Some thermal aspects of magnesium-potassium dichromate and related systems.

A Thesis presented by Anthony Gary Callegari to the Faculty of Science of the University of London in submission for the degree of Master of Science

Department of Chemical Physics
The University of Surrey, May 1969.
Only those who manage to pass that fire test emerge into the ultimate kingdom, which is of this earth and not in the hereafter, where all bounds are shattered and man transcends himself.

.... John Philip Lundin, Ph.D.
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Abstract.

This report is concerned with an investigation of magnesium-potassium dichromate, magnesium oxide-potassium dichromate and magnesium chromate (VI) systems at elevated temperatures using differential thermal analysis (DTA) and thermogravimetry (TG). Other methods used were chemical and X-ray diffraction powder analyses and determinations of the time-to-ignition of the magnesium-potassium dichromate system.

The magnesium-potassium dichromate system gave an exothermic reaction between 400° and 600°. A reaction mechanism is proposed in which magnesium chromate (V) is an intermediate. The Borchardt and Daniels theory of DTA was adapted to determine the activation energy for the reaction between 490° and 560° which was shown to be \(-87.86 \pm 0.35\) kcal/mole. The results suggested that the initial reaction step involved chemisorption of chromium (VI) oxide onto magnesium oxide to form magnesium chromate (VI). After subtraction of the heat of formation of the chromium-oxygen bond, the true activation was shown to be either \(+9.14 \pm 0.05\) kcal/mole or \(+14.14 \pm 0.05\) kcal/mole. The heat of activation for the system determined by time-to-ignition measurements was shown to be \(9.105\) kcal/mole (0.005 standard deviation) between 450° and 535°.
The magnesium-potassium dichromate system gave two endotherms (607°-620°, 620°-630°) on heating and three exotherms (615°-605°, 605°-585°, 585°-550°) on cooling probably associated with unit changes in the oxidation state of chromium:

\[
\text{Cr(VI)} \rightarrow \text{Cr(V)} \rightarrow \text{Cr(IV)} \rightarrow \text{Cr(III)}
\]

The exothermic reaction was limited by the formation of a coherent layer of magnesium chromite around each particle of magnesium.

The magnesium oxide-potassium dichromate system decomposed between 575° and 630° with the formation of magnesium chromite.

Magnesium chromate (VI) decomposed in two endothermic stages (607°-620°, 620°-677°) to form magnesium chromite.
1. INTRODUCTION.

1.1 Reason for undertaking the present work.

A recent study of the thermal decomposition of a large number of chromates and dichromates by Charsley and Redfern suggested that each series of compounds decomposed according to a common pattern. The methods which they used were mainly differential thermal analysis (DTA) and thermogravimetry (TG) together with chemical and infra-red analysis of the decomposition products.

It seemed desirable to extend this work to binary systems as there was little in the literature on the topic.

The first system chosen for study was that of a metal and potassium dichromate. Magnesium was selected as the metal because it was available reasonably pure and because of its frequent use in pyrotechnic compositions.

1.2 Thermal decomposition of chromates (VI) and polychromates (VI).

One of the first and most spectacular experiments carried out in the school laboratory is to heat crystals of ammonium dichromate in a shallow pan causing them to ignite and emit a
shower of sparks. The experiment is designed to demonstrate that the reaction is self-propagating once it has started.

However, the study of the thermal decomposition of chromates and polychromates has been scant and sporadic until recently. A summary of some of the more important investigations is given below.

Ammonium dichromate.

Maus¹ and Bottger² showed that decomposition of ammonium dichromate began at 170⁰ and occurred rapidly to give a residue of chromium (III) oxide. Harbard and King³ showed that this oxide contained oxygen in excess of that required by the stoichiometric ratio. Ammonium dichromate heated at below the decomposition temperature gave a solid residue which they suggested was either anhydrous or hydrated chromium (IV) oxide. Fishbeck and Spingler⁴,⁵ suggested that decomposition at reduced pressure proceeds according to equation (I).

\[
(NH_4)_2Cr_2O_7 = N_2 + Cr_2O_3.3H_2O + 3H_2O \quad \ldots \quad (I)
\]

Other chromates (VI) of the ammonium ion.

Ammonium chromate is unstable in air at normal temperatures and loses appreciable weight with the loss of ammonia and water to produce the dichromate⁶,⁷.
Maus showed that the compound decomposed rapidly on heating above 100°. Fishbeck and Spingler showed that the decomposition occurred autocatalytically with oxidation of the cation by the anion according to equation (2).

\[
2(NH_4)_2CrO_4 = 2NH_3 + N_2 + Cr_2O_3 \cdot H_2O + 4H_2O
\]  
\[\text{(2)}\]

They also showed that ammonium trichromate decomposed according to equation (3).

\[
2(NH_4)_2Cr_3O_10 = 2N_2 + 5/2 O_2 + (Cr_2O_3) \cdot H_2O + 5H_2O
\]  
\[\text{(3)}\]

Jaeger and Kruss prepared the tetrachromate of ammonia, \((NH_4)_2Cr_4O_{13}\), and showed that it was unstable in moist air, giving the dichromate and chromic acid, and that it darkened on heating to 160°. It began to decompose at 170° and at 175° nitric oxide was evolved leaving chromium (III) oxide.

There is little similarity between the thermal decomposition of ammonium polychromates and polychromates of other elements.

**Chromates and polychromates of Group IA.**

Stanley showed that sodium dichromate decomposed at a temperature slightly above its melting point (320°) with evolution of oxygen commencing at 400°.
The decomposition was shown to be explosive at dull red heat to give the products sodium chromate, chromium (III) oxide and oxygen according to equation (4).

$$2\text{Na}_2\text{Cr}_2\text{O}_7 = 2\text{NaCrO}_4 + \text{Cr}_2\text{O}_3 + \text{O}_2 \quad \ldots \quad (4)$$

The product also contained a small amount of alkali.

Grosschuff found that potassium dichromate decomposed considerably at 1000°. Hempel and Schubert reported that decomposition commenced at 500° and was complete at 1500°.

Flood and Muan investigated the effect of varying cation size on the thermal stability of the dichromates of sodium, potassium and thallium (I). They showed that the stability of the dichromates, which decomposed according to equation (5), increased in the order Tl < Na < K.

$$\text{Cr}_2\text{O}_7^{2-} = \text{CrO}_4^{2-} + \frac{1}{2}\text{Cr}_2\text{O}_3 + \frac{3}{4}\text{O}_2 \quad \ldots \quad (5)$$

Flood and Muan concluded that the thermal stability of the oxygen bridge (–Cr–0–Cr–) was dependent on the size and polarizing power of the cation.

By contrast, Spitsyn and co-workers investigated the effect of varying anion size on the thermal stability of the polychromates of potassium. Using DTA, TG and X-ray diffraction
analysis, they showed that:

(i) the stability of the polychromate decreased as the number of \( \text{CrO}_3 \) groups attached to the \( \text{CrO}^{2-} \) ion increased,

(ii) the tri- and tetrachromates decomposed at their melting points (243° and 210° respectively) by dissociation to give potassium dichromate and chromium (VI) oxide, according to equations (6) and (7),

\[
\begin{align*}
K_2\text{Cr}_3\text{O}_{10} & = K_2\text{Cr}_2\text{O}_7 + \text{CrO}_3 \quad \ldots (6) \\
K_2\text{Cr}_4\text{O}_{13} & = K_2\text{Cr}_2\text{O}_7 + 2\text{CrO}_3 \quad \ldots (7)
\end{align*}
\]

Sutra\textsuperscript{16} suggested that the dichromate ion also dissociates when potassium dichromate melts.

Spitsyn and co-workers also studied the thermal decomposition of the tri- and tetrachromates of sodium\textsuperscript{15} and those of rubidium and caesium\textsuperscript{14}. They concluded that in these cases fusion is not accompanied by decomposition of the anion. Fusion and decomposition temperatures are given in Table I.1. Spitsyn and co-workers concluded\textsuperscript{12,15} that:

(i) increase in the number of chromium atoms in the polychromate ion for a given cation leads to a decrease in the melting points and thermal stabilities due to polarizing action of chromium
atoms on oxygen atoms since the ratio $\text{Cr} : 0$ decreases from 4 in $\text{CrO}_4^{2-}$ to 3.25 in $\text{Cr}_4\text{O}_{13}^{2-}$.

(ii) in a series of polychromates with the same anion, the stability increases as the radius of the alkali metal cation increases.

**Other Group chromates and dichromates.**

Charsley and Redfern$^{17}$ showed that the thermal stabilities of a large range of chromates and dichromates increase with increase in cation radius (see Table 1.2). The methods which they used were DTA, TG, chemical and infra-red analysis. The TG studies were carried out up to $1400^\circ$ in static air, flowing air and flowing nitrogen atmospheres. They also carried out simultaneous DTA-TG up to $1000^\circ$.

Their results showed that most of the chromates decomposed endothermically according to equation (8).

$$2\text{M}_x\text{CrO}_4 = \text{M}_x\text{Cr}_2\text{O}_7 + \text{M}_x\text{O} + \frac{3}{2} \text{O}_2 \quad \cdots (8)$$

$$(\text{M} = \text{a metal}; \ x = 1 \text{ or } 2)$$

The dichromates were shown to decompose according to the general pattern given in equation (9).

$$2\text{M}_x\text{Cr}_2\text{O}_7 = 2\text{M}_x\text{CrO}_4 + \text{Cr}_2\text{O}_3 + \frac{3}{2} \text{O}_2 \quad \cdots (9)$$

$$(\text{M} = \text{a metal}; \ x = 1 \text{ or } 2)$$
### Table I.1

**Fusion temperatures** \((T_f)\) and **decomposition temperatures** \((T_d)\) of Group IA trichromates and tetrachromates\(^{14}\).

<table>
<thead>
<tr>
<th>Cation</th>
<th>trichromate</th>
<th>tetrachromate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(T_f)</td>
<td>(T_d)</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>232</td>
<td>337</td>
</tr>
<tr>
<td>K(^+)</td>
<td>243</td>
<td>243</td>
</tr>
<tr>
<td>K(_b^+)</td>
<td>276</td>
<td>366</td>
</tr>
<tr>
<td>Cs(^+)</td>
<td>261</td>
<td>370</td>
</tr>
</tbody>
</table>

### Table I.2

**Chromates** (C) and **dichromates** (D) studied by Charsley and Redfern\(^{17}\).

<table>
<thead>
<tr>
<th>Group</th>
<th>IA</th>
<th>IIA</th>
<th>VIIA</th>
<th>VIII</th>
<th>IB</th>
<th>IIB</th>
<th>IIIB</th>
<th>IVB</th>
<th>VB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li;D</td>
<td>Mg;C</td>
<td>Ca;CD</td>
<td>Mn;C</td>
<td>Co;C</td>
<td>Cu;C,D</td>
<td>Al;C*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na;C,D</td>
<td></td>
<td>Sr;C</td>
<td></td>
<td>Ni;C</td>
<td></td>
<td>Zn;C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K;C,D</td>
<td></td>
<td>Ba;C,D</td>
<td></td>
<td></td>
<td></td>
<td>Ag;C,D</td>
<td>Cd;C</td>
<td>Hg;C,D</td>
<td></td>
</tr>
<tr>
<td>Cs;C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pb;C</td>
<td>Bi;C</td>
<td></td>
</tr>
</tbody>
</table>

* not normal chromates
Some exceptions to the patterns shown in equations (8) and (9) were found\textsuperscript{17}. For example, silver chromate (VI) decomposed endothermically in the range 720°-860° according to equation (10).

\[
2\text{Ag}_2\text{CrO}_4 = 2\text{Ag} + \text{Ag}_2\text{Cr}_2\text{O}_7 + 2\text{O}_2 \quad \ldots \quad (10)
\]

The deviation from the general pattern was attributed to the thermal instability of silver oxide intermediate at the decomposition temperature of silver chromate (VI).

Basic copper chromate was found to decompose according to the general pattern in the range 450°-510° but decomposed further above 850° with reduction of copper occurring according to equation (11).

\[
\text{CuCr}_2\text{O}_4 + \text{CuO} = \text{Cu}_2\text{Cr}_2\text{O}_7 + \frac{3}{2}\text{O}_2 \quad \ldots \quad (11)
\]

The trend towards greater thermal stability with increase in cation size was shown by their results which are given in Table I,3.

It was shown that the chromates in an A Group were more stable than those of the corresponding B Group. This was attributed to the more favourable conditions for covalent bonding in the B Group\textsuperscript{17}.

Charsley and Redfern also showed that chromates (VI) are more stable than the corresponding dichromates (see Table I,4).
### Table I.3

**Decomposition temperatures of chromates (VI)**

<table>
<thead>
<tr>
<th>Group</th>
<th>IA</th>
<th>IIA</th>
<th>IB</th>
<th>IIB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na, 800(1)</td>
<td>Mg, 630-720</td>
<td>Cu, 450-510(5, 6)</td>
<td>Zn, 500-600</td>
<td></td>
</tr>
<tr>
<td>K, 980(1)</td>
<td>Ca, 1050-1400(2, 3)</td>
<td>Ag, 720-860(6)</td>
<td>Cd, 600-720(6)</td>
<td></td>
</tr>
<tr>
<td>Cs, 955(1)</td>
<td>Ba(2, 4)</td>
<td></td>
<td>Hg, 360-440(7)</td>
<td></td>
</tr>
</tbody>
</table>

1. peak temperature
2. reversible decomposition dependent on $P_{O_2}$
3. decomposition incomplete at 1400°
4. little decomposition up to 1400°
5. basic chromate
6. complex decomposition reaction
7. partial decomposition only of Hg(II) chromate (VI).

### Table I.4

**Decomposition temperatures of chromates compared to corresponding dichromates**

<table>
<thead>
<tr>
<th>Group</th>
<th>Cation</th>
<th>Decomposition temperature range</th>
</tr>
</thead>
<tbody>
<tr>
<td>IA</td>
<td>Na$^+$</td>
<td>1000 - 1400</td>
</tr>
<tr>
<td>IIA</td>
<td>Ba$^{2+}$</td>
<td>above 1400</td>
</tr>
<tr>
<td>IB</td>
<td>Ag$^+$</td>
<td>720 - 860</td>
</tr>
<tr>
<td>IIIB</td>
<td>Hg$^{2+}$</td>
<td>360 - 440</td>
</tr>
</tbody>
</table>
They attributed the lower stability of dichromates as compared to the corresponding chromates (VI) to the greater polarisability of dichromates.

No thermal studies have been reported for trichromates and tetrachromates of any elements apart from those of Group 1A as they are either unknown or only formed in solution.

**Lanthanide chromates.**

A number of investigations have shown that the chromate (V) ion, \( \text{CrO}_4^{3-} \), is intermediate in the decomposition reactions of the lanthanide chromates \(^{18,19,20,21}\). Darrie and Doyle \(^{21}\) suggested that the decomposition proceeds according to equations (12a) and (12b).

\[
\text{VI} \quad \text{M}_2(\text{CrO}_4)_3 = 2\text{MCrO}_4 + \frac{1}{2}\text{Cr}_2\text{O}_3 + \frac{5}{4}\text{O}_2 \quad \ldots \quad (12a)
\]

\[
2\text{MCrO}_4 + \frac{1}{2}\text{Cr}_2\text{O}_3 = 2\text{MCrO}_3 + \frac{1}{2}\text{Cr}_3\text{O}_3 + \text{O}_2 \quad \ldots \quad (12b)
\]

\( (M = \text{metal}) \)

They suggested that chromium (III) oxide acts catalytically in reaction (12b). They also showed that the decomposition of samarium (III) chromate (VI) proceeds by a contracting sphere mechanism.

**Thermal decomposition of magnesium chromate (VI).**

Magnesium chromate (VI), \( \text{MrCrO}_4 \), has been the subject of a number of decomposition studies \(^{20,21,22}\).
Some controversy has arisen regarding the mechanism of decomposition. The various theories have been discussed by Charcosset and co-workers\textsuperscript{22}. The dispute concerns the nature of the intermediate decomposition product. Henrich\textsuperscript{23} suggested that the intermediate was a mixture of magnesium chromite and magnesium oxide whilst others\textsuperscript{24, 25, 26} proposed a basic chromite whose composition varied between $6\text{MgO} \cdot 5\text{Cr}_2\text{O}_3$ and $2\text{MgO} \cdot \text{Cr}_2\text{O}_3$. Ryss\textsuperscript{26} proposed a decomposition mechanism according to equations (13a) and (13b).\textsuperscript{27}

$$2\text{MgCr}_4 \rightleftharpoons \text{Mg}_2\text{Cr}_2\text{O}_5 + \frac{3}{2} \text{O}_2 \quad \cdots (13a)$$

$$\text{Mg}_2\text{Cr}_2\text{O}_5 \rightleftharpoons \text{MgCr}_4 + \text{MgO} \quad \cdots (13b)$$

Charcosset also considered that the mechanism was represented by equations (13a) and (13b). Darrie\textsuperscript{27} did not agree with this mechanism and suggested that the intermediate was magnesium chromate (V), $\text{Mg}_3\text{(CrO}_4\text{)}_2$. Darrie and Doyle\textsuperscript{21} found that the decomposition of magnesium chromate (VI) occurred in two stages with activation energies of 30 and 57 kcal/mole respectively. They did not however characterise the intermediate.

Deren and Haber\textsuperscript{28} investigated the decomposition of magnesium chromate (VI) formed 'in situ' in aqueous mixtures of magnesium oxide and chromium (VI) oxide.
They determined the overall oxidation state of chromium in the mixtures as a function of temperature by the Bunsen-Rupp method and concluded that between 400° and 800° either

(i) chromium (IV) ion is stabilised on the surface of the magnesium oxide, or

(ii) magnesium chromate (IV), Mg₂CrO₄, is formed on the surface of magnesium oxide.

Scholder prepared barium chromate (IV), Ba₂CrO₄, and later, with Schwarz, also prepared chromates (V) of some elements of Groups IA and IIA; although magnesium chromate (V) was not prepared. Klemm showed that the magnetic susceptibilities of chromates (V) and chromates (IV) were consistent with one and two unpaired electrons respectively.

Magnesium dichromate.

Hartford prepared the monohydrate and pentahydrate of magnesium dichromate. Both hydrates were found to be deliquescent. The anhydrous compound could not be prepared from the monohydrate because heating resulted in decomposition to give magnesium chromite, magnesium chromate (VI), oxygen and chromium chromates.

I.2.1. Investigations concerning chromium (VI) oxide.

The thermal decomposition of chromium (VI) oxide
has been investigated using thermoanalytical methods\textsuperscript{12, 33, 34}. Lorthior and Michel\textsuperscript{34} showed that the decomposition of chromium (VI) oxide occurred in three stages:

(i) \( \text{CrO}_3 \rightarrow \text{Cr}_2\text{O}_5 \cdot 23, \ 288^\circ - 332^\circ \) (exothermic)

(ii) \( \text{Cr}_2\text{O}_5 \cdot 23 \rightarrow \text{Cr}_2\text{O}_4 \cdot 87, \ 385^\circ - 416^\circ \) (exothermic)

(iii) \( \text{Cr}_2\text{O}_4 \cdot 87 \rightarrow \text{Cr}_2\text{O}_3, \ 458^\circ - 472^\circ \) (endothermic)

The empirical formula \( \text{Cr}_2\text{O}_5 \cdot 23 \) was shown to correspond to that for chromium dichromate, \( \text{Cr}_2(\text{Cr}_2\text{O}_7)_3 \), but the formula \( \text{Cr}_2\text{O}_4 \cdot 87 \) could not be explained simply.

Rode's account\textsuperscript{33} of the decomposition is quite different to that of Lorthior. Using vacuum DTA on chromium (VI) oxide, Rode showed that four endothermic peaks occurred. The first was attributed to fusion and the other three were attributed to the consecutive decomposition of the decachromate, dichromate and monochromate of chromium. In addition, a small exothermic effect just after melting was given and attributed to polymerisation and solidification of the melt corresponding to composition \( \text{Cr}_2\text{O}_7 \cdot 96 \).

Sutra\textsuperscript{16} suggested that fusion of potassium dichromate is accompanied by dissociation of the dichromate ion, \( \text{Cr}_2\text{O}_7^{2-} \). By analogy with pyrosulphates which contain an oxygen bridge and
decompose according to equation (14)\(^35\), the
dissociation of \(\text{Cr}_2\text{O}_7^{2-}\) should be according to the
equilibrium equation (15).

\[
\begin{align*}
(\text{O}_3\text{S}-\text{O}-\text{S}_3)_{\text{melt}}^{2-} & \rightleftharpoons \text{SO}_4^{2-}_{\text{melt}} + \text{SO}_3(g) \quad \text{.... (14)} \\
(\text{O}_3\text{Cr}-\text{O}-\text{Cr}_3)_{\text{melt}}^{2-} & \rightleftharpoons \text{Cr}_4^{2-}_{\text{melt}} + \text{Cr}_3^{3-}_{\text{melt}} \quad \text{.... (15)}
\end{align*}
\]

The difference between equations (14) and (15)
is in the gaseous and liquid states of the trioxides
at the fusion temperatures of the poly-acids.
Chromium (VI) oxide would be expected to be found in
molten potassium dichromate and DTA should give
thermal effects showing its presence. However, the
only effect which has been shown to occur\(^37\) in the
DTA of potassium dichromate, apart from the fusion
endotherm at 398°, is the commencement of endothermic
drift at 500° associated with decomposition. This
suggests that if dissociation of \(\text{Cr}_2\text{O}_7^{2-}\) does occur,
the degree of dissociation is very small.

Further support for the proposed dissociation
mechanism, equation (15), is given by the results
of investigations of potassium dichromate and
chromium (VI) oxide dissolved in molten salts\(^36,38,39\).

Duke and Iverson\(^36\) investigated the kinetics
of the rate of precipitation of heavy metal chromates
from a solution of potassium dichromate in molten potassium nitrate-sodium nitrate eutectic mixture. They found that potassium dichromate was stable in the melt but that on adding a soluble salt of lead, cadmium or barium, a precipitate was immediately produced. The overall reaction for the addition of lead nitrate took place according to equation (16),

$$\text{Cr}_2\text{O}_7^{2-} + 2\text{NO}_3^- + 2\text{Pb}^{2+} = 2\text{PbCrO}_4 + \text{gases} \quad \ldots (16)$$

The gases which were evolved were oxygen and oxides of nitrogen. Duke and Iverson considered that the dissociation reaction (15) possibly occurred followed by reaction between chromium (VI) oxide and nitrate ion according to reaction (17),

$$\text{CrO}_3^- + \text{NO}_3^- = \text{CrO}_4^{2-} + \text{NO}_2^+ \quad \ldots (17)$$

Assuming reaction (17) to be rate controlling, they found that the kinetics proceeded according to the expression (18),

$$\frac{d}{dt} \left[ \text{Cr}_2\text{O}_7^{2-} \right] = k_1 \cdot K_e / K_5 \left[ \text{Cr}_2\text{O}_7^{2-} \right] \left[ \text{Pb}^{2+} \right] \quad \ldots (18)$$

where $k_1$ is a pseudo-first order specific velocity involving the nitrate concentration in the rate controlling reaction (16), $K_e$ is the equilibrium
constant for reaction (15) and $K$ is the solubility product of lead chromate.

However, the dissociation mechanism was rejected in favour of the direct combination reaction (19),

$$\text{Cr}_2\text{O}_7^{2-} + \text{NO}_3^+ \rightleftharpoons 2\text{Cr}_2\text{O}_4^{2-} + \text{NO}_2^+ \ldots \quad (19)$$

The reasons for this were:

(i) the rate dependence on lead increased in order from one to two at low lead concentrations,

(ii) the rate increased by bubbling inert gas through the melt.

To account for the first observation (i), they proposed the formation of a stable complex between the dichromate ion and the heavy metal ion. They derived an expression which explained the second order dependence at low lead concentrations but which could not explain the greater retarding effect of $\text{Ba}^{2+}$ compared with $\text{Cd}^{2+}$ on the decomposition of $\text{Cr}_2\text{O}_7^{2-}$ which was expected.

They considered that the second observation (ii) was strong evidence for the presence of gaseous products in equilibrium with the reactants in the melt. The gas was thought to be nitrogen pentoxide formed by a reaction between nitronium ion and nitrate ion according to equation (20).
On the basis of the evaporative mechanism they derived expression (21) which explains the second order dependence in lead,

\[
\frac{d}{dt} \left[ \text{Cr}_2\text{O}_7^{2-} \right] = \frac{k_3}{k_s^2} \left[ \text{Cr}_2\text{O}_7^{2-} \right] \left[ \text{Pb}^{2+} \right] \quad \ldots (21)
\]

where \( k_3 \) is a complex constant comprising two diffusion terms and a unimolecular decomposition term.

The evaporative rate expression can also be explained, however, if chromium (VI) oxide is assumed to be the equilibrium product which undergoes evaporation. It has been shown \( 33,37 \) that chromium (VI) oxide readily volatilises above its melting point. It is therefore surprising that the dissociation mechanism of \( \text{Cr}_2\text{O}_7^{2-} \) and evaporation of chromium (VI) oxide was not considered especially as they found that lead chromate was precipitated from a solution of chromium (VI) oxide in molten nitrates at the same rate as from a solution of potassium dichromate in molten nitrates of the same strength. They also showed that chromium (VI) oxide gave a stable solution in molten nitrates with little or no reaction in the absence of heavy metal ions. Similarly, a solution of potassium dichromate in molten nitrates was shown
to be stable in the absence of heavy metal ions and they proposed that the equilibrium reaction (19) lies far to the left hand side. If this is so, then it is difficult to explain Van Norman's results.

Van Norman studied solutions of potassium dichromate in mixtures of molten nitrates (KNO$_3$-LiNO$_3$) by absorption spectrophotometry. He found that in this solvent, the spectra of potassium chromate, potassium dichromate and chromium (III) chloride are all similar and attributable to the chromate ion, CrO$_4^{2-}$. These results suggest that if the equilibrium reaction (19) proposed by Duke and Iverson does occur then it must lie well to the right hand side. This contradicts Duke and Iverson's suggestion that reaction (19) lies well to the left hand side.

This contradiction may be explained if the dissociation mechanism (15) occurs in the following scheme:

$$\text{Cr}_2\text{O}_7^{2-} \rightleftharpoons \text{CrO}_4^{2-} + \text{CrO}_3$$  \hspace{1cm} (15)

$$\text{CrO}_3 + \text{N}_2\text{O}_5 \rightleftharpoons \text{CrO}_4^{2-} + \text{N}_2\text{O}_5^+$$  \hspace{1cm} (17)

$$\text{N}_2\text{O}_5^+ + \text{N}_2\text{O}_5^- \rightleftharpoons \text{O}_2\text{O}_5$$  \hspace{1cm} (20)

If the reaction (15) lies well to the right hand side, the spectrum associated with chromate (VI) may be
explained whilst the rate controlling reaction (17) would explain the apparent stability of the system if its rate was low. Support for this scheme is given by the differential spectrum of 30 mg K$_2$Cr$_2$O$_7$ v 40 mg K$_2$Cr$_2$O$_7$ in 40 g molten LiN0$_3$-KN0$_3$. The melt had the characteristic colour of dichromate. Van Norman concluded that only part of the dichromate was converted to chromate (VI).

The differential spectrum gave a maximum absorbance at 415 mp and was similar to the spectra given by potassium chromate (VI), potassium dichromate and chromium (III) chloride in molten silver nitrate. The absorption at this wavelength was attributed to the dichromate ion. It was suggested that the chromate (VI) could be converted to dichromate according to equation (22).

$$2 \text{Ag}^+ + 2\text{CrO}_4^{2-} = \text{Cr}_2\text{O}_7^{2-} + \text{Ag}_2\text{O} \quad \ldots (22)$$

An alternative mechanism to the tetramolecular reaction (22) could be a step-wise series of bimolecular reactions as follows:

$$\text{CrO}_4^{2-} + \text{Ag}^+ = \text{AgO}^- + \text{Cr}_3 \quad \ldots (23)$$

$$\text{AgO}^- + \text{Ag}^+ = \text{Ag}_2\text{O} \quad \ldots (24)$$

$$\text{Cr}_3 + \text{CrO}_4^{2-} = \text{Cr}_2\text{O}_7^{2-} \quad \ldots (15)$$
It is unfortunate that this investigation did not include a measurement on the spectrum of chromium (VI) oxide in molten salts.

However, the most conclusive evidence in support of the dissociation reaction (15) is given indirectly from the results of the potentiometric titration of potassium dichromate and chromium (VI) oxide in molten potassium nitrate carried out by Shams el Din. He titrated solutions of potassium dichromate with potassium hydroxide and found one equivalent point at a \( K_2Cr_2O_7 : KOH \) ratio of 1:2 in accordance with reaction (25),

\[
Cr_2O_7^{2-} + 0^{2-} = 2CrO_4^{2-} \quad \ldots \ (25)
\]

The oxide ion was produced in accordance with reaction (26),

\[
2KOH = 2K^{+} + H_2O + 0^{2-} \quad \ldots \ (26)
\]

Shams el Din also attempted to neutralize chromium (VI) oxide step-wise according to equations (27) and (28),

\[
2CrO_3 + 0^{2-} = Cr_2O_7^{2-} \quad \ldots \ (27)
\]

\[
Cr_2O_7^{2-} + 0^{2-} = 2CrO_4^{2-} \quad \ldots \ (28)
\]

However, only one equivalent point was given at a \( CrO_3 : KOH \) ratio of 1 : 0.94-1.04. The possibility that
reaction (29) occurred was ruled out as the expected
CrO$_3$:KOH ratio would have been 1:2.

\[
\text{CrO}_3 + \text{O}^2- = \text{CrO}_4^{2-} \quad \ldots \ (29)
\]

The production of brown fumes during the melting
period suggested that reaction (30) occurred and
explained the observed ratio 1:0.94 - 1.04.

\[
2\text{CrO}_3 + 2\text{KN}_3 = \text{K}_2\text{Cr}_2\text{O}_7 + \text{N}_2\text{O}_5 \quad \ldots \ (30)
\]

However, when a molten solution of potassium
hydroxide in potassium nitrate was titrated with
potassium dichromate two equivalent points were
given at KOH:K$_2$Cr$_2$O$_7$ ratios of 1:0.35 - 0.42 and
1:0.49 - 0.51 whereas previously, when potassium
dichromate was titrated with potassium hydroxide,
only one equivalent point was given at a KOH:K$_2$Cr$_2$O$_7$
ratio of 1:0.5.

Moreover, the first neutralisation step at
KOH:K$_2$Cr$_2$O$_7$ ratio of 1:0.35 - 0.42 was not sharp (see
Fig. 1.1). This would be expected if reaction (15)
occurring because:

(i) when potassium dichromate was added to the
solution of potassium hydroxide in potassium
nitrate, chromium (VI) oxide produced by reaction
(15) reacted more rapidly with oxide ion than
the dichromate ion did. The first neutralisation
Fig. I.I. Titration of KOH with $K_2Cr_2O_7$ at 370° (after Shams el Din$^{39}$).
step was given in accordance with reaction (29) but as the concentration of chromate (VI) in the melt increased due to this reaction, it increasingly opposed the extent of dissociation of dichromate ion as more potassium dichromate was added to the melt. When the dissociation was sufficiently suppressed, the second neutralisation step began to occur according to equation (25).

(ii) when the solution of potassium dichromate in potassium nitrate was prepared, reaction (30) occurred appreciably before titration with potassium hydroxide commenced so that a neutralization step due to the presence of chromium (VI) oxide would not be given.

I.3. Oxidation of magnesium.

The oxidation of magnesium has been the subject of a number of investigations\(^{40, 41, 42, 43, 44, 45}\). These were all concerned with oxidation of magnesium in oxygen or air. There is little in the literature concerning oxidation of magnesium by agents other than oxygen. A notable exception is to be found in the field of pyrotechnic studies where the oxidants are normally molten oxy-acids.
1.4. Pyrotechnics

The history and development of pyrotechnics, which has been defined as an art, has been reviewed by Clarke and Cackett.

More recently, pyrotechnics have been subjected to scientific investigation.

A number of workers have used, or modified, the Mallard-LeChatelier gaseous phase combustion theory to investigate the burning mechanism of solid compositions. The theory assumes that the burning is propagated solely by the forward conduction of heat.

Japanese workers suggested that flow of hot gas through the composition was an important factor which the purely thermal theory ignored. Nakahara criticised the modified Mallard-LeChatelier theory as applied to the solid phase because the characteristics and reaction mechanisms of the solid phase were ignored.

However, the hot gas flow mechanism also ignores solid-state reaction mechanisms.

Hill and co-workers investigated the slow-burning of a wide range of compositions in terms of the Mallard-LeChatelier theory. They concluded that the theory is probably a sound basis for
examining the systems. However, they also emphasized that:

(i) there is no simple relationship between the mathematical expression of the theory and experimental results,

(ii) physical parameters which enter into the expression can neither be easily defined nor readily measured,

(iii) the heat of reaction, which is a parameter in the expression (31), depends on the actual reaction mechanism occurring, which may be composite, of different nature in different temperature zones, and incomplete.

The fundamental differential equation representing the Mallard-LeChatelier theory is:

\[
VQ \rho \frac{d\varepsilon}{dx} + k \frac{d^2T}{dx^2} - V \rho \ c \ \frac{dT}{dx} = 0 \quad ... \ (31)
\]

where \(\varepsilon\) = rate of propagation

\(Q\) = heat of reaction per gram

\(\rho\) = density of unburnt material

\(\varepsilon\) = fraction reacted of component not in excess

\(x\) = linear co-ordinate

\(k\) = thermal conductivity of unburnt material

\(c\) = specific heat of unburnt material

\(T\) = absolute temperature.
I.4.1. Methods used to study pyrotechnic compositions.

Although Hill and co-workers used a variety of methods to attempt to examine the validity of expression (31) with respect to the systems under investigations, their summary implied that they were not able to arrive at definitive conclusions because of a lack of data for heats of reaction and chemical reaction rates.

Furthermore, Amster questioned the wisdom of continuing to develop more refined computing systems for investigating self-heating mechanisms when the precision of kinetic and thermodynamic data remained so limited.

The methods which Hill and co-workers used were closed bomb calorimetry, X-ray and chemical analysis of residues, and measurements of the rate of burning, ignition and temperature and temperature profiles of compacted compositions. Bond has reviewed these and some of the other methods which have been used to study pyrotechnic compositions which include thermogravimetry, differential thermal analysis, time-to-ignition and self-heating measurements.

Calorimetry.

Clarke used closed bomb calorimetry to study the binary system magnesium-barium nitrate.
He ignited pellets of the binary system in an atmosphere of argon inside the calorimeter and found the heats of reaction suggested a reaction mechanism which proceeded according to equations (32) and (33).

\[
\begin{align*}
\text{Ba(NO}_3\text{)}_2 & = \text{BaO} + \text{N}_2 + \frac{5}{2} \text{O}_2 \quad \ldots \quad (32) \\
\text{Mg} + \frac{1}{2}\text{O}_2 & = \text{MgO} \quad \ldots \quad (33)
\end{align*}
\]

Hill and co-workers\(^{57}\) also used closed bomb calorimetry to investigate a wide range of binary slow-burning compositions in which the fuel was a powder of one of the following: iron, manganese, molybdenum, silicon. The oxidants were one of the following compounds: barium peroxide, potassium permanganate, potassium nitrate, strontium nitrate, potassium dichromate. However, in the majority of cases, they found that the heats of reaction determined calorimetrically suggested that the reactions in the burning pellet were incomplete or different at different temperature zones in the pellet.

Closed bomb calorimetry can not be used to determine kinetic parameters.
X-ray powder diffraction analysis.

Hill and co-workers\(^5^7\) used X-ray powder diffraction analysis to characterise the residues of burnt compositions.

X-ray powder diffraction analysis can not be readily adapted to allow determinations to be made of the kinetics of burning compositions.

Chemical analysis.

Hill and co-workers\(^5^7\) used chemical analysis in an attempt to elucidate the products of reaction of burnt compositions. However, they did not analyse the systems as a function of time to enable kinetic data to be determined.

Thermogravimetry.

Bond\(^5^9\) used thermogravimetry to investigate the binary system between magnesium and sodium nitrate. He showed that the decomposition of sodium nitrate occurred in two stages, the first proceeding according to equation (34).

\[
2\text{NaN}_3 = 2\text{NaN}_2 + \text{O}_2 \quad \ldots (34)
\]

The nitrite decomposed subsequently according to equations (35) and (36).
When magnesium was present, the two stage mechanism was not given and decomposition proceeded in one stage. Bond suggested that reaction (35) did not occur in the presence on magnesium because the nitrite ion began to react with magnesium rapidly according to equations (37) and (38).

\[
\begin{align*}
2\text{NaNO}_2 &= \text{Na}_2\text{O} + 2\text{NO} + \frac{1}{2}\text{O}_2 \\
\text{Na}_2\text{O} + 3\text{NO} &= 2\text{NaNO}_2 + \frac{1}{2}\text{N}_2
\end{align*}
\]  \hspace{1cm} \ldots (35)  \\
\hspace{1cm} \ldots (36)

Krien\textsuperscript{60} used thermogravimetry to study a number of pyrotechnic compositions. The method was carried out with simultaneous differential thermal analysis. He was also able to investigate several explosive materials by simultaneous TG-DTA.

Krien also determined energies of activation for the decomposition of some explosive materials using his results in the Borchardt and Daniels equation for DTA.

Although Krien was able to use TG to study pyrotechnic compositions and explosive materials,
it is not always appropriate to use TG due to the risk of damage to the thermobalance resulting from explosive reactions\textsuperscript{61}. In addition, some pyrotechnic compositions react and burn without any appreciable change in weight\textsuperscript{59} and are known as 'gas-less compositions'. Such compositions can not be studied by TG.

**Differential thermal analysis.**

Freeman and Gordon\textsuperscript{62} used differential thermal analysis to investigate the systems magnesium-lithium nitrate and magnesium-sodium nitrate. They showed that the ignition reactions of these two systems were not proceeded by pre-ignition reactions but they did not propose a mechanism for the ignition reactions.

Gordon and Campbell\textsuperscript{63} used differential thermal analysis, closed bomb calorimetry and determinations of the time-to-ignition to investigate the pre-ignition and ignition reactions of the ternary pyrotechnic system zinc-hexachlorobenzene-potassium perchlorate.

**Time-to-ignition.**

Freeman and Gordon\textsuperscript{62} also used time-to-ignition measurements to study the systems magnesium-lithium nitrate and magnesium-sodium nitrate. Observed ignition
times were in agreement to the same order of magnitude
with those calculated on the basis of the theory
of absolute reaction rates.

I.5. **Theory and practice of differential thermal analysis.**

The technique of differential thermal analysis
originated in the late nineteenth century after
early investigations by LeChatelier and Roberts-
Austen. Smothers and Chiang have reviewed the
field of DTA up until 1965, including a comprehensive
bibliography, whilst the Stanton Instrument Company
publish quarterly the Thermal Analysis Review
edited by Redfern which includes abstracts of
all papers published since 1962 on DTA and associated
thermoanalytical techniques.

The theoretical aspects of DTA have been discussed
by a number of workers.

Various workers have proposed theories
in which the shape of a differential thermal
analysis curve can be used to determine kinetic
parameters for the thermal decomposition of solids
or liquids. In the early investigations it was
found that results were not always reproducible
and were sometimes at variance with the results
obtained by more conventional methods. The basis of Kissinger's theory\textsuperscript{71} was questioned by Reed, Weber and Gottfried\textsuperscript{73} who also showed that the Borchartdt and Daniels theory\textsuperscript{72} provides a satisfactory basis for the determination of kinetic data from DTA curves.

However, a number of restrictions are imposed in formulating the Borchartdt and Daniels theory. These are:

(i) the temperature of the sample must be homogeneous,

(ii) the temperature of the thermal source must be homogeneous,

(iii) a complete curve without any overlapping from neighbouring peaks is necessary for analysis.

In view of the uniform temperature requirement (i) above, it would appear that the method cannot be applied in cases where a temperature gradient exists within a system. A temperature gradient is set up in solids which are heated from a thermal source whose temperature is rising as a function of time. A temperature gradient may also arise as a result of internal self-heating which occurs in decomposition of explosives and pyrotechnic compositions. Nevertheless, the method has been used with some success to study systems containing
Krien used the method to determine the kinetics for the decomposition of six common explosive materials but his results were in considerable disagreement with existing literature values.

Rabovskii, Kogan and Furman suggested methods for overcoming errors inherent in the Borchardt and Daniels method.

I.5.1. The Borchardt and Daniels method for the determination of kinetic data by DTA.

The form of apparatus used is illustrated in Fig. I.2. The temperature of the heating bath is raised at a suitable rate. One cell contains the sample and the other contains the inert reference material. Matched thermocouples are inserted into each cell and connected in opposition so that the difference in temperature between the two cells can be measured. The experiment is started at a suitably low temperature at which the reaction rate is sensibly zero and the temperature of the system is raised until the reaction is essentially completed. A typical curve obtained is shown in Fig. I.3.

Theory.

The homogeneous temperatures of the sample, reference and thermal source are represented by
Fig. I.2. DTA apparatus for obtaining kinetic data for reactions occurring in solution.

Fig. I.3. Typical DTA curve obtained using apparatus depicted in Fig. I.2.
The total heat capacities of the sample and reference materials are represented by $C_s$ and $C_r$ respectively.

The increase in enthalpy of the sample is given by equation (39),

$$C_s \cdot dT_s = dH + K_s (T_b - T_s) \, dt \quad \ldots \quad (39)$$

where $dH$ is the heat evolved by the reaction in time $dt$ and $K_s$ is the heat transfer coefficient of the sample container. For the reference cell,

$$C_r \cdot dT_r = K_r (T_b - T_r) \, dt \quad \ldots \quad (40)$$

where $K_r$ is the heat transfer coefficient of the reference container. If both containers are made equal so that $K_s$ equals $K_r$ and if $C_s$ is made equal to $C_r$, subtracting equation (40) from (39) gives:

$$dH = C_p \cdot d \Delta T + K_s \cdot \Delta T \cdot dt \quad \ldots \quad (41)$$

where $K_s = K_r = K$, $C_s = C_r = C_p$, and $\Delta T = T_s - T_r$.

The total heat transferred ($\Delta H$) is given by integrating equation (41) between $t = 0$ and $t = \infty$.
according to equation (42),

$$\Delta H = C_p (\Delta T_o - \Delta T) + K \int_0^\infty \Delta T \, dt \quad \cdots (42)$$

Since $\Delta T = \Delta T_o = 0$, equation (42) reduced to

$$\Delta H = K \cdot A \quad \cdots (43)$$

where $A$ is the total area under the curve.

The heat of reaction per mole is given according to equation (44),

$$\Delta H_r = \frac{K \cdot A}{n_o} \quad \cdots (44)$$

where $n_o$ is the initial number of moles of reactant.

The Borchardt and Daniels theory then postulates that the heat evolved in a small time interval is directly proportional to the number of moles reacting in that time according to equation (45),

$$dH \propto -dn \quad \cdots (45)$$

$$\therefore \quad dH = -K \cdot A \cdot \frac{dn}{n_o} \quad \cdots (46)$$

assuming that the heat of reaction remains constant during the reaction under consideration.

Substituting for $dH$ from equation (46) into equation (41) and differentiating with respect to time gives the rate of reaction in terms of DTA parameters according to equation (47),
\[ \frac{-dn}{dt} = \frac{n_0}{K \cdot A} (C_p \cdot \frac{d \Delta T}{dt} + K \cdot \Delta T) \quad \ldots \quad (47) \]

For a homogeneous reaction, the number of moles present at any instant \( n \) is given by equation (48),

\[ n = n_0 - \int_0^t (-\frac{dn}{dt})dt \quad \ldots \quad (48) \]

Substituting equation (47) in equation (48) gives

\[ n = n_0 - \frac{n}{K \cdot A} (C_p \cdot \Delta T + K \cdot a) \quad \ldots \quad (49) \]

where \( a \) is the partial area under the curve from \( t = 0 \) to \( t = t \).

The specific rate of reaction of order \( x \) with respect to one component is by equation (50),

\[ k = (-V^{x-1} \cdot \frac{dn}{dt})/n^x \quad \ldots \quad (50) \]

where \( V \) is the volume of the system containing \( n \) moles.

Substituting in equation (50) for \((-\frac{dn}{dt})\) from equation (47) and for \( n \) from equation (49) gives the specific rate in terms of DTA parameters according to equation (51),

\[ k = \left( \frac{(K \cdot A \cdot V/n_0)^{x-1} (C_p \cdot \frac{d \Delta T}{dt} + K \cdot \Delta T)}{[K(A-a) - C_p \cdot \Delta T]^x} \right) \quad \ldots \quad (51) \]

For a homogeneous reaction of the type represented by equation (52), the specific rate is given by the general equation (53),
mM + nN + \ldots = \text{products} \quad \ldots \quad (52)

\[
k = \frac{K\text{AV}^{m+n-1}}{M_o} \left( C_p \frac{dT}{dt} + K \cdot \Delta T \right)
\]

\[
\left[ K(A-a) - C_p \cdot \Delta T \right]^m \left[ K(N_0 A/M_o - na/m) - C_p \cdot \Delta T \right]^n
\]

where the rate expression is given by equation (54),

\[
dz/dt = (M-z)^m (N-nz/m)^n \quad \ldots \quad (54)
\]

and \(z\) represents the number of moles of M reacted in time \(t\) for a reaction of order \((m + n + \ldots - 1)\), \(M_o\) and \(N_o\) the initial number of moles of M and N respectively.

For reactions in the solid state, different expressions have been obtained\(^{74,76}\) for the specific rate.
2. EXPERIMENTAL RESULTS.

2.1 Materials.

Magnesium.

All magnesium used in this work was in fine powder form as supplied by the R.A.R.D.E., Langhurst. The powder was quoted to contain not less than 96% of magnesium, the main impurities being oxygen and hydrogen in the form of oxide and hydroxide.

Three grades of magnesium were supplied, namely grade 3, grade 5 and atomised grade. Microscopic examination (section 2.6) showed that each grade consisted of spherical particles. However, grade 5 appeared to have essentially the same range of distribution of particle size as the atomised grade but contained a larger degree of irregularly shaped particles. Accordingly, little use was made of grade 5 material.

The particle size distribution of the other two grades was determined by sieve analysis and is given in Table 2.1.

Initial work was carried out using the material as supplied but later work used the fraction of the atomised grade between BS sieves No. 300 and No. 350, i.e. 45-53 μ. No additional treatment was carried out on the magnesium powder which was used with an oxide film.
**Potassium dichromate.**

AnalaR grade potassium dichromate (Hopkin & Williams Ltd.) was used throughout this work. The dichromate was ground in an agate mortar, dried at 110° and stored over silica gel before use. Further purification was carried out for the DTA studies of potassium dichromate as described in section 2.3.2(c).

**Chromium (VI) oxide.**

Research reagent grade chromium (VI) oxide (Harringtons) was dried at 110°, ground rapidly in an agate mortar and stored over silica gel before use. Additional purification for DTA studies was carried out by vacuum sublimation at 175°.

**Aluminium oxide.**

Chromatography grade aluminium oxide (Fruka) was used as a reference material in DTA studies. The material was screened to pass a BS sieve No. 350. The material was dried by heating to dull red heat and allowed to cool in a desiccator before use in each DTA experiment.

**Other materials used.**

A list of the other materials used in this work is given in Table 2.2. Further details are given in the relevant sections.
Table 2.2

Other materials used

<table>
<thead>
<tr>
<th>Material</th>
<th>Formula</th>
<th>Grade</th>
<th>Brand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium chromate</td>
<td>MgCrO$_4$.H$_2$O</td>
<td>Laboratory</td>
<td>B.D.H. Ltd</td>
</tr>
<tr>
<td>Barium nitrate</td>
<td>Ba(NO$_3$)$_2$</td>
<td>AnalaR</td>
<td>&quot;</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Potassium chromate</td>
<td>K$_2$CrO$_4$</td>
<td>&quot;</td>
<td>Hopkin &amp; Williams</td>
</tr>
<tr>
<td>Magnesium sulphate</td>
<td>MgSO$_4$.7H$_2$O</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Disodium diaminoethanetetracetic acid</td>
<td>C$<em>{10}$H$</em>{14}$O$_8$N$_2$Na$_2$.2H$_2$O</td>
<td>&quot;</td>
<td>&quot;</td>
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<td>Eriochrome Black T</td>
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<td>&quot;</td>
</tr>
<tr>
<td>Potassium hydrogen phthalate</td>
<td>C$_8$H$_4$O$_4$.HK</td>
<td>Research</td>
<td>Harringtons</td>
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<td>-</td>
<td>Permutit</td>
</tr>
<tr>
<td>ZeoKarb 225</td>
<td>-</td>
<td>-</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
2.2. Chemical analysis.

The possible products of reaction were shown to be magnesium chromite, soluble chromate (VI) ion and magnesium ion. It was also necessary to establish the presence or otherwise of chromium (III) oxide and magnesium oxide.

Where appropriate, the chemical analyses were carried out on reactants and products by the methods outlined below. Further details are given in the appropriate sections.

2.2.1. Methods of chemical analysis.

Chromate (VI) and dichromate.

The concentrations of chromate (VI) ion and dichromate ion were determined by the simultaneous method suggested by Khodakov. The solution to be analysed is treated with excess barium nitrate solution causing dichromate to be precipitated quantitatively according to equation (2.1),

\[ \text{Cr}_2\text{O}_7^{2-} + 2\text{Ba}^{2+} + \text{H}_2\text{O} = 2\text{BaCrO}_4 + 2\text{H}^+ \]  \( \ldots (2.1) \).

The hydrogen ion formed is titrated against standard alkali. The barium chromate (VI) precipitate formed according to equation (2.1) is determined gravimetrically along with the barium chromate (VI)
produced from the chromate (VI) ion which was originally present in the solution, which is thus given by equation (2.2),

\[ \text{Cr}_4^{2-} = \text{Cr}_4^{2-} - \text{Cr}_4^{2-} \] (total titration) ... (2.2).

This method prevents any uncertainty in the colour change of an indicator (in a redox titration for dichromate ion) due to displacement of the equilibrium reaction (2.3),

\[ \text{Cr}_2O_7^{2-} + H_2O \rightleftharpoons 2\text{Cr}_4^{2-} + 2H^+ \] ... (2.3).

However, in this study it was found that the presence of colloidal barium chromate (VI) made it difficult to observe the end-point using phenolphthalein indicator. Instead, a potentiometric method was used to determine the end-point using a pH meter (E.I.L., Ltd., model 38A) and glass-calomel electrodes.

**Magnesium**

The concentration of magnesium ion was determined by complexometric titration against 0.02 M EDTA after removal of dichromate ion and chromate (VI) ion on a column of anion exchange resin (De-acidite FF, 100 - 200 mesh, Permutit Ltd.). This was found to be necessary because the presence of chromates and dichromates completely masked the end-point using
Eriochrome Black T indicator. The resin was discarded after each exchange because of the adverse effect of dichromate ion on the resin. The column was repacked with sufficient fresh resin to effect complete removal of chromate (VI) and dichromate but allow a fast elution rate. The repacked columns were eluted with distilled water (250 ml) before each exchange.

Analysis of standard solutions of chromate (VI) ion, dichromate ion and magnesium ion.

Standard solutions (0.01 M) of potassium dichromate, potassium chromate and magnesium sulphate heptahydrate were made up and used to prepare solutions containing various ratios of the three salts (Table 2.3).

Aliquots (10 or 25 ml) of each solution were pipetted into a conical flask, excess saturated barium nitrate solution was added and the acid produced was titrated potentiometrically against 0.03 N sodium hydroxide solution. The end-point occurred at a pH of 7.7 - 8.0. The sodium hydroxide solution was prepared from AnalR grade material. The pellets were thoroughly washed with distilled water to remove surface carbonate before making up standard solutions. The sodium hydroxide solution was stored in a plastic bottle (polyvinyl chloride)
and standardised against 0.02 N potassium hydrogen phthalate before each batch of titrations.

Because barium chromate was deposited on the electrodes, it was necessary to carry out the gravimetric analyses independently of the acidimetric analyses. The electrodes were washed with 10% hydrochloric acid to remove barium chromate (VI) and washed several times with distilled water before each titration.

The results of the analysis of solutions containing potassium dichromate, potassium chromate (VI) and magnesium sulphate are shown in Table 2.3. The results agreed to within ± 2% of the expected values which was of sufficient accuracy for analysing the solutions discussed in section 2.2.2.

2.2.2. Preparation and analysis of the products of reaction at 429° between magnesium and potassium dichromate.

Preparation of reaction mixture.

Atomised grade magnesium powder in the range 45 - 53 μ was accurately weighed (0.2432 g) into a Pyrex test tube (6" x 5/8"). Potassium dichromate (2.9422 g) was also accurately weighed into the test tube. The tube was closed with a glass stopper and shaken to ensure thorough mixing of the components. The tube was reweighed to ensure that no material had been lost on shaking. The mixture was levelled
### Table 2.1

Sieve analysis of Magnesium powder (supplied by R.A.R.D.E.)

<table>
<thead>
<tr>
<th>Magnesium</th>
<th>B.S. Sieve No.</th>
<th>Size</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade 3 <em>(i)</em></td>
<td>on 72</td>
<td>210</td>
<td>nil</td>
</tr>
<tr>
<td></td>
<td>72-100</td>
<td>210-150</td>
<td>&lt;7</td>
</tr>
<tr>
<td></td>
<td>100-240</td>
<td>150-63</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>passing 240</td>
<td>63</td>
<td>&lt;15</td>
</tr>
<tr>
<td>Atomised grade</td>
<td>on 200</td>
<td>75</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td></td>
<td>200-240</td>
<td>75-63</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>240-300</td>
<td>63-53</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>300-350</td>
<td>53-45</td>
<td>17.2</td>
</tr>
<tr>
<td></td>
<td>passing 350</td>
<td>45</td>
<td>63.9</td>
</tr>
</tbody>
</table>

*(i)* reference 47.

### Table 2.3

Results of analysis of standard mixed solutions containing magnesium ion chromate ion and dichromate ion in varying ratios.

<table>
<thead>
<tr>
<th>Mixed solution of</th>
<th>Percentage error in concentration of dichromate by titrtn.</th>
<th>chromate by gravim.</th>
<th>Mg$^{2+}$ by titrtn.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_2Cr_2O_7$ 0.01 M (ml)</td>
<td>25</td>
<td>+1.8</td>
<td>-0.2</td>
</tr>
<tr>
<td>$K_2CrO_4$ 0.01 M (ml)</td>
<td>25</td>
<td>+1.9</td>
<td>-0.3</td>
</tr>
<tr>
<td>$MgSO_4.7H_2O$ 0.01 M (ml)</td>
<td>25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>25</td>
<td>10</td>
<td>-</td>
</tr>
</tbody>
</table>
at the bottom of the tube by gently tapping the
test tube which was then immersed in a stirred
molten lead bath (section 2.4) which was maintained
to \( \pm 1^\circ \). Mixtures were heated for periods of 0.5
to 8 hours measured with a stop-clock.

By locating a thermocouple (Pt v 13% Rh-Pt)
at the centre of the mixture and measuring the
output on a Rikadenki Kogyo Co. B3, (f.s.d. <
one second) potentiometric recorder, it was
shown that the temperature of the mixture rose to
within 2° of the bath temperature in 3.5 minutes.

The isothermal heating period was taken as
the measured period of immersion less 3.5 minutes.

It was shown that no self-heating occurred in
the mixture under these conditions.

Extraction and chemical analysis of the products
of reaction at 429°.

Extraction.

After heating, each mixture was allowed to
cool in a desiccator. A hard crust had formed on
the surface of each sample which consisted mainly
of magnesium (see Table 2.10) whose density (1.74
g/cc) is less than that of potassium dichromate
(2.69 g/cc).

The mixture was lixiviated in boiling distilled
water to loosen the hard crust.
The insoluble portion of the extract was collected quantitatively on a No. 5 sintered glass crucible (1.8 μ mean pore diameter), washed with distilled water, dried at 110° and weighed as (A).

The filtrate and washings were collected quantitatively and made up to 0.5 l. of solution at 20°, (B).

A small quantity of gas was evolved during lixiviation of all samples. The amount was determined for one sample by breaking the test tube to extract the solid mass, grinding and placing the powder in a boiling tube in water covered by a simple eudiometer arrangement consisting of a filter funnel and microburette (2 ml). Levels were equalised in a measuring cylinder filled with water and the volume of gas evolved after 16 hours, when evolution had ceased, was found to be 0.73 ml (uncorrected for S.V.P.). Because of the limited amount evolved, no attempt was made to characterise the gas.

The water-insoluble residue (A) was washed with 1% hydrochloric acid until no more gas was evolved, washed with distilled water, dried at 110° and weighed as (C). The filtrate and washings were collected quantitatively and made up to 0.25 l. of solution at 20°, (D).

The full scheme for extraction and analysis is shown in Fig. 2.1.
Mixtures 0.01 mole K₂Cr₂O₇ + 0.01 g. ion Mg heated at 429⁰ for 0.5-8 hours, cooled, extracted in distilled water, filtered

Water insolubles:
dried at 120⁰ and weighed as (A).
Washed with HCl (1%) until effervescence ceased, and distilled H₂O.
Washings collected quantitatively.

Water solubles:
made up to 0.5 l.
(B) and estimated for magnesium ion and dichromate ion.

Gas:
volume measured (5 hour product only) at S.T.P.

Acid insolubles:
dried at 120⁰ and weighed as (C).

Acid solubles:
made up to 0.25 l (D) and estimated for magnesium.

Fig. 2.1 Scheme for extraction and analysis of products of isothermal experiments.
2.2.3. Results

The weights of (C) found for the different heating periods are given in Table 2.4 and Fig. 2.2.

The weights of magnesium in the water soluble products (B) are given in Table 2.5 and Fig. 2.2.

Table 2.4

Weight of 1% HCl insoluble product (C) at 429°.

<table>
<thead>
<tr>
<th>Time hour</th>
<th>Wt. of Mg₂Cr₂O₇ mg</th>
<th>mole x 10⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>35.7</td>
<td>1.856</td>
</tr>
<tr>
<td>0.75</td>
<td>47.1</td>
<td>2.449</td>
</tr>
<tr>
<td>1.0</td>
<td>63.0</td>
<td>3.276</td>
</tr>
<tr>
<td>1.5</td>
<td>72.2</td>
<td>3.754</td>
</tr>
<tr>
<td>2.0</td>
<td>81.8</td>
<td>4.253</td>
</tr>
<tr>
<td>2.5</td>
<td>86.1</td>
<td>4.477</td>
</tr>
<tr>
<td>3.0</td>
<td>86.4</td>
<td>4.492</td>
</tr>
<tr>
<td>4.0</td>
<td>92.0</td>
<td>4.783</td>
</tr>
<tr>
<td>5.0</td>
<td>95.0</td>
<td>4.930</td>
</tr>
<tr>
<td>6.5</td>
<td>104.4</td>
<td>5.428</td>
</tr>
<tr>
<td>8.0</td>
<td>111.6</td>
<td>5.802</td>
</tr>
</tbody>
</table>

The weights of magnesium in (D), determined volumetrically (EDTA), are compared with the difference (A-C) in gravimetric weights and are shown in Table 2.6. The accuracies of volumetric and gravimetric analyses were estimated to be better than ± 0.3 and ± 0.1 mg, respectively. Since the volumetric and gravimetric results agree closely, it may be assumed that the
Fig. 2.2. Weights of magnesium chromite and soluble magnesium ion formed at 429°.
water insoluble-HCl soluble product (D) was predominately magnesium, i.e., magnesium oxide was not one of the main products of the reaction.

Table 2.5

Weight of magnesium in water soluble product (B) at 429°.

<table>
<thead>
<tr>
<th>Time (hour)</th>
<th>Weight of Mg^{2+} g. ion x 10^4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>4.80</td>
</tr>
<tr>
<td>0.75</td>
<td>4.92</td>
</tr>
<tr>
<td>1.0</td>
<td>5.58</td>
</tr>
<tr>
<td>1.5</td>
<td>6.79</td>
</tr>
<tr>
<td>2.0</td>
<td>6.89</td>
</tr>
<tr>
<td>2.5</td>
<td>7.46</td>
</tr>
<tr>
<td>3.0</td>
<td>7.24</td>
</tr>
<tr>
<td>4.0</td>
<td>7.73</td>
</tr>
<tr>
<td>5.0</td>
<td>7.90</td>
</tr>
<tr>
<td>6.5</td>
<td>8.90</td>
</tr>
<tr>
<td>8.0</td>
<td>8.91</td>
</tr>
</tbody>
</table>

Table 2.6

Comparison between the weight of water insoluble-1% HCl soluble product and the weight of magnesium at 429°.

<table>
<thead>
<tr>
<th>Time (hour)</th>
<th>Volumetric (D) mg. Mg^{2+}</th>
<th>Gravimetric (A-C) mg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>221.9</td>
<td>218.6</td>
</tr>
<tr>
<td>2</td>
<td>215.3</td>
<td>221.4</td>
</tr>
<tr>
<td>3</td>
<td>207.3</td>
<td>206.8</td>
</tr>
<tr>
<td>4</td>
<td>212.3</td>
<td>213.7</td>
</tr>
<tr>
<td>5</td>
<td>208.5</td>
<td>208.7</td>
</tr>
</tbody>
</table>
Determination of amount of potassium dichromate remaining in the reaction products formed at 429°.

The amount of potassium dichromate remaining in the reaction products at 429° is given in Table 2.7 and Fig. 2.3.

<table>
<thead>
<tr>
<th>Time (hour)</th>
<th>Weight of K₂Cr₂O₇ remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g.</td>
</tr>
<tr>
<td>0.5</td>
<td>2.648</td>
</tr>
<tr>
<td>0.75</td>
<td>2.637</td>
</tr>
<tr>
<td>1.0</td>
<td>2.559</td>
</tr>
<tr>
<td>1.5</td>
<td>2.563</td>
</tr>
<tr>
<td>2.0</td>
<td>2.533</td>
</tr>
<tr>
<td>2.5</td>
<td>2.464</td>
</tr>
<tr>
<td>3.0</td>
<td>2.554</td>
</tr>
<tr>
<td>4.0</td>
<td>2.465</td>
</tr>
<tr>
<td>5.0</td>
<td>2.399</td>
</tr>
<tr>
<td>6.5</td>
<td>2.369</td>
</tr>
<tr>
<td>8.0</td>
<td>2.396</td>
</tr>
</tbody>
</table>

The volumetric accuracy for the dichromate determination was better than ± 0.2% and the results were reproducible to within ± 1.5%.

Determination of chromate (VI) formed in the product at 429°.

The reason for determining the chromate (VI) concentration was two-fold. First, it was to attempt to show that the soluble magnesium in the product at
Fig. 2.3. Weight of potassium dichromate remaining.
429° was present as magnesium chromate (VI). Second, a knowledge of the extent of formation of potassium chromate was required.

The results of the gravimetric determination of chromate (VI) are shown in Table 2.8.

**Table 2.8**

Weight of barium chromate precipitated from 25 ml aliquot of solution of water-soluble product (B).

<table>
<thead>
<tr>
<th>Time (hour)</th>
<th>Weight of BaCrO₄ pptd.</th>
<th>Mean variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2611</td>
<td>+1.00</td>
</tr>
<tr>
<td></td>
<td>0.2572</td>
<td>-0.56</td>
</tr>
<tr>
<td></td>
<td>0.2575</td>
<td>-0.44</td>
</tr>
<tr>
<td>1</td>
<td>0.2616 (1)</td>
<td>-3.20</td>
</tr>
<tr>
<td></td>
<td>0.2760 (1)</td>
<td>+2.10</td>
</tr>
<tr>
<td></td>
<td>0.2735 (1)</td>
<td>+1.10</td>
</tr>
<tr>
<td>2</td>
<td>0.2528</td>
<td>-1.40</td>
</tr>
<tr>
<td></td>
<td>0.2585</td>
<td>+0.88</td>
</tr>
<tr>
<td></td>
<td>0.2576</td>
<td>+0.52</td>
</tr>
<tr>
<td>3</td>
<td>0.5312 (2)</td>
<td>+3.22</td>
</tr>
<tr>
<td></td>
<td>0.4952 (2)</td>
<td>-4.00</td>
</tr>
<tr>
<td></td>
<td>0.5189 (2)</td>
<td>+0.78</td>
</tr>
<tr>
<td>4</td>
<td>0.2815</td>
<td>+4.26</td>
</tr>
<tr>
<td></td>
<td>0.2631</td>
<td>-2.59</td>
</tr>
<tr>
<td></td>
<td>0.2655</td>
<td>-1.67</td>
</tr>
<tr>
<td>5</td>
<td>0.2588</td>
<td>+11.51</td>
</tr>
<tr>
<td></td>
<td>0.2194</td>
<td>-5.60</td>
</tr>
<tr>
<td></td>
<td>0.2186</td>
<td>-5.91</td>
</tr>
</tbody>
</table>

(1) : Magnesium removed on ion-exchange resin.
(2) : Precipitated from 50 ml aliquot.

Some of the determinations diverged appreciably outside the experimental accuracy of ± 0.05% of weighing.

The degree of divergence appeared to increase with increase in time.
It was thought that the large divergencies may have been due to co-precipitation of magnesium hydroxide but the repeatability was not improved when magnesium ion was removed on an ion-exchange resin (Zeo-Karb 225, sodium form; Permutit Ltd.).

The weight of chromate (VI) ion in the product at 429° was calculated on the mean of the two closest results and is given in column 6 of Table 2.9.

The weight of chromate (VI) ion in the product at 429° as potassium chromate (column 7, Table 2.9) was calculated from the amount of potassium dichromate that had reacted (column 5, Table 2.9) using the equation

\[ K_2Cr_2O_7 = K_2CrO_4 + CrO_3 \quad \ldots (2.5) \]

The weight of chromate (VI) ion, after subtraction of chromate (VI) ion as potassium chromate, is given in column 8 of Table 2.9.

The ratio of chromate (VI) ion to magnesium ion is given in column 10 of Table 2.9. The ratio was greater than unity which would have been expected for magnesium chromate (VI), MgCrO_4. This may be explained as follows:

The product at 429° contained magnesium chromate (V), Mg_3(CrO_4)_2, which on lixiviation in water
Table 2.9
Cumulative table of results including weight of chromate (VI) not present as \( \text{K}_2\text{Cr}_2\text{O}_7 \) and its ratio to the weight of magnesium ion.

<table>
<thead>
<tr>
<th>Time (hour)</th>
<th>Wt. of BaCrO(_4) pptd. g</th>
<th>Wt. of BaCrO(_4) mean g</th>
<th>Equiv. wt. of Cr(_2\text{O}_7) g. ion x 100</th>
<th>Wt. of Cr(_2\text{O}_7) at 4290 g. ion x 100</th>
<th>Wt. of Cr(_2\text{O}_7) as ( \text{K}_2\text{Cr}_2\text{O}_7 ) g. ion x 100</th>
<th>Wt. of Cr(_2\text{O}_7) not as ( \text{K}_2\text{Cr}_2\text{O}_7 ) (col.6-col.7) g. ion x 100</th>
<th>Wt. of ( \text{Mg}^{2+} ) g. ion x 100</th>
<th>Ratio ( \frac{\text{CrO}_2^-}{\text{Mg}^{2+}} )</th>
<th>Ratio ( \frac{\text{CrO}_2^-}{\text{Mg}^{2+}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2575</td>
<td>0.2573</td>
<td>2.031</td>
<td>0.8699</td>
<td>0.2912</td>
<td>0.1301</td>
<td>0.1611</td>
<td>0.0558</td>
<td>2.887</td>
</tr>
<tr>
<td>2</td>
<td>0.2585</td>
<td>0.2580</td>
<td>2.036</td>
<td>0.8610</td>
<td>0.3140</td>
<td>0.1390</td>
<td>0.1750</td>
<td>0.0689</td>
<td>2.54</td>
</tr>
<tr>
<td>3</td>
<td>0.5312</td>
<td>0.5251</td>
<td>2.073</td>
<td>0.8682</td>
<td>0.3361</td>
<td>0.1318</td>
<td>0.2048</td>
<td>0.0724</td>
<td>2.83</td>
</tr>
<tr>
<td>4</td>
<td>0.2631</td>
<td>0.2643</td>
<td>2.086</td>
<td>0.8378</td>
<td>0.4099</td>
<td>0.1622</td>
<td>0.2477</td>
<td>0.0773</td>
<td>3.20</td>
</tr>
<tr>
<td>5</td>
<td>0.2194</td>
<td>0.2190</td>
<td>1.729</td>
<td>0.8155</td>
<td>0.0957</td>
<td>0.1845</td>
<td>(negative)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>0.2588</td>
<td>0.2588</td>
<td>2.042</td>
<td>0.8155</td>
<td>0.4110</td>
<td>0.1845</td>
<td>0.2265</td>
<td>0.079</td>
<td>2.87</td>
</tr>
</tbody>
</table>

(1) Column is the ratio of column 8 : column 9.
disproportionated according to equation 2.6,

\[ V \quad VI \quad III \]
\[ 3 \text{Cr} = 2 \text{Cr} + \text{Cr} \quad ...(2.6) \]

The overall reaction may be represented by equation 2.7,

\[ 3\text{Mg}_3(\text{Cr}_2\text{O}_4)_2 + 4\text{H}_2\text{O} = \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{CrO}_4 + 9\text{MgO} \quad ... \quad (2.7) \]

If the magnesium oxide formed by reaction 2.7 was precipitated whilst the chromic acid was taken up into solution, then chromate (VI):magnesium ratios greater than unity would be obtained.

Results for estimation of the degree of separation of magnesium chromite.

The possibility that formation of magnesium chromite on the surface of each magnesium particle may determine the reaction rate was investigated.

The hard residue formed in the test tube (section 2.2.2) after 7.5 hours at 450°C was extricated by carefully breaking the test tube. The hard cylindrical core was cleaved at the junction between the surface crust (grey) and the lower layer (orange). The weight of material in each layer which was insoluble in 10% hydrochloric acid was determined. The results are given in Table 2.10.

Each of the acid insoluble residues was
examined by X-ray powder diffraction analysis (see section 2.5) and each residue gave a pattern which corresponded exactly with that given by magnesium chromite.

Table 2.10

<table>
<thead>
<tr>
<th>Layer</th>
<th>Weight</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper</td>
<td>138.5</td>
<td>83.2</td>
</tr>
<tr>
<td>Lower</td>
<td>27.9</td>
<td>16.8</td>
</tr>
</tbody>
</table>

Only one sixth of the magnesium chromite formed was found in the lower layer although its specific gravity (4.5 g.cm$^{-3}$) is greater than that of potassium dichromate (2.69 g.cm$^{-3}$).

2.3 Results of Thermal Analysis.

2.3.1 Thermogravimetry.

Thermogravimetry was carried out using two automatically recording thermobalances. The first was a Stanton model HT-F balance with a sensitivity of 0.2 mg. The TG head was made of Sintox (high density fused alumina) and is shown in Fig. 2.4(a).

Each sample was investigated using the same platinum crucible sample holder (0.5" diameter x 1/8").
Fig. 2.4. Sintonx heads used in thermogravimetry, actual size.
Thermogravimetry was carried out in a flowing argon atmosphere (175 ± 25 ml min⁻¹). The argon (B.O.C. Ltd.) was stated to contain not more than 500 ppm nitrogen. The buoyancy correction for the empty platinum crucible at this flow rate was small and is shown in Fig. 2.5.

The second balance was a Stanton model HT-D thermobalance with a sensitivity of 0.1 mg which had been modified to enable simultaneous DTA-TG to be carried out. The balance incorporated a Sintox head (Fig. 2.4(b)) into which dimpled platinum DTA crucibles (6 mm diameter x 8 mm depth) could be inserted over Pt vs. 13% Rh-Pt thermocouple junctions. The buoyancy correction using this assembly was greater than before and is shown in Fig. 2.6.

Most runs were carried out at a heating rate of approximately 3 °C min⁻¹. In the first balance, the sample temperature was measured by a Pt vs 13% Rh-Pt thermocouple touching the base of the platinum crucible. In the second balance, the temperature was measured at the centre of the sample.

2.3.1(a) Thermogravimetry of the system Mg-K₂Cr₂O₇.

Thermogravimetry was carried out on mixtures of magnesium powder and powdered potassium dichromate.
Fig. 2.5. Buoyancy correction for HT-F thermobalance using TG head (Fig. 2.4),
type a) at an argon flow rate of 175 ± 25 ml/min. (downwards).
Fig. 2.6. Buoyancy correction for TG head (Fig. 2.4., type b) at an argon flow rate of 75 ± 5 ml/min. (downwards).
containing 10%, 50% and 70% of magnesium by weight respectively. The results are shown in Figs. 2.7, 2.8 and 2.9.

The mixture containing 10% Mg gave less than 0.25% weight increase between ambient temperature and 650\(^\circ\). This result was checked by repeating the experiment in argon and also under a flowing oxygen atmosphere of 150 ml/min. (see Fig. 2.10). The mixture gave virtually no weight change under argon but gave 0.85% weight increase between 20\(^\circ\) and 650\(^\circ\) under oxygen.

The mixture containing 50% Mg lost 2 mg between 160\(^\circ\) and 605\(^\circ\) and 1 mg between 605\(^\circ\) and 620\(^\circ\).

The mixture containing 70% Mg gained 7.5 mg in weight between 510\(^\circ\) and 650\(^\circ\).

2.3.1(b) Thermogravimetry of the system MgO-K\(_2\)Cr\(_2\)O\(_7\).

Thermogravimetry was carried out on mixtures of magnesium oxide and potassium dichromate containing 5%, 10% and 50% MgO by weight respectively. The results are shown in Figs. 2.11, 2.12 and 2.13.

The mixture containing 5% MgO gave a gradual weight loss up to 400\(^\circ\) amounting to 1.8 mg. A further weight loss stage began at 570\(^\circ\) which was incomplete at 710\(^\circ\).

The mixture containing 10% MgO lost 2 mg between 290\(^\circ\) and 370\(^\circ\) and began to lose weight at 575\(^\circ\). The stage
Fig. 2.7. Thermogravimetric curve for 503.6 mg 10% Mg( atomised)-K₂Cr₂O₇ at 3°C/min. in dynamic argon atmosphere (175 ml/min.).
Fig. 2.8. Thermogravimetric curve for 253.3 mg 50% Mg(atomised)-\(\text{K}_2\text{Cr}_2\text{O}_7\) at 3°C/min. in dynamic argon atmosphere (175 ml/min.).
Fig. 2.9. Thermogravimetric curve of 258.4 mg 70% Mg(atomised)-K_2Cr_2O_7 at 3°C/min. in dynamic argon atmosphere (175 ml/min.).
Fig. 2.10. Effect of atmosphere on thermogravimetric curves for 10% Mg (atomised).

$K_{2}Cr_{2}O_{7}$ : I, oxygen; 2, argon; 3, argon.
Fig. 2.11. Thermogravimetric curve of 207.3 mg 5% MgO-K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} at 3 C/min.
in dynamic argon atmosphere (175 ml/min.).
Fig. 2.12. Thermogravimetric curve of 221.9 mg 10% MgO-K₂Cr₂O₇ at 3°C/min.

Atmosphere: argon at 175 ml/min.
Fig. 2.13. Thermogravimetric curve for 219.5 mg 50% MgO–K₂Cr₂O₇ at 3°C/min in dynamic argon atmosphere (175 ml/min.).
was not completed at 710°.

The mixture containing 50% magnesium oxide lost weight steadily up to 400°. A further weight loss occurred between 575° and 630°.

The pattern of the TG for the system containing 50% MgO was different from those given by the systems containing 5% and 10% MgO respectively. The difference was probably caused by magnesium oxide in the mixture containing 50% MgO reacting with dichromate almost quantitatively. That this was so is shown in the following calculation:

\[ K_2Cr_2O_7 = K_2CrO_4 + Cr_2O_3 \quad (2.8) \]

Assuming that the net weight loss was associated with the following reaction scheme

\[ Cr_2O_3 + MgO = MgCrO_4 \quad (2.9) \]
\[ MgCrO_4 = \frac{1}{2}MgCr_2O_4 + \frac{1}{2}MgO + \frac{3}{2}O_2 \quad (2.10) \]

then

\[ K_2Cr_2O_7 \equiv Cr_2O_3 \equiv \frac{3}{2}O_2 \quad (2.11) \]

294.19 100.01 24

The sample weight was 219.5 mg which contained 109.75 mg \( K_2Cr_2O_7 \). This weight of dichromate is equivalent to 8.95 mg \( O_2 \). Now, the weight loss in the mixture
containing 50% Mg0 in the range 575° - 630° was 7.4 mg.
The discrepancy between these two values was probably
due to physical contact not being maintained between
potassium dichromate and magnesium oxide during the
final stages of the reaction. On removing the
crucible from the thermobalance, it was observed
that a small amount of solidified melt remained in
the crucible and this was not in contact with the
bulk of the product which was a light orange powder.

The residues produced after TG to 710° of the
mixtures containing 5% and 10% Mg0 were dark red in
colour and hard-packed suggesting that potassium
dichromate was still present to a large extent.

The second weight loss stage commenced at 575°
in the mixtures containing 5%, 10% and 50% Mg0; this
is the temperature at which magnesium chromate (VI)
was found to decompose (see section 2.3.1(c)).

2.3.1(c) Thermogravimetry of magnesium chromate (VI).

Simultaneous DTA-TG was carried out on
magnesium chromate, MgCrO₄.H₂O. The result is
shown in Fig. 2.14.

The hydrated magnesium chromate lost weight
in three stages between 60° and 440° which suggested
that the original material contained the dihydrate
Fig. 2. Th. Simultaneous DTA-TG of 91 mg magnesium chromate monohydrate.

Differential temperature, endothermic

Heating rate: 4°C/min.
Atmosphere: argon at 70 ml/min.

Weight loss (mg)
and the pentahydrate of magnesium chromate in addition to the monohydrate.

Anhydrous magnesium chromate (VI) was formed quantitatively at 430° which was stable up to 575° under argon atmosphere.

The anhydrous magnesium chromate (VI) lost weight in one stage between 575° and 720°. However, the part of the DTA curve corresponding to this weight-loss stage showed two closely spaced endotherms (see Fig. 2.14). This suggested that the decomposition of magnesium chromate (VI) occurred in two stages.

2.3.1(d) **Thermogravimetry of potassium dichromate.**

Thermogravimetry was carried out on potassium dichromate in a flowing argon atmosphere (175 ± 25 ml/min.). The experiment was carried out using the 0.2 mg sensitivity balance and the sample was placed in a dimpled platinum crucible covered by a platinum lid with a small opening for gas to escape. This was done to reduce volatilisation which occurs when potassium dichromate is heated above its melting point 37.

The result is shown in Fig. 2.15. No significant weight changes occurred up to 652°.
Fig. 2.15. Thermogravimetry of 108.6 mg potassium dichromate at 3 °C/min.
in dynamic argon atmosphere (175 ml/min.).
2.3.1(e) Thermogravimetry of magnesium powder.

Thermogravimetry of magnesium powder was not carried out.

2.3.2 Results of differential thermal analysis studies.

2.3.2(a) Preliminary differential thermal analyses.

Apparatus

Because there was a possibility of explosion with some of the mixtures, it was necessary to carry out preliminary investigations to determine the explosive properties of the mixtures of potassium dichromate and magnesium using an inexpensive and easily replaceable DTA sample-cell assembly.

The apparatus used is shown in Fig. 2.16 and was similar to that designed by Rogers. The combined sample and reference cell assembly was made from 5/32" diameter stainless steel rod (Tube Investments Ltd., cutting grade). The sample was loaded into one compartment and weighed. An equal amount of fused alumina was loaded into the other compartment and weighed. The holder was placed into a metal block (B). The block used initially was made of stainless steel but this was changed later to a brass block of the same design to reduce the large temperature drop which occurred between
Fig. 2.16. Preliminary DTA apparatus (actual size).
the furnace wall and sample holder.

The junctions of chromel-alumel thermocouples were pushed into the sample and reference materials and held rigid by tightening the screws (S) against the thermocouple insulators (K). The whole assembly was placed at the centre of a horizontal furnace (F). The thermocouple wires were connected in opposition and the connections placed in a melting ice cold junction. The leads were connected to a Leeds and Northrup Speedomax W potentiometric recorder which had been modified to give two inputs, one of which was switched in for ten seconds every ten minutes to record the temperature of the reference material \( T_r \). The differential temperature \( \Delta T \) was recorded continuously through the other input.

The preliminary experiments were carried out in a static air atmosphere because the apparatus was not readily suited to carrying out analyses under various atmospheres. A heating rate of \( 6^\circ \text{C. min}^{-1} \) was attained using an Ether Transitrol 994/2 temperature programmer.

Since \( T_r \) was only recorded every ten minutes, considerable uncertainty existed in the \( T_r \) record particularly when a reaction occurred.
Preparation of mixtures.

About 5 g of each mixture to be investigated was prepared by weighing the requisite amounts into a dry specimen tube. The tube was corked and shaken to mix the two components thoroughly. Each mixture was stored over silica gel until ready for use.

Preliminary differential thermal analysis of mixtures of magnesium and potassium dichromate.

Differential thermal analysis was carried out using the apparatus just described on mixtures containing 16%, 28.5%, 42% and 64.5% of magnesium (grade 5) by weight. Two DTA runs were carried out for each mixture to assess reproducibility. Essentially similar results were obtained on repetition in each case. The results are shown in Figs. 2.17, 2.18, 2.19 and 2.20.

The mixtures containing 16%, 28.5% and 42% magnesium gave essentially the same DTA pattern consisting of

(i) an endotherm commencing at between 380° and 400° attributable to the fusion of potassium dichromate.

(ii) a broad exotherm between 400° and 600°, the peak temperature of which decreased from 500° to 455° with increase in the percentage of magnesium in the mixture.
Fig. 2.17. DTA of 16\% Mg (grade 5) - K2Cr2O7.
Fig. 2.18. DTA of 28.5% Mg (grade 5(-K$_2$Cr$_2$O$_7$).
Fig. 2.19. DTA of 42% Mg (grade 5) - K₂Cr₂O₇.
Fig. 2.20. DTA of 64.5% Mg (grade 5) - K2Cr2O7.

Sample temperature (°C)

Endothermic

Exothermic

Differentiation temperature (°C)

-909
(iii) an endotherm between $620^\circ$ and $640^\circ$. In one of the 16% magnesium mixtures, the endotherm was resolved into two closely spaced peaks at $629^\circ$ and $633^\circ$.

(iv) an endotherm at $650^\circ$ attributable to fusion of magnesium. The fusion endotherm was not completed in mixtures containing more than 16% magnesium because ignition of the sample occurred during the fusion period of magnesium or before. Temperatures of ignition are listed in Table 2.11.

Table 2.11

<table>
<thead>
<tr>
<th>Magnesium %</th>
<th>Ignition temperature $^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>677</td>
</tr>
<tr>
<td>16</td>
<td>685</td>
</tr>
<tr>
<td>28.5</td>
<td>650</td>
</tr>
<tr>
<td>28.5</td>
<td>654</td>
</tr>
<tr>
<td>42</td>
<td>631</td>
</tr>
<tr>
<td>42</td>
<td>633</td>
</tr>
<tr>
<td>64.5</td>
<td>640</td>
</tr>
<tr>
<td>64.5</td>
<td>652</td>
</tr>
</tbody>
</table>

The mixture containing 64.5% magnesium gave a completely different DTA pattern compared to the other
cases in that the broad exotherm between 400° and 600° and the endotherm between 620° and 640° were missing.

Two very small thermal effects occurred at 315° and 455°. These did not occur in experiments carried out after (see section 2.3.2(b)) using isolated Pt v. 13%Rh–Pt thermocouples and may possibly have been caused by a reaction between the thermocouple junctions and the mixture.

The baseline was found to vary considerably from run to run and it was decided that further investigations be carried out using the more elaborate Stanton DTA assembly up to temperatures just below the ignition temperatures given in Table 2.21.

2.3.2(b) Differential thermal analyses using a Stanton DTA assembly.

Apparatus

The second DTA assembly which was used is shown in Fig. 2.21. It consisted of a vertical nichrome wound tube furnace with a DTA head and base assembly as used in the Stanton DTA apparatus. Analyses could be carried out in dynamic gas atmospheres by means of a top-entry ceramic sheath (C). The DTA head consisted of a stainless steel block with two symmetrically placed wells to receive dimpled platinum crucibles (6mm x 8mm)
Fig. 2.21. Stanton DTA head (actual size).
which were supported on Pt v 13\% Rh-Pt thermocouple beads. However, the platinum crucible was severely attacked after heating with magnesium powder so that some experiments were carried out using stainless steel crucibles of the same diameter but without a dimp. These had considerably lower sensitivity than the platinum crucibles.

Details of experiments carried out with this apparatus are given in Table 2.12.

From this series of experiments the following deductions were made:

(i) Magnesium powder gave no exothermic reactions in the absence of an oxidising atmosphere,

(ii) Potassium dichromate gave no exothermic reactions up to $600^\circ$,

(iii) Mixtures of magnesium powder and potassium dichromate gave an exothermic reaction between $400^\circ$ and $600^\circ$ and endothermic reactions between $620^\circ$ and $640^\circ$. The nature of the reactions was not significantly affected by the atmosphere above the mixture,

(iv) Mixtures of magnesium oxide and potassium dichromate gave no exothermic reactions up to $700^\circ$. 
Experiments carried out with the Stanton DTA apparatus at a heating rate of 6 °C/min.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Material/Mixture</th>
<th>Atmosphere</th>
<th>Weight mg</th>
<th>Crucible Material</th>
<th>Exotherm</th>
<th>Endotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Magnesium (atom)</td>
<td>Argon / 150</td>
<td>74.2</td>
<td>Platinum</td>
<td>-</td>
<td>635</td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>Air / 0.2 torr</td>
<td>88</td>
<td>&quot;</td>
<td>460-540</td>
<td>150-320</td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>Static air</td>
<td>75</td>
<td>&quot;</td>
<td>505-610</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>&quot;</td>
<td>167</td>
<td>Stainless steel</td>
<td>-</td>
<td>398</td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>Argon / 500</td>
<td>130</td>
<td>&quot;</td>
<td>400-600</td>
<td>500</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>Static air</td>
<td>123.6</td>
<td>&quot;</td>
<td>400-600</td>
<td>620-640</td>
</tr>
<tr>
<td>7</td>
<td>16% Mg-K₂Cr₂O₇</td>
<td>&quot;</td>
<td>118.5</td>
<td>&quot;</td>
<td>398</td>
<td>620-640</td>
</tr>
<tr>
<td>8</td>
<td>25% Mg-K₂Cr₂O₇</td>
<td>&quot;</td>
<td>127</td>
<td>&quot;</td>
<td>400-570</td>
<td>620-640</td>
</tr>
<tr>
<td>9</td>
<td>42% Mg-K₂Cr₂O₇</td>
<td>&quot;</td>
<td>110.2</td>
<td>&quot;</td>
<td>398</td>
<td>620-640</td>
</tr>
<tr>
<td>10</td>
<td>30% MgO-K₂Cr₂O₇</td>
<td>&quot;</td>
<td>126.6</td>
<td>&quot;</td>
<td>392;660</td>
<td>-</td>
</tr>
</tbody>
</table>
Fig. 2.22. DTA of 74.2 mg magnesium (atomised) at 6°C/min. in dynamic argon atmosphere (150 ml/min.).
Fig. 2.23. DTA of 88 mg magnesium (atomised) powder at 6°C/min. at 0.2 torr air.
Fig. 2.24. DTA of 75 mg magnesium (atomised) powder at 6°C/min. in static air.
Fig. 2.25. DTA of 166.9 mg K₂Cr₂O₇ at 6°C/min. in static air atmosphere.
Fig. 2.26(a). DTA of 16% Mg-K₂Cr₂O₇ at 6°C/min. in dynamic argon atmosphere (500 ml/min.), 130 mg of mixture containing atomised grade magnesium.
Fig. 2.26(b). DTA of 123.6 mg 16% Mg-K$_2$Cr$_2$O$_7$ at 6°C/min. in static air atmosphere.
Fig. 2.26(c). DTA of 118.5 mg 25% Mg-K₂Cr₂O₇ at 6°C/min. in static air atmosphere.

ignition

495

635-

675-
Fig. 2.26(d). DTA of 127 mg 25% Mg-K$_2$Cr$_2$O$_7$ at 6°C/min. in static air atmosphere.
Fig. 2.27. DTA of 126.6 mg 30% MgO-K₂Cr₂O₇ at 6°C/min. in static air atmosphere.
2.3.2(c) **Differential thermal analysis using the University of Surrey - R.A.R.D.E. apparatus.**

One of the reasons for undertaking the present work was to attempt to use DTA to obtain quantitative data for the reactions occurring in pyrotechnic compositions. This required:

(i) a satisfactory theory of quantitative DTA,
(ii) a suitable system for examination,
(iii) an apparatus capable of giving results to a sufficient degree of accuracy.

The first requirement is covered in section 1.5.1.

The preliminary investigations of the system containing magnesium powder and potassium dichromate which gave the broad exotherm between 400° and 600° suggested that this system was suitable for quantitative analysis.

The third requirement was for a DTA instrument which had the following features:

A high degree of base line stability is essential since an accurate base line is required between the point of commencement and completion of the peak. This can only be done when the base line is sufficiently constant and reproducible between experiments. Ideally, a base line should be obtained in which there is no deviation in $\Delta T$. 


from shorted input conditions when no thermal changes are occurring in the sample. However, in practice deviations from $\Delta T = 0$ occur for the following reasons:

(i) thermal effects such as fusion, phase change, reaction,

(ii) mismatch in the instrument e.g. thermocouples, sample and reference cells, geometry of DTA head relative to furnace,

(iii) changes in thermal conductivity, specific heat and density as the reactants go to products.

This will give rise to a change in the baseline position from prior to a thermal effect of type (i) above to following its completion. The effect has been referred to as 'off-set' (see Fig. 3.1).

Interpretation of small thermal effects which take place slowly e.g. slow oxidation of magnesium (Fig. 2.24) is made difficult when this is superimposed upon effects (ii) and (iii) above. It is therefore necessary to have a DTA instrument in which provision is given for adjusting the position of the DTA head relative to the position of the sheath and furnace as well as for adjusting the position of the thermocouple
beads so that a reproducible base line can be obtained with little or no drift due to effect (ii) above.

The differential thermal analysis apparatus which was designed by Charsley and Redfern in association with the R.A.R.D.E. was used for the bulk of the present work. The apparatus was designed with the objective of carrying out quantitative DTA and incorporated the required features (vide supra).

The University of Surrey - R.A.R.D.E. DTA apparatus.

A full description of the apparatus will be given by Charsley.

The apparatus was assembled as shown in Fig. 2.28. The DTA head (H) was made of inconel and was positioned as accurately as possible in the hot zone. Use was made in later work of a copper DTA head of the same dimensions as the inconel head. The copper head was plated with silver to prevent oxidation.

The head was supported on a hollow ceramic tube of 0.5 mm wall thickness. Dimped platinum crucibles (6 mm diameter x 8 mm depth) were used with the DTA head and were supported on Pt v 13% Rh-Pt thermocouple beads. The thermocouple wires were obtained from Johnson, Matthey & Co. and conformed to BS 1826. Experiments using the copper DTA head were carried out using Platinel II thermocouples.
Fig. 2.28. Differential thermal analysis head used in University of Surrey-R.A.R.D.E. apparatus.
(35% Pd-65% Au v 14% Au-31% Pt-55% Pd) because the sensitivity of the copper head was lower than that of inconel. The wires were 0.008" diameter and were supplied with calibration charts$^{90}$ by Engelhard Industries. The thermocouple beads of Platinel were made by arc-welding against a carbon rod.

The thermocouple wires were insulated in the furnace using 1.55 mm twin bore alumina tube made to a special order of 200 mm length by Degussa in Degussit AL 23 alumina.

The thermocouple wires were connected in opposition and connected to shielded copper wires to take the differential output to a DC amplifier (Rikadenki, model A 10). The thermocouple wire connections to copper wire were maintained in a melting ice cold junction during an experiment. The amplified differential output signal was recorded simultaneously with the output from the sample thermocouple on a Rikadenki three pen potentiometric recorder (model B 31) using two channels. The accuracy of the amplifier was ± 1% with a drift of less than 1 µV after stabilisation. The recorder was calibrated using a Croydon Precision Instruments thermocouple potentiometer (model P4) of 0.01 mV accuracy. This enabled the sample temperature to be measured to an accuracy of 1°C. The recorder amplifiers were adjusted
to give the maximum gain at critical damping which did
not induce oscillation.

Differential thermal analyses were carried out in
static air or in flowing argon where necessary. Argon was
passed into and out of the sheath via tubes.

Experiments were carried out at a heating rate of
$3^\circ C \cdot min^{-1}$.

Differential thermal analysis of the system $Mg-K CrO$.

Mixtures of magnesium powder and potassium dichromate
were investigated using the University of Surrey-R.A.R.D.E.
DTA apparatus in the following sets of experiments:

Set A. Variation of surface area of magnesium.

The percentage of magnesium in the mixture was
kept constant at 10% by weight and the surface
area of the magnesium varied by using the various
grades of magnesium as supplied i.e. grade 3,
grade 5 and atomised grade. The particle size
distribution of grade 3 and atomised grade magnes-
ium is given in Table 2.1. The particle size
distribution of grade 5 magnesium was not
determined as this contained irregularly shaped
particles (see section 2.6). The order of size
of the particles in grade 5 was similar to that
of atomised grade.

The results are shown in Fig. 2.29. The area under
Run 1: mixture containing 24.8 mg Mg (grade 5), 23.4 mg Mg (atomised), 23.7 mg Mg (grade 3).

Fig. 2.29. Effect of surface area of magnesium in DTA of Mg-K2Cr2O7.
the curve using grade 3 magnesium (coarse) was much less than the areas under the curves using grade 5 (fine) and atomised grade (fine) magnesium.

Set B. Variation of % w/w Mg.

The surface area of the magnesium was kept constant by using only grade 3 magnesium and the percentage of magnesium in the mixture was varied. Mixtures containing 2.5%, 7.5%, 10%, 20%, and 40% by weight of magnesium were investigated.

The results are shown in Fig. 2.30. The area under the exotherm (400° - 600°) increased as the percentage of magnesium in the mixture increased.

Set C. Effect of atmosphere.

In this set of experiments, the mixture containing 10% by weight of atomised magnesium was investigated under static air, argon and oxygen atmospheres.

The results are shown in Fig. 2.31. The atmosphere did not exert any appreciable effect on reactions occurring in the mixture.

Set D. Effect of different reference materials.

The mixture was investigated using fused alumina as the reference material. The same material (10% w/w Mg atomised grade) was then investigated using potassium dichromate as the reference material.

The results are shown in Fig. 2.32. The base line 'off-set' varied as follows:
Fig. 2.30. DTA of mixtures Mg(grade 3)-K$_2$Cr$_2$O$_7$:

Run I; 185 mg 40% Mg-K$_2$Cr$_2$O$_7$ containing 74 mg magnesium,

" 2; 241 mg 20% " " " 48 mg "
" 3; 237 mg 10% " " " 23 mg "
" 4; 252 mg 7\% " " " 19 mg "
" 5; 258 mg 2\% " " " 6 mg "

Differential temperature (°C)
Fig. 2.31. Effect of atmosphere on DTA of 10% Mg (atomised) - \( \text{K}_2\text{Cr}_2\text{O}_7 \); Run 1, 244.6 mg in argon (75 ml/min.); Run 2, 158.3 mg in static air; Run 3, 234 mg in oxygen (75 ml/min.).
Run I: 250.3 mg 10% Mg-K$_2$Cr$_2$O$_7$
containing 225 mg K$_2$Cr$_2$O$_7$
versus 228 mg K$_2$Cr$_2$O$_7$.

Run 2: 244.6 mg 10% Mg-K$_2$Cr$_2$O$_7$
versus 150 mg alumina.

Fig. 2.32. Effect of reference material on 'off-set'.
(i) exothermic \(0.25^\circ C\) using alumina reference.

(ii) very slightly exothermic \(0.03^\circ C\) using potassium dichromate reference.

The potassium dichromate in the mixture began to melt before the pure dichromate. These results suggest that the thermal diffusivities of the mixture and reference materials were in the order

\[
10\% \text{Mg-K}_{2}\text{Cr}_{2}O_{7} > K_{2}\text{Cr}_{2}O_{7} \gg \text{Al}_{2}O_{3}.
\]

The high thermal diffusivity of the mixture is one reason why it should be possible to obtain kinetic data for reactions occurring in the mixture by DTA using the Borchardt and Daniels theory (see section 1.5.1) since it means that assumption (i) (p.40) is approximated to.

Set E. Use of DTA head of different material.

In these two experiments, the 10\% w/w Mg-K\(_2\)Cr\(_2\)O\(_7\) was investigated under identical conditions using first the inconel DTA head and then the silver-plated copper head.

The results are shown in Fig. 2.33. The area of the fusion endotherm at 398\(^\circ\) of potassium dichromate using the copper head was about half that obtained when the inconel head was used. The relaxation time from peak \(\Delta T\) was also reduced by a factor of two. These
Run I: 244.6 mg 10% Mg (atomised) - K$_2$Cr$_2$O$_7$ using inconel DTA head.

Run 2: 236.5 mg 10% Mg (atomised) - K$_2$Cr$_2$O$_7$ using silver-plated DTA head.

Fig. 2.33. Effect of thermal diffusivity of head on DTA of 10% Mg-K$_2$Cr$_2$O$_7$. 
reductions occurred when the thermal diffusivity of the material of which the head was made was reduced from that for inconel \((0.13 \text{ cm}^2 \cdot \text{sec}^{-1})\) to that for copper \((1.09 \text{ cm}^2 \cdot \text{sec}^{-1})\).

In addition, the shape of the broad exotherm \((400^\circ - 600^\circ)\) was changed. The exotherm, which using the inconel head was shown to be a single stage, was resolved into three thermal effects using the copper head:

(i) \(420^\circ - 440^\circ\), small exotherm
(ii) \(450^\circ - 560^\circ\), large exotherm
(iii) \(495^\circ - 502^\circ\), small exotherm superimposed on (ii).

The experiment was repeated using the copper head again but replacing the Pt v 13% Rh-Pt thermocouples by the Platinel combination. The heating rate was reduced in an attempt to resolve effects (i) to (iii) above as much as possible. The results are shown in Fig. 2.34.
234 mg 10% Mg (atomised) K2Cr2O7 and 38% silver powder at 1.6°C/min. in dynamic argon atmosphere (75 ml/min.).

Fig. 2.34. DTA of 10% Mg-K2Cr2O7 using copper DTA head and platinal thermocouples.
The following thermal effects occurred:

(iv) $398^\circ - 408^\circ$, endothermic drift,
(v) $408^\circ$, exothermic effect similar to (i) above,
(vi) $408^\circ - 557^\circ$, exotherm similar to (ii) above,
(vii) $447^\circ$, exothermic effect by increase in $\frac{d\Delta T}{dt}$ superimposed on (vi)
(viii) $450^\circ$, plateau ($\frac{d\Delta T}{dt} = 0$) for one minute.

The explanation for these additional thermal effects being shown using the copper head in place of inconel is possibly related to the increase in thermal diffusivity of the head.

The thermal effects with the more 'responsive' copper head may be explained on the basis of the proposed mechanism (see section 3.1).

Differential thermal analysis of the system MgO-K$_2$Cr$_2$O$_7$.

The mixture containing 10% MgO by weight was investigated using the inconel head. A static air atmosphere and a heating rate of 3°C min$^{-1}$ were used. The results are shown in Fig. 2.35.

The only significant thermal effect was an endotherm at $390^\circ$ associated with fusion of potassium dichromate. The following effects also occurred:

$500^\circ - 510^\circ$, small exothermic effect
585° - 675°, endothermic drift.

Infra-red analysis showed that the product at 675° consisted mainly of potassium dichromate.

A mixture containing 40% MgO by weight was investigated under an argon atmosphere (80 ml/min.). The following effects occurred (see Fig. 2.36.):

510° - 535°, erratic exothermic effect
540° - 600°, erratic endothermic effect

Infra-red analysis showed that the product at 650° consisted mainly of chromate (VI) ion and magnesium chromite.

Further differential thermal analyses using the University of Surrey - R.A.R.D.E. DTA apparatus.

Differential thermal analyses using the University of Surrey - R.A.R.D.E. apparatus were carried out on

(i) potassium dichromate
(ii) the system $K_2Cr_2O_7 - CrO_3$
(iii) the system $K_2Cr_2O_7 - K_2CrO_4$.

Details are given in Tables 2.13 and 2.14.

The first DTA on potassium dichromate (run 1, Table 2.13) gave a plateau during the initial stages of fusion (Fig. 2.39 (a)). This was thought to be due to a packing effect of the sample in the crucible.
### Table 2.13

**Differential thermal analyses of potassium dichromate using the University of Surrey-R.A.R.D.E. apparatus**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pretreatment</th>
<th>Weight mg</th>
<th>Atmosphere</th>
<th>Mesh size μm</th>
<th>Heating rate °C/min.</th>
<th>Block</th>
<th>Run</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_2Cr_2O_7$</td>
<td>see sect. 2.1</td>
<td>135.2</td>
<td>static air</td>
<td>45-53</td>
<td>3</td>
<td>inconel</td>
<td>1</td>
<td>Fig.2.39(a)</td>
</tr>
<tr>
<td>&quot;</td>
<td>premelted</td>
<td>&quot;</td>
<td>&quot;</td>
<td>solid mass</td>
<td>3</td>
<td>&quot;</td>
<td>2</td>
<td>Fig.2.39(b)</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>3</td>
<td>&quot;</td>
<td>3</td>
<td>Fig.2.39(c)</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>204.9</td>
<td>&quot;</td>
<td>&quot;</td>
<td>3</td>
<td>&quot;</td>
<td>4</td>
<td>Fig.2.40</td>
</tr>
<tr>
<td>&quot;</td>
<td>see sect. 2.1</td>
<td>246.0</td>
<td>Argon at 75 ml/min.</td>
<td>43</td>
<td>3</td>
<td>&quot;</td>
<td>5</td>
<td>Fig.2.41</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>200.0</td>
<td>Oxygen at 75 ml/min.</td>
<td>43</td>
<td>3</td>
<td>&quot;</td>
<td>6</td>
<td>Fig.2.42</td>
</tr>
<tr>
<td>&quot;</td>
<td>premelted</td>
<td>205.2</td>
<td>Static air</td>
<td>solid mass</td>
<td>1.4</td>
<td>copper</td>
<td>7</td>
<td>Fig.2.43</td>
</tr>
</tbody>
</table>
Table 2.14

Differential thermal analyses of the systems potassium dichromate-chromium (VI) oxide and potassium dichromate-potassium chromate by University of Surrey-R.A.R.D.E. apparatus.

<table>
<thead>
<tr>
<th>Sample w/w</th>
<th>Pretreatment</th>
<th>Weight mg</th>
<th>Atmosphere</th>
<th>Heating rate, °C/min.</th>
<th>Block</th>
<th>Run</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂Cr₂O₇ - 0.7% CrO₃</td>
<td>AR. K₂Cr₂O₇ recrystallised, CrO₃ sublimed</td>
<td>231.9</td>
<td>Static air</td>
<td>3</td>
<td>Inconel</td>
<td>1</td>
<td>Fig. 2.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>205.2</td>
<td>&quot; &quot;</td>
<td>3</td>
<td>&quot; &quot;</td>
<td>2</td>
<td>Fig. 2.45</td>
</tr>
<tr>
<td>K₂Cr₂O₇ - 30% CrO₃</td>
<td>(section 2.1)</td>
<td>261.2</td>
<td>&quot; &quot;</td>
<td>3</td>
<td>&quot; &quot;</td>
<td>3</td>
<td>Fig. 2.46(a)</td>
</tr>
<tr>
<td>K₂Cr₂O₇ - 10% K₂CrO₄</td>
<td>( &quot; &quot; )</td>
<td>257.4</td>
<td>&quot; &quot;</td>
<td>3</td>
<td>&quot; &quot;</td>
<td>4</td>
<td>Fig. 2.46(b)</td>
</tr>
</tbody>
</table>
Fig. 2.35. DTA of I56.5 mg I0% MgO-K2Cr2O7 at 3°/min. in static air atmosphere.

Temperature (°C)
Fig. 2.36. DTA of 150 mg 40% MgO-K₂Cr₂O₇ at 3°C/min. in dynamic argon atmosphere.
Fig. 2.39. Effect of sample density (bulk) on shape of fusion endotherm in DTA of 135.2 mg \( \text{K}_2\text{Cr}_2\text{O}_7 \) at 3°C/min. in static air: (a) hard-packed powder (45-53 μ), (b) sample from run (a) after fusion and cooling to solidification, (c) sample from run (b).
The sample from Run 1 was allowed to cool and completely solidify. It was then reheated (Run 2, Fig. 2.39 (b)). The plateau did not occur a second time. The amplitude and the 'off-set' of the fusion endotherm were both less than those given in Run 1.

The sample from Run 2 was allowed to cool and solidify and was again reheated (Run 3, Fig. 2.39 (c)). The shape of the fusion endotherm was similar to that given in Run 2.

On removing the sample from the apparatus it was found that the dimp of the crucible was not completely covered by the sample.

The experiment was repeated after having premelted a sufficient amount of potassium dichromate (204.9 mg) in the crucible to ensure that the dimp would not be uncovered during the DTA run. The result is shown in Fig. 2.40. A plateau occurred on the fusion endotherm.

Differential thermal analysis of potassium dichromate was carried out under argon to investigate the effect of atmosphere (Fig. 2.41). The curve began to behave erratically at 565°C. It was found that considerable volatilisation of potassium dichromate had occurred during the experiment. Differential thermal analysis was also carried out under oxygen (Fig. 2.42). After the fusion endotherm had occurred, no
Fig. 2.40. Fusion endotherm in DTA of pre-melted $K_2Cr_2O_7$
$(204.9 \text{ mg})$ at $3^\circ C/\text{min.}$ in static air atmosphere.
Fig. 2.41. DTA of 246 mg K$_2$Cr$_2$O$_7$ at 3°C/min. in dynamic argon atmosphere (75 ml/min.).
Fig. 2. DTA of 200 mg K$_2$Cr$_2$O$_7$ at 3°C/min, in dynamic oxygen atmosphere (75 ml/min)
Thermal effects occurred up to $750^\circ$ except for a slight endothermic drift commencing at $500^\circ$.

It was thought that the 'plateau effect' ($390^\circ \text{ to } 391^\circ$, Fig. 2.40) may have been associated with the dissociation of the dichromate ion during fusion which had been suggested by Sutra$^{16}$. If the dissociation occurred according to equation (15) (section 1.2.1), then admixing either potassium chromate or chromium (VI) oxide to potassium dichromate should suppress the dissociation and the 'plateau effect' would not be given. To investigate this further, the following analyses were carried out:

(i) DTA of potassium dichromate (recrystallized AnalAr grade), which had been premelted, using the more responsive copper DTA head, platinum thermocouples and a lower heating rate. The result is shown in Fig. 2.43. The 'plateau effect' was given.

(ii) DTA of mixtures of potassium dichromate and chromium (VI) oxide. The result for a mixture containing $0.7\% \text{ CrO}_3$ by weight is shown in Fig. 2.44. No 'plateau effect' was given. The result for a mixture containing $30\% \text{ CrO}_3$ by weight is shown in Fig. 2.45. The shape of the fusion endotherm of potassium dichromate
Fig. 2.43. Plateau effect at start of fusion in DTA of 205.2 mg K$_2$Cr$_2$O$_7$ at 1.4 °C/min.
Fig. 2. DTA of 231.9 mg 0.7% \( \text{CrO}_3 - \text{K}_2\text{Cr}_2\text{O}_7 \) at 3°C/min. in static air.
Fig. 2.45. DTA of 205.2 mg 30% CrO₃-K₂Cr₂O₇ at 3°C/min. in static air.
was considerably transformed due to the presence of chromium (VI) oxide.

(iii) DTA of mixtures of potassium dichromate and potassium chromate. The results for mixtures containing 10% and 40% K₂CrO₄ by weight are shown in Fig. 2.46. Neither mixture gave a 'plateau effect'.

The 'plateau effect' was not given in any of the DTA of the Mg$_2$K₂Cr₂O₇ mixtures.

Cooling, reheating and isothermal curves by differential thermal analysis.

In order to investigate particular effects, DTA was carried out on Mg$_2$K₂Cr₂O₇ mixtures in the following ways:

(i) under cooling conditions

(ii) reheating conditions

(iii) isothermal conditions.

Details of these experiments are given in Table 2.15.

The DTA on 248.5 mg 10% Mg (grade 5)-K₂Cr₂O₇ (Fig. 2.29, Run 1) gave an exotherm in the range 407° - 607° followed by an endotherm at 650°. This showed that magnesium was still present in the
Run (a): 261.2 mg 10% $K_2CrO_4$-$K_2Cr_2O_7$
Run (b): 257.4 mg 40% $K_2CrO_4$-$K_2Cr_2O_7$

Fig. 2.46. DTA of $K_2CrO_4$-$K_2Cr_2O_7$ systems.
Table 2.15

Differential thermal analyses of $10\% \text{Mg-K}_2\text{Cr}_2\text{O}_7$ under cooling, reheating and isothermal conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pretreatment</th>
<th>Weight (mg)</th>
<th>Atmosphere</th>
<th>Heating rate $^\circ\text{C/min.}$</th>
<th>Apparatus</th>
<th>Run</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10% \text{Mg (5)-K}_2\text{Cr}_2\text{O}_7$</td>
<td>as in Run 1, Fig. 2.29.</td>
<td>248.5</td>
<td>Static air</td>
<td>3</td>
<td>U. of S. - R.A.R.D.E.</td>
<td>1</td>
<td>Fig. 2.47(a)</td>
</tr>
<tr>
<td>$10% \text{Mg (atomised) - K}_2\text{Cr}_2\text{O}_7$</td>
<td>as in Run 1, Fig. 2.32</td>
<td>250.3</td>
<td>Argon at 80 ml/min.</td>
<td>3</td>
<td>&quot;</td>
<td>2</td>
<td>Fig. 2.47(b)</td>
</tr>
<tr>
<td>&quot;</td>
<td>None</td>
<td>269.7</td>
<td>&quot;</td>
<td>3</td>
<td>&quot;</td>
<td>3</td>
<td>Fig. 2.47(c)</td>
</tr>
<tr>
<td>&quot;</td>
<td>as in Run 3, Fig. 2.47 (c).</td>
<td>269.7</td>
<td>&quot;</td>
<td>3</td>
<td>&quot;</td>
<td>4</td>
<td>Fig. 2.47(d)</td>
</tr>
</tbody>
</table>

The apparatus was used with the inconel head and Pt v 13% Rh-Pt thermocouples.
mixture after the process which gave rise to the
exotherm which was completed at 607°. The sample
was allowed to cool from 652° to 255°. The only
thermal effects which were given were exotherms at
650° and 350°, the latter attributable to the
solidification of supercooled potassium dichromate.
The sample was reheated at 3 °C/min. from 255° to
480°. The result is shown in Fig. 2.47 (a). The
fusion endotherm of potassium dichromate was given
at 398°, although the amplitude was less than in
the first heating cycle (Fig. 2.29, Run 1). However,
the exotherm, which was previously given between
407° and 607° was not given a second time.

This experiment showed that the process giving
rise to the exotherm (407° - 607°) was irreversible.

The DTA on 250.3 mg 10% Mg (atomised)-K$_2$Cr$_2$O$_7$
at 3 °C/min. under argon atmosphere gave two
endotherms (607° - 620°, 620° - 630°) on heating to
632°. On cooling from 632° at 3 °C/min., two exotherms
were given at 614° - 603° and 600° - 580° with the
suggestion of a third in between these two. The
result is shown in Fig. 2.47 (b).

Differential thermal analysis was carried out
on 269.7 mg 10% Mg (atomised)-K$_2$Cr$_2$O$_7$ at 3 °C/min.
but allowing the temperature of the mixture to
Fig. 2.47(a). DTA of product of DTA heated to 650° of 10% Mg-K₂Cr₂O₇.
Fig. 2.47(b). Heating and cooling in DTA of 10% Mg-K₂Cr₂O₇.
remain constant for limited periods of time. This was done by switching off the temperature controller. The differential temperature was measured during isothermal periods at 427°, 465°, 502°, 545° and 590°. The atmosphere was flowing argon (80 ml/min.). The result is shown in Fig. 2.47 (c).

Very little exothermic reaction occurred up to 427°. On raising the temperature, a large exotherm commenced immediately which continued when the temperature of the sample was constant at 465° for three minutes. On raising the temperature again, the magnitude of the differential temperature increased and the exothermic reaction continued isothermally for 2.5 minutes at 502°. After the differential temperature had levelled at the 'off-set' position, the temperature was raised and held at 545°. This gave a small exothermic effect but on raising the temperature to 590° essentially no further exothermic effect was given.

This experiment showed that the main part of the exothermic reaction, which under dynamic heating conditions is given in the approximate range 400° - 600°, is given between 427° and 500° when the heating is interrupted.
Fig. 2.47(c). Heat generated under isothermal conditions in DTA of 10% Mg-K₂Cr₂O₇.
The sample from the previous experiment (Fig. 2.47 (c)) was heated finally to 630° at 3 °C/min. under argon and allowed to cool at 23 °C/min. to 495°. The result is shown in Fig. 2.47 (d).

Two endotherms were given during the heating period at 607° - 620° and 620° - 630° but three exotherms were given in the same temperature range during cooling at 615° - 605°, 605° - 585°, 585° - 550°.

These results suggest that the complex reactions in the ranges 607° - 630° (endothermic, heating) and 615° - 550° (exothermic, cooling) may be associated with unit changes in the oxidation state of chromium as follows:

<table>
<thead>
<tr>
<th>Heating temperature</th>
<th>change in oxidation state</th>
<th>Cooling temperature</th>
<th>change in oxidation state</th>
</tr>
</thead>
<tbody>
<tr>
<td>607° - 620°</td>
<td>Cr(VI) to Cr(V) or Cr(IV)</td>
<td>615° - 605°</td>
<td>Cr(III) to Cr(IV)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>605° - 585°</td>
<td>Cr(IV) to Cr(V)</td>
</tr>
<tr>
<td>620° - 630°</td>
<td>Cr(V) or Cr(IV) to Cr(III)</td>
<td>585° - 550°</td>
<td>Cr(V) to Cr(VI)</td>
</tr>
</tbody>
</table>

Differential thermal analysis of magnesium chromate.

Differential thermal analysis was carried out on magnesium chromate monohydrate. The result is shown in Fig. 2.48. Endotherms occurred at 607° - 620° and 620° - 677°.
Fig. 2.47(d). DTA curve of 10% Mg-K₂Cr₂O₇ for heating and rapid cooling (23°C/min.).
Fig. 2.47(e). DTA curve of 10% Mg-K₂Cr₂O₇ after reheating (3°C/min) and cooling (3°C/min).
Weight of MgCrO$_4$$\cdot$H$_2$O: 134 mg
Atmosphere: Argon at 75 ml/min.
Heating rate: 1.4 °C/min.

Fig. 2.48. DTA curve for magnesium chromate(VI) between 580° and 680°.
The DTA curve over this temperature range resembled those obtained for the Mg-K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} mixtures (low Mg content) in the same range.

2.3.2(d) Quantitative differential thermal analysis.

In this section the results are given of attempts to obtain quantitative data for the reactions in the system Mg-K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}. Two methods were used:

(i) a simulated Borchardt and Daniels method using a stirred molten lead bath with stirred sample and reference systems.

(ii) application of the Borchardt and Daniels theory to the DTA curves obtained from the Mg-K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} system.

Differential thermal analysis of the stirred system Mg-K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} (liquid) using a stirred thermal source.

Apparatus

The lead bath (section 2.4) was modified to take the sample and reference assembly shown in Fig. 2.49. The sample and reference tubes were made from 0.06" wall thickness stainless steel tube (Tube Investments Ltd., 18/8) of 1" diameter and 9" length. Stainless steel caps (0.06" thick) were welded to one end of each tube.
Fig. 2.49. Lead bath adapted for stirred DTA.

Scale: 0.4"=1".
The tubes fitted tightly into the brass plate of the stirrer gear assembly. The stirrers were made of 0.1" pyrex glass rod flattened to form paddles (0.07" x 0.25" x 2"). The speed of rotation was one revolution/second. Shielded chromel-alumel thermocouple wires were passed through steel guides (6" x 0.25") into the sample and reference liquids. The reference was potassium dichromate.

Method.

Potassium dichromate (AnalaR) was weighed into each steel tube to give a depth of molten dichromate of 2.5". This required 27.7 g of potassium dichromate. The thermocouple junctions were adjusted to reach 1.25" below the surface of the molten dichromate in each tube.

The temperature of the lead bath was maintained at 490° ± 1° and the temperature of the molten dichromate in each tube allowed to reach equilibrium. The differential temperature of the stirred samples was plotted for 45 minutes (Fig. 2.50). The base line gave a rhythmic oscillation due to stirring of less than ±0.02° but the drift over 45 minutes from the mean position was indetectable.

Magnesium powder (0.546 g) was inserted into one tube and the temperature of the sample adjusted to 405°. With stirring, ΔT was plotted for 30 minutes (Fig. 2.50 (b)). The bath temperature was raised at 1.4°/min to 550°. The DTA obtained is shown in Fig. 2.50 (c).
Fig. 2.50. Differential output at 490° between stirred samples of K₂Cr₂O₇ (27.7 g) using apparatus shown in Fig. 2.49.
Fig. 2.50. Stirred DTA of 1.9% Mg (atomised) - K₂Cr₂O₇.
The amplitude of the oscillations increased as the temperature increased and at 550° equalled ± 3° giving an exothermic differential temperature of 20° ± 3°.

The method was discontinued in favour of the unstirred method.

Application of Borchardt and Daniels theory to the DTA curves of the unstirred system Mg-K₂Cr₂O₇.

The exothermic curves in the range 400° - 600° in the DTA of unstirred systems Mg-K₂Cr₂O₇ were smooth and showed no oscillation as was observed in the experiments reported in the previous section.

The values which must be measured from the DTA curve to apply the Borchardt and Daniels theory are:

(i) The total area (A) under a complete curve
(ii) the differential temperature (ΔT) at a given instant
(iii) the partial area (a) under the curve from the start of the reaction.

To a first approximation, the base line under the curve was taken as the straight line AB in Fig. 3.1. so that A, ΔT and a could be measured.

Measurements were made from the 400° - 600° curve
in Fig. 2.18 obtained using the apparatus shown in
Fig. 2.16 and substituted in the simplified Borchardt
and Daniels expression (2.12) for the specific
velocity constant,

\[ k = \frac{\Delta T}{(A-a)^x} \] (2.12)

where \( x \) is the order of reaction.

The results for different values of \( x \) are
shown in Fig. 2.51. The most linear plot was
given when \( x \) was equal to 2.

This analysis warranted further investigation
of the curves obtained using the Stanton DTA apparatus
(section 2.3.2 (b)). The 400° - 600° exothermic curves
in Figs. 2.26 (c) and 2.26 (b) were analysed for
values of \( x = \frac{1}{2}, 1, 1\frac{1}{2}, 2 \) and 3. The results are
shown in Figs. 2.52 and 2.53 respectively. This
time, the plots for \( x = 2 \) were not strictly linear.

Further analyses were carried out using the
University of Surrey-R.A.R.D.E. DTA apparatus in a
manner by which errors in measuring \( A, \Delta T \) and \( a \)
were minimised. This was done by using the fastest
chart speed available on the recorder (120 cm/min.)
and adjusting the amplification so that the curve
spread over most of the chart width of 10 inches.
Measurements were made from the 400° - 600° exotherm
shown in Fig. 2.54 against the base line AB. Plots
Fig. 2.51. Plot of $\log k = \frac{\Delta T}{(A-a)^x} v I/T$ for $400^\circ -600^\circ$ exotherm in Fig. 2.18.
Fig. 2.5: Preliminary method of analysing exotherm in Fig. 2.29, (Run 2).
Fig. 2.55. Plot of $\log_{10} k = T/(A-a)^x$ for 400° - 600° exotherm in Fig. 2.54.
when $x = \frac{1}{2}, 1, 1\frac{1}{2}, 2$ and 3 in equation 2.12 are shown in Fig. 2.55. The most linear plot was obtained when $x = 2$.

Further kinetic analysis of other curves was not carried for the reasons given in section 3.

2.4 Results of time-to-ignition experiments.

Apparatus

The apparatus used is shown in Fig. 2.56. The molten lead bath (approximately 50 lb.) was stirred and the temperature maintained to $\pm 1^\circ$ using an AEI resistance thermometer temperature controller (type RT3/R Mark II with PRT4 thermometer). Serious oxidation of the lead was overcome by:

(i) inserting a stainless steel guide through which the stirrer shaft was mounted below the surface of the lead,

(ii) passing nitrogen over the surface,

(iii) covering the lead surface with graphite powder which was also used to lubricate the stirrer guide.

The ignition time was determined electrically using the circuit shown in Fig. 2.57. The accuracy of the timer (Advance, model SCI) was 0.01 sec. plus mains stability. It was started by contact between the sample holder (copper tube) and the lead bath. Light from the ignition process decreased the resistance of the cadmium sulphide photocell (Proops Bros. Ltd., Cat. No. S-193) allowing current to
Photocell to vacuum

Sliding stop

Motor

Fixed stop

Stirrer

Control heater

Sample tube

N₂

Main heater winding

Molten lead

Vermiculite insulation

Fig. 2.56. Lead bath adapted for time-to-ignition.
Fig. 2.57. Electronic method for measuring ignition time.
pass through the valve V (Sylvania, type 6V6) to actuate the relay and stop the timer. The ignition times were checked manually using a stop-watch (Admiralty surplus) reading to 0.02 second. Readings agreed to within ± 0.08 second. The bath temperature was measured to within ±0.1° using a Pt v 13% Rh-Pt thermocouple and potentiometer (Cropico, model P4).

Mixtures containing atomised magnesium and potassium dichromate (sieved to pass B.S.S. 350) were prepared containing 40.8% Mg and 48.4% Mg w/w. The samples were mixed by shaking and stored over silica gel before use.

A sample of a mixture was weighed to 150 ± 10 mg in a copper blasting cap (6, mm dia. x 85 mm), supplied by R.A.R.D.E., and the tube was tapped to settle the mixture at the bottom of the tube. The tube was then pushed into the tight fitting flange F (Fig. 2.56). The tube was rapidly inserted into the lead bath to a depth of 75 mm.

The procedure detailed above was carried out in triplicate at a given temperature for each mixture. Measurements were made at temperatures in the range 430° - 560°.

Experiments were also carried out on samples of 50 ± 5 mg to investigate the effect of mass.
Experiments were also carried out at a pressure of 100 mm Hg of air to investigate the effect of atmosphere.

The results are given in Tables 2.16, 2.17 and 2.18 and are plotted in Figs. 2.58 and 2.59.

The following effects occurred:

(i) the ignition time decreased with decrease in mass,
(ii) the ignition time increased with increase in the amount of magnesium in the system,
(iii) the ignition time increased with decrease in atmospheric pressure.

For experiments carried out on 48.4% \( \text{Mg-K}_2\text{Cr}_2\text{O}_7 \) at normal pressure, a first order polynomial least squares fit gave a heat of activation of 9.564 kcal/mole with 0.006 standard deviation.

However, experiments carried out at temperatures below 450° did not always result in ignition and those that did result in ignition gave values which tended to diverge from the least squares plot. A first order least squares fit was recalculated for experiments carried out above 450° where ignition occurred in every case. This gave a heat of activation of 9.105 kcal/mole with 0.005 standard deviation.

The heat of activation for experiments carried out at 100 mm Hg of air was calculated to be 10.4 kcal/mole with 0.008 standard deviation.
Table 2.16

Results of time-to-ignition experiments on $48.4\% \text{Mg-K}_2\text{Cr}_2\text{O}_7$:
atmospheric pressure.

<table>
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<th>Weight mg</th>
<th>Temperature $^\circ\text{C}$</th>
<th>Time sec.</th>
<th>Weight mg</th>
<th>Temperature $^\circ\text{C}$</th>
<th>Time sec.</th>
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continued overleaf...
Table 2.16, continued

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<th>Time sec.</th>
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</table>

DNI: Did not ignite.

Table 2.17

Results of time-to-ignition experiments on 40.8% Mg-K_2Cr_2O_7 at atmospheric pressure.

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<th>Weight mg</th>
<th>Temperature °C</th>
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<th>Time sec.</th>
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</tr>
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<td>11.37</td>
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<td></td>
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<td>147.1</td>
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<td>DNI did not ignite.</td>
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</table>

DNI: Did not ignite.
Table 2.18
Results of time-to-ignition experiments on 48.0% Mg$_2$Cr$_2$O$_7$

at reduced atmospheric pressures.

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<th>Time sec.</th>
<th>Pressure mm Hg air.</th>
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<td>100-90</td>
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</table>
Fig. 2.58. Plot of $\log(\text{time})$ vs $\frac{1}{T}$ for ignition of mixtures at 760 mm air pressure.

Mixture:
1. $40.8\%$ Mg-$K_2Cr_2O_7$
2. $48.4\%$ Mg-$K_2Cr_2O_7$
Fig. 2.59. Plot of log(time) vs I/T for ignition of 48% Mg-K$_2$Cr$_2$O$_7$ at 100 torr.
2.5 Results of X-ray diffraction analysis.

The nature of the products formed in DTA, in TG and in isothermal experiments in the range 400° - 660° was investigated by X-ray powder diffraction analysis.

In each case samples were obtained by removing the furnace during an experiment and allowing the sample to cool in a desiccator over silica gel.

The samples were mounted on glass fibres and irradiated [Cu(Kα), weighted mean \( \lambda = 1.5418 \, \text{Å} \)] for between 4 to 6 hours.

The diffraction patterns were recorded photographically and measured using a travelling microscope. Weaker lines were measured using a Solus Schall Cu(Kα) direct reading Å scale. The intensity of each line was estimated visually.

2.5.1 X-ray diffraction patterns of hydrochloric acid insoluble products of DTA, TG and isothermal experiments on the system Mg-K\(_2\)Cr\(_2\)O\(_7\).

The product of DTA (Fig. 2.29) to 650° on a 20% Mg (grade 3)-K\(_2\)Cr\(_2\)O\(_7\) mixture was treated with water, boiled and filtered. The insoluble residue was further treated with 10% HCl until no further effervescence occurred, filtered, washed and dried. The lattice
The pattern of the lines was similar to that quoted for magnesium chromite in the University of Surrey Crystallography Department X-ray catalogue. The very weak line at 2.94 Å was also distinguishable but there were no lines to indicate the presence of chromium (III) oxide.

The DTA product from a 40% MgO - 60% K2Cr2O7 mixture heated to 652°C (Fig. 2.36) was similarly treated. The result is shown in Table 2.19. The pattern was also similar to that quoted for magnesium chromite.

The product from the isothermal experiment (section 2.2.2.) at 429°C for 5 hours (which had been extracted in boiling water, washed with 1% HCl, washed and dried) was investigated by X-ray analysis. The pattern obtained (Fig. 2.19) was similar to that quoted for magnesium chromite.

2.5.2. X-ray diffraction patterns of untreated products of DTA and TG on the system Mg-K2Cr2O7.

The product from TG to 560°C on 10% Mg-K2Cr2O7 (Fig. 2.7) was analysed by X-ray diffraction and gave the pattern shown in Table 2.20.

The probable assignment for each line is given in column 3 of Table 2.20. The presence of α-K2CrO4 was
X-ray diffraction patterns of acid (dilute HCl)-insoluble residues of products of DTA and isothermal experiments.

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<th>5 hour isothermal experiment at 429°</th>
<th>Lattice spacings and intensities of magnesium chromite prepared at NBS</th>
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<td>DTA of 20%Mg-K₂Cr₂O₇ to 650°</td>
<td>DTA of 40%MgO-K₂Cr₂O₇ to 652°</td>
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</tr>
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<td>d Å (1) Intensity</td>
<td>d Å (2) Intensity</td>
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<td>1.1666 9</td>
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(1) measured with travelling microscope
(2) measured with Solus Schall d scale.
Table 2.20

X-ray diffraction pattern of untreated product of TG to 560°C of 10% Mg-K₂Cr₂O₇.

<table>
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<th>Intensity</th>
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<th>(85)</th>
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<td>strong</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.19</td>
<td>weak</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.06</td>
<td>&quot;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.96</td>
<td>strong</td>
<td>Mg, 2.780</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.78</td>
<td>weak</td>
<td>Mg, 2.606</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.60</td>
<td>&quot;</td>
<td>Mg, 2.453</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.28</td>
<td>strong</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.148</td>
<td>v. weak</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.085</td>
<td>&quot;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.604</td>
<td>weak</td>
<td>Mg, 1.605</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.474</td>
<td>strong</td>
<td>Mg, 1.473</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

MgCr₂O₄, 4.30, 4.27
K₂Cr₂O₇, 3.68
K₂Cr₂O₇, 3.49
K₂Cr₂O₇, 3.32
α-K₂Cr₂O₇, 3.078
K₂Cr₂O₇, 2.99, 2.96
" , 2.60
" , 2.286

?
shown. There were no lines which could be assigned to chromium (III) oxide (see Table 2.21) or to magnesium oxide (see Table 2.22).

The product from TG to $455^\circ$ on 10% Mg-K$_2$Cr$_2$O$_7$ was investigated by X-ray analysis and gave the pattern shown in Table 2.23.

The strongest line in the pattern for magnesium at 2.510 Å could not be distinguished. Lines could be assigned to potassium dichromate and magnesium (see Tables 2.24 and 2.25). The remaining lines co-incided very closely with those in the X-ray diffraction pattern obtained for calcium chromate (V), $\text{Ca}_3(\text{CrO}_4)_2$. It was considered that this indicated the presence of magnesium chromate (V), $\text{Mg}_3(\text{CrO}_4)_2$ and an attempt was made to show that magnesium chromate (V) is formed in the decomposition of magnesium chromate (VI).

2.5.3. X-ray pattern of TG and DTA carried out in argon on magnesium chromate (VI).

The product from TG to $540^\circ$ on magnesium chromate monohydrate (Fig. 2.14) gave the X-ray pattern shown in Table 2.26, column 1.

The product from DTA to $612^\circ$ on magnesium chromate monohydrate (Fig. 2.48), which had completed only the first endotherm, gave the X-ray pattern shown in Table 2.26, column 2.
### Table 2.21

X-ray diffraction pattern of chromium (III) oxide

<table>
<thead>
<tr>
<th>d, Å</th>
<th>1</th>
<th>d, Å</th>
<th>1</th>
<th>d, Å</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.633</td>
<td>74</td>
<td>2.176</td>
<td>38</td>
<td>1.4314</td>
<td>40</td>
</tr>
<tr>
<td>2.666</td>
<td>100</td>
<td>1.8156</td>
<td>39</td>
<td>1.239</td>
<td>17</td>
</tr>
<tr>
<td>2.480</td>
<td>96</td>
<td>1.672</td>
<td>90</td>
<td>1.1731</td>
<td>14</td>
</tr>
</tbody>
</table>

### Table 2.22

X-ray diffraction pattern of magnesium oxide

<table>
<thead>
<tr>
<th>d, Å</th>
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<th>d, Å</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.431</td>
<td>10</td>
<td>0.9419</td>
<td>17</td>
</tr>
<tr>
<td>2.106</td>
<td>100</td>
<td>0.860</td>
<td>15</td>
</tr>
<tr>
<td>1.216</td>
<td>12</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.23

X-ray diffraction pattern of untreated product of TG of 10% Mg-K$_2$Cr$_2$O$_7$ to 455°.

<table>
<thead>
<tr>
<th>d, Å</th>
<th>Angle 2°</th>
<th>Intensity</th>
<th>Inference</th>
<th>d, Å</th>
<th>2θ°</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.4</td>
<td></td>
<td>weak</td>
<td></td>
<td></td>
<td>?</td>
</tr>
<tr>
<td>4.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>?</td>
</tr>
<tr>
<td>3.68</td>
<td>24.1</td>
<td>strong</td>
<td>K$_2$Cr$_2$O$_7$, 3.68</td>
<td></td>
<td>Mg$_3$(CrO$_4$)$_2$, 25.3</td>
</tr>
<tr>
<td>3.48</td>
<td></td>
<td>weak</td>
<td></td>
<td></td>
<td>?</td>
</tr>
<tr>
<td>3.30</td>
<td></td>
<td>strong</td>
<td></td>
<td></td>
<td>?</td>
</tr>
<tr>
<td>3.28</td>
<td>27.0</td>
<td></td>
<td></td>
<td></td>
<td>27.0</td>
</tr>
<tr>
<td>3.05</td>
<td>29.3</td>
<td>weak</td>
<td></td>
<td></td>
<td>28.8</td>
</tr>
<tr>
<td>2.96</td>
<td>30.2</td>
<td>strong</td>
<td>Mg, 2.78</td>
<td></td>
<td>30.3</td>
</tr>
<tr>
<td>2.87</td>
<td>31.2</td>
<td>weak</td>
<td>Mg, 2.606</td>
<td></td>
<td>31.5</td>
</tr>
<tr>
<td>2.78</td>
<td>33.4</td>
<td>v. weak</td>
<td>Mg, 2.453</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.68</td>
<td></td>
<td>weak</td>
<td></td>
<td></td>
<td>39.0</td>
</tr>
<tr>
<td>2.60</td>
<td></td>
<td>strong</td>
<td></td>
<td></td>
<td>42.2</td>
</tr>
<tr>
<td>2.45</td>
<td></td>
<td>weak</td>
<td></td>
<td></td>
<td>43.2</td>
</tr>
<tr>
<td>2.32</td>
<td>38.7</td>
<td>weak</td>
<td></td>
<td></td>
<td>45.6</td>
</tr>
<tr>
<td>2.14</td>
<td>42.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>2.07</td>
<td>43.7</td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>1.97</td>
<td>45.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.90</td>
<td></td>
<td></td>
<td>Mg, 1.901</td>
<td></td>
<td>51.8</td>
</tr>
<tr>
<td>1.765</td>
<td>51.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.605</td>
<td></td>
<td></td>
<td>Mg, 1.605</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.47</td>
<td>v. weak</td>
<td></td>
<td>Mg, 1.473</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.44</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.39</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.37</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

176.
Table 2.24

X-ray diffraction pattern of potassium dichromate

<table>
<thead>
<tr>
<th>d, Å</th>
<th>Intensity</th>
<th>d, Å</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.82</td>
<td>3</td>
<td>2.645</td>
<td>3</td>
</tr>
<tr>
<td>6.59</td>
<td>7</td>
<td>2.616</td>
<td>3</td>
</tr>
<tr>
<td>4.92</td>
<td>7</td>
<td>2.554</td>
<td>3</td>
</tr>
<tr>
<td>4.55</td>
<td>1</td>
<td>2.546</td>
<td>3</td>
</tr>
<tr>
<td>3.73</td>
<td>15</td>
<td>2.45</td>
<td>3</td>
</tr>
<tr>
<td>3.68</td>
<td>20</td>
<td>2.407</td>
<td>1</td>
</tr>
<tr>
<td>3.49</td>
<td>30</td>
<td>2.394</td>
<td>5</td>
</tr>
<tr>
<td>3.32</td>
<td>100</td>
<td>2.255</td>
<td>1</td>
</tr>
<tr>
<td>3.08</td>
<td>7</td>
<td>2.25</td>
<td>1</td>
</tr>
<tr>
<td>3.02</td>
<td>9</td>
<td>2.157</td>
<td>1</td>
</tr>
<tr>
<td>2.88</td>
<td>7</td>
<td>2.064</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 2.25

X-ray diffraction pattern of magnesium

<table>
<thead>
<tr>
<th>d, Å</th>
<th>Intensity</th>
<th>d, Å</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.780</td>
<td>35</td>
<td>1.343</td>
<td>9</td>
</tr>
<tr>
<td>2.606</td>
<td>41</td>
<td>1.303</td>
<td>2</td>
</tr>
<tr>
<td>2.453</td>
<td>100</td>
<td>1.0296</td>
<td>7</td>
</tr>
<tr>
<td>1.901</td>
<td>20</td>
<td>1.0112</td>
<td>3</td>
</tr>
<tr>
<td>1.605</td>
<td>18</td>
<td>0.9751</td>
<td>2</td>
</tr>
<tr>
<td>1.473</td>
<td>15</td>
<td>0.8988</td>
<td>4</td>
</tr>
<tr>
<td>1.389</td>
<td>2</td>
<td>0.8729</td>
<td>2</td>
</tr>
<tr>
<td>1.366</td>
<td>16</td>
<td>0.8337</td>
<td>2</td>
</tr>
</tbody>
</table>
X-ray diffraction pattern of magnesium chromate monohydrate after heating to 540°, 612° and 752°.

<table>
<thead>
<tr>
<th>2 x Scattering angle° of product at</th>
<th>Inference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MgCr₂O₄, MgCrO₄, anhydrous</td>
</tr>
<tr>
<td>540°</td>
<td>612°</td>
</tr>
<tr>
<td>20.0</td>
<td>19.6</td>
</tr>
<tr>
<td></td>
<td>21.5 - 22.0</td>
</tr>
<tr>
<td>23.6</td>
<td>23.6</td>
</tr>
<tr>
<td>25.3</td>
<td>25.35</td>
</tr>
<tr>
<td>26.8</td>
<td>26.9</td>
</tr>
<tr>
<td>28.15</td>
<td>28.15</td>
</tr>
<tr>
<td>29.30</td>
<td>29.40</td>
</tr>
<tr>
<td>32.30</td>
<td>32.60</td>
</tr>
<tr>
<td>35.10</td>
<td>35.10 - 35.70 (broad)</td>
</tr>
<tr>
<td></td>
<td>37.10</td>
</tr>
<tr>
<td>40.65</td>
<td>40.75</td>
</tr>
<tr>
<td></td>
<td>43.20</td>
</tr>
<tr>
<td>45.50</td>
<td>45.35</td>
</tr>
<tr>
<td></td>
<td>47.35</td>
</tr>
<tr>
<td>54.72</td>
<td>54.85</td>
</tr>
<tr>
<td></td>
<td>57.35</td>
</tr>
<tr>
<td></td>
<td>62.90</td>
</tr>
<tr>
<td></td>
<td>66.45</td>
</tr>
</tbody>
</table>
The product from TG to 752° on magnesium chromate monohydrate (Fig. 2.14) gave the X-ray pattern shown in Table 2.26, column 3.

The pattern of the product of decomposition of magnesium chromate to 612°, which it was thought might contain magnesium chromate (V), gave lines which could only be attributed to anhydrous magnesium chromate (VI) (Table 2.26, column 1) and magnesium chromite. The broad line in the X-ray pattern of the product at 612° at 2θ = 21.5°-22.0° was not given the products formed at 540° and 752°.

2.6. Results of microscopic examination.

Apparatus

Examination of the grades of magnesium used in this work and the products of TG, DTA and isothermal reaction products were investigated microscopically using a Gillett and Sibert, model M 19431 microscope with travelling platform at 400 magnification.

Microphotographs were taken using an Examatic, model 35 mm camera.

Thin sections (thickness 0.1 μ) were prepared using a LKB, model 4801/2/A microtome. The reaction product from a 10% Mg (atomised)–K₂Cr₂O₇ mixture heated to 490°
at 10°/minute was encapsulated in an araldite mixture prepared to the following formula:

Hardener 20 ml
Resin 20 ml
Accelerator 0.6 ml
Dibutyl phthalate 2 ml

The mixture was polymerised at 60° for 24 hours before sections were cut.

2.6.1. Microscopy of magnesium.

Photomicrographs of the three grades of magnesium used in this work are shown in Plate 1.

2.6.2. Treatment and microscopic examination of reaction product

The product of TG to 490° of 10% Mg (atomised)-K$_2$Cr$_2$O$_7$ was extracted in warm water, filtered, washed and dried at 110°. A small amount of the product was spread over a microscope slide which had been lightly smeered with vaseline. The material was covered with 2–3 ml of distilled water in a thin layer. Hydrochloric acid (1%) was added dropwise at one edge of the pool of water. The microscope was focussed on the solid particles. Bubbles began to form slowly usually at one point on the surface of each particle. The dark central region of each particle gradually reacted leaving hollow transparent shells which eventually collapsed.
(a) Magnesium (atomised grade). Magnification x 1150

(b) Magnesium (grade 5). Magnification x 1150.

(c) Magnesium (grade 3). Magnification x 1150.

(d) I μ section of magnesium (atomised) particle covered with magnesium chromite. Magnification x 3500.
This suggested that each magnesium particle was covered with a rigid protective film. An attempt to estimate the thickness of the film is described in section 2.6.3.

2.6.3. Treatment of lamina of residue under microscope.

A small amount of the product which had been extracted in water, washed and dried (see section 2.6.2) was encapsulated in the epoxy resin and 0.1 μ sections prepared as described above (section 2.6, Apparatus). The sections were transferred to a greased microscope slide. Laminae of the particles were generally elliptical in shape but a small number were essentially circular (see Plate 1).

The perimeter of the circular section was much darker in colour than the central region which appeared to be semi-transparent.

The sections were covered with a thin layer of distilled water and 1% HCl was added dropwise to the edge of the layer of water. The central region of the circular particle (in Plate 1) became transparent almost immediately. It was not possible to distinguish with any degree of certainty that there were any remains of the dark product which was previously around the perimeter of the circular section (Plate 1).
3. DISCUSSION.

3.1. The thermal decomposition of potassium dichromate.

The work of Charsley and Redfern\textsuperscript{17} and previous workers\textsuperscript{9,10,11} established that potassium dichromate begins to decompose at 500\textdegree and proceeds according to the overall equation (3.1),

\[ K_2Cr_2O_7 \rightarrow K_2CrO_4 + \frac{1}{3}Cr_2O_3 + \frac{3}{2}O_2 \quad \ldots \quad (3.1) \]

However, it is possible that decomposition occurs by a more complex series of reactions than is represented by equation (3.1). By comparison with the decomposition of other pyro-oxy anions, e.g. pyrosulphate, it might be expected that the initial stage in the decomposition of potassium dichromate consists of dissociation of the dichromate ion according to equation (3.2),

\[ Cr_2O_7^{2-} \text{ (liq.)} \rightleftharpoons CrO_4^{2-} \text{ (solid)} + CrO_3 \text{ (liq.)} \quad \ldots \quad (3.2) \]

Sutra\textsuperscript{16} calculated the entropy of fusion of potassium dichromate and suggested that this indicated that fusion of potassium dichromate is accompanied by a dissociative mechanism. However, no attempts have been made to show experimentally that dissociation does occur. The most conclusive experimental evidence that dissociation does occur was given indirectly by the results of Shams-
el-Din's titration of a solution of potassium hydroxide in molten potassium nitrate by potassium dichromate (see section 1.2.1).

Clearly, if equation (3.2) does occur, it must lie well to the left hand side below $500^\circ$ because molten potassium dichromate can be kept indefinitely at temperatures below $500^\circ$ without loss in weight associated with loss of oxygen whereas chromium (VI) oxide, if it were present in an appreciable amount, would have completely decomposed at $475^\circ$ (see section 1.2.1).

Rode showed using DTA that fusion of chromium (VI) oxide was immediately followed by a small exothermic effect which he attributed to polymerisation and solidification. Moreover, Spitsyn showed by DTA that potassium dichromate heated above its melting point gave a small exotherm at $244^\circ$ on cooling which he attributed to the presence of potassium trichromate. Spitsyn also concluded that, when potassium trichromate and potassium tetrachromate are heated above their melting points, only free chromium trioxide undergoes decomposition.

These results suggest that when potassium dichromate is heated to melting, a series of equilibrium reactions is established according to equations (3.2) to (3.5).

$$\text{CrO}_3 + \text{Cr}_2\text{O}_7^{2-} \leftrightarrow \text{Cr}_3\text{O}_2^{2-} \quad \ldots (3.3)$$
The probability of reactions (3.4) and (3.5) occurring may be lower than for reaction (3.3) but as the temperature increases, the polychromates decompose producing an increasing concentration of chromium (VI) oxide so that at 500° reaction (3.5) begins to proceed at a detectable rate.

3.2. The thermal decomposition of potassium dichromate in the presence of magnesium powder.

The results of this work showed that the presence of magnesium powder in molten potassium dichromate accelerated decomposition. A smooth exothermic DTA curve was given by the magnesium-potassium dichromate mixture which began as soon as the dichromate had melted. The peak temperatures of the exotherms decreased as the amount of magnesium in the mixture increased. The temperature at which the exotherm was completed appeared to be a function both of heating rate and the amount of magnesium in the mixture. In some cases, the exotherm was not completed when two endotherms, closely spaced, were given between 620° and 640°.

At 650°, a further endotherm occurred associated with magnesium fusion which was generally accompanied by ignition of the mixture when higher heating rates (6°C/min.) were
used. Little or no attempt has been made to study the system at or above 650°.

Chemical analysis of the products of isothermal reaction at 429° between magnesium and potassium dichromate showed that the reaction was essentially completed when only about one sixth of both of the initial reactants had been consumed.

The results of both DTA and chemical analysis suggested that the reaction was limited by the formation of a protective layer around the magnesium particles. This was confirmed by microscopic examination.

Analysis by X-ray diffraction showed that magnesium chromite was formed during the early stages of the exothermic reaction process.

Chemical analysis of the product of isothermal reaction at 429° showed that the magnesium chromite, confirmed by X-ray diffraction, was retained in the layer of magnesium particles which was produced above the more dense layer of potassium dichromate although magnesium chromite is more dense than potassium dichromate.

Analysis by X-ray diffraction of the products of DTA experiments on the system magnesium-potassium dichromate in the range 400° to 600° gave patterns which could be attributed to the presence, apart from magnesium and
potassium dichromate, of magnesium chromite, anhydrous magnesium chromate (VI) and another possible product, the pattern of which was similar to that quoted for calcium chromate (V) by Scholder. It suggested that magnesium chromate (V), Mg₃(CrO₄)₂, was formed 'in-situ' in the reaction between magnesium and potassium dichromate.

The DTA of magnesium chromate (VI) monohydrate in a dynamic argon atmosphere (75 ml/min.) at 1.4°C/min. gave two closely spaced endotherms, the first commencing at 610°C, the shapes of which were similar to the two closely spaced endotherms in the system magnesium-potassium dichromate in the range 620°C to 640°C. However, the second endotherm in the DTA of magnesium chromate (VI) was not completed until 670°C. Attempts were made to examine the product produced at the stage between the two endotherms in the DTA (under argon) of magnesium chromate (VI) to see if magnesium chromate (V) be indicated. However, the only products which could be identified with certainty were anhydrous magnesium chromate (VI) and magnesium chromite. It is likely that the failure to identify magnesium chromate (V) is because of its instability but that it was identified in the products of the reacted system magnesium-potassium dichromate because it was protected against reaction with oxygen and water (atmospheric) in the solidified matrix of potassium dichromate.
Analysis by X-ray diffraction of the products of reaction in the system magnesium-potassium dichromate showed that there was no appreciable production of magnesium oxide nor chromium (III) oxide. Chemical analysis confirmed that little or no magnesium oxide accumulates in the reacting system magnesium-potassium dichromate between 400° and 600°.

It was shown using thermogravimetry that the exothermic reaction between 400° and 600° in the system magnesium-potassium dichromate occurred without any significant weight change.

### 3.2.1. Proposed reaction mechanism for reaction in the system magnesium-potassium dichromate above 400°.

On the basis of the results obtained in this work and the results of previous workers, the following reaction mechanism is proposed to explain the occurrence of the broad exotherm in the DTA of the system magnesium-potassium dichromate between 400° and 600°.

First, dissociation of potassium dichromate occurs according to equation (3.6):

\[ \text{K}_2\text{Cr}_2\text{O}_7 \text{(liq.)} \rightleftharpoons \text{K}_2\text{CrO}_4 \text{(s)} + \text{CrO}_3 \text{(liq.)} \quad \ldots \quad (3.6) \]

Chromium (VI) oxide is absorbed at oxide sites on the initial film of magnesium oxide covering the magnesium particles producing chromate (VI) ions according to equation (3.7),
Two chromate (VI) ions on adjacent sites are joined by diffusion with a magnesium ion, Mg$^{2+}$, and electrons (e/MgO)(i) from the conduction band of magnesium oxide to form magnesium chromate (V) according to equation (3.8),

\[
2\text{MgCrO}_4 + \text{Mg}^{2+} + 2(e/\text{MgO}) \rightarrow \text{Mg}_3(\text{CrO}_4)_2 \quad \ldots (3.8)
\]

Reaction (3.8) begins at 400° and is rapidly followed by decomposition of magnesium chromate (V) according to reaction (3.9),

\[
\text{Mg} \left[ \text{CrO}_4 \right]_2 \rightarrow \text{MgCr}_2\text{O}_4 + 2\text{MgO} + 2\text{O}_2 + 4(e) \quad \ldots (3.9)
\]

where (e □ ) is a positive hole.

Magnesium oxide produced by reaction (3.9) offers the same number of sites as were present initially for reaction (3.7) to continue whilst oxide ions also produced by reaction (3.9) offer further sites for reaction. Oxide ions thus act autocatalytically.

Magnesium is converted to magnesium ion at the oxide magnesium-magnesium interface according to equation (3.10),

\[
\text{Mg} = \text{Mg}^{2+} + 2(e/\text{MgO}) \quad \ldots (3.10)
\]

The magnesium ion and electrons produced by reaction (3.10) diffuse to the melt-oxide/chromite interface to
react with magnesium chromate (VI) according to reaction 3.8 and to maintain neutrality for the oxide ions and positive holes produced by reaction (3.10).

The sequence of reactions from (3.7) to (3.10) is repeated continuously at a branching factor of three.

3.2.2. Rate expression for the reaction between magnesium and potassium dichromate above 400°.

If the dissociation mechanism (3.6) and diffusion of magnesium ion and electrons are eliminated, the rate determining step may be associated with one of the reactions from (3.7) to (3.10).

Up to 500°, the concentration of chromium (VI) oxide may be controlled at a low level by the equilibrium reaction (3.6) and the rate of diffusion of chromium (VI) oxide from the melt to the melt-oxide/chromite interface may be slower than the rate at which oxide ions are produced by reaction (3.9). Below 500°, the expression would therefore contain a term representing the diffusion of chromium (VI) oxide through the melt.

Above 500°, potassium dichromate begins to decompose readily so that the concentration of chromium (VI) oxide increases to an excess.

Assuming reaction (3.8) to then be the slowest step, the rate expression is given according to equation (3.11),
Assuming magnesium ion to be in excess in the interface, expression (3.11) reduces to expression (3.12),

\[
\frac{-d[MgCrO_4]}{dt} = k \left[ MgCrO_4 \right]^2 \left[ Mg^{2+} \right] \quad (3.12)
\]

If chromate (VI) ions are not mobile on the surface, during the initial stages of reaction some chromate (VI) ions will not be on adjacent sites and reaction (3.8) will not be possible. But, because of the rapid production of chromium (VI) oxide at 500°C, the surface then becomes rapidly saturated with chromate (VI) ions after which expression (3.12) will hold.

The concentration of magnesium chromate (VI) present at any time is given according to equation (3.13),

\[
\left[ MgCrO_4 \right] = -\int_{t=0}^{t} (-d[MgCrO_4]/dt) dt \quad (3.13)
\]

Using the Borchardt and Daniels postulate for DTA, then the heat change in a small time interval is proportional to the number of moles of magnesium chromate (VI) reacting and is given by equation (3.14),

\[
dH = -K \Delta n \cdot d \left[ MgCrO_4 \right] \quad (3.14)
\]

Differentiating equation (3.14), rearranging and substitution
of equation (41) from section (1.5.1) gives equation (3.15),
which on integrating gives equation (3.16),

\[
\frac{d}{dt} \left[ \text{MgCrO}_4 \right] = -\frac{n_o}{KA(C_p \cdot d\Delta T/dt + K \cdot \Delta t)} \ldots (3.15)
\]

\[
[\text{MgCrO}_4] = -\frac{n_o}{KA(C_p \cdot \Delta T + K \cdot \alpha)} \ldots (3.16)
\]

\(n_o\) represents the initial number of moles of MgCrO\(_4\).

Substituting from equations (3.15) and (3.16) into equation (3.12) gives the specific rate of reaction
according to equation (3.17),

\[
k = -\frac{KA/n_o \cdot (C_p \cdot d\Delta T/dt + K \cdot \Delta T)}{(C_p \cdot \Delta T + K \cdot \alpha)^2} \ldots (3.17)
\]

Assuming \(K \cdot \Delta T \gg C_p \cdot d\Delta T/dt\) and \(K \cdot \alpha \gg C_p \cdot \Delta T\),
expression (3.17) reduces to equation (3.18),

\[
k = -(A/K \cdot n_o) (\Delta T/\alpha^2) \ldots (3.18)
\]

3.2.3. Evaluation of DTA parameters, \(\Delta T\), \(A\), and \(\alpha\).

Although a linear baseline \((d \Delta T/dt = 0)\) was given before the onset and after the completion of the 400\(^0\)-600\(^0\)
exotherm in most experiments, there was generally an 'off-set' (see Fig. 3.1) between the baseline positions. For Run 2
in Fig. 2.29, the 'off-set' was equal to 1.15 \(\mu\)V. This is
associated with changes in the specific heats \( (c_p) \), thermal conductivities \( (k') \) and densities \( (\rho) \) in the system as reagents go to products via intermediates. The rate at which these properties change during the 400\(^\circ\)-600\(^\circ\) exothermic process must be proportional to the rate determining step according to equation (3.19),

\[
\frac{d}{dt} \sum_{i} \left( c_{pi} k_{i}^p \rho_{i} \right) \propto \text{MgCrO}_4 \quad \ldots (3.19)
\]

Using (3.16), where \( K.a \gg C_p \Delta T \), in (3.19) gives equation (3.20),

\[
\frac{d}{dt} \sum_{i} \left( c_{pi} k_{i}^p \rho_{i} \right) \propto (a/A)^2 \quad \ldots (3.20)
\]

Expression (3.20) was used to estimate the base line under the curve which would be due to changes in \( c_p, k \) and \( \rho \) alone. Because errors were greater in measuring \( \Delta T \), the estimated base line was only used to correct for measured values of \( \Delta T \) as follows:

(i) a straight line AB (Fig. 3.1) under the curve was assumed for the purpose of measuring A and a to a first approximation,

(ii) the approximate values of A and a were used to calculate corrections \( (c_i) \) to \( \Delta T \) at different temperatures using equation (3.21).

\[
c_i = (a_i/A)^2 \times \text{'off-set'} \quad \ldots (3.21)
\]

(iii) corrections \( c_i \) were subtracted from the values
of $\Delta T$ measured between the curve boundary and AC. The corrected base line was sigmoid in shape and is shown in Fig. 3.1.

The Arrhenius expression was plotted using the value of $k$ given by equation (3.18), where $\Delta T$ was corrected as described above and $(A/Kn_0)$ was assumed to be unity. The result is shown in Fig. 3.2, in which points evaluated at temperatures of $490^\circ$ and above lie on a straight line. The points are shown more accurately in Fig. 3.3 which gives an apparent activation energy of minus 87.86 kcal./mole. An estimation of the errors involved in measuring $\Delta T$ and $a$ is given in Table 3.1.

The errors due to neglecting the terms $C_p \cdot d\Delta T/dt$ and $C_p \cdot \Delta T$ are given in Table 3.2, columns 7 and 8, expressed as percentage ratios.

3.2.4. **Significance of the negative apparent activation energy for the exothermic reaction at $400^\circ-600^\circ$ in the system magnesium-potassium dichromate.**

The negative activation energy determined by DTA for the reaction between magnesium and potassium dichromate in the temperature range $490^\circ-560^\circ$ is readily explained if the initial reaction stage is absorption of chromium (VI) oxide at the magnesium oxide-melt interface according to
Fig. 3.2. Plot of $\log k = \Delta T{\text{(corrected)}}/a^2$ for exotherm in Fig. 2.29, (Run 2).
Fig. 3.3. Arrhenius plot for $\log k = \Delta T(\text{corrected})/a^2$ for exotherm in Fig.
Table of values measured from DTA curve (Fig. 2.29, Run 2) used to plot Figs. 3.2 and 3.3.

<table>
<thead>
<tr>
<th>ΔT_1</th>
<th>a_1</th>
<th>temperature</th>
<th>1/°K</th>
<th>(a/A)^2 x BC</th>
<th>ΔT_c</th>
<th>log_{10} k</th>
<th>Estimated Errors(^{(%)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm</td>
<td>g</td>
<td>°C</td>
<td>°K</td>
<td>cm</td>
<td></td>
<td>cm</td>
<td>ΔT_1 (\pm) 2 a_1</td>
</tr>
<tr>
<td>0.92</td>
<td>0.0492</td>
<td>455.7</td>
<td>728.9</td>
<td>1.3720</td>
<td>0.0006</td>
<td>0.92</td>
<td>2.93785</td>
</tr>
<tr>
<td>2.33</td>
<td>0.1352</td>
<td>472.9</td>
<td>746.1</td>
<td>1.3404</td>
<td>0.0046</td>
<td>2.33</td>
<td>2.46336</td>
</tr>
<tr>
<td>5.46</td>
<td>0.3502</td>
<td>490.1</td>
<td>763.3</td>
<td>1.3102</td>
<td>0.0306</td>
<td>5.43</td>
<td>2.00418</td>
</tr>
<tr>
<td>7.83</td>
<td>0.7988</td>
<td>507.3</td>
<td>780.5</td>
<td>1.2813</td>
<td>0.1595</td>
<td>7.67</td>
<td>1.43792</td>
</tr>
<tr>
<td>5.27</td>
<td>1.1652</td>
<td>524.5</td>
<td>797.7</td>
<td>1.2537</td>
<td>0.3393</td>
<td>4.93</td>
<td>0.91809</td>
</tr>
<tr>
<td>2.52</td>
<td>1.3685</td>
<td>541.7</td>
<td>814.9</td>
<td>1.2272</td>
<td>0.4681</td>
<td>2.05</td>
<td>0.39729</td>
</tr>
<tr>
<td>1.32</td>
<td>1.4559</td>
<td>558.9</td>
<td>832.1</td>
<td>1.2018</td>
<td>0.5298</td>
<td>0.79</td>
<td>-0.07059</td>
</tr>
</tbody>
</table>

ΔT_1 measured between curve and initial base line position AC (see Fig. 3.1) in cm.

a_1 " " " " straight line AB (see Fig. 3.1) in g. by weighing sections.

A measured between curve and AB (see Fig. 3.1), tracing and weighing equalled 1.5089 g.

BC ('off-set' in Fig. 3.1) equalled 0.57 cm. (1.15 \(\mu\)V).

ΔT_c equals ΔT_1 minus (a/A)^2 x BC

k equals ΔT_c/(a/A)^2

\(\delta \Delta T_i\) equals error in travelling microscope (0.001 cm.) plus twice error in line width (\(\pm\) 0.01 cm.)
Errors due to neglecting terms $C_p \cdot d T/\text{dt}$ and $C_p \cdot T$ in expression (3.18) for specific rate.

<table>
<thead>
<tr>
<th>$\Delta T_i$ cm</th>
<th>$d \Delta T_i/\text{dt}$ $\mu$/cm</th>
<th>$\Delta T_i$ $^\circ$C/sec</th>
<th>$\Delta T_i$ cal./min</th>
<th>$K \cdot \Delta T_i$ cal./min</th>
<th>$C_p \cdot d \Delta T_i/\text{dt}$ $p$ %</th>
<th>$C_p \cdot \Delta T_i$ $p$ %</th>
<th>Total error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.92</td>
<td>0.170</td>
<td>0.058</td>
<td>0.00446</td>
<td>0.307</td>
<td>0.164</td>
<td>2.71</td>
<td>2.76</td>
</tr>
<tr>
<td>2.33</td>
<td>0.335</td>
<td>0.112</td>
<td>0.00853</td>
<td>0.777</td>
<td>0.415</td>
<td>2.06</td>
<td>2.54</td>
</tr>
<tr>
<td>5.46</td>
<td>0.575</td>
<td>0.192</td>
<td>0.01476</td>
<td>1.810</td>
<td>0.996</td>
<td>1.53</td>
<td>2.28</td>
</tr>
<tr>
<td>7.83</td>
<td>-0.060</td>
<td>-0.020</td>
<td>-0.00154</td>
<td>2.557</td>
<td>1.356</td>
<td>-1.13</td>
<td>1.41</td>
</tr>
<tr>
<td>5.27</td>
<td>-0.590</td>
<td>-0.197</td>
<td>-0.01514</td>
<td>1.643</td>
<td>0.877</td>
<td>-1.73</td>
<td>0.62</td>
</tr>
<tr>
<td>2.52</td>
<td>-0.330</td>
<td>-0.110</td>
<td>-0.00846</td>
<td>0.683</td>
<td>0.365</td>
<td>-2.32</td>
<td>0.22</td>
</tr>
<tr>
<td>1.32</td>
<td>-0.150</td>
<td>-0.050</td>
<td>-0.00384</td>
<td>0.263</td>
<td>0.140</td>
<td>-2.74</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Conversion of $T$ from cm. to $^\circ$C calculated using $1 \text{ cm} = 2 \mu \text{V} = 1/3 \ ^\circ\text{C}$.  

$C_p$ calculated using $c_p (K_2Cr_2O_7) = 97.3 \text{ cal.}/^\circ\text{C/mole}^{92}$, $c_p (\text{Mg}) = 7.2 \text{ cal.}/^\circ\text{C/mole}^{92}$.  

$K$ calculated using $\Delta H = K \cdot A$ on DTA fusion curve (0.3500 g) in Fig. 2.29, Run 2 where  

$H(\text{fusion}) = 8510 \text{ cal./mole}^{92}$ and 1 g of paper = 32.069 min. $^\circ\text{C}$.  

Total error equals column 7 plus twice error in column 8.
equation (3.7).

The heat of chemisorption due to the formation of the chromium-oxygen bond must be subtracted from apparent activation energy to give the true activation energy for the rate controlling step (3.8),

The bond dissociation energy (Q) for the Cr-O bond has been quoted to be 97 kcal./mole and 102.0 kcal./mole. The true activation energy (E) is given by equation (3.22) in which \( E_a \) is the apparent activation energy.

\[
E = E_a + Q \quad \ldots (3.22)
\]

\[
= (-87.86) + (+97) \text{ or } (+102.0)
\]

\[
= +9.14 \text{ or } 14.14 \text{ kcal./mole.}
\]

These values may be compared with the value of the heat of activation of 9.105 (standard deviation 0.005) kcal./mole determined by time-to-ignition measurements (section 2.4) at temperatures of 450\(^\circ\) for the system 48.4\% Mg-K\(_2\)Cr\(_2\)O\(_7\).

3.2.5. Conclusions.

The activation energy for the rate determining step in the reaction between magnesium and potassium dichromate in the range 400\(^\circ\) - 600\(^\circ\) as determined by DTA was in agreement with that determined by time-to-ignition measurements. This would have been unlikely
if the theoretical bases of either or both methods were questionable.

3.3. Suggestions for further work.

1. The results of this work suggest that there is a relationship between the rate determining step chemical reaction in a binary redox system (consisting of a powdered metal and a molten oxy-acid) and the pre-ignition reactions occurring in the system when subjected to high rates of heat input.

   It might prove useful to examine the burning rates of pyrotechnic compositions in relation to a suitably modified theory (e.g., the Mallard-LeChatelier theory) in which the rate data for the chemical reactions can be used having been determined by the Borchardt and Daniels-DTA method.

2. From this study it is clear that the exact chemical composition of molten potassium dichromate between its melting point (338°C) and up to its decomposition temperature (500°C) is not known with any degree of certainty. It might prove useful if this was investigated.

3. The results of this and previous studies have shown that DTA coupled with the Borchardt and Daniels theory can be used to determine kinetic data for chemical reactions occurring in the solid state.
Undoubtedly, improvements can be made in the method, in particular improvements associated with the method of heating the samples. For example, it might prove valuable if DTA were carried out using a stirred liquid (e.g., Wood's metal, m.p. 79°C) which meets the requirements of the Borchardt and Daniels theory for a homogeneous thermal source.
References.


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