THERMAL DECOMPOSITION

OF

AMMONIUM DICHROMATE

Thesis presented for the degree of Doctor of Philosophy

by

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WITH GRATEFUL THANKS TO

MY PARENTS.
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Introduction.

Since the alchemists of the Middle Ages, science has used heat as one of the main sources of energy in chemical reactions. Priestley, in 1774, discovered oxygen by heating mercuric oxide, and with the intensive study in the following century of the gaseous products of the combustion of most known substances much data accumulated. With the progress of thermodynamical theory, and the rapid expansion of the knowledge of the fine structure of crystalline solids, following Bragg's elucidation of potassium chloride in 1917, attention was focussed on the reaction mechanisms and kinetics of solid state decompositions. From the early nineteen-twenties, in an attempt to find a general mechanism for these decompositions, the conditions and methods of decomposition have been standardised, and a classification of the results can now be made, due among others to the work of the Garner school at Bristol, and the later Tompkins' school in London.

Three main methods of solid state decomposition, or dissociation, may be employed: thermolysis with the energy supplied as heat, photolysis with the energy supplied in the form of photons of light, and the application of energy in the form of X- and γ-radiation, α-particles, etc. Most workers have used thermal methods, which require a relatively simple apparatus, and have the advantage of
giving a more flexible approach to solid state problems than the other methods. Early investigators decomposed the substances in air; this was later improved by decomposing the solid in an atmosphere of a known (sometimes inert) gas. Lewis (1), in his classical work on silver oxide, decomposed the substance in oxygen. Since the advent of reliable methods of obtaining high vacua, the reactions have been mainly studied at low pressures.

There are three arbitrary classes of thermal decomposition: purely organic reactions, endothermic inorganic reactions, and exothermic inorganic reactions. Organic decompositions (2), such as organic azides and acids, are very dependent on lattice structure, which is usually of the molecular type, and thus involves liquefaction or sublimation, either prior to, or simultaneous with, the actual thermal decomposition. This leads to a wide variety of end products and very complex kinetics, as little progress has been made in reducing the overall process to a series of simple chemical changes with simple kinetics, so that relatively few detailed investigations have been made in this field. The information about nucleation processes and the mechanisms of interface reactions provided by endothermic inorganic reactions are worth the experimental and theoretical complications caused by the occurrence of both dissociation and recombination processes. Work in this field has been restricted to the dehydration of salt hydrates and the dissociation of metal carbonates (3).
Exothermic inorganic decompositions, in which category ammonium dichromate lies, are irreversible and have been studied fairly systematically, especially the azide salts and the oxalates of heavy metals.

The majority of the reactions which have been investigated are of the type,

$$ A_{\text{solid}} \rightarrow B_{\text{solid}} + C_{\text{gas}} $$

although two, or more, solids or gases may be obtained. Generally, a decomposition is classified into a certain reaction type for which the formal kinetics are deduced on the basis of an a priori mechanism and these are compared with the experimental kinetics. Reactions of the above type may easily be followed by simply measuring the pressure of the evolved gases, or the loss in weight of the solid A.

Exothermic Decompositions.

A convenient classification of irreversible reactions is given by the form of the sigmoid pressure-time curves. The sigmoid shape indicates a primary nucleation stage, followed by an autocatalytic stage and a final decay stage. The three main reaction types are illustrated in Fig. 1.

In Fig. 1(a) the most rapid rate of reaction occurs near the beginning of the decomposition. This form of curve is typical of reactions in which nuclei of the new phase B are very rapidly formed, and cover the surface of the decomposing material almost instantaneously with a
film of the solid product. Lead (4) and silver azides (5) are examples of this type.

In Fig. 1(b) an apparent induction period, due to the slow rate of formation of nuclei, forms the first part of the curve. If the rate of formation is sufficiently low these nuclei grow to sizes which may be examined microscopically, as in the case of barium azide. (6).

Fig. 1(c) differs from Fig 1(b) in that there is a small initial evolution of gas, which is most rapid at the beginning of the heating. This is followed by an acceleration of the reaction corresponding to that in Fig. 1(b). Examples of this type of decomposition are mercury fulminate (7), (8), (9), (10), lithium aluminium hydride (11), and potassium azide (12), (13). In general, the crushing, or grinding, of whole crystals reduces the induction period. Complications may arise due to melting during the decomposition, as in the case of potassium perchlorate (14), and the form of the curve may not fit the above classification.

In most of the known cases, the pressure-time curves have been interpreted as a three-stage process: (i) an initial reaction occurring on the surface of the crystals; (ii) formation of the nuclei of the product phase B, and; (iii) a reaction occurring at the interface between phase A and phase B. The surface reaction has no definite characteristics as yet, and much work remains to be done to clarify its nature - it may be limited to one layer, or
It may spread diffusely into the interior of the crystal. The nuclei are formed as a result of this initial reaction and are normally three-dimensional increasing in area as the square of the time. Mampel (15) has developed the most general mathematical treatment of the formation and growth of nuclei.

Nucleation implies the formation of the new solid phase B at special sites in the lattice of A: when local fluctuations in the lattice energy are sufficient to allow the formation of B, decomposition will begin. The calculation of the rate of decomposition cannot be treated as a straightforward exercise in probability theory, as this implies the molecules in a crystal are merely an array of dimensionless points and disregards an important consequence of their finite size. Whereas the first-formed fragments of phase B, embedded in a matrix of A, may retain the molecular volume and lattice type of A, larger particles of B will almost always have a different molecular volume and lattice type from the surrounding matrix. Strain due to local deformation of the lattice must therefore occur and will have an associated extra energy, the 'strain energy.'

For a fragment of B, containing \( m \) molecules and a strain energy per unit area of interface \( \gamma \), the free energy change accompanying its formation is

\[
\Delta G = m\Delta G_B + \sigma \gamma \tag{1}
\]
where $\sigma$ is a shape factor (4$\pi r^2$ for a spherical interface) and $\Delta G_B$ is the bulk free energy change per molecule accompanying the reaction

$$\text{Asolid} \rightarrow \text{Bsolid} + \text{Cgas}$$

Assuming that the fragments of B are spherical, and if $V_m$ is the volume per molecule of the product phase, then

$$m = \frac{4\pi r^3}{3V_m} \quad (2)$$

which on substituting in equation (1) gives the general form,

$$\Delta G = am^3 - bm \quad (3)$$

where $a$ is proportional to the strain energy, and $b$ is the negative of the bulk free energy change per molecule.

Although the nuclei have been considered as spherical for simplicity, both experimental observations and theoretical considerations suggest that disc- or needle-shaped clusters, with definite preferred orientations with respect to the parent lattice, should be considered (16). Similarly, any rigorous theory should consider the strain energy arising from lattice deformations: such energy forms part of the free energy of formation of the germ nucleus (17).

Although the strain energy is a minimum for disc-shaped nuclei, the anisotropy of the interfacial energy of reactant and product often controls the shape of the nucleus, since there will be a definite crystallographic relationship between A and B. In fact, Frank (18) suggests that the interface growth of B into A may be regarded as a dislocation climb process.
Fig. 2 shows the plot of $\Delta G$ against $m$ for equation (3). If $\gamma$ is positive, $\Delta G$ passes through a maximum at $m=m^*$, when a fragment of B has the critical size to be in equilibrium with its surroundings. Because of the strain caused by the formation of the new phase small fragments of B, with the number of molecules less than $m^*$, are unstable and revert back to phase A. These are 'germ nuclei' and will disappear unless local energy fluctuations permit further additions to the nucleus until $m>m^*$. If $m$ is greater than $m^*$, $S\Delta G/Sm$ is negative, so that the nuclei can grow freely - hence, these are 'growth nuclei'. X-ray diffraction evidence would seem to point to the presence of nuclei of varying composition and stability in the lattice of A.

Since most real crystals are imperfect and contain many dislocations and thermal defects, such as Frenkel and Schottky defects, growth of nuclei will be preferred in those crystal elements with dislocations in their vicinity, since large stresses cannot be supported there, so that nucleation will be easier at the sub-boundaries of the crystal. This has been experimentally shown by Hedges and Mitchell (19) for the photolysis of silver bromide. Solute atoms of B will form an atmosphere round the dislocation until the concentration of B approaches $m^*$ when a stable nucleus will grow. In
thermal decompositions, the concept of discrete nuclei is favoured in interpreting results of kinetic studies, and a theory of diffuse nuclei has not been developed.

The autocatalytic nature of the reaction can thus be explained as due to the relatively rapid growth of these nuclei following their formation at certain localised points in the reactant lattice. If the free energy of activation of the interface reaction between the nucleus of B and the solid matrix A is less than that for nucleus formation, then growth of existing nuclei predominates, and B assumes the form of compact discrete nuclei distributed in a matrix of A: if, however, the free energies are comparable a large number of sub-microscopic nuclei will be formed. In such cases the acceleratory period is greatly reduced. The general form of the sigmoid curves can thus be qualitatively explained by the above mechanism, and, on this basis, certain assumptions lead to the prediction of the kinetic equations. (20).

'Normal' growth of nuclei is considered to occur according to a power law, viz. \( p \propto t^n \), where \( p \) is the pressure at any time \( t \), \( n \) is an integer, and there is no overlap between individual nuclei. This law holds very well for barium azide (6), (21), calcium azide (22), and silver oxide (23); however, since complications such as the cracking of the solid due to strain and the
occurrence of small liquid inclusions in the crystal may exist, departures from a simple power law relationship may occur, as in the case of lead azide and potassium permanganate.

Again, the oxalates of silver (24), (25) and lead (26) show the reaction spreading through the solid by a 'branching chain' mechanism following an exponential law. The detailed picture of what constitutes the chain process remains obscure: they are definitely not 'energy chains' as this concept would require very rapid rates of reaction, and yet quite slow and very fast decompositions have comparable activation energies. Also, any interruption of the decomposition by cooling and reheating has no effect on the rate as Garner and Hailes (27) showed for mercury fulminate. How far this branching is due to effects arising from a diffuse, initial spreading reaction is not yet clear, but it is now accepted that the concept of linear chains must be modified, as the rapid propagation of such chains through a crystal would tend to separate it into mosaic blocks which would decompose slowly. Branching plate-like nuclei of a constant average width would, however, overcome this objection and still follow an exponential law. In some cases, notably mercury fulminate (7), (8), (9), (10), barium (6) and calcium (22) azides and silver oxalate (24), (25), a further reinvestigation has shown
that these decompositions can be best interpreted in the light of a power relationship.

The neglect of probable interference between branching nuclei is a serious fault in the above chain theory, as the chains would then terminate. By postulating a further term, inclusive of both the probability of branching and the probability of termination factors, a theoretical equation is obtained, namely

$$\log \frac{\alpha}{1-\alpha} = kt + c \quad (4)$$

where $\alpha$ is the fraction decomposed at time $t$ and $k$ is the probability of branching. Prout and Tompkins were the first to apply this equation to the decomposition of potassium permanganate (28), which gave an excellent fit up to $\alpha = 0.9$. Two values were needed for $k$, fitting the portion of the curve up to the maximum rate and the decay period respectively. This requirement was a consequence of the asymmetry of the decomposition curve: for a curve symmetrical about the inflexion point, one constant value is obtained for $k$.

A further complication became apparent in silver permanganate (29), where equation (4) only fitted up to $\alpha = 0.1$; but, if the equation were modified by assuming that the branching coefficient $k$ is not independent of
time, but varies inversely with this parameter, then the resulting modified equation,

\[ \log \frac{\alpha}{1-\alpha} = k' \log t + c \quad (5) \]

fits the results well, as Prout and Tompkins demonstrated.

Further equations to fit cases where the surface is rapidly covered by a film of solid product, followed by a rate-determining progression of the resulting interface towards the centre of the crystal, as in Fig. 1(a), may be theoretically derived. For normal growth following after the random nucleation of the reactant with a low probability, the amount of decomposition should vary as the fourth power of the time. Fischbeck and Spingler (30) found this was the case for the chromates of ammonia. A complex mathematical treatment of the problems of ingestion and overlap of nuclei has been developed by Mampel (15); the final formulae are rather complex and cannot be directly applied to practical data as yet, although this work represents the most detailed attempt yet made to work out the course of a solid reaction.

The final stage of any thermal decomposition, the decay period, has been the subject of much attention. After reaching the maximum rate stage, the rate is usually proportional to the amount of material left undecomposed, and this is referred to as the unimolecular decay law.

\[ \log \frac{1}{1-\alpha} = kt \quad (6) \]
This simple law is a consequence of a tendency for the contracting interface, between product and reactant phases, to collapse before the completion of the reaction, leaving isolated blocks of undecomposed material. Since each molecule in a block has an equal chance to decompose, then the rate becomes simply proportional to the amount of initial material left undecomposed.

Any a posteriori agreement between theoretical and experimental rate equations does not, of course, confirm the basis on which these equations are derived, so that further information about the decomposition, in addition to the $\alpha - t$ curve, is of great value. A standard complementary study is that of direct microscopic observations of the solid as it decomposes, although experimental difficulties exist, viz. the difficulty of growing single crystals and the temperature limitation. The most effective results have been obtained by Wischen (6) for barium azide. However, by cooling the partially decomposed material to room temperature, the nuclei, frozen in a matrix of the original substance, may be studied as has been done for silver oxalate and mercury fulminate.

Surface area measurements are of value when a knowledge of the depth of penetration of the reaction in the prenucleation stages is desired. Although, as yet, not fully certain in the interpretation of the
results, the measurement of the electrical conductivity of solids is of great qualitative value, giving an activation energy value for the conduction process, which may be compared with that for the rate-determining stage of the reaction. Its use in showing the coalescence of metallic nuclei at the maximum rate stage, when the nuclei are three-dimensional, has been shown for the alkaline earth azides (22). For lithium aluminium hydride (11) Garner and Haycock have used its semi-conducting properties to show the initial production of F' -centres, and their diffusion from the surface into the lattice where they increase the conductivity: the association of these F' -centres causes a sharp drop in conductivity when they form nuclei, and the conductivity then remains constant until the metallic nuclei coalesce, when the material becomes a pure metallic conductor. This method promises to be a valuable tool in future work on thermal decompositions.

**Ammonium Salts.**

The thermal decomposition of ammonium salts of oxyacids is highly complex. The large range of possible products, following the oxidation of the cation, is complicated by the temperature dependence of this oxidation process: a stoichiometrical equation is seldom obtained. A further kinetical complication is the possible sublimation, melting,
or explosion of the salt at what are normally regarded as low temperatures.

The importance of ammonium nitrate (31), (32), (33), (34), (35), as an explosive has led to a fairly extensive examination of the salt at both high and low temperatures. Between 210° - 260°C the nitrate decomposes exothermically into nitrous oxide and water to the extent of 98% reaction, although a little nitrogen is also present. The occurrence of a simultaneous endothermic dissociation of the salt into ammonia and nitric acid, and the small interaction between these two gaseous products to give nitrogen, makes the kinetics very complex.

Extensively studied by Bircumshaw et al, ammonium permanganate (36) gave unsatisfactory results in vacuo and was finally studied whilst immersed in Apiezon B oil, which altered the kinetics considerably. Complexity in the interpretation of results is due to the fact that, not only is the ammonium ion oxidised during the decomposition, but one of the products, viz. ammonium nitrate, is thermally unstable, and its breakdown is catalysed by one of the other products, manganese dioxide.

Bircumshaw and his co-workers have also investigated ammonium perchlorate (37) with respect to the kinetics of the decomposition, and found ten gaseous products. Below 300°C, the products are substantially as given by

\[ 4\text{NH}_4\text{ClO}_4 \rightarrow 2\text{Cl}_2 + 3\text{O}_2 + 8\text{H}_2\text{O} + 2\text{N}_2\text{O}. \]
Above 300°C the proportion of nitric oxide became appreciable, and above 350°C,

\[ 2\text{NH}_4\text{ClO}_4 \rightarrow 4\text{H}_2\text{O} + \text{Cl}_2 + \text{O}_2 + \text{NO}, \]

was considered most representative, although there were many possible additional products. Together with this complexity of products was the thermal transition from the rhombic form below 240°C to the cubic form above this temperature. The kinetics and mechanism postulated by Bircumshaw will be discussed later.

**Ammonium Dichromate.**

A survey of previous work on the thermodecomposition of ammonium dichromate reveals a great deal of conflicting results, both qualitatively and quantitatively, in the kinetics and the reaction products. Although the physical properties of the salt are well established (38), (39), (40), (41), the variation in the nature of the reaction products and the decomposition temperature range is probably accounted for by the different experimental conditions employed.

The earliest workers had reported that at red-heat in air the main products were chromic oxide and water. Darby (42) reported that at 200°C, in addition to these products, nitrogen and ammonia were formed, whereas Siewert (43), using an explosive decomposition in air, found nitric oxide and oxygen as the main gaseous products.
Following this early work, Jäger and Krüss (44) in 1869, showed that the ammonium chromates gave off some ammonia on decomposing. Hooton (45) whilst confirming the presence of nitrogen and water in the gaseous products, also found large quantities of oxygen and oxides of nitrogen, whether the decomposition was performed in air or vacuo: if slowly decomposed in air below 90°C to constant weight, atmospheric oxygen was reported to take part in the reaction giving a hydrated chromium dioxide, \((\text{CrO}_2)_2\text{H}_2\text{O}\), a glistening black powder which, on strong heating, yielded oxygen, water and chromic oxide. In the absence of oxygen, heating below 190°C gave a dull green-black powder, chromic oxide hydrate \(\text{H}_2\text{Cr}_2\text{O}_4\), a substance which was brightly incandescent at 400°C, giving water and compact chromic oxide, but no gaseous products.

Ball (46) in a study of the slow decomposition of the ammonium chromates, found that, between 185° - 205°C, the dichromate slowly turned brown and then black, giving off nitrogen, water, and ammonia. After several days heating the composition was \(\text{Cr}_2\text{O}_3\ 83.89\%\), active oxygen 9.00%, water 6.93%, that is nearly \((\text{CrO}_2)_3\text{H}_2\text{O}\), but this composition was not constant: at an intermediate stage the residue contained one-half of the total original nitrogen, and the approximate composition was \(2\text{CrO}_3\cdot\text{Cr}_2\text{O}_3\cdot2\text{NH}_3\cdot\text{H}_2\text{O}\). Henrich (47) stated that ammonium dichromate, at 135°C in air, decomposed violently
into nitrogen, oxygen and chromic oxide, plus a small amount of ammonia.

In 1923 Moles and Gonzales (41) in addition to studying the physical properties of ammonium dichromate, found that slow decomposition began at 225°C with the evolution of nitrogen, ammonia, and nitrous acid. The solid residue was not chromic oxide, but black chromium dioxide with 6 - 7% of water.

In 1938, in a study of the reaction products of the thermal decomposition of the three chromates of ammonia in vacuo, Fischbeck and Spingler (48) claimed that relatively uniform products were obtained in contrast to the diversity of results previously described. They formulated

$$(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \rightarrow \text{N}_2 + \text{Cr}_2\text{O}_3\cdot\text{H}_2\text{O} + 3\text{H}_2\text{O},$$

as the main decomposition equation, with 14 - 18% of the nitrogen present as ammonia, the residue being an amorphous black solid. There was no temperature dependence in the amount of ammonia evolved during the decomposition. Nitric oxide only occurred amongst the products after explosive decomposition in vacuo.

The kinetics suggested for the thermolysis of ammonium dichromate show a similar large divergence in the interpretation of experimental results. The first mechanism was put forward by Hinshelwood and Bowen (49) in 1920, who explained the observed acceleration of the decomposition on the basis of a progressive disintegration.
of the crystal structure with a consequent increase in effective surface, and that the reaction was confined to surface-adjacent zones. Solution in another solid caused a reduction in the rate of reaction. Roginskii and Schultz (50), in 1928, found an induction period and an autocatalytic period to the decomposition of the dichromate, both as crystals and as finely powdered material, the latter having a much faster rate. They rejected Hinshelwood's suggested mechanism, stating that there were definite reaction centres on the surface which spread throughout the crystal. There were two stages to the reaction; firstly, a free growth of reaction nuclei in all directions in the crystal and, secondly, a decreasing velocity stage occurring when the whole surface was covered and propagation of the reaction was to the interior only. Catalysis of the reaction was caused by the reaction products, which, if present in large amounts, completely changed the character of the reaction, no induction or autocatalytic period being observed. Garner (51), with evidence that the reaction product grew into the crystal interior in the form of needle-shaped nuclei, suggested that ammonium dichromate decomposed as the result of a branching structural chain reaction which was dependent on the crystal structure.

Following their analysis of the decomposition products, Fischbeck and Spingler (30) studied the kinetics of the
decomposition of the three chromates of ammonia. Their results for the dichromate are of especial interest as they are the most detailed of the early work and will be discussed more fully later. Briefly, Fischbeck reported a characteristic induction period of t' minutes, which was followed by an autocatalytic stage of the sigmoid pressure-time curve, the pressure measured being that of evolved nitrogen, fitting the equation
\[ x = k(t - t')^4, \]
up to 30% decomposition, where \( x \) was the amount of change at any time \( t \), and \( k \) a velocity constant. This simple power law is indicative of the growth of spherical nuclei, whose number increases linearly with time. From 30% decomposition, i.e. the maximum rate, to 100% decomposition the equation for a contracting sphere mechanism was obeyed, namely
\[ k(t - t_0) = 1 - (1 - x)^{3/2}, \]
where \( t_0 \) was the time at which the maximum rate occurred. In other words, the reactant is imagined as a collection of spheres fully nucleated on the surfaces, and with the reaction interface contracting inwards at a constant rate.

Taylor (52), in a reinvestigation of the problem using small crystals of 0.1 - 0.2 mm. in size, could not repeat Fischbeck's results, and suggested that a better equation would be the modified Prout-Tompkin's relationship,
\[ \log \frac{\alpha}{1 - \alpha} = k' \log t + c, \]
with but a single value for $k'$ in place of the more normal two values. The activation energy of 33 kcaIs/mole he obtained for the accelerator period was much lower than that reported by Fischbeck, namely 49 kcaIs/mole.

Object of this Research.

The research described in this thesis was undertaken with the idea of extending Taylor's reinvestigation to the case of large single crystals, c. 10 - 20 mg. in weight, and comparing the results obtained with the previous work in an attempt to reconcile the different reaction products and mechanisms proposed. To this end the reaction products were re-examined, and the usual pressure measurements supplemented by studying the loss in weight and the electrical conductivity, and by microscopic observations of the ammonium dichromate as it decomposed.
I. Growth of Crystals.

Analytical ammonium dichromate, 99.8% pure, was used as the initial material. Early attempts to grow single crystals soon showed that what appeared to be growth bands occurred in the crystal interior. As these growth bands would be tantamount to a series of crystal surfaces within the crystal, either requiring fresh nucleation when the product-reactant interface had grown in from the true external surface, or alternatively, being nucleated simultaneously with the true surface nucleation, they had to be eliminated before the crystals were suitable for use.

Although MacMasters, Abbott and Peters (53), in a study of the crystallisation characteristics of the dichromate group, reported that crystallisation in the presence of ammonium nitrate was effective in suppressing these growth bands, experiment gave material showing little, if any, improvement in form. Furthermore, other considerations militate against this practice. Thus, Dode (54) suggested that ammonium nitrate would be a product in the low-temperature decomposition of ammonium salts of sufficiently oxygenated acids. For both ammonium permanganate (36) and ammonium chlorate (55) this was the case, and Bircumshaw and Newman (37) found...
traces of nitrate ion in the sublimate from ammonium perchlorate, whose induction period was also halved in the presence of nitrate ion. The additional fact that ammonium nitrate itself decomposes in a temperature range similar to that of the dichromate, and that its decomposition is catalysed most strongly by dichromates (34) at the lower end of the temperature range, c. 220°C, provided another strong reason for not pursuing this method further.

The effect of varying the initial concentration, stirring during cooling, the rate of cooling and evaporation, the time of growth, etc., was investigated and, finally, the following procedure was adopted.

A saturated solution of ammonium dichromate was prepared at 30°C, i.e. 47.2 g. salt in 100 ml. of dust-free distilled water, and left to evaporate slowly at room temperature in a draught of air. The batch of extremely large, coarse, opaque crystals with strongly ridged faces, which quickly grew, were set aside and, after another day, hundreds of little crystals, from 5 - 20 mg. in weight, appeared and from these suitable samples could be chosen.

These crystals were selected by hand, thoroughly dried on filter paper, and stored in a desiccator over P₂O₅ if not used immediately. It was experimentally determined that 300 mg. of crystals, dried in the above manner, contained 1.5 mg. water, i.e. a 0.5% water content.
This water was either removed by storage in the desiccator, or by the overnight evacuation to which every crystal was subjected before a decomposition run was started.

The large rejected crystals were redissolved and the solution once more made saturated at 30°C, the above process then being repeated. Thus the analar material was recrystallised several times from solution, and the resulting crystals were probably as pure as could be obtained. A limit to this recrystallisation process occurred when the solution was perceptibly darker than a freshly prepared solution. This darkening would seem to be due to a slight photochemical decomposition of the solution, or alternatively, to repeated heating at 30°C, as the early experiments had shown that solutions heated above 50°C definitely decomposed. These 'dark' solutions gave crystals which were noticeably darker than 'normal' crystals, and also gave decomposition curves which were not typical. Any solution was rejected when it was considered to have darkened, and a fresh solution prepared.

II. Microscopic Observations of the Solid.

Two separate procedures were employed; (i) observations with the hot-stage microscope as the temperature was slowly increased and, (ii) microscopic examination after partial decomposition in vacuo and cooling to room
temperature.

Although the literature (38), (39), (40) describes ammonium dichromate as monoclinic, growing in the form of rhombs, typical crystals, that is those which were used in this work for the decomposition runs, were flat tabular hexagons, and it was noted that any rhombs obtained were in fact hexagons with two side faces inhibited (Fig. 4). The faces, consisting of two main pinacoids and four, or six, small side faces, were in general flat under the microscope with no ridges or hollows, and the edges and corners were sharp and bright, but these tended to become dull and rounded with age.

Initially, some ammonium dichromate crystals were heated in air on a slide on the hot-stage microscope with a temperature increase of 1°C per minute. The salt was stable up to 100°C after which temperature the original bright red-orange colour, gradually and irreversibly, became a red-brown and, as the temperature rose, a rich dark ruby-red colour. At 170°C black patches appeared on the lower surface and their number increased with increasing temperature. These black nuclei were first noticed on the upper surface at 185°C: the earlier growth on the lower face was presumably due to the better heating contact between the lower face and the hot-stage. Under high-power magnification it was seen that these black nuclei were diamond shaped (Fig. 3a), and had a distinctly linear
crack running along the main diagonal of the diamond: these nuclei appeared to grow very slowly at this temperature, whereas new ones were continually 'jumping' into view on the surface. At 205°C the nuclei were beginning to grow slowly by spreading out at the ends of the diamond cracks in the form of a spear-like front (Fig. 3b), whilst the cracks lengthened: small fern-like subsidiary cracks also appeared growing normal to the main crack in big nuclei (Fig. 3c).

Meanwhile, the body of the crystal was growing noticeably darker independently of these surface nuclei. At 215°C the number of nuclei on the surface increased rapidly and the crystals began to jump about on the hot-stage: the nuclear cracks grew to sizeable dimensions and spread across the crystal with many of the nuclei appearing in the region of these cracks. By 225°C half of the upper surface was covered with large-sized nuclei and was very cracked, but the bulk of the crystal was, by this time, an extremely dark red. By 230°C the whole crystal was black throughout and parts of the edges had been blown away.

The behaviour of crystals grown in the presence of ammonium nitrate was examined in a similar manner. The reddening process occurred as before from 100°C onwards, but nuclei did not appear until 190°C and were spherulitic in shape rather than diamond type. This form of nucleus did not grow appreciably and little happened, apart from the
increasing darkening of the crystal, until 215°C where, after many audible "cracking" noises, the crystal explode. The indications were that nitrate ion inhibited the surface nucleation process, but not the general darkening process, and caused an explosive decomposition at 215°C in place of a more normal "slow" decomposition.

Crystals of the dichromate were then examined as they were heated in vacuo. Half of the closed end of a glass tube was sliced off and a flat glass window cemented in its place by means of "Araldite" thermosetting resin; the crystal was placed under the glass window and the open end of the tube connected to a Hyvac oil pump. The glass tube was surrounded by a pile of copper turnings to spread the heat from the hot-stage more evenly. General darkening of the crystal bulk began at 100°C: nuclei appeared on the lower face at 190°C, and on the upper at 200°C. A rapid increase in the number of these diamond nuclei occurred at 215°C and the surface was riddled with cracks by 220°C. Shattering of the crystal began at 225°C with many small pieces being blown off the edges, and by 230°C the sample was completely black throughout. In general, the phenomena were the same as those observed in air, with a general darkening process followed by the appearance of nuclei.

A study of the crystals' appearance at successive stages of the general decomposition curve (Graph 1) was then made at a fixed temperature, 195.5°C, in order to determine
whether the darkening in bulk or the surface nucleation was the dominant process in the decomposition. The amount of decomposition at each stage was fixed as a percentage of the amount of nitrogen experimentally expected from the complete decomposition of that weight of crystals at that temperature. Each observation was on a batch of five or more crystals, and was repeated four times. The estimate of the amount of surface covered by black nuclei is merely a visual average, and the estimate of the rate of darkening is only relative to the preceding stage.

At 0.1% decomposition, that is immediately the induction period had finished, the samples were ruby-red to the naked eye, but quite light in transmitted light under the microscope. No nuclei were seen at this stage, but in specimens with poor faces an unusual growth of spherulitic nuclei appeared resembling bubbles on the surface of the crystals and standing up from the surface level, in contrast to the fact that diamond nuclei appeared to lie in the actual surface layer.

At 0.5% decomposition the crystals were very much darker to the unaided eye: under the microscope the material was still light red and a few small nuclei had now appeared. These latter were tiny pinheads with diffuse tails and were seemingly aligned in one direction: the spherulites, meanwhile, had grown no larger nor increased in number. At this stage the product was still completely soluble in
water giving a light yellow colour.

When 1% decomposition had occurred the material was very dark red to the eye although still quite transparent to bright light. Small patches of nuclei had appeared around any rough patches on the surface and were much larger than the spherulites which could only be seen under very high power, whereas the diamonds were visible with low magnification. The samples were still soluble in water.

At the 2% stage the material was extremely dark red to the eye, although just dark red with strong illumination. The nuclei had not increased significantly in number but were noticeably larger, covering about one-hundredth of the surface area: no new incipient nuclei could be seen. The material was soluble in water, giving a dull yellow colour with a few tiny insoluble black specks.

At 5% decomposition the crystals were jet-black and opaque to the unaided eye, but under the microscope showed up as very dark red. The diamond nuclei were now quite large and covered approximately one-tenth of the surface area. The main crack running along the diagonal had now appeared as well as the smaller subsidiary cracks. An earlier tendency for the nuclei to be diffuse at one end of the main diagonal, as if growth was occurring at a slight angle to the surface, had now disappeared and the nuclei lay flat on the surface. The alignment of the nuclei in one direction was now strongly pronounced in all the crystals.
examined and in no case did this phenomenon fail to occur. The substance was still soluble in water, giving a greenish-yellow colouration with some black insoluble particles.

At 10% decomposition very little light was transmitted through the crystals under the microscope. Whilst now an extremely dull red in bulk, it was still possible to see that the black nuclei covered one-half of the surface and cracks were beginning to develop on the two main faces. The bulk of the material was soluble, but gave a dark green colour with a noticeable amount of insoluble black specks.

By 18% decomposition, which was one-quarter of the sigmoid section of the curve, the material was completely black and opaque under the microscope with the cracks now showing the alignment in the same crystallographic direction as the main nuclear diagonals had pointed. From this stage onwards the solubility of the material decreased rapidly. By the maximum rate stage, 34% decomposition, the number of these cracks had increased greatly and at the top of the sigmoid, 70% general decomposition, the surface was very badly cracked when examined microscopically, although to the unaided eye it presented an adamantine lustre. From here to complete decomposition no significant change in physical appearance was observed, although the material at the 70% stage was negligibly soluble whereas the final product was completely insoluble in water. The final product, especially for larger crystals, had in many cases split
into two or more parts and the edges had blown off. In addition, microscopic observations of the final product using surface illumination showed that the cracks were approximately one-half the crystal width in dimension and were all aligned parallel to the b-axis: many small, fine cracks could be seen at right angles to the array of major cracks.

X-ray crystallographic measurements were made to determine the alignment of the diamond nuclei, and it was found that the main diagonal cracks lay in the plane of the b-axis with the other diagonal in the plane of the c-axis, and with the actual nuclei normal to the a-axis. Fig. 4(A) shows the large (100) face of a typical hexagonal crystal with an arrow showing the direction of the main diagonal of the nuclei. Fig. 4(B) shows the modification of a hexagonal crystal to a rhomb, but the nuclei still point to the inhibited faces.

An important corollary to these external visual observations was the fact that, when the crystals were broken open at each stage, the diamond nuclei were confined to the surface faces, whereas the darkening was homogeneous, apart from one or two amber patches which were random in occurrence and not central.

The conclusions drawn from this microscopic work were that the general darkening phenomenon was the primary decomposition process, and was in fact occurring before the
acceleration period began. The diamond nuclei, which appeared to occur principally on the pinacoid 100 faces, and in every case were aligned in one crystallographic plane with the main diagonal pointing parallel to the b-axis, were confined to the surface, grew very slowly, and contributed only in a minor degree to the decomposition. The cracks noticed in the final product were probably the results of stresses in the lattice, but whether they were caused by the diamond nuclei or the darkening process it was not possible to show.

The following four plates are photomicrographs of partially decomposed crystals of ammonium dichromate, showing some features of the diamond nuclei.
Plate I (x 340) shows the alignment of the nuclei with respect to the crystal orientation. The face shown is the (100) pinacoid and the diamonds point to a partly inhibited (010) face. Through illumination only.

Plate II (x 1050) is a close-up of a section of Plate I and shows the perfect alignment of the nuclei and the main diagonal cracks. The mixture of through and surface illumination shows that the nuclei are on the surface and the cracks run into the crystal.

Plate III (x 4500) is a close-up of an individual nucleus showing the diamond shape and the main diagonal crack with the network of subsidiary cracks at right angles. Black material fills many surface fissures which may mark subgrain boundaries. Through illumination only.

Plate IV (x 680) shows the surface of the final material. The product is pseudomorphous with the initial crystal and the micrograph illustrates the many cracks on the surface all pointing in the direction of the b-axis as did the nuclei. Surface illumination only.

As the photographs were taken on 35 mm. film the magnifications given in brackets are those calculated from the respective lens combinations used in the microscope for each plate combined with the magnification due to the enlarging of 35 mm. film to the plate size.
III. (a) **Apparatus.**

The experimental system used (Fig. 5) was based on an apparatus described by Garner and Haycock (11). It is a simple static system in which the pressure increase in a known volume due to the gases evolved during the decomposition was measured by either a McLeod or a Bourdon gauge. The reaction vessel RV was seated in the electrically-heated furnace F, so that the bottom of the vessel, and also the thermocouple Th, was centrally situated. The sample S, contained in a small bucket constructed from 2cm.$^2$ of 0.025 mm. thick platinum foil, could be lowered into, or raised from, the furnace at any given time by means of the winch W to which the bucket was connected by fine platinum wire. The furnace was stabilised to better than 0.05°C by the use of a Sunvic Resistance Thermometer Controller Type RT2 with the A.C. mains power supply further stabilised by a voltage stabiliser. The thermocouple, with one joint at the very bottom of the reaction vessel and the other held in ice, was calibrated in steps of 5°C from 30°C to 300°C against a standard platinum resistance thermometer: the voltage was read to 0.001 mv. on a Tinsley Potentiometer Type 3184D.

The gases from the reaction vessel passed through a trap T₁ into the vacuum line to be expanded into a known volume V. V consisted of three bulbs of known volume, each of which, or all of which, could be connected into the
vacuum line to give pressures in a desired range. The water condenser C adequately cooled the upper part of the reaction vessel. \( M_1 \) was a McLeod gauge measuring from \( 10^{-5} \text{ mm.} \) to \( 0.16 \text{ mm.} \), and \( M_2 \) a McLeod gauge measuring from \( 10^{-5} \text{ mm.} \) to \( 5.5 \text{ mm.} \), any greater pressure being measured on a manometer \( M_3 \) connected to the system. The trap \( T_2 \) prevented mercury vapour from the McLeods distilling into the reaction line. In later work a Bourdon gauge \( B_2 \) of sensitivity \( 0.0159 \text{ mm.}/\text{scale division of the telescope} \), was built into the line to measure gaseous products including water and ammonia.

The pumping system consisted of an Edwards metal two-stage mercury diffusion pump backed by a Speedivac rotary oil pump, the unit giving a vacuum of \( 10^{-6} \text{ mm.} \). Apiezon L grease was used for all joints and taps, except for the joint used in the winch where Apiezon T grease was used.

The volume of each section of the system was measured by expanding a known pressure of dry air from a known volume through the air-leak \( A \) into each section, and measuring the resultant pressure on the manometer. From Boyle's Law the volume of each section was then calculated. Small volumes, e.g. of connecting tubing, were calculated from their dimensions. The volumes given are a mean of three determinations, and were estimated with the reaction vessel and both traps at room temperature.
### Section of Apparatus

<table>
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<th>Description</th>
<th>Mean Volume</th>
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</thead>
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</tr>
<tr>
<td>flask 1</td>
<td>1097 cc.</td>
</tr>
<tr>
<td>flask 2</td>
<td>2351 cc.</td>
</tr>
<tr>
<td>flask 3</td>
<td>2300 cc.</td>
</tr>
<tr>
<td>McLeod gauge M₁</td>
<td>376 cc.</td>
</tr>
<tr>
<td>total volume (added)</td>
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</tr>
<tr>
<td>Bourdon gauge: spoon + connections</td>
<td>40 cc.</td>
</tr>
<tr>
<td>jacket + connections</td>
<td>430 cc.</td>
</tr>
</tbody>
</table>

### III. (b) Experimental Procedure

With the weighed crystal in the platinum bucket the total volume was pumped out overnight for 15 hours until a vacuum of $10^{-6}$ mm. was attained. The system was isolated from the pumps and, if after one hour no leak had developed, the sample was lowered into the furnace so that it made good contact with the bottom of the pocket containing the thermocouple. The thermocouple indicated a maximum heating-up period of about 5 minutes, and gave no evidence of self-heating of the crystals during decomposition.

With liquid nitrogen round the traps T₁ and T₂, M₁ measured the pressure of the nitrogen gas evolved during the decomposition: readings were taken every five minutes at lower temperatures and every two minutes at higher temperatures. With phosphorus pentoxide in both traps, M₁ measured the combined pressure of nitrogen and nitrous oxide. For each run a final pressure reading was taken.
after 24 hours decomposition had occurred.

To estimate water and ammonia in the condensate trap $T_1$ was replaced by a U-tube which was surrounded by liquid air. The ammonia was estimated by titration with decinormal hydrochloric acid, and an attempt made to measure the water by weighing.

The pressure of the total gaseous products was measured by means of the Bourdon gauge alone with a minimum backing volume of reaction vessel, vacuum line and the two traps at room temperature.

IV. Analysis of the Reaction Products.

(a) The Gaseous Products.

In view of the wide variation in the reported gaseous products referred to in the Introduction, it was decided to reinvestigate this aspect of the decomposition. The gases were first tested for qualitatively and then, when identified, estimated quantitatively by their partial pressures in the apparatus described above. The gases analysed were obtained at a standard decomposition temperature of 195.5°C.

Qualitative Analysis. With liquid nitrogen round the traps, the condensate was examined. Ammonia was identified by Nessler's reagent as being present in large amounts. The presence of traces of nitrite and nitrate was indicated by the sulphanilic acid - α-naphthylamine hydrochloride test described in Section VIII (e): from 100 mg. ammonium
dichromate only 5 μg. of these ions were obtained. The presence of ice in the condensate indicated that water was evolved in sizable amounts.

Nitrous oxide was identified by gas phase chromatography (56). With as small a volume as possible, about 70 cc., sufficient ammonium dichromate was slowly decomposed in vacuo at 196° C to give 10 mm. of non-condensable gas when a small U-tube in the system was surrounded with liquid nitrogen, the pressure being measured on a manometer. When the decomposition was finished, this non-condensable gas was flushed out of the system by the carrier gas, nitrogen, into any one of four chromatographic columns, which were calibrated for various gases. The actual technique used was adsorption chromatography, and the gas detector was a thermal conductivity gauge, the method having a fairly high sensitivity of the order of micromoles. This 10 mm. of gas had the same thermal conductivity as the carrier gas and was thus nitrogen. The condensate in the U-tube was warmed with hot water and flushed into the chromatographic columns. A gas passing through a silica gel column maintained at 35° C in 8 minutes was identified as nitrous oxide: the water and ammonia were too strongly adsorbed to the chromatographic columns and could not be identified in this manner. This method of gas analysis, however, eliminated the possibility of oxygen, or any of the other oxides of nitrogen, being significant products of the
decomposition of ammonium dichromate under these experimental conditions, as had been previously claimed. If the decomposition occurred explosively, however, some nitric oxide was found in the gaseous products.

**Quantitative Analysis.** With liquid nitrogen round the traps the accumulative nitrogen pressure was measured on the McLeod gauge; with $P_2O_5$ in the traps the accumulative nitrogen plus nitrous oxide pressure was measured. Titration of the condensate with $0.1N$ hydrochloric acid, using a mixed indicator of methyl red and bromocresol green, gave the ammonia content. By converting these results, obtained after complete decomposition had been attained, to the amount of gas evolved from a 10 mg. crystal in a fixed volume (6684 cc.), and calculating the amount of nitrogen expected from this weight of ammonium dichromate on the basis of Fischbeck's equation,

$$ (NH_4)_2Cr_2O_7 = N_2 + 3H_2O + Cr_2O_3 \cdot H_2O, $$

it was found that 100% nitrogen ammonium dichromate gave 53.5% as free nitrogen, 23.5% as nitrous oxide, and 20.5% as ammonia gas at 195.5°C; that is, a total of 97.5% of the theoretical value. This theoretical value was calculated on the basis of

$$ \text{pressure} = \text{constant} \times \frac{\text{weight} \times \text{room temperature (°A)}}{\text{volume of system}} $$

where the constant includes the corrections for N.T.P. For the standard corrected values of a 10 mg. crystal in 6684 cc. at 18°C this pressure is $108.4 \times 10^{-3}$ mm.
By connecting a gas cell, with sodium chloride end-windows, to the reaction system, and by decomposing sufficient material to give a final pressure of c. 20 mm. of total gaseous products, the infra-red spectrum of the latter could be traced on a Hilger R800 Spectrophotometer. The presence of nitrous oxide, ammonia, and water was confirmed, but no trace of any other oxides of nitrogen was found, (99) (see Fig. 10).

(b) Nature of the Solid Residue.

The final solid product of the reaction at 195.5°C was a hard, black, brittle adamantine material pseudomorphic with the initial crystal of ammonium dichromate. An X-ray powder photograph showed that this substance was amorphous as Fischbeck had reported (48), but the loss in weight of the crystal found during the decomposition did not correspond to the formula given by him, namely chromic oxide hydrate, \( \text{Cr}_2\text{O}_3\cdot\text{H}_2\text{O} \). He stated that this material was homogeneous, and gave as the main reaction mechanism,

\[
(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + \text{Cr}_2\text{O}_3\cdot\text{H}_2\text{O},
\]

with approximately 14% of the nitrogen being evolved as ammonia in a small initial surface reaction.

Earlier workers had variously described the solid residue as \( \text{Cr}_2\text{O}_3\cdot\text{H}_2\text{O} \) (45), (48), non-homogeneous \( (\text{CrO}_2)_3\cdot\text{H}_2\text{O} \) (46), and \( \text{CrO}_2 \) with 7% of water in it (41). In 1938 Harbard and King (57) reinvestigated this black material which they found to be a solid solution with the composition by weight, as
Cr 61.2; N₂ 3.0; N₂O 4.5; H₂O 2.0; O (by difference) 29.3%.

In spite of its apparent physical homogeneity, they suggested there was no simple formula and the substance was probably a solution of two or more compounds, or else the gases are sorbed in some manner to the surface of some simple oxide.

In an attempt to decide which of the work in the literature was most reliable, the final black product was analysed as follows.

Chromium was estimated by the standard method of fusion with sodium peroxide to give sodium chromate (58). Addition of sulphuric acid formed the dichromate, which was then reduced by a known excess amount of ferrous ammonium sulphate, and the excess determined by back-titration with standard potassium dichromate.

Water was estimated by roasting a known weight of black material in an evacuated silica tube at 800°C, and measuring the resultant increase in weight of a U-tube containing P₂O₅.

Nitrous oxide was measured by gas phase chromatography (56) in a similar manner to that previously described. 0.5g. of black material was roasted at 800°C in a small evacuated silica tube connected to the U-tube which was surrounded by liquid air. The non-condensable evolved gas was flushed into the chromatographic columns by nitrogen; this gas came through a charcoal column maintained at 25°C in two
minutes, which fixed it as oxygen and not nitrogen as found by Harbard and King. On warming the condensate in the U-tube, the evolved gas came through a silica gel column at 35°C in 8 minutes, indicating nitrous oxide. No other gases could be found within the experimental limits of the method. By connecting the silica tube to the reaction line at the air-leak A (Fig. 5), evacuating, and roasting a known amount of the black solid at 800°C, the gases evolved could be quantitatively measured on the McLeod gauge.

The composition of the product, by percentage weight, was found to be

Cr 60.1; H₂O 8.1; N₂O 1.2; O₂ (free) 2.8; O (difference) 27.8.

The chromium, fixed oxygen, and water content correspond approximately to chromic oxide hydrate which requires Cr 61.2; O 28.2; H₂O 10.6%, the small amount of nitrous oxide and oxygen being held in the material in some way.

This was borne out by the average loss in weight, which was found to be 31.8% at 195.5°C, as opposed to an expected value of 32.6%, if ammonium dichromate (M.W. 252.1) were to decompose to chromic oxide hydrate (M.W. 170.0). That is, the salt has not fully decomposed, although all pressure measurements indicated that the reaction was complete. Furthermore, as discussed below, if the green material obtained on roasting the black product at 800°C was assumed to be chromic oxide, then a loss in weight of 10.6% would
be expected, whereas experimentally this was found to be 12.1%.

Since Harbard and King had reported that the gases were evolved slowly from 260°C upwards, with an explosive evolution at 385°C - 390°C, it was considered that the kinetics of this decomposition might shed some light on the mechanism of the primary dichromate decomposition. Unfortunately, the evolution of the gases was not simple, and also was very dependent on the thermal history of the sample. For material prepared at 195.5°C the small residue of N₂O came off very quickly from 230°C upwards and remained constant: little, if any, oxygen was evolved until 385°C where it came off explosively and was then slowly sorbed back into the solid, as Harbard and King had found, although the amount of N₂O remained constant and was not resorbed in any way. An X-ray powder photograph of this material, taken when the gases had evolved explosively at 385°C, showed that approximately 50% of the solid had recrystallised, the lines on the photograph being superimposable on a Cr₂O₃ powder photograph by direct comparison. If black material prepared at 215°C were decomposed, no nitrous oxide could be found, although the same amount of free oxygen was found with the explosive temperature again at 385°C.

Hnard and King had found that roasting the black material at 350°C gave a chromium content of 67.3%, which
increased to 67.8% after roasting with a Meker burner. It was found in this work that the material left at 385°C after the explosive decomposition was a dull grey-green with a chromium content of 67.4±0.3%. Roasting in air for two hours with a Meker burner gave a chromium figure of 67.7±0.3%, the residue being a pale blue-green colour. Analysis of commercial Cr₂O₃, a bright emerald green colour, gave a figure of 68.4±0.4% for the chromium content, indicating that the material prepared from ammonium dichromate contained an excess of oxygen although X-ray powder photographs gave no indication of this.

The 1.2% nitrous oxide by weight in the black residue corresponded to 5.6% of the nitrogen in the initial weight of ammonium dichromate, so that the final nitrogen balance was N₂ 53.5%; N₂ as N₂O (free) 23.5%; N₂ as N₂O (in solid) 5.6%; N₂ as NH₃ 20.5%, after correcting the pressures to a fixed volume, all the values being determined at 195.5°C the standard reference temperature. This gave a total nitrogen figure of 103.1%, i.e. an error of 3.1% which, considering the additive errors involved, appeared reasonable.

V. Kinetics of the Decomposition.

(a) The evolution of Nitrogen.

As described in the experimental procedure, the pressure was measured every five minutes for the slower decompositions, and every two minutes for the faster runs on a McLeod gauge.
The decomposition of single crystals was studied at seven temperatures in the range 188° - 215°C and four runs were done at each temperature.

The form of the pressure-time curve was a sigmoid form with a pronounced induction period, as found for barium azide (6). At the end of the sigmoid a new feature occurred, namely the appearance of a straight-line portion to the curve, as found by Taylor (52) for very small crystals. After this linear portion, which was present at all temperatures, the decomposition curve died off in an indeterminate manner.

Graph 1 shows a typical run for each temperature examined with the tables of results given below. These pressures have all been corrected as coming from a 10 mg. crystal decomposing in a volume of 6684 cc. This was justified by the fact that Taylor found that both the maximum rate and the constant rate stage were directly proportional to the initial weight of the sample. The value $p_f$ was estimated as that pressure where the sigmoid portion of the curve finished and the linear part of the curve began.

In the following tables $t$ denotes the time of reaction in minutes, $p$ the pressure of accumulated gas, and the values are given for the Prout-Tompkins factor $\log \frac{p}{p_f - p}$. The estimated value of $p_f$ is given as is the length of the induction period $\uparrow$ minutes.
### Table 1.

**Run A4.** 188.1°C. \( pf = 40.7 \times 10^{-3} \text{mm.} \) ~ 65 minutes.

<table>
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<th>t (mins.)</th>
<th>( p \times 10^3 ) mm.</th>
<th>3 + log ( \frac{P}{pf-p} )</th>
<th>t (mins.)</th>
<th>( p \times 10^3 ) mm.</th>
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Run B3.  192.0 C.  $p_f = 40.8 \times 10^{-3}$ mm.  ~ 50 minutes.

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Table 3.

Run C3. \(195.5^\circ C.\) \(p_f = 40.6 \times 10^{-3} mm.\) \(\sim 45\) minutes.

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Table 4.

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Run E2.  \(205.2^\circ\text{C.} \quad P_f = 43.5 \times 10^{-3}\text{mm.} \sim 20\text{ minutes.}\)

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<th>$p \cdot 10^3$ mm.</th>
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</table>
Graph 2 illustrates the plot of $\log \frac{\alpha}{1-\alpha}$ against time, substituting $p/p_\text{f}$ for $\alpha$. This, in nearly every case, is the best fit to the results, the exceptions being discussed later. This plot gives one straight line in every case, and is fairly reproducible from curve to curve for a given temperature. Below, in Table 8, a summary is given of the

Table 7.

<table>
<thead>
<tr>
<th>Run G1. 213.4°C. $p_\text{f} = 43.5 \times 10^{-3}$mm.</th>
<th>10 minutes.</th>
</tr>
</thead>
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<td>$t$ (mins.)</td>
<td>$p \times 10^3$ (mm.)</td>
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<td>10</td>
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<tr>
<td>15</td>
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</table>

24 hrs. 60.2
GRAPH 1

THE EVOLUTION OF NITROGEN

CURVES B AND E ARE DISPLACED 20 MINUTES TO THE RIGHT

PRESSURE (×10^-2 atm)

TIME (MINUTES)
CURVES B AND E ARE DISPLACED 20 MINUTES TO THE RIGHT AND TO THE LEFT RESPECTIVELY
maximum rates, the slopes of the constant-rate process, and the values of the Prout-Tompkins $k$ calculated from each plot of $\log \frac{P}{P_0-P}$ against time, all values being corrected to 10 mg.

**Table 8.**

<table>
<thead>
<tr>
<th>Run</th>
<th>$T^\circ C$</th>
<th>maximum rate $10^4$ mm./min.</th>
<th>linear rate $10^5$ mm./min.</th>
<th>$k \times 10^2$</th>
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</thead>
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</tr>
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<td>192.0°</td>
<td>2.35</td>
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</tr>
<tr>
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<td>4.40</td>
<td>1.127</td>
</tr>
<tr>
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<td>4.00</td>
<td>1.192</td>
</tr>
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<td>6.29</td>
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<td>7.45</td>
<td>1.561</td>
</tr>
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<td>3.84</td>
<td>9.44</td>
<td>1.730</td>
</tr>
<tr>
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<td>6.00</td>
<td>1.527</td>
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<td>9.44</td>
<td>1.806</td>
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<td>9.16</td>
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</table>
These values are plotted on Graphs 3, 4 and 5 as activation energy curves, giving the following values for $E$:

- 36.6 kca/mol from the maximum rate values,
- 34.3 kca/mol from the Prout-Tompkins $k$ values,
- 41.0 kca/mol from the linear rate values.

The error in estimating the best slope of each of these sets of values is of the order of ±2 kca/mol.

(b) The evolution of Nitrogen and Nitrous Oxide.

The measurement of these two gases on a McLeod gauge with $P_2O_5$ in the traps was studied in the same manner as for nitrogen alone. The same form of decomposition curve was found and Graph 6 shows seven typical runs in the range 188.1°C - 215°C with the corresponding experimental results tabulated in Tables 9 - 15. Again the Prout-Tompkins equation $\log \frac{p}{p_f - p} = kt + c$ was the best fit and Graph 7 illustrates the fit of the chosen examples. Only one straight line was obtained once more.

Table 16 summarises the maximum rates, linear rates, and Prout-Tompkins $k$ values obtained at the temperatures given, the values being corrected to 10 mg. and 6684 cc.
<table>
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<th>Run A5</th>
<th>188.1°C.</th>
<th>$p_f = 52.1 \times 10^{-3}$mm.</th>
<th>↑ 40 minutes.</th>
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<tbody>
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<td>t mins.</td>
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<td>$3 + \log \frac{p}{p_f-p}$</td>
<td>t mins.</td>
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24 hours: 84.2
Table 10.

Run B5. 192.0°C.  \( p_f = 51.6 \times 10^{-3} \text{mm}. \) ~ 50 minutes.

<table>
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<th>t (mins.)</th>
<th>p ( \times 10^{-3} ) mm.</th>
<th>3 + log ( \frac{P}{P_f-P} )</th>
<th>t (mins.)</th>
<th>p ( \times 10^{-3} ) mm.</th>
<th>3 + log ( \frac{P}{P_f-P} )</th>
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### Table 12.

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*24 hrs.* 86.0
Table 13.

Run E5. 205.2°C. \( p_f = 54.0 \times 10^{-3} \text{mm} \). ~ 20 minutes.

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Run P4. 209.7°C. \( p_f = 55.0 \times 10^{-3} \text{mm} \) \( \sim 15 \text{ minutes} \).

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24 hrs. 89.0
Table 15.

Run G5. 215.0°C.  $p_f = 63.0 \times 10^{-3}$ mm.  ~10 minutes.

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CURVES C, E, F, ARE DISPLACED 20 MINUTES AND CURVE A 40 MINUTES TO THE RIGHT
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<th>linear rate $10^5$ mm./min.</th>
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These values are plotted on Graphs 8, 9 and 10 as activation energy curves giving the following values for E:

- 42.1 kca/s./mole from the maximum rate values,
- 35.3 kca/s./mole from the Prout-Tompkins k values,
- 41.1 kca/s./mole from the linear rate values.

The error in each of these values of E is about $\pm 2$ kca/s./mole.
(c) **The evolution of Ammonia.**

In this work the trap adjacent to the reaction vessel was replaced by a U-tube of known weight, which could be removed from the reaction line by means of two Quickfit joints. During the decomposition of 500 mg. samples, the bucket could be raised at any desired fractional decomposition, as measured on the nitrogen curve, and the condensate in the U-tube examined.

With liquid air round the U-tube and after a certain fraction of decomposition the reaction was stopped, the U-tube removed, and stoppers placed over the U-tube joints and fixed in place by means of spring supports. The U-tube was allowed to come to room temperature, the outside carefully cleaned and dried, and the whole weighed. After cooling once more to liquid air temperature, the stoppers were removed, 10 ml. 0.1N HCl added, and the contents washed into a beaker. The excess acid was determined by titration with standard 0.1N NaOH, using a methyl red-bromocresol green mixed indicator, and the amount of ammonia thus estimated. The U-tube was carefully dried and cleaned inside and outside, the stoppers replaced, and the whole weighed once more.

Theoretically, knowing the weights of ammonia, nitrogen, and nitrous oxide evolved, the remainder of the gain in weight in the U-tube should have been water. Unfortunately, in many cases the weight of total gaseous
products exceeded the loss in weight, as determined from the partially decomposed crystals, by as much as 10% and it was concluded that the excess weight was primarily due to distillation of mercury from the McLeod gauge, and also to some condensation of water and carbon dioxide from the air into the U-tube during manipulation when weighing.

The determination of water by this method was abandoned, and as the exact composition of the nitrogen, nitrous oxide, and ammonia gaseous content was not known at any given time, the combined weight of these gases could not be estimated and subtracted from the actual loss in weight to give the weight of water at that time. The experimental obstacle to this was the fact that the gases had to be determined in separate runs, and because of the variable nature of the induction period, no confident relationship could be made between values obtained at any given point on the time scale.

However, an estimate of the manner in which ammonia was evolved in the decomposition was obtained, and a typical set of results is given below in Table 17. The corresponding points on a general decomposition are shown on Graph 11.

The molar ratios of ammonia to nitrogen are given in Table 18. By partial ratio at any point is meant the ratio of the amount of gases evolved in that one small range of the curve, and by total ratio the amounts of gases evolved
from the point 0 up to the end of that part of the curve.

Table 17.

<table>
<thead>
<tr>
<th>Range on curve</th>
<th>nitrogen moles x 10^{-3}</th>
<th>total moles x 10^{-3} at points</th>
<th>ammonia moles x 10^{-3}</th>
<th>total moles x 10^{-3} at points</th>
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<td>0 - A</td>
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<td>4.40 0.157</td>
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<td>6.84 0.244</td>
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<td>0.55 0.032</td>
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<td>(24 hrs.)</td>
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Table 18.

<table>
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<tr>
<th>Range on curve</th>
<th>partial ratio of NH_3:N_2</th>
<th>total ratio of NH_3:N_2</th>
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</thead>
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<td>1.71:1</td>
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<td>A - B</td>
<td>1.27:1</td>
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<td>B - C</td>
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<td>1.30:1</td>
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<td>C - D</td>
<td>1.09:1</td>
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<td>D - E</td>
<td>0.075:1</td>
<td>0.765:1</td>
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The results in Tables 17 and 18 were obtained from an initial weight of 530.7 mg. (NH_4)_2Cr_2O_7 at 195.5°C in a volume of 6684 cc.; the weight of solid residue was 360.8 mg.
GRAPH II
THE EVOLUTION OF AMMONIA

MOLES OF GAS (x 10^3) EVOLVED

TIME (MINUTES)

N\textsubscript{2}
N\textsubscript{H}_3

50 100 150 200 250 300 350 400
0 0 0 0 0 0 0 0

24 HOURS
Those curves indicate that there is no constant molar relationship between the evolution of nitrogen and ammonia. In the early stages of the reaction nearly twice as much ammonia as nitrogen is evolved, but this ratio decreases until at the maximum rate stage of the general decomposition curve it is approximately mole for mole. Just before the top of the sigmoid, at D, more than 97% of the ammonia has been evolved whereas only 63% of the experimentally determined nitrogen has come off here. Other similar determinations indicated that all the ammonia was evolved by the end of the sigmoid portion of the nitrogen pressure-time curve, very little, if any, being evolved during the constant-rate process and final decay period.

\[ 530.7 \text{ mg.} \ (\text{NH}_4)_2\text{Cr}_2\text{O}_7 \longrightarrow 12.0 \text{ mg.} \ N_2 + 0.55 \text{ mg.} \ \text{NH}_3 + 360.8 \text{ mg.} \ \text{Cr}_2\text{O}_3\text{H}_2\text{O}. \] (assumed formula)

\[ \therefore 2.13 \times 10^{-3} \text{ moles} \ (\text{NH}_4)_2\text{Cr}_2\text{O}_7 \longrightarrow 1.152 \times 10^{-3} \text{ moles} \ N_2 + 0.881 \times 10^{-3} \text{ moles} \ \text{NH}_3 + 2.12 \times 10^{-3} \text{ moles} \ \text{Cr}_2\text{O}_3\text{H}_2\text{O}. \]

\[ \therefore 1 \text{ mole} \ (\text{NH}_4)_2\text{Cr}_2\text{O}_7 \longrightarrow 0.54 \text{ moles} \ N_2 + 0.414 \text{ moles} \ \text{NH}_3 + 0.996 \text{ moles} \ \text{Cr}_2\text{O}_3\text{H}_2\text{O}. \]

From four such analyses at 195.5°C this general effect of a much greater evolution of ammonia than nitrogen in the early stages of the decomposition was borne out, and little, if any, ammonia was evolved after the top of the sigmoid. The average total amount of ammonia determined was 0.410 moles from 1 mole ammonium dichromate.

Fischbeck (48) has stated that the amount of ammonia
evolved during the decomposition is constant, i.e. it is temperature independent. A survey of the results obtained in this work showed that the nitrogen final pressures were independent of temperature, being \(54.2\%\) of the theoretical nitrogen content of the salt when corrected to 10 mg., 6684 cc., and an allowance made for the temperature effect on the traps and reaction vessel. The combined nitrogen-nitrous oxide pressures varied from 73\% at 138.1\(^\circ\)C to 83\% at 205\(^\circ\)C upwards of the theoretical nitrogen content, indicating that the amount of nitrous oxide evolved is temperature dependent. This effect was also noted by Taylor (52).

At 195.5\(^\circ\)C the decomposition equation would appear to be

\[
(NH_4)_2Cr_2O_7 \rightarrow 0.535 N_2 + 0.235 N_2O + 0.410 NH_3
+ Cr_2O_3.H_2O.N_2O.O_2 + 2.6 \text{ (approx.) } H_2O.
\]

(d) **The total gaseous evolution.**

In a further attempt to determine the nature of the water evolution, a Bourdon gauge was incorporated in the reaction line and, using as small a volume as possible (600 cc., of which 40 cc. were the volumes of the gauge spoon and connections), decompositions of single crystals were followed with no traps employed in the system, i.e. the total gaseous pressure was allowed to build up. Readings were taken every five minutes at 195.5\(^\circ\)C and converted to the standard crystal weight of 10 mg. and 6684 cc. Because
of the sensitivity of the Bourdon gauge, 0.0159 mm./scale division of the telescope, it was necessary to equilibrate the gauge and the jacket about seven times during a decomposition. Before beginning a run, both sides of the gauge were evacuated independently with the vacuum tap across the gauge shut (Fig. 5): the pumps were shut off and a run started, so that the gases evolved filled the gauge spoon and the deflection was read on a telescope focussed on the end of the spoon. When the spoon had moved a full deflection across the telescope scale the connecting tap was opened, the spoon allowed to come back to its zero position, the tap shut once more, and the scale deflections again read as the reaction proceeded. This procedure was repeated each time a full scale deflection occurred until the decomposition was finished. The scale deflections were translated into pressure readings and these were added together to give the pressure of accumulated gas.

The variation in the final experimental pressures measured was of the order of \( \pm 5\% \) of the mean of the six runs performed at 195.5°C. This error was probably due in the main to the adsorption of water, and perhaps ammonia, on the glass surfaces as the pressure built up, but the fact that the gauge and jacket had to be equilibrated about seven times during a decomposition (and as each equilibration required thirty seconds this would have a considerable effect, especially in the accelerating stage of the reaction)
probably introduced a large variable error.

Despite this error the decomposition curves obtained were of the usual sigmoid type, but with a very pronounced linear portion of over six hours, as compared with the two hour constant-rate stage found for both the nitrogen and nitrogen-nitrous oxide curves at this temperature. This would indicate that the presence of water and/or ammonia preserved this linear interface reaction by some means.

Graph 12 is a typical example of the curve obtained with the corresponding experimental measurements in Table 19, the values being corrected to 10 mg. and 6684 cc. Again the Prout-Tompkins equation of \( \frac{P}{P_f - P} \) against time is the best fit with one value of \( k \) being obtained (Graph 12). The existence of a pronounced induction period of 60 minutes is indicative that no measurable amount of water, or ammonia, is evolved in this early part of the curve before nitrogen or nitrous oxide is evolved.

In spite of the lack of concordancy, the average of all runs gave a final total pressure of \( 312.10^{-3} \text{mm.} \). In the same volume, and from the same weight of ammonium dichromate (10 mg.), it can be calculated from previous runs that \( 58.0.10^{-3} \text{mm.} \) \( N_2 \), \( 25.5.10^{-3} \text{mm.} \) \( N_2O \), and \( 44.5.10^{-3} \text{mm.} \) \( \text{NH}_3 \) are evolved, i.e. \( 128.0.10^{-3} \text{mm.} \) total gas pressure.

Thus \( (312.0-128.0).10^{-3} \text{mm.} = 184.10^{-3} \text{mm.} \) is the water pressure i.e. 10 mg. material in 6684 c.c. evolves
0.0146 g. water, or 1 mole \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\) \(\rightarrow\) 2.042 moles \(\text{H}_2\text{O}\).

Table 19.

<table>
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<tr>
<th>t mins.</th>
<th>(p \times 10^3) mm.</th>
<th>3+log (\frac{p}{p_f-p})</th>
<th>t mins.</th>
<th>(p \times 10^3) mm.</th>
<th>3+log (\frac{p}{p_f-p})</th>
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<td>1.345</td>
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</tr>
<tr>
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<td>4.091</td>
<td>525</td>
<td>266.6</td>
<td></td>
</tr>
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<td>4.233</td>
<td>555</td>
<td>269.3</td>
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<tr>
<td>200</td>
<td>215.0</td>
<td>4.405</td>
<td>570</td>
<td>270.5</td>
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<tr>
<td>205</td>
<td>222.3</td>
<td>4.637</td>
<td>585</td>
<td>272.1</td>
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<tr>
<td>210</td>
<td>226.9</td>
<td>4.839</td>
<td>600</td>
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<tr>
<td>215</td>
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<td>24 hrs.</td>
<td>275.2</td>
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<td>225</td>
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<td>5.080</td>
<td></td>
<td>281.1</td>
<td></td>
</tr>
</tbody>
</table>

However, by converting the known pressures of \(N_2\), \(N_2O\) and \(NH_3\), in 6684 cc. into the corresponding weights of these gases, and subtracting these added weights from the experimentally determined loss in weight, it was calculated...
GRAPH 12

TOTAL GASEOUS EVOLUTION

TIME (MINUTES)
that this figure should be in the region of 2.6 moles of water. On summing the oxygen and hydrogen contents of the gaseous and solid products, and comparing them with the oxygen and hydrogen content of the initial ammonium dichromate, it was found that there is a deficiency of these two gases in the products in approximately the ratio needed for 0.5 mole water. Probably this water, 20% of the expected 2.6 moles, is adsorbed by the glass and makes an accurate determination of the water impossible. These deductions are not strictly valid for two reasons: (a) the fact that ammonia is also probably adsorbed on the glass would affect the hydrogen-oxygen balance, and (b) as stated earlier the crystals have a small water content, of less than 0.5%, which would probably have a very slight effect on this part of the work.

(e) **The Induction Period.**

Approximately thirty runs were done at 195.5°C in an attempt to discover what effects age, shape, condition, mode of crystallisation, interruption of the decomposition, weight, and number of crystals had on the induction period, maximum rate, and amount of decomposition. The term induction period is arbitrarily defined as that part of the curve occurring before the pressure has reached $10^{-4}$ mm, when the acceleration period begins.

Early runs were done with the top of the containing platinum bucket open but, as the crystal occasionally split
and bits of material were ejected, later runs were done with the top of the bucket closed. This had no noticeable effect on the induction period, maximum rate, nor the amount of gas evolved.

The induction period obtained at 195.5°C was extremely variable, from 0 - 80 minutes, and it was found that this significant effect was related to the age of the crystal after it had been taken from solution and dried by filter-paper. It was noticed that crystals taken straight from solution, dried, and evacuated overnight in the apparatus before being decomposed, had an induction period of 40 minutes. This overnight evacuation involved 15 hours pumping at a hard vacuum of $10^{-5}$ mm. A few runs done after only 4 hours pumping at $10^{-5}$ mm. showed a tendency to a longer induction period of about 60 minutes, and in one case of 80 minutes. Crystals stored in a desiccator over $P_2O_5$ for a week or more had a shorter induction period of approximately 15 - 20 minutes. It may be that this inhibitory effect is due to the small amount of water present in the crystals. After a week's storage over $P_2O_5$ the water content of the crystal would be much smaller, giving a shorter induction period. This point will be discussed in more detail later.

This question of age was followed up by slowly decomposing crystals of varying ages at 180.5°C in a small volume of 600 cc. The results are shown on Graph 13,
Graph 13

Aging Effects

Pressure (x10^3 mmHg)

Two Years Old Crystal

Six Days Old Crystal

New Crystal

Time (Minutes)

20 40 60 80 100 120 140 160 180 200 220 240 260 280 300
where a two-year old crystal has no induction period, a six-day old crystal has a 50 minute induction period, and a new crystal has an induction period of 120 minutes. This bears out the sequence found at 195.5°C. This work also shows that there is no measurable increase in nitrogen pressure during the induction period.

Apart from this ageing effect the induction period is temperature dependent as found by Fischbeck (30) and Taylor (52). Table 20 lists the average induction periods at various temperatures for new crystals.

<table>
<thead>
<tr>
<th>Temperature in °C</th>
<th>Length of Induction Period T minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>180.5°</td>
<td>120</td>
</tr>
<tr>
<td>188.1°</td>
<td>70</td>
</tr>
<tr>
<td>192.0°</td>
<td>50</td>
</tr>
<tr>
<td>195.5°</td>
<td>40</td>
</tr>
<tr>
<td>200.0°</td>
<td>30</td>
</tr>
<tr>
<td>205.2°</td>
<td>20</td>
</tr>
<tr>
<td>209.7°</td>
<td>15</td>
</tr>
<tr>
<td>215.0°</td>
<td>10</td>
</tr>
</tbody>
</table>

At the higher temperatures the difference in the length of induction period between "aged" and "new" crystals is not very marked as the values are small in any case.

If $\frac{1}{\tau}$ is taken as a measure of the "rate of reaction"
during the induction period and plotted in the form of an activation energy curve, as in Graph 14, a value for E of \(31.4 \pm 1.5\) kcal/mol is obtained.

The other contributory effect to the induction period was the method of crystal preparation. The values listed in Table 20 were from normal crystals i.e. those grown as described in Section I. If Taylor's method \((52)\) of quick growth from a solution at 40°C is used a very much reduced value of \(\tau\) is found (15 minutes), and for crystals which are very poor in form and highly ridged no induction period is found. Crystal habit, size and weight seemed to have no effect on the length of the induction period.

The effect on the maximum rate and the constant-rate stage of various factors was also studied. It was found that at all temperatures the maximum rate for nitrogen runs occurred at 35% of the final nitrogen pressure and the estimated \(p_f\) at 70% decomposition: as mentioned earlier the final nitrogen pressure was the same at all temperatures. For the nitrogen-nitrous oxide runs, the maximum rate occurred at a constant pressure value at all temperatures, approximately \(26.10^{-3}\) mm. under the experimental conditions, and the estimated \(p_f\) at \(51.5.10^{-3}\) mm. at all temperatures.

As mentioned earlier, the final pressure of nitrous oxide increased with increasing temperature but the \(p_f\) and maximum rate remained constant, so that the "extra" nitrous oxide must be evolved during the indeterminate decay period
following the constant-rate process.

When the maximum rate measured and the linear rate measured were converted to the standard 10 mg. and 6684 cc., it was found that a variation in mass from 1 - 30 mg. at 195.5°C had no measurable effect on these quantities over and above any experimental error variation, nor had the use of a collection of half a dozen small crystals, c. 2.0 mg. each.

<table>
<thead>
<tr>
<th>mass of crystals mg.</th>
<th>max. rate ( \times 10^4 ) corrected to 10 mg. mm./minute</th>
<th>linear rate ( \times 10^5 ) corrected to 10 mg. mm./minute</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>3.98</td>
<td>8.31</td>
</tr>
<tr>
<td>6.5</td>
<td>4.43</td>
<td>9.70</td>
</tr>
<tr>
<td>10.0</td>
<td>4.02</td>
<td>8.76</td>
</tr>
<tr>
<td>15.0</td>
<td>4.26</td>
<td>7.84</td>
</tr>
<tr>
<td>20.0</td>
<td>4.17</td>
<td>8.35</td>
</tr>
<tr>
<td>15.0 (collection of 6 crystals)</td>
<td>4.52</td>
<td>9.10</td>
</tr>
</tbody>
</table>

Taylor (52) had found a similar result for small crystals. For very poor material the maximum rate was about four times the normal maximum rate and the linear rate varied considerably in value. Apart from this, crystal habit and age had no effect on the values, or positions on the decomposition curve, of maximum rate nor linear rate.
GRAPH 16

DECOMPOSITION INTERRUPTED AT END OF Sigmoid STAGE
GRAPH 17

DECOMPOSITION INTERRUPTED AT LINEAR RATE STAGE

TIME (MINUTES)
Runs were interrupted at various stages to see if cooling and reheating the crystal had any effect on the decomposition rates. As Graphs 15, 16 and 17 illustrate, the rates were the same before and after cooling.

The significance of these effects, and the degree of ambiguity in the fit of the Prout-Tompkins equation is discussed later.

VI. Loss in Weight Studies.

(a) Normal Decompositions.

To supplement the work on the gaseous products, and as a substitute for the unsuccessful study of the total pressure by means of a Bourdon gauge, the loss in weight of ammonium dichromate was measured isothermally as a function of time at four temperatures.

The apparatus used was a simple modification of the McBain-Bakr sorption balance (Fig. 6). The spring, of beryllium-copper alloy, hung from a glass hook fixed to the walls of the reaction vessel; from the spring was suspended a very fine glass rod hooked at both ends. The closed platinum bucket, containing the sample, was fixed to the lower hook and the furnace, containing the lower half of the reaction vessel, was then raised up and the two portions connected by a "Quickfit" joint. This joint was built into a water-condenser for cooling purposes and Apiezon T grease used to complete the seal. Air was left in the
apparatus for five minutes to facilitate heating the sample to the required temperature, and the tap to the rotary oil pump was then opened for the whole of the decomposition. A movable telescope, with a scale of 100 divisions in the ocular, was focussed on the point where the top hook of the glass rod met the spring: this point could be maintained in focus as the decomposition progressed. A trap was placed between the vessel and the pumps.

100 mg. samples, approximately 10 single crystals, were used giving a loss in weight of just over 30 mg. which covered the 100 scale divisions. The spring was calibrated for the range "weight of bucket plus 100 mg." to "weight of bucket plus 70 mg." and, as Graph 18 shows, a straight line relationship existed in this range, so that the contraction of the spring is a direct measure of the loss in weight. The sensitivity of the spring was 2.72 scale divisions/mg. The temperature of the furnace, regulated to ±0.05°C, was measured by a thermocouple placed in a pocket inside the reaction vessel.

Graph 19 illustrates the loss in weight curves obtained at the four temperatures investigated. Above 200°C the crystals tended to crack and split with consequent agitation of the spring which made readings impossible, so that no runs were done above this temperature. Below 188°C the decomposition was too slow to be comfortably followed. Tables 22 - 25 give the results for four
GRAPH 18

CALIBRATION OF SPRING

LOAD (mg)
typical runs where $x$ is the contraction of the spring.

### Table 22.

<table>
<thead>
<tr>
<th>Run AL2</th>
<th>188.0°C. $x_f = 69.4$ units; first 50 minutes obscured by vibration of spring.</th>
</tr>
</thead>
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<td>$t$ (mins.)</td>
<td>$x$ (units)</td>
</tr>
<tr>
<td>50</td>
<td>6.0</td>
</tr>
<tr>
<td>75</td>
<td>6.6</td>
</tr>
<tr>
<td>60</td>
<td>7.4</td>
</tr>
<tr>
<td>65</td>
<td>8.1</td>
</tr>
<tr>
<td>70</td>
<td>9.1</td>
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<td>75</td>
<td>10.1</td>
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<td>80</td>
<td>11.1</td>
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<tr>
<td>85</td>
<td>12.2</td>
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<td>90</td>
<td>13.3</td>
</tr>
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<td>95</td>
<td>14.5</td>
</tr>
<tr>
<td>100</td>
<td>15.9</td>
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<tr>
<td>105</td>
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<td>56.5</td>
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<tr>
<td>220</td>
<td>57.7</td>
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### Table 23.

**Run B11. 192.0°C.** $x_f = 65.0$ units; first 50 minutes obscured by vibration of the spring.

<table>
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<tr>
<th>$t$ (mins.)</th>
<th>$x$ (units)</th>
<th>$2+\log \frac{x}{x_f-x}$</th>
<th>$t$ (mins.)</th>
<th>$x$ (units)</th>
<th>$2+\log \frac{x}{x_f-x}$</th>
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<td>2.0925</td>
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<tr>
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<td>230</td>
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<tr>
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<td>7.5</td>
<td>1.1145</td>
<td>235</td>
<td>61.0</td>
<td>3.1832</td>
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<td>245</td>
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<td>3.3802</td>
</tr>
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<td>1.3181</td>
<td>250</td>
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<td>3.4166</td>
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<tr>
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<td>300</td>
<td>66.0</td>
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<td>1.7959</td>
<td>310</td>
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<tr>
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<td>1.8657</td>
<td>320</td>
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<td>3.7822</td>
</tr>
<tr>
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<td>29.5</td>
<td>1.9191</td>
<td>330</td>
<td>67.3</td>
<td>3.7822</td>
</tr>
<tr>
<td>135</td>
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<td>1.9731</td>
<td>340</td>
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<td>435</td>
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Table 24.

Run CL3. 195.5°C.  {\( x_f = 68.0 \) units;  \( T = 25 \) minutes.}

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<tr>
<th>t (mins.)</th>
<th>x (units)</th>
<th>2+log ( \frac{x}{x_f-x} )</th>
<th>t (mins.)</th>
<th>x (units)</th>
<th>2+log ( \frac{x}{x_f-x} )</th>
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<tr>
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Table 25.

Run DL1. 200.0°C. \( x_f = 66.5 \) units; first 20 minutes obscured by vibration of spring.

<table>
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<th>t mins.</th>
<th>x units</th>
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<th>t mins.</th>
<th>x units</th>
<th>2+log ( \frac{x}{x_f-x} )</th>
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</table>

24 hrs. 89.0
$2 + \log_{10}\left(\frac{x}{x_0}\right)$

Curves A, B, C, and D are plotted on the graph. The graph shows the relationship between time (in minutes) and the logarithmic term. The text at the bottom of the graph states: "Curve A is displaced 20 minutes to right."
In many cases, the readings for the first 40 - 50 minutes of the run could not be taken due to violent vibrations in the spring, indicating cracking was occurring at this stage. In the main, however, the curves obtained were the same general sigmoid form with a final linear portion as found in the pressure-time measurements. The best fit was the Prout-Tompkins equation \[ \log \frac{X}{X_f - X} = kt + c, \] where \( X_f \) was the estimated loss in weight at the top of the sigmoid portion of the curve. One value of \( k \) was again obtained and a table of temperatures, maximum rates, linear rates and \( \log k \)'s is given below (Table 26), with the corresponding activation energy curves shown on Graphs 20, 21 and 22.

**Table 26.**

<table>
<thead>
<tr>
<th>Run</th>
<th>( T°C )</th>
<th>maximum rate</th>
<th>linear rate ( 10^2 )</th>
<th>( k \times 10^2 )</th>
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<tr>
<td></td>
<td></td>
<td>divs./minute</td>
<td>divs./minute</td>
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<tr>
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<td>0.875</td>
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Although the scatter in results is considerable (much greater than that found in the pressure experiments) the
activation energies obtained from these values were respectively 35.3 kcal./mole, 41.3 kcal./mole, and 34.3 kcal./mole. The error in estimating these quantities is of the order of ±4 kcal./mole.

(b) **Effect of the Gaseous Products on the decomposition.**

In Section VI(a) the loss in weight runs were performed with continuous evacuation and with liquid nitrogen round the trap. By varying the conditions of the trap and allowing the pressure of the gaseous products to build up, the inhibitory or catalytic effect could be studied.

The procedure followed was as in the previous section but, when the furnace had been raised, the vessel was evacuated for 5 minutes and then the tap leading to the pump was closed and the telescope focussed on the hook. With liquid nitrogen round the trap the effect of the nitrogen on the decomposition could be studied; and with P₂O₅ in the trap the effect of nitrogen and nitrous oxide studied. With barium oxide, a water absorbent, in the trap the combined effect of ammonia, nitrogen and nitrous oxide was studied; and with no trapping agent used, the effect of allowing all the gases to build up was noted.

As ten times the "normal" weight (i.e. a 100 mg. sample in place of the 10 mg. crystal used in pressure runs) of ammonium dichromate was used and only one-tenth of the "normal" volume (650 cc. in place of 6684 cc.), the final pressures of gas obtained were about one-hundred times the
"normal" values obtained for the pressure measurements (i.e. 10 mm. nitrogen instead of 0.1 mm.). This gave rise to difficulties due to distillation effects of ammonia and water in the experimental system, but it was found that, if a tube containing either P₂O₅ or BaO was placed directly above the spring, these effects were removed.

Graph 23 illustrates the effect of altering the conditions at 192°C. The build-up in the nitrogen and nitrous oxide pressures over P₂O₅ had no apparent effect on the decomposition curve, a typical sigmoidal curve being obtained (cf. Graph 19) but the linear rate was about twice as fast as in a "normal" decomposition. With BaO in the traps the rate of decomposition was greatly reduced and the sigmoid became indeterminate in form; examination of the surface of the BaO by Nessler's reagent showed only a trace of ammonia, indicating that only water was being absorbed out of the gaseous products.

The effect of allowing all the gaseous products to build up was to suppress the decomposition greatly, the loss in weight being very slow; after three hours heating, by which time the decomposition should have been nearing the end of the straight line section of the curve, only one-fifth of the expected loss in weight had occurred. The tap to the pump was then opened and the rate at once increased to give a typical decomposition curve. This compared with the fact that in the same time, with ammonia
CONTRACTION OF SPRING 2

A. P₂O₅ IN TRAPS
B. BaO IN TRAPS
C. NO TRAPS USED

STARTED EVACUATING AT 330 MINUTES.

TIME (MINUTES)
building up but not water, only four-fifths of the expected loss in weight had occurred. A run was attempted with no absorbent in the traps and an atmosphere of air kept in the system, but no loss in weight occurred even after 24 hours: when this system was evacuated the sample decomposed to give a typical curve at 192°C.

This work indicated that with a pressure of approximately 10 mms. of gaseous products building up, nitrogen and nitrous oxide have no catalytic effect on the decomposition, but that in the presence of ammonia and water the reaction is inhibited, water having a much greater effect than ammonia. The inhibitory effect of air may be due to its water content, or to the atmospheric oxygen.

(c) **Effect of the Solid Product on the decomposition.**

90 mg. of finely ground material was made into a pellet and the loss in weight curve followed at 186.3°C. A typical sigmoid curve with a linear portion was obtained (Graph 24). A similar weight of dichromate, intimately mixed with 10 mg. of black solid product, was compressed into pellet form and decomposed at the same temperature. In both cases liquid nitrogen was placed round the trap and the apparatus continually evacuated.

With the solid product present initially the curvature in the lower half of the sigmoid is practically eliminated, and the linear section of the decomposition is extended from 2 hours to approximately 4 hours. The rate of reaction
is also increased to some extent, indicating catalysis of
the reaction by the solid product. Since finely crushed
material decomposes at a very fast rate in any case, the
apparent catalytic effect of the black material is not
exceptionally great but it is quite definite.

VII. Electrical Conductivity Measurements.

(a) Apparatus and Procedure.

The apparatus used (Fig. 7) was a modification of that
devised by Jacobs (59) to measure the specific ionic
conductance of azides in the range $10^{-9} - 10^{-13}$ ohms$^{-1}$ cm.$^{-1}$
by means of D.C. amplification to avoid large field strengths.
E was an Osram electrometer triode type ET1 of high input
impedance, with the power supply consisting of four 2-volt
60Ah accumulators. The filament current of 100 ma,
indicated by the ammeter A, was regulated by resistors $R_{10}$
(variable) and $R_{11}$; the mid-point of the filament was
approximately +2v, when point y was earthed. To obtain
minimum possible electrical leakage, the operating grid
potential was kept greater than two volts negative with
respect to the negative end of the filament by means of
$R_9$; the circuit containing $S_1$, $R_{14}$, $R_{13}$, $R_{12}$ was used to
zero the galvo G, $R_{12}$ being a coarse control and $R_{13}$ a
fine control. The internal and external guard rings and
and electrostatic shield GR of valve E were connected to
the negative end of the filament. With these conditions
the drift in the filament current was very slow and could be corrected by $R_{10}$.

The grid leak, $R_g$, was a vacuum-sealed calibrated resistor supplied by the Welwyn Electrical Laboratories with a guaranteed tolerance of $\pm 1\%$: a $10^8$ ohms and a $10^{10}$ ohms resistors were soldered to the point $x$, and either could be switched into the circuit by attaching it to the grid by means of a screw connection with the other resistor hanging free. These calibrated resistors were supplied in pairs and were checked against each other with one in place of the cell: the ratio was within $0.5\%$ of that calculated from the makers' calibration, remaining constant over the period the work was carried out. The leads to the cell $c$ consisted of polythene-insulated coaxial cable and all earthing connections were brought to one point, $y$, which was then earthed on a three-pin plug: this common earth terminal was necessary otherwise stray electrical leaks occurred. The points $J$ were breaks in the coaxial cable used in zeroing the circuit, whereas $s_1$ and $s_2$ were normal two-way switches, and $s_3$ a selector switch.

The network of resistors at the left of the diagrammatic circuit was, as in Jacobs' original circuit, to calibrate the voltage source as the maximum voltage recorded by the Tinsley potentiometer $P$ was 1.8 volts. The applied voltage across $R_g$ is $S = s \times p$, where $s$ is the calibrated
voltage measured in positions 1 and 5 of the switch $s_3$, and a factor dependent on the ratio of resistor to $R_7$. This network gave a range of voltages from 1 volt to 120 volts and extended the resistance range to $10^{13}$ ohms ($\pm 2\%$). All resistors were high quality wire-wound with a tolerance of $1\%$, apart from $R_9$ which was vacuum sealed. The complete circuit, apart from the switches $s_2$ and $R_8$, cell, potentiometer, galvo G, and power supply, was contained in an airtight aluminium box containing silica gel to preserve a dry atmosphere.

The dichromate, ground to a fine powder, was compressed into cylindrical pellets of 6.52 mm. diameter and about 2 - 3 mm. length by means of a pellet press and vice giving a pressure of 3 tons/in.$^2$: this high compression avoided any spurious results due to bad contact between individual crystal fragments in the pellets (50). Fig. 8 is a diagram of the cellholder. A strip of brass, 3mm. thick, was bent to the form shown, and a hole bored and tapped for a $\frac{3}{8}$ inch nut and bolt: over the end of the bolt was fitted a piece of quartz tubing $T$, of $\frac{3}{8}$ inch diameter and closed and flattened at one end, which could slip neatly into the quartz sleeve $S$. The pellet $P$ sat inside this sleeve on a platinum electrode, 1 cm. square, which was insulated from the brass holder by a quartz plate insulator $I$. The other platinum electrode lay between the closed end of $T$ and the top of the cylindrical pellet:
Resistor Values

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<th>Value</th>
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</thead>
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<tr>
<td>R_5</td>
<td>120kΩ</td>
</tr>
<tr>
<td>R_6</td>
<td>30kΩ</td>
</tr>
<tr>
<td>R_7</td>
<td>10kΩ</td>
</tr>
<tr>
<td>R_8</td>
<td>10^6Ω</td>
</tr>
<tr>
<td>R_9</td>
<td>22Ω</td>
</tr>
<tr>
<td>R_{10}</td>
<td>50Ω</td>
</tr>
<tr>
<td>R_{11}</td>
<td>15Ω</td>
</tr>
<tr>
<td>R_{12}</td>
<td>10kΩ</td>
</tr>
<tr>
<td>R_{13}</td>
<td>500Ω</td>
</tr>
<tr>
<td>R_{14}</td>
<td>15kΩ</td>
</tr>
</tbody>
</table>

**FIG. 7**

**Key to FIG. 8.**

- BRASS
- PELLET
- QUARTZ
- PLATINUM

**SECTION OF CELL**

**FIG. 8**
welded to the electrodes were platinum leads which were insulated by alumina capillary tubing. The cell hung from a glass hook in the reaction vessel by the brass support L, and the electrical leads were taken out of the Pyrex reaction vessel by means of seals in "Quickfit" B10 cones. The leak resistance in parallel with the pellet is composed of the quartz insulators at the temperature of reaction and the Pyrex glass and Apiezol L grease between the two seals. At \(10^{-6}\) mm, the empty cell had a resistance of greater than \(10^{16}\) ohms.

For any pellet the apparatus was outgassed for 24 hours to remove water vapour and then the furnace, at the required temperature, was raised, the temperature being measured by a thermocouple in a pocket in the reaction vessel. In order to avoid spurious effects a standard procedure was evolved. With the connections to the applied voltage removed, and the cell connections broken at \(J_1\) and \(J_2\) and the potentiometer P shunted out by \(s_2\), \(s_1\) was switched on and the galvo G set at zero by \(R_{12}\) and \(R_{13}\). With \(s_2\) opened and \(J_1\) and \(J_2\) connected, a known voltage \(S\) was applied across the cell. The galvanometer was then zeroed again by applying a known voltage through a voltage dividing box DB. This applied voltage was accurately determined by the potentiometer and the resistance of the pellet is

\[
R = \frac{R_0}{u} (S-u),
\]
where \( u \) is the voltage required to zero the galvanometer.

In Jacobs' work the potentiometer was combined with an automatic switch which continuously changed the direction of the applied voltage \( S \) every thirty seconds, i.e. a low frequency pulse technique was used. Since in this work the resistance of the pellet could be determined in less than a minute this feature was omitted. However, to avoid polarisation, the next reading was always taken with a voltage of opposite sign applied across the cell, and a reversing switch RS ensured that the potentiometer voltage was of the correct sign to balance the galvo.

(b) Results.

Graph 25 is the plot of log specific conductivity, \( K \), against the reciprocal of temperature, and the values for a typical pellet are tabulated below (pellet 1). The pellet dimensions were measured by a micrometer. \( R_8 \) is \( 9.34 \times 10^9 \) ohms.

<table>
<thead>
<tr>
<th>( T ) ( {^\circ}C )</th>
<th>( S ) volts</th>
<th>( u_+ ) volts</th>
<th>( u_- ) volts</th>
<th>( R ) ohms</th>
<th>( K ) ohm(^{-1} ) cm(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>37.0</td>
<td>110.0</td>
<td>0.0270</td>
<td>0.0271</td>
<td>3.79 \times 10^{13}</td>
<td>4.114 \times 10^{-14}</td>
</tr>
<tr>
<td>40.9</td>
<td>110.0</td>
<td>0.0310</td>
<td>0.0310</td>
<td>3.23 \times 10^{13}</td>
<td>4.697 \times 10^{-14}</td>
</tr>
<tr>
<td>67.5</td>
<td>27.50</td>
<td>0.1230</td>
<td>0.1234</td>
<td>2.08 \times 10^{12}</td>
<td>7.499 \times 10^{-13}</td>
</tr>
<tr>
<td>85.2</td>
<td>27.50</td>
<td>0.4684</td>
<td>0.4684</td>
<td>5.38 \times 10^{11}</td>
<td>2.994 \times 10^{-12}</td>
</tr>
<tr>
<td>98.4</td>
<td>4.564</td>
<td>0.1940</td>
<td>0.1940</td>
<td>2.11 \times 10^{11}</td>
<td>7.389 \times 10^{-12}</td>
</tr>
<tr>
<td>107.1</td>
<td>4.564</td>
<td>0.3493</td>
<td>0.3494</td>
<td>1.13 \times 10^{10}</td>
<td>1.380 \times 10^{-11}</td>
</tr>
<tr>
<td>132.2</td>
<td>1.304</td>
<td>0.4662</td>
<td>0.4662</td>
<td>1.76 \times 10^{9}</td>
<td>8.892 \times 10^{-11}</td>
</tr>
<tr>
<td>141.7</td>
<td>1.304</td>
<td>0.6230</td>
<td>0.6233</td>
<td>1.02 \times 10^{9}</td>
<td>1.531 \times 10^{-10}</td>
</tr>
<tr>
<td>161.8</td>
<td>1.304</td>
<td>0.9505</td>
<td>0.9509</td>
<td>3.49 \times 10^{9}</td>
<td>4.457 \times 10^{-10}</td>
</tr>
</tbody>
</table>

One straight line (A) is obtained fitting the equation
GRAPH 25
CONDUCTIVITY DATA

- Pellet 1
- Pellet 2
- Pellet 3
- Pellet 4

\( \frac{1000}{T(A)} \)
\[
\log \kappa = -8.05 - \frac{20.2^{\pm 0.5}}{2.303 \, RT}
\]

This value of activation energy is less than that normally associated with ionic conductance, e.g. 30 kcals, as suggested by Jacobs and Tompkins for solid azides (61) and the alkali metal halides (87) suggesting that the ammonium ion (the probable main ionic conduction carrier because of its size and mobility) decomposes before making any significant direct contribution to the electrical conductivity. This is borne out by the fact that above 150°C values of conductivity slowly increased with time, indicating slow decomposition above this temperature. Below this temperature conductivities obtained on heating up were the same as those at corresponding temperatures on cooling down.

The material used was the analar salt, recrystallised as in Section I, and ground in a mortar to a very fine powder. Graph 25 shows that the reproducibility from pellet to pellet for four runs was better than 2%. The straight line of lower slope (B) is that for a pellet which had decomposed for 48 hours at 180°C and was then cooled down. This gave an activation energy of 12.4 kcals./mole, indicating the formation of a new conduction carrier in the decomposed material. The nature of the conducting species in ammonium dichromate could not be determined by transport number experiments because of the decomposition of the pellets with prolonged heating.

A temperature, 186.3°C, was chosen so that the
isothermal change in pellet conductivity could be followed and compared with the pressure increase during the decomposition measured by the McLeod gauge, range $10^{-5}$ to 5.5 mm. An experiment in which one join of a thermocouple, of very fine copper-Bureka wire, was fixed in the middle of a pellet and the other join in the pocket inside the reaction vessel, showed that no self-heating of the pellet occurred during decomposition. Since the cell had to be suspended freely in the reaction vessel, these were at room temperature when the furnace was raised, and consequently an unfortunately long warming-up period for this mass was required. Thus the first 40 minutes of the reaction was indeterminate, but at the chosen temperature it was found that this was a negligible effect in the 12 hours during which the run was studied. Liquid nitrogen was placed round the traps in the line, so that only the pressure of evolved nitrogen was measured. Graph 26 illustrates the results given in Table 28.

It will be noted that the decomposing pellet gives a typical sigmoid form with an extended linear portion, the induction period being obscured by the afore-mentioned heating-up period. No features were observed in the plot of $R$ against $t$ similar to those found in the case of lithium aluminium hydride (11), which also darkened in bulk on being thermally decomposed; but the plot of $\log \chi$ against time gave a straight line which extended until the sigmoid pressure
curve was finished, and then came to a steady value of \( \log \kappa \) during the linear portion of the pressure curve before finally decreasing considerably in value. This exponential increase in specific conductivity, and hence in conduction carriers, occurred in all ten pellets thus examined. The range of temperature in which this increase in conductivity with time could be studied was less than 10°C, as above 166°C the sigmoid portion of the curve was quickly over and below 180°C the sigmoid portion extended for nearly 12 hours: however, at 170°C a very slow exponential increase of carriers with time was present.

If the slope of \( \log \kappa \) against time was calculated and plotted as a log value against \( 1000/T \), an activation energy of the order of 40 kcales./mole was obtained. The error in this, due to the small temperature range which could be employed, was considerable and the value cannot be accurately determined. This value of \( E \) is obtained from the plot of a log "rate" (where "rate" is measured as \( \log \kappa /\text{time} \)) against the reciprocal temperature, and is probably associated with the process which causes the increase in conduction rather than with the actual conduction process itself. In this case, a value of about 40 kcales./mole is what would be expected from the values of \( E \) obtained in the earlier sections.
EXponential Increase in Conductance.
Table 28.

Pellet at 186.3°C; \( l = 0.2390 \) cm.; \( r = 0.3258 \) cm.

<table>
<thead>
<tr>
<th>( t ) mins.</th>
<th>( R \times 10^{-7} ) ohms.</th>
<th>( 9 + \log \kappa )</th>
<th>( t ) mins.</th>
<th>( p \times 10^{3} ) mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>49.2</td>
<td>0.1711</td>
<td>45</td>
<td>26</td>
</tr>
<tr>
<td>50</td>
<td>44.9</td>
<td>0.2136</td>
<td>55</td>
<td>38</td>
</tr>
<tr>
<td>60</td>
<td>40.3</td>
<td>0.2590</td>
<td>65</td>
<td>56</td>
</tr>
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<td>70</td>
<td>36.5</td>
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<td>75</td>
<td>66</td>
</tr>
<tr>
<td>80</td>
<td>32.9</td>
<td>0.3481</td>
<td>85</td>
<td>93</td>
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<td>30.0</td>
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<td>116</td>
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<td>27.7</td>
<td>0.4222</td>
<td>105</td>
<td>148</td>
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<td>110</td>
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<tr>
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<td>22.0</td>
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<td>125</td>
<td>217</td>
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<td>130</td>
<td>19.8</td>
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<td>135</td>
<td>239</td>
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<tr>
<td>140</td>
<td>17.9</td>
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<td>145</td>
<td>271</td>
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<tr>
<td>150</td>
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<td>165</td>
<td>328</td>
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<tr>
<td>170</td>
<td>13.7</td>
<td>0.7183</td>
<td>175</td>
<td>356</td>
</tr>
<tr>
<td>180</td>
<td>12.6</td>
<td>0.7549</td>
<td>185</td>
<td>375</td>
</tr>
<tr>
<td>190</td>
<td>11.6</td>
<td>0.7900</td>
<td>195</td>
<td>414</td>
</tr>
<tr>
<td>200</td>
<td>10.5</td>
<td>0.8320</td>
<td>205</td>
<td>424</td>
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<td>210</td>
<td>9.39</td>
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<td>215</td>
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<td>220</td>
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<td>452</td>
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<tr>
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<td>490</td>
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<td>660</td>
</tr>
<tr>
<td>500</td>
<td>13.26</td>
<td>0.7328</td>
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<td></td>
</tr>
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</table>

(a) X-Ray Crystallographic Measurements.

Byström and Wilhelmi (62) determined the fine structure of ammonium dichromate, and Fig. 9 shows the projection on the (010) face. The chromium atoms are surrounded by four oxygen atoms situated at the corners of a distorted tetrahedra: two tetrahedra share one corner so that a Cr$_2$O$_7$ group is formed. The angle found for the Cr — O — Cr is $115^\circ$, whereas in CrO$_3$ this angle is $136^\circ$ (63). They consider that the most stable arrangement would consist of equilinear bonds between the two joined tetrahedra, and suggest the strong distortion of the angle may be due to the formation of strong N — H — O bonds, which implies that the Cr — O — Cr angle in the dichromates of alkali metals should be $180^\circ$. However, in sodium dichromate dihydrate (64) the angle is approximately $120^\circ$, and in a review of the X — O — X angles determined in X$_2$O$_7$ groupings Cox (65) suggests that the grouping is essentially non-linear, c. $123^\circ$ in an isomorphous series to which potassium dichromate belongs. The bending of the X$_2$O$_7$ group would seem to depend on the steric effect of the XO$_3$ groups rather than on hydrogen bonding, although this may occur in the ammonium dichromate. From the evidence the dichromate grouping would appear to be under no strain in the crystal lattice.

In the course of the work, Byström's results were
checked experimentally and the cell parameters found were in good agreement. As described earlier, the diamond nuclei were found by X-ray and goniometric measurements to be aligned parallel to the b- and c-axes and normal to the a-axis on the main faces. From the projection it will be seen a strong cleavage exists in the (100) plane, which is the plane in which the nuclei grow; the literature also cites a strong (101) cleavage, which is clearly seen in Fig. 9. It can also be seen that the ammonium ions are coplanar in this cleavage direction and sit beside one oxygen atom. The ammonium ion appears to be rotating in the crystal at ordinary temperatures, as found from thermal transition work (66), (67), and nuclear magnetic resonance work. If interaction occurs between the ammonium ion and its neighbouring oxygen atom then, by the symmetry of the space group C2/c, it is possible to imagine a symmetrical diamond product being formed in the (100) plane which would be essentially two-dimensional in its growth. The dimensions of the diamond would be fairly equal in length and breadth as the b- and c-parameters are comparable, 7.54 Å and 7.74 Å respectively, and this is reflected in the photomicrographs. This picture was confirmed by building a model of the cell and joining the coplanar \( \text{NH}_4^+ \) ions. A diamond nucleus is a possible result of this.

X-ray measurements on a darkened single crystal at the 1% decomposition stage showed no change in the positions of
Projection on the (010) face

\[ a = 13.26 \pm 0.01 \text{ Å} \]
\[ b = 7.54 \pm 0.02 \text{ Å} \]
\[ c = 7.74 \pm 0.02 \text{ Å} \]
the reflected intensities determined for the original undecomposed crystal. Thus, within experimental error of 1%, no new species existed in the darkened crystal.

Unfortunately, the fully decomposed material, although a pseudomorph of the initial crystal, was amorphous and no indication of its nature could be obtained.

(b) **The Induction Period.**

As mentioned previously (p. 71) the length of the induction period varied considerably at the standard temperature of 195.5°C, and some reasons were given for this. Nevertheless, five minutes heating at this temperature was sufficient to cause a definite general darkening of the crystal without, however, any detectable evolution of nitrogen or nitrous oxide. No diamond nuclei could be detected during this early process. It was concluded, however, that, irrespective of the length of this induction period, the ammonium dichromate was essentially decomposing as shown by the general darkening process. This is analogous to mercury fulminate which became brown in depth before the acceleration process began.

(c) **Visible Spectrum of Ammonium Dichromate.**

In an attempt to determine whether the early darkening was the result of the formation of a new species, such as F-centres, the visible spectrum of the salt at various stages of decomposition was examined in the Unicam SP600 spectrophotometer. Tompkins and Young (68) found that
colour centres, i.e. F- or F'-centres, were formed by photolysis and thermal decomposition of potassium azide crystals, and Heal (69) found that irradiated sodium azide crystals also gave these centres. It was considered as possible that on heating ammonium dichromate F-centres were produced resulting in the dark-red colouration and that on the aggregation of these colour centres nuclei of the black product were formed.

Four large clear crystals of the salt were selected with as uniform a thickness as possible. The spectrum of the undecomposed crystal was obtained by fixing the crystal in a definite position over a 2 mm. diameter hole bored in a 1 mm. thick piece of aluminium, which was held in the Unicam cell-holder. The light beam of the instrument was first passed through a comparable hole in a similar aluminium strip as a standard, and the crystal then switched into the beam. Graph 27 shows the spectrum of the initial dichromate crystal: there are no significant peaks in the range measured, apart from the sharp cut-off at 550 m\(\mu\).

The crystal was removed and heated for varying periods of time (10 to 180 minutes) at 195.5\(^\circ\)C, and then returned to the original position on the aluminium strip. Although obviously darkened to the unaided eye the log density measured was far from reproducible from stage to stage of the heating.

It was concluded that the large variation in the
GRAPH 27

VISIBLE SPECTRUM OF AMMONIUM DICHROMATE

WAVELENGTH (mλ)

AMMONIUM DICHROMATE

"DARKENED" AMMONIUM DICHROMATE.
optical density readings was due to the impossibility of returning the crystal to exactly the same position in the light beam, so that any slight difference in crystal thickness would have a large effect. However, the qualitative results obtained demonstrated that no new absorption bands occurred in the visible region of the spectrum, even for quite dark crystals, and that the darkening was due to the production of some black material, which merely increased the optical density of the crystal (and not to the formation of F− or F′-centres).

(d) **Infra-red Spectra of Ammonium Dichromate and its Decomposition Products.**

Examination of the gaseous products by infra-red spectroscopy showed only water, ammonia and nitrous oxide (Fig. 10). Consideration was given to following the evolution of water by this means, but the same experimental difficulties of water adsorption on glass walls in the early stages of the decomposition would still occur.

Examination of spectra obtained from Nujol mulls of the ammonium dichromate and the black residue indicated that the decomposition could be followed quantitatively by making KBr discs of the material at various stages of decomposition. At first, the use of a single disc of KBr/(NH₄)₂Cr₂O₇, which could be examined at successive stages of decomposition, was contemplated, but the presence of a strong oxidising group mixed with the bromide would
probably complicate the spectrum and this idea was never attempted.

The following procedure was adopted which gave semi-quantitative results. 50 mg. of crystals were taken to a known percentage decomposition, weighed, and ground in an agate mortar to a fine powder. A 1/2 mixture of this material in dried KBr was intimately mixed in an agate ball-mill and, after twenty minutes shaking, 140 mg. were weighed into a stainless steel press and made into a thin transparent disc under a pressure of 5 tons/sq. inch. The press was evacuated whilst the disc was being made, so that little water would be occluded in the mixture. The infra-red spectrum was traced by a Hilger H800 spectrophotometer using a double-beam method in which a disc of the mixture was run against a standard KBr disc. Due to the formation of solid intermediaries in the decomposition, and the consequent change in the base line, it was impossible to follow the change in the peak heights quantitatively, but an approximate estimate of the course of the decomposition can be obtained from the spectra shown in Fig. 12.

Fig. 12 (a - h) are the initial ammonium dichromate and the final black material with a range of intermediate partially decomposed material, whose nature is shown on the general decomposition curve in Fig. 11: Fig. 12 (i) is black material which has been roasted to the blue-green final material. Fig. 13 (a - f) shows the standard spectra
used in comparison, namely potassium dichromate, ammonium monochromate, ammonium nitrate, sodium nitrite, sodium nitrate, and chromic oxide. These standard spectra were all obtained from KBr discs made by the above procedure, and compare reasonably well with the spectra obtained from Nujol mulls by Miller and Wilkins (70).

A study of the intermediate spectra revealed some interesting developments: a list of the more important bands in the spectra is given below.

The literature (70) gives:

\[
\begin{align*}
\text{NH}_4^+ & \quad 3300-3030 \text{ cm}^{-1} \text{ vs, } 1430-1390 \text{ cm}^{-1} \text{ s.} \\
\text{Cr}_2\text{O}_7^{2-} & \quad 890-845 \text{ cm}^{-1} \text{ m, } 765-735 \text{ cm}^{-1} \text{ m.} \\
\text{CrO}_4^{2-} & \quad 950-910 \text{ cm}^{-1} \text{ w, } 875-860 \text{ cm}^{-1} \text{ s, } 860-790 \text{ cm}^{-1} \text{ m.} \\
\text{H}_2\text{O} & \quad \text{approx. } 3500 \text{ cm}^{-1} \text{ s, approx } 1630 \text{ cm}^{-1} \text{ s.} \\
\text{NO}_2^- & \quad 1250-1230 \text{ cm}^{-1} \text{ vs, } 840-800 \text{ cm}^{-1} \text{ vw.} \\
\text{NO}_3^- & \quad 1380-1350 \text{ cm}^{-1} \text{ vs, } 840-815 \text{ cm}^{-1} \text{ m.}
\end{align*}
\]

s strong, m medium, w weak.

From the standards in Fig. 13 (a - f) the following reference values were taken:

\[
\begin{align*}
\text{NH}_4^+ & \quad \text{shoulder at } 3200 \text{ cm}^{-1} \quad 1420 \text{ cm}^{-1} \\
\text{NO}_3^- & \quad 1425 \text{ cm}^{-1} \quad 825 \text{ cm}^{-1} \\
\text{NO}_2^- & \quad 1260 \text{ cm}^{-1} \\
\text{Cr}_2\text{O}_7^{2-} & \quad 940 \text{ cm}^{-1} \quad 750 \text{ cm}^{-1} \\
\text{CrO}_4^{2-} & \quad 940 \text{ cm}^{-1} \quad 875 \text{ cm}^{-1} \quad 750 \text{ cm}^{-1} \\
\end{align*}
\]

Since the $\text{NH}_4^+$ band around 3250 cm$^{-1}$ is a broad shoulder, and is very close to the water band at 3500 cm$^{-1}$,
the comparison in relative rates of disappearance of the
NH$_4^+$ and Cr$_2$O$_7^{--}$ ions was made at the lower end of the
spectrum. Unfortunately, Cr$_2$O$_7^{--}$ and CrO$_4^{--}$ species
absorb equally strongly in the same regions, and any
breakdown of Cr$_2$O$_7^{--}$ into CrO$_4^{--}$ groups would not be
detectable. The formation of NO$_2^-$ ions can be definitely
established by the 1250-1230 cm$^{-1}$ peak: NO$_3^-$ has a strong
absorption at the same range as NH$_4^+$ ion and, as the
NH$_4$NO$_3$ spectrum shows, these peaks are unresolvable.
Fortunately, the NO$_3^-$ has a medium strong peak at
840-815 cm$^{-1}$ (cf. NaN$_3$ and NH$_4$BO$_3$) which can be detected,
and is not attributable to the weak NO$_2^-$ peak in this region,
nor the CrO$_4^{--}$ peak which occurs about 50 cm$^{-1}$ higher.
The estimate of water present is very rough as the decomposed
material is usually slightly hygroscopic, and some of the
spectral water may be due to this.

Fig. 12(a) shows the spectrum of the original dichromate
and the peak height of the NH$_4^+$ ion is roughly greater than
the Cr$_2$O$_7^{--}$ peak height. Fig. 12(b), which has decomposed
1% by the nitrogen evolution, has no new peaks, although
the water content seems to have increased slightly; the
NH$_4^+$ peak is slightly larger than the Cr$_2$O$_7^{--}$ peaks. In
Fig. 12(c), which has decomposed 17%, the NH$_4^+$ peak is
slightly lower than the Cr$_2$O$_7^{--}$ peak, which is beginning
to lose its fine structure: a trace of NO$_2^-$ ion can be
detected at 1260 cm$^{-1}$, but no other new product appears.
In Fig. 12(d), 34\% decomposition and the maximum rate stage, the NH$_4^+$ peak heights are now definitely reduced in comparison to the Cr$_2$O$_7^{2-}$, and the water content appears to have increased. The NO$_2^-$ peak is now quite pronounced and, although the Cr$_2$O$_7^{2-}$ fine structure appears to be similar to Fig. 12(c), a trace of NO$_3^-$ seems to occur in the 825 cm$^{-1}$ position. Fig. 12(e), at 53\% decomposition, shows both NH$_4^+$ peaks much reduced in size in comparison to the Cr$_2$O$_7^{2-}$ ion. NO$_2^-$ ion is now present in a sizable amount, as is the NO$_3^-$ ion which is now definitely present in the changing Cr$_2$O$_7^{2-}$ grouping, in which only one definite peak at 940 cm$^{-1}$ remains. In Fig. 12(f), the top of the sigmoid portion of the curve and 69.0\% decomposition, the NH$_4^+$ ion shoulder at 3200 cm$^{-1}$ has a very flat maximum, indicating that this ion has practically vanished: the NO$_2^-$ and NO$_3^-$ ions have now reached their maximum values, and it is probable that much of the 1420 cm$^{-1}$ peak is due to NO$_3^-$ absorption rather than NH$_4^+$. H$_2$O is still present in sizable amounts, but the fine structure of the Cr$_2$O$_7^{2-}$ ion has completely disappeared, though a large absorption still occurs in this area, apart from that due to the NO$_3^-$ peak.

In Fig. 12(g), 71.5\% decomposition and half-way up the linear portion of the decomposition curve, there is no NH$_4^+$ left whilst the absorption in the Cr$_2$O$_7^{2-}$ region is greatly reduced: the NO$_2^-$ ion concentration has approximately halved and the NO$_3^-$ ion concentration is
also reduced. In the final product Fig. 12(h), i.e. 100% decomposition by nitrogen evolution, no \( \text{NO}_2^- \), \( \text{NH}_4^+ \), or \( \text{Cr}_2\text{O}_7^{--} \) is left, but a small amount of \( \text{H}_2\text{O} \) and \( \text{NO}_3^- \) seems to be present. Fig. 12(i), of material which has been roasted for 5 hours at 800°C, has no features and corresponds to the \( \text{Cr}_2\text{O}_3 \) spectrum cf. Fig. 13(f).

It would appear from the above interpretations of the spectra that little structural change occurs in the dichromate during the early nucleation period, but that water is being produced very early in the reaction. When the autocatalytic period has begun, small amounts of nitrite are being produced and the ammonium content is decreasing. By the maximum rate stage significant amounts of nitrite are forming and traces of nitrate appear in the spectrum. The nitrite and nitrate content reaches a maximum at the top of the sigmoid portion of the curve, i.e. when the lower activation energy reaction has finished and the ammonium ion peak has vanished. These two anions are consumed during the linear interface decomposition, and the final black material has no nitrite, but there is a trace of nitrate and an indication that this substance is a hydrate, or at least contains water in some form. The indications are that water is produced during the decomposition, but no sign of any nitrous oxide or ammonia held in the solid can be found.
(a) $(NH_4)_2C_2O_7$

(b) 1% DECOMPOSITION

(c) 17% DECOMPOSITION

FIG. 12
(d) 34% Decomposition

(e) 53% Decomposition

(f) 69% Decomposition

FIG. 12
(a) 71.5% Decomposition

(b) 100% Decomposition

(c) Pale Green Residue

FIG. 12
(a) $K_2Cr_2O_7$

(b) $(NH_4)_2CrO_4$

(c) $NH_4NO_3$

FREQUENCY IN CM$^{-1}$
(d) NaNO₂

(e) NaNO₃

(f) Ca₂O₃

FIG 13
(e) **Evidence from Chemical Analysis of Partially Decomposed Material.**

In an attempt to confirm the results from the infra-red analyses, material which was 37%, 54% and 70% decomposed, respectively, was examined for nitrite ions. The nitrite was estimated by the coupling reaction between α-naphthylamine and sulphanilic acid (71). 30 mg. of the material was ground in an agate mortar with (i) 5 ml. of 1N hydrochloric acid, (ii) 10% sodium hydroxide solution, and (iii) water, respectively, and the mixtures filtered. To each filtrate was added 1 ml. sulphanilic acid reagent (0.6 g. recrystallised sulphanilic acid dissolved in 70 ml. hot water, cooled, 20 ml. conc. HCl added, and made up to 100 ml. with water). After 5 minutes, 1 ml. α-naphthylamine hydrochloride was added (0.6 g. in 1 ml. conc. HCl, made up to 100 ml.) and 1 ml. 2M sodium acetate. These solutions, after standing 10 minutes, were visually compared with M/5,000 and M/10,000 sodium nitrite solutions treated the same way and with blanks of the reagents. No trace of nitrite could be found in the test solutions. This negative result indicates that the nitrite does not exist in the decomposed material, which would dissolve with the above treatment, but is probably co-ordinated in some way to the chromium atoms, perhaps in the form of a polynuclear complex.

As the test for nitrate (72) involves boiling off any
nitrite present and reducing the solution with zinc dust to form nitrite ions which are estimated as above, this was tried with the filtrates but with no positive results. To boil the mixture of solvent and black material to remove any hypothetical nitrite involves further decomposition of the material; hence this test was not tried and it was concluded that no determinable nitrate was present in the material.

Examination of the solubilities of the partially decomposed material (p. 29) showed that very concentrated solutions of 20 - 30% decomposed ammonium dichromate were a yellow-green colour. A possibility that some chromic ion might be present, suggested by this colouration, was investigated by a spectrophotometric method (73). Englis has shown by this means that chromic ion, in fairly concentrated amounts, could be determined in the presence of hexavalent chromium compounds. Other methods were invalidated by the probability of the chromic ion being oxidised to chromate ion. After decomposing some crystals to 28% decomposition at 195.5°C, dissolving the product in as small a volume of water as possible, filtering, and making the filtrate up to 10 ml., the optical density of this solution at 587 m\textmu was measured on a Unicam SP600 spectrophotometer and compared with various standard concentrations of chromic sulphate and ammonium dichromate. It was found that the maximum amount of chromic ion produced
in the decomposition was 1.5% of the chromium in the initial dichromate. No chromic ion was present at the end of the induction period, and after the maximum rate stage the product was only slightly soluble. The significance of this small amount of chromic ion will be discussed later.

The presence of chromic ion was confirmed by adding dilute \( \text{NH}_4\text{OH} \) and \( \text{NH}_4\text{Cl} \) to the above solution, boiling for a few minutes and centrifuging down the small precipitate which formed. This precipitate was suspended in a little water, boiled with a little \( \text{Na}_2\text{O}_2 \), and the resulting clear yellow solution acidified by acetic acid. Lead acetate was added and a yellow precipitate formed positively identifying \( \text{Cr}^{+++} \) ion.

(f) Effects of \( \gamma \)-Radiation.

Two sets of ammonium dichromate crystals were subjected to irradiation from a \( ^{60}\text{Co} \) isotope bomb: one set were sealed in an evacuated tube and the other set merely corked in a tube. As these tubes were only receiving approximately 10% of the total radiation intensity, the crystals were examined microscopically every fortnight for four months.

After the first fortnight no change could be seen in either set of irradiated crystals, either by eye or with the aid of the microscope, but after one month's irradiation both sets had become a rich red colour in place of the original orange-red colour: no sign of nuclei, or any like phenomenon, was present. The darkening continued to
increase during the remainder of the irradiation, but after
the four months there was no diamond nuclei, or incipient
nuclei, to be seen, although to the unaided eye the crystals
were definitely a very dark red. By comparison, the colour
at this end stage would only be that obtained after
approximately fifteen minutes heating at the control
temperature of 195.5°C: that is, somewhere in the induction
period.

500 mg. of crystals were sealed off in a volume of
25 cc. attached to a small manometer, and irradiated for
four months as in the above paragraph. After one month's
irradiation, an increase in gas pressure of 2 mm. had occurred,
and this slowly increased until, at the end of four months,
a pressure of 10 mm. was registered. In terms of a 10 mg.
crystal in a volume of 6684 cc. this represented a pressure
of 0.75 \times 10^{-3} \text{ mm}; in other words towards the end of the
induction period. As full irradiation could not be
obtained continuously this work was concluded after the
four months.

Four of the crystals were thermally decomposed after
being irradiated for four months. A normal sigmoid
pressure-time curve was obtained with no appreciable change
in the value of the maximum rate. Because of the variable
nature of the induction period no definite conclusion as to
any effect of the irradiation on this part of the curve
can be made.
Table 29.

\( \gamma \) -irradiated crystal, 195.5°C, \( p = 4.0 \times 10^{-3} \text{ mm}, \tau \approx 50 \text{ minutes.} \)

<table>
<thead>
<tr>
<th>t mins.</th>
<th>( p \times 10^3 \text{ mm.} )</th>
<th>( 3 + \log \frac{d}{Pf-P} )</th>
<th>t mins.</th>
<th>( p \times 10^3 \text{ mm.} )</th>
<th>( 3 + \log \frac{d}{Pf-P} )</th>
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<td>50</td>
<td>0.18</td>
<td>0.6902</td>
<td>205</td>
<td>34.2</td>
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<tr>
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<td>0.29</td>
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<tr>
<td>70</td>
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<tr>
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<td>3.6365</td>
<td>24 hrs.</td>
<td>57.6</td>
<td></td>
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</table>

However, as a typical run from one of these irradiated crystals shows, (Graph 28, Table 29), the Prout-Tompkins against time plot has broken into two straight lines, and a power law does not fit at all. The break occurs before the maximum rate. This lower portion has a \( k_1 \) value of 0.023 and the \( k_2 \) value is 0.015. This \( k_2 \) is of the order
GRAPH 28
DECOMPOSITION OF \( \gamma \)-IRRADIATED CRYSTAL

\[ 3 + \log_{10} \frac{P}{P_0} \]

TIME (MINUTES)
0.0175 found for k in unirradiated crystals at this temperature of 195.5°C, and suggests that irradiation increases the probability of branching, which then falls to the normal value in the latter part of the decomposition.

The use of ultra-violet pre-irradiation of ammonium dichromate had no obvious physical effects on microscopic examination, although the induction period was slightly reduced on subsequent thermal decomposition.

Addendum.

The knowledge of the surface area of a decomposing substance is valuable when it is required to know the depth of penetration of the reaction in the prenucleation stages of a solid reaction. It was considered, however, that any attempt by standard methods to measure the changes of surface area of single crystals brought about during the thermal decomposition would be subject to considerable error and no practical work was carried out on this aspect.

Ammonium dichromate emits light on slow thermal decomposition, and, if the frequency and change in intensity of this light during the thermal decomposition could be measured then an insight into the fundamental mechanism of the reaction might be gained (5). Unfortunately, the light requires a photomultiplier for its detection and could not be sufficiently amplified to pass through a prism to determine the frequency and so this work was rejected as unpromising.
Another project considered was that of making pellets of ammonium dichromate with the length equal to the diameter, and comparing the kinetics of the decomposition with those deduced for such a cylinder fully nucleated on the surface and the resultant interface contracting inwards at a constant rate. The kinetics of some comparable pellets, used in the conductivity studies, had shown no agreement with the equation formulated by Fischbeck and Spingler (30) for the decay period \( k(t-t_0) = 1 - (1-x)^{\frac{1}{3}} \), which is for a fully nucleated sphere with the interface contracting inwardly at a constant rate. The derived equation, however,

\[
x_{\text{cylinder}} = x_{\text{sphere}} - \frac{Zk}{a} t (1 - \frac{k}{a} t) (1 - \frac{k}{a} t)
\]

was rather intractable, containing various powers of time, and this work was not pursued.

- \( x \) is fraction decomposed.
- \( k \) is a constant.
- \( a \) is the radius of the cylinder and sphere and equals the length of the cylinder.
- \( t \) is the time.
Discussion of Results.

From published work it is evident that the experimental results obtained in thermal decompositions can be very dependent on the past history of the samples. Changes occurring in the crystal during crystallisation and after its preparation (ageing effects) may be at least partly responsible for the lack of agreement amongst the results of the various workers described in the introduction to this thesis. Work on silver oxalate (25) and mercury fulminate (10) has shown that the kinetic expressions which best fit the acceleratory process of the decomposition of fresh and aged material are different, although the activation energies are the same. This would suggest that these differences are associated with changes of structure of the material and not with alternative reaction mechanisms.

The fact that many solid state physical and chemical phenomena, e.g. electrical transport of matter and optical properties, depend upon the existence of structural imperfections led to the concept of lattice defects in crystalline solids. These defects, of which the Frenkel and Schottky types are the most important, are arbitrarily scattered throughout the crystal but in certain individual lattice positions they give rise to localised regions of disturbance. The ability of these defects to move through the lattice was obviously of importance in postulating
mechanisms whereby nuclei could grow in the reactant matrix during a thermal decomposition. Mott (74) interpreted the data on barium azide on the basis of mobile interstitial cations, which was later modified by Tompkins (21) in that nucleus formation was considered to be due to the formation of $F^\prime$-centres which interacted with vacant lattice sites, thus acquiring mobility and these aggregated to form nuclei. Work on lithium aluminium hydride and the various azide salts seemed to indicate that defects played an important part in thermal decompositions. Information regarding these prenucleation processes comes mainly from the study of the photochemical processes and conductivity measurements.

Recent advances in dislocation theory have proved promising when applied to thermal decompositions. Apart from the external surface itself, the most extensive imperfections in solids are subgrain boundaries which divide the crystals into blocks, or subgrains, of linear dimensions 1 - 10 microns. These boundaries often comprise arrays of parallel edge dislocations in the principal lattice planes of the crystal (tilt boundaries), but more generally consist of two-dimensional arrays of dislocations with mixed character, e.g. screw and edge dislocations. These disordered regions generally arise from the presence of impurities and are known to have enhanced reactivity, e.g. it is probable that each dislocation line provides a
route along which diffusion will occur more rapidly than routes through the undisturbed crystal lattice. This theoretical possibility is due to the enhanced concentration of vacancies, and to more frequent atomic rearrangements in the relatively disorderly arrangement of atoms at the core of the dislocation. This reactivity is borne out by Hedges and Mitchell’s micrographs of the interior precipitation of photolytic silver in silver bromide (19): they found that the very small particles of precipitated silver marked out line networks in the interior of the crystals, forming grids typically half a micron apart. These two-dimensional dislocation nets were joined together dividing the crystal into cells of the order of magnitude 10 microns across, the material within these cells being free from lines, or containing only a few. The material used was of high purity, crystallised from the melt and annealed before exposure to light: less well-annealed material showed lines which were in less orderly arrangements of an essentially three-dimensional character. There is no doubt that these lines show the positions of dislocation lines, and probably all the dislocation lines, in the material.

Recent investigations of azide decompositions by means of the electron microscope (75), (76), (77), have shown that these substances crack and split violently along crystallographic planes forming blocklets of $10^{-2}$ microns
across as measured on lead and cadmium azides; silver azide formed blocklets with dimensions of 0.3 micron. This work showed that the surface cracked first and the behaviour of the substances was consistent with preferential reaction at a network of dislocations. Singh (78) in a microscopic study of mercury fulminate undergoing thermal decomposition, has observed preferential decomposition along (010) and (100) planes, and interprets these results in terms of redistribution of dislocations on heating; he also observed the formation of small yellow-brown nuclei along growth marks on the surface. Tompkins (10), in a more detailed study of mercury fulminate, which shall be more fully discussed in the section of the decomposition kinetics of ammonium dichromate, found no evidence of discrete nuclei but did find parallel surface cracks, occurring about 10 microns apart, which he ascribed to dislocation effects. Discrepancies in experimental results for the decomposition of silver oxalate have been satisfactorily accounted for by Tompkins and his co-workers (25) on the basis of dislocation theory. Further development of the theory of dislocations and its application to solid decompositions will probably overcome theoretical difficulties inherent in the defect theory, which depends on the mobility of the defects.

In this present work the initial surface of the crystals used appeared to have no obvious defects apart
from small channels from which water had been removed on drying. As the micrographs show black diamond-shaped nuclei appeared on the surface, and it was suggested that this shape is a reflection of the chemical reaction occurring during the decomposition, viz. the interaction of an ammonium ion and its nearest oxygen neighbour. If lines are drawn joining each ammonium ion position in the (100) plane, a planar diamond is formed. The crack along the main diagonal would appear to be due to stress effects as it does not appear until the nucleus has attained a certain size. This crack is parallel to the strong (101) cleavage plane and the strain induced by the misfit at the reactant-product interface is probably relieved by splitting along this cleavage plane. It would also appear that decomposed material (apart from the diamond nuclei) lies along a network of lines and grows into the interior giving the effect of a general darkening in bulk, which has been described as the main process with the surface nuclei contributing but little to the decomposition. It may be that these networks are indications of the positions of dislocations in the crystal as they in no way resemble the pattern of growth lines found in poor crystals. The violent agitation of the spring in the loss in weight experiments indicating the occurrence of cracking processes, and the fact that the final material is riddled with surface cracks oriented in the direction of the
b-axis, suggests a crystallographic effect in which the cracks develop analogous to the cracks in the nuclei rather than from dislocations as suggested by Singh.

X-ray measurements on a darkened crystal which was only very slightly decomposed, showed no difference in the positions of the reflection intensities so that the ammonium dichromate cell parameters had not changed. The fact that the visible spectrum of similar darkened material showed no new absorption peaks indicated that no detectable F-centres were being formed which could aggregate to form nuclei. An absorption band due to F-centres, if absorbing in the region below 600\(\mu\) would be undetectable because of the strong dichromate ion absorption in this range: the indications, however, are that the darkening effect is due to the formation of black product in the crystal bulk.

The infra-red spectrum of material which had been 1% decomposed, i.e. just at the end of the induction period, showed no new peaks which could be ascribed to products, although some water might be produced in this period. The fact that colour centres can be produced in certain crystals by X- and \(\gamma\)-radiation (68), (69), (79), (80), (81), suggested the experiments in which ammonium dichromate was subjected to \(\gamma\)-irradiation. As has been described the same general effects were found but no nuclei accompanied the darkening process, although the kinetics of the later thermal decomposition were affected. The low specific
electrical conductivity, approximately $5 \times 10^{-10}$ ohms$^{-1}$cm$^{-1}$ at $160^\circ$C, and the large size of the ions, would seem to preclude any general mobility of the ions through the lattice. This section of the experimental work would suggest that the black solid product forms in the subgrain boundaries formed by dislocations and grows into the crystal interior down these boundaries causing the effect of darkening of the crystal bulk. This diffusion of product down the subgrain boundaries has been suggested by Tompkins for mercury fulminate (10) and by Hill and Wallace (82) for the diffusion of molybdenum impurities during the thermal decomposition of mixtures of molybdenum and potassium permanganate.

The fact that monoclinic ammonium dichromate is isomorphous with monoclinic potassium dichromate, and that the potassium salt is polymorphic giving a triclinic form, suggested that the initial reddening effect observed on heating the ammonium salt might be due to polymorphism. No reference to such an effect could be found in the literature, and the microscopic work confirmed that the reddening effect was irreversible, so that the possibility of a polymorphic change complicating the decomposition, as found in ammonium perchlorate (37), can be discounted. The occurrence of spherulitic nuclei in poorly formed crystals instead of the normal diamond nuclei has a parallel in barium azide. Tompkins (83) found that
circular nuclei were formed initially and grew to a critical size, from whence the nuclei became diamond shaped. He suggests this is due to the crystal structure of the azide and that at the nucleus-matrix interface the entropy of activation for growth of the nucleus is a maximum along the diagonals of the diamond; as found in this work growth of the diamond nuclei occurs preferentially along the diagonals of the diamond. He further found that rapidly formed crystals had only circular nuclei. It may be that the kinetics of the decomposition of ammonium dichromate depend wholly on the mode of preparation and age of the crystals and this will be discussed later.

**Kinetics of the decomposition.**

For convenience, the decomposition curve for both the pressure runs and the loss in weight runs may be divided into two parts: (I) the sigmoid pressure-time section, and (II) the linear constant-rate process. To thus regard the two parts of the curve as distinct processes is justified by their respective values of activation energy, 35 kcals./mole and 41 kcals./mole, and by the fact that the value of $p_f$ chosen to fit the Prout-Tompkins relationship lies at the top of the sigmoid and the beginning of the straight line.

I. The Sigmoid Decomposition Curve.

This curve would seem to fit Fig. 1(b) in the general classification given in the introduction, i.e. an apparent induction period exists due to the slow rate of formation of
nuclei. It can be analysed best on the basis of three stages, (a) the induction period, (b) the acceleration period, and (c) the decay period.

(a) The induction period. As defined earlier, this was the time required to reach a pressure of $10^{-4}$ mm. starting from a vacuum of better than $10^{-5}$ mm. Reddening of the crystal indicated that a decomposition process was occurring and an approximate value of 31.5 kcaal./mole was calculated as an activation energy for this process. The fact that shorter induction periods were found for minute and ground crystals by Taylor (52), and that ageing and $\gamma$-irradiation altered the mechanism somewhat, suggested that Tompkins' mechanism for mercury fulminate (10) might be applicable to ammonium dichromate. Crushing would fracture crystals along the original subgrain boundaries forming individual blocks, which may be covered with a superficial layer of the black solid product formed by the frictional heat generated during crushing, although this is not experimentally noticeable; if not, then the surface available for nucleation will have been "activated" in some manner. $\gamma$-irradiation would have a similar effect but only to a slight extent, since the pre-irradiated crystals which were thermally decomposed had an induction of 30 minutes instead of the normal 40 minutes at 195.5°C. Ultra-violet pre-irradiation appeared to have no effect, although solutions of dichromate darkened after 3 - 4 weeks standing in the daylight, undergoing a
photochemical decomposition and crystals grown from these solutions were dark red in colour and decomposed with no induction period.

Ageing may also effect the separation of the crystal into largely independent blocks. Graph 13 shows that a two-year old crystal had no induction period at 180.5°C whereas a new crystal had one of 120 minutes; although no colour change was noted in old crystals they appeared to have very dull surfaces and rounded edges when compared with the glossy surfaces and sharp edges and corners of new crystals. It may be that crushing reduces crystals to particles of subgrain dimensions, the applied stress being relieved by slip along dislocations and subgrain boundaries; ageing would also give a collection of non-contiguous subgrains within the crystal due to the loss of water, and perhaps ammonia, over the P₂O₅ in the desiccator, any subsequent strain being reduced by the formation of subgrains. The surfaces of these crystalline particles would be very active in both cases. It would appear from the varying lengths of the induction period that ageing and crushing do tend to divide the crystals into activated non-contiguous subgrains, whereas new crystals will have these subgrains predominantly contiguous. A six-day old crystal had an induction period of 50 minutes at 180.5°C and probably had some of the subgrains contiguous and some non-contiguous.

The fact that new crystals were darkening during the
induction period indicated that decomposition was occurring in this period although no measurable amount of gas was evolved. In aged and crushed material rapid nucleation of the non-contiguous subgrains would form the gaseous products of the decomposition which could be freely evolved and thus measured as a pressure: hence no induction period would appear. In new material prenucleation processes can only occur on external surfaces and on internal surfaces in the region of dislocations: hence any gas formed inside the crystal would be trapped and not measurable resulting in an apparent induction period, although the crystal was actually decomposing and darkening in bulk. The fact that fragments are blown off the crystals at higher temperatures suggests that it is the pressure exerted by gases inside the crystal which causes this explosive effect.

(b) The accelerating process. It has been concluded from the above discussion on the induction period that the prenucleation process consists of the formation of non-contiguous subgrains with loose interstitial detrital material in aged and crushed material, whereas for new crystals only a little of this material is formed between the subgrains which are essentially contiguous. It may be that the 0.5% water content in new crystals "heals" any non-contiguous subgrains by solution of the loose interstitial material and its recrystallisation as a "bridge" across the subgrain boundary, i.e. a process akin to annealing.
It has been stated that the relationship, 
\[ \log \frac{\alpha}{1-\alpha} = kt + c, \]
is the best fit for the decompositions and that only one value of \( k \) is obtained. Mathematically, this implies that the curve is symmetrical about the point of inflection, i.e. \( \alpha = \frac{1}{2} \) at the inflection point and hence \( p_f = 2p_{\text{max}} \), where \( p_{\text{max}} \) is the pressure at the maximum rate. For all pressure runs and loss in weight runs this condition is satisfied. The activation energies obtained give an average value for this reaction of 35.1±2 kcals./mole, but one value, obtained from the maximum rate values of nitrogen-nitrous oxide runs gives a value of 42.1 kcals./mole. This discrepancy is apparently anomalous since the value obtained from the Prout-Tompkins \( k \) in the same experiment is in agreement with the figure of 35.1 kcals./mole, and \( k \) can be mathematically related to the maximum rate in a simple fashion. This suggests the discrepancy arises in the estimation of the maximum rates for the nitrogen-nitrous oxide runs but as the values of maximum rate were estimated for nitrogen runs in an exactly similar manner this does not seem possible. The additional fact that nitrogen and nitrous oxide appear to be evolved simultaneously (Graph 29) suggests that these arise from the same mechanism and the same activation energy would be anticipated.

Graph 30 shows the fit, for run C9 (a new crystal) at 195.5°C, of some other possible kinetic expressions for the acceleratory period, viz.
GRAPH 29

EVOLUTION OF N₂ AND N₂O AT 200°C.
A. \( p = Ce^{kt} \) linear branching reaction,
B. \( p = kt^n \) power law,
C. \( p = k(t-t')^4 \) Fischbeck's equation.

These fit over a very small range of pressure change, giving the lengthiest fit since the Prout-Tompkins equation reduces to this expression for small values of \( p \). For new crystals the power law did not fit in any case, but for a two-year old crystal this expression always fitted up to the maximum rate stage with \( n = 3 \) (Graph 31). For crystals with ages ranging from one week to a year it was found that, whilst the major portion of the sigmoid fitted the Prout-Tompkin's relationship, the early part up to \( \alpha = 0.2 \) fitted a power law relationship but \( n \) varied considerably from 2.5 - 5.5, although the average value tended to lie between \( n = 3 \) and \( n = 4 \). Corresponding to this change from an interfering branching chain reaction mechanism to a power law mechanism was the shortening of the induction period. This agrees with Tompkins idea that aged, crushed, or pre-irradiated material will fit a cubic power law following the separation of the substance into non-contiguous subgrains, whereas new material should fit an exponential type expression.

From the determined values of the activation energies, 35.1 kcal/mole for the acceleratory process and 31.5 kcal/mole for the prenucleation process, a difference of \( 10^{2-3} \) in the respective pre-exponential factors is
GRAPH 31
TWO YEAR OLD CRYSTAL

(A) \( \text{PRESSURE (x10^3 \text{ mm})} \)

(B) \( 1 + \log_{10}(\text{PRESSURE}) \)

(A) \( \log_{10}(\text{TIME}) \)

(B) TIME (MINUTES)
indicated, assuming equal rates of reaction and equal interfaces at some point towards the end of the induction period — but due to a variation of the interface, caused by the cracking of the crystal, this estimate of $10^{2-3}$ is probably significantly out. The fact that the $E$ values are so close would suggest that the rate of growth of nuclei would be much the same, or just slightly less, than the rate of production of nuclei and this would explain the darkening of the solid as due to the production of sub-microscopic nuclei spreading diffusely through the crystal. The diamond nuclei probably form at spots on the surface where local lattice fluctuations are favourable, e.g. on minute surface cracks or where dislocations emerge at the surface, and grow comparatively slowly. This would indicate that the sub-microscopic nuclei may also be diamond-shaped, two-dimensional and aligned as on the surface.

In aged material the detrital dichromate between non-contiguous subgrains is quickly decomposed to black solid product with the rapid evolution of gases as the absence of an induction period indicates. When all the subgrains are nucleated, the strain set up by the misfit at the interface of the reactant and product causes secondary cracking in directions predominantly normal to the interface, as found on the surface where stress in the nuclei is relieved by cracking along the main diagonal followed by
a network of cracks perpendicular to this. This secondary cracking produces discontinuities (cleavage steps) at intervals down the cracks. The decomposition spreads simultaneously over the faces of the secondary cracks, increasing the volume strain energy which is somewhat relieved by slip at the cleavage steps when isolated sub-blocks, comparable to the mosaic blocks of classical crystal theory, are formed within the subgrains of the dichromate crystal. The high ratio of the pre-exponential factors in mercury fulminate \((10^{2.5}:1)\), this ratio referring to an initial interface reaction growing at a constant rate followed by an accelerating reaction spreading according to either a power law mechanism or an exponential law mechanism, suggested that when a reaction in sub-block had been initiated it was completely decomposed by a co-operative process propagated rapidly \((84), (85)\). The wholly decomposed sub-block would then detach itself from the reactant matrix, and "trigger-off" the decomposition of an adjacent sub-block by a Burgers-Mott type of mechanism, the process being statistically independent of the direction and requiring a certain activation energy. In the case of ammonium dichromate, however, no such clear-cut decision can be made as the ratio of pre-exponential factors is perhaps \((10^{2.3}:1)\) for acceleration:induction period and this is of the order of the error allowed for experimental conditions in the determination of the lattice frequency,
\[ \chi, \text{ in the Polanyi-Wigner equation} \]

\[ \frac{dx}{dt} = N \chi e^{-E/RT}. \]

It may be supposed that a sub-block of ammonium dichromate molecules is completely decomposed by such a process as Tompkins envisages. This sub-block will detach itself from the reactant matrix and "trigger-off" an adjacent sub-block, this process being, as Tompkins observes, statistically independent of direction and requiring in this case an activation energy of 35 kcals./mole, although in this work aged material has not been sufficiently examined to discover whether this value found for new material will also be found for aged material. The fact that Taylor obtained a value of 33 kcals/mole for this salt but a different mechanism, indicates that this is a distinct possibility. The product matrix thus comprises a conglomerate of sub-blocks, approximately hemispherical in shape and bounded by the original subgrain boundaries. The whole process therefore corresponds to three-dimensional growth of reaction centres, all of which are created at approximately the same time \( \tau \), which in the case of fully aged crystals is zero, the appropriate rate expression being \( p = k(t-\tau)^3 \), where \( k \) contains a term denoting the total number of blocks.

With fresh material the much longer induction period indicates that very little, if any, decomposed material exists in the inter-subgranular material at the beginning.
of the decomposition. It may be that the small amount of water held in the crystal from the crystallisation process inhibits the decomposition which will not commence until this water has been expelled from the crystal. It is suggested that only between a few favourable subgrain boundaries is any black product produced in the early stages, and in these areas, as for aged material, secondary cracks are locally produced, but instead of ultimately terminating, as in aged crystals, at fully decomposed subgrain boundaries, most will meet undecomposed boundary material. The subgrains of fresh material are not largely independent and non-contiguous, but are linked to each other by bridges of undecomposed reactant. The sub-block formation does not spread uniformly throughout the individual subgrains as in aged crystals, but extends tree-like through the whole crystal via the bridges in a branching manner, because cracking can only originate in each subgrain from that part of the surface which has been covered by the decomposition product. The mechanism of the sub-block decomposition and the "triggering-off" of adjacent sub-blocks is the same as for aged material, and the activation energy should be the same, although as mentioned no proof exists for this in the present work as it does for mercury fulminate. Taylor's material with an activation energy of 33 kcals./mole may correspond to slightly aged material and the fact that a mechanism is
proposed of an interfering branching chain reaction with
the probability of branching falling off with time, suggests
that many of the "bridges" existing in new crystals have
been destroyed in some manner, perhaps involving Taylor's
method of crystallisation. The initial reaction centres
present at the end of the induction period \( \tau \) are mostly
concentrated at the external surfaces, or in the region of
dislocations, since only here can the original material be
fully nucleated. However, many of the initial centres of
reaction do not continue to propagate the decomposition in
every direction since this is only possible where the
adjacent sub-blocks are of undecomposed material. In the
transference of reaction from block to block more than one
bridge is normally available, so that branching takes place
leading to an exponential law. Depending on the number of
initial reaction centres which continue to grow, interference
in the branching would be expected leading to the Frank-
Tompkins relationship: this is the case for ammonium
dichromate.

However, an alternative argument might be that in fresh
material with the presence of water, and possibly ammonia,
which have been shown to strongly inhibit the decomposition,
the reaction may be inhibited preferentially along certain
planes leading to a chain process. In the absence of any
inhibitors, i.e. in aged material where water and ammonia
have been removed by storage over \( \text{P}_2\text{O}_5 \), the reaction would
be more three-dimensional in character. These mechanisms might require different values of activation energy for fresh and aged material. Since continued evacuation of the gaseous products during the loss in weight experiments failed to alter the Prout-Tompkins mechanism and the activation energy of the decomposition, it seems this argument may be safely discounted. It would also seem for both fresh and aged material that as the reaction proceeds the water and ammonia that are formed might lead to the linking up of the subgrains by the annealing effect mentioned previously — this would perhaps explain the fit of the Prout-Tompkins kinetic expression in the later stages of the decomposition in aged and fresh material.

The acceleratory process is associated with the higher activation energy (35.1 kcals./mole), as found also in the case of mercury fulminate, and this energy requirement is sufficient to initiate the decomposition of a chain of dichromate molecules. The nucleation processes, which initiate the acceleratory period, have a lower activation energy requirement, again as in mercury fulminate. Consequently, the nucleation processes are quickly swamped by the acceleratory process (whose $A$ factor is assumed to become much larger because of the increased interface formed by the cracking processes), the speed of travel of this through the crystal being so much faster. The ageing process, extending over months, is so slow that relaxation
processes have ample time to occur, whereas in the rapid process of "bridging" the subgrains during decomposition these processes cannot occur. Confirmation is found in the case of week-old or month-old crystals where the $P_2O_5$ in the desiccator has not had time to remove all the water from the crystal surfaces and subgrain boundaries. Hence a power law is found for the first small part of the decomposition varying from $\alpha = 0.05$ to $\alpha = 0.25$ depending on the age of the crystal, and this is followed by an interfering branching chain reaction. This involves the assumption that the power law process is "faster" than the branching process, which in turn assumes that more initial centres of reaction are concentrated in a certain volume of the crystal than are scattered over the surface as centres for the exponential process. These aged parts of the crystal will decompose quickly and predominate in the early part of the decomposition, and the pressures of evolved gas measured here should be due to this process: when these decomposed blocks reached an undecomposed subgrain boundary probably two or more paths for "triggering-off" adjacent sub-blocks become available and the process becomes an exponential type. Thus, the fact that the extent of a power law fit in the early stages of the decomposition will depend on ultimately the "age" of the crystal, since the time the crystal stands over the drying agent, $P_2O_5$, determines the number of initial
centres of reaction, becomes understandable and agrees with experimental observations, which show fresh material fitting the Prout-Tompkins relationship very well, two-year old material fitting a cubic power law up to the maximum rate stage, and material with ages lying between these two values fitting the cubic law at the early stages of the decomposition and the Prout-Tompkins in the later stages, the extent of the power law fit depending entirely on the age of the crystal. Experimental results also confirm that the rate of the exponential process in the initial stages of decomposition is slower than the rate of the cubic process. This cubic process and exponential process and their interrelationship have been noticed in all the pressure-time curves and the loss in weight runs. The variation in the value of $n$ noticed for crystals of intermediate age is probably due to interference of the two processes in early stages giving pressure readings which reflected the occurrence of both processes. This variation of $n$ was especially noticeable in crystals which were only two or three days old, and the tendency was for the value of $n$ to approach 3 for the early power law part of the curve the older the crystal was.

$\gamma$-pre-irradiated crystals decomposed to give results fitting the Prout-Tompkins relationship, the straight line breaking into two parts early in the decomposition at $\alpha = \frac{1}{3}$. The lower straight line has a value of slope 1.5 times that
normally found at 195.5°C, and implies that pre-irradiation has increased the number of ways by which decomposing material can bridge the sub-blocks. After a certain time these extra "bridges" are used up and the probability of branching comes back to the usual value: this is found experimentally.

The activation energy of 35.1 kcals./mole obtained in this work is in fairly good agreement with Taylor's estimated value of 33 kcals./mole, but is appreciably less than that given by Fischbeck and Spingler (49 kcals./mole). The material used by Taylor was small crystals (0.1 - 0.2 mm.) obtained by rapid recrystallisation of Analar salt at 40°C and decomposed in 5 - 14 mg. samples. This technique, in which the pressure of nitrogen and nitrous oxide was allowed to accumulate, gave results which best fitted the modified Prout-Tompkins relationship, \[ \log \frac{p}{p_f - p} = k' \log t + c, \] i.e. a structural branching chain reaction in which the chains interfere and the probability of branching decreases inversely as the time. Values of \( k' \) varied erratically with temperature and the \( E \) of 33 kcals./mole was derived from the maximum rate dependence on temperature. When single crystals of ammonium dichromate were grown in the present work in the manner described by Taylor very poor crystals of 10 mg. were obtained. On decomposition (Graph 32) at 195.5°C a very fast reaction occurred, and the results best fitted the kinetic equation given by Taylor. In both cases
one value of \( k' \) was again obtained. These results of Taylor's can be fitted into the mechanism given above if it is considered that rapid crystallisation will produce many more defects and dislocations in the crystal and greatly increase the probability of branching. This will be greatest at the beginning but will decrease with time, giving the kinetic expression \( \log \frac{P}{P_f - P} = k' \log t + c \). The fact that Fischbeck's results fit the equation

\[ \alpha = k(t-t')^4 \]

suggests that he used old material. That the products in Fischbeck's work were continually evacuated should not matter, as in the present work the results obtained from loss in weight experiments, where continual evacuation was employed, gave exactly the same kinetic expressions and values for \( E \) as the pressure runs where the gases were allowed to accumulate. In addition, whether the decomposing sample were held in a closed or open bucket made no difference to the decomposition. Taylor found that Fischbeck's equation fitted his results only approximately and \( n \) varied between 2 and 3. Fischbeck's equation theoretically implies the decomposition occurs by a collection of spheres fully nucleated on the surface and whose number increases linearly with time. This concept could be fitted into the Tompkins mechanism of adjacent zones "triggering off" each other, but does not agree with the cubic law found for aged crystals in the present work. Garner's suggestion in 1935, on the basis of observing
needle-shaped nuclei (these were observed in this work for certain poor elongated crystals and were regarded as very elongated diamond shapes), was that this substance decomposed by a branching chain reaction.

The large difference in geometric form between ammonium dichromate, monoclinic, $a = 13.26^\circ$, $b = 7.54^\circ$, $c = 7.74^\circ$, $\beta = 93.2^\circ$, and one of the solid products, chromic oxide hydrate, where chromic oxide is hexagonal with $a = 5.35^\circ$ and $\alpha = 54^\circ 58'$, suggests that the idea of strain at the reactant-product interface is feasible. The cracking of the crystal is noticeable from quite early in the decomposition and at the higher temperatures is quite violent.

(c) The decay process. As discussed above, the Prout-Tompkins relationship $\log \frac{D}{P_t-P} = kt + c$ holds up to the end of the sigmoid portion of the curve, one value of $k$ being obtained on either side of the maximum rate stage. This is unusual as for most substances which fit this kinetic expression two values of $k$ are obtained, the change in $k$ value occurring at the maximum rate point. The fact that Taylor found one value of $k'$ for the modified Prout-Tompkins relationship (as was also found in four comparable crystals in the present work), suggests that this phenomenon involves the fine crystal structure of the material, and perhaps is associated with the nature of the two-dimensional nuclei indicated on the surface by diamond shapes. The fact that
the decay period of both fresh and aged material fits the Prout-Tompkins expression with the same value of $k$ in both cases may be due, as discussed on p. 129, to the formation of bridges across the subgrain boundaries by an annealing effect due to the production of water and ammonia during the decomposition. In fresh material this might maintain the probability of branching $k$ at a constant value throughout the decomposition, and in aged material cause the "cubic" growth to become exponential with time as bridges were formed during the decomposition. In $\gamma$-pre-irradiated material the increased value of $k$ during the early stages of thermal decomposition would fall to the normal value in the later stages as the water and ammonia were formed during the reaction.

Neither a unimolecular nor a bimolecular decay law, nor Fischbeck's equation $kt = 1-(1-x)^{3/2}$ fitted the results (Graph 33). However, Taylor found that this latter expression fitted his results moderately well from the maximum rate to the end of the sigmoid, giving an activation energy of 35 kca/s./mole (a value in agreement with the present results) as opposed to Fischbeck's value of 49 kca/s./mole. This discrepancy of 14 kca/s./mole seems too large to ascribe to self-heating effects, although they did use 300 mg. samples, which the present work indicated were liable to decompose explosively at $200^\circ$C and above, whereas single crystals could be taken to $225^\circ$C before this
GRAPH 33

THE DECAY PERIOD

\[ \log_{10} \left( \frac{P_f}{P} \right) \]

\[ \frac{2P - P_f}{P_f} \]

\[ 1 - \left( \frac{t}{\tau} \right) \]

TIME (MINUTES)

TIME (MINUTES)
effect occurred. Otherwise the differences in kinetics cannot be due to different experimental conditions because (a) in both cases the pressure of residual water vapour is estimated to be less than $10^{-4}$ mm. and (b) experiment showed that the decomposition of the salt was unaffected by the presence of nitrogen or nitrous oxide, but that water and ammonia vapour inhibited it greatly.

In the above kinetic expressions involving $p_f$, an estimated experimental pressure, an assumption is made that either the linear interface reaction is insignificant during the autocatalytic stage, or that the pressure due to the latter process at any time is a constant fraction of the whole.

II. The Interface Reaction.

At the end of the sigmoid decomposition stage the material is a black, insoluble amorphous crystal highly riddled with cracks. From here the decomposition followed a constant-rate stage, indicating a linear interface reaction (13): this effect was also noted by Taylor but appears to have been regarded as part of the decay period by Fischbeck. In this work an activation energy of 41.1 kcals./mole was obtained for this process compared to 36 kcals./mole reported by Taylor.

The fact that an amorphous material may decompose at low temperatures has already been reported by Schmitz-Du Mont (86) for cobalt and chromium amides which split
off ammonia to give crystalline cobalt nitride and amorphous chromium nitride. In the present work the substance, both at the beginning of the constant-rate stage and at the end of the decomposition, is amorphous to X-rays. This section of the decomposition curve is very dependent on how the material has decomposed during the earlier part of the decomposition. For unaged crystals the slope of the constant-rate process is reproducible, but for aged material this was not so, as was also the case in the loss in weight where a considerable scatter in the results was noted. The process was envisaged as a reaction spreading from the surface, with an interface of constant area, and moving through the amorphous crystal with the surface being constantly regenerated. The fact that the presence of very low pressures of water (and ammonia) as shown by the Bourdon runs, greatly extends this stage of the reaction indicates that some form of "solvent" effect may be present which effectively "preserves" the interface. The fact that mixtures of ammonium dichromate and the black solid product also have extended constant-rate stages may originate more from chemical effects, e.g. the black material acting as a bridge in an electron transfer process, rather than from purely mechanical effects.

After this linear rate process the decomposition dies away indeterminately and, at higher temperatures, very rapidly. In conclusion, it is clear from the present work,
from work on silver oxalate and mercury fulminate, that ageing brings about changes in the physical structure of freshly prepared material which determine to varying degrees the kinetics of the decomposition. The theoretical approach devised by Tompkins, for mercury fulminate in particular, has been applied to ammonium dichromate, and would appear to offer a reasonable explanation of the present results and some reconciliation of divergent earlier results.

The Electrical Conductivity of Ammonium Dichromate.

The application of conductivity data to thermal decompositions is in its infancy at the present time. There are difficulties inherent in the use of powders (in the form of pellets) which have not yet been completely surmounted. It is difficult to distinguish between electronic and ionic conductivity without elaborate experimental techniques, and there is as yet no certain method of distinguishing between surface and bulk conductivity, apart from the differences in the activation energies associated with each process and the temperatures at which the different effects appear. The apparatus used in this work, a modification of the Jacobs circuit (59), gave results reproducible within 2% from pellet to pellet, and polarisation effects seem to have been successfully avoided.

Theoretical aspects of ionic conductance in solid salts have been treated by Tompkins and Jacobs (87) but no attempt has been made to apply these in the present work,
apart from certain qualitative conclusions which have been made. The fact that only one straight line occurs expressing the temperature variation of the specific conductivity, viz. 

\[ \kappa = 1.122 \times 10^{-8} e^{-20.2/RT} \]

suggests that only defect conduction makes any significant contribution to \( \kappa \) in the range of temperatures examined. This view is supported by the value of \( E \) (20.2 kcal./mole), which is in the range of values reported for "structure-sensitive conductance" for the alkali halides (87) and "bulk structure-sensitive conductance" for the azides (61). It is higher than the \( E \) expected for surface conductance (4.5 kcal./mole) in azides and lower than that expected for the characteristic ionic conductance of most salts (c. 30 kcal./mole) which have been investigated. The characteristic bulk ionic conductance region is never reached as experiment showed that the salt was decomposing steadily above 160°C and this was reflected in the conductivity values. Ammonium dichromate has a thermal transition point at -2.4°C and from this, and magnetic resonance measurements, it is considered that ammonium ion is rotating in the lattice. From its general size and mobility it is probable that the value of \( E \) found is a measure of the mobility of ammonium ion defects in the lattice, as dichromate ions are too bulky to occur interstitially or to move through the lattice.

The fact that the conductivity increases exponentially with time at a fixed temperature in the range 180° - 186°C,
comes to a fixed value, and then dies away, is significant in view of the kinetic mechanism proposed earlier. The value of E of 40 kcais./mole though subject to a large error, probably 30 - 40%, due to the small temperature range employed, (less than 6°C), would indicate that the process giving rise to the increase in conductivity is associated with the process occurring in the pressure measurement runs. In other words, the exponential increase is associated with the decomposition mechanism and not with the general conductance properties of the ammonium dichromate lattice. It is envisaged that an intermediate solid product is formed, reaching a maximum value at the top of the sigmoid (e.g. the section on the chemical mechanism of the decomposition), and this intermediate gives rise to the increased conductivity. The fact that the intermediate postulated in the next section is a large polynuclear complex which would be unlikely to move through the lattice need not invalidate this idea, since it could increase the conductivity by contributing electrons to the conduction band. When the sub-blocks of decomposed material are formed these contribute to the conduction process: as each new sub-block is "triggered off" in new material the number of sub-blocks increases exponentially, and thus so does the conductivity. This fit will be good at the beginning but later in the decomposition, due to interference between chains, the fit of the exponential straight line in the plot log $\kappa$ against
should fall off slightly, as is found experimentally. On reaching the top of the sigmoid the number of decomposed sub-blocks, consisting of the intermediate solid product, has reached a maximum value and the conductivity thus becomes constant. It is considered that the constant-rate process then occurs, changing the intermediate solid to the final solid product obtained on complete decomposition. The conductivity may thus fall off after the steady value and this view is experimentally valid.

This mechanism assumes that the material in the pellets decomposes in a manner analogous to new crystals although the material has been finely ground at first. It is imagined that the subgrains formed by grinding will once more become contiguous in the pellet form because of the high compression used and so will decompose by a chain process. Graph 34 shows the loss in weight curve of a pellet decomposed at 195.5°C and in Graph 35 the fit of two power law expressions are compared with the Prout-Tompkins equation. It can be seen that the pellet decomposes in a manner which fits the chain process idea very well, but not the power law mechanism which would be expected for ground material. This would suggest that the subgrains are contiguous and that the assumed mechanism is valid.

Thus it may be concluded that the conductivity results bear out the kinetic mechanism proposed earlier. No significant changes in conductivity occur in the early stages
GRAPH 34

PELLET DECOMPOSITION

TIME (MINUTES)
of the decomposition which could be ascribed to the formation of F-centres, and although the bulk conductivity seems too small to allow for a mechanism involving these it is of the same order as that found for barium azide (c. $10^{-11}$ ohms) for which the production of F-centres has been put forward, (21). The low mobility of the ions may also explain why the final material is amorphous, although the value of 12.4 kcal/mole obtained as the activation energy for pellets of the final black solid product of the decomposition suggests that it might recrystallise at a higher temperature where the mobility of the ions is greater.

**Chemistry of the Decomposition.**

The varying nature of the products of the thermal decomposition of ammonium dichromate as reported by earlier workers has been noted in the Introduction. The results of the very earliest workers in this field will not be considered, as many of them were obtained from experiments performed in air under widely differing conditions. The present work agrees with previous results in that nitrogen, water, and ammonia are found as major gaseous products, but this appears to be the first time that nitrous oxide has been reported as present as a gaseous constituent, although Moles and Gonzales (41) found nitrous acid. The only previous quantitative estimate of the gaseous products was made by Fischbeck and Spingler (48) who found that the decomposition fitted the equation,
(NH₄)₂Cr₂O₇ → N₂ + 3H₂O + Cr₂O₃·H₂O,

after 14 - 18% of the nitrogen content of the initial salt had been evolved as NH₃ during a primary surface reaction: a check of the figures given in their paper reveals that only 41% of the theoretically expected nitrogen figure is obtained at 211°C. In the present work the balance of the nitrogen contents of the original undecomposed material and of the gaseous and solid products is fairly satisfactory being within 3.1% of each other at 195.5°C. Expressed as a percentage of the total nitrogen in the original solid, the gaseous products contained 53.5% as nitrogen, 23.5% as nitrous oxide, 20.5% as ammonia, and 5.6% as nitrous oxide held in the solid residue. No other gases could be found within the experimental limits of the methods of analyses employed, but the presence of minute traces of nitrate and nitrite in the condensate in the traps gave a possible indication of nitric oxide and nitrogen dioxide in the gaseous products.

With regard to the solid products of the decomposition the position is not so clear cut. The varying compositions reported by the early workers may be due to varying amounts of oxygen from the air taking part in the reaction. Fischbeck assumed the formula of the black material to be Cr₂O₃·H₂O from the loss in weight occurring during the decomposition, but carried out no chemical analysis for the chromium. Harbord and King (57) regarded this black
material as a solid solution of two, or more, compounds, or a non-stoichiometric substance containing nitrogen and nitrous oxide, but certainly not a simple hydrate or high oxide of chromium, although the chromium content (61.2%) was equivalent to the composition CrO\textsubscript{2}, as had been reported by earlier workers. They suggested that the varying compositions, which had previously been reported, were due to the assumption that after ignition the composition corresponded to Cr\textsubscript{2}O\textsubscript{3} which they showed was not justified. The Cr\textsubscript{2}O\textsubscript{3} was non-stoichiometric itself, there being an excess of 1.1% oxygen over the theoretical value. As the experimental results show the black product in this present work was non-stoichiometric, but 2.8% oxygen was found in place of the nitrogen found by Harbard and King. The evolution of nitrous oxide from black material prepared at 195.5°C can be explained on the assumption that it originated from the small amount of nitrate ion-chromium complex left in the solid at this temperature, as indicated by the infrared work. Material prepared at 205°C and above evolved no nitrous oxide on further heating, though the oxygen content was the same: this "missing" nitrous oxide had been evolved in the primary low-temperature reaction where the estimate of nitrous oxide was experimentally determined 5.6% higher at 205°C than at 195.5°C.

The oxygen from the residue was evolved explosively at 385° - 390°C and bore a close resemblance to one of the
stages in the thermal decomposition of chromium trioxide. Harold and King (88) had studied this reaction and found the formation of two intermediate non-stoichiometric oxide ranges \( \text{CrO}_2 \, .2-2.6 \) and \( \text{CrO}_{1.7-1.9} \), but later workers rejected these values. Ward (89), using X-ray diffraction and chemical analysis, found three stoichiometric oxides as intermediaries, \( \text{Cr}_3\text{O}_8 \), \( \text{Cr}_2\text{O}_5 \) and \( \text{CrO}_2 \). Below 360°C mixtures of \( \text{Cr}_3\text{O}_8 \) and \( \text{Cr}_2\text{O}_5 \) were formed, from 360°C - 460°C mixtures of \( \text{Cr}_2\text{O}_3 \) and \( \text{CrO}_2 \) were obtained: the \( \text{Cr}_3\text{O}_8 \) was readily soluble in water giving \( \text{Cr}_2\text{O}_7^{-} \) and \( \text{Cr}^{4+} \) ions, whereas \( \text{Cr}_2\text{O}_5 \) would only dissolve in boiling perchloric acid. The pressures of evolved oxygen were not measured, but Glemaer and his co-workers (90), in an investigation of the decomposition of \( \text{CrO}_3 \) in a stream of oxygen, used magnetic measurements, as well as X-ray diffraction and chemical analysis, and found three phases, corresponding to Ward's from the diffraction data, but having the formulae \( \text{CrO}_{2.48} \), \( \text{CrO}_{2.48} \), \( \text{CrO}_2 \). Although \( \text{CrO}_{2.48} \) and \( \text{CrO}_{2.48} \) could be isolated, the \( \text{CrO}_2 \) only occurred with the \( \text{Cr}_2\text{O}_3 \) and appeared to be formed simultaneously with the \( \text{Cr}_2\text{O}_3 \). Glemaer found at 390°C a sudden change from \( \text{CrO}_{2.48} \) to \( \text{CrO}_{1.6} \) (i.e. a mixture of \( \text{Cr}_2\text{O}_3 \) and \( \text{CrO}_2 \)), accompanied by the sudden evolution of oxygen and a sharp rise in the magnetic susceptibility. This material \( \text{CrO}_{1.6} \) was grey-green in colour, as King had found, instead of the bright green of pure \( \text{Cr}_2\text{O}_3 \). This colour is probably due to a
mixture of the two oxides and not to a single non-stoichiometric oxide with excess oxygen, as Anderson (91) has shown that the limits of deficiency or excess of oxygen in Cr$_2$O$_3$ are very narrow and do not cover the "chromic oxide" obtained by Harbard and King from ammonium dichromate.

The explosive evolution of oxygen at 385°C from the black residue, giving a pale green residue of the same composition, Cr$_{0.7}$, as that found by Harbard and King, implies that some Cr$_2$O$_5$ is present decomposing to CrO$_2$-Cr$_2$O$_3$ with the evolution of oxygen.

Although the major proportion of the black solid at 195.5°C has a composition corresponding to chromic oxide hydrate, containing a little nitrate complex, the evolution of 2.8% by weight as oxygen indicates that 16.1% of the solid is Cr$_2$O$_5$. The detection of 1.5% of the total chromium as chromic ion (i.e. 100 Cr$_2$O$_7^{2-}$ ions give rise to 3 Cr$^{+++}$ ions) just before the maximum rate stage would indicate the soluble oxide Cr$_3$O$_8$. The fact that the decomposing material is insoluble from the top of the sigmoid onwards would indicate that by this stage of the decomposition the Cr$_3$O$_8$ has decomposed to Cr$_2$O$_5$. The low melting point of CrO$_3$ (c. 197°C) would preclude its formation in the decomposition of ammonium dichromate other than as a very transient intermediate. Many hours roasting of the pale-green residue Cr$_{0.7}$ at 800°C gave a blue-green material
containing less oxygen, CrO\textsubscript{1.55}. It would seem that the black residue is a solution of chromic oxide hydrate and Cr\textsubscript{2}O\textsubscript{5}, with a nitrate content which depends on the temperature of formation of the material. Glemsen had also examined the final black material formed in the decomposition of ammonium dichromate, but found it to be amorphous and of an indeterminate composition. No CrO\textsubscript{2} could be found by X-ray diffraction work nor by magnetic measurements (the most reliable method for determining CrO\textsubscript{2} since it is ferromagnetic) but on heating at 400°C, or higher temperatures, Cr\textsubscript{2}O\textsubscript{3} was formed.

The fact that the amorphous black solid recrystallises after the evolution of oxygen at 385°C is of interest. It was noted by Russian workers (92) that the temperature of transition of amorphous chromium oxide hydrate into crystalline chromic oxide occurred just below 400°C, and only took place when the substance had lost the last traces of chemically bound water. Other workers (93) found that amorphous Cr\textsubscript{2}O\textsubscript{3} recrystallised at 380° - 415°C in an atmosphere of oxygen, and that chromic oxide monohydrate is stable at 220°C (94). No Cr\textsubscript{2}O\textsubscript{5} can be found in the X-ray diffraction photographs which are completely amorphous for the black material, but the recrystallised material is definitely chromic oxide. The fact that Cr\textsubscript{2}O\textsubscript{5} changes to Cr\textsubscript{2}O\textsubscript{3} with the evolution of oxygen at the same temperature range in which amorphous chromic oxide hydrate recrystallises
to chromic oxide, obscures the above relationships but does not invalidate them, since the energies of activation for both processes may have minimum values at 390° - 400°C.

Chemical Mechanism of the Decomposition.

The mechanism postulated by Bircumshaw for ammonium perchlorate (37) seems to have certain attractions when applied to the dichromate salt. An electron transfer reaction between a dichromate anion, occupying a lattice site, and an interstitial ammonium cation is probably the essential initial step in the decomposition. The ion NH$_4^+$ would be expected to be stable since

$$\text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}^+ \text{  } 200 \text{ to } 220 \text{ kca}s.$$  

The fact that the potassium and sodium dichromate salts are fairly stable to heat indicates that the thermal breakdown of the dichromate ion is unlikely to be the first step in the decomposition.

The initial electron transfer reaction will be

$$\text{Cr}_2\text{O}_7^{2-} + \text{NH}_4^+ \rightarrow \text{Cr}_2\text{O}_7^- + \text{NH}_4 \text{ followed by}$$

$$\text{NH}_4^- \rightarrow \text{NH}_3 + \text{H}.$$  

This dichromate radical formed in the bulk of the crystal probably cannot break up since it will be stabilised by the crystalline force fields, and it must pick up either an electron from a neighbouring Cr$_2$O$_7^{2-}$ ion, or a hydrogen atom to form HCr$_2$O$_7^-$. This electron transfer process will eventually produce a Cr$_2$O$_7^-$ radical on the surface which will then be able to decompose. The point on the surface
where the \( \text{Cr}_2\text{O}_7^{\text{-}} \) radical has been formed and decomposed has lost an electron (or two) and must therefore be a positive hole. This positive charge can be removed either by the entry of an electron from the crystal interior to form an F-centre, or the migration of an \( \text{NH}_4^{+} \) ion from a nearby lattice site; this \( \text{NH}_4^{+} \) ion would become an interstitial ion which could take part in another electron transfer reaction in the neighbourhood of the decomposition site. Continuation of the process would give rise to a nucleus. The low conductivity of the ammonium dichromate, and the fact that decomposition occurs before any significant ionic conductance can be observed, precludes the second possibility (although there may be a migration of \( \text{NH}_4^{+} \) ions at the surface or along dislocation zones occurring with a low activation energy), and indicates that the aggregation of F-centres is the probable mode of formation of nuclei. This would explain the appearance of surface nuclei and the evolution of ammonia gas. However, no features are observed in the increase of conductivity with time of decomposition, or in the visible spectrum of very slightly decomposed material, which would indicate the aggregation of F-centres in the substance. Possibly once a sub-block of the crystal is fully nucleated it "triggers off" other sub-blocks and the consequent exponential increase of conductivity with time hides any F-centre contribution to the conductivity. It may be that the same process of F-centre formation and
aggregation to form nuclei occurs within the crystal at dislocations and accounts for the darkening effect noticed in the induction period of new crystals.

The two products of the breakdown of the NH₄ radical

\[ \text{NH}_4 \rightarrow \text{NH}_3 + \text{H} \ (26 \pm 10 \text{ kca}s.) \]

may diffuse to the surface and escape, or more probably the H atom will meet a \( \text{Cr}_2 \text{O}_7^- \) radical in the interior, or surface, in which case \( \text{HCr}_2\text{O}_7^- \) is formed and effectively no decomposition occurs. This \( \text{HCr}_2\text{O}_7^- \) ion may react with another H atom as

\[ \text{H} + \text{HCr}_2\text{O}_7^- \rightarrow \text{H}_2\text{Cr}_2\text{O}_7^-; \]
\[ \text{H}_2\text{Cr}_2\text{O}_7^- \rightarrow \text{H}_2\text{O} + \text{Cr}_2\text{O}_6^-; \]
\[ \text{Cr}_2\text{O}_6^- \rightarrow 2\text{CrO}_3 + \text{e}^- . \]

Water and ammonia vapours are known to inhibit the decomposition and this would suggest that they inhibit by preventing the diffusion of \( \text{NH}_3 \) gas out of the lattice, or by reversing the above method of forming water. Or again, the reaction

\[ \text{Cr}_2\text{O}_7^{2-} + \text{NH}_4^+ \rightarrow \text{Cr}_2\text{O}_7^- + \text{NH}_4; \]
\[ \text{NH}_4 \rightarrow \text{NH}_3 + \text{H}; \]

may be reversible in the crystal and the addition of ammonia would thus reduce the rate of decomposition.

The possibility of the formation of \( \text{CrO}_3 \) (probably as a very transient intermediate) is suggested by the respective crystal structures of the dichromate ion (Fig. 9) and chromium trioxide. The \( \text{Cr}_2\text{O}_7^{2-} \) grouping consists of two
tetrahedra, with chromium atoms at their centres, linked at one corner of the tetrahedra by a common oxygen atom, the Cr — 0 — Cr angle being 115° and the distance between paired Cr atoms 3.2 Å. CrO₃ consists of long chains of tetrahedra joined by oxygen atoms the Cr — 0 — Cr angle being 136° and the Cr — Cr distance in a chain 3.3 Å. The fact that the crack along the main diagonal of the diamond nuclei may lie in the (101) cleavage plane, suggests that the ammonium dichromate lattice, by splitting along this cleavage, would divide the crystal into a number of "chains" of dichromate molecules (Fig. 9). If two adjacent NH₄ radicals attack the nearest oxygen atoms then it may be imagined that one molecule of NH₃ gas will be formed and one molecule of water and these will be evolved: the other oxygen will join to the Cr of the adjacent molecule to satisfy valency forces. Since this will happen for each temporary Cr₂O₆⁻ grouping a chain is formed and is essentially CrO₃. The second NH₄ group will become co-ordinated to the Cr atoms as an amide grouping NH₂⁺ which could then be oxidised to NO₂⁻ — NO₃⁻ forming the intermediate polynuclear complex. So the Cr₂O₆⁻ grouping, essentially the dichromate ion, could "polymerise" into CrO₃ chains. This "polymerisation" process might be imagined as involving a number of dichromate ions and might possibly be equated with the "triggering-off" process visualised for the kinetic mechanism. At certain positions in these chains Cr₃O₈
groupings could occur which would break down to give \( \text{Cr}_2\text{O}_7^{2-} \), the evolved oxygen being used to oxidise \( \text{NH}_2^+ \) groups to \( \text{NO}_2^- - \text{NO}_3^- \) groupings. The \( \text{CrO}_3 \) chains would be stabilised by the co-ordinated \( \text{NH}_2^+ \), \( \text{NO}_2^- \) groupings as discussed in the next paragraph.

It is of interest that Ryss (100) finds that \( \text{CrO}_3 \) decomposes as a first step to \( \text{Cr}_5\text{O}_{13} \) (i.e. \( \text{Cr}_3\text{O}_8 \)) with an activation energy of 33.97 kca/l/mole (cf. the E of 35.1 kca/l/mole found in this work). This mechanism would seem to account for the \( \text{Cr}^{+++} \) content of the partially decomposed material more satisfactorily than postulating the ion-electron half reaction

\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{+++} + 7\text{H}_2\text{O}
\]

which would be accompanied by an oxidation reaction, probably of the ammonium radical.

The occurrence of nitrate and nitrite ions from the infra-red work implies that these occur as intermediate compounds in the decomposition. The fact that ammonia comes off earlier than nitrogen or nitrous oxide and has been completely evolved by the top of the sigmoid, whereas the other two gases are evolved throughout the whole decomposition (and their presence has no effect on the rate of the reaction), supports this view. At this temperature, c. 200°C, it is unlikely that ammonia, once evolved, would be resorbed on the surface of the solid and oxidised directly to give nitrogen and nitrous oxide, especially as
ammonia inhibits the decomposition. No data has been found to argue this on the basis of energetics, but the experimental evidence points to nitrogen and nitrous oxide being evolved from an intermediate $\text{NO}_3^- - \text{NO}_2^-$ complex. This would arise from the $\text{NH}_4^+$ radical being oxidised to the $\text{NO}_2^-$ and also $\text{NO}_3^-$, the $\text{NO}_2^-$ appearing first in the infra-red spectra. The fact that these ions cannot be detected chemically suggests that they are bonded to the chromium oxide complex, probably in the form of a polynuclear complex. It has been mentioned earlier that amorphous chromium and cobalt amides decompose autocatalytically to give the corresponding nitrides at similar temperatures. These substances are without doubt high polymers, and the chromium amide is given as

It is suggested that the $\text{NO}_2^-$ and $\text{NO}_3^-$ groups are stabilised on the $\text{CrO}_3$ chains in a similar manner, forming a polynuclear complex for which a tentative structure is given below.
although the end groupings may possibly be -CrO\textsubscript{3} groups.

This is feasible as polynuclear complexes derived from 6-co-ordinated metal ions have been studied extensively, and commonly contain such bridging groups as -OH, -O-, -O\textsubscript{2}-, -NH\textsubscript{2}, -NH-, and -NO\textsubscript{2} (95). One, two, or three such groups are common to both co-ordination spheres. This complex is formed simultaneously with the initial reactions in which the ammonia and water are formed, and it decomposes to give essentially nitrogen, nitrous oxide and Cr\textsubscript{2}O\textsubscript{3}.H\textsubscript{2}O and Cr\textsubscript{2}O\textsubscript{5} (from Cr\textsubscript{3}O\textsubscript{6}). Much of the water formed in the decomposition as a whole will occur as a result of the oxidation of NH\textsubscript{4} to NO\textsubscript{3}\textsuperscript{-} and NO\textsubscript{2}\textsuperscript{-}; it may be that an amide type polynuclear complex, similar to chromium amide, is formed first and the NH\textsubscript{2}\textsuperscript{+} is oxidised to the NO\textsubscript{2}\textsuperscript{-} complex. No positive evidence of NH\textsubscript{2}\textsuperscript{+} groups can be found in the spectra, as they absorb in the same region as water, c. 1630 cm\textsuperscript{-1}. This NO\textsubscript{2}\textsuperscript{-} complex would be stable and give nitro grouping absorption peaks in the infra-red spectra, as has been found in the case of the inorganic complexes dinitrotetramminecobalt chloride and sodium.
hexanitrocobaltate (101) where it has been shown the $\text{NO}_2^-$ group is bonded to the central metal atom by a direct $\text{N} \rightarrow \text{Co}$ bond as in nitro-alkanes and not as an alkyl nitrite type $\text{N} \rightarrow \text{O} \rightarrow \text{Co}$. Further oxidation would give $\text{NO}_3^-$ group and it is generally accepted that $\text{NO}_3^-$ groups are poor co-ordinators: hence the complex would tend to become unstable and break down to give $\text{N}_2$ and $\text{N}_2\text{O}$ and $\text{H}_2\text{O}$ as gaseous products. The fact that the maximum concentration of $\text{NO}_3^- - \text{NO}_2^-$ complex occurs at the top of the sigmoid and is destroyed from there onwards suggests that the presence of water lengthens the constant-rate process by preserving the linear interface reaction which causes the breakdown of this polynuclear complex. The small retention of $\text{NO}_3^-$ ion at 195.5°C means that all the complex has not decomposed, the $\text{NO}_3^-$ probably being associated in some way with the $\text{Cr}_2\text{O}_3\cdot\text{H}_2\text{O}$ which occurs at the end of the reaction. The molecule of water will probably be chemically bound to the $\text{Cr}_2\text{O}_3$ and has to be removed before the $\text{Cr}_2\text{O}_3$ will recrystallise: probably this chemically bound water lowers the mobility of the ions and prevents crystallisation. The strength of this bond is probably due to $\text{OH}$ groups being bonded to the $\text{Cr}_2\text{O}_3$ phase through a hydrogen bond to an oxygen atom (96). The stability of the nitrous oxide at this temperature over chromic oxide has been demonstrated by Stone (97) who states that the gas is stable over this catalyst up to 650°C.
It is of interest to note the mechanism put forward by Shidlovskii for the combustion of ammonium dichromate pellets in oxygen, and in which the combustion appears to take place in the gaseous phase (98). He suggested

\[(\text{NH}_4)_2\text{Cr}_2\text{O}_7 = 2\text{NH}_3 + \text{H}_2\text{O (vapour)} + 2\text{CrO}_3 - 64.5 \text{ kcals.,}\]

\[2\text{CrO}_3 = \text{Cr}_2\text{O}_3 + 1.5\text{O}_2 - 5.6 \text{ kcals.,}\]

\[2\text{NH}_3 + 1.5\text{O}_2 = \text{N}_2 + 3\text{H}_2\text{O (vapour)} + 151.3 \text{ kcals.,}\]

this last reaction being the rate-determining step. In the present work the presence of intermediate nitrate and nitrite probably rules out this last step, but the first two steps are possible. Following

\[(\text{NH}_4)_2\text{Cr}_2\text{O}_7 = 2\text{NH}_3 + \text{H}_2\text{O} + 2\text{CrO}_3,\]

the second step would involve the stepwise breakdown of

\[2\text{CrO}_3 \rightarrow 2\text{Cr}_3\text{O}_8 + \text{O}_2 (E = 33.97 \text{ kcals./mole})\]

and it would appear that this step may be the rate-determining reaction.

Finally it may be said that more work is necessary on the enthalpy properties of the various intermediates in this decomposition before a complete mechanism can be forwarded with any confidence. The use of magnetic susceptibility measurements to follow the decomposition might be of use in unravelling the complex formation of oxides of chromium and the positive presence of a polynuclear complex. A more detailed examination of aged material could be rewarding from the kinetic aspect, and electrical conductivity data for decomposing aged and fresh material might support the
physics of the mechanism proposed, if the method could be extended to make use of single crystals.
Summary.

A brief outline of the present knowledge of thermal decompositions of crystalline solids has been given in the Introduction, together with a description of the principal mechanisms that have been put forward in explanation of the experimental results. The kinetic expressions derived for these mechanisms have also been noted. The disparity between the results of previous workers on ammonium dichromate has been described and in the present work an attempt has been made to reconcile these anomalies.

From a chemical viewpoint the variation in the products of the decomposition would seem to arise from the lack of standardisation in experimental conditions. The present work found nitrogen, nitrous oxide, ammonia and water as the gaseous products and a black solid product whose composition would appear to be

$$\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O} \cdot (\text{Cr}_2\text{O}_5)_x \cdot (\text{Cr}-\text{O}-\text{N complex})_y$$

under the experimental conditions employed. No simple chemical mechanism can be applied to the decomposition and it is suggested that the reaction proceeds via an intermediate compound, whose nature would appear to be a polynuclear complex formed by "polymerisation" of chains of dichromate ions in the (101) plane of the crystal lattice to form -Cr-O-Cr-O-Cr- chains, to which nitrite and nitrate groups are co-ordinated in some way. The only evidence for this is that given by the infra-red spectra of partially
decomposed samples of ammonium dichromate.

With regard to the kinetics of the decomposition the present work differs from previous results. An expression representing a branching chain mechanism in which the chains interfere, viz. \( \log \frac{x}{1-x} = kt + c \) best fits the results of both pressure measurements and loss in weight measurements with only one value of \( k \) required as against the more usual requirement of two values of \( k \). The fact that "aged" crystals, i.e. crystals which had been kept for two years, fitted a power law expression \( p = kt^n \) with \( n=3 \), led to the application of dislocation theory to the mechanism involved in the thermal decomposition, on the basis of Tompkins' work on mercury fulminate and silver oxalate.

The occurrence of two stages in the decomposition curve, a sigmoid portion fitting the mechanism quoted above and with an activation energy of \( 35 \pm 2 \) kals./mole, followed by a linear constant-rate interface reaction with an activation energy of \( 41 \pm 2 \) kals./mole, agrees with Taylor's work on minute crystals but has no analogy in earlier work by Fischbeck and Spingler.

Electrical conductivity measurements on pellets of ammonium dichromate gave results which could be fitted in with the idea of a branching chain mechanism and the formation of a polynuclear complex. Microscopic observations showed that the crystals were decomposing during the apparent induction period but neither X-ray
diffraction measurements, electrical conductivity measurements, nor the visible spectrum of the decomposed material could offer any clue to the nature of this prenucleation process. From microscopic observations the darkening in this induction period appears to be due to the formation of diffuse sub-microscopic nuclei.
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