by an exothermic peak at 1000° C. At this stage product layer grows inwards into the grains of MgO, and Cr_{20}_{3} is being transported by diffusion of chromium ions through this layer to the MgO/product interface at which the reaction proceeds. The DTA peak corresponding to this second step appears only in the nitrogen atmosphere.

For the $Z_{n0}-Cr_{2}O_{3}$ system the initial reaction step (an exothermic peak at around 700 to 800°C) proceeds under the catalytic action of Zn0 in a similar manner as that in the MgO-Cr₂O₃ system. But it was considered that the catalytic mechanism for Zn0 differs from that for MgO. Although these catalytic mechanisms are not clear however, it is suggested that the active oxygen absorbed on the surface of the MgO, and the oxygen ions in the ZnO lattice, play important roles in the oxidation of $Cr_{2}O_{3}$ to CrO_{3} in the initial step. The second reaction step (exothermic peak at about 1100° C) proceeds at the same temperature regardless of atmosphere.

Ishii et al [35] have also studied the effect of fluoride additives LiF, NaF and CaF_2 on the solid-state reactions in the MgO-Cr₂O₃ and ZnO-Cr₂O₃ systems. From the results on MgO-Cr₂O₃ - MF (M=Li,Na) systems they concluded that the melting of the fluoride additives plays an important role, accelerating the second reaction step at around 1000°C. On the other hand for the ZnO-Cr₂O₃ -MF(M=Li,Na) system a great acceleration by the additives was observed in the first reaction step at around lower temperature than the fluorides. The effect of CaF₂ was not clear in either system.

Campbell and Weingarten [36] made a thermoanalytical study of the ignition reactions of black powder. On the basis of their DTG and DTA measurement, the first step in the combustion of black powder is a pre-ignition reaction, between sulfur and potassium nitrate, which is sufficiently exothermic to provide required energy to activate a propagative combustion reaction between charcoal and potassium nitrate.

(1) $S + 2KNO_3 \longrightarrow K_2SO_4 + 2 NO$ (2) $3 C + 2 KN)_3 \longrightarrow K_2CO_3 + N_2 + CO_2 + CO_3$

In the reaction (1) sulfur being in molten state and potassium nitrate in its thermally active trigonal form, in the reaction (2) the charcoal is in the solid state, potassium nitrate in molten condition. They found that the presence of oxyhydrocarbons in the charcoal does not seem to be the essential factor in the pre-ignition reactions however, the propagative ignition reaction is the same as advanced by Blackwood and Bowden [37].

Zimmer-Galler [38] made a detailed study on the mechanism of the reaction and intermediate stages of the combustion of tungsten with barium chromate and chlorate. He measured burning time and potassium effect of pressure on burning time of the mixtures, in and pressures up to 12000 psi. The amount of vacuum non-condensing gas formed during the combustion was measured by a manometric method. Differential thermal analysis was used to study interactions between the components, and calorific values were determined by delay compositions in a Parr bomb burning the calorimeter, under various environmental conditions. He also obtained temperature distribution profiles and the effect of metal concentration on the temperature distribution along the lateral surface of the burning delay composition with a low-colorpyrometer. From the results he concluded that,

(a) Tungsten delay composition have no reaction zone

(b) Heterogeneous decomposition reactions of the oxidising agent are involved in the burning process and consequently there is a pressure dependence of the burning process,

(c) An interaction between W and $KClo_4$ is the initiating step in the combustion process,

(d) The burning rate of the metal delay powder is primarily controlled by the thermal conductiity of the system.

Collins and co-workers [39] investigated the ignition of titanium subhydride/potassium perchlorate composition by an electrostatic discharge. They showed that the ignition is due to the metal/air reaction rather than the pyrotechnic reaction as previously supposed, and proposed a model which related to electrostatic sensitivity of the titanium subhydrates to the surface activity of the powder. According to the data obtained, the electrostatic energy input required for the initiation, decreased as the metal powder surface area increased. Dehydration of titanium fuel

also decreased the required initiation energy, the humidity was found to be a moderator in the electrostatic ignition process. From the data on the effect of atmosphere on the electrostatic initiation of the $TiH_{x}/KClO_{4}$ system, they suggested that the blends of these pyrotechnic mixtures can be handled safely in an inert atmosphere.

Collins (40) also investigated the ignition of $TiH_x/KC10_4$ compositions by thermal methods. Data obtained from differential scanning calorimetry and electron spectrometer studies, suggested that two primary factors associated with titanium which influence the are ignition process. They are, dissolution and reoxidation of the particle surface. As titanium powder is being heated, the oxide coating the metal particles dissolves into the bulk metal to generate a surface, the surface being reoxidised reactive immediately by oxygen gas from the surrounding atmosphere, but insufficient heat being generated for sustained combustion. Kinetically, ignition is determined by the rate of dissolution of the oxide coating versus rate of the reoxidation.

Charsley et al [41] have developed a differential thermal analysis unit, for the study of the ignition

reactions of pyrotechnic systems. The main objectives of their design in the study of ignition reactions were.

(a) To minimise heat losses from the sample and hence promote ignition.

(b) Provide reproducible temperature measurements, over a large number of experiments, without the need for recalibration.

(c) Resist attack from ignition products.

To measure the precise ignition temperature they used a silicon photodetector cell. It is positioned at the top of the sample container and is connected to the digital temperature unit. The detector signal, on ignition, is used to freeze the ignition display, enabling a direct ignition temperature measurement.

The unit was applied to measure the ignition temperatures of eight pyrotechnic systems. On the effect of sample weight on the ignition temperature, they found that with the same compositions a dramatic decrease in ignition temperature occurs when sample weight increases above a certain level. They gave the pyrotechnic composition containing magnesium, barium peroxide and acaroid resin as an example, suggesting
that at the high sample weight, the ignition occurs at the temperature range of the first exothermic, and at low sample weights at second exothermic peak.

Al-Kazraji and co-workers [42] studied the decomposition kinetics and activation energies of thermal decomposition of Pb_3O_4 by a thermogravimetric method under isothermal and dynamic conditions. From the results obtained they concluded that, in the case of isothermal decompositions, the rate of diffusion of gaseous products is the controlling factor, while in the dynamic decomposition nucleation and growth within the Pb_3O_4 particles is important and it has a larger activation energy than the isothermal decomposition.

Goodfield and Rees [43] have investigated the application of an automatic recording pyrometer and optical focussing system on the measurement of the ignition temperature of fast pyrotechnic reactions of lead monoxide and silicon systems. They measured ignition temperatures of the compositions in the range of 70/30 to 96/4 Pb0/Si, and compared this with the calculated reaction temperature. They discussed the advantages of the infra-red pyrometer and its practical utility in the field of pyrotechnics.

Laye and Tipping [44] investigated the rate of heat

transfer in the ignition of a gasless delay composition by the analysis of the temperature/time history of the combustion wave. Their tests with the propagation mixture of tungesten and potassium dichromate (35/65% Wt ratios) indicated that radial conduction, ahead of the reaction zone and axial conduction behind it, exert only a small influence on the combustion wave.

Al-Kazraji and co-workers [45] suggested a mathematical model in the analysis of temperature profile data to calculate the propagation velocities and activation energies of Pb $_{3}0_{4}$ /Si delay compositions. They assumed a low thermal diffusivity for the Pb $_{3}0_{4}$ /Si system and also for the reaction rate co-efficient they assumed,

$$K = \left(\frac{\beta}{\alpha}\right) \qquad \left(\frac{t}{\alpha}\right)^{\beta-1}$$

Different values of β and \propto and the related T (temperature) were obtained from temperature profiles of the combustion of solid mixtures of different compositions, and by plotting in $\ln\beta/\propto$ versus $\frac{1}{T}$ the activation energy was obtained.

Boddington and co-workers [46] have developed techniques to measure thermal diffusivity of pyrotechnic delay mixtures pressed into the form of cylinders.

Both techniques use a modified commercial differential thermal analysis apparatus to monitor the temperature gradient inside the cylinder when the ambient temperature is increased, either linearly with time or suddenly from one constant value to another. They correlated theoretically the temperature gradient with the thermal diffusivity and used both methods to measure thermal diffusivity of different mixtures of tungsten and potassium dichromate.

Hossjer [47] studied the gasless pyrotechnic composition of lead chromate, copper oxide and tin in the proportions of 61:15:24 by weight, utilising the temperature profile method. To measure temperature the mixture was compressed into 30 mm long copper tubes, and a small hole at the centre of the tube was drilled. Through this hole a thin quartz capillary was threaded inside this capillary one junction of the and thermocouple was placed. The other junction consisted of mercury contacts placed in a metal block with a The temperature profile curves showed thermometer. that there is a slow rise of temperature in the centre before the reaction zone arrives, then there comes a rapid rise of temperature to 1000°C or more which is followed by fairly rapid cooling towards the heat He measured the temperature at the equilibrium. equilibrium directly from the curve and compared these

with values calculated thermochemically.

Speros and Debesis [48] studied the dependence of combustion of solid state reactions in fuel/oxidant systems, on the oxidant dissociation pressure, and the rate of evolution of oxygen from the dissociation. They used a combustion cell with a controllable atmosphere and a glass lid. Ignition of the sample was carried out by an igniter device employed in flash Observations and measurements were carried out lamps. by high speed photography and spectroscopy. The temperature was measured as a function of time by the method of "blue-to-red" ratio at two wavelengths of the spectral continuum and the decomposition kinetics of the oxidants were studied using differential scanning calorimetry and thermogravimetry. They suggested a selection method of oxidant based on their dissociation pressures and kinetics of oxygen evolution, in a multi-oxidant pyrotechnic system such as $Zr/Co_{3}O_{4}$, $BaCrO_{4}$,

 Fe_2O_3 which could help in the amplification of combustion rate.

McLain [49] studied the solid state reactions of boron/barium chromate and silicon/lead dioxide delay systems. From the results of measurements of heat output and propagation rate and their variation with fuel/oxidant ratio, it was concluded that their

behaviour conforms to the heat transfer mechanism of propagation suggested by Spice, Staveley [4] and Hill [26]. The following equations were found to represent the chemical reactions taking place in combustion of the above mentioned systems.

> $4B + BaCrO_4 \longrightarrow 4BO + Ba + Cr$ $PbO_2 + Si \longrightarrow Pb + SiO_2$

The reaction between selenium and barium peroxide was studied by Johnson [50], with the aim of producing more closely timed delay fuses in order to be used more effectively and safely in mining. It was found that reaction between selenium and barium peroxide the powders takes place by three processes. The effect of the first he claimed can be measured after the powdered mixture is heated to temperatures as low as 50 $^{\circ}$ C for as little as 32 hours, there is a slight lowering of the heat output and activation energy, and an increase in burning rate. The second process appears to be a slow, exothermic product forming reaction between the materials, which is not self-sustaining. The third is an ignition reaction which begins at 265°C is extremely exothermic and is self-sustained.

The chemical role of organic binders in the reaction of pyrotechnic compositions have been investigated by Charsley and co-workers [51]. They examined a wide range of binders on four metal/oxidant systems based on the metals magnesium and titanium and the oxidants sodium nitrate and strontium nitrate.

The influence of the binder on DTA curves of the metal/oxidant reactions, heat output and light output have been shown. They used equal parts by weight of metal and oxidant incorporating small amounts of binder (below 10%) in every experiment.

DTA curves for the ternary compositions showed that the presence of a binder could result in additional pre-ignition exotherms. The magnitude of these could be altered by increasing the concentration of the binder and this sometimes resulted in ignition taking place at a lower temperature exothermic reaction.

The ignition temperature of titanium/strontium nitrate compositions decreased from 670° C to 483° C by increasing alloprene from 1 to 10%. They showed that all pyrotechnic parameters measured have been profoundly altered by the presence of the binder.

Ywenkeng [52] studied the influence of the

additives on the burning rate of molybdenum/potassium perchlorate delay compositions. Different quantities of various additives, such as, $BaCrO_4$, Sb_2S_3 , Cu, Se, MoO₃ were tested on the rate of ignition.

On the addition of $BaCr0_4$ to the stoichiometric mixture they measured the ignition temperature to be above $1500^{\circ}C$ therefore causing the decomposition of $BaCr0_4$.

The released oxygen from the decomposition helps the ignition of Mo therefore increasing the rate of burning. Compositions with above 3% BaCrO₄ decreased the rate of burning. This is suggested to be due to the insufficient heat release to cause the decomposition of BaCrO₄, and is only absorbed on melting. Addition of Cu in small quantities increases thermal conductivity therefore increasing rate of burning. With higher amounts the heat absorption by Cu exceeds the better thermal conductivity effect therefore a decrease of burning rate results.

With Sb_2s_3 the decomposition and oxidation take place at above 300 °C releasing a large amount of heat which causes an increase in rate of burning.

$$2 \text{ Sb}_2 \text{ S}_3 + 9 \quad 0_2 \rightarrow 2 \text{ Sb}_2 0_3 + 6 \text{ So}_2 \Delta \text{ H}_f = 634 \text{ kcal}$$

This process, like addition of $BaCrO_4$, can also be reversed with the increase in the amount of Sb_2O_3 . Sublimation of MoO₃ causes a decrease in rate of burning, and addition of selenium shows a very similar effect as that of Sb_2S_3 .

Ward and co-workers [53] investigated the burning rate of the Mg/NaNO stoichiometric composition at above atmospheric pressure. They made pressed strands of magnesium and sodium nitrate for the burning rate determinations, the binder was not added and nitrogen was used as pressurizing gas in all experiments.

The measurements were carried out in a gas cylinder, equipped with two directly opposed viewing ports, through which the burning strands were photographed with a high speed camera. They found that in contrast to gas or rocket propellants, the burning rate at above 2 MPa is relatively insensitive to pressure.

When the experiments were carried out with oxygen as the pressurising gas, it resulted in a similar rate of burning as under N_p atmosphere. It was therefore

concluded that the reason for the insensitivity to the pressure is due to the absence of gaseous reactions.

Hossjer [54] used a special method to investigate the reaction mechanism and ignitability of gasless delay compositions. He considered that the chemical reaction between the reactant particles takes place in the form of transportation of material, from one particle to another, to form products.

This being possible in three different ways -

- (a) Transport in gas phase
- (b) Transport in liquid phase
- (c) Transport in solid phase diffusion.

When the composition, in the shape of a column, is divided into two parts by a thin membrane of some heat resistant material, and the composition ignited at one end, if besides the heat transfer gas or liquid transport is necessary for the progress of the reaction, it should cease when the transport is stopped at the membrane. If the material transport does not involve gas transport, but instead diffusion between neighbouring particles in the solid phase controlled

mainly by the heat wave, the presence of the membrane should have a small effect on reaction rate.

Mica was chosen as a suitable material for a membrane and experiments were carried out on three types of compositions -

(a) Sn/Cu.PbCr04

(b) CuO/Sn

(c) ZrNi/BaCrO₄.

The compositions type (a) and (c) were affected very little by the presence of the membrane, whereas the composition type (b) did not ignite even with a very thin (0.01mm) membrane, and the obtained weight loss confirmed the occurrence of a gas phase reaction.

CHAPTER THREE

SCOPE OF THE PRESENT WORK

Self-sustained reaction between finely powdered antimony and potassium permanganate in various proportions has been investigated. Measurements have been made of the linear rate of propagation reaction and heats of reaction in compressed form. The temperature of the combustion is measured using (a) non-contact optical pyrometer, (b) by a temperature profile technique. The possibility of the involvement of both gas-solid and solid-solid stages in the main propagation reaction has been examined and the mechanism of the reaction is discussed.

A detailed thermoanalytical study of the system including the reactions of individual components was carried out. Since potassium permanganate releases oxygen at a relatively low temperature $(300^{\circ} C)$, therefore thermogravimetric studies were carried out in order to examine the mass change during the main reaction.

Differential scanning calorimetry and hot stage microscopy were used to study the non-ignition and

ignition reactions of the compositions.

The ignition process was observed as the temperature of the sample increased rapidly and the effect of the atmosphere on the occurrence of the ignition was tested. The gas-solid oxidation characteristics of antimony was studied separately.

Thermal decomposition of whole crystals and finely powdered KMnO₄ were studied utilising all available thermoanalytical techniques, under three different atmospheres of air, nitrogen and argon. The data obtained were used for the kinetical analysis of the decomposition process. The activation energy was calculated applying a number of different methods, and the results were compared with the isothermal evaluation of the activation energy.

CHAPTER FOUR

BIPERIMENTAL TECHNIQUES

4.1. <u>MATERIALS</u> :

Potassium permanganate was supplied by B.D.H. Chemicals Ltd., with 99.5% minimum purity. For the kinetic and thermal analysis studies of KMnO₄ fresh crystals were prepared.

A solution of 250 cc of KMnO_4 with carbon dioxide gas passing through the solution was saturated at 60 °C. After saturation it was cooled to room temperature and filtered through a No. 4 porosity sintered glass filter-funnel, to remove any MnO_2 , and the filtrate was left in the dark for 48 hours at 20°C. The supernatant liquour was then decanted and the crystals were rapidly dried. For each thermal analysis test, the crystal was selected by hand and was left at 100°C for 30 minutes to ensure the evaporation of the water before each run.

Powdered $KMn0_4$ was prepared by rubbing the crystals in an agate mortar. The sample was then

sieved and its surface area was measured which was found to be 0.46 m $^2/g$.

Antimony powder with 98.5% purity was supplied by B.D.H. Chemicals Ltd., the mean particle size of the material was 4.6μ m with 0.509 m²/g surface area.

Antimony trioxide and antimony pentoxide were both supplied in powdered form by B.D.H. Chemicals Ltd., with a minimum purity of 99% and 98.5% respectively.

The preparation of Sb/KMnO₄ mixtures was carried out in a Portakabin located outside the main laboratory. Since pyrotechnic mixtures are usually sensitive to accidental ignition by static electricity impact and friction, therefore adequate safety measures are necessary in mixing and pelleting of the compositions. The electric points of the Portakabin were all located externally. It has two specially designed escape doors and is equipped with a fire extinguisher. Safety clothing including fire proof overall, electrically conductive shoes, protective glasses, gloves and respirators were used.

The firing of delay elements was carried out behind an armoured safety screen and away from any other ignitable materials. The mixtures were stored in

plastic and glass containers in the Portakabin at steady temperature.

4.2. DETERMINATION OF SURFACE AREA OF THE MATERIALS

A Strohlein area meter (Model OPI-Bb 119-E) was utilised to measure surface area of the powdered materials. The method is based on low temperature nitrogen adsorption, according to Brunauer, Emmet and Teller (BET Method).

The most commonly used gas for the measurement of reasonably high surface area is nitrogen at liquid temperature. Since volumes of the gas adsorbed are high the consequent changes in the pressure can be measured accurately by the manometer. However, for powders of low surface areas the fraction of the nitrogen gas in the system that is absorbed is low, resulting in negligible pressure changes, so that manometric pressure measurement cannot be used. In such cases ethylene at liquid oxygen temperature and krypton at liquid nitrogen temperature have been used as the absorbate gas.

The measuring principle of the instrument used

was based on the use of two glass absorption vessels of the same volume, one of them is filled with the sample while the other remains empty (reference vessel) both vessels are filled at ambient temperature with nitrogen at atmospheric pressure. They are then cooled in the cold bath to the temperature of the liquid nitrogen.

The adsorption of the nitrogen on the sample results in a pressure difference between sample and reference vessel which is indicated on the manometer. From the pressure difference and sample weight the specific surface area could be calculated.

$$S_g = \frac{A \Delta h}{m} + \frac{B}{\rho_p}$$

Where $\Delta h = pressure difference$ m = sample weight $\rho_{p} = specific weight of sample$

A and B are coefficients. Coefficients A and B are dependent only on \triangle h and filling pressure which can be determined from the nomogram.

A most important preliminary to the accurate measurement of an adsorption isotherm is the preparation of the absorbant surface. In their usual state all

solid surfaces are covered with a physically absorbed film which must be removed before any quantitiative measurements are made.

Therefore before each test the sample in the vessel was placed in the heating block and purged with the test gas (nitrogen) at 130° C for four hours. It was then cooled to room temperature without interrupting the purging gas and closed with a stopper and stored for the measurement.

4.3. DETERMINATION OF PARTICLE SIZE :

Coulter Counter Model TA was used to measure particle size of powdered antimony.

The counter technique is a method of determining the number and size of particles, suspended in an electrolyte, by causing them to pass through a small orifice on either side of which is immersed an electrode. The changes in resistance as particles pass through the orifice generate voltage pulses whose amplitudes are proportional to the volumes of the particles. The pulses are amplified, sized and counted, and from the derived data the size distribution of the suspended phase is determined.

The technique was originally applied to blood counting (55), modified instruments were soon cell developed with which particles could be sized as well as counted. The operating principle of the technique could be followed by referring to Figure (4.3.1). A controlled vacuum initiates flow through a sapphire orifice let into a glass tube and unbalances a mercury The system is then isolated from the vacuum siphon. source by closing tap A and flow continues due to the balancing action of the mercury siphon. The advancing column of mercury activates the counter by means of start and stop probes, so placed that a count is carried out while a known volume of electrolyte passes through the orifice. The resistance across the orifice is monitored by means of immersed electrodes on either side. As each particle passes through the orifice it changes this resistance, thus generating a voltage pulse which is amplified, sized and counted and from the derived data the size distribution of the suspended phase is determined. The amplified voltage pulses are fed to a threshold circuit, where the actual sizing occurs. Sized particle pulses are then sent to their respective integrators where they are converted to a voltage representative of size of particles. The integrator voltages are then fed to the multiplexer card where they are sampled one by one for differential data

and added one by one for cumulative data. The output of the multiplexer card is fed to the AGC card which adjusts these signals electronically for x-y recorder presentation, relative to 100% for total sample.

4.4. <u>PREPARATION OF THE COMPOSITIONS AND DELAY</u> PELLETS :

The difference between the present pyrotechnic system and those which have been used previously in this laboratory, is that the oxidising agent (KMnO $_4$) is soluble in water. Therefore the dry method of preparation of the granules of compositions were examined first.

The thoroughly mixed composition was lightly pressed into a pellet shape using a manually operated press. The resulting pellet was broken and sieved in order to obtain suitable size of granules. In this way it was possible to prepare granules of dry mixed composition, however this process needed a considerable period of time since in each attempt only a small size of pellet resulted and from each pellet only part of the sample ended in granule form.

Addition of graphite powder to the mixture in

order to help its flow in the compressor was examined. This was also found to be a slow process since a longer period of time was needed between loading and pressing operations, in order to feed enough sample to the delay element before each pressing.

The most convenient way for the preparation of granules was found to be the use of a binder. A very small amount of carboxymethyl cellulose solution, just enough to form a hard cake of the mixture was used. The sample was left in the oven at 50° C for a period of two hours to dry, the dried sample was broken and sieved through a large aperture ($850\,\mu$ m). In order to separate finer granules the resulting sample was again sieved with a smaller aperture sieve ($300\,\mu$ m). The final mixtures were found to flow readily from the container to the delay tube in loading and pressing operations.

The mean burning time of 20 delay elements prepared by the dry mixing method was found to be very close to those prepared by using binder. However standard deviation was lower with dry mixed compositions. The granulated compositions were loaded into zinc die-cast delay elements using an air operated hydraulic compressor. The pressure in the main tube was indicated by a pressure gauge in lbs/in², the actual dead load on the composition was measured by using a

stattimeter. Measured dead load was then divided by the surface area of the tube in contact with loading punch to obtain loading pressure of the composition. Further details on the operation of compressor and the assembling of delay units have been given by Al-Kazraji (74).

The burning time was measured by using a Racal universal counter-timer Model No. 9901. The timer and delay element both were connected to a firing circuit so that the timer started simultaneously with the operation of firing and stopped by a signal coming through a photoelectric cell sensitive to the light emitted from the end of the burning delay composition. A schematic diagram of the delay time measuring apparatus is shown in Figure (4.4.1).

4.5 <u>MEASUREMENT OF HEAT OUTPUT</u> :

The heats of reactions of consolidated mixtures were determined using a Parr 1421 semimicro Bomb Calorimeter. A cross-section of the bomb with identification of the main parts is shown on Figure (4.5.1).

This instrument has a working temperature of 20

to 30 °C and it is capable of measuring an energy change from approximately 200J to 5 kJ. Temperature sensing is achieved by the use of a thermistor in the water jacket. The heat capacity of the calorimeter (water equivalent) was determined by burning a known weight of calorimetry standard benzoic acid in the bomb under an oxygen atmosphere at 30 atmospheres pressure. The heat of combustion of benzoic acid is available and from the temperature rise obtained, the energy equivalent of the bomb was calculated to be 2026.3 $\stackrel{+}{=}$ 12.2 J/ °C.

At the start of each test three of the aluminium tubes, each containing a delay element and a fuse head, were placed inside the bomb and connected to the firing circuit. The total weight of the sample in each experiment was approximately 0.7 g.

The bomb containing sample, and with ignition lead attached, is immersed in a glass Dewar flask containing 400 ± 0.1 g of water which is situated in a thermally insulated air can. The initial temperature of the water in each experiment was kept at 23 °C.

The air can cover with the mechanical stirrer attached is then fitted and the thermistor probe is inserted into the calorimeter water through the hole in the cover. The stirrer drive belt is then fitted and

the stirrer motor started.

The temperature measuring system in this calorimeter consists of a thermistor probe and a special bridge designed for use within the ten degree span from 20 to 30 °C. The electronic bridge within this range can be adjusted to produce a zero voltage output. At the temperature range of 20 to 30 °C the thermistor output is linear, with each 100 microvolt change representing a temperature range of exactly 0.001 °C.

In present experiments the full scale deflection of the chart recorder was adjusted to 1° C and the temperature change with different compositions varied between 0.4 to 0.7° C.

One advantage of the present calorimetry technique is that the temperature equilibrium before and after the reaction could readily be noticed from the linearity of the temperature trace. In Figure (4.5.2) a typical example of the type of temperature recording is shown. The midpoint vertical distance between the extrapolated pre-period and post-period portions of the temperature trace is shown by R, while ΔT_c is the corrected temperature rise measured at 0.63R.

The heat output is calculated by multiplying the

net corrected temperature rise, ΔT_c , by the calorific value, c of the calorimeter.

Heat generated by the electrical igniters was measured by separate experiments, and was deducted from the total heat output. These experiments were carried out under conditions identical to those used in the actual heat of reaction measurements.

4.6. <u>MAXIMUM TEMPERATURE OF THE REACTION</u> :

Two principally different techniques were utilised to measure maximum temperature of combustion of delay mixtures.

(1) The automatic optical pyrometer which measures the temperature of the object without contact by sensing infra-red radiation from its surface. Detailed description of the technique and its application to pyrotechnics has been given by Goodfield and Rees [43]. The apparatus consists of a sensing head, electronic module and a temperature indicator. The sensing head is focussed to one end of delay pellet through the perspex disc and it is ignited from the other end. The signal from the sensing head is fed to the electronic module, which then amplifies and

linearises the signal and provides a variety of electronic output signals linear to the temperature. The focussing of the sensing head, and the judgement of its distance from the object, is an important factor for obtaining reproducible results from the optical pyrometer.

This is particularly important when the temperature difference of the mixtures, with small differences in the proportions of the contents (5 or 10%) are involved. Therefore to ensure stable and similar conditions for all measurements, a cylindrical block was made so that the sensing head was placed at one end, looking at the delay element through the cylinder at the other end.

The distance between the sensing head and the delay element was 6 inches, which is the optimum focussing distance for the 22A05 model sensing head. The resulting temperature measurements were found to be more accurate and reproducible. Figure (4.6.1) shows the block diagram of the temperature measurement system.

(2) This method is in principle similar to the temperature profile technique introduced by Hill [26] and was applied by Al-Kazraji [74] to the Si/Pb $_{3}^{0}_{4}$ system at this laboratory. However the recording of

the temperature was carried out by a newly developed system, the DMS-6430-Digital memoryscope.

The memoryscope is a desk-top type waveform memory system for memorising to the semiconductor memory the electrical one-shot phenomenon, repeated phenomena and electrical signals of optics, dynamics, mechanical vibration, chemical and temperature changes. These signals are converted by various transducers for reproducing the signals on the CRT screen, and external pen recording for permanent record. It has the facility to display a portion of the memorised waveform and to be enlarged before final print out.

The thermocouple used was Pt/Pt - 10% Rh of 0.05mm diameter wires, and it was directly connected to the memoryscope. The thermocouple junction was embedded in the pelleted delay compositions, and the temperature was recorded as the combustion wave moved from the point of ignition until it reached the thermojunction.

4.7. THERMAL ANALYSIS EQUIPMENT :

Thermal analysis studies of the reactants and the mixtures were carried out utilising,

thermogravimetry (Perkin Elmer TGS - 2), differential scanning calorimetry (Perkin Elmer DSC-2), and hot-stage microscopy (Stanton Redcroft HSM-5). Technical aspects and facilities provided by each technique have been described in a previous study.[11] Here the emphasis will be put on details concerning the techniques and their application.

Thermogravimetry is a most widely used 4.7.1. technique to study heterogeneous processes. In this technqiue a gas-solid system must be involved in which the gaseous component is either a reactant or product of Phase transition such as solid - gas the reaction. could also be investigated by this technique. Data obtained from the TG are usually more quantitative than Since in the thermogravimetry technique DSC or DTA. the sample is suspended and being continuously weighed, this creates problems for the direct temperature Therefore in all measurements of the sample. thermogravimetry systems only the temperature of the furnace chamber is continuously monitored.

For the accuracy of the reaction kinetic studies, the exact temperature of the sample is required. Manch and Carroll [56] developed a fast response transducer in physical contact with the sample,

in which its temperature information is instantaneously relayed to an indicating device through a non-mechanical coupling. It consists of using a unijunction transistor relaxation oscillator with a thermistor as the resistive part. The entire primary circuit, including the power supply, is made part of the balance suspension and is weighed along with the sample. Unfortunately the temperature range was rather limited from 25 to 160 °C. The use of substances having magnetic transitions for the temperature calibration of TG systems have proven to be very effective. [57]

The ferromagnetic standard is suspended from the balance beam in a magnetic field which is oriented and a vertical component of magnetic force acts on the sample. When the sample is heated through its Curie point, the equivalent magnetic mass diminishes to effectively zero and the balance will indicate an apparent weight loss.

The effect of various gaseous atmospheres on thermal decomposition reactions using thermogravimetry been discussed by Wiedeman [58]. He also has effect of sample holders on the investigated the Self-generated TG TG system. performance of the atmospheres have been reviewed by Newkirk [59], this type of atmosphere consists of decomposing solid sample in a crucible that has a small vapour volume with a

small opening to the atmosphere. As a consequence, except for the air initially present, decomposition occurs in an atmosphere of gaseous decomposition products, hence a self-generating atmosphere.

4.7.2. : Differential Scanning Calorimetry:

DSC is a new system of DTA with one fundamental difference. In differential thermal analysis the difference temperature between a substance and a reference material is measured as a function of temperature whilst the substance and reference material are subjected to a controlled temperature programme. Whereas in DSC the difference in energy inputs into substance and reference material is measured as a function of temperature, whilst the substance and reference material are subjected to a controlled temperature programme.

Among various types of DSC instruments, introduced by various industrial firms, there are two basically different types based on two different principles of operation. Most of the DSC instruments are based on the principle of DTA rather than that of a dynamic calorimeter.

There are numerous disadvantages of the DTA type over those of DSC instruments [60] Perhaps the most widely used true DSC instrument has been the Perkin-Elmer DSC2. This has a temperature range of up to 725° C with high calorimetric sensitivity and good base line repeatability and linearity.

4.7.3. Hot Stage Mic roscopy :

HSM allows visual observations of the sample, at various magnifications, under a controlled heating and cooling programme.

The most important application of high temperature microscopy according to McCrone [61] are : study of crystal growth, crystal lattice strain, analysis of binary mixtures, characterisation and identification of pure compounds, determination of purity. Various hot-stage furnaces for use up to maximum temperature of 2000 $^{\circ}$ C have been described [62]

A hot stage microscope which can also be used as a micro-DTA instrument has been described by Sommer and Co-workers. [63] The apparatus is based on the use of two opposed viewable thermocouple microfurnaces which may be rapidly heated or quenched and the sample weight

as low as one milligram can be tested.

Charsely and Kemp [64] for the first time applied the hot stage microscopy technique for the study of pyrotechnic reactions. They discussed the advantage of using hot stage microscopy to aid the interpretation of DTA and TG results.

A similar technique has been used in the present work, a Stanton Redcroft hot stage unit, with a separate programmer, with the necessary connections so that it could be handled easily and placed on the microscope stage, and removed for the sample change. It has a temperature range of 20 - 1000° C with heating rates from 1 to 100° C/min.

The sample atmosphere may be varied according to requirements. Due to the low mass of the water cooled furnace, it is possible to obtain fast heating and cooling rates together with good temperature response, and the isotherm could be established within a few seconds of switching the programmer to hold position.

The microscope used for the viewing of the sample was an Olympus X-Tr stereoscopic microscope fitted with trinocular head for photomicrography.









Block diagram of delay time measuring system



FIGURE (4.5.1)

Cross Sectional diagram of Parr Semimicro bomb calorimeter.



FIGURE (4.5.2)

TIME AXIS



Block diagram of temperature measuring system using optical pyrometer.

FIGURE (4.6.1)
CHAPTER FIVE

RESULTS AND DISCUSSIONS ON THE REACTION OF COMPACTED MIXTURES

5.1. DELAY TIME OF VARIOUS Sb/KMn04 COMPOSITIONS :

Antimony/potassium permanganate mixtures varying from 20 to 80% antimony were prepared using carboxymethyl cellulose as binder. Since KMnO, is soluble in water a small amount of a solution of binder was added to the thoroughly mixed composition in order to prepare granules of the mixture. The final composition contained less than 0.3% C.M.C. and was compacted into a 10mm delay tube under 61 x 10^{-6} Nm⁻² pressing load. In Figure (5.1.1) the variation of delay time against percentage antimony is shown. It can be seen that the burning time decreases as the fuel content of the mixture increases and reaches to a minimum at 65% Sb in the mixture. With further increase of the Sb in the mixture, the burning time increases up to 80% Sb above which compositions fail to initiate.

From the X-ray diffraction analysis it was possible to detect Mn_2O_3 and smaller amounts of Mn_3O_4 , there was also an X-ray pattern relating to the presence of \propto - Mn, stronger with compositions containing lower percentage of fuel.

Identification of the main reaction responsible for the propagation is difficult due to the variable valencies of manganese and presence of a number of stable oxides of antimony.

Hill [24] on the reaction of $Fe/KMn0_4$ system suggested the formation of $K_20_{.2}$ Mn0_{1.89}. Herbstein [20] in a recent work on the thermal decomposition of KMn0₄ also detected formation of oxide of manganese with an intermediate amount of oxygen.

The stable oxides of antimony are Sb_2O_3 , Sb_2O_4 , and Sb_2O_5 , Sb_2O_3 is stable up to $360^{\circ}C$. Above this temperature Sb_2O_3 vapourizes and in presence of oxygen it oxidises to Sb_2O_4 and Sb_2O_5 . Sb_2O_5 is stable up 400 °C where it begins to lose oxygen and by 950°C it decomposes to $\propto - Sb_2O_4$. [105]

The X-ray diffraction results did not show strong patterns relating to the oxides of antimony, it is possible that they are present in inorganic glass form amorphous to X-rays.

The products of the reaction of $Sb/KMnO_{\frac{1}{2}}$ mixtures from thermal analysis experiments, showed clear

X-ray patterns relating to the formation of $\frac{5b_{2}0}{23}$ (cubic) and $\propto - \frac{5b_{2}0}{4}$.

Where KMn0_4 was decomposed at 300 $^{\text{o}}\text{C}$ in air and was then mixed with antimony none of the resulting compositions propagated. This indicates that the oxygen resulting from the decomposition of KMn0_4 is necessary for the propagation of the composition.

Further evidence was obtained from the thermal analysis studies of the reaction of antimony with solid decomposition products of $KMnO_4$.

When the heating of various compositions was observed by a microscope under inert atmosphere $\binom{N}{2}$, Ar), even at very fast heating rates neither of the mixtures ignited. Whereas under oxygen containing atmosphere, the ignition took place. Ignition originated from a hot spot and advanced with a glow front through the mixture.

In compacted delay compositions this oxygen is provided from the decomposition of $KMnO_{A^*}$

The measurements of the temperature of various compacted mixtures showed that they vary between 890 to $1280 \,{}^{\circ}\text{C}$. Therefore Sb_20_3 formed initially from

oxidation of antimony, will be present in vapour form $(Sb_2O_3$ vapourises at above 360°C).

In the presence of oxygen resulting from the decomposition of KMnO₄ it will probably further oxidise to higher oxides of antimony (to Sb_2O_5 and preferably to Sb_2O_4).

From the results obtained, and from the consideration of chemical and physical characteristics of the reactant and the possible products, the following steps for the propagation reaction of Sb/KMn0 $_4$ mixtures could be suggested.

(a) Solid-state decomposition of $KMn0_4$ to give gaseous oxygen and solid products.

(b) Reaction of antimony with the products of decomposition to form Sb_2O_3 vapour.

(c) Further reaction of Sb_20_3 with the oxygen to form higher oxides of antimony.

(d) Solid-solid reaction of antimony with solid products of decomposition of $KMnO_4$.

After decomposition of KMnO $_4$, no preference

could be given to any other stages, they could probably take place simultaneously.

Hill and Wallace [25] in an investigation of the reaction of molybdenum with $KMn0_4$, showed that the temperature profile of the system consists of two steps. The first step being completed at 120 °C and the second step at 850 °C. Thus the heat evolved at first stage is roughly one-eighth of the total. They attributed the first step to a solid-solid reaction taking place between Mo and $KMn0_4$ by diffusion of Mo through the dislocation network of $KMn0_4$, and resulting in the coverage of internal surface with the products.

Such a reaction is also possible with $Sb/KMn0_4$ system and is responsible for the aging of the compositions.

5.2 EFFECTS OF LOADING PRESSURE ON RATE OF BURNING

Propagation rates of various mixtures of Sb/KMnO₄ were measured at several different loading pressures (from 20 to 240 x 10^{+6} N/m²). The compositions were prepared and tested within 24 hours, and a 10mm delay element was used in each test.

The results of rate of propagation at various loading pressures are shown on Figure (5.2.1) and (5.2.2).From the graphs it can be seen that in all compositions rate of burning decreased as the loading pressure increased. However, the effect of pressing load on compositions containing a large amount of excess Sb was found to be different from those containing high excess of KMn0,. When a Sb/KMn0, mixture containing 80% Sb was examined it was found that up to 110 x 10⁺⁶ N/m^2 all 15 delay elements ignited, at 168 x 10⁺⁶ N/m² almost half of the number of the delay elements failed, and at 240 x 10 +6 N/m² and above none of the delay elements propagated. It should be added that when the mixture did propagate a decrease in burning rate at higher compaction was observed.

With the compositions containing a large amount of excess $KMnO_4$ (20 and 25% Sb), the decrease in pressing load resulting in a more significant decrease in rate of burning. The standard deviation was also higher with such compositions.

When the loading pressure of a self-contained pyrotechnic mixture is increased, depending on the mechanism of the propagation reaction, it could either increase or decrease the rate of burning. If the

propagation wave only involves solid-solid reaction without vapour phase products, the increase in loading pressure should increase the rate of burning. This is mainly due to the higher density and therefore better surface contact of the reactant particles. At high density there is also better thermal conductivity of the mass, however this has been shown to have a small part in the increase of burning rate. When a gas-phase reaction is also involved in the propagation reaction of the composition or the reaction results in vapour phase products, the higher pressing load is expected to decrease the rate of propagation.

In this case the heat transport is carried out by the gaseous phase, diffusing through the voids to raise the temperature of the next layer to that of the ignition temperature. Therefore the increase of loading pressure, which reduces the voidage will inhibit the rate of burning of compositions.

In the combustion of Sb/KMnO₄ mixtures, as described previously, there is a very strong possibility of gas-solid oxidation of antimony to form vapourized Sb₂O₃ and its further oxidation in the gas-phase to form Sb₂O₄. Therefore at high densities the gas phase reaction is being suppressed and hence a decrease in burning rate is expected. When the composition with a

large amount of Sb is examined, since there is just enough oxidser to sustain the ignition, at high density the restricting of gas phase reaction causes the propagation to cease and therefore a large number of ignition failures are observed.

However, when the $Sb/KMn0_4$ mixtures with high excess of $KMn0_4$ are being tested (20 and 25% Sb) since at higher density a large mass of the sample is present in the delay tube, and the resulting gases from the decomposition of unreacted $KMn0_4$, causes a pressure build-up inside the delay tube. This results in erratic burning rates and often bursts in the aluminium delay tube.

5.3 <u>HEATS OF REACTIONS</u> :

Heats of reactions of various mixtures of $Sb/KMn0_4$ were determined using a Parr 1421 semimicro bomb calorimeter. On Figure (5.3.1) the variation of measured heat output per gram of the mixture is plotted against percentage antimony content in each composition.

From the graphs it can be seen that there is a

single maximum obtained at 50% Sb, this is 15% lower than the combustion rate maximum.

The closest calorific values to the experimentally measured heat outputs were found to be provided by the chemical equation

$$2 \text{ Sb} + 2 \text{ KMn0}_4 \longrightarrow \text{Sb}_2^0_4 + \text{Mn}_2^0_3 + \text{K}_2^0$$

However as can be seen from the Figure (5.3.1) the calculated heats of reactions are still higher than those found experimentally for all compositions. Similar results have been reported in the reactions of Mo/ KMnO₄, Fe/ KMnO₄, Mn/ KMnO₆ systems by Rees. [65]

When a chemical equation, suggested for the ignition process of a delay composition, is the only reaction taking place, the experimentally measured heat outputs are usually expected to be lower than the theoretical values calculated from the suggested chemical equation. This is mainly due to the heat loss from the measuring equipment and also incomplete oxidation of fuel particles. Therefore, when an excess heat is observed, there must be a highly exothermic reaction, more exothermic perhaps than the main reaction to account for the overall excess heat.

In some pyrotechnic systems the amount of excess heat measured experimentally is significantly high. In previous work carried out on the $Ti/BaCr0_4$ system higher calorific values, up to 45% greater were measured (11). Similar results have been reported by Miller [66] in the reaction of $Ti/PbCr0_4$.

McLain [49] Goodfield [67] and Harris [68] on the ignition reactions of pyrotechnic systems involving boron as the fuel $(SnO_2$, PbO, BaCrO₄ as oxidisers) reported higher experimental calorific values than those obtained theoretically.

With non-stoichiometric mixtures, it is reasonable to expect that the excess fuel or oxidant may take part in side reactions, and contribute to the heat output which is not accounted for in the theoretical calculations. However, the excess heat output provided by such reactions should decrease as the compositions approach the stoichiometric value.

Examination of the graphs obtained and those reported in the literature show that, in most of the above mentioned systems, the excess heat with the stoichiometric mixture is as much as the non-stoichiometric mixtures.

This raises an additional possibility that a side reaction partly responsible for the excess heat, involves fuel or oxidant in the composition, regardless of the proportions of the reactants.

Intermetallic reaction between the fuel and the metal resulting from the reduction of oxidiser is one possibility which could result in a considerable energy increase. Alloying reactions of boron, titanium, zirconium and a number of transition elements have been investigated by Hardt and Phung[69,70]. They showed that intermetallic reaction between finely powdered metals are highly exothermic, and suitable mixtures of these metals in compacted form can propagate in a self-sustained manner. They reported the heat output from 900 to 4800 J/g, raising the temperature of the sample between 2400 to 3770°C.

On Figure (5.3.2) the determined calorific values per mole of KMnO₄ are plotted against percentage antimony. It can be seen that the quantity H increases up to the point 50% antimony above which it remains almost constant. This point has been suggested to relate to the stoichiometry of the reaction where the amount of reducing agent is equal to the oxidising agent. Further increase in the reducing agent uses up all the oxidising agent and (H) becomes constant.

Figure (5.1.1) shows that the rate of propagation reaches a maximum at 65% Sb, whereas the maximum heat output is obtained with 50% antimony mixture. This is in accord with Spice and Staveley's [4] findings, where they state that the propagation rate usually reaches to a maximum at a higher and never a lower percentage of reducing agent, than that at which the heat out-put has its highest value.

They explained this occurrence on the basis that the oxidation of a fuel particle is fast initially when a large surface is available and it gets slower as the reaction proceeds. Therefore, when excess fuel is present, the reaction is faster for the above reasons and this outweighs the effect of lower heat output per unit mass [4].

In a previous work (11) on the PbO/Si and Pb_{30}_{4}/Si

systems, the thermal analysis results showed the occurrence of the surface reaction taking place more readily at lower temperature than the bulk reaction. Thus confirming that, if a layer-to-layer combustion reaction can propagate without the need for the reaction to advance to the bulk of the particles, such reactions will have a faster propagation rate than the reaction with bulk oxidation.

In the present system $Sb/KMnO_4$, reaction in thermal analysis studies was found to be different from the reaction in consolidated form. The principal difference being the absence of gas phase reaction, due to the early stage decomposition of $KMnO_4$ and loss of oxygen. Whereas in compacted form, as shown previously, the gas phase reaction was essential for the propagation to take place.

DSC studies of the oxidation of powdered antimony in air resulted in a double exothermic peaks. The first peak relating to the surface oxidation of Sb. Therefore it is possible that in consolidated form the oxidation takes place through the surface reaction. With compositions containing excess fuel the reaction proceeds faster, until the effect of lower heat output increases and the rate of burning begins to decrease.

5.4 <u>REACTION_TEMPERATURE_MEASUREMENTS</u>

Ignition temperature of mixtures was measured by (a) an optical pyrometer and (b) a temperature profile method.

When the optical pyrometers are being used, the

major requirement for accurate and repeatable temperature measurements is the knowledge of the emittance of the target. Goodfield [67] in a detailed investigation, on the application of the pyrometer to a number of pyrotechnic delay systems showed that the change of emittance of the system from 0.1 to 0.9 results in a temperature difference of 350 °C. He put forward a method by which it was possible to measure emittance of each delay system, prior to the final temperature measurements.

To obtain the emittance value the ignition product of a 50/50 mixture of Sb/KMn0₄ was chosen. A suitable amount of powdered sample was placed in an Inconel sample pan and was heated to 750 $^{\circ}$ C under nitrogen atmosphere in a Stanton-Redcroft microfurnace. The sensing head was then focussed on the sample and the emittance control on the electronic module varied until the correct temperature was displayed on the digital meter. The emittance value obtained in this way (0.55) was used in all temperature measurements of the pelleted mixtures.

Eight measurements for each composition were made in order to ensure the repeatability of the results. In Figure (5.4.1) the measured temperatures are plotted against the variation of fuel content of the

mixtures. It can be seen that the maximum temperature, 1227 $^{\circ}$ C is attained with a 50/50 composition. At this temperature the manganese and the possible oxides of manganese formed are in a solid form. Manganese melts at 1240 $^{\circ}$ C, Mn₃0₄ melts at 1564 $^{\circ}$ C and Mn₂0₃ begins to lose oxygen at 1050 $^{\circ}$ C.

The most stable oxide of antimony is $\propto -$ Sb₂0₄ which begins to decompose to Sb₂0₃ vapour and oxygen at 930 °C. At this temperature any excess antimony present will be in molten form, since it transforms to liquid at 630 °C. Unlike Ti/BaCrO₄ and PbO/Si systems the final products of Sb/KMnO₄ mixtures, preserved their original pelleted form.

There was no formation of a hollow in the centre of pellet, which is usually due to the melting of a large amount of product to the cooler sides.

In the measurements by the temperature profile method, which is an extension of the method originally published by Hill and co-workers [6], the temperature change across the burning zone is measured directly using a thermocouple.

The measurements were carried out using Platinum/Platinum - 10% Rhodium thermocouples of 0.05 mm

diameter. The mixture is compacted into an open delay train 20 mm long. The thermocouple junction is embedded at the mid-point of the pelleted mixture. The delay element was ignited at one end of the train and the thermocouple signal was captured and stored by a memoryscope. The stored signal was examined visually on the CRT screen before the final print out.

The results obtained were not as repeatable and reproducible as those obtained by the pyrometer. This was mainly due to the thermocouple failure and imperfect contact between the thermocouple head and the sample. However, under the right condiditons, when the complete profile of the mixtures were obtained, the maximum temperatures were found to be in a very good agreement with those obtained by the pyrometer.

In Figure (5.4.2) the temperature profile obtained directly from the ignition of a 55/45 mixture of Sb/KMnO₄ is shown. In Figure (5.4.3) the temperature rise of the combustion is enlarged four times. It can be seen that, there is a linear temperature rise up to 120° C. This is followed by acceleratory rate of temperature rise, and within 980 msec temperature increases to 1200° C. There is an inflection point at 400° C above which the rate of temperature increase begins to fall.

Hill [24] from a detailed analysis of temperature profiles of the $Fe/KMnO_4$ system, and from the effect of inert materials on the reaction kinetics proposed a mechanism. He suggested that the reaction takes place by the way of the gas phase and solid-solid interface. The relative importance of these reactions vary with the density of the mixtures.

Thermal analysis studies of the Sb/KMnO₄ system in loose form, and the individual components, showed that the ignition reaction takes place only under oxygen containing atmosphere. The study of the compacted mixtures, as reported in sections 5.1 and 5.2, showed that the rate of propagation decreases with the increase of density. This indicates that at the higher density the main reaction is in solid-solid interface, and that the decrease in the rate of propagation is due to the restriction on gas-solid phase reaction caused by higher density.

A useful information on the reaction of non-stoichiometric mixtures of $Sb/KMn0_4$ with excess $KMn0_4$ is probably to know whether the excess oxygen in the product is in the form of gaseous oxygen or in the form of solid products of $KMn0_4$ decomposition. With compositions containing a very large amount of $KMn0_4$

unreacted gaseous oxygen is expected.

In the hot-stage microscope studies, even with compositions containing enough excess of KMnO_4 so that, after losing oxygen at first stage of decomposition of KMnO_4 , there was enough oxygen left in the composition to satisfy the complete oxidation of Sb, still ignition did not take place. It is possible that all oxygen resulting from the first stage of decomposition of KMnO $_4$ reacts with antimony. The excess gaseous oxygen is due to the second stage of decomposition, which also releases oxygen, and from the other oxides if the temperature is high enough.













0/0







FIGURE (5.4.2)



Time (seconds)

CHAPTER SIX

THERMAL ANALYSIS STUDIES

6.1 <u>APPLICATION OF THERMAL METHODS OF ANALYSIS</u> <u>TO THE STUDY OF PYROTECHNIC REACTIONS</u>

Perhaps the most widely used DSC instrument has been the Perkin-Elmer DSC-1 introduced in 1963 and Model DSC-2 introduced in 1971 [71]. This has an extended temperature range up to $725^{\circ}\dot{C}$ improved baseline repeatability and a higher calorimetric sensitivity.

No attempts will be made here to discuss technical aspects of DSC. Details of theory and design of DSC have been given by Watson et al [72] and O'Neill [71]. McNaughton and Mortimer [73] have discussed the advantages of differential scanning calorimetry to the conventional DTA, in which both sample and reference are heated by a single heat source.

DSC instruments other than Perkin-Elmer have been introduced with high temperature range up to 1500 °C. However, since they are designed on the basis of a single furnace, they carry the disadvantages of DTA, and are referred to as indirect DSC [60]. In the literature, the majority of the thermal analysis studies on the pyrotechnic reactions have been carried out utilising the DTA technique, where a large amount of sample is used and the system is designed to resist heat

from the highly exothermic reactions.

Perkin-Elmer DSC-2 is principally designed for the determination of physical constants of substances, enthalpies of phase changes, and chemical reactions with low exothermicity.

However, if in the study of pyrotechnic reactions by DSC-2, necessary precautions (such as choice of the system, weight of the sample, rate of heating, choice of atmosphere) were taken, DSC traces with more detailed information can be obtained. This is demonstrated by Al-Kazraji [74] and Goodfield [67] in a detailed investigation of a number of pyrotechnic systems.

On Figure (6.1.1) a DSC trace obtained from the solid-solid reaction of Si/PbO system is shown. The reactions of Si with PbO have previously been reported [11]. Two exothermic peaks at the temperature range of 550 to 770° C represent the reactions, the first peak is always the smaller of the two peaks. Similar peak patterns were obtained on the oxidation of antimony in air, and from the reaction of antimony with PbO₂. However, when at the temperature of the reactants was in molten form the resulting DSC traces were found to be different from the solid-solid reaction.

In Figure (6.1.2) the DSC curve corresponding to the reaction of selenium with barium peroxide obtained under argon atmosphere is given. Selenium melts at around 217 °C, and a sharp endothermic phase change at this temperature is observed. The exothermic reaction of molten Se with BaO₂ begins at around 350 °C and forms only a single exothermic peak at around 420 °C before returning to the base line at 510 °C.

The reaction of boron with potassium dichromate under argon atmosphere is given in Figure (6.1.3) where the oxidant is in molten form. It can be seen that a single exothermic peak appears at the melting point of potassium dichromate at around 400° C. The reaction of molybdenum with $K_2 Cr_2 O_7$ also resulted in a single exotherm in the DSC trace, as shown on Figure (6.1.4).

The melting of $K_2 Cr_2 O_7$ and oxidation of the metal takes place simultaneously, with fast heating rates it is possible to separate the two processes, Figure (6.1.5). Review of the results at this stage shows that:

(a) In a metal oxidant system physical changes of the fuel do not result in its immediate reactivity, selenium

melts at 217 °C, but its reaction wih $Ba0_2$ begins long after at around 350 °C. Whereas with the $K_2Cr_20_7$ / metal systems the reaction begins at the melting point of oxidant with both metals. Therefore it could be suggested that the temperature, at which physical or chemical change occurs in the oxidant, has a more important role on the start of the main reaction. This is true at least with the $K_2Cr_20_7$ / metal system and in the literature there are a number of reports concerning the importance of the decomposition of oxidant on the reaction of the pyrotechnic system. [24,25,74,75]

(b) With molten fuel or oxidiser only a single exothermic peak, represents the reaction on the DSC trace, whereas with the single stage solid-solid reaction, a small exotherm prior to the large exothermic peak appears.

Further information was obtained from the DTG traces of the oxidation of powdered Fe in static air atmosphere. The reaction of Fe in air results in two major peaks, in Figure (6.1.6), curve (a) corresponds to the oxidation of iron up to 730 ^OC which is the end of the first peak, when the sample was cooled and reheated as shown by curve (b), no further reaction takes place at this temperature range. Curve (c) shows the weight gain

after the sample (b) was re-ground mechanically and was reheated.

Similar results were obtained from the reaction of Si with PbO, the first peak was irreversible and on re-grinding the sample reaction at the temperature range of the first peak was detected.

The occurrence of the reaction after grinding the sample is due to the formation of the fresh surface, therefore the first exothermic peak could be associated with the surface reaction of particles. The nature of the chemical reaction, corresponding to the first exotherm is probably similar to the slow surface reaction occurring during the storage of the mixtures. This is associated with a small amount of reactants and is responsible for the ageing of the compositions.

The effect of ageing on $Ti/BaCr0_4$ and $Sb/KMn0_4$ compositions has been studied. The ageing was brought about by subjecting the mixtures to a constant temperature for a certain period of time.

In general the increase of the temperature or the time to which the sample was subjected, decreased the burning rate and heat output. This is usually accompanied with an increase in the number of ignition

failures. Therefore it could be concluded that the extent of the chemical reaction responsible for the ageing of the mixture could be affected with time and temperature.

In the DSC experiments, when the mixture is being heated, the reaction begins on the surface, similar to the reaction occurring during the storage.

However, since the temperature is being increased continuously, the reaction probably will not be limited to a small amount. It advances deeper into the particles up to a point where the accumulation of the product will interfere with the reaction.

The emergence of this point is a relatively gradual process on the DSC trace. A decrease in the rate of the reaction is noticeable, which is the completion of the first peak and beginning of the second peak.

Further continuation of the reaction now would depend on the diffusion of one of the reactants through the product layer. This stage of the reaction, could be called bulk reaction which relates to the second exothermic peak and involves a larger amount of the sample.

When either of the reactants is in molten form, the formation of the products is in a solid/liquid interface, and it would not be a barrier to the advance of the liquid phase. This is probably the main reason for a single exotherm on the DSC trace.

DSC curves of pyrotechnic mixtures with multiple exothermic peaks have been reported and these are usually associated with various stages of reduction of oxidizer by the fuel.

Charsley and Ottaway [76], reported five exothermic peaks on the reaction of boron with molybdenum trioxide. From the X-ray diffraction analysis at selected temperatures, they showed that, the first two exotherms correspond to the reduction of MoO₂ to MoO₂. The three other exotherms are due to the reduction of MoO₂ to $\frac{1}{2}$ metallic Mo through three different stages.

6.2 THERMAL ANALYSIS OF POTASSIUM PERMANGANATE

Thermal behaviour of $KMnO_4$ in the temperature range ambient to 720 °C was studied under oxygen, nitrogen and argon atmosphere\$, utilising thermogravimetry, differential scanning calorimetry, and hot stage microscopy techniques.

In Figure (6.2.1) TG/DTG curves of ground and single crystal KMnO $_{L}$ tested under nitrogen atmosphere at a heating rate of 5° C/min. are shown. With the ground sample the reaction rate begins to increase at 231 $^{\rm O}$ C accelerates up to 289°C, makes a maximum at this point and returns to zero at 304°C. With the single crystal sample there is a long period of constant rate of decomposition up to 274° C from which the reaction rate begins to increase up to 285° C, followed by a decline at about the same rate to the base-line at 310° C. The results indicate that there is a very small difference in peak temperature maximum between the two forms of KMnO $_4$, but the distribution of the extent of reaction with temperature differs significantly. With the single crystal sample, up to 287.5 °C only 7.5% of material had reacted, while with the ground sample at this temperature 62.5% had reacted. The result would be that with the crystal of KMnO,, much more sample would be left to decompose at substantially higher temperature, which would take place at a higher rate.

A similar but less significant effect probably exists at the isothermal conditions. Before the beginning of the acceleratory stage, the crystallised sample being subjected to the temperature for a much longer period of time (induction period) than the ground

sample. The reason for the ground sample reacting more readily at a lower temperature is due to the larger surface area and the formation of potential nuclei, resulting from the local heating effects of grinding.

Percentages of the weight loss were calculated from the minimum of five tests for each heating rate, and it was found that the weight loss generally increases with the increase of the heating rate in a limited range.

To examine the influence of high density on thermal behaviour of $KMnO_4$ the crystallised sample was compacted before thermogravimetric analysis. This was carried out manually using a pellet press. A disc of $KMnO_4$ which was around 9 times denser than the loose powder sample, was obtained from the press, this was then broken to grains and a suitable weight was chosen for TG/DTG tests.

Decomposition of compacted KMnO_4 , together with the ground and single crystal sample, at the heating rate of 10 $^{\text{O}}$ C/min, under nitrogen atmosphere are shown in Figure (6.2.2). It can be seen that, although during the compaction the KMnO_4 crystals break down further, its decomposition begins at a higher temperature than the ground sample, and it results in a sharper DTG

curve.

The final product was in one piece and was as hard as the sample before test.

Changing the atmosphere from oxygen to argon increased the temperature of decomposition slightly around 14 ^OC and the weight loss with argon was lower, this was found to be highly reproducible.

To describe the decomposition of $KMnO_4$ most authors have used the following equation :

 $2 \ \text{KMn0}_{4} \longrightarrow \text{K}_{2} \text{Mn0}_{4} + \text{Mn0}_{2} + \text{O}_{2} \qquad (1)$

Corresponding to the weight loss of 10.12%. In most experimental studies the weight loss from the decomposition of KMnO₄ was found to be higher than the above mentioned value.[17].

Herbstein and co-workers [20] suggested a mechanism according to which the products in air at above 200 9 C are manganate "K₄Mn₇0" phase and oxygen

10 KMnO₄ \longrightarrow (2.65 K₂MnO₄ + 2.35 K₂O + 7.35 MnO_{2.05}) + 60₂ This is referred to as the Herbstein mechanism which agrees with the products of equation (1) and satisfies
the higher weight loss which is 12.15%. However Boldyrev et al [22] have recently suggested that the crystalline phase K₃(MnO₄)₂ is formed at first stage and that K₂MnO₄ is formed in a later stage. If the reaction follows the Boldyrev's mechanism then most of the earlier studies particularly of the Prout and Tompkins type will have to be reinterpreted. In the present work the weight loss obtained varied with both temperature and atmosphere in the range of 10.5 to 12.8%.

DSC experiments were also carried out under three different atmospheres. On Figures (6.2.3,4,5) DSC traces obtained at 5° C/min for ground and crystallised KMnO₄ under oxygen, nitrogen and argon are shown respectively. It can be seen that with ground KMnO₄ like DTG experiments the reaction takes place in a broader temperature range, beginning at a lower temperature than the crystallised sample. With single crystal KMnO₄ a noticeable rate of decomposition is reached at higher temperature and it produces much sharper peaks.

The effect of atmosphere on the temperature of DSC traces is small (around 14 $^{\circ}$ C) Figures (6.2.3,4,5) However the major difference was that under oxygen and nitrogen atmosphere exothermic DSC curves for the

decomposition of KMnO_4 were obtained whereas under argon atmosphere, after an initial tendency towards exotherm, the main decomposition peak is endothermic. In order to make sure of such an occurrence different forms of KMnO_4 , from different sources, were examined by DSC under various atmospheres. The results were principally the same as shown on Figures (6.2.3,4,5). On Figure (6.2.6) the DSC trace for the 30/70 mixture of Sb/KMnO $_4$ obtained under argon atmosphere is shown. The reaction of antimony begins after complete decomposition of KMnO $_4$.

The endothermic peak of the decomposition of $KMnO_4$ can be clearly seen, being in the opposite direction to the exothermic peaks of Sb reactions.

Numerous peak patterns similar to the Figure (6.2.6) were obtained with different Sb/KMn0₄ mixtures, under argon atmosphere.

Exothermic decomposition of $KMnO_4$ in air is widely known. Herbstein et al [20] and Booth et al [23] have shown exothermic DTA curves of $KMnO_4$ decomposition in air. If equation (1) describes the whole chemical process then the reaction under inert atmosphere should be exothermic as well. No inert atmosphere other than nitrogen, has been used in thermal decomposition of $KMnO_4$. Beck and Brown [77] also showed the exothermic decomposition of $KMnO_4$ under N₂

atmosphere. Under argon atmosphere the decomposition reaction begins exothermally by initial diversion towards exotherm, however it seems to be suppressed by unfavourable atmosphere Figure (6.2.5).

Thermogravimetric measurements show that the weight loss under 0_2 , N_2 and Ar atmosphere differs in a reproducible and small range, however the weight loss under argon is always lower than N_2 and 0_2 atmospheres. The exothermic decomposition could be one of the reasons for higher weight loss, causing further decomposition of products and KMn0₄ under 0_2 and N_2 atmospheres.

The reactivity of the products of the decomposition of $KMnO_4$ obtained under O_2 , N_2 and Ar atmospheres were compared by their reaction individually with antimony, no significant differences on the resulting DSC curves were obtained.

Up to the present time there has not been a final agreement on the chemical nature of the decomposition products of $KMn0_4$. Herbstein et al found that the " $K_4Mn_7O_{16}$ " phase and oxygen were the products of decomposition in air, whereas Boldyrev et al's results suggested the formation of $K_3(MnO_4)_2$ crystals at the first stage.

There have been further publications from both authors, Herbstein et al [21] and Boldyrev et al [78] with results supporting their earlier findings.

The agreement with either of the above mentioned mechanisms should accompany a detailed X-ray investigation on the reaction intermediates and products, with a specially designed system to register diffraction patterns continuously as the sample temperature is changed.

When the sample of $KMn0_4$ after decomposition was heated to higher temperature, further decomposition occurred, resulting in a single endothermic peak at 627 $^{\circ}C$

Figure (6.2.7). This endotherm corresponds to the decomposition of K_2 MnO $_4$, and is represented by the following chemical equation (1).

$$10 \ \text{K}_{2}\text{MnO}_{4} \longrightarrow 5.7 \ \text{K}_{3}\text{MnO}_{4} + 0.5 \ (2.9 \ \text{K}_{2}\text{O} \ . \ 8.6 \ \text{MnO}_{2.1}) \\ + 3.40_{2}$$

The reaction under air, nitrogen and argon atmospheres was found to be endothermic. However under air atmosphere, when the sample after decomposition was cooled and reheated the endothermic peak appeared in smaller size. This indicates that the reaction is at least partially reversible.

Thermogravimetry results showed that the change

of atmosphere from air to argon has a reverse effect on the weight loss at the second stage, to that of first stage of decomposition.

In air atmosphere the weight loss at first stage of decomposition of $KMn0_4$ was 12.8% and at the second stage 3.7%. Whereas under argon atmosphere the following values, 10.7% and 5.2% were obtained at first and second stage of decomposition respectively. Each value mentioned above is the mean value taken from the results of five experiments under each different atmosphere at the heating rate of 5°C/min. Results indicate that under air atmosphere, partial decomposition of products takes place at the first stage resulting in a lower weight loss at the second stage of decomposition.

On the mechanism of decomposition of $KMnO_4$ (first stage) Prout and Tompkins [12] suggested that a chain branching nucleation process is responsible for the acceleratory decomposition of $KMnO_4$. The chain branching being due to the crack formation in the crystals. The cracks being the result of strains induced by the surface product molecules of different dimensions in the undecomposed crystal (they assumed MnO_2 being one of the products where the unit cell geometry and dimensions are different from that of $KMnO_4$).

Hill [14,15] however believed that the chains were diffusion chains, rather than strings of immobile He suggested that the atoms or ions of the nuclei. products diffuse through the dislocation network and reach the nucleus forming a site, and fertilisation takes place. When decomposition of single crystal of KMnO_h was observed visually under a hot-stage microscope, the visible fragmentation occurred by the internal disruptions. The fresh surface created by the pattern and original fragmentations kept its bronze-brown colour for a long time. There was no indication of immediate decomposition on the surface. Although it is expected that the nucleation at the favourable points on the surface will occur, however, this is not as effective as internal decomposition to cause cracking of the crystal. The effect of surface deomposition probably increases with the decrease of size of the fragments, up to a range, where the continues through the surface fragmentation decomposition, this could be the beginning of the acceleratory stage.

Rate of nucleation of potential nuclei will depend on the rate of diffusion of products, which will increase with the increase of temperature. In Table (6.2.1) the effect of the heating rate on the extent of

the acceleratory stage (> max) is shown, it can be seen that the $<max}$ max is increased with the increase of temperature. This could be explained by the chain diffusion mechanism (79). Application of chain diffusion theory has shown that the nucleation efficiency increased from 10⁻⁴ at 140 °C to 10⁻¹ at 220 °C

6.3 <u>OXIDES OF ANTIMONY</u>

Three stable oxides of antimony are known, $S_2^0_3$, $Sb_2^0_4$ and $Sb_2^0_5$.

There are two forms of antimony trioxide, cubic Sb_2O_3 (senarmontite) and orthorhomic Sb_2O_3 (valentinite). Both oxides when heated begin to vaporize at around 360 °C, the cubic Sb_0 transforms to orthorhomic form at the temperature region of 573 to 510 °C

with the heat of transformation of $\triangle H = 3.4$ kJ/mole. The enthalpy of vaporization is 50 kJ/mole and the gaseous product of vaporization has been shown to be a dimer of $Sb_2 0_3$, i.e. $Sb_4 0_6$, and it condenses to senarmontite $Sb_2 0_3$.

When $Sb_{2} 0_{3}$ is heated in air (either form), the oxidation takes place and the final product is $Sb_{2} 0_{4}$. DSC and TG/DTG analysis of cubic $Sb_{2} 0_{3}$ have been carried

out under argon and static air atmosphere. When the sample was heated in air, the volatilization and oxidation begin simultaneously. The final outcome of the two counteracting weight change processes was 18.5% weight loss between 360 to 600 °C Fig (6.3.1), the remaining material did not show any weight change when heated to 1000 °C.

In the DSC studies of cubic $Sb_2 0_3$, low sensitivity had to be used to minimise the continuous endothermic drift due to the vaporisation of $Sb_2 0_3$, the exothermic oxidation peak begins at 560 °C and reaches to a maximum at 626 °C. The endothermic deviation still continues with a slower rate after the oxidation, and no other significant change is evident Fig (6.3.2). When the sample was heated in argon atmosphere 92% weight loss occurred by 780 °C.

Orthorhombic \propto - Sb $_2$ 0 $_4$ (cervantite) is considered to be a very stable oxide, and under inert or oxygen atmosphere it undergoes no chemical or physical changes up to 950 °C.

In the oxidation of antimony $\propto -$ Sb₂0₄ is the final product. Transformation of $\propto -$ Sb₂0₄ to monoclinic phase takes place at above 960°C, Rogers and Skapski [80] have suggested that the β - Sb₂0₄ is

formed in the following manner:

$$2 \propto -Sb_20_4(solid) \longrightarrow Sb_40_6(vapour) + 0_2 \longrightarrow 2\beta Sb_20_4(solid)$$

Cubic $\frac{\text{Sb}_{2}}{25}$ is also a stable oxide of antimony up to 400°C above this temperature it dissociates to $\propto -\frac{\text{Sb}_{2}}{4}$.

Rosenberg et al [31], in the isothermal oxidation of antimony, found that at early stages of oxidation, $Sb_2 0_5$ together with $Sb_2 0_3$ are formed on the surface of Sb, where the $Sb_2 0_3$ is an inner layer close to antimony and $Sb_2 0_5$ being the outer layer.

Thermogravimetric analysis on the $\text{Sb}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ were carried out under air and argon atmosphere. On Figure (6.3.3) the TG/DTG curves obtained under static air atmosphere at the 20°C/min heating rate are shown. The results agree with Cody et al [105] findings, dehydration ends at 600°C which results in 10% weight loss. Further weight loss due to the dissocation of Sb $_2\text{O}_5$ to Sb $_2\text{O}_4$ takes place at the temperature range of 680 to 750°C with 4.8% weight decrease.

6.4 OXIIDATION OF ANTIMONY

The solid-gas oxidation reaction of finely powdered antimony under an oxygen containing atmosphere studied by differential scanning calorimetry and was thermogravimetry. In Figure (6.4.1) the DSC trace of the oxidation of Sb in static air at 5° C/min heating rate is shown. Under these conditions a controlled and non-ignition reaction takes place. The reaction begins at around 360° C and two peak maxima at 501 and 552° C are The valley between the two peaks is either due formed. to the evaporation of Sb 0_{23} or, because of the formation of products on the surface of the antimony which interfere with the reaction.

X-Ray diffraction analysis showed that the final product is $\propto -$ Sb₂0₄, which is stable at the temperature of the reaction. The linearity of the base line, after completion of the reaction on Figure (6.4.1), shows the stable products formed. On the X-Ray diffraction film, a weak pattern corresponding to the formation of small amounts of cubic Sb₂0₅ was also present.

Thermogravimetric results, obtained under similar experimental conditions as DSC experiments, are

shown on Figure (6.4.2). The weight gain occurs at two stages, the first taking place at the temperature range of 370 to 498° C with 7% weight gain, the second at the temperature range $498 - 610^{\circ}$ C with the mass increase of 11%.

The possible oxidation steps with corresponding mass increase and reaction enthalpies are :

 $2Sb_{(s)} + 3/2 \xrightarrow{0}{2} \xrightarrow{Sb_2_0_3} (s) \xrightarrow{19.7\%} \Delta H = 348 \text{ kJ/mole}$

$$Sb_20_3 + \frac{1}{2}0_2 \longrightarrow Sb_20_4$$
 (s) 6.5% $\Delta H = 99.4 \text{ kJ/mole}$

The results indicate that the oxidation process is not divided into two stages in accordance with the two above chemical equations, but in every stage both reactions are taking place. Sb_20_3 being formed first and then reoxidized to Sb_20_4 in each stage some Sb_20_3 being lost due to the vaporization, and in a complete oxidation process all final products are Sb_20_4 .

Nakahara [82] showed that the oxidisation of Sb in air results in a total mass gain of 25% occurring in two approximately equal stages. Beck and Brown [77] obtained a 1% (weight) gain at 300° C, followed by 16% weight increase at the temperature from 300° C to 540° C.

The value of $\triangle H$ obtained from the total area under the exothermic peaks in the DSC trace was 376kJ/mole which is lower than calculated value, 448 kJ/mole.

Deviation from the expected mass and enthalpy change is due to the vaporization of $\text{Sb}_{2}0_3$, during the oxidization. In Figures (6.4.3) and (6.4.4) DSC and TG/DTG traces for the oxidation of antimony in air, obtained at a faster heating rate and higher sample weight are shown. It can be seen that the second peak is very sharp, vaporization and/or melting of Sb_20_3 and unreacted Sb follow immediately. This is also apparent on the DTG curve, a rapid decrease in rate of weight gain occurs after the second stage of weight gain. This most probably is due to the fast temperature rise resulting from the oxidation reaction, which causes the vaporization of Sb₂0₃ and melting of unreacted Sb.

When the oxidation of antimony was observed with a hot stage microscope, at around $530 \, ^{\circ}$ C the first needle shaped white crystals above the mass of antimony appeared. This probably corresponds to the simultaneous formation and vaporisation of $\rm Sb_2\,0_3$ changing to cubic white crystals at the top of black antimony, follwed by very rapid and simultaneous mass contraction and its conversion to white $\rm Sb_2^0_4$.

6.5 REACTIONS OF Sb/KMn04 COMPOSITIONS

In Figure (6.5.1) and (6.5.2) DSC and TG/DTG traces of the reaction of a 40/60 mixture of Sb/KMnO₄ under argon atmosphere are shown. The endothermic peak at around 300 °C corresponds to the first stage in the decomposition of KMnO₄ the oxygen released at this stage leaves the sample without reacting with antimony.

The corresponding TG and DTG curves show 7.1% weight loss (60% KMnO $_4$) at the same temperature range Figure (6.5.2). The reaction of antimony begins after complete decomposition of KMnO $_4$, this being observed from the exothermic deviation of DSC curve.

It can be seen from Figure (6.5.1) that in the temperature range of 350 to 490°C comparatively broad overlapping exothermic peaks are formed, this is followed by a sharp and intense exotherm. This peak has the characteristics of a very fast exothermic reaction, and it is much larger under air atmosphere when the ignition reaction takes place.

When the $Sb/KMnO_4$ mixture was heated in air, the oxygen resulting from the decomposition of $KMnO_4$ again left the sample. However a gradual weight gain began shortly after decomposition, and continued up to

520 °C where the ignition reaction took place, this resulted in a rapid weight gain of about 19% Figure (6.5.2). In the DSC trace the ignition is represented by a sharp and strong peak at the corresponding temperature range.

occurrence of the ignition reaction The depended on the rate of heating and mass of the sample. The major difference between the reaction of the Sb/KMn0 $_4$ in compacted delay elements and that of the loose powder in thermal analysis methods, is that in the ignition of the compacted mixtures in delay assemblies, the oxygen released from the decomposition of KMnO $_{m L}$ takes part in the ignition of the sample. Whereas in DSC and TG/DTG experiments, as the results showed, the oxygen resulting from the KMnO $_{f L}$ decomposition leaves the sample without reacting with antimony. The use of air as the carrier in thermal analysis experiments, provides an gas unlimited amount of oxygen and therefore the oxidation is always expected to be complete, regardless of the amount of KMnO4 present in the composition.

In the study of Sb/KMnO₄ mixtures in the inert atmosphere when the loss of oxygen from the decomposition of KMnO₄ was taken into account, the stoichiometric amounts were calculated to be Sb 27.5%, KMnO₄ 72.5%.

- $2 \text{ KMnO}_4 \longrightarrow \text{K}_2 \text{MnO}_4 + \text{MnO}_2 + \text{O}_2$ $2 \text{ K}_2 \text{MnO}_4 + 2 \text{ MnO}_2 + 2\text{Sb} \longrightarrow \text{Sb}_2 \text{O}_4 + \text{K}_2 \text{O} + \text{Mn}_2 \text{O}_3$
- $4 \text{ KmnO}_4 + 2\text{Sb} \longrightarrow \text{Sb}_2\text{O}_4 + 3 \text{ Mn}_2\text{O}_3 + 3 \text{ K}_2\text{O} + \text{O}_2 27.5\% \text{ St}$

The stoichiometric values are calculated on the assumption that all of the antimony is completely oxidised to Sb_20_4 . In practice however, some of the antimony remains unreacted, and from the reacted antimony some vaporises as the Sb_20_3 form, before further oxidization to Sb_20_4 . DSC traces of various Sb/KMn0₄ mixtures show that the highest exothermicity is closer to 40/60 than 30/70 Sb/KMn0₄ composition.

Figures (6.5.1,3,4,5) show the DSC traces of various Sb/KMnO₄ compositions under argon atmosphere. It can be seen, that with the increase of proportion of KMnO₄ in the mixture, the size of the endothermic decomposition peak increases, and at the same time the endothermic peak relating to the melting of unreacted Sb becomes smaller. With 10/90 and 70/30 Sb/KMnO₄ mixtures, the sharp exothermic peak at the ignition temperature is absent, it appears with more active mixtures and becomes stronger as the mixture ratio

approaches the stoichiometric value.

When the variation of fuel/oxidant ratio was studied under air atmosphere there was little difference on DSC traces except that with high Sb proportions larger exothermic peaks resulted. This is due to the availability of the gaseous oxygen from air which results in complete oxidization of Sb.

The differences on TG/DTG traces were more noticeable, the compositions with higher KMnO_4 showed higher weight loss at the decomposition of KMnO_4 and less weight gain at the oxidation of Sb.

When the compositions were observed with a hot-stage microscope while it was being heated, at around 300° C decomposition of KMn0₄ took place which was accompanied by physical activity of the particles. After the decomposition of KMn0₄ up to the ignition temperature, or fast Sb oxidisation region, no physical changes were noticed. This is mainly due to the dark colour of the reactants which make it difficult to observe the contact points of particles. The ignition reaction occurs only under air atmosphere, this originates at a hot spot in the sample and rapidly progresses to the unreacted mixture.

With most samples the bright red reaction front had a non-molten appearance. This was confirmed by testing the final product, it was hardened to one piece, but could easily be powdered by hand pressure. With compositions containing high percentage of Sb (above 60%) Sb molten reaction front was visible, and the product was in solid form and usually in one piece.

Under inert atmosphere (nitrogen and argon) no ignition reaction was observed. With compositions close to the stoichiometric value, the occurrence of a rapid oxidation reaction at above 470° C was noticeable, accompanied with the contraction of the sample.



 $\frac{dH}{dt}$ mcal/sec



 $\frac{dII}{dt}$ mcal/sec







 $\frac{dH}{dt}$ mcal/sec



dw dt mg/min



FIGURE (6.2.2) TG and DTG traces of various forms of $KMnO_4$ under nitrogen atmosphere at $10^{\circ}C/min.$



Temperature ^oC





dt















TG and DTG traces of $Sb_20_5 2H_20$ heated under static

dw dt mg∕min

Ехо 1 mcal/sec 400 Oxidation of powdered Sb under static air atmosphere at 5°C/min Temperature ^OC FIGURE (6.4.1) 450 500 550 600

 $\frac{dH}{dt}$ mcal/sec








dw dt mg∕min









mcal/sec

TABLE (6.2.1)

Since deviation of the experimental weight loss from the theoretical values, varies with the variation of temperature, therefore the \propto max values for each experiment were taken, considering the full weight loss at $\propto =1$.

Sample Form	Sample Weight mg	Heating Rate ^O C/min	Weight Lo ss %	∝ _{max}
Single				
Crystal	7.7	10	126	0.75
tt	7.41	5	11.8	0,684
n	7.47	2.5	115	0.642
n	8.13	1.25	11.1	0.638
n	7.04	1.25	10.9	0.618
n	7.65	0.62	10,6	0.58
Ground	7.00	10	11.5	0.66
17	7.11	5	11-2.5	0.62

CHAPTER SEVEN

KINETICS

7.1 THEORETICAL ASPECTS OF THERMAL ANALYSIS

The term decomposition is applied to a chemical process when there is a breakdown of one or more constituents of the reactants into simpler molecules. Thermal decomposition is intended to imply that such a change is brought about by a temperature increase. Thermal decomposition of solids usually results in a solid residue of different chemical identity from that of the reactant, and it can be represented by :

$$A(s) \xrightarrow{B}(s) + C(g)$$

where A is the reactant, B and C are the products and (s) and (g) specify the solid and gaseous phases respectively. The solid-solid interactions could be represented by :

 $A(s) + D(s) \longrightarrow products$

where the products may be solid, liquid and/or gaseous.

Two alternative methods have been used in kinetic and mechanism investigation of thermal decomposition and other reactions of solids : in the first, \propto - time measurements are made while the sample is maintained at constant temperature, while in the second the sample is subjected to a controlled rising temperature. Measurements using both techniques have been widely utilised in the determination of kinetic characteristics and parameters.

The term \propto in the reactions of solids represents the fraction of material reacted, or the extent of the reaction. In isothermal methods the weight or pressure change with time is represented by \propto and in dynamic methods \propto at any temperature is calculated by dividing the partial peak area (of DSC, DTA and DTG curves) at that temperature by the total area under the curve.

The first stage of an experimental study of thermal decomposition of solids by the isothermal method is usually the determination of a curve representing the plot of fraction decomposed as a function of time. On Figure (7.1.1) a plot of \propto versus t is shown. A is an initial reaction associated with the decomposition of impurities or unstable superficial material, B is the

induction period, which is usually regarded as a stage where the nuclei of the product(s) are being formed and is usually terminated by the development of stable nuclei. In general, crushing or grinding whole crystals and with some substances pre-irradiation and pre-heating [15,19,12] shortens the induction period, it is usually completed at a low value of \propto . C is and the acceleratory period of growth of nuclei formed during induction period, perhaps accompanied by further nucleation. For some substances the acceleratory period is of relatively short duration and it can even be altered by storage or pre-heating of the sample. The acceleratory period continues up to the maximum rate of reaction D or inflection point. Thereafter the continued expansion of nuclei is no longer possible due to the overlap of nuclei and consumption of reactant, and this leads to deceleratory or decay period E, which is continued until completion of reaction F. One or more of these features (except D) may be absent or negligible, variation in their relative importance, results in the appearance of a wide variety of different types of kinetic behaviour, [83,84].

After determination of a series of \propto - time values the kinetic studies are usually carried out, through the comparison of these data with the theoretical functions, derived from various assumed

models for products, phase nucleation and growth in solids. The problem could be regarded as the identification of the functional relationship between \propto and time, f (\propto) = kt where k is the rate coefficient. The most commonly used expressions, summarised in Table (7.1.1) are given in a publication by Sharp et al.[85]

To test the obedience of the isothermal kinetic data obtained to the theoretical equations the following general approaches have been made :

- (1) Testing the linearity of a plot of $f(\alpha)$ against time, the slope is the rate coefficient for the overall reaction.
- (2) Comparison of shapes of \propto reduced time plots with those calculated for various functions. This method has been suggested by Sharp et al and tabulated data for each function is available.
- (3) Comparison of measured $d \propto /dt$ reduced time plots which can enhance the ease of discrimination between alternative kinetic obedience [86].
- (4) Comparison of measured $d \propto /dt \propto$ values with master curves.

When the reduced time method is used the equation can be expressed in the form of $f(\propto) = A(t/t_{0.5})$ where $t_{0.5}$ is the time for 50% reaction and A is a calculable constant depending on the form of $f(\propto)$. A particular advantage of the technique is that if isothermal measurements have been determined at several different temperatures, all data can be collected as a single plot, by the use of an appropriate scaling factor, for comparison with the theoretical curves. A disadvantage in the reduced time method of analysis, is

that it involves comparison of curves [83,87].

Another method of identification of the rate equation, which has been widely used in the isothermal decomposition of solids is through the plot of the form

 $\ln \left[-\ln(1 - \alpha)\right] = n \ln t + constant$

Where different values of n correspond to the different theoretical expressions given in Table (7.1.1). Values of n for the diffusion limited equation are usually between 0.53 and 0.58, for the contracting area and volume relations are 1.08 and 1.04 respectively, for the Avrami-Erofeev equation are 2.00, 3.00 etc.[88] This method has been criticised from the point of view that the lnln plot is not very sensitive.

Tang and Chauderi [89] suggested an alternative method for the discrimination between $f(\propto)$ functions by plotting $[-ln(l-\propto)]^{1/m}$ versus time, showing that the value of m differs significantly between different groups of $f(\propto)$.

Doulah [90,91] in a method similar in principle to the method of Hancock and Sharp [88] suggested the identification of a kinetic expression through the plot of the form :

$$\ln\ln\left(\frac{1}{1-\alpha}\right) = \beta \ln t - \beta \ln y$$

where the value of β has mechanistic significance. This method is also used for the kinetic evaluation of data obtained by the dynamic method, and it will be discussed in more detail in the following section.

After the determination of which of the available rate expressions provides the most acceptable fit to the experimental temperatures, the Arrhenius equation is used to establish the activation energy.

$$d \propto /dt = K f(\propto)$$

 $K = A e^{-E/RT}$
 $lnk = lnA - \frac{E}{RT}$

where E = activation energy

- A = frequency factor
- K = universal gas constant
- T = absolute temperature

In the kinetic study of solid-solid interactions, the experimental methods used for the investigation of the thermal decomposition of solids, are equally useful. However, those methods which rely on the measurement of the weight or pressure change cannot be applied to those solid-solid reactions where no gas is evolved such as :

$$2 B + 3 Pb0 \longrightarrow B0 + 3 Pb$$

Isothermal and non-isothermal measurement of enthalpy changes (DSC, DTA) offer attractive experimental approaches for the kinetic investigation of reactions of the type mentioned above.

However there are a number of experimental difficulties associated with the kinetic analysis of enthalpy change methods which have been the subject of a detailed investigation by Goodfield [67].

Exothermic reactions particularly pyrochemical mixtures normally exhibit multiple peak patterns which complicates extraction of useful data.

There are also difficulties associated with zeroline (base line) where its linearity is a basic requirement in the kinetic analysis of DSC and DTG curves. Although at a low and limited temperature range it is possible to obtain an acceptable linear base line, however, high differences between the heat capacities of the reactants and the products can introduce non-linearity on either side of the reaction When, on the reaction of two solids, gaseous peak. products are formed the methods of weight loss and pressure change measurements can be used to study the reaction kinetics, provided that the evolution of gas and the solid-solid reaction is strictly a single step process.

Information concerning the mechanism of solid-solid reaction has been obtained by many diverse experimental approaches mainly depending on the system under investigation.

Spice and Stavely followed the progress of the reaction of iron with barium peroxide by magnetic

measurements [3]. In some solid-solid reactions the dissolution of one component from the reactant product mixture, coupled with the chemical analysis at various experimental conditions has been used to obtain kinetic information.

Herbert and Smoak [92] in the kinetic study of the magnesium oxide and chromium oxide reaction

$$Mg0 + Cr_2 O_3 \longrightarrow MgCr_2 O_4$$

extracted and measured chemically the unreacted MgO from the reactant and product mixture by dissolving it in dilute HC1.

Dynamic methods of studying kinetics of decomposition and reactions of solids involves measuring the reaction rates under conditions of a continuous temperature change, theoretically making it possible to determine complete kinetic behaviour by a single experiment.

 $\frac{d\alpha}{dt} = A f(\alpha) \exp(-E/RT)$

Although close agreement between values of E, determined by isothermal and non-isothermal methods, has been reported for a number of decompositions [93], in

other systems agreement has been less than satisfactory. Zsako and Arz [94] found that the activation energies of $CaCO_3$, derived by means of different calculation techniques from dynamic thermogravimetry, are much more scattered than those obtained from isothermal studies.

In the literature there has been much discussion about the advantages, disadvantages and limitations of the non-isothermal approach to the kinetic studies of the solids. It is obvious that the problems associated with the identification of a rate equation for \propto - time data, through a curve fitting method, are even greater when temperature is an additional variable.

When thermal analysis techniques are used the problem which can arise is the use of programmed heating, which necessitates heat flow. The material, in direct contact with heat source is at higher temperature than that within the reactant mass, and such differences are enhanced during an endothermic process. The reverse can also be the case when highly exothermic pyrochemical reactions are involved. One way of reducing temperature gradient, as suggested by Goodfield [67] is to use compositions of as low a heat output as possible and to programme at as low a heating rate as possible.

Since the introduction of non-isothermal methods especially with the development of differential thermoanalytical techniques (DSC, DTA and DTG), numerous methods for kinetic analysis of data obtained on solid state reactions, have been suggested. Originally proposed by Skramovsky, the first use of DTA in the study of reaction kinetics was made by Murray and White [97].

They studied the kinetics of dehydration of clays first isothermally which were shown to obey a first order law, and generated a theoretical DTA curve which was found to be similar to the DTA curve obtained by the dynamic method. The authors also found that the heating rate has a marked effect on the peak maximum temperature obtained, it being displaced to higher temperature as the heating rate is increased.

Kissinger [98] extended the work of Murray and White [97] and developed an equation which related the variations of peak maximum temperature with the rate of heating.

$$d(\ln \Theta/T_m^2) / d(1/T_m) = \frac{E}{R}$$

where Θ = heating rate

T_ = peak maximum temperature

Thus, by measuring the peak maximum temperature at a number of different heating rates and plotting $\ln \theta/T^2_{m}$ versus $1/T_{m}$ a straight line of slope $\frac{E}{P}$ is obtained.

Friedman [99] suggested a method for kinetic analysis of thermal degradation of plastics, from the data obtained using the dynamic method of TGA. In this method the rate of the reaction at various temperatures has been used to calculate the activation energy without previous knowledge of the form of $f(\cong)$. Considering the general kinetic equation

 $d \propto /dt$ = A . e -E/RT f(\propto)

in logarithm form

 $\ln d \propto /dt = \ln A - E/RT + \ln f(\propto)$ (a)

If, from the DTG curves at various heating rates, for fixed values of \propto the values of d \propto /dt and T were determined, the plot of $\ln(d \propto /dt)$ against reciprocal of the temperature results in a straight line which in accordance with equation (a), its slope giving the activation energy. Friedman selected a dozen values of \propto ranging from 0.675 to 0.950 and found that the activation energy varies from 50 to 72 kcal/mol with mean value of 57.7 kcal/mol.

Friedman's method allowed the determination of activation energy, however it does not permit the discrimination of the kinetic law obeyed by the reaction.

Credo and Ortega [100] in a recent work proposed a method which overcame this drawback. They took into account that in accordance with equation (a) \propto can be calculated as a function of $\ln d \propto /dt + E/RT - \ln A$. They assumed for $f(\propto)$ the theoretical functions used in the literature for describing kinetics of solid state reactions Table (7.1.1). For the experimetal values, once the value of E is found by the Friedman method, the plot of experimental values of \propto against $\ln d \propto /dt + E/RT$ must be superimposed upon the master curve corresponding to the actual kinetic law of the reaction by a lateral shift. The length of this lateral shift being equal to -lnA.

Ozawa [101] proposed a method for kinetic analysis of data obtained for the decomposition of polymethylmethacrylate. In this method first the activation energy was estimated by utilising the linear relation between the logarithm of the heating rate and the reciprocal absolute temperature at a given conversion or at peak of the DTA curve. Then, in order to find the rate equation and the pre-exponential

factor, the curve between reduced time of the conversion and reduced rate of the conversion was drawn and compared with the corresponding theoretical curve by curve-fitting.

Tang and Chaudri [102] provide a critical and comprehensive review of the methods for the analysis of isothermal and dynamic kinetic data from solid state reactions. They suggested that the reliability of non-isothermal results can be improved if the isothermal $f(\propto)$ - time relation is determined independently.

Rogers and Morris [106] suggested a method of estimating activation energy using differential scanning calorimetry. Data extracted from the DSC curves are in the form of distances between reaction curve and the baseline at the related absolute temperature. The distance measured is proportional to the rate of heat evolution or absorption and is therefore proportional to the rate constant.

The activation energy is calculated from the equation :

$$- E = R \frac{\ln d_1 - \ln d_2}{1/T_2 - 1/T_1} = \frac{4.58\ln(d_1/d_2)}{1/T_1 - 1/T_2}$$

Where d_1 and d_1 are any two distances from the base line

at the related absolute temperatures T_1 and T_2 . Neither sample weight nor heat of reaction needs to be known to calculate the activation energy.

Doulah [90,91] suggested a method which is based on the expansion of the Erofeev [104] equation of the probability of an elementary event to describe the rate of solid-state reaction.

$$d \propto / dt = P(1 - \alpha)$$

Where P is the mean probability for reaction of an individual molecule. For a decomposition process P is function of temperature and time and is expressed by : $P = (\beta / \gamma) (t / \gamma)^{\beta - 1}$

the rate of decomposition :

$$d \propto /dt = (\beta / \gamma) (t / \gamma)^{\beta - 1} (1 - \alpha)$$

In which β and χ are functions of temperature, for a given system β and χ vary only with temperature.

Integration of the equation above leads to :

$$\propto = 1 - \exp\left(-\left(\frac{t}{y}\right)^{\beta}\right)$$

the double ln of this equation results :

$$\ln\ln\left[1/(1-\infty)\right] = \beta \ln t - \beta \ln y$$

 β and χ being obtained from the plot of $\ln\ln(\frac{1}{1-\alpha})$ versus lnt. At $\alpha = 0.63$ the t = χ which results $d\alpha/dt$ = $(\frac{\beta}{\chi})(1-\alpha)$.

Therefore $(\frac{\beta}{\chi})$ becomes a specific rate constant at a first order decay law.

Considering the Arrhenius law

$$\ln \frac{\beta}{\gamma} = E/RT 0.63 + \ln k.$$

where $T_{0.63}$ is the Kelvin temperature at $\propto = 0.63$

 $T_{0.63}$ is the temperature of decomposition under isothermal conditions. For the decomposition carried out under dynamic condition $T_{0.63}$ will vary with the variation of heating rate, the value of the β having mechanistic significance.

7.2 <u>ISOTHERMAL DECOMPOSITION OF POTASSIUM</u> <u>PERMANGANATE</u>

Isothermal studies on single crystals of KMnO_4 and with Analar samples as received from the manufacturer (BDH) were carried out under static air atmosphere at the temperature range 215 - 245°C. The weight loss obtained at this temperature range agree well with the results of others.

On Figure (7.2.1) a plot of extent of the reaction and rate of the reaction v time for a recrystallized sample at 237 °C is shown. A similar result was obtained with Analar sample. When crystals were ground by rubbing in an agate mortar it resulted in a shorter induction period, Fig (7.2.2). This is due to the formation of potential nuclei, resulting from the lateral heat at the grinding process.

The acceleration stage with most samples was found to be more complex and on the plot of rate of the reaction $v \propto at$ the range of \propto , 0.1 to 0.35 deviations from the straight acceleration line were observed (15). On the corresponding isothermal DTG curve, which was obtained simultaneously with TG measurements, the complex decomposition behaviour at the acceleration stage was accompanied with noisy signals of the recorder pen, Figure (7.2.3). This behaviour was more frequent with the Analar samples.

Hill and co-workers [26] found that the complex behaviour of the decomposition of $KMnO_4$ at the acceleratory stage is related to the internal structure

of the crystals and their purity, which could be controlled by the method of the preparation of the crystals.

They introduced carbon dioxide atmosphere, thus suppressing the decomposition of aqueous solution by maintaining slightly acid conditions. The resulting crystals were left in the dark in the mother liquor for 40 hours at 20 °C before filtering off and drying the sample. Crystals prepared in this way showed a straight acceleration line on their decomposition. In order to determine the time taken for the sample to attain furnace temperature (zero time), Curie point effect of the ferro-magnetic materials was used.

ferro-magnetic substances with the The transition temperature close to the temperature range of interest (215 - 245 °C) were Alumel (Ni 95%, Mn 2%, Al 2%) at 163 °C and Nickel at 345 °C. At the transition temperature they lose their ferro-magnetism and become 2mm of the wire of each merely para-magnetic. substance (weighing between 2 to 3mg each) were embedded in the powdered KMnOL in an aluminium sample pan, and was covered by aluminium lid. After the suppression of the whole weight of the sample pan and its contents, the magnet was set around the furnace and the total magnetic effective weight was expanded to the full scale

deflection of the recorder pen.

The upper limit temperature was set to $163^{\circ}C$ and the sample was heated at a rate of $160^{\circ}C/min$, this heating rate was usually used on actual experiments of isothermal decomposition of KMnO₄.

The time was recorded from the moment of temperature reaching upper limit to the Curie point (extrapolated point of total loss of ferro-magnetism), Figure (7.2.4).

Similar experiments were carried out with Nickel being embedded in the product of decomposition.

The time taken from the isothermal point to the Curie point could be considered as the time taken for the sample to attain furnace temperature. At the end of this period of time in the thermal decomposition of KMnO_L the recording of reaction v time was began.

In most solid state reactions, including thermal decomposition of $KMnO_4$, the exact initiation point of acceleration stage in reaction - time curves is difficult to find since it is obscured by the presence of an induction period.

In the present work the times t were corrected for an induction period by considering acceleratory decomposition at above $\propto = 0.05$ as shown by Phillips and Taylor [16].

The extent of the acceleration stage depended on the temperature of the reaction. On Figure (7.2.5) the tan θ (the slope of \propto - time curve at various \propto values, which is proportional to the rate of the reaction) is plotted against \propto , it can be seen that at 218°C a straight line resulted at between 0.05 and 0.2, whereas on Figure (7.2.6) at 231°C the acceleratory decomposition is continued up to $\propto = 0.5$.

In Table (7.2.1) the results corresponding to the thermal decomposition of ground KMnO₄ at the temperature range of 215 to 245°C are given. The data are treated in accordance with the method suggested by Hancock and Sharp [88] and Doulah [90]. The value of the 'n' obtained as shown on Table (7.2.2) is between 1.745 and 1.904, relating to the Avrami-Erofeev equation:

 $kt = (-\ln(1 - \alpha))^{\frac{1}{2}}$

The variation of the rate coefficient k with temperature is plotted on Figure (7.2.7) by the least square method, the activation energy obtained at \propto range between 0.1

and 0.9 is 34.37 kcal/mole. The Avrami-Erofeev equation indicated by the above method, was applied directly to obtain rate coefficients for acceleratory and deceleratory stages. The extent of the acceleratory stage was found by the inspection of the \propto -time and d \propto /dt v \propto plots, and the value of the rate coefficient and E were calculated by the least square method. The results are shown on Table (7.2.3). It can be seen that the rate coefficient increases with the increase of temperature, on Figure (7.2.8) the logarithm the rate coefficient for acceleratory stage is of plotted against $\frac{1}{T}$. The value of E found, in accordance with Arrhenius equation, was 34.62 and 37.75 kcal/mole for acceleratory and deceleratory stages respectively. The results could be compared with those found by Prout and Tompkins [12]. They calculated the rate costant, in accordance with the equation:

 $kt = \ln \left(\frac{\infty}{1-\infty}\right)$

and values of E for ground $KMn0_4$ were found to be 33.1 and 34.5 kcal/mole for acceleratory and deceleratory stages respectively.

7.3 NON-ISOTHERMAL DECOMPOSITION OF KMn0 4 DYNAMIC METHOD

Heating rates from 0.62 to 20 °C/min were used in both differential scanning calorimetry and

thermogravimetry analysis, in air and inert atmosphere. Powdered KMnO₄ was used in order to avoid the loss of the sample from the container, due to the disintegration at the early stage of decomposition, under programmed heating conditions. With the sample weight 5 to 15mg and fast recording chart speed it was possible to obtain broad and large DSC peaks, suitable for the kinetic analysis, Figure (7.3.1). The partial peak areas were measured at regular temperature intervals (time) across the peak, this enabled measurement of the extent of the reaction at any desired temperature. The rate of the reaction was determined from the height of the peak at corresponding temperature.

Three methods were used to calculate the activation energy. The first is the Rogers and Morris [103] method which suggests the use of a single DSC or DTG curve to obtain the activation energy. Second is the Kissinger [98] method in which a number of DSC and DTG curves, obtained at various heating rates, are involved, and the activation energy is correlated to the variation of reaction temperature with the rate of heating. Ozawa [101] has suggested a similar method which utilises the following approximate relation, for a given conversion, to calculate the activation energy, log Θ + 0.4567 E/RT = constant. Plotting log against the reciprocal absolute temperature for a given

value, the activation energy can be estimated.

The third is the method suggested by Friedman [99], this also involves a number of DSC and DTG curves at various heating rates with the difference that variation of rate of the reaction (at any chosen values) with the rate of heating, is used to obtain activation energy.

In Tables (7.3.1 - 7) the data obtained from the analysis of DSC curves are presented. It can be seen that the vlue of E obtained from each heating rate differs substantially and they scatter at the range of 12.4 to 43.7 kcal/mole. From the thermogravimetric data, Table (7.3.7 - 14) the activation energies, calculated at various heating rates, varied between 21.05 and 66.05 kcal/mole.

The value of E obtained in accordance with the Kissinger method Table (7.3.8) from the DSC results, was 33.75 kcal/mole, this is in close agreement with the value of E, calculated from the thermogravimetric data 34.5 kcal/mole. Similar results were obtained from application of the Ozawa [101] method. One possible reason for such a close agreement between DSC and DTG results is that the Kissinger and Ozawa methods of evaluation of E, are based on the variation of reaction

temperature with the rate of heating, and this should depend very little on the nature of technique used.

Using Friedman's method, the activation energies from both DSC and DTG results were calculated at different stages of the reaction. It can be seen from the Tables (7.3.15,16) that, using the thermogravimetry data, the closest value of E to those obtained from isothermal methods are E = 30.27, 35.3 and 36.97, kcal/mole at the \checkmark values of 0.7,0.5 and 0.3 respectively. The activation energies obtained from the DSC data were found to be much lower.

In order to test the obedience of the kinetic law on the basis of non-isothermal data, a method suggested by Credo and Ortega [100] was used. In this method the value of E is used to plot the \propto against lnd /dt + E/RT, the resulting curve is compared with the theoretical in order to distinguish the corresponding rate equation. On Figure (7.3.2) the theoretical master curve, based on the $f(\propto)$ function commonly used in literature, Table (7.1.1) are shown. The plot of experimental values is compared with Avrami-Erofeev and Prout and Tompkins equations on Figure (7.3.3).

The review of the results obtained from the isothermal and non-isothermal methods show that :

(a) The reliability of reaction constants, based on non-isothermal single experimental data could be tested by determining the influence of the heating rate on kinetic characteristics, and comparing the results with those obtained from isothermal data,

(b) More accurate reaction constants can be obtained from these non-isothermal methods which involve a number of DSC or DTG experiments relating to various heating rates.

From this group, when the methods based on variation of the reaction temperature with the heating rate were used, it was found that the reaction constants obtained from DTG and DSC experiments are always in close agreement. This is thought to be due to the fact that, the influence of the rate of heating is independent of the technique employed. Whether a thermogravimetry or differential scanning calorimetry system is used, the higher heating rate causes the reaction to take place at higher temperature.

(c) When the non-isothermal method, based on variation of rate of the reaction with the heating rate is used, the results show that the thermogravimetry data are more accurate than the DSC results.

Finally it should be added that, in general, when dynamic methods involving different heating rates are used, the advantage of the non-isothermal method which is the utilisation of a single experiment, is reduced. Furthermore the analysis of the results of each heating rate, which involves the partial peak area measurements at regular temperature intervals, is a time-demanding process. One might just as well perform a series of isothermal measurements, for which the subsequent analysis will be both more accurate and much simpler.





Time (minutes)
















FIGURE (7.2.7)



FIGURE (7.2.8)



mcal/sec d|H





Master curves for the kinetic analysis of DTG Curves in accordance with Criado and Ortega method (100). The symbols of Sharp et al (85) have been used for the naming of $f(\alpha)$ functions.



TABLE (7.1.1)

Type of reaction	$f(\alpha)$
1 - Acceleratory - time curves P1 power law E1 exponential law	$\frac{1/n}{a}$ ln \propto
2 - Sigmoid - time curves A2 Avrami - Erofeev A3 Avrami - Erofeev A4 Avrami - Erofeev B1 Prout - Tompkins	$ \begin{pmatrix} -\ln(1-\alpha) \end{pmatrix}^{\frac{1}{2}} \\ \begin{pmatrix} -\ln(1-\alpha) \end{pmatrix}^{\frac{1}{3}} \\ \begin{pmatrix} -\ln(1-\alpha) \end{pmatrix}^{\frac{1}{4}} \\ \ln\left(\frac{\alpha}{1-\alpha}\right) \end{pmatrix} $
 3 - Deceleratory - time curves 3.1 - Based on geometrical models R2 Contracting area R3 Contracting volume 	$1 - (1 - \alpha)^{\frac{1}{2}}$ 1 - (1 - \alpha)^{\frac{1}{3}}
 3.2 - Based on diffusion mechanisms D1 One-dimensional diffusion D2 Two-dimensional diffusion D3 Three-dimensional diffusion D4 Ginstling - Brounshtien 	$\begin{array}{c} 2 \\ \propto \\ (1 - \alpha) \ln (1 - \alpha) + \alpha \\ \left(1 - (1 - \alpha)^{\frac{1}{3}}\right)^{2} \\ (1 - 2\alpha/3) - (1 - \alpha)^{\frac{2}{3}} \end{array}$
3.3 - Based on order of reaction F1 first order F2 second order F3 third order	$-\ln (1 - \alpha)$ $\frac{1}{(1 - \alpha)}_{2}$ $\left(\frac{1}{(1 - \alpha)}\right)$

TABLE (7.2.1)

t ₂₁₈	^t 225	t ₂₃₁	8	^t 237	^t 242	$(-\ln(1-\alpha)^{\frac{1}{2}})$
10.8	8.2	4.8	0.05	3.1	1.6	0.2265
18.36	14.2	9.4	0.1	6.1	3.63	0.3246
25.6	17.9	12.1	0.15	8.2	5.1	0.4031
31.6	21.6	14.2	0.2	9.95	6.3	0.4729
36.6	25.4	16.1	0.25	11.5	7.5	0.5364
42	29.3	18.2	0.3	13.12	8.45	0.5972
46.6	32.4	20.1	0.35	14.65	9.5	0.6563
52	36.1	21.5	0.4	15.8	10.5	0.7147
57.2	39.4	20.0	0.45	16.8	11.5	0.7732
62.7	42.8	25.3	0.5	18.08	12.4	0.8326
68.2	46	27.3	0.55	19	13.2	0.8936
73.6	48.8	29.7	0.6	20	14	0.9573
79.64	51.8	32.6	0.65	21.5	14.6	1.0246
83.7	54.5	35.8	0.7	22.82	15.45	1.0973
92.7	57.6	39.8	0.75	25	16.2	1.177
98.84	60.8	45.2	0.8	27.45	18.75	1.2686
	64.2	52.8	0.85	31.1	19.7	1.3774
	68		0.9	34	19.75	1.5174

The time values measured at the temperature range of 218 to 242° C.

TABLE (7.2.2)

Т	n	8	$\frac{n}{y}$	$\ln \frac{n}{\delta}$
4.91 4.98 504 510	1.745 1.899 1.813 1.904	70.095 48.75 31.054 21.56	0.249 0.0389 0.0584 0.0883	-3.393 -3.245 -2.84 -2.427
515	1.806	13.95	0.129	-2.045

The values of n calculated in accordance with Hancock and Sharp method and in accordance with Doulah's method.

TABLE (7.2.3)

Acceleration and Deceleration constants, in equation $(-\ln(1-\infty))^2 = kt$ measured at various temperatures.

Т	^k 1	lnk ₁	k ₂	lnk ₂
491	0.085	-4.309	0.0131	-4.33
498	0.1090	-3.927	0.0209	-3.867
504	0.1615	-3.398	0.0218	-3.825
510	0.210	-3.037	0.0388	-3.249
515	0.280	-2.682	0.0968	-2.335

 ${\bf k}_1$ and ${\bf k}_2$ represent the rate coefficients for acceleratory and

deceleratory stages respectively.

TABLE (7.3.1)

Data obtained from the DSC curve on the thermal decomposition of ground $KMnO_4$ at the heating rate $0.62^{\circ}C/min$ (d is the distance from the base line, which is proportional to the rate of the reaction)

0.01 774.2 4.5 0.0097 -4.636 496 0.0245 967.7 7.5 0.0161 -4.125 498 0.0288 1161.3 10.5 0.0226 -3.788 500 0.04201 1354.8 14 0.0302 -3.501 502 0.0646 1548.4 19 0.041 -3.195 504 0.0765 1742.0 24 0.0517 -2.962 506 0.0954 1935.5 31 0.0668 -2.706 508 0.1425 2129 40 0.0862 -2.451 510 0.1814 2322.6 53.5 0.115 -2.160 512 0.2611 2516.1 74 0.159 -1.836 514 0.345 2709.7 102 0.219 -1.515 516 0.451 2903.2 128.5 0.277 -1.284 518 0.586 3096.8 140 0.302 -1.198 520 0.726 3290.3 133 0.287 -1.249 522	\propto	t(s)	d (mm)	d∝/dt	lnd∝/dt	T(K)
0.0245 967.7 7.5 0.0161 -4.125 498 0.0288 1161.3 10.5 0.0226 -3.788 500 0.04201 1354.8 14 0.0302 -3.501 502 0.0646 1548.4 19 0.041 -3.195 504 0.0765 1742.0 24 0.0517 -2.962 506 0.0954 1935.5 31 0.0668 -2.706 508 0.1425 2129 40 0.0862 -2.451 510 0.1814 2322.6 53.5 0.115 -2.160 512 0.2611 2516.1 74 0.159 -1.836 514 0.345 2709.7 102 0.219 -1.515 516 0.451 2903.2 128.5 0.277 -1.284 518 0.586 3096.8 140 0.302 -1.198 520 0.726 3290.3 133 0.287 -1.249 522	0.01	774.2	4.5	0.0097	-4.636	496
0.02881161.310.50.0226-3.7885000.042011354.8140.0302-3.5015020.06461548.4190.041-3.1955040.07651742.0240.0517-2.9625060.09541935.5310.0668-2.7065080.14252129400.0862-2.4515100.18142322.653.50.115-2.1605120.26112516.1740.159-1.8365140.3452709.71020.219-1.5155160.4512903.2128.50.277-1.2845180.5863096.81400.302-1.1985200.7263290.31330.287-1.249522	0.0245	967.7	7.5	0.0161	-4.125	498
0.042011354.8140.0302-3.5015020.06461548.4190.041-3.1955040.07651742.0240.0517-2.9625060.09541935.5310.0668-2.7065080.14252129400.0862-2.4515100.18142322.653.50.115-2.1605120.26112516.1740.159-1.8365140.3452709.71020.219-1.5155160.4512903.2128.50.277-1.2845180.5863096.81400.302-1.1985200.7263290.31330.287-1.249522	0.0288	1161.3	10.5	0.0226	-3.788	500
0.06461548.4190.041-3.1955040.07651742.0240.0517-2.9625060.09541935.5310.0668-2.7065080.14252129400.0862-2.4515100.18142322.653.50.115-2.1605120.26112516.1740.159-1.8365140.3452709.71020.219-1.5155160.4512903.2128.50.277-1.2845180.5863096.81400.302-1.1985200.7263290.31330.287-1.249522	0.04201	1354.8	14	0.0302	-3.501	502
0.07651742.0240.0517-2.9625060.09541935.5310.0668-2.7065080.14252129400.0862-2.4515100.18142322.653.50.115-2.1605120.26112516.1740.159-1.8365140.3452709.71020.219-1.5155160.4512903.2128.50.277-1.2845180.5863096.81400.302-1.1985200.7263290.31330.287-1.249522	0.0646	1548.4	19	0.041	-3.195	504
0.09541935.5310.0668-2.7065080.14252129400.0862-2.4515100.18142322.653.50.115-2.1605120.26112516.1740.159-1.8365140.3452709.71020.219-1.5155160.4512903.2128.50.277-1.2845180.5863096.81400.302-1.1985200.7263290.31330.287-1.249522	0.0765	1742.0	24	0.0517	-2.962	506
0.14252129400.0862-2.4515100.18142322.653.50.115-2.1605120.26112516.1740.159-1.8365140.3452709.71020.219-1.5155160.4512903.2128.50.277-1.2845180.5863096.81400.302-1.1985200.7263290.31330.287-1.249522	0.0954	1935.5	31	0.0668	-2.706	508
0.18142322.653.50.115-2.1605120.26112516.1740.159-1.8365140.3452709.71020.219-1.5155160.4512903.2128.50.277-1.2845180.5863096.81400.302-1.1985200.7263290.31330.287-1.249522	0.1425	2129	40	0.0862	-2.451	510
0.26112516.1740.159-1.8365140.3452709.71020.219-1.5155160.4512903.2128.50.277-1.2845180.5863096.81400.302-1.1985200.7263290.31330.287-1.249522	0.1814	2322.6	53.5	0.115	-2.160	512
0.3452709.71020.219-1.5155160.4512903.2128.50.277-1.2845180.5863096.81400.302-1.1985200.7263290.31330.287-1.249522	0.2611	2516.1	74	0.159	-1.836	514
0.451 2903.2 128.5 0.277 -1.284 518 0.586 3096.8 140 0.302 -1.198 520 0.726 3290.3 133 0.287 -1.249 522	0.345	2709.7	102	0.219	-1.515	516
0.586 3096.8 140 0.302 -1.198 520 0.726 3290.3 133 0.287 -1.249 522	0.451	2903.2	128.5	0.277	-1.284	518
0.726 3290.3 133 0.287 -1.249 522	0.586	3096.8	140	0.302	-1.198	520
	0.726	3290.3	133	0.287	-1.249	522
0.833 3483.9 111 0.239 -1.430 524	0.833	3483.9	111	0.239	-1.430	524
0.928 3677.4 68 0.147 -1.920 520	0.928	3677.4	68	0.147	-1.920	520
0.975 3870.9 25 0.054 -2.921 528	0.975	3870.9	25	0.054	-2.921	528

TABLE (7.3.2)

\propto	t(s)	d (mm)	d∝/dt	lnd∝/dť	́Т(К)
0.0442	900	32.7	0.0704	-2.6525	514
0.0644	996	45.8	0.0987	-2.3156	516
0.0825	1092	64.1	0.1381	-1.9794	518
0.116	1188	82.6	0.1780	-1.726	520
0.1508	1284	103	0.2219	-1.505	522
0.269	1380	154.2	0.3319	-1.103	524
0.35	1476	184.8	0.398	-0.926	526
0.447	1572	213.2	0.4595	-0.777	528
0.596	1668	227.8	0.4909	-0.7114	530
0,752	1764	221.0	0.4763	-0.7417	532
0.838	1860	195.9	0.4222	-0.862	534
0.94	1956	124.0	0.2672	-1.3	536
0.976	2052	67.2	0.1448	-1.932	538
	i			<u> </u>	

Data obtained on the thermal decomposition of $\rm KMn0_{4}$ from DSC Curve at 1.25 $^{\rm O}\rm C/min.$

TABLE (7.3.3)

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DSC results on thermal decomposition of KMn0_4 at 2.5 ^{\rm O}C/min
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×	d (mm)	d∝/dt	lnd∝⁄dt	т(к)	t(s)
0.035	18	0.076	-2.556	527.25	330
0.047	25.5	0.11	-2.208	528.5	360
0.064	37.5	0.162	-1.822	529.75	390
0.089	51.5	0.222	-1.505	531	420
0.127	66.5	0.286	-1.249	532.25	450
0.16	81	0.349	-1.052	533.5	480
0.210	99	0.426	-0.852	534.75	510
0.279	116	0.5	-0.693	536	540
0.344	134	0.577	-0.549	537.25	570
0.426	148	0.638	-0.449	538.5	600
0.510	157	0.676	-0.391	539.75	630
0.600	158	0.681	-0.381	541	660
0.777	153.5	0.661	-0.413	542.25	690
0.847	140.5	0.606	-0.502	543.5	720
0.900	117.5	0.506	-0.680	541.75	750
0.950	89.5	0.386	-0.95	546	780
0.975	56	0.241	-1.42	547.25	810

TABLE (7.3.4)

DSC results on thermal decomposition of $KMn0_{\mu}$ at $5^{\circ}C/min$

×	t (s)	d (mm)	d∝/dt	lnd∝/dt	т(К)
0.044	222	11.25	0.0969	-2.333	536.5
0.059	237	15.5	0.134	-2.013	537.75
0.079	252	22	0.189	-1.663	539
0.107	26 7	29.5	0.254	-1.369	540.25
0.138	282	36.5	0.315	-1.156	541.5
0.149	297	45	0.388	-0.947	542.75
0.224	312	54	0.465	-7.646	544
0.274	327	63.5	0.547	-0.602	545.25
0.342	342	74	0.638	-0.449	546.5
0.403	357	85	0.733	-0.311	547 .7 5
0.480	372	94.5	0.815	-0.205	549
0.564	387	103	0.888	-0.119	550.25
0.639	402	107	0.922	-0.081	551.5
0.715	417	106.8	0.9207	-0.0826	552.75
0.789	432	101.5	0.875	-0.134	554
0.865	447	91.5	0.789	-0.237	555.25
0.909	462	75.4	0.65	-0.431	556.5
0.938	477	57	0.491	-0.711	557.75
0.964	492	38	0.328	-1.116	559

TABLE (7.3.5)

X	T(K)	d (mm)	d∝⁄dt	lnd∝/dt	t(s)
0.0485	550	11	0.2371	-1.439	144
0.08425	552	18.2	0.392	-0.936	156
0.112	554	28.6	0.616	-0.4839	168
0.132	556	41.6	0.897	-0.109	180
0.211	558	56.1	1.209	0.189	192
0.311	550	77.0	1.659	0.506	204
0.433	562	86.8	1.8701	0.626	216
0.495	564	95	2.046	0.716	228
0.626	566	94.5	2.036	0.711	240
0.7196	568	85	1.831	-0.605	252
0.814	570	67	1.44	0.367	264
0.876	572	44.2	0.953	-0.0486	276
0.921	574	26.0	0.559	-0.58	288
1	1	1		I	

<u>TABLE (7.3.6)</u>

DSC results on thermal decomposition of $\rm KMn0_4$ at 20 $^{\circ}_{\rm C}/\rm min.$

X	Т(К)	d (mm)	d∝/dt	lnd∝/dt	t(s)
0.402	565	18.5	0.797	-0.226	63
0.05787	567	31	1.336	0.289	75
0.099	569	46.5	2.004	0.695	87
0.1388	571	64.5	2.78	1.022	99
0.195	573	84	3.62	1.286	111
0.265	575	102	4.396	1.480	123
0.346	577	116	5	1.609	135
0.442	579	126.5	5.45	1.696	147
0.527	581	127.7	5.504	1.70	159
0.645	583	118.5	5.108	1.631	171
0.726	585	101	4.35	1.47	183
0.795	587	81	3.391	1.250	195
0.874	589	60	2.586	0.950	207
0.899	591	45	1.94	0.6625	219
0.927	593	32.5	1.401	0.337	231
0.946	595	24.5	1.056	0.0543	243

<u>TABLE (7.3.7)</u>

Activation energies calculated from each single DSC and DTG experiment

Heating Rate ^O C/min	E(DSC) kcal/mole	E(DTG) kcal/mole	
20	12.4	66.65	
10	32.4	46.19	
5	18.58	30.2	
2.5	38.18	21.05	
1.25	43.7	28.4	
0.62	29.2	23.64	

<u>TABLE (7.3.8)</u>

Data are presented in accordance with Kissinger method, and the activation energies for two different techniques are calculated by least square method.

Heating Rate	DSC		D	TG
°C/min	т _т (к)	$\ln \frac{\Theta}{T_m}^2$	т _m (к)	$\ln \frac{\Theta}{T_m^2}$
20	580.6	-9.73	576.95	09.72
10	565	-10.371	562.05	-10.36
5	552.2	-11.018	548.15	-11.00
2.5	540.7	-11.669	536.85	-11.655
1.25	529.5	-12.32	527.15	-12.312
0.62	520	-12.986	522.75	-12.996
Activation Energy	32.4	kcal/mole	34.5 kca	l/mole

TABLE (7.3.9)

Thermogravimetry results on decomposition of KMnO_{μ} at 0.62°C/min . d is the distance from the base line which is proportional to the rate of the weight loss.

X	t(s)	d (mm)	d∝/dt	lnd∝⁄dt	т(к)
0.05	2661.3	3	0.006	-5.116	489.65
0.1	3648.4	8.9	0.0178	-4.028	499.85
0.2	4480.6	16.3	0.0326	-3.423	508.45
0.3	4964.5	25.2	0.0504	-2.987	513.45
0.4	5303.2	33	0.066	-2.718	516.95
0.5	5564.5	41.5	0.083	-2.489	519.65
0.6	5758.1	46.2	0.0924	-2.382	521.65
0.7	5951.6	46	0.092	-2.386	523.65
0.8	6145.2	41	0.082	-2.501	525.65
0.9	6387.1	29	0.058	-2.847	528.15
0.95	7441.9	19.5	0.039	-3.244	539.05

TABLE (7.3.10)

Thermogravimetry results on decomposition of $KMn0_4$ at $1.25^{\circ}C/min$

×	t(s)	d (mm)	d∝∕dt	lnd∝⁄dt	т(К)
0.05	708	9.8	0.0196	-3.932	499.9
0.1	988.8	21.5	0.043	-3.147	505.75
0.2	1320	41	0.082	-2.501	512.65
0.3	1512	55	0.110	-2.207	516.65
0.4	1670.4	65.5	0.1310	-2.033	519.95
0.5	1800	78.5	0.157	-1.852	522.65
0.6	1920	87	0.174	-1.748	525.15
0.7	20304	88	0.176	-1.737	527.45
0.8	2136	80.5	0.1611	-1.826	529.65
0.9	2263.2	5 7	0.114	-2.172	532.3
0.95	2409.6	32	0.064	-2.749	535.35

TABLE (7.3.10)

Thermogravimetry results on decomposition of $KMn0_4$ at 1.25°C/min

×	t(s)	d (mm)	d∝∕dt	lnd∝⁄dt	т(к)
0.05	708	9.8	0.0196	-3.932	499.9
0.1	988.8	21.5	0.043	-3.147	505.75
0.2	1320	41	0.082	-2.501	512.65
0.3	1512	55	0.110	-2.207	516.65
0.4	1670.4	65.5	0.1310	-2.033	519.95
0.5	1800	78.5	0.157	-1.852	522.65
0.6	1920	87	0.174	-1.748	525.15
0.7	20304	88	0.176	-1.737	527.45
0.8	2136	80.5	0.1611	-1.826	529.65
0.9	2263.2	57	0.114	-2.172	532.3
0.95	2409.6	32	0.064	-2.749	535.35

TABLE (7.3.11)

Thermogravimetry results on decomposition of $KMn0_{4}$ at 2.5 $^{\circ}C/min$

×	t(s)	d (mm)	d∝⁄dt	lnd∽⁄dt	T(K)
0.05	403.2	20.8	0.045	-3.10	510.95
0.1	552	44.1	0.095	-2.354	517.15
0.2	696	78.88	0.17	-1.778	523.15
0.3	799.2	106.7	0.23	-1.47	527.45
0.4	873.6	131.1	0.283	-1.264	530.55
0.5	936	156.6	0.338	-1.086	533.15
0.6	991.2	169.3	0.365	-1.008	535.45
0.7	1044	169.3	0.365	-1.008	537.65
0.8	1101.6	149.8	0.323	-1.130	540.05
0.9	1176	87.0	0.1875	-1.674	543.15
0.95	1264.8	19.7	0.0425	-3.158	546.85

TABLE (7.3.12)

Thermogravimetry results on decomposition of $KMn0_4$ at $5^{\circ}C/min$.

×	t(s)	d (mm)	d∽/dt	lnd∽⁄dt	Т(К)
0.05	194.4	19.95	0.086	-2.45	512.35
0.1	290.4	38.28	0.165	-1.802	520.35
0.2	360	71.9	0.31	-1.171	526.35
0.3	410.4	109.7	0.473	-0.749	530.35
0.4	442.8	147.3	0.635	-0.454	533.05
0.5	468	176.3	0.76	-0.274	535.15
0.6	492	192.6	0.83	-0.1863	537.15
0.7	516	194.2	0.837	-0.1779	539.15
0.8	541.2	170.5	0.735	-0.308	541.35
0.9	576	92.8	0.40	-0.916	544.15
0.95	662.4	6.96	0.3	-3.507	551.35

TABLE (7.3.13)

Thermogravimetry results on decomposition of $KMn0_4$ at $10^{\circ}C/min$

			inu jut	T(K)
98.1	16.24	0.14	-1.966	535.15
135.9	34.3	0.296	-1.217	541.8
177.6	66.8	0.576	-0.552	548.75
201.6	100.9	0.87	-0.1393	552.75
216.6	138	1.19	0.1739	555.25
237	171.7	1.49	0.3988	558.65
247.8	196	1.69	0.5247	560.45
252	208.9	1.801	0.5883	561.15
264	205.3	1.77	0.571	563.15
277.2	153	1.32	0.2776	565.35
	98.1 135.9 177.6 201.6 216.6 237 247.8 252 264 277.2	98.1 16.24 135.9 34.3 177.6 66.8 201.6 100.9 216.6 138 237 171.7 247.8 196 252 208.9 264 205.3 277.2 153	98.1 16.24 0.14 135.9 34.3 0.296 177.6 66.8 0.576 201.6 100.9 0.87 216.6 138 1.19 237 171.7 1.49 247.8 196 1.69 252 208.9 1.801 264 205.3 1.77 277.2 153 1.32	98.1 16.24 0.14 -1.966 135.9 34.3 0.296 -1.217 177.6 66.8 0.576 -0.552 201.6 100.9 0.87 -0.1393 216.6 138 1.19 0.1739 237 171.7 1.49 0.3988 247.8 196 1.69 0.5247 252 208.9 1.801 0.5883 264 205.3 1.77 0.571 277.2 153 1.32 0.2776

TABLE (7.3.14)

Thermogravimetry results on decomposition of $KMn0_4$ at 20 $^{\circ}C/min$

×	d (mm)	d∽/dt	lnd∽/dt	Т(К)	t(s)
0.05	7.19	0.155	-1.864	549.15	51
0.1	14.14	0.305	-1.187	556.35	72.6
0.2	29.9	0.645	-0.438	563.65	94.5
0.3	48.7	1.05	0.0488	567.3	105.45
0.4	68.4	1.475	0.388	569.75	112.8
0.5	85.8	1.85	0.6152	571.65	118.5
0.6	102	2.2	0.788	573.15	123.0
0.7	116	2.5	0.916	574.95	128.4
0.8	124	2.675	0.984	576.55	133.2
0.9	116	2.5025	0.917	578.55	139.2
0.95	89.3	1.925	0.655	580.65	145.5

<u>TABLE (7.3.15)</u>

Heating	0.3		0.	5	0.8	
Rate ^O C/min	т(к)	lnd $\frac{d \epsilon}{dt}$	т(к)	$\ln \frac{d\omega}{dt}$	Т(К)	$\ln \frac{d\alpha}{dt}$
20	576.04	1.561	580.54	1.704	587.08	1.232
10	559.8	0.3216	564.08	0.711	569.55	0.306
5	545.64	-0.542	549.18	0.159	554.18	-0.138
2.5	536.58	-0.626	539.6	-0.397	542.39	-0.423
1.25	524.75	-1.03	528.7	-0.754	533.116	-0.793
0.62	515.151	-1.654	518.73	-1.246	523.38	-1.404
Activation Energy	28.8 kcal/mole		27.8 k	cal/mole	23.2 kc	al/mole

DSC data in accordance with Friedman's method, activation energies are calculated at various of values.

TABLE (7.3.16)

Heating	0.3			0.5		.7
Rate ^O C/min	Т(К)	$\ln \frac{d x}{dt}$	т(к)	$\ln \frac{d\alpha}{dt}$	T(K)	$\ln \frac{d\alpha}{dt}$
20	567.3	0.0488	571.65	0.6152	574.95	0.916
10	522.75	-1.393	558.65	0.3988	561.15	0.588
5	530.35	-0.749	535.19	-0.274	539.15	-0.1778
2.5	527.45	-1.47	533.15	-1.086	537.65	-1.008
1.25	516.65	-2.207	522.65	-1.852	527.45	-1.737
0.62	513.45	-2.987	519,15	-2.849	523.65	-2.386
Activat- ion Energy	36.97	kcal/mole	35.3	kcal/mole	30.27	kcal/mole

CHAPTER EIGHT

CONCLUSIONS

Thermal analysis studies of the decomposition of potassium permanganate, at the temperature range of ambient to 720 O C, showed that the reactions take place at two different stages.

The first stage of decomposition occurs at $300^{\circ}C$ and the weight loss due to the release of oxygen, was found to differ, depending on the sample atmosphere and temperature. At any fixed rate of heating, the weight loss under static air, nitrogen and argon atmosphere differed as air > N_o > Ar.

The amount of weight loss at the first stage of decomposition seemed to have a reverse effect on the weight loss at the second stage of decomposition which takes place at 627° C.

DSC studies of the reactions showed that, the decomposition at first stage, under air and nitrogen atmosphere is an exothermic process. However the experiments under argon atmosphere revealed some unusual results. The decomposition reaction resulted in an endothermic peak at 300 °C.

On Figures (6.5.1,3,4,5) DSC traces corresponding to Sb/KMnO₄ reactions under argon atmosphere are shown. It can be seen that the endothermic decomposition of KMnO₄ formed a peak in the opposite direction to that of exothermic oxidation peaks of antimony.

These results raise a possibility that the exothermicity of the reaction is responsible for the higher weight loss at first stage of decomposition, causing further decomposition of products at this stage. This could also be the reason for the increase of weight loss with the temperature which has been subject of much discussion [17].

Considering the different mechanisms suggested for the decomposition reaction [12,22,15,20], the exact nature of the final products is still uncertain, with the exception that the oxygen is released. The decomposition at the second stage under any three different atmospheres mentioned above, resulted in an endothermic peak, and it was found that under air atmosphere reaction is partially reversible.

The gas-solid oxidation of powdered antimony in static air resulted in two exothermic peaks at 501°C and

552 °C. No ignition reaction was observed on the heating of antimony on its own in air, using similar experimental conditions to that of Sb/KMnO $_4$ compositions.

Thermogravimetry results showed a two stage weight gain on the oxidation of Sb at the temperature range of 370 to 610° C. The weight gain was 7% at first stage and 11% at the second stage.

Both thermogravimetry and differential scanning calorimetry results on the reactions of Sb/KMnO₄ mixtures, showed that the oxygen resulting from the first stage decomposition of KMnO₄ leaves the sample without reaction with antimony. Samples of Sb/KMnO₄ mixtures undergo ignition reaction only under oxygen containing atmosphere (510° C). In the layer-to-layer combustion of the mixtures, in sealed delay elements the oxygen required is supplied by the first stage of decomposition of KMnO₄.

Further evidence was obtained from the reaction of solid decomposition products of $KMnO_4$ with Sb. The $KMnO_4$ was decomposed in air at 300 °C, it was then mixed with Sb in various proportions. Such mixtures in compacted form were non-propagative. However in air atmosphere when viewed under a hot stage microscope, the

ignition reaction was observed $(510^{\circ}C)$ using suitable sample weight and heating rate. The results show conclusively the presence of both gas-solid and solid-solid phase reactions in the combustion of the Sb/KMn0₄ system, and that both reaction phases are essential for the propagation to take place.

The increase of density in all compositions resulted in a lower propagation rate which is due to the restriction caused by higher density on gas-solid phase reaction (24,25).

The closest agreement with the experimentally measured calorific values is provided by the chemical equation:

$2 \text{ Sb} + 2 \text{ KMn0}_{4} \longrightarrow \text{Sb}_{2}^{0}_{4} + \text{Mn}_{2}^{0}_{3} \times \text{K}_{2}^{0}_{2}$

When the heat outputs were calculated per mole of $KMn0_4$ it was found that with mixtures containing above 50% antimony the heat output remains constant.

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