THE THERMAL DECOMPOSITION OF AZODICARBONAMIDE

by

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THE THERMAL DECOMPOSITION OF AZODICARBONAMIDE

SUMMARY

Azodicarbonamide (A.C.), commercially known as Genitron A.C., is an industrial blowing agent for cellular plastics. The present work, presented in two parts, reveals two separate aspects of the thermal decomposition of A.C.

PART I

AZODICARBONAMIDE ON ITS OWN

In this part of the investigation an attempt has been made to obtain detailed information regarding the mechanism of the decomposition of A.C.

A.C. on thermal decomposition forms four major solid components, namely, urea, urazole, biurea and cyanuric acid. A method for the quantitative analysis of these components has been devised and the variation in the percentage of these components as a function of time at two temperatures has been studied.

The gaseous components other than nitrogen have been identified by infra-red spectroscopy. They are found to contain carbon monoxide and iso-cyanic acid at 171.5°C and carbon monoxide and ammonia at 191.5°C. Positive evidence for the presence of iso-cyanic acid has been obtained for the first time. The iso-cyanic acid polymerises slowly to cyanuric acid and cyamelide which makes the analysis extremely difficult. A special apparatus has been

designed for the quantitative analysis of all the gaseous components present.

On the basis of the analytical data obtained, a mechanism for the decomposition of pure A.C. has been proposed. The experimental data are in good agreement with the theoretically calculated data.

The iso-cyanic vapour has been found to react readily with water vapour and ammonia. An attempt to prevent the formation of cyanuric acid, originating from iso-cyanic acid, has been made by heating A.C. in the presence of ammonium benzoate, ammonium sulphate, ammonium chloride and hydrated aluminium ammonium sulphate. None of these materials are found to succeed in preventing the formation of cyanuric acid at 171.5°C.

PART II

AZODICARBONAMIDE AND ACTIVATORS

The decomposition temperature of A.C. is greatly influenced by different additives known as 'activators' or 'kickers'. In this part of the investigation, an attempt has been made to learn the role these additives play in the catalytic decomposition of A.C.

The kinetics of the decomposition of A.C. and zinc oxide mixtures have been followed isothermally by measuring the pressure of the gas evolved as a function of time. The decomposition reaction takes place in two steps, unlike that of A.C., which is one step reaction under the same conditions. A detailed

investigation has revealed that the first step is a surface reaction and follows first order reaction kinetics. The activation energy of the first step is lower than the second step.

The oxides of cadmium and lead behave similarly to that of zinc, whereas magnesium oxide has practically no catalytic effect. With cadmium oxide, the second step becomes explosive at a lower temperature than with any of the other oxides investigated, and this is attributed to the rate of heat production and local temperature rise during the first step being greater with this oxide than with any of the others.

The effects of the stearates of cadmium, lead, barium and zinc, zinc octoate, and urea on the decomposition of A.C. have been studied. All these materials react with A.C. in two steps, in a manner similar to the metal oxides.

C O N T E N T S

CHAPTER 1

INTRODUCTION

Azodicarbonamide has been known since the end of the last century, but its various industrial applications have been recognized only recently. It has several trade names dependent on the manufacturer. One of the most common is 'Genitron' A.C. It is extensively used in industry as a blowing agent for expanding plastics.

The practice of expanding plastics is over fifty years old. Plastics were originally expanded by means of gas, a method which was later replaced by adding inorganic salts which liberate gas on being heated, such as ammonium nitrite and metallic bicarbonates. All these inorganic compounds had certain limitations and so attention was turned to organic compounds which evolve gases on thermal decomposition. Reed[1] has mentioned the properties of an ideal blowing agent. Azodicarbonamide (A.C.), although not possessing all these properties, satisfies most of the requirements.

To begin with, it liberates mainly nitrogen which is an ideal gaseous product because it is inert, non-toxic and non-inflammable, and in addition has a low permeability in most resins. The greater the permeability, the more gas is required for equal foaming[2]. Carbon dioxide is not suitable because of its relatively high permeability in most plastic foams. Thus, nitrogen releasing organic compounds of which A.C. is a good example, dominate the chemical foaming agent field.

Secondly, in contrast to most organic blowing agents which ignite and decompose when touched with a flame, A.C. is self extinguishing and therefore presents little or no storage hazard. Finally, although insoluble in most common solvents, because of fine particle size, A.C. is readily dispersed in resin and plastic mixes. Thus A.C. possesses most of the properties desired of a good blowing agent.

The thermal decomposition of A.C. has been widely reported in the literature[3-5]. The work has mostly been carried out under the industrial conditions of blowing plastics and very little information is available regarding the mechanism and kinetics of the thermal decomposition of the pure material.

It has been found[1,6] that the composition of the gaseous products from pure A.C. varies with both temperature and the conditions under which the decomposition is carried out, but the reason for this behaviour is not known.

On decomposition, A.C. forms some white solid material along with the gases, a portion of which is in the form of a sublimate. In the previous investigations[1,6] some of the products were identified but the complexity of analysis did not allow the mechanism to be established.

The utility of A.C. is limited by its high decomposition temperature. It has a decomposition temperature of about 235-240°C, when in the pure state. It has been found in recent years that its decomposition temperature can be altered by different activators. This technique provides a wide range of working temperatures for A.C.

covering many of the temperatures at which different types of plastics need to be blown. The most important activators are fatty acid salts of Group II and Group IV elements. The metallic oxides have also been used frequently as activators. Some organic compounds such as urea, ethanolamine and glycols are also considered as good activators.

The technique of decreasing the decomposition temperature of A.C. by different additives is widely used but it has remained unknown why certain activators are more efficient than others. To date, there has been no systematic effort to discover the role which the 'kickers' play and the factors responsible for decreasing the decomposition temperature of A.C.

PART 1

AZODICARBONAMIDE ON ITS OWN

PART 1

AZODICARBONAMIDE ON ITS OWN

CHAPTER 2

LITERATURE SURVEY AND THEORY

2.1. INTRODUCTION

Azodicarbonamide (A.C.) is prepared by oxidising hydrazodicarbonamide (biurea). Biurea itself is prepared by reacting urea with hydrazine[1] according to the following equations:-

$$2\ H_2N.\ CO.\ NH_2 + N_2H_4 \longrightarrow H_2N.\ CO.\ NH.\ NH.\ CO.\ NH_2 + 2\ NH_3$$

$$\downarrow \text{ oxidation}$$

$$H_2N.\ CO.\ N{:}N.\ CO.\ NH_2$$

The oxidation of biurea to A.C. has been carried out with several oxidising agents under different conditions such as potassium dichromate[7], alkali metal chlorates[8] and chlorine[9].

The purification of crude A.C. by crystallization has proved very difficult due to two reasons. The first is that A.C. is insoluble in most of the common organic solvents and the second that there is a possibility of hydrolysis occurring particularly at high temperatures[10]. It is, however, slightly soluble in hot water. Williams and co-workers[7] and Bryden[11] have succeeded in crystallizing A.C. from hot water in small quantities, but it seems unlikely that this method could be used for a large scale purification. Swann[10] has purified A.C. by dissolving it in dimethylsulphoxide at room temperature and reprecipitating it with cold water. He has pointed out that this method eliminates

the possibilities of 'prereaction'.

Armand[12] has studied the physical properties of some azo-compounds from a structural point of view and has confirmed the following structure of A.C.

$$H_2N\ (C : O)\ N : N\ (C : O)\ NH_2$$

A wide range of decomposition temperatures of pure A.C. from 240°C to 180°C [1,13], has been reported in the literature. This variation in the decomposition temperature is most probably due to variations in the degree of purity, and in the procedure for determining the decomposition temperature. Lasman and Blackwood[14] have reported that in addition the particle size is an important factor in determining the decomposition temperature of A.C.

Williams and co-workers[7] have studied the heat of combustion of several azo-bis formamides by bomb-calorimetry and they have reported that the heat of combustion of A.C. is -254.83 ± 0.25 k cal mol^{-1}, and that of biurea is -273.87 ± 0.14 k cal mol^{-1}.

A.C. is a strong oxidising agent capable of liberating iodine from potassium iodide solution. Glicksman and Morehouse[15] have studied the electrochemical behaviour of A.C. and have suggested that the reduction of A.C. takes place according to the following equation:-

$$H_2N - \overset{O}{\overset{\|}{C}} - N = N - \overset{O}{\overset{\|}{C}} - NH_2 + 2\ H_2O + 2\ e^- \longrightarrow H_2N - \overset{O}{\overset{\|}{C}} - NH - NH - \overset{O}{\overset{\|}{C}} - NH_2 + 2\ OH^-$$

The oxidising property of A.C. has been studied by other workers[16] and their findings suggest that the reduction of A.C. depends on the reducing agent, the solvent and the temperature of the reaction.

The ease of reduction of A.C. has also been observed in industry. When A.C. is used in flour maturing, biurea, a reduction product of A.C., is recovered quantitatively[17]. The thermal decomposition product also contains a significant quantity of biurea[6]. In this particular case, since there is no reducing agent present, it is believed that amidic hydrogen must be involved in the reduction process.

2.2. THE MECHANISM OF THE DECOMPOSITION

The thermal decomposition of azo compounds has been widely reported in the literature [18,19]. Most of the investigators agree that the decomposition takes place by the evolution of nitrogen and the production of two free radicals and this is the first and rate determining step

$$A - N = N - B \longrightarrow A^{\cdot} + B^{\cdot} + N_2$$

Good evidence for the production of two free radicals has been found in most cases. A careful study of the decomposition of some azocompounds has shown that the rate of production of scavengeable radicals is usually less than the rate of decomposition[18,19]. The discrepancy is attributed to the coupling and disproportionation of geminate radical pairs, formed by the

primary decomposition process, before they have been separated by diffusion. This effect is known as the 'cage' effect since the time of encounter is prolonged, relative to the gas phase, through the geminate pair being surrounded by a 'cage' of solvent molecules.

It has been reported[20] that the thermal decomposition of A.C. in solution takes place in a manner similar to other azo-compounds, i.e., with the formation of two free radicals and a molecule of nitrogen.

The situation in the solid state is quite different from that in solution. In this case there is no solvent present and the evidence for the formation of free radicals is difficult to obtain. Thus these theories cannot be applied directly to solid state decomposition reactions.

The thermal decomposition of A.C. in the solid phase was first studied by Thiele[21]. He found that the material when heated at 180 - 200°C turned white with the evolution of ammonia gas. The white residue was identified as cyanuric acid. His investigation was brief so it was not possible to learn much about the mechanism of the decomposition.

According to U.S. Rubber and other sources [22,23] the gaseous product in the decomposition of A.C. has the following composition by weight:-

Nitrogen	62 %
Carbon monoxide	35 %
Ammonia and Carbonic acid	3 %

Owing to the lack of complete analytical data, it was not possible to suggest the mechanism of the decomposition of A.C.

A complete analysis of the gaseous and solid products was carried out by Reed[6,23]. He found that when A.C. was heated at 190°C in an open flask, the products and their proportions by weight were as follows:-

Urazole	39%
Biurea	2%
Cyanuric acid	26%
Cyamelide	1%
Gaseous products	32%

Reed[1] also reported that the proportions of the products varied considerably according to the conditions of the decomposition. For example, when the decomposition was carried out at the same temperature under liquid paraffin, the products were as follows:-

Urazole	27%
Biurea	34%
Cyanuric acid	5%
Gaseous products	34%

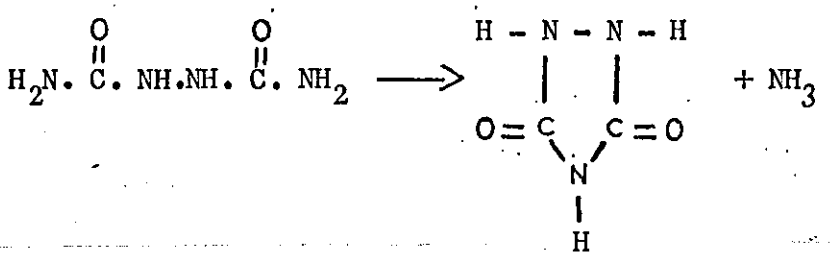
On the basis of these results, Reed[6] suggested that the primary decomposition of A.C. follows two routes:-

(1) $H_2N-\overset{O}{\overset{\|}{C}}-N{:}N-\overset{O}{\overset{\|}{C}}-NH_2 \longrightarrow N_2 + CO + \left[H_2N.\overset{O}{\overset{\|}{C}}.NH_2 \rightleftharpoons HNCO + NH_3\right]$

(2) $2\,H_2N-\overset{O}{\overset{\|}{C}}-N{:}N-\overset{O}{\overset{\|}{C}}-NH_2 \longrightarrow H_2N.\overset{O}{\overset{\|}{C}}.NH.NH.\overset{O}{\overset{\|}{C}}.NH_2 + 2\,HNCO$

The formation of biurea was explained by reaction (2).

Thiele and Stange[24] have studied the thermal decomposition of biurea. They reported that urazole was formed by heating biurea at 180°C or above, according to the following reaction:-

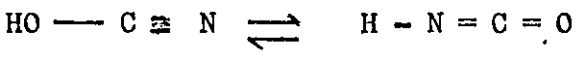


This reaction also takes place at lower temperature in the presence of hydrochloric acid gas. Reed's experimental conditions were suitable for this reaction to take place, so he suggested that urazole was formed in this manner. If this is the mechanism for the formation of urazole, it is difficult to explain the absence of about 6.6% of ammonia which is the amount expected to be produced during the formation of 39% urazole. Reed did not report the presence of ammonia gas in the gaseous components or postulate its consumption in secondary reactions.

Swann[10] found the gaseous products to consist solely of nitrogen and carbon monoxide, roughly in the ratio 3:1. He also found, however, that the ratio varied with the extent of decomposition and temperature. There was no evidence that either carbon dioxide or ammonia were present in the gas evolved.

Reed[6] suggested that the formation of cyanuric acid and cyamelide took place by polymerization of cyanic acid.

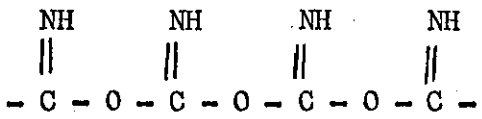
The polymerization of cyanic acid has been studied by Werner and Fearon[25]. They have postulated that the acid in solution is an equilibrium mixture of keto and enol forms.



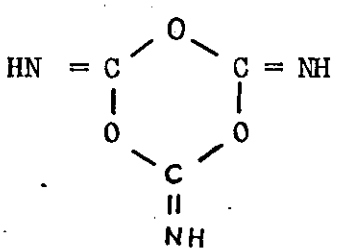
Enol Keto

A more recent study of the infra-red spectrum by Herzberg and Reid[26] has confirmed that cyanic acid in the vapour phase consists solely of H - N = C = O (isocyanic acid) molecules. The proportions of cyanuric acid and cyamelide formed are a function of the temperature with the formation of cyanuric acid being favoured at higher temperatures[25].

Cyamelide is a white inert material, almost insoluble in most of the common solvents. It is believed to have either of the following two structures:-



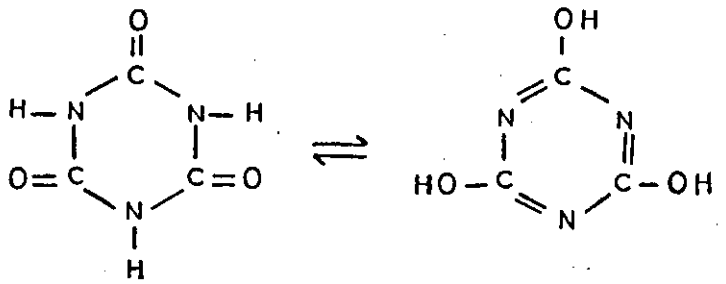
(I)



(II)

Some of the authors believe that cyamelide is more likely to have the structure (II)[27].

Cyanuric acid is a colourless, crystalline solid, reacting as a mono, di and tribasic acid. It has a cyclic structure and is believed to be tautomeric[27].



Keto Enol

Reed's suggestion that cyamelide and cyanuric acid are formed by the polymerization of cyanic acid (or isocyanic acid) seems very likely but there is no evidence that cyanic acid (or isocyanic acid) is a primary product of the decomposition of A.C.

Reed's[6] analysis of the decomposition products accounts for 100% of the material but the data have not been looked at quantitatively. Table 2.1 shows the percentages of elements present in the individual components of the product. The sum of the percentages of each element is expected to be equal to that of the percentage present in pure A.C.

TABLE 2.1

Percentage of elements in different products[6]

Component	Percentage by weight			
	Carbon	Hydrogen	Nitrogen	Oxygen
Urazole	9.27	1.16	16.22	12.35
Biurea	0.41	0.10	0.95	0.54
Cyanuric acid	7.26	0.60	8.47	9.67
Cyamelide	0.28	0.02	0.33	0.37
Nitrogen			20.80	
Carbon monoxide	4.32			5.76
Carbon dioxide	0.31			0.81
Total	21.85	1.88	46.77	29.50
Azodicarbonamide	20.68	3.44	48.28	27.60

If allowance is made for experimental error, the percentages of carbon, nitrogen and oxygen in the products may be considered as reasonable, but the percentage of hydrogen is significantly low. This suggests that there is an unaccounted component with a high hydrogen content, the other elements of which are difficult to assess from the present set of data.

Reed[1] elsewhere reported that nitrogen and ammonia were present in the gaseous products and oxamide was an additional solid product. The production of oxamide could be accounted for by the following reactions:-

$$H_2N.\,CO.\,N{:}N.\,CO.\,NH_2 \longrightarrow 2\,H_2N.\,CO. + N_2$$

$$2\,H_2N.\,CO. \longrightarrow H_2N.\,CO.\,CO.\,NH_2$$

Oxamide

The formation of ammonia may be due to the decomposition of biurea as described earlier. But the quantity of ammonia produced would be expected to be far more than the value obtained. Ammonia reacts easily with cyanic acid (or isocyanic acid) to form urea and ammonium cyanate[25]. It is possible that a portion of the ammonia might have been used up in this process. This argument suffers from the fact that no urea or ammonium cyanate have been reported among the solid products.

2.3. THE KINETICS OF THE DECOMPOSITION

a) General Comment

Kinetic studies of chemical reactions in the homogeneous phase have shown that the reaction rate is directly proportional to the concentration of the reactant molecules raised to a power known as the 'reaction order'. If the reaction rate $-\frac{dc}{dt}$ is directly proportional to the reactant concentration C, then the reaction is said to be first order. In a solid state reaction the time behaviour is not controlled by molecularity or chemistry alone, but is controlled also by the physical properties and geometry of the system[28].

There are difficulties in defining the rate constants for the reactions of solids[29]. Some of the complications involved when the experimental rate constants of solid state reactions are under consideration, have been summarised by Toplin[30]. He has pointed out four complications normally observed in a solid state reaction. The first three are due to the combination of simple rate constants in which case the observed rate constant may or may not obey the Arrhenius equation exactly. The fourth is due to a temperature-dependent factor which may be attributed to some property of a solid phase in the system, e.g., the permeability of a coherent layer of the product.

There are two important factors responsible for the reactivity of a solid. Firstly, the reactivity of a solid substance is often dependent on the history of the particular sample. This contrasts with the behaviour of liquids and gases since it is only solid particles which retain the scars of handling or preparation which in turn may influence their subse-

-quent reactivity. It is believed that the chemical changes of solids may occur most readily in the most highly deformed or defective regions of the lattice. Thus, the reactivity depends on the total concentration of such sites. Secondly, the rate at which a chemical process involving a solid occurs is often controlled by the surface area of that solid, since the reactions are frequently initiated at surfaces and these are the regions of contact between a pair of reactants. The reaction kinetics of a process may thus be influenced by the average crystallite size and the particle size distribution about this value.

There are several different types of decomposition reaction reported in the literature but much attention has been devoted to kinetic studies of the reactions of following general type:-

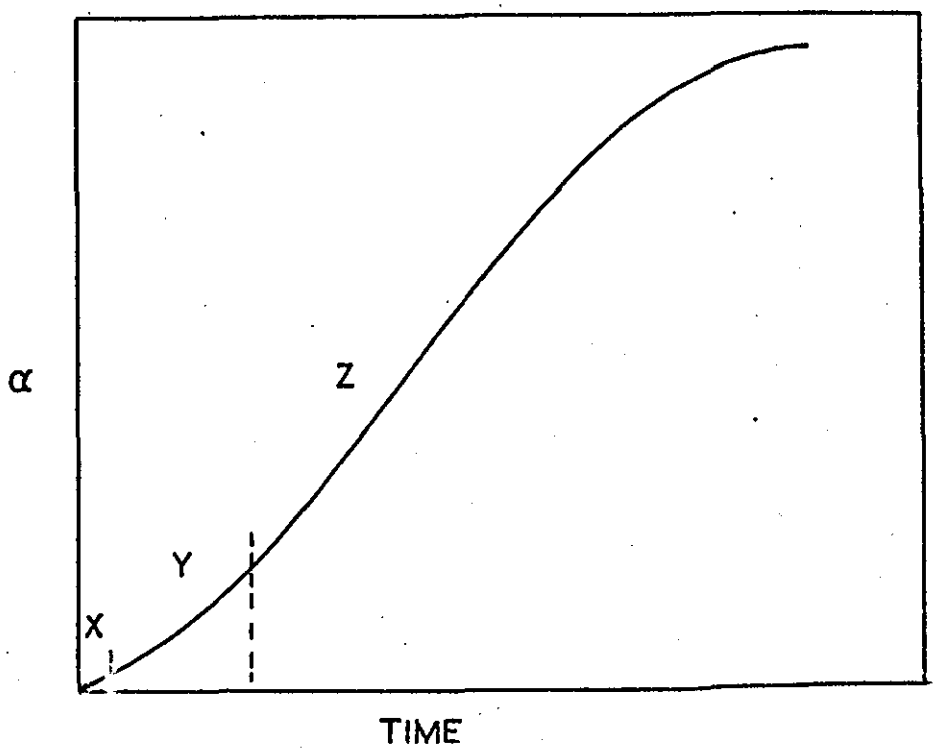
$$A\ (solid) \longrightarrow B\ (solid) + C\ (gas)$$

The extent of the reaction, α, is determined from the pressure or volume of the gas evolved or the reactant weight loss.

The α-time relationship for a typical solid phase thermal decomposition reaction is shown in FIGURE 2.1.

Section X is termed the induction period and is characterised by a slow formation of the product, so slow in some cases as to be scarcely measurable. For many solids, there may be a significant time interval between the time that the reactant reached reaction temperature and the detection of significant product formation. During this interval 'germ' nuclei of the solid product are being established at a limited number of points on the reactant surfaces.

FIGURE 2.1



It is usually not possible to determine the temperature coefficient of the product formation during the induction period, but it is sometimes possible to assign a duration to the induction period and thus obtain an activation energy. However, this activation energy has very little meaning because of the error involved in an accurate analysis of Section Y.

Once nuclei have been established, there is a constant rate of advance of the reaction interface through the solid for a reaction at constant temperature. The growth of nuclei results in an increase in the area of product nuclei-reactant surface contact. Thus, there is an increase in the rate of product formation and the reaction is acceleratory (Section Y).

After a continued growth of nuclei a point is reached where reaction interfaces from different nuclei begin to overlap and at these junctions the reaction interface is eliminated. The overlap reduces the rate of interface expansion (and thus of product formed) and the acceleration is decreased. Subsequently, this factor progressively increases in importance so that thereafter the reaction becomes deceleratory (Section Z). When the point has been reached where those regions of the solid which comprised the original surfaces of the reactant have been decomposed and the solid products incorporated in growing nuclei, the existing reaction interfaces may still continue growth towards the centre, unreacted, regions of the crystal. During this stage there is a progressive decrease in the interfacial area and the reaction rate steadily slows up until complete decomposition of the reactant has occurred.

There are several mathematical equations available in the literature for the treatment of the kinetic data of thermal decomposition reactions of solids. Sharp [31] has summarised nine commonly used equations corresponding to different types of solid state reactions. He has also published values of the reduced time $t/t_{0.5}$ (where $t_{0.5}$ = time at $\alpha = 0.5$) and of the function $F(\alpha)$, which depends on the mechanism controlling the reaction, and on the size and shape of the reacting particles, as a function of α for each equation. It will be noticed later that certain limitations do not permit the mechanism of the thermal decomposition of A.C. to be studied by these methods so these theories are not discussed in detail.

b) The Decomposition of Azodicarbonamide

An attempt was made by Swann[10] to study the kinetics of the thermal decomposition of A.C. by thermogravimetric analysis and by measurement of the gas evolved.

(i) Thermogravimetric Method

The isothermal decomposition curve obtained by this method exhibited three sections. Initially, a slowly increasing rate was observed which was followed by a constant rate of decomposition producing a long linear portion in the thermogram. The measurable reaction ended quite sharply but the weight continued to decrease slowly and a constant value was never obtained.

For the linear portion of the curve, where the rate of decomposition was constant, the rate of the reaction was independent of the extent of decomposition, suggesting, therefore, zero order kinetics.

The rate constants at different temperatures were obtained from the slope of the linear portion of the curve and the activation energy was determined by an Arrhenius plot. It was found to be 54.4 kcal mol^{-1}.

It was observed that the sample size had no effect on the activation energy or on the order of the reaction.

(ii) Gas Analysis Method

An accurate determination of the gaseous volume revealed some interesting features of the reaction during its early stages. The rate of reaction initially increased rapidly. This was followed by a portion in which the rate was considerably depressed. After a short time, the rate gradually increased to its maximum value. This phenomenon was not possible to observe during the runs at high temperatures.

The isothermal gas evolution curves were very similar in shape to those obtained from the thermogravimetric analysis. The feature observed during the early stages of decomposition in an accurate gaseous volume analysis was not noticed in the general volume-time plot, suggesting that the initial decomposition was extremely small in comparison with the overall reaction. The final volume of the gas did not reach a constant value even after a long time. The activation energy was calculated in the same way as in the case of the thermogravimetric analysis method, and it was found to be 50.7 kcal mol^{-1}. The values of the activation energy obtained by the two methods were in good agreement.

Owing to the difficulty in obtaining the value of V_∞ (the volume at the end of the decomposition reaction), an accurate determination of the extent of the reaction, α, was not possible. Swann[10] calculated α by considering an approximate value of V_∞, when the increase in volume was found to be very small, and made an attempt to use some known equations for solid state decomposition reactions to study the mechanism.

A generalised kinetic equation based on the nucleation process was derived by Avrami[32] and Erofeev[33]. They made the following assumptions in deriving the equation associated with their names:-

i) That the rate is proportional to the area of the reactant/product interface.

ii) That the nucleation is dependent on defects of some kind and that the concentration of defects may be constant or may increase with time.

Avrami - Erofe'ev equation may be written in the form

$$\alpha = 1 - e^{-kt^n} \qquad (1)$$

Where α represents the fraction of the decomposition at time t and k is a constant. The value of n indicates the sum of two factors β and λ, where β represents the nucleation stage and λ the dimension of growth of the nuclei. For example, the thermal decomposition of large single crystals of ammonium perchlorate follows Avrami - Erofe'ev equation with $n = 4$ during the early stages of decomposition ($\alpha < 0.2$)[34]. Thus, the reaction may be regarded as single-stage nucleation ($\beta = 1$) with three dimensional growth ($\lambda = 3$). After completion of the initial reaction when the nuclei overlap ($0.2 < \alpha < 0.9$) the reaction follows the equation with $n = 3$. It is believed that complete decomposition of the original crystal surface precludes further nucleation (thus $\beta = 0$) and the solid is decomposed by the three-dimensional growth of existing nuclei.

Taking logarithms of the expression (1)

$$-\log_{10}(1-\alpha) = \frac{k\,t^n}{2.303}$$

and again

$$\log_{10}\left[-\log_{10}(1-\alpha)\right] = \log_{10}\frac{k}{2.303} + n\log_{10}t$$

Thus, a plot of $\log_{10}\left[-\log_{10}(1-\alpha)\right]$ versus $\log_{10}t$ should be linear with its slope equal to n.

Swann[10] used the data obtained from the decomposition of A.C. and found that a plot of $\log_{10}\left[-\log_{10}(1-\alpha)\right]$ versus $\log_{10}t$ gave a good straight line. The value of n obtained from the slope was very close to 2.

Table 2.2 shows the variation of n with temperature obtained by this method.

TABLE 2.2

Variation of 'n' in Avrami - Erofe'ev equation with temperature [10]

Temperature °C	n
171.0	2.1
176.0	1.9
176.5	1.6
180.0	2.2
183.0	2.0

Although there is an appreciable divergence in the values of 'n', there is no sign that n is temperature dependent. It has a value 2, which indicates that the nuclei are flat.

The crystal structure of A.C. has been studied by Bryden[11].

He has found that the crystals obtained by crystallizing A.C. with water are monoclinic with elongation in the direction of the a axis. Each molecule of A.C. is hydrogen bonded to four surrounding molecules in the same plane, thus forming sheets which are nearly parallel to the (101) plane. The forces holding these sheets together are of the Van der Waal's type. Because the molecules form sheets, the two dimensional growth of nuclei is more than likely and fits in with the findings of the kinetic studies.

CHAPTER 3

EXPERIMENTAL

3.1. THE PURIFICATION OF AZODICARBONAMIDE

The purification of azodicarbonamide (A.C.) by crystallization was found to be difficult because of the low solubility of A.C. in common organic solvents. Mixtures of dimethylsulphoxide with organic solvents such as acetone, methanol and tetrahydrofuran in different proportions were first tried but no crystalline material was obtained. A mixture of dioxane and water in different proportions produced the same result. Crystalline material was obtained in small quantity from a single solvent system, such as hot water or pyridine, after long standing, but it was found impossible to use these solvents for large scale purification owing to the very limited extent to which A.C. dissolved in them.

The material used in the present investigation was purified with the method used by Swann[10].

Procedure:-

The commercial material, Genitron A.C., was dissolved in dimethylsulphoxide at room temperature. The saturated solution was filtered and distilled water was added slowly to the stirred solution at room temperature until fine crystals of A.C. were obtained. The crystals were filtered at the pump, washed with distilled water, then with alcohol and finally with ether. The recrystallization was carried out three times using this method. The material was finally dried in vacuo and stored in a dark coloured bottle.

3.2. THE DECOMPOSITION OF AZODICARBONAMIDE

During preliminary investigation and for the analysis of solid products the decomposition was carried out in an apparatus similar to the one shown in FIGURE 3.1. The apparatus consisted of two 50 ml boiling tubes connected together with a ground glass quick-fit joint. The top tube had a stopcock near the sealed end, which was used for evacuating the apparatus before decomposition was carried out.

In order to permit the analysis of both gaseous and solid products the decomposition tube was slightly modified (see FIGURE 3.1). The lower tube was extended making it now 11 inches in length. During the decomposition, the joint between the two tubes was sealed with picein wax and a spiral water condenser was fitted round the upper part of the lower tube. This was designed to condense the sublimate at this point and to prevent it from undergoing further decomposition at the time of warming the picein wax to disconnect the two tubes.

To allow a series of decompositions to be carried out at one time, a large (30 cm x 28 cm working space) oil bath was used. Before carrying out the decomposition, the temperature variation at different positions and depths of the bath was checked. The maximum variation was found to be $\pm$ 0.2°C.

Procedure

A known weight of A.C. was weighed in a 50 ml quick-fit boiling tube and covered with a tube of the same size as shown in FIGURE 3.1. The tube was evacuated to 1 mm mercury pressure (or to less than 0.1 mm where stated) and immersed in the thermostatically controlled oil bath.

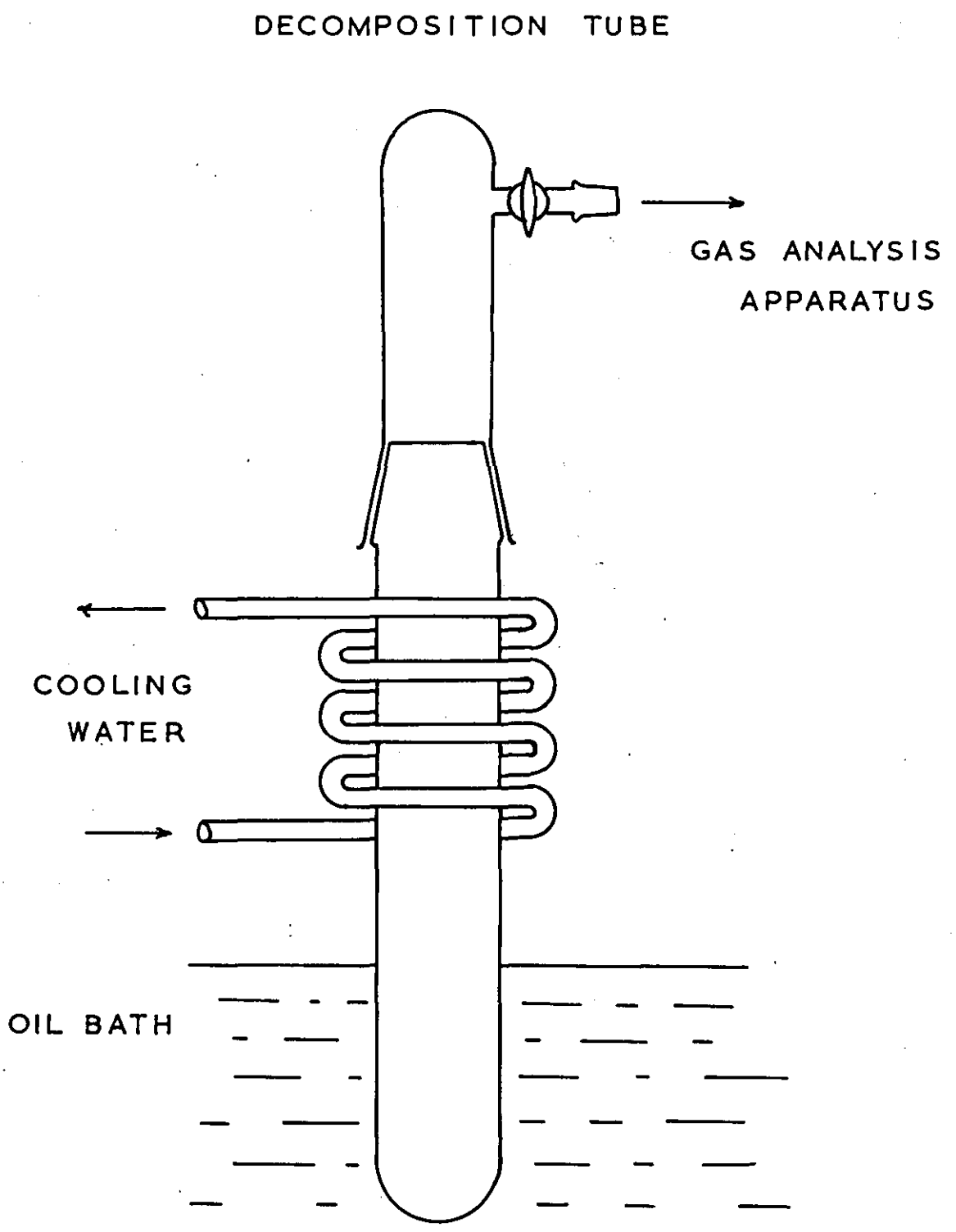

DECOMPOSITION TUBE
GAS ANALYSIS
APPARATUS
COOLING
WATER
OIL BATH

FIGURE 3.1

A constant sample weight of 232 mg was used when only the solid products were to be analysed, with the exception of the wet sample when the weight of A.C. used was 116 mg. It was no longer possible to keep the sample size exactly constant when the modified apparatus with a longer tube was in use. In this case, the weight of the sample varied within $\pm$ 5 mg of 232 mg.

3.3. ANALYSIS OF THE SOLID PRODUCTS

a) QUALITATIVE EXAMINATION

The decomposition products in the solid phase were obtained in the form of a sublimate and a residue. Both were white in colour with practically no smell. Previous workers[1,6] reported that the composition of the solid products varied with the experimental conditions so it was thought essential to find out the number of components formed when A.C. decomposed under the present experimental conditions. Chromatographic techniques are very common ways of obtaining this type of information and the gas liquid chromatographic (G.L.C.) technique is particularly advantageous because it can be used both for qualitative and quantitative analysis. But owing to the non-volatile nature of the products this method was considered unsuitable. The possibility of using G.L.C. after preparing volatile derivatives of the products was ruled out because of the lack of information regarding the chemical nature of the components. The products were found to be soluble in warm water and, although the solubility was not very great, only a trace of the white material remained insoluble. Thus, it was decided to use thin-layer chromatography (T.L.C.) to obtain the information regarding the components in the water soluble portion of the solid products.

After obtaining the information from T.L.C., an attempt was made to confirm the identities of the components by infra-red spectroscopy and by mass spectrometry.

THIN-LAYER CHROMATOGRAPHY

A preliminary investigation was carried out with Silicagel GF_{254} (Merck) as a stationary phase. After discovering a suitable solvent system good resolution of the components was obtained and therefore the same adsorbent was used throughout the investigation.

It was found almost impossible to detect all the spots on the T.L.C. plate with a single reagent, so different reagents were used for developing each component.

Procedure

i) Preparation of the Thin-layer Plates

The thin-layer plates of thickness 0.25 mm were prepared by standard procedure[35], using Silicagel GF_{254} (Merck) as adsorbent in an aqueous suspension. The plates were activated at 110°C for one hour and preserved in a cabinet over dry silicagel.

ii) The Solvent System

The solvent used for the separation was a mixture of dioxane, benzene and acetic acid in the volume ratio 80:20:2. Urea, urazole and cyanuric acid all moved in this solvent, but biurea did not.

iii) The Detection of the Components

Urazole:- The plate on drying was exposed to iodine vapour for two minutes. Urazole appeared as a yellow spot.

A more specific reagent for urazole was also available[36]. This reagent was prepared by adding 2 ml of 5% aqueous sodium nitroprusside solution to 1 ml of 10% aqueous sodium hydroxide solution and 5 ml of 3% perhydrol (hydrogen peroxide) solution, and finally diluting to 15 ml with water. The reagent was freshly prepared each time before use. It was fairly sensitive, with urazole appearing as a blue spot.

Cyanuric acid:- The plate used to detect urazole by exposure to iodine vapour, after marking the urazole spot with a pencil, was left in an oven at 100°C for five minutes to remove the absorbed iodine.

The plate was then sprayed with the following reagents:-

Spray solution I:- 0.25 g of mercuric acetate was dissolved in 100 ml of 96% (by volume) ethanol and a few drops of acetic acid added.

Spray solution II:- 0.05 g of diphenyl carbazide was dissolved in 100 ml of 96% (by volume) ethanol.

Solution I was sprayed first. Then solution II was sprayed until the plate became uniformly faint violet. The plate was heated in an oven at 120°C for a few minutes. The cyanuric acid appeared as a light violet spot.

Biurea could also be detected by the same procedure and reagents

but the sensitivity was poor.

Urea:- 2 g of p-dimethylaminobenzaldehyde was dissolved in 50 ml of 96% (by volume) ethanol, and 10 ml of concentrated hydrochloric acid added. The solution was diluted to 100 ml with 96% ethanol. On spraying with this reagent, urea appeared as a yellow spot at room temperature.

Biuret could also be developed with this reagent by heating at 110°C for 2 - 3 minutes.

Biurea:- After removal of the solvents from the plate, the latter was sprayed uniformly with concentrated nitric acid and then heated in an oven at 120°C for 15 minutes. Biurea appeared as a yellow spot which was more distinct under ultraviolet irradiation.

iv) Application of the Products on to the Plates

The solid products in the decomposition tube were dissolved in a minimum quantity of warm water and spotted on to the plates. Pure samples of possible products were spotted on to the same plate for reference and the R_f values (i.e., the distance travelled by each spot with respect to the solvent front) compared. To permit the detection of all the components by spraying with different reagents, three plates were run for each set of products.

INFRA-RED SPECTROSCOPY

From the thin-layer chromatographic technique it was found that the major components in the water soluble portion of the sublimate were cyanuric acid and urea, and those in the residue were biurea, urazole and cyanuric acid. Infra-red spectroscopy was used to obtain further evidence regarding the presence of these components in the solid products.

An attempt was made to separate individual components of the sublimate but only urea was separated successfully. This was carried out by extracting the mixture with hot acetone. Urea being slightly soluble in acetone and cyanuric acid almost insoluble, the extract on concentration gave urea in a fairly pure state. It was still further purified by recrystallization. The infra-red spectrum of the isolated sample was compared with the spectrum of an authentic sample of urea.

The acetone insoluble portion of the sublimate contained cyanuric acid, traces of urea and most probably some cyamelide. The spectrum of this mixture was taken and an attempt was made to identify all the major absorption peaks.

The residue which contained urazole, biurea and cyanuric acid was completely soluble in hot water. An attempt to isolate urazole in the pure state by fractional crystallization with water was unsuccessful. Thus, it was decided to compare the spectrum of the residue with a synthetic mixture of authentic samples of cyanuric acid, urazole and biurea.

All the spectra were recorded on an Unicam SP.200 G, Infra-red Spectrophotometer, using the KBr disc technique[37].

MASS SPECTROMETRY

This technique was used to obtain further information regarding the components of the solid products. As mentioned earlier, it was not possible to isolate the components in a pure state, except in the case of urea. Mass spectra of mixtures were therefore obtained, both in the case of the sublimate and of the residue. Most of the components were identified by the molecular ion peaks and by comparison with the mass spectra of authentic samples.

b) QUANTITATIVE DETERMINATION OF THE COMPONENTS

The quantitative analysis of the individual components of the water soluble solid products was carried out by ultraviolet and visible spectroscopy. The weight of the insoluble residue was also determined. It was found extremely difficult to separate the sublimate from the residue so all the soluble solid products were dissolved together and the analysis was carried out on this solution.

i) The Analysis of Urazole and Cyanuric Acid

The method employed was very similar to that used by Finkelshtein, Boitsov and Mushkin[38] and Boitsov and Finkelshtein[39] in the determination of biuret, cyanuric acid, melamine, ammeline and ammelide. The authors[38, 39] suggest that by a suitable choice of the pH of the medium, it is possible to select wave lengths at which a good difference in the molar absorption coefficients of the components exists. Thus, by measuring the absorbances at different wave lengths and solving the simultaneous equations, the amounts of the different components can be determined.

The absorption bands of urazole and cyanuric acid were almost superimposable in aqueous solutions. It was found that in 0.1 (N)

borax solution (pH 9.25) the absorption of cyanuric acid at 216.5 nm was appreciably higher than that of urazole, while in 0.1 (N) hydrochloric acid (pH 1) the absorption of urazole at 220 nm was higher than that of cyanuric acid. TABLE 3.1 shows the molar absorption coefficients of the water soluble solid products of A.C. in 0.1 (N) borax and 0.1 (N) hydrochloric acid.

TABLE 3.1

Molar absorption coefficients of the solid products of A.C.

Products	Medium	
	Hydrochloric acid 0.1 (N)	Borax 0.1 (N)
	Wave length 220 nm	Wave length 216.5 nm
Cyanuric acid	38.1	12350
Urazole	1332.5	4150
Biurea	<8	<2
Urea	<5	<1

Although there was no absorption maximum in either case in the wave length region 210–250 nm, it was possible to determine the two components in a mixture by measuring the absorptions at the two wave lengths and at the two pHs mentioned, and solving two simultaneous equations.

The compositions of three synthetic mixtures of urazole and cyanuric acid were determined to test the validity of the method. TABLE 3.2 shows the expected and experimentally determined values of the two components.

TABLE 3.2

Expected and determined values of urazole and cyanuric acid in three synthetic mixtures

Mixture No.	Urazole		Cyanuric acid	
	Expected	Found	Expected	Found
1	1.000×10^{-4} M	0.982×10^{-4} M	10.00×10^{-4} M	10.00×10^{-4} M
2	5.000×10^{-4} M	5.009×10^{-4} M	5.000×10^{-4} M	4.985×10^{-4} M
3	5.000×10^{-4} M	5.028×10^{-4} M	0.500×10^{-4} M	0.598×10^{-4} M

It is observed that the method results in a significant error in the determination of cyanuric acid when a large excess (~ ten times) of urazole is present. But this situation never occurred in the present investigation.

ii) Determination of Urea

Urea was determined by a colorimetric method used by Brown[40]. With p-dimethylaminobenzaldehyde in the presence of hydrochloric acid urea forms a greenish yellow complex which has a maximum absorption at 420 nm. Cline and Fink[41] have studied the mechanism of this reaction and have found that the complex is very stable at room temperature. They have suggested that most of the factors which slightly influence the intensity of the colour can be eliminated by keeping the reagent concentrations in large excess of the amounts necessary for the formation of the complex.

It was found that urazole in quantity interfered very slightly in this determination but the molar absorption coefficient of urazole is very low and the quantity in which it is present in the product mixture from A.C. decomposition is such as to make the interference negligible.

iii) Determination of Biurea

The colorimetric method used for the determination of biurea was similar to that used by Ellis and Formaini[42] for the determination of biuret. Biurea, with the Fehling's solution recommended in the latter method, forms a complex which has a maximum absorption at 410 nm. The biuret complex has a maximum absorption at 555 nm and does not absorb at 410 nm.

Urazole, however, also forms a complex whose absorption occurs at a similar wavelength to that of the biurea complex and, although considerably weaker, is nevertheless significant. Urazole was therefore determined first by the method described earlier and a correction applied to allow for its presence in the determination of the biurea.

Procedure for the Quantitative Analysis of the Solid Products of A.C.

A known weight of A.C. was decomposed in an evacuated decomposition tube as described in Section 3.2. The solid products in the decomposition tube were extracted with warm water (below 50°C). The extract, after being cooled to room temperature, was filtered through a sintered glass crucible (G.4) and washed several times with distilled water. The combined filtrate and washings were made up to 250 ml. The analyses of urazole, cyanuric acid and biurea were carried out as described earlier. For the urea analysis, the products were extracted with a minimum quantity of water. Since urea is highly soluble in water, complete recovery of urea was not difficult. After filtering and washing, the total volume was made up to 50 ml in this case.

The amount of insoluble matter was determined only in those cases when the A.C. was decomposed completely. The determination was carried

out by measuring the difference in weight of the sintered glass crucible before and after filtration. The crucible was heated in an oven at 110°C and cooled in a silica-gel desiccator. The exercise was repeated to a constant weight each time.

3.4. ANALYSIS OF THE GASEOUS PRODUCTS

a) IDENTIFICATION OF THE COMPONENTS

The information available from the published papers[1,6] suggested that the major gaseous components in the decomposition products of A.C. were nitrogen, carbon monoxide, carbon dioxide and ammonia. The question remained why ammonia and carbon dioxide were formed under certain conditions whereas nitrogen and carbon monoxide were the sole products under other conditions. Swann[10], for example, never found any gaseous product other than nitrogen and carbon monoxide when he analysed the products of A.C. on decomposition over the temperature range 166.5 - 183.0°C. Since there has never been any doubt of nitrogen being a major component under all conditions, it was decided to obtain more information regarding the gaseous products other than nitrogen, and for this purpose an infra-red spectroscopic technique was used.

The infra-red spectra of the gaseous products of A.C. obtained at different temperatures were recorded and compared with the spectra of authentic samples of carbon monoxide, carbon dioxide and ammonia recorded under the same conditions.

It was discovered that the gaseous products of A.C. at 171.5°C had a condensable component which was neither ammonia nor carbon dioxide.

This component was identified as iso-cyanic acid vapour by comparing the spectrum with the spectrum of a prepared sample of iso-cyanic acid, recorded under the same conditions, and with published data[26].

The reactions of iso-cyanic acid with moisture and ammonia were studied in the vapour phase with this technique to obtain some information regarding the decomposition mechanism of A.C.

Procedure

Infra-red spectra of the gaseous products of A.C.

A.C. was decomposed in an evacuated (less than 0.1 mm of Hg) tube as described earlier. The decomposition tube containing the gaseous products was immersed in liquid nitrogen and then rewarmed to room temperature. The gaseous products were allowed to expand directly into an evacuated infra-red gas cell with sodium chloride windows and a 10 cm path length. The spectrum was recorded against air as reference on an Unicam SP.200 G Infra-red Spectrophotometer capable of recording over the range 650 - 4000 cm^{-1}.

Infra-red spectrum of iso-cyanic acid

Iso-cyanic acid was prepared by thermal depolymerization of cyanuric acid[43]. A decomposition tube containing about one gram of pure cyanuric acid was evacuated and then filled with a small pressure ($\sim$ 10 mm Hg) of dry nitrogen gas. The cyanuric acid was heated with a bunsen burner, the top portion of the tube being cooled with a spiral condenser. The infra-red spectrum of the vapour produced was recorded as described earlier.

A similar experiment was carried out by using urea in place of cyanuric acid and the spectrum was recorded.

Reaction of iso-cyanic acid with ammonia and moisture

A 250 ml flask was filled with ammonia gas and opened gently to an infra-red cell containing a low pressure of iso-cyanic acid vapour. The spectrum of the resultant vapour was recorded.

A 3 litre flask containing moist air at atmospheric pressure was opened to a decomposition tube containing iso-cyanic acid. After mixing had taken place the vapour was expanded into an evacuated infra-red cell and the spectrum was recorded.

b) QUANTITATIVE DETERMINATION OF THE GASEOUS PRODUCTS

Infra-red analysis showed that the gaseous products of A.C. at 171.5°C consisted of iso-cyanic acid and carbon monoxide in addition to nitrogen. It was also found that ammonia was one of the components in place of iso-cyanic acid when A.C. decomposed at 191.5°C. Thus a method capable of analysing all the four components, namely, nitrogen, carbon monoxide, ammonia and iso-cyanic acid was needed.

Difficulties were encountered in the analysis due to the presence of iso-cyanic acid vapour. This material has a melting point of -86.8°C and a boiling point of +23.5°C. It polymerises slowly in the vapour-phase forming both cyamelide and cyanuric acid. The polymerization appears to be a surface reaction, being very slow in a clean surface but being catalysed by polymer deposited on the vessel surface[44]. The reaction is also promoted by metal surfaces[26]. Smith and Jonassen[45] found that at low pressures at 30°C the polymerization could be followed

over a period of seven days. To remove the iso-cyanic acid from the gaseous mixture attempts were made to promote the polymerization by altering the temperature and exposing the vapour to metal surfaces. But it was found almost impossible to remove the traces of iso-cyanic acid vapour from the mixture by this method.

The method used in this investigation for the separation and determination of different gaseous components was based on their volatilities and chemical reactivities. The condensable gas cyanuric acid (or ammonia) was separated from the rest of the mixture by freezing the mixture at liquid nitrogen temperature. The volume of the non-condensable gas, i.e., nitrogen and carbon monoxide, was measured. The carbon monoxide was oxidised to carbon dioxide by passing over hot cupric oxide and the carbon dioxide formed was separated by freezing. The volume of nitrogen was measured and that of carbon monoxide calculated by difference. The carbon monoxide volume was further checked by measuring the volume of carbon dioxide formed from it.

The condensable portion of the mixture, iso-cyanic acid, was determined by titrating with dry ammonia gas in the vapour phase. When ammonia was in the condensable portion, the volume was measured directly after equilibrating at room temperature.

The Apparatus

A special apparatus was designed and built to carry out the quantitative determinations of the gases. This is shown diagrammatically in FIGURE 3.2.

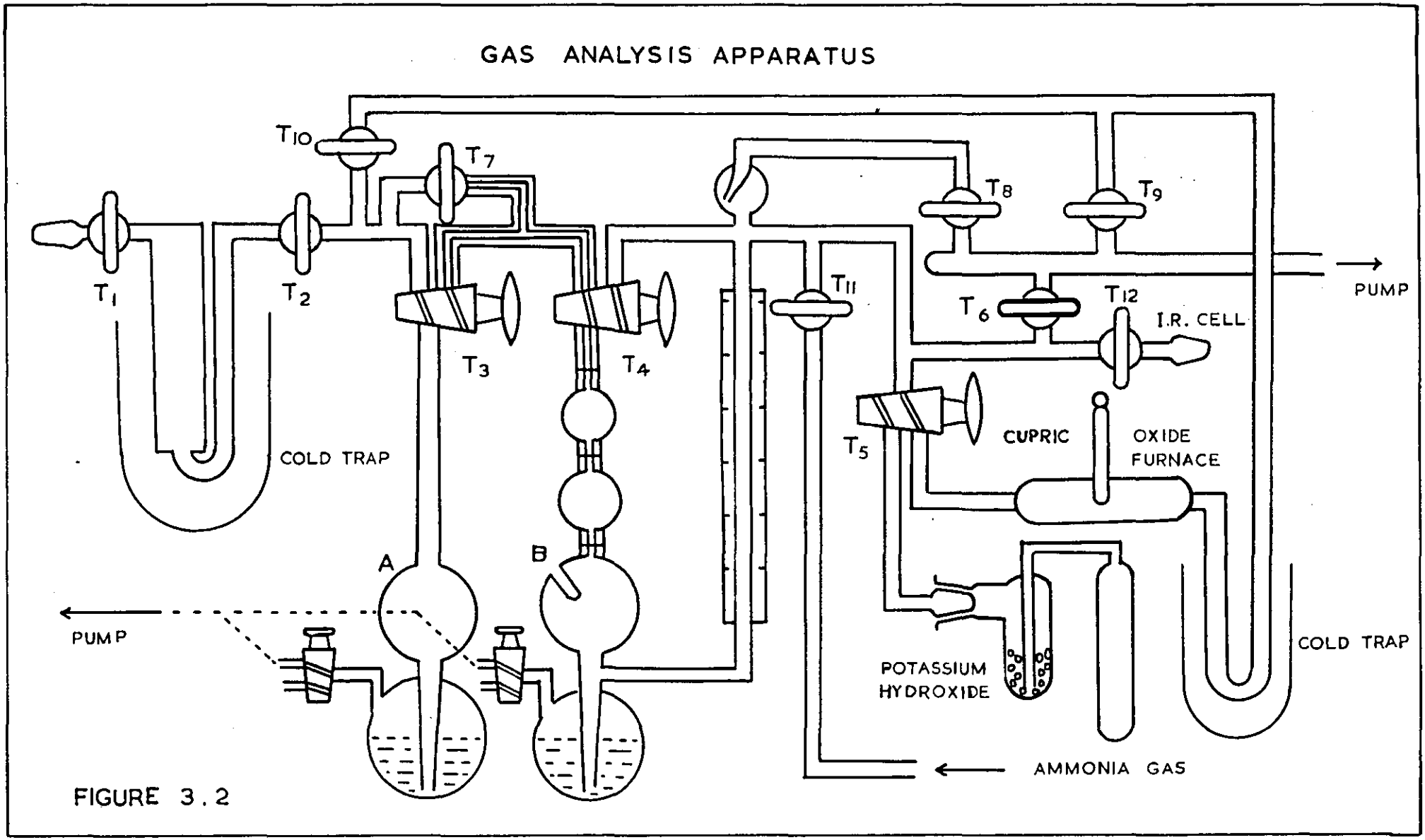

GAS ANALYSIS APPARATUS
T10
T7
T8
T9
T1
T2
T11
T6
T12
PUMP
I.R. CELL
T3
T4
T5
CUPRIC
OXIDE
FURNACE
COLD TRAP
A
B
PUMP
POTASSIUM
HYDROXIDE
COLD TRAP
AMMONIA GAS

FIGURE 3.2

It consists of two sets of glass bulbs, A and B, connected together by thick-walled capillary tubing. The bottom bulb of each set is connected to a two-way tap, one end of which is attached to a vacuum pump. The top two bulbs of set B have predetermined volumes and the third has a built-in test-tube inside it. The other end of the two-way tap at the top of set B is connected to the potassium hydroxide tube and the cupric oxide furnace. In addition, there is provision for introducing ammonia gas and attaching an infra-red gas cell between the cupric oxide furnace and B.

A preliminary investigation into the efficiency of the cupric oxide in oxidising carbon monoxide to carbon dioxide was carried out at a temperature 285-290°C with a glass tube 10 cm in length and 1 cm in diameter filled with cupric oxide (wire-form, Fisons Scientific Apparatus Ltd.). Owing to there being a small amount of carbon monoxide in the presence of a large amount of nitrogen, a complete oxidation of carbon monoxide into carbon dioxide became a tedious process. To overcome this difficulty a longer tube ($\sim$ 40 cm) in the shape of a spiral was used. This modified form was found to be very efficient.

The outlet from the cupric oxide tube and the reaction vessel containing the gaseous mixture to be analysed are connected to the other side of A. Both these tubes have cold traps to freeze out the condensable gases.

The gaseous volume is determined in each case by measuring the pressure of the gas at constant volume with the help of the set of bulbs B, behind which is attached a scale.

Procedure

Before carrying out the analysis, the apparatus was evacuated by

opening the taps T_2 to T_{10} to the vacuum line and maintaining the cupric oxide furnace at 285-90°C overnight. The lower portion of the decomposition tube described earlier and containing the gaseous products was cooled with liquid nitrogen and then connected to the vacuum frame with a ground glass quick-fit joint. Apiezon-N grease was used at all the joints and taps throughout the apparatus. Tap T_1 was opened and the portion of the tube between the frame and the decomposition tube was evacuated. The U-tube was cooled with liquid nitrogen and the taps T_2 - T_{10} were closed. The tap in the decomposition tube was slowly opened and the gases were allowed to pass through the cold trap. The non-condensable gases were transferred into A by lowering the mercury level and opening the taps T_2 and T_3. The gases in A were then transferred into B by raising the mercury level in A and opening the taps T_4 and T_3 towards B. This operation was repeated until a complete transfer of non-condensable gases from the decomposition tube to B was achieved. The volume of the gas was measured by raising the mercury level in B to one of the three marks. The highest mark, which still permitted the pressure to be measured on the scale, was the one normally used.

The gaseous mixture in B was then passed over hot cupric oxide by raising the mercury level in B. The carbon dioxide formed was condensed in the cold trap. The uncondensed gas (nitrogen) was transferred back into B with the help of A and the volume was measured. The operation was repeated until a constant pressure of nitrogen was observed which indicated complete oxidation of carbon monoxide to carbon dioxide. The volume of carbon dioxide formed was measured separately by transferring it into B. The transfer of carbon dioxide was facilitated by filling the built-in test-tube in B with liquid nitrogen. The carbon dioxide was finally transferred into the infra-red cell through T_{12} and the

spectrum was recorded to confirm its identity.

The condensable fraction of the gaseous products of A.C. obtained at 171.5°C was iso-cyanic acid. The titration of this vapour was carried out in the vapour phase by introducing ammonia gas into B, through T_{11}. The volume of ammonia was measured and it was then allowed to react with the iso-cyanic vapour in the decomposition tube at room temperature. The reaction takes place almost instantaneously as indicated by the white fumes formed inside the decomposition tube. The tube was cooled to liquid nitrogen temperature and then rewarmed to ensure the completeness of the reaction. The volume of the unreacted ammonia was measured at room temperature.

The gaseous products at 191.5°C contained ammonia as a condensable component. In this case, the volume of the condensable fraction was measured directly without reacting with ammonia gas.

Each time a gas volume and pressure were recorded, room temperature was noted with a thermometer kept close to B.

3.5. THE REACTION OF ISO-CYANIC ACID WITH A.C.

This reaction was attempted under two conditions:-

(i) The iso-cyanic acid vapour was produced by heating cyanuric acid in a current of nitrogen gas. The vapour was collected in a tube as a liquid at liquid nitrogen temperature. The tube was connected to an evacuated reaction vessel containing solid A.C. and fitted with a heating and stirring device. The reaction vessel was maintained at 140°C and the iso-cyanic acid allowed to expand into it slowly. The reaction was continued for eight hours. The gas in the vessel was analysed by infra-red spectroscopy and the residue by thin-layer chromatography.

(ii) The iso-cyanic acid vapour produced by method (i) was dissolved in dry carbon tetrachloride. The suspension of A.C. in this solution was heated at 80°C for eight hours with continuous stirring. The residue was analysed by the method mentioned earlier.

3.6. THE DECOMPOSITION OF A.C. IN THE PRESENCE OF AMMONIA AND AMMONIUM SALTS

(i) Decomposition in the presence of ammonia

For this exercise, the decomposition tube containing a known weight of A.C. was evacuated and then dry ammonia gas was allowed to enter until a required pressure was observed.

The solid products were examined qualitatively by the thin-layer chromatographic technique and the quantitative determinations of the components were carried out as described in Section 3.3.

The gaseous products were first examined by the infra-red spectroscopic technique and then quantitative analyses of nitrogen and carbon monoxide were carried out.

(ii) Decomposition in the presence of ammonium salts

A.C. and the ammonium salts were weighed into a ball-mill mortar and vibrated for two hours. The decomposition of the mixture was carried out as described in Section 3.2.

The solid and the gaseous products were examined only qualitatively, in this instance, by the method described earlier.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. THE IDENTIFICATION OF THE SOLID PRODUCTS

FIGURE 4.1 shows the chromatographic separation of the components in both sublimate and residue obtained on decomposing azodicarbonamide (A.C.). The R_f values of the components are tabulated in TABLE 4.1.

TABLE 4.1

R_f values of the solid products of A.C.

Components	R_f value	
	Sublimate	Residue
Cyanuric acid	0.72	0.72
Urazole	-	0.47
Urea	0.30	-
Biurea	-	does not move

The identities of the components were confirmed by the characteristic colours of the spots developed with different reagents. The biurea spot has not appeared in the photograph because it was only clearly visible under ultra-violet irradiation. The R_f values compared well with those of the authentic samples run on the same plate.

This evidence indicates that the sublimate consists of urea and cyanuric acid and the residue of urazole, cyanuric acid and biurea.

The infra-red spectrum of urea isolated from the sublimate compared well with the published spectrum of urea[46,47] and it was superimposable

PHOTOGRAPH OF THE CHROMATOGRAPHIC PLATE

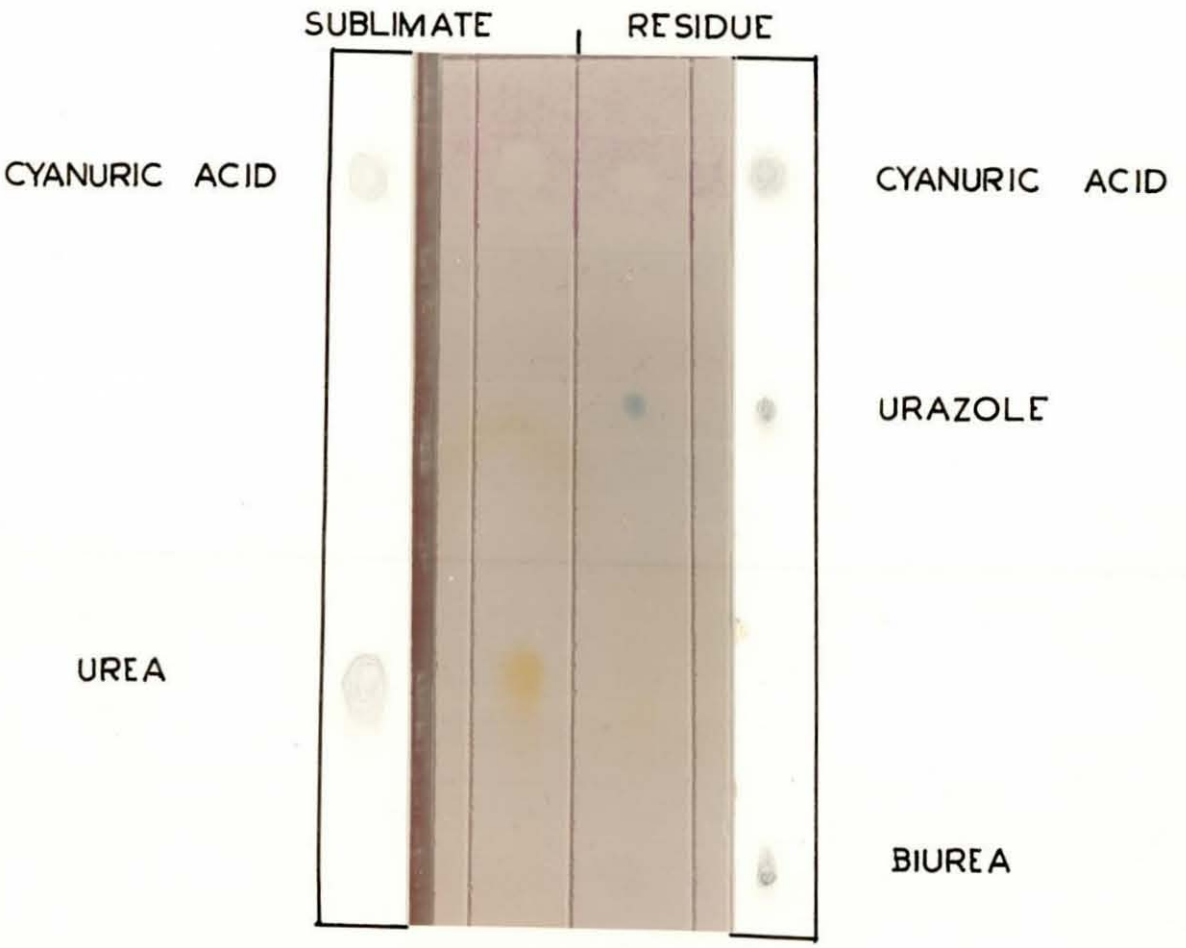


FIGURE 4.1

TABLE 4.2

Major Infra-red Absorption Bands of the Solid Products of A.C.

Sublimate			Residue		
Wave number	Intensity	Assign-ment	Wave number	Intensity	Assign-ment
758	w	Cy	740	w	C, Ur
780	w	U	760	s	Ur
785	vw	U	1000	m	B
1060	m	C	1045 - 1055	m	Ur, B
1170	w	U	1115	s	B
1200	sh	Cy	1245	w	Ur
1410	s	C	1410 - 1420	s	C
1440	s	Cy	1465	m	C,Ur,B
1468	s	U	1490 - 1510	m	B,Ur
1629	s	U	1595 - 1605	s	B
1660 - 1685	s,b	U,Cy	1620	sh	Ur
1710	s	C	1670	s,b	B
1800	m	C	1680 - 1710	vs,b	B,Ur
3210)			1795	w	Ur
3350)	s,b	U,C,Cy	2780	w	Ur
3440 - 3470)			2900	w	C
			3020 - 3060	s,b	Ur,C
			3180	vs	Ur,B
			3270	m	B
			3370	vs	B

Key:- w - weak, vw - very weak, m - medium, sh - shoulder, s - strong vs - very strong; C - cyanuric acid, Cy- cyamelide, U - urea, Ur - urazole, B - biurea.

on the spectrum obtained from an authentic sample.

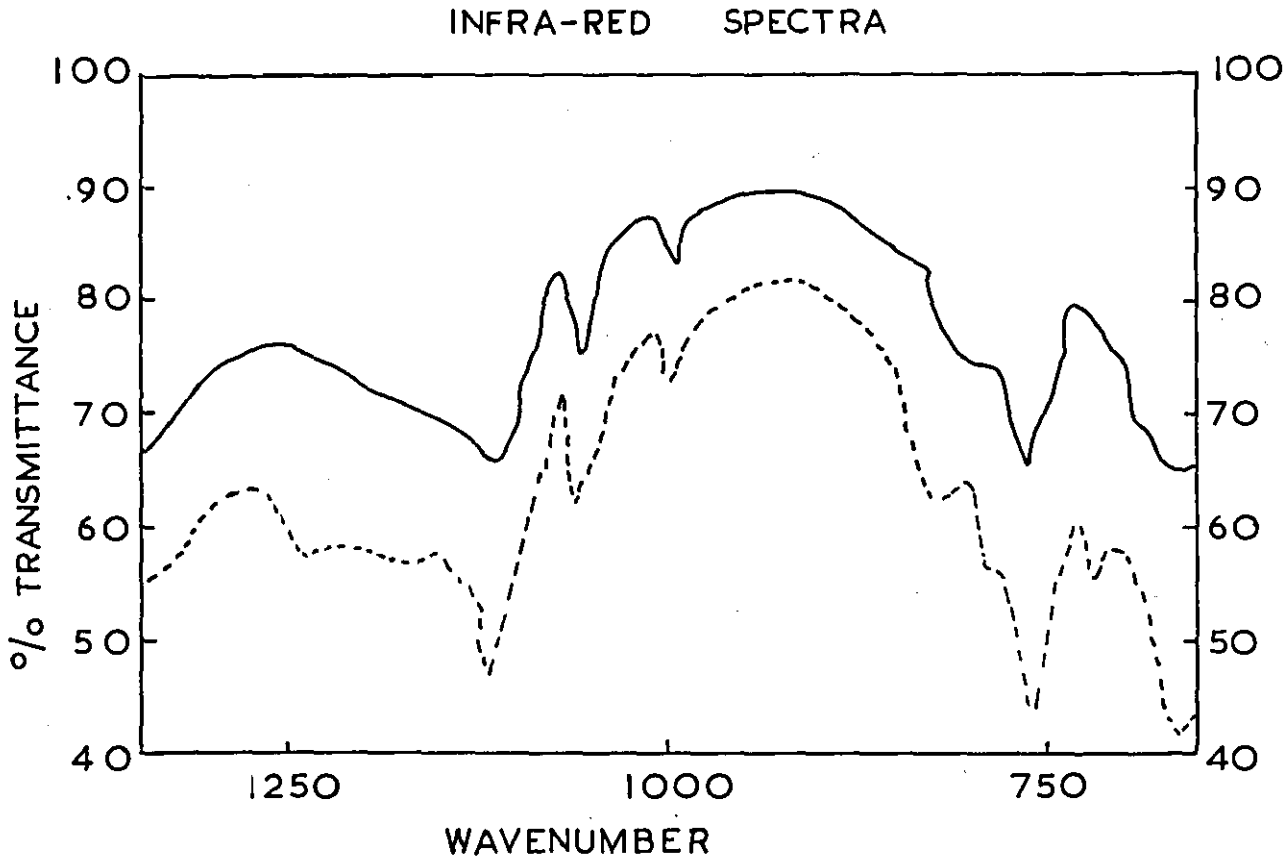
Cyanuric acid, which is a major component of the sublimate, has been found to associate with the alkali halides[48] normally used in the preparation of discs for recording infra-red spectra. This, together with the presence of three materials, namely, urea, cyanuric acid and cyamelide (a polymer of iso-cyanic acid, which will be discussed later) in unknown proportions made it impossible in the infra-red spectrum of the sublimate to obtain fine details of the absorptions due to the individual components.

The major absorption frequencies observed in the spectrum are shown in TABLE 4.2. In the region 3000 - 3500 cm^{-1}, where N - H and O - H stretching frequencies normally appear, the sublimate spectrum has a strong unresolved absorption showing peaks at 3210, 3350 and 3440 - 60 cm^{-1}. Cyanuric acid[49,50], in this region, absorbs at 3210 and 3060 cm^{-1}, urea[47] at 3311 and 3413 cm^{-1}, and cyamelide at 3410 and 3120 cm^{-1}. The peak at 3210 cm^{-1} is most likely due to cyanuric acid because of the latter's very strong absorption at this wavelength. The carbonyl stretching frequency of cyanuric acid at 1800 cm^{-1} is quite distinguishable from that of urea which appears at 1684 - 6 cm^{-1}. The cyanuric acid would be expected to have a very strong carbonyl absorption at 1710 cm^{-1} but owing to a broad absorption of cyamelide at 1660 - 1720 cm^{-1} the resolution is poor. The absorptions due to the triazene ring of cyanuric acid appear at 1470 and 1050 - 65 cm^{-1}, but in the spectrum the former is difficult to identify due to overlap with the C - N stretching frequency of urea at 1464 - 1468 cm^{-1}. The absorption at 1660 cm^{-1}, however, is a definite indication of the presence of this ring. The cyamelide band at 758 cm^{-1} has prevented the resolution of a weak band of cyanuric acid at 765 cm^{-1},

The thin-layer chromatographic technique revealed that the residue consisted of three major components, namely, urazole, cyanuric acid and biurea. The infra-red spectra of the residue and a mixture of authentic samples of these three components are shown in FIGURES 4.2A and 4.2B. It is noticed that the intensities of the absorption peaks of the two spectra are not identical. This is due to differences in the proportions of the components in the residue and in the artificial mixture. But the wavelengths at which the peaks appear in the two spectra are identical.

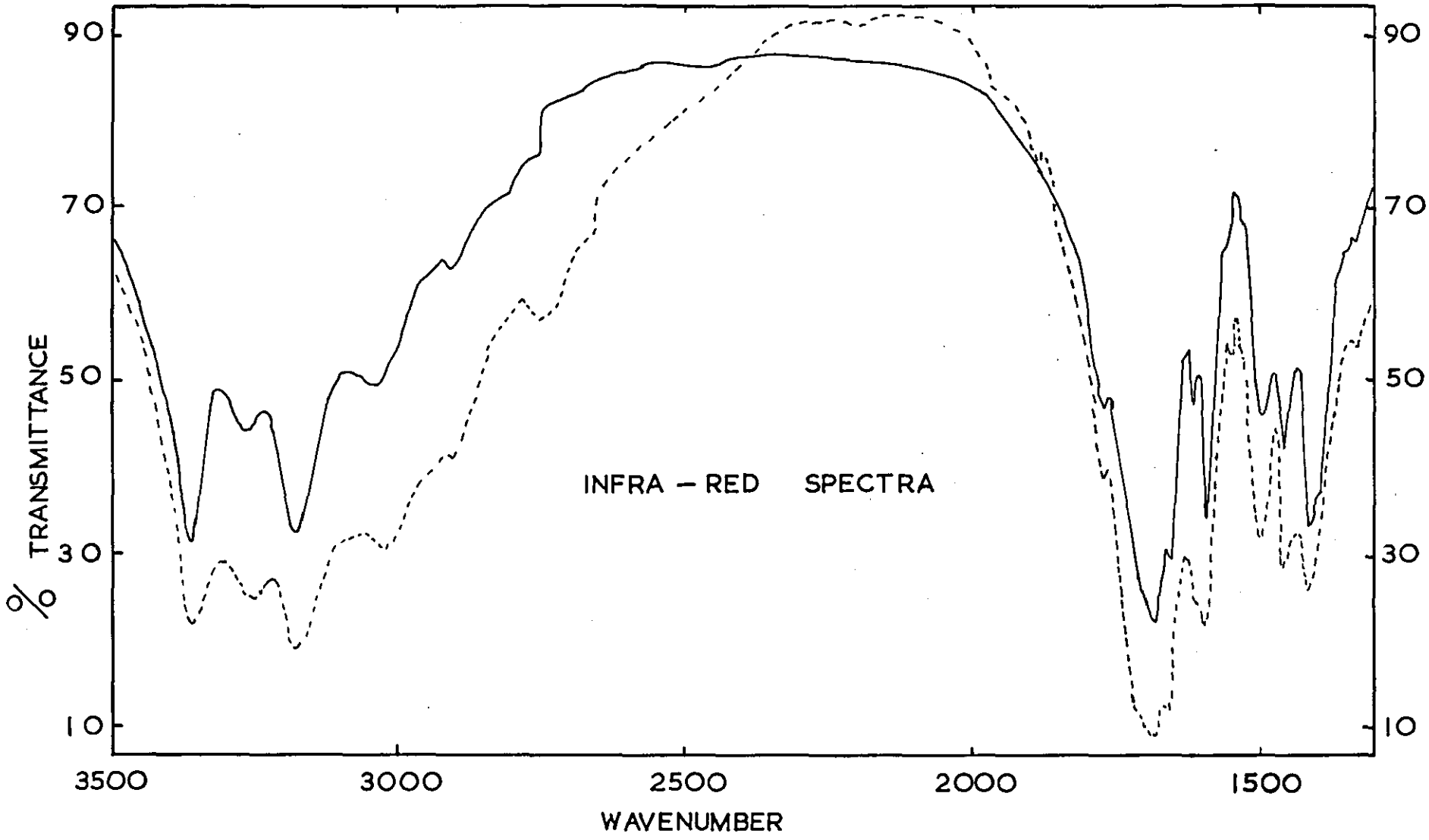
Owing to the lack of finer details, due to the same causes as in the case of the sublimate, the exact interpretation of the residue spectrum is impossible. The major absorption peaks observed in the spectrum and their most likely assignments are tabulated in TABLE 4.2. It is noticed that most of the strong absorption peaks are due to biurea which indicates that the residue has a large proportion of this material. The other peaks due to urazole and cyanuric acid are weak in comparison. The strong but poorly resolved peaks in the region 3000 - 3500 cm^{-1} are attributed to the N - H stretching frequencies of the three materials. The biurea peak[51,52] at 3370 cm^{-1} is well defined but that at 3180 - 90 cm^{-1} overlaps with the urazole peak which is expected at 3195 cm^{-1}. The cyanuric acid absorptions at 3210 cm^{-1} and 3060 cm^{-1} are also not resolved.

Several absorptions are observed in the region 1300 - 1600 cm^{-1}. The absorption at 1465 cm^{-1} is difficult to assign to any one particular material because urazole[51] absorbs fairly strongly at 1460 cm^{-1}, the triazene ring of cyanuric acid appears at 1464 - 70 cm^{-1} and C - N stretching frequency of biurea occurs at 1465 cm^{-1}. The carbonyl



SOLID LINE - RESIDUE (TRANSMITTANCE SCALE 10 % INCREASED)
BROKEN LINE - A SYNTHETIC MIXTURE OF BIUREA, URAZOLE AND CYANURIC ACID

FIGURE 4.2A



MATERIALS — SAME AS FIGURE 4·2A

FIGURE 4·2B

TABLE 4.3

Mass Spectra Data of the Products and Authentic Samples

m/e	% Abundance with respect to the highest peak					
	Products		Authentic samples			
	Sublimate	Residue	Urea	Urazole	Biurea	Cyanuric acid
129	28.7	11.3				38.1
118		1.3			2.0	
102		1.8		2.3		
101		50.0		68.6	5.0	
100		2.6				
87	1.0					
86	6.7	3.1				5.0
85		4.1		1.0		
75		3.1			10.2	
70	5.3	15.0		15.2	1.3	8.1
69					1.9	
61	2.6		11.3			
60	66.7	41.3	12.7			36.3
59		4.0		1.0		
58		40.0		44.5		
57					2.0	
56				1.0	1.7	
55					2.6	
45	4.3	3.0	9.9	1.4	2.0	
44	100	100	86.0	61.0	37.0	100
43	66.7	98.8	93.1	89.0	20.4	93.8
42	14.7	81.3	97.3	25.4	6.3	16.3
41	3.5	13.8	91.7	5.1	3.9	7.5
40			16.9		1.5	
32		2.8	18.3		48.1	8.8
31	3.8	22.5	93.1	14.0	16.7	5.0
30	2.8	26.3	97.3	100	3.5	1.3
29	12.7	28.8	9.9	99.1	10.0	18.8
28	20.0	37.5	100	33.0	100	87.5
27	4.7	26.3	93.1	14.0	3.3	10.0
26	1.7	10.0	90.2	2.5	1.7	3.8

absorption of biurea is observed at 1680 - 1690 cm^{-1} without interference. The assignments of the other absorption peaks of the spectrum have been made with the help of the published spectra of the individual materials[47,51,52].

The infra-red spectrum of the water insoluble product is shown in FIGURES 4.3A and 4.3B. The spectrum of an authentic sample of cyamelide (shown in the same figures with dotted lines) is found to be superimposable on this spectrum. The material, therefore, is undoubtedly cyamelide.

The conclusion from T.L.C. and infra-red spectroscopy that the sublimate contains cyanuric acid as a major component is also supported by mass spectroscopic study. TABLE 4.3 shows the percentage abundances of the fragment ion peaks of the solid products of A.C. and authentic samples of urea, urazole, biurea and cyanuric acid.

While the presence of three components in unknown proportions makes detailed analysis of the mass spectrum of the sublimate impossible, the molecular ion peak at m/e = 129 suggests the presence of cyanuric acid. The presence of urea is difficult to assess accurately because cyanuric acid has a fragment peak at m/e = 60 with a relative abundance of 36.3% of the highest peak. However, a percentage abundance of 66.7 at m/e = 60 with the sublimate in relation to the 28.7 per cent molecular ion peak of cyanuric acid is much higher than can be accounted for by cyanuric acid alone. This higher percentage abundance suggests the presence of another material with mass number 60, which is most likely to be urea.

In the mass spectrum of the residue (TABLE 4.3) there is a peak at m/e = 129 which corresponds to cyanuric acid. The other peak at

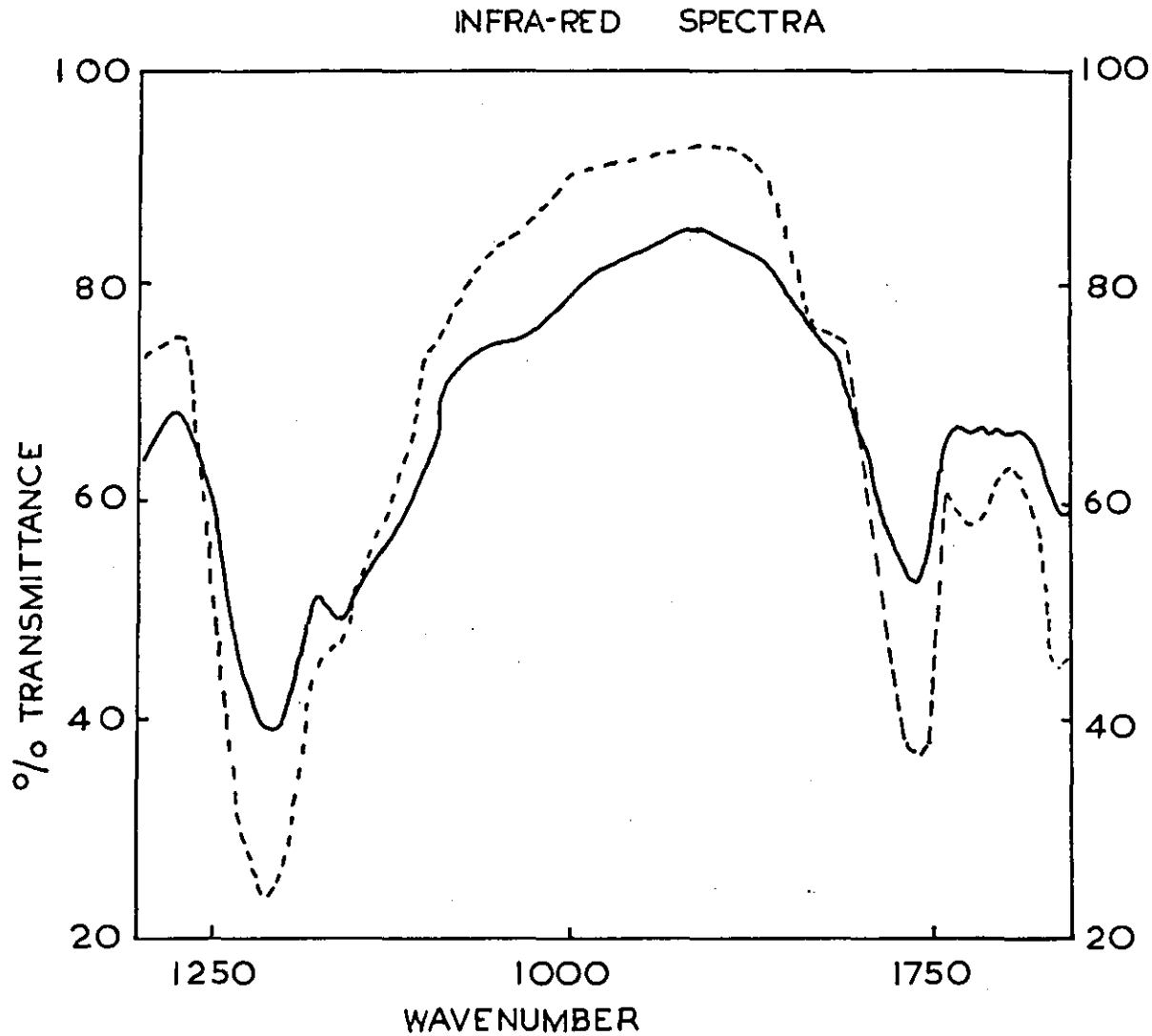
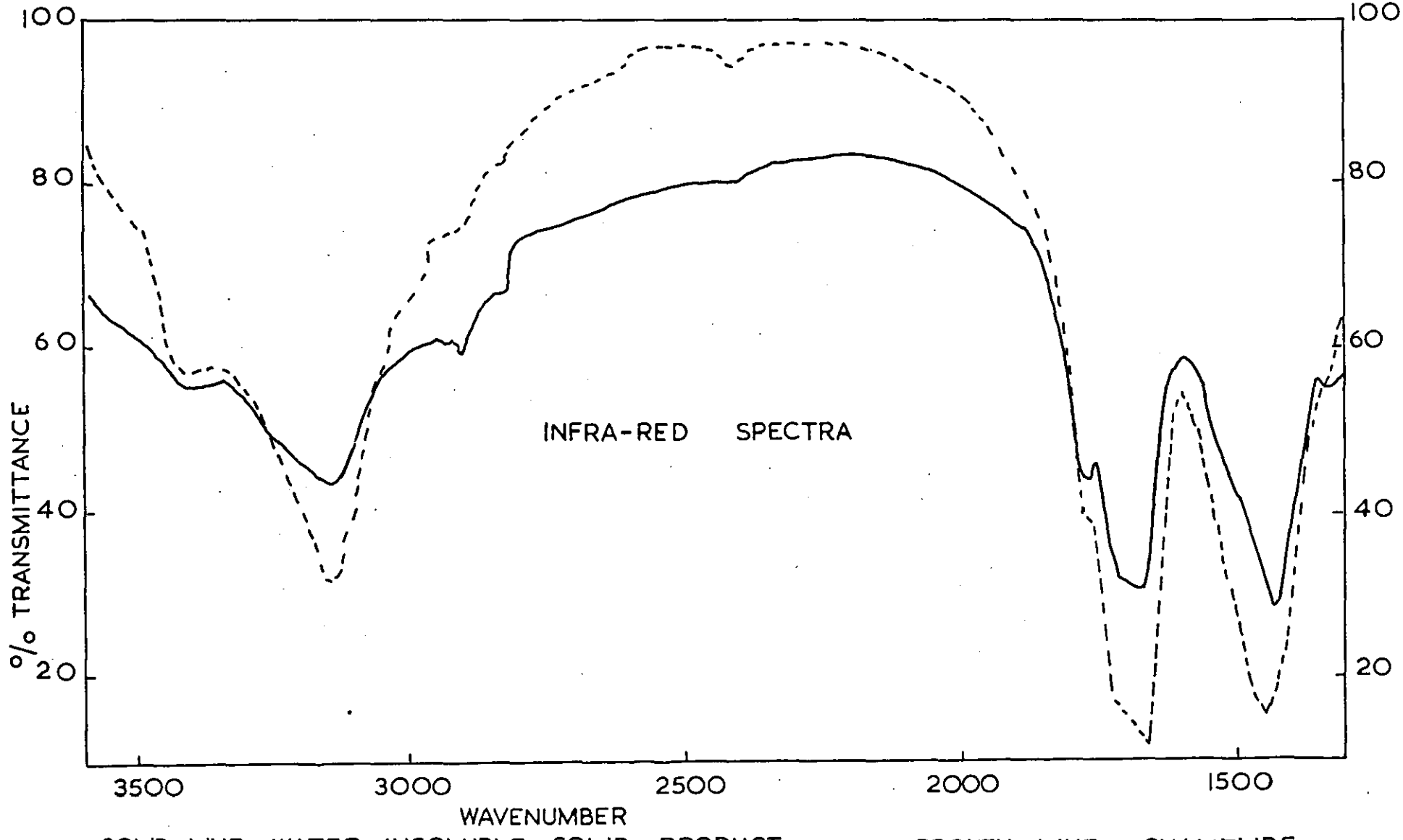

INFRA-RED SPECTRA
100
80
60
40
20
% TRANSMITTANCE
1250
1000
1750
WAVENUMBER
SOLID LINE - WATER INSOLUBLE SOLID PRODUCT
BROKEN LINE - CYAMELIDE

FIGURE 4.3A



SOLID LINE – WATER INSOLUBLE SOLID PRODUCT BROKEN LINE – CYAMELIDE

FIGURE 4.3B

m/e = 118 must be the molecular ion peak of biurea because cyanuric acid has no fragment with this mass number. A peak at m/e = 101, which corresponds to the molecular ion peak of urazole, also corresponds to a fragment of biurea having about 5.0 per cent abundance relative to the highest peak of pure biurea. An approximate estimate shows that biurea, on the basis of the 1.3 per cent abundance of the peak at m/e = 118, should contribute about 3.3 per cent abundance at mass number 101. The observed value of 50 per cent abundance, therefore, is a clear indication for the presence of urazole.

The presence of oxamide as one of the solid products of A.C.[1] was ruled out on the evidence of T.L.C. The infra-red spectrum of oxamide[51,53] was compared with the observed spectrum of the residue. Oxamide absorbs mostly in the same region of the infra-red as do the other solid products of A.C. Thus, it is difficult to assess the absence of oxamide from this evidence. However, the absence of a peak at m/e = 88 in the mass spectrum, corresponding to the molecular ion, confirms that oxamide is not present in the solid products.

4.2. THE IDENTIFICATION OF THE GASEOUS PRODUCTS

The curve A in FIGURE 4.4 shows the infra-red spectrum of the gaseous products after A.C. had been heated at 171.5°C for 8 hours. The spectrum has two strong absorptions - one parallel band at 2274 cm^{-1} and a second band at 3500 - 3535 cm^{-1}. These absorptions agree closely with the positions of the two strongly absorbing fundamental bands of iso-cyanic acid observed by Herzberg and Reid[26]. These authors recorded the spectrum with varying pathlengths and pressures of iso-cyanic acid vapour in order to resolve the fine details. As it was impossible to

INFRA-RED SPECTRUM OF GASEOUS PRODUCTS OF A.C. DECOMPOSED AT 171·5°C.

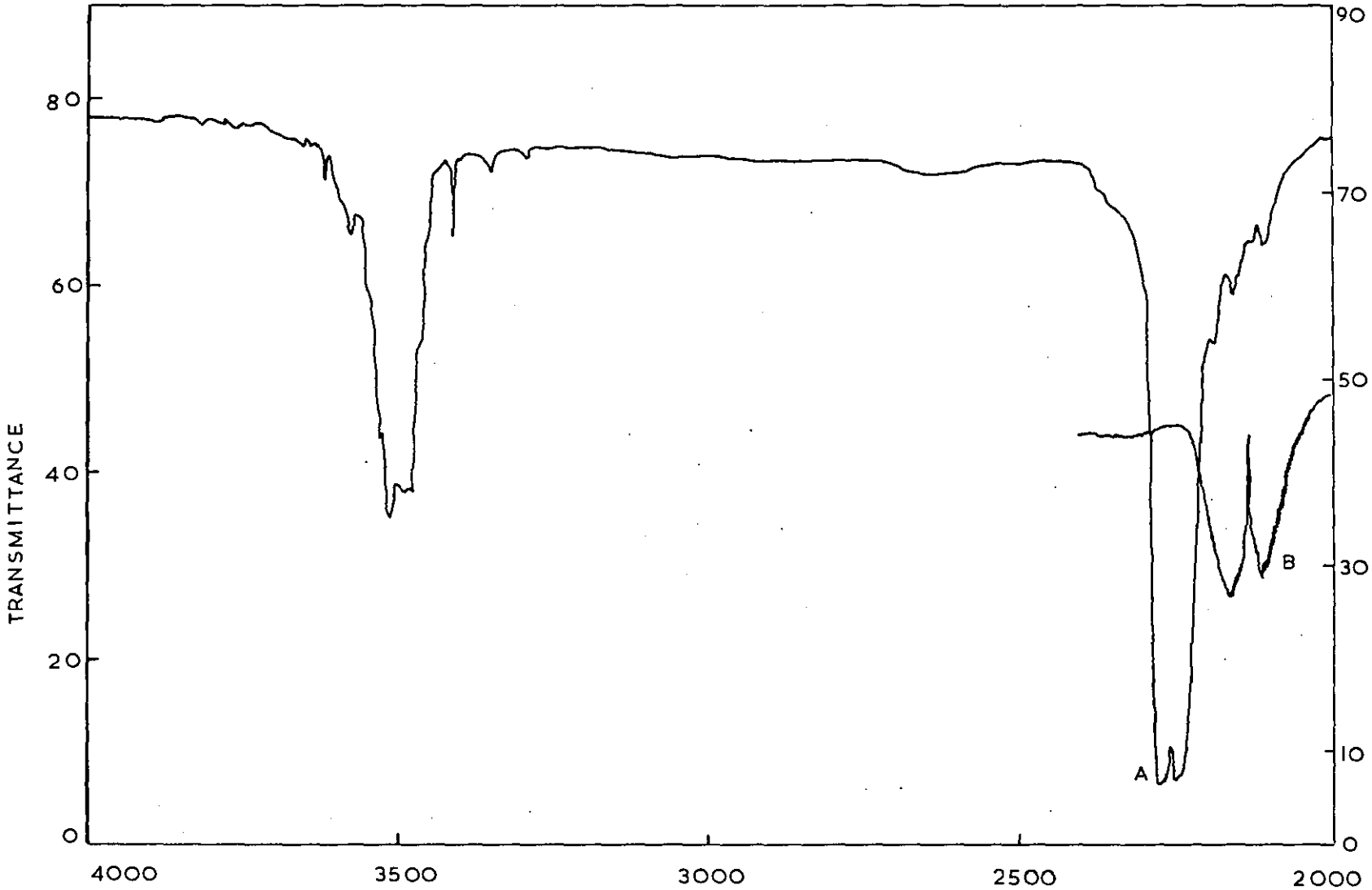


FIGURE 4.4

B — BASELINE 30% DECREASED

apply this procedure in the present work, the other, weaker absorptions of iso-cyanic acid are not well defined in the spectrum shown in FIGURE 4.4. For comparison, a spectrum of pure iso-cyanic acid, produced by thermal depolymerization of cyanuric acid, was recorded under the same experimental conditions. The two spectra were found to be superimposable.

When the gaseous products were allowed to age at room temperature for 48 hours and then re-examined in the infra-red cell, a considerable decrease in the absorption at 2274 cm^{-1} and almost negligible absorption at 3500 - 3535 cm^{-1} were observed. This fits in with a steady loss of iso-cyanic acid through polymerization[45] into cyanuric acid and cyamelide. Two broad absorptions at 2110 and 2164 $\pm$ 5 cm^{-1} now became visible as shown in curve B of FIGURE 4.4. These two bands agree with the bands of carbon monoxide[54].

The gaseous products, when A.C. was heated at 191.5°C for three hours, gave a quite different infra-red spectrum (see FIGURES 4.5A and 4.5B). This spectrum has two absorptions at 2110 cm^{-1} and 2164 cm^{-1} similar to curve B in FIGURE 4.4, and three sets of multiple bands at 710 - 1230 cm^{-1} (maxima at 930 and 965 cm^{-1}), 1400 - 1800 cm^{-1} (maximum at 1620 cm^{-1}) and 3130 - 3500 cm^{-1} (maximum at 3310 cm^{-1}). The first two bands are again attributed to carbon monoxide, whereas the three multiple bands are those of ammonia[47]. The spectrum of an authentic sample of ammonia gas compared well with this spectrum. The iso-cyanic acid vapour no longer appears to be present in this mixture.

In order to confirm the identity of the iso-cyanic acid some properties of this vapour were investigated.

INFRA-RED SPECTRUM OF GASEOUS PRODUCTS OF A.C. DECOMPOSED AT 191·5°C.

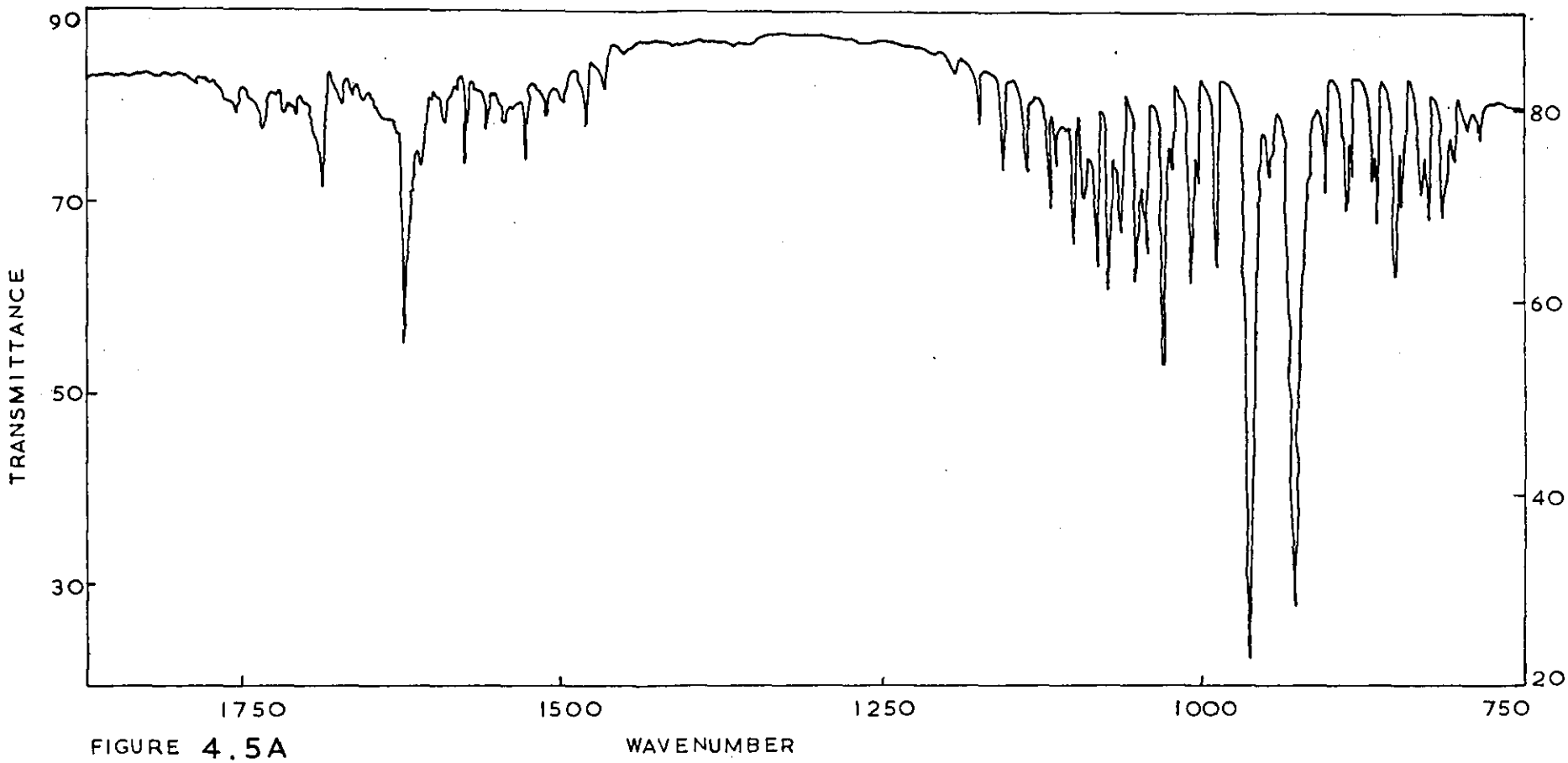


FIGURE 4.5A

INFRA-RED SPECTRUM OF GASEOUS PRODUCTS OF A.C. DECOMPOSED AT 191·5°C.

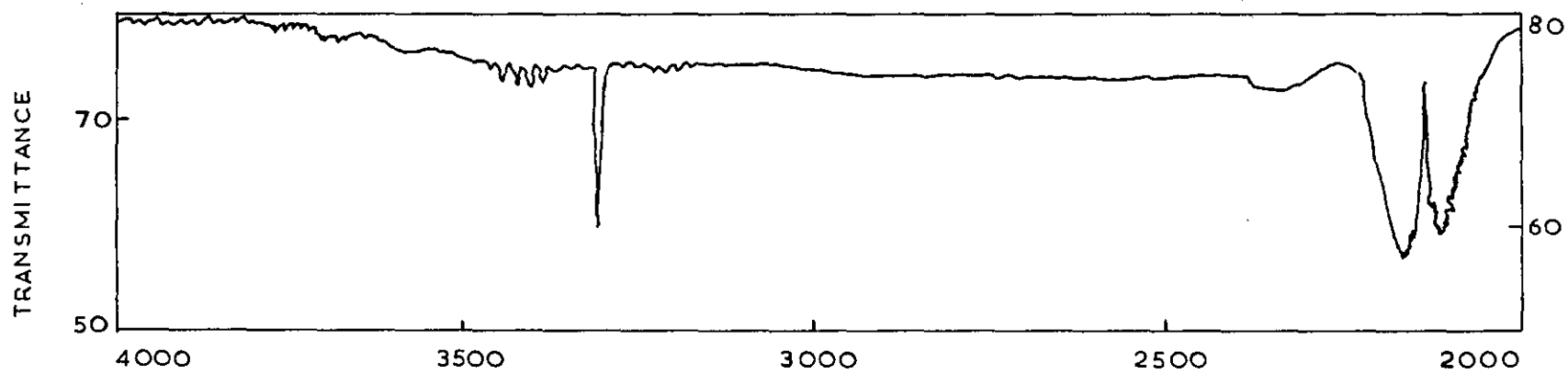


FIGURE 4.5B

(a) The reaction of iso-cyanic acid with ammonia

In this experiment when excess of ammonia was introduced into an infra-red cell containing iso-cyanic acid the cell immediately became slightly foggy and the only gas detectable in the infra-red spectrum recorded as soon afterwards as possible was ammonia. It is clear that the reaction between ammonia and iso-cyanic acid to form urea is an extremely rapid one which effectively prevents the two gases co-existing together in the gas phase. This experiment also explained why no iso-cyanic acid was present in the gas phase when A.C. was decomposed at 191.5°C, a result which is discussed more fully later when the formation of urazole is considered.

(b) The gaseous products of urea decomposition

This experiment was carried out to confirm the findings of the reaction of iso-cyanic acid with ammonia. The infra-red spectrum of the gaseous products obtained on heating urea shows the presence of ammonia only. Heating urea should produce iso-cyanic acid and ammonia in equi-molar quantities:-

$$NH_2 . CO . NH_2 \longrightarrow NH_3 + HNCO$$

But if some of the iso-cyanic acid polymerizes to give cyanuric acid and cyamelide, an excess of ammonia will result. If the back reaction is rapid, only ammonia will be left in the gas phase to be detected in the infra-red spectrum.

(c) The reaction between iso-cyanic acid and water-vapour

On introducing moist air into a tube containing iso-cyanic acid and then recording the infra-red spectrum, both carbon dioxide and iso-cyanic acid were detected. The removal of iso-cyanic acid was not

complete probably because insufficient water vapour had been added. When moist cyanuric acid was heated to produce iso-cyanic acid, the vapour after standing showed the presence of carbon dioxide and ammonia. It appears that the reaction between iso-cyanic acid and water-vapour is rapid and takes place in the following manner:-

$$HNCO + H_2O \longrightarrow NH_3 + CO_2$$

The reaction goes to completion only when the water-vapour is in excess. If the water is not in excess, any ammonia formed reacts with iso-cyanic acid to form urea, leaving only carbon dioxide and surplus iso-cyanic acid to be detected in the gas phase.

4.3. THE MECHANISM OF THE DECOMPOSITION OF A.C.

The analytical information suggests that the solid products of A.C. contain four major components in the water soluble portion, namely, urazole, cyanuric acid, urea and biurea, and that the water insoluble material is mainly cyamelide. The gaseous products consist of nitrogen, iso-cyanic acid and carbon monoxide when A.C. is decomposed for 8 hours at 171.5°C. Under these conditions there was no carbon dioxide or ammonia present in the gas phase.

A complete analysis of both solid and gaseous products formed under the same conditions is shown in TABLE 4.4.

The percentages on addition indicate that nearly 96% by weight of the A.C. is accounted for. When the analytical data is examined with

TABLE 4.4

Percentages of the product components of A.C. decomposition at 171.5°C

Gaseous products % by weight			Solid products % by weight				
N_2	CO	HNCO	Biurea	Urazole	Cyanuric acid	Insoluble matter	Urea
15.8	3.8	5.3	37.3	13.6	9.9	4.0	-
16.2	3.8	-	-	-	-	-	5.9

respect to the percentage of the individual elements present in each component, the following results are obtained (see TABLE 4.5).

TABLE 4.5

Percentages of different elements present in each component

Components	Percentage by weight of A.C.			
	carbon	Hydrogen	Nitrogen	Oxygen
Biurea	7.59	1.90	17.70	10.11
Urazole	3.23	0.40	5.66	4.31
Urea	1.18	0.39	2.75	1.57
*Iso-cyanic acid	5.36	0.45	6.25	7.14
+Nitrogen	-	-	16.00	-
+Carbon monoxide	1.63	-	-	2.17
Total	18.99	3.14	48.36	25.30
A.C.	20.68	3.44	48.28	27.59

* Sum of the cyanuric acid, iso-cyanic acid and the insoluble matter, i.e., cyamelide.

+ Mean of duplicate determinations.

This break-down shows that the products account for the whole of the nitrogen present in the original A.C. but only 92% of the carbon, hydrogen and oxygen. The discrepancy may be due to a cumulation of analytical errors or it may represent the failure to detect in the water soluble solid products a small quantity of a compound containing these three elements only with an approximate empirical formula CH_2O.

THE EFFECT OF TEMPERATURE ON THE SOLID PRODUCTS

The slow polymerization of the iso-cyanic acid vapour made it difficult to analyse the gaseous products quantitatively and for this reason only the variation of the solid products with temperature was studied. The results are shown in TABLE 4.6.

It is observed that the proportion of cyanuric acid increases with temperature while that of the insoluble residue decreases. The insoluble residue has been identified as cyamelide by infra-red spectroscopy. That when iso-cyanic acid polymerises, higher temperatures favour the formation of cyanuric acid and lower temperatures the formation of cyamelide is in accordance with published work[25]. It is, therefore, reasonable to deduce that both cyanuric acid and cyamelide are secondary products formed as a result of the polymerization of iso-cyanic acid.

THE FORMATION OF URAZOLE

It is also noticed from TABLE 4.6 that at higher temperatures (i.e., above 177.0°C) the proportion of urazole increases while that of biurea

TABLE 4.6

Variation in the quantities of products with temperature

Temp. °C	Time Hours	Percentage by weight of A.C.				
		Biurea	Urazole	Cyanuric acid	Urea	Insoluble matter
171.4	8.0	35.8	13.2	11.7	5.8	4.9
177.0	6.0	38.2	13.9	10.1	6.6	4.7
177.0	6.0	39.5	13.9	10.1	6.7	4.0
182.0	3.0	36.7	16.9	11.1	7.9	1.8
182.0	3.0	36.6	16.6	11.3	7.8	1.0
187.0	2.5	16.5	20.9	13.6	14.7	0.7
187.0	2.5	17.0	20.7	13.8	14.3	1.3
191.5	2.5	16.4	24.6	13.1	14.5	0.5
191.5	2.5	16.0	24.2	13.7	14.9	0.9

decreases. Biruea is known to decompose into urazole and ammonia above 180°C and at lower temperatures in the presence of gaseous hydrogen chloride[24]. It was thought likely that iso-cyanic acid acts, like the hydrogen chloride, as a catalyst enabling the decomposition of biurea into urazole to occur at a lower temperature. In an attempt to ascertain whether urazole is solely a secondary product arising entirely as a result of biurea decomposition the amounts of the four water soluble components were determined as a function of time at two temperatures. The results are shown in TABLES 4.7 and 4.8 and plotted in FIGURES 4.6 and 4.7 respectively.

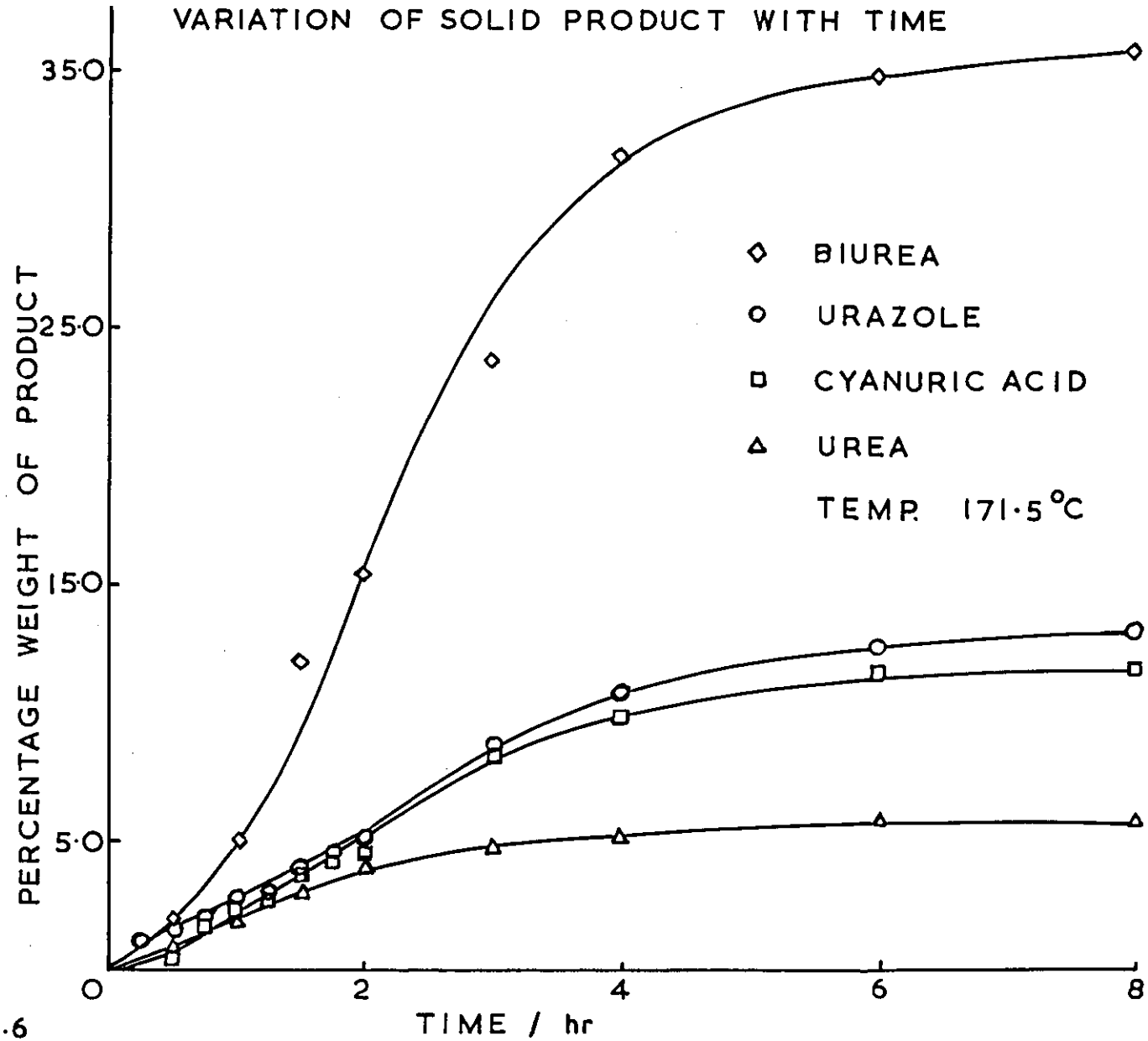

VARIATION OF SOLID PRODUCT WITH TIME
PERCENTAGE WEIGHT OF PRODUCT
35·0
25·0
15·0
5·0
0
2
4
6
8
TIME / hr
BIUREA
URAZOLE
CYANURIC ACID
UREA
TEMP. 171·5 °C

FIGURE 4·6

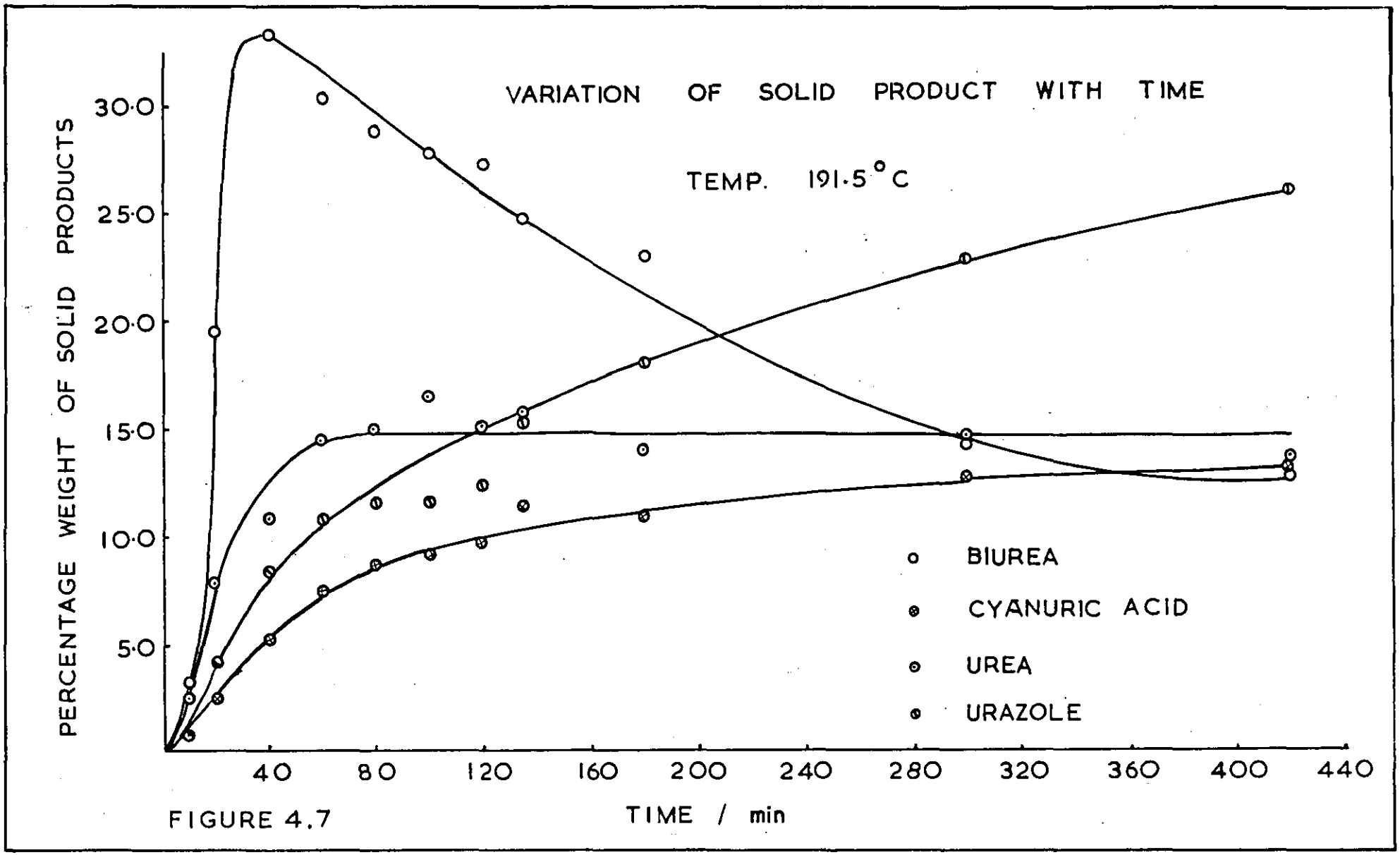

VARIATION OF SOLID PRODUCT WITH TIME
TEMP. 191·5 °C
PERCENTAGE WEIGHT OF SOLID PRODUCTS
30·0
25·0
20·0
15·0
10·0
5·0
40
80
120
160
200
240
280
320
360
400
440
TIME / min
BIUREA
CYANURIC ACID
UREA
URAZOLE

FIGURE 4.7

TABLE 4.7

Variation in the quantities of solid products with time at 171.5°C

Time	Percentage by weight of A.C.			
Hours	Biurea	Urazole	Cyanuric acid	Urea
0.25	-	1.1	-	-
0.50	2.0	1.7	0.4	0.7
0.75	-	2.0	1.7	-
1.00*	5.0	2.7	2.2	1.9
1.25	-	3.1	3.1	-
1.50*	12.1	3.9	3.5	3.1
1.75	-	4.6	4.2	-
2.00*	15.4	5.2	4.4	4.1
3.00	23.8	8.8	8.4	4.9
4.00	31.8	10.7	9.8	5.1
6.00	34.7	12.6	11.6	5.9
8.00	35.8	13.2	11.7	5.8

* Mean of duplicate determinations.

TABLE 4.8

Variation in the quantities of solid products with time at 191.5°C

Time Mins	Percentage by weight of A.C.				
	Biurea	Urazole	Cyanuric acid	Urea	S+
10	3.3	0.8	2.4	0.8	
20	19.4	4.2	8.0	2.4	
40	33.2	8.6	10.9	5.2	
60	30.2	10.8	14.6	7.4	32.8
80*	28.9	11.5	15.1	8.4	32.3
100	27.8	11.6	16.5	9.1	31.3
120	27.3	12.2	15.1	9.7	31.5
135	24.7	15.2	15.7	11.4	32.4
180	23.0	18.0	14.0	11.1	34.0
300	14.3	22.9	14.6	12.8	31.0
420	12.7	26.1	13.7	13.3	31.2

* Mean of duplicate determinations.

\+ S = Biurea, experimental amount + an amount equivalent to the increase in the urazole.

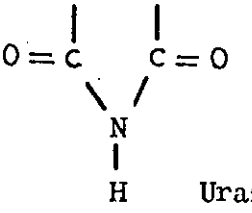
At both temperatures urazole is formed at the very start of the reaction and at 171.5°C, as the reaction nears completion, no decrease occurs in the amount of biurea, as would be expected if the latter were decomposing into urazole and ammonia. At 191.5°C, however, prolonged heating beyond the time (~ 40 min) at which the initial reaction is virtually complete does result in a decrease in the quantity of biurea and a corresponding increase in the amount of urazole. Calculation shows that within experimental error the biurea loss is exactly matched by the urazole gain, as demonstrated by the nearly constant values of S. As mentioned earlier the infra-red spectrum of the gaseous products

after heating A.C. for 420 mins at 191.5°C (FIGURES 4.5A and 4.5B) revealed the presence of carbon monoxide and ammonia and the absence of iso-cyanic acid. It is clear that at 191.5°C a slow secondary reaction does occur in which biurea decomposes into urazole and ammonia. In this process sufficient ammonia is formed to convert all the iso-cyanic acid in the gas phase into urea and leave excess ammonia present.

But this secondary process cannot at either temperature account for the urazole formed initially and it appears that this urazole is a primary product formed directly from A.C. and not from biurea. The evidence, therefore, points to two primary processes occurring concurrently, namely,

$$2\ NH_2.\ CO.\ N{:}N.\ CO.\ NH_2 \longrightarrow NH_2.\ CO.\ NH.NH.\ CO.\ NH_2 + N_2 + 2\ HNCO \quad (1)$$

$$2\ NH_2.CO.N{:}N.CO.NH_2 \longrightarrow \text{Urazole} + N_2 + 2\ HNCO + NH_3 \quad (2)$$



Urazole

An alternative to reaction (2) is

$$2\ NH_2.CO.N{:}N.CO.NH_2 \longrightarrow \text{Urazole} + N_2 + NH_2.CO.NH_2 + HNCO \quad (3)$$

But at the temperature at which A.C. decomposes urea itself is unstable and dissociates to form ammonia and iso-cyanic acid[55].

$$NH_2.\ CO.\ NH_2 \longrightarrow NH_3 + HNCO \quad (4)$$

It is impossible therefore to distinguish between reaction (2) and the combination of reactions (3) and (4). The urea determined experimentally undoubtedly results from the combination of ammonia and iso-cyanic acid (i.e., the occurrence of the reverse of reaction (4)) in the cooler parts of the reaction tube.

THE FORMATION OF CARBON MONOXIDE

In the present work the variation in the quantities of gaseous components formed as a function of time was not studied. But the chromatographic analysis in previous work[10] of the gas evolved when A.C. was decomposed between 166.5 and 183°C showed that at the very start of the reaction little carbon monoxide was formed and the nitrogen to carbon monoxide ratio was greater than 15:1. By the time 10% decomposition had occurred the rate of the carbon monoxide formation relative to the nitrogen formation had reached a maximum and the nitrogen to carbon monoxide ratio had fallen to below 3:1. For the remaining 90% of the decomposition the rate of carbon monoxide formation fell relative to the nitrogen formation slightly but steadily and the nitrogen to carbon monoxide ratio increased again to a final value close to 4:1.

These observations are explained if the carbon monoxide is formed as a result of the reduction of the unreacted A.C. by iso-cyanic acid:-

$$NH_2.CO.N{:}N.CO.NH_2 + 2\ HNCO \longrightarrow NH_2.CO.NH.NH.CO.NH_2 + N_2 + 2\ CO \quad (5)$$

Being formed by this secondary process, carbon monoxide does not appear initially but only once appreciable iso-cyanic acid has been formed. Reaction (5) competes with the polymerization of iso-cyanic acid to form cyanuric acid and cyamelide and as the A.C. decomposition proceeds the depletion of unreacted A.C. shifts the balance away from carbon monoxide formation and towards polymer formation so that less carbon monoxide is formed per molecule of A.C. decomposed by reactions (1) and (2). Since the bulk of the nitrogen is formed by reactions (1) and (2) a steady fall occurs in the rate of carbon monoxide formation relative to that of nitrogen formation over the last 90% of the reaction.

An attempt to carry out the reaction of iso-cyanic acid vapour with A.C. (reaction 5) at 140°C produced a negative result. The solid product was found to contain cyanuric acid and A.C. only. It was thought that the vapour pressure of iso-cyanic acid was inadequate for the reaction so the reaction was carried out in carbon tetrachloride solution. This experiment also gave the same negative result. It seems that the reaction does not take place at lower temperatures but no attempt was made to carry out the reaction at higher temperatures because of the possibility of decomposing the A.C.

RELATIVE IMPORTANCE OF DIFFERENT REACTIONS

If reactions (1), (2) and (5) are the only ones responsible for the formation of nitrogen, urazole and biurea, an equality should exist between the number of moles of nitrogen formed and the sum of the moles of biurea and urazole. A calculation of the molar quantities of the three components from the experimental data in TABLE 4.4 reveals that the molar quantity of nitrogen formed is larger than the sum of the molar quantities of biurea and urazole. This may be due to the experimental error or may indicate that a small percentage of A.C. decomposes to give nitrogen without biruea or urazole by a mechanism such as:-

$$NH_2.CO.\ N{:}N.\ CO.NH_2 \longrightarrow N_2 + 2\ NH_2CO\cdot \longrightarrow 2\ N_2 + 2/n\ (H_2CO)_n \qquad (6)$$

If at 171.5°C, 53% of the A.C. decomposes by reaction (1), 31% by reaction (2) and 8% by each of reaction (5) and (6), and all the ammonia produced in reaction (2) reacts with iso-cyanic acid to form urea, the percentage of the products formed would be expected to be those shown in TABLE 4.9. These values are in good agreement with the experimental percentages.

TABLE 4.9

Predicted and the experimental percentages of the products of A.C.

Components	Percentage by weight of A.C.	
	Theoretically predicted	Experimentally found
Nitrogen	15.9	16.0
Carbon monoxide	3.9	3.8
Iso-cyanic acid	19.5	19.2
Urea	8.0	5.9
Urazole	13.5	13.6
Biurea	35.1	37.3

Note:- The iso-cyanic acid represents the sum of the percentages of the cyanuric acid, insoluble matter (i.e. cyamelide) and the iso-cyanic acid in the vapour phase.

The figure for urea may be slightly low because of the partial formation of ammonium iso-cyanate by the reaction of iso-cyanic acid with ammonia.[25]

Thus, it appears that reactions (1) and (2) are the major primary reactions in the decomposition of A.C. taking place in an approximate ratio 1.7 : 1 at 171.5°C. The important secondary reactions all stem from the reactivity of the iso-cyanic acid formed in (1) and (2), most of which either polymerizes, combines with ammonia or reacts with A.C.

THE CRYSTAL STRUCTURE OF A.C.

The crystal structure of A.C. determined by Bryden[11] suggests that the molecules are near planar and lie in sheets parallel to the (101) plane. A model built with the available information revealed that it

is quite possible for all the products biurea, urazole, urea, iso-cyanic acid, nitrogen and carbon monoxide to be formed directly through the crystal cracking in different patterns and the hydrogen atoms moving slightly. It is, however, difficult to estimate the extent to which each cracking pattern takes place and hence a theoretical estimation of the relative amounts of the different products is not possible.

4.4. THE DECOMPOSITION OF A.C. IN THE PRESENCE OF AMMONIA GAS

A qualitative examination of the products of A.C. decomposed in an atmosphere of ammonia gas is shown in TABLE 4.10. This suggests that there is no formation of cyanuric acid in the sublimate and the gaseous products contain no iso-cyanic acid. The other products are the same as those found with pure A.C. This investigation confirms that the iso-cyanic acid produced during the decomposition of A.C. cannot exist in the gas phase in the presence of ammonia.

TABLE 4.11 shows a quantitative analysis of the solid and gaseous products formed when A.C. was decomposed at 171.5°C for 8 hours in 250 mm Hg pressure of ammonia gas.

The percentages of the gaseous components, i.e., N_2 and CO, are slightly lower than those from pure A.C. (see TABLE 4.4). This may be due to the fact that the ammonia, by reaction with iso-cyanic acid produced from the two primary reactions (1) and (2) in the proposed mechanism, reduces the extent of a secondary reaction (i.e., reaction (5)) in which iso-cyanic acid reacts with A.C. to form nitrogen, carbon monoxide and biurea.

TABLE 4.11

Percentage of different products of A.C. decomposed under ammonia

Gaseous Products percentage by weight of A.C.			Solid products percentage by weight of A.C.				
N_2	CO	HNCO	Biurea	Urazole	Cyanuric acid	Insoluble matter	Urea
15.3	3.2	nil	32.7	16.1	10.4	nil	-
15.0	3.0	nil	-	-	-	-	23.4

It is also observed that the percentage of urazole is greater, whereas that of biurea is less under the present experimental conditions. This may be due to the fact that the change in the experimental conditions alters the ratio of the rates at which reactions (1) and (2) take place. It is difficult to say, under the present experimental conditions, how much urea is formed originally from the A.C. because a certain amount of urea is also formed by the reaction of ammonia with the iso-cyanic acid vapour.

4.5. THE EFFECT OF AMMONIUM SALTS ON THE DECOMPOSITION PRODUCTS OF A.C.

This investigation was carried out with the object of learning whether the presence of an ammonium salt alters the components in the products obtained from pure A.C. The results of a qualitative examination of the products of A.C. and ammonium salt mixtures decomposed at 171.5°C are summarised in TABLE 4.10 It is observed that ammonium benzoate prevents the formation of cyanuric acid in the sublimate but the residue still contains cyanuric acid just as it does with pure A.C. This is most probably due to the polymerization of iso-cyanic acid vapour before it can escape into the gas phase. The trace of carbon dioxide in

TABLE 4.10

Material	Molar ratio	Temp °C	Time hours	Gaseous Products			Sublimate		Residue		
A.C. + Ammonium benzoate	1:1	171.5	8	NH_3 (traces)	CO	CO_2 traces)	Urea	-	Biurea	Urazole	Cyanuric acid
A.C. + Ammonium sulphate	1:1	171.5	8	NH_3 (traces)	CO	-	Urea	Cyanuric acid	Biurea	Urazole	Cyanuric acid
A.C. + Ammonium chloride	1:1	171.5	8	NH_3	CO	-	Urea	Cyanuric acid	Biurea	Urazole	Cyanuric acid
A.C. + $Al(NH_4).(SO_4)_2$ $12\ H_2O$	2:1	171.5	8	-	CO	CO_2	Urea	-	Biurea	Urazole	Cyanuric acid
A.C. in ammonia atmosphere	250 mm NH_3	171.5	8	NH_3	CO	-	Urea	-	Biurea	Urazole	Cyanuric acid

the gaseous products of ammonium benzoate is due to traces of moisture which react with iso-cyanic acid vapour to produce ammonia and carbon dioxide.

Ammonium chloride and ammonium sulphate have a similar effect on the decomposition products of A.C. to that of ammonium benzoate except that their sublimates contain cyanuric acid as one of the components. This could be due to the evolution of ammonia being slow owing to the fact that the decomposition temperatures of these salts are much higher than the present working temperature. The effect of hydrated aluminium ammonium sulphate can be explained in a similar manner.

PART 2

AZODICARBONAMIDE AND ACTIVATORS

PART 2

AZODICARBONAMIDE AND ACTIVATORS

CHAPTER 5

THE FUNCTION OF ACTIVATORS IN THE DECOMPOSITION OF AZODICARBONAMIDE

Azodicarbonamide (A.C.) decomposes at about 235 - 240°C when it is in a pure state. Lasman and Blackwood[14] have found that the rate of decomposition of A.C. is greatly influenced by its particle size. In general, the smaller the particles the more rapid is the decomposition rate. The industrial application of A.C. has been limited due to its high decomposition temperature. But, recently, it has been possible to reduce the decomposition temperature of A.C. with the help of different additives. These additives, commonly known as 'activators' or 'kickers', have been effective in lowering the decomposition temperature of A.C. to varying extents.

There are several types of activators in use at present but the most important ones are fatty acid salts of Group II and Group IV metals[56-59]. Most of the work on A.C. has been carried out under the industrial conditions of expanding cellular plastics. The progress of decomposition of a material is normally monitored by measuring the pressure or volume of the gaseous product formed as a function of time at a constant temperature. But in industry the measurement of apparent density of an expanded foam affords a convenient means for measuring the extent of decomposition of the blowing agent[14]. An apparent density may be measured as a function of time at a constant

temperature or as a function of temperature with a constant heating rate. Nass[60] has investigated the thermal decomposition of A.C. in the presence of the octoates, stearates, iso-butyl benzoates and phthalates of cadmium, lead, zinc and barium by this method. The results with the octoates of the four metals are shown in FIGURE 5.1.

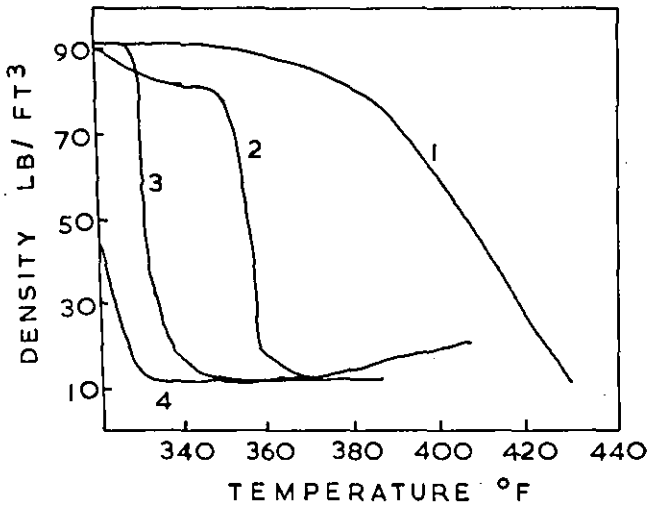
A sharp decrease in the density represents an approximate decomposition temperature. It is observed that the cadmium octoate is the most effective and that the barium octoate is the least. In the same investigation a comparative study of the 2-ethylhexanoates of different metals showed that barium 2-ethylhexanoate did not exert any marked influence on the decomposition of A.C. These results indicated that barium salts may act as retarders for A.C. functioning in such a way as to stabilize the blowing agent at its normal decomposition temperature.

The mechanism of the catalytic decomposition of A.C. in the presence of metallic salts is not yet clear. It is known that A.C. undergoes hydrolysis in cold aqueous sodium hydroxide to yield sodium azo-dicarboxylate[61]:

$$NH_2.\ CO.\ N{:}N.\ CO.\ NH_2 + 2\ NaOH \longrightarrow NaOOCN{:}NCOONa + 2\ NH_3$$

The latter decomposes in hot water to yield sodium carbonate and hydrazine[14]. Sodium azodicarboxylate also precipitates the insoluble and unstable lead, cadmium and zinc azodicarboxylates when treated with appropriate solutions of the salts of these metals. The azodicarboxylates of lead, cadmium and zinc decompose at once with rapid gas evolution. Nass[60], therefore, suggested that the activating effect by these metals in vinyl foam systems proceeds via the formation of the intermediate metallic azodicarboxylate which is less stable than A.C. The inertness or retarding effect of barium salts can be

VARIATION IN THE DENSITY OF FOAM EXPANDED BY AZODICARBONAMIDE IN PRESENCE OF DIFFERENT OCTOATES



(1) BARIUM OCTOATE (2) ZINC OCTOATE
(3) LEAD OCTOATE (4) CADMIUM OCTOATE

FIGURE 5.1

explained by the same hypothesis. Barium azodicarboxylate does not decompose immediately but instead is stable to such an extent that temperatures in excess of 450°C are necessary to cause this salt to yield gas. This explanation for the activation of A.C. by metallic salts assumes that A.C. in a vinyl foam system first undergoes alkaline hydrolysis. This is theoretically possible since the metallic 'stabilizers' (materials used for the protection of the polymers against thermal degradation[61]) normally employed in expanding the plastics are slightly alkaline. But this theory fails to explain the activation of A.C. by metallic salts in the absence of 'stabilizers'.

A comparative study of the catalytic action of lead, cadmium and zinc octoates in the decomposition of A.C. has also been carried out by Lally and Alter[62]. They have found that lead initiates the decomposition at a lower temperature than zinc, while cadmium activates at lower temperature than either lead or zinc. Their investigations were also carried out in the presence of polymeric material so it is difficult to say whether the results were completely free from the influence of other materials present. However, the observations agreed well with the findings of Nass[60].

The metallic stearates have been used widely as activators for decreasing the decomposition temperature of A.C.[63,64]. TABLE 5.1 shows the effect of calcium, barium and lead stearates on the decomposition temperature of A.C. when they are added in different proportions.

It is observed that out of the three stearates studied lead stearate is most effective in decreasing the decomposition temperature of A.C.

TABLE 5.1.

The effect of metallic stearates on the decomposition temperature of A.C.

Addition by weight of A.C. %	Decomposition Temperature °C		
	Calcium Stearate	Barium Stearate	Lead Stearate
3	205	175	160
2	215	185	170
1	225	190	180

It has been found that inorganic salts also affect the decomposition temperature of A.C. but they are comparatively less effective than the salts of organic acids. Metallic chromates and dichromates, for example, decrease the decomposition temperature of A.C. only by 5 to 10°C. The effects of metallic chromates and dichromates on the decomposition temperature of A.C. are shown in TABLE 5.2.

TABLE 5.2

The effects of metallic chromates and dichromates on the decomposition temperature of A.C.[65]

Cations	Decomposition Temperature °C	
	Chromate	Dichromate
Sodium	194.1	193.1
Potassium	191.3	192.1
Ammonium	195.0	194.5
Calcium	196.3	195.8
Barium	192.7	194.9
Lead	194.6	196.1
A.C. (alone)	201.5 201.1	

It is observed that altering the cation causes very little difference in the decomposition temperature. In the same investigation it was also found that the decrease in the decomposition temperature of A.C. is a function of the amount of additive. FIGURE 5.2 shows the effect of a variation in the amount of the potassium dichromate addition on the decomposition temperature of A.C. It is noticed that beyond a certain level of addition of potassium dichromate, there is no further decrease in the decomposition temperature.

With the present uncertain knowledge of the mechanism for the catalytic decomposition of A.C. it is not known whether only the metal ions are responsible for decreasing the decomposition temperature or whether the anions also take part in the catalytic activity. Lally and Alter[62], who studied the role of activators in expanding p.v.c. with A.C., observed that the activator performance is influenced by the anion structure and the acidity of the activator. They also found that the rate of decomposition of A.C. is increased by an increase in the activator concentration.

It is interesting to note that several organic compounds such as urea[6], monophenyl urea[66], biurea[67] and glycols[6] have also been used in catalysing the decomposition reaction of A.C. Owing to the large variety of activators being used, each to varying degrees of success, it is difficult to say whether a single type of chemical reaction such as the one proposed by Nass[60] is occurring in the catalytic decomposition of A.C.

In the present investigation it was decided to investigate the effect of comparatively less complex compounds such as metal oxides, on the decomposition reaction of A.C. The study was later extended to

EFFECT OF POTASSIUM DICHROMATE ON THE DECOMPOSITION TEMPERATURE OF A.C.

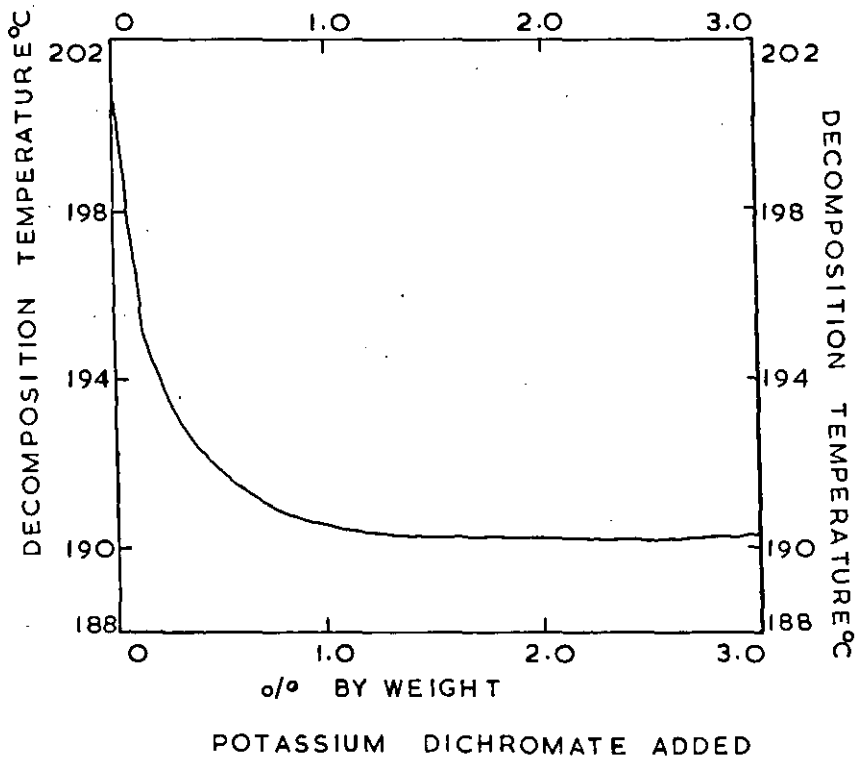


FIGURE 5.2

the other type of compounds commonly used as activators.

THE THEORY OF CATALYTIC ACTIVITY OF METAL OXIDES

One of the most important factors in the catalytic behaviour of metal oxides is the electronic factor associated with crystal defects. On this basis oxides are classified into two groups:-

(i) Semiconductor oxides

(ii) Insulator oxides

The semiconductor oxides are again divided into two parts, n-type and p-type. Both originate from a non-stoichiometric defect of the compound. A non-stoichiometric compound is a solid in which there is an excess or a deficiency of one component of the ions present (found by chemical analysis)[68]. Some non stoichiometric compounds display only a very small departure from the stoichiometric composition, others exhibit marked departures, but in all of them the number of atoms of one component to the number of atoms of the other component does not correspond exactly to the whole number ratio expressed by the formula.

A good example of a n-type semiconductor is zinc oxide. It often contains excess metal incorporated as interstitial zinc ions and the electrons removed through ionization remain close to the excess (defect) metal. Crystals containing such defects show semiconducting properties since the loosely bonded electrons may be readily promoted to the conduction band of the solid where migration through the lattice is possible. The impurity atom generates a local electron accommodating level somewhat below the conduction band and an electron may be readily promoted from this level to give conducting properties in the solid. This is called an n-type semiconductor, since the negative

electron, on promotion to the conduction band, is the normal current carrying species.

The p-type semiconductor oxides on the other hand depart from stoichiometry through metal ion vacancies. Nickel oxide is an example of this type of semiconductor. The nickel ion vacancy due to non-stoichiometry results in the formation of two Ni^{3+} ions to preserve the electrical neutrality. In this type of solid each defect provides an unoccupied impurity level at an energy just greater than the upper limit of the valence band and to which an electron may be promoted with reduction of the defect in charge:-

$$Ni^{3+} + e^{-} \longrightarrow Ni^{2+}$$

A vacancy in the valence band is thus generated. Such a gap is known as 'positive hole' and the migration of a positive hole in one direction is equivalent to the migration of an electron in the opposite direction. The positive-hole migration results in p-type semiconductivity.

The insulator type of oxides such as barium oxide and magnesium oxide do not exhibit catalytic activity (from an electronic point of view) so they are not discussed here.

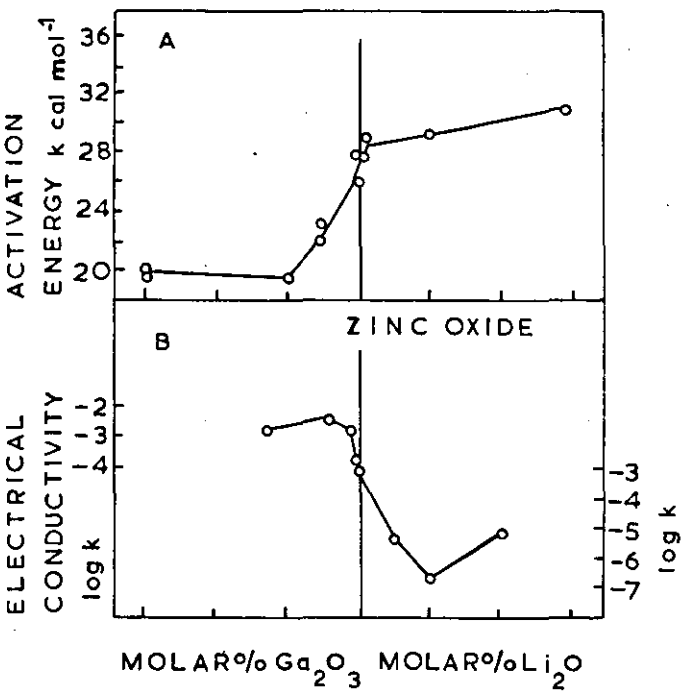
In a large number of reactions the catalytic activation consists in a transfer of electrons from the molecule to the catalyst or vice versa. As a first approximation reactions may be divided into two groups. The first group consists of donor reactions, in which the electrons must be transferred to the catalyst, and the second group of acceptor reactions involving molecules with high electron affinities such as O_2 or H_2O_2. Thus, the semiconducting property of an oxide is

related to its catalytic activity by the observation that p-type oxides catalyse the former group and n-type the latter one. This theory has been further strengthened by the experiments carried out by Schwab[69] with 'doped' (i.e. the deliberate addition of small amounts of cations of valency different from that of the cations of the host lattice[68]) oxides. The p and n character of an oxide can be altered by doping and thus the catalytic efficiency varied. The influence of the addition of altervalent ions on the conductivity of zinc oxide and on the activation energy of the oxidation of carbon monoxide is shown in FIGURE 5.3. The addition of lithium ions causes a decrease in the number of free electrons and hence a decrease in conductivity of the n-type semiconductor, whereas the addition of tervalent gallium ions increases the conductivity by increasing the number of free electrons. It can be seen that the activation energy of the catalytic reaction increases as the concentration of added lithium ions decreases and that the addition of gallium causes a marked decrease in the activation energy. These observations are consistent with the conclusion that the catalytic oxidation of carbon monoxide over zinc oxide involves the chemisorption of oxygen as the slow step. As oxygen is an electron acceptor, the greater the supply of electrons at the surface of the semiconductor, the easier will be the formation of the surface oxygen ions and hence the lower the activation energy of the catalysed reaction.

In spite of several examples available it is difficult to say whether a simple relation does exist between the semiconducting property and catalytic activity of an oxide. In the first place, evidence has come to light[68] which strongly suggests that the precise

EFFECT OF DOPING ZINC OXIDE WITH THE OXIDES OF LITHIUM AND GALLIUM

(A) ACTIVATION ENERGY FOR THE OXIDATION OF CARBON DIOXIDE



(B) ELECTRICAL CONDUCTIVITY FOR ZINC OXIDE DOPED WITH OXIDES OF GALLIUM AND LITHIUM[69]

FIGURE 5.3

degree of the semiconductivity of a metal oxide may differ considerably in the bulk phase from that prevailing at the surface. Secondly, much remains to be learned about the nature of the defects. For example[70], the extent of the localization of the holes and electrons, and the tendency of individual point defects to interact with one another, needs to be investigated. The third difficulty is that too much attention has been paid to the number or concentration of positive holes and other point defects but very little attention has been given to the mobility of the defects[68].

CHAPTER 6

THE INFLUENCE OF ZINC OXIDE ON THE DECOMPOSITION TEMPERATURE OF AZODICARBONAMIDE

Zinc oxide either alone or in combination with the other materials has been used extensively as an activator for decreasing the decomposition temperature of azodicarbonamide (A.C.)[6]. A temperature as low as 140 - 150°C has been achieved with the addition of zinc oxide, while the decomposition temperature of pure A.C. is about 235-240°C. Owing to the lack of information regarding the reaction between pure A.C. and zinc oxide the mechanism of the catalytic behaviour of the latter is not known. It is not even known whether the activation of A.C. by zinc oxide takes place via a chemical process such as the one suggested by Nass[60] (CHAPTER 5) for the fatty acid salts of Group II and Group IV metals.

The present work shows the effect of zinc oxide on the decomposition temperature of A.C. In order to learn about the decomposition of A.C. in the presence of zinc oxide, no other additive has been used in the reaction system. The effects of grinding and compressing the two particles together on the decomposition temperature have been studied. Information regarding the effect of grinding on the physical state of the particles has been obtained from electron micrographs. Finally, a complete chemical analysis of the solid and gaseous products of an A.C. and zinc oxide mixture has been carried out to learn whether a significant quantity of zinc oxide is chemically involved in the activation of A.C.

EXPERIMENTAL

THE MATERIALS

(i) Zinc Oxide

The zinc oxide used in this investigation was 'Analytical Reagents' quality supplied by Fisons Industrial Chemicals, Loughborough. The material was dried over a bunsen burner (~ 400-500°C) for one hour and cooled to room temperature in a silicagel desiccator before it was mixed with A.C.

(ii) Azodicarbonamide

The purified sample of A.C. used in this investigation was the same as that used in the previous experiments (see CHAPTER 3).

THE PREPARATION OF MIXTURES

Two different methods were used for preparing the mixtures.

(i) Ground mixture

The A.C. and zinc oxide were weighed into a ball-mill mortar and vibrated for different lengths of time. The same vibrator speed was used for preparing all the mixtures.

The mixture of A.C. and zinc oxide used for the complete quantitative analysis of the products was ground for two hours.

(ii) Unground mixture

Known quantities of dried zinc oxide and A.C. were suspended in dry chloroform (2% w/v) and stirred at room temperature with a magnetic stirrer for one hour. The chloroform was then removed on a rotary

evaporator, the temperature being kept below 40°C. This procedure produced good mixing with minimum change in particle size.

THE PREPARATION OF A DISC

The mixture of zinc oxide and A.C. was transferred into a thick walled steel die. The pressure was applied to a constant level with a hydraulic press for a certain length of time, with the die under vacuum.

A small portion of the disc was used for the determination of the decomposition temperature each time.

THE DETERMINATION OF THE DECOMPOSITION TEMPERATURE

The decomposition temperature was determined with a DU-PONT 900 Differential Thermal Analyzer. The peak maximum of the thermogram was taken as the decomposition temperature. The heating rate was 15°C per minute up to 140°C and then was reduced to 5°C per minute. The heating rate was kept constant and the sample size was maintained at 5 - 6 mg throughout the investigation.

THE ANALYSIS OF THE DECOMPOSITION PRODUCTS

The mixture of A.C. and zinc oxide in the ratio 4:1 (w/w) prepared by grinding was decomposed in an evacuated tube as described earlier (CHAPTER 3). A preliminary analysis of the solid products was carried out with the thin-layer chromatographic technique and the gaseous products were examined by infra-red spectroscopy.

The technique used for the quantitative analysis of the solid products of pure A.C. (CHAPTER 3) was slightly modified for the analysis of the solid products of the A.C. and zinc oxide mixture. The aqueous extract of the solid products contained suspended zinc oxide which was extremely difficult to filter. The extract, therefore, was centrifuged and the clear liquid filtered through Whatman 542 filter paper. The insoluble residue was washed several times with warm water, the washings centrifuged and the clear liquid filtered. The filtrate and the washings were mixed together and diluted to a constant volume. This combined solution was then used to determine the water soluble components as described earlier (CHAPTER 3).

The insoluble residue was dissolved in 4 N hydrochloric acid (5 - 7 ml), filtered and the insoluble portion washed. The solution was neutralized to pH 7 with 4 N sodium hydroxide solution.

The determination of Zn^{++} was carried out in both the above solutions by titrating with 0.01 M E.D.T.A. solution using Eriochrome-black-T as indicator[71].

RESULTS AND DISCUSSION

TABLE 6.1 shows the decomposition temperatures of pure A.C. and mixtures of A.C. and zinc oxide

TABLE 6.1

The decomposition temperatures of A.C. and (A.C. + ZnO) mixtures

Sample	Ratio (w/w)	Decomposition temperature ^{o}C
A.C. unground	-	237
A.C. ground for 12 hours	-	236
*A.C. unground + ZnO	4:1	224
*A.C. ground for 12 hours + ZnO	4:1	212

* The two components were mixed without grinding (see EXPERIMENTAL)

The observed decomposition temperature of 237°C for pure unground A.C. is very close to the reported decomposition temperature. The decomposition temperature, however, does not change significantly on grinding for 12 hours in a ball mill. When the unground A.C. is mixed with zinc oxide in a 4:1 ratio without grinding the decomposition temperature is decreased by about 13°C. There is a further decrease of about 12°C when a ground sample of A.C. is mixed with zinc oxide in the same way. The only difference existing between the two mixtures is the difference in the particle size of the A.C. The ground A.C. having a larger surface area increases the interfacial contact area with the zinc oxide. Thus, it is evident that the decomposition temperature of the mixture is dependent on the interfacial contact area of the two particles.

The grinding of A.C. and zinc oxide together has a more dramatic effect on the decomposition temperature than mixing a preground sample of A.C. with zinc oxide. TABLE 6.2 shows the variation in the decomposition temperature of mixtures of zinc oxide and A.C. with grinding time.

TABLE 6.2

The effect of grinding time and percentage of zinc oxide on the decomposition temperature of A.C. and zinc oxide mixtures

2 hours grinding		4 hours grinding		8 hours grinding	
% ZnO	Decomposition temperature °C	% ZnO	Decomposition temperature °C	% ZnO	Decomposition temperature °C
0	237	0	233	0	238
5	223	8	211	10	177
10	217	12	201	20	176
20	198	20	188	30	174
30	194	30	181	50	167
50	187	50	171		

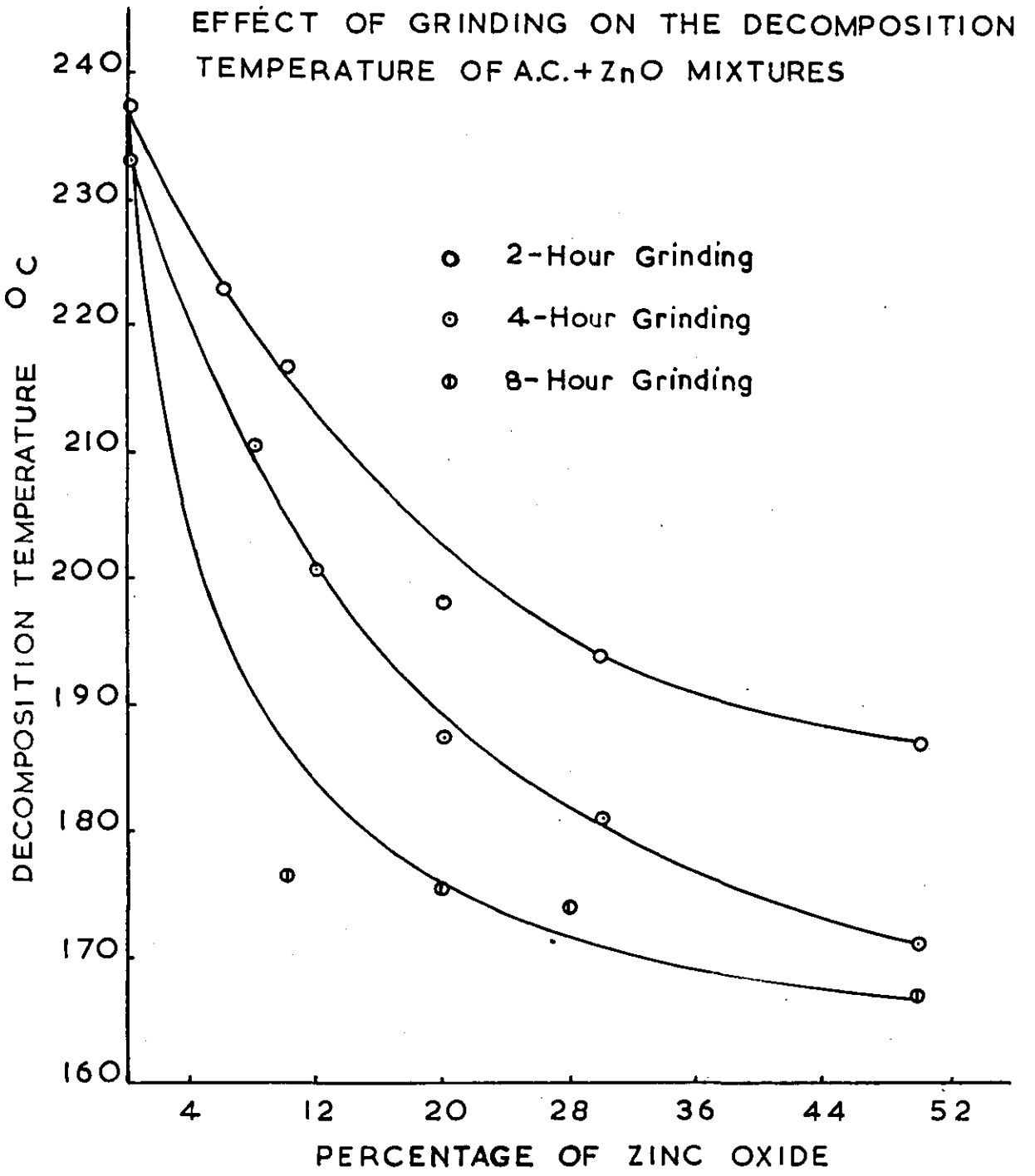
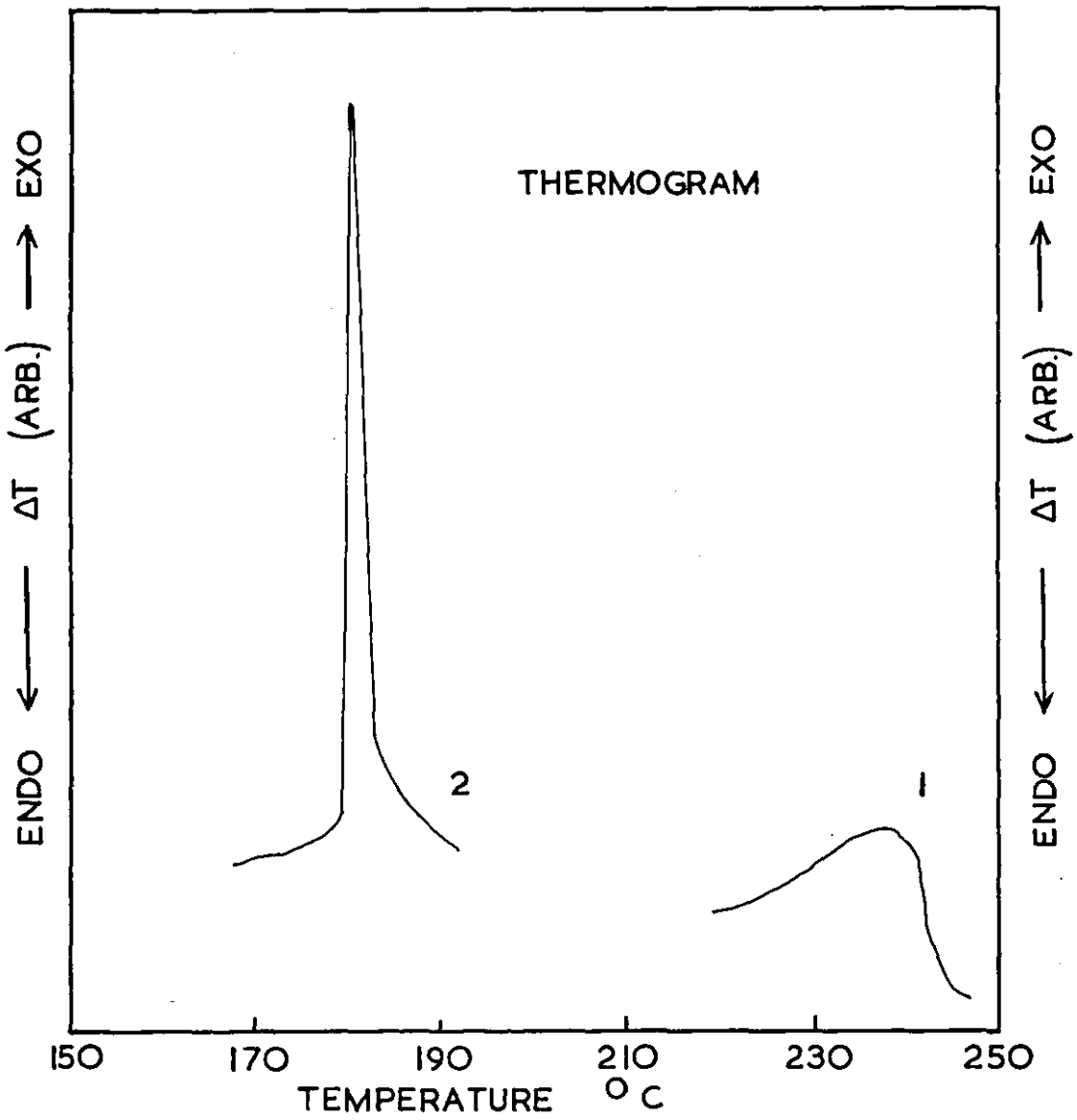

EFFECT OF GRINDING ON THE DECOMPOSITION TEMPERATURE OF A.C.+ZnO MIXTURES
240
230
220
210
200
190
180
170
160
DECOMPOSITION TEMPERATURE °C
2-Hour Grinding
4-Hour Grinding
8-Hour Grinding
4
12
20
28
36
44
52
PERCENTAGE OF ZINC OXIDE

FIGURE 6.1

It is noticed that the decrease in the decomposition temperature depends on the degree of grinding. The decomposition temperature also depends on the proportion of zinc oxide but above the 30% level the change is not significant (see FIGURE 6.1).

It is observed that the shape of the thermogram of pure A.C. is quite different from that of its mixture with zinc oxide when both thermograms are recorded under similar conditions (FIGURE 6.2). The former has a broad exothermic thermogram whereas the latter gives a very sharp single peak thermogram as though an explosion has occurred.

The marked effect of zinc oxide on the decomposition temperature of A.C., particularly when the two solids are ground together, is difficult to explain. To learn more about the effect of grinding on the physical state of the particles, electronmicrographs of the ground and unground mixtures as well as of pure A.C. were taken. The three electronmicrographs are shown in FIGURES 6.3A and 6.3B. The micrograph of pure A.C. shows that the material is crystalline (the cracks appeared as a result of the adverse effect on A.C. of the conditions under which the micrographs were produced). The ground mixture of A.C. and zinc oxide shows that the particles are very fine and that they are close to each other. In fact, it is difficult to identify the two materials in the micrograph. In the unground mixture the zinc oxide particles being smaller in size are sitting on the larger A.C. particles. The A.C. particles, in this case, are not completely covered with zinc oxide particles. It is clear, therefore, that the ground and unground mixtures differ in interfacial contact area. The former has a better interfacial contact area than the latter. It would appear, therefore, that the cause of the more effective kick-



1. A.C. 2. A.C. + ZnO (7:3) – GROUND FOR 4 HOURS

FIGURE 6.2

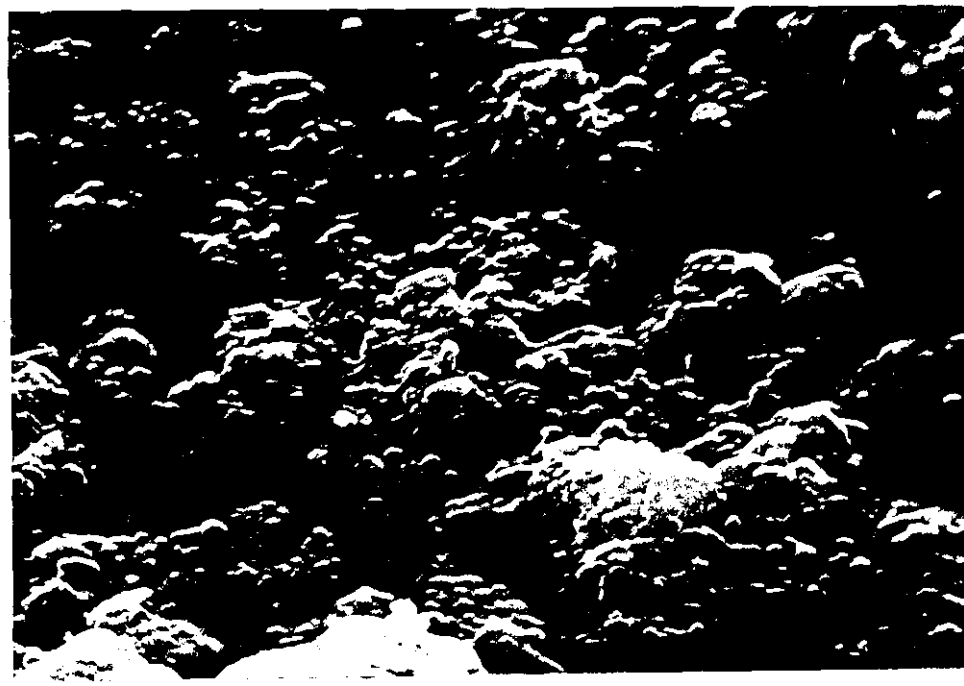
ELECTRONMICROGRAPH

AZODICARBONAMIDE (A.C.)

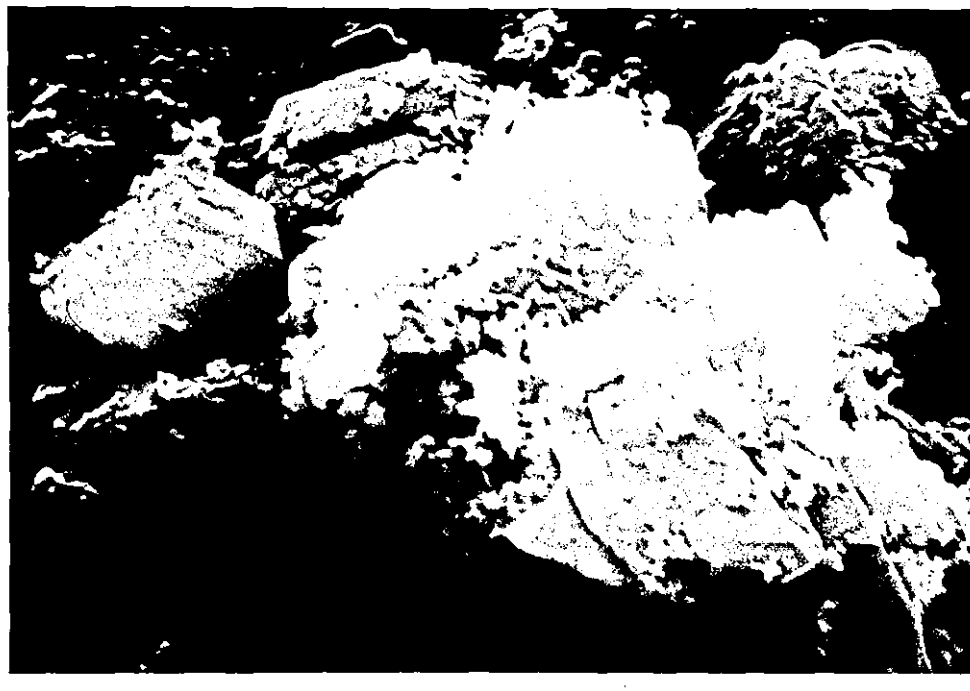
magnification 4500

FIGURE 6.3A

ELECTRONMICROGRAPHS



A.C. + ZnO Ground



A.C.+ ZnO Unground

magnifications same as 6.3A

FIGURE 6.3B

-ing observed in the ground mixture is the better interfacial contact between the two solids resulting from the grinding.

The effect of increased interfacial contact in lowering the decomposition temperature was further confirmed by compressing the A.C. and zinc oxide particles together in the form of a disc. The results of this exercise are summarized in TABLE 6.3.

TABLE 6.3

Effect of compression on the decomposition temperature of A.C. and zinc oxide mixtures

Sample	Ratio	Pressure tons/in^2	Time min	Decomposition temperature ^{o}C
A.C. + ZnO Unground	4:1	Unpressed	-	225
A.C. + ZnO Unground	4:1	16	5	209
A.C. + ZnO Ground	4:1	16	5	161
A.C. + ZnO Unground	4:1	32	5	171
A.C. Ground	-	16	5	229

When the particles are unground the decomposition temperature decreases by 16^{o}C and there is a further decrease of about 38^{o}C, when the pressure is increased to 32 tons/in^2. Although the ground mixture has a decomposition temperature of 176^{o}C (TABLE 6.2), the compression decreases this further by about 15^{o}C. It seems that the decrease in the decomposition temperature is also dependent on the compactness of the two particles.

The evidence suggests that the effectiveness of zinc oxide in decreasing the decomposition temperature of A.C. is dependent upon the degree of grinding and the extent of compression of the two solids. The question remains whether the zinc oxide takes part chemically in catalysing the decomposition reaction of A.C. In an attempt to answer

this, it was decided to analyse the solid and gaseous products obtained on decomposing a mixture of A.C. and zinc oxide.

The qualitative analysis of the solid products by thin-layer chromatography and the gaseous products by infra-red spectroscopy showed the presence of the same components as were found when A.C. was decomposed alone (CHAPTER 4). The results of a quantitative analysis of the components of A.C. and zinc oxide (4:1) mixture are shown in TABLE 6.4.

TABLE 6.4

Products of an A.C. and ZnO mixture decomposed at 171.5 °C for 8 hours

Gaseous products % by weight of A.C.			Solid products % by weight of A.C.					
N_2	CO	HNCO	Biurea	Urazole	Cyanuric acid	Urea	ZnO as Zn^{++}	ZnO unchanged
15.4	2.8	3.3	37.2	13.7	11.2	-	1.9	18.1
15.1	2.7	2.7	-	-	-	5.4	-	-

The percentages of the products are very similar to those obtained from pure A.C., except that there is a decrease in the percentage of carbon monoxide. This may be due to the variation in the proportions of the reactions (1), (2) and (5) in the mechanism proposed for the decomposition of A.C. alone (CHAPTER 4). A slight amount of Zn^{++} (represented as ZnO) is found in the solid products. This is, presumably, due to the formation of traces of zinc iso-cyanate. From the results it appears that the zinc oxide does not take part chemically in any major reaction occurring during the decomposition of the mixture under the conditions employed.

From the information available it seems that the decrease in the decomposition temperature of A.C. in the presence of zinc oxide is due to a surface reaction taking place between the two solids. The bulk of the zinc oxide remains unchanged. The explosion phenomenon is difficult to explain but it is possible that initially an exothermic surface reaction takes place between A.C. and zinc oxide. The rate of production of heat is greater than the rate of loss to the surroundings by conduction and convection, and this causes the self heating of the solid which accelerates the reaction to an explosion. If this is so, then one would expect the decomposition of the mixture to occur in two steps, the first involving the surface reaction and the second the normal decomposition of A.C. The thermogram of the A.C. and ZnO mixture, however, does not indicate that the reaction is occurring in two steps. It is likely that the present experimental conditions are unsuitable for the resolution of the two peaks expected from two separate steps. Isothermal decomposition at low temperatures, however, might provide more suitable conditions with which to demonstrate a two step process and confirm the tentative conclusions of this chapter.

CHAPTER 7

THE CATALYTIC DECOMPOSITION OF AZODICARBONAMIDE IN THE PRESENCE OF METAL OXIDES

It has been found both in the present investigation and in the work carried out in industry for expanding plastics[6] that zinc oxide decreases the decomposition temperature of azodicarbonamide (A.C.). Aleseenko and Denisenko[72] have studied the kinetics of gas evolution during the decomposition of A.C. with the dosage of zinc oxide in various proportions. Their results show that the plot of gaseous volume as a function of time has a similar shape to that obtained from A.C. alone. In this investigation no particular attention was paid to the degree of mixing which, as was shown in the previous chapter, does have a great influence on the decomposition temperature. In addition, the investigation provided practically no information regarding the mechanism of the catalysis.

Takahashi and Tsutsumi[73] have studied the effect of mechanical treatment on the physical properties of zinc oxide. They have found that the primary particles of zinc oxide on progressive grinding aggregate and this is accompanied by a growth of secondary particles. The sensitivity of the zinc oxide to mechanical treatment depends on its origin. In the same investigation it has also been pointed out that the catalytic activity of zinc oxide is closely related to the primary structural change and the lattice distortion caused by mechanical treatment.

In this investigation the isothermal decomposition of mixtures of A.C. and metal oxides has been studied by measuring the pressure

of the gaseous product as a function of time. Particular attention has been paid to the influence of temperature and the extent of grinding on the decomposition rate. It was hoped that the information obtained would provide a better understanding of the role the metal oxides play in catalysing the decomposition reaction of A.C.

EXPERIMENTAL

The Materials

The sample of zinc oxide used in this investigation was treated in a similar manner to that described in CHAPTER 6. Lead oxide (PbO), cadmium oxide, magnesium oxide and barium oxide were Laboratory Reagent grade which were dried in a similar manner to zinc oxide.

The sample of A.C. was the same as that used in the previous experiments.

Preparation of the mixtures

The ground mixtures of A.C. with different oxides were prepared by grinding the two solids together as described in CHAPTER 6.

The unground mixture was prepared by suspending the two solids in dry chloroform as described in the same chapter.

Preparation of the pre-heated samples

The mixture of A.C. and zinc oxide was heated at 144.5^{o}C for 2.5 hours in an evacuated decomposition tube. The mixture was

divided into two parts. The first part was used for the decomposition at 180°C. The second part was reground for two hours and then the decomposition was carried out at the same higher temperature.

The pre-heated mixture of A.C. and cadmium oxide was prepared by heating a mixture of the two solids in an evacuated decomposition tube for two hours at 144.5°C. The tube was removed from the bath and cooled to room temperature. Care was taken to avoid the production of fresh surfaces during handling. The decomposition was carried out at 171.5°C.

The decomposition procedure and the measurement of gaseous pressure

The apparatus consisted of a 50 ml quick-fit boiling tube, the top portion of which was connected via a cold trap to a U-tube mercury manometer sealed at one end and to a vacuum pump. The apparatus was similar to the one shown in FIGURE 7.1. The pump, manometer and the decomposition tube were separated by two stop-cocks.

The sample was weighed into the decomposition tube and connected to the rest of the apparatus with a ground glass joint sealed with picein wax. The apparatus was evacuated to less than 0.1 mm mercury pressure and the trap was cooled with liquid nitrogen. After closing off the pump the decomposition tube was immersed in a constant temperature oil bath and the stop-watch was switched on. The rise in pressure was measured at different intervals of time.

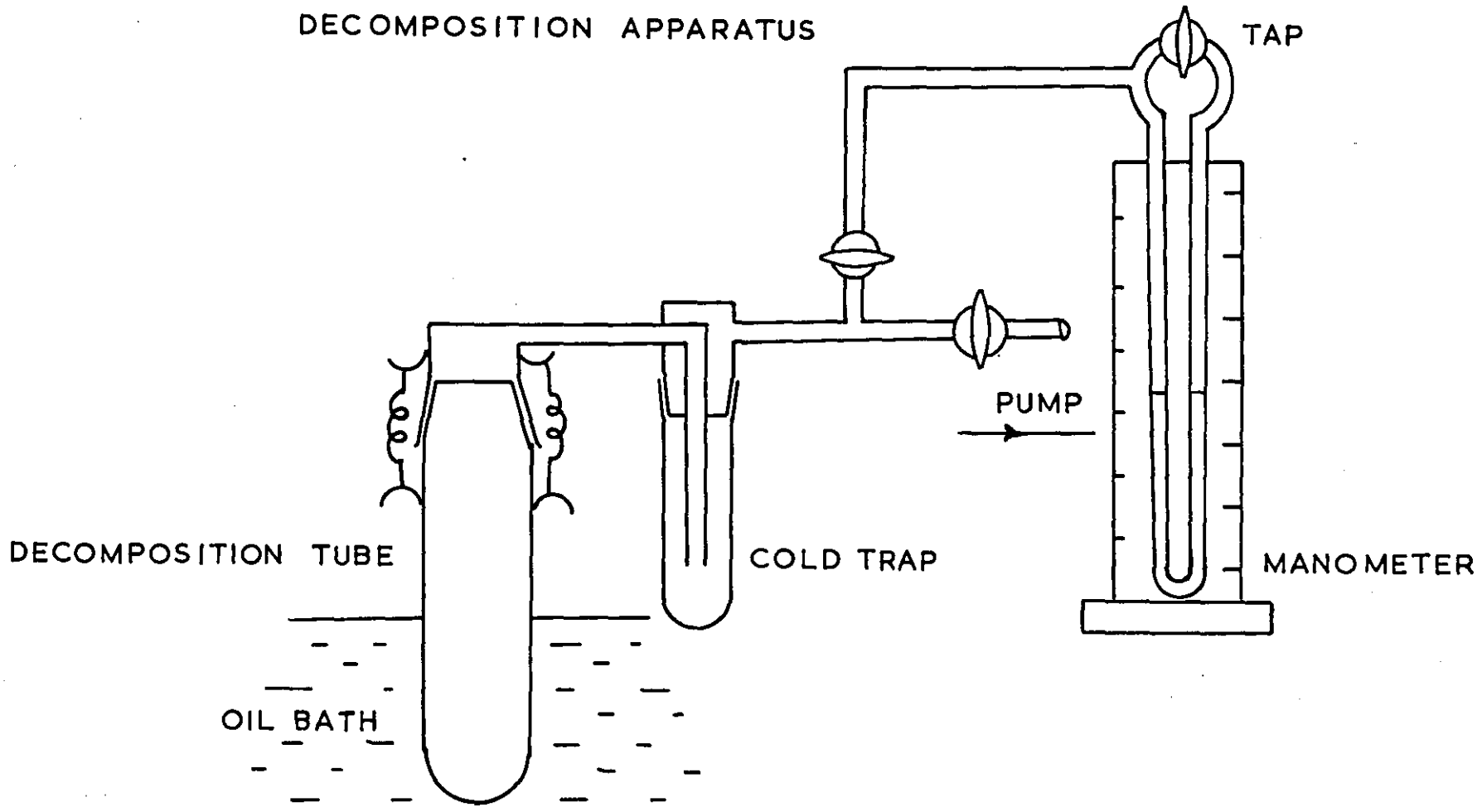

DECOMPOSITION APPARATUS
TAP
PUMP
DECOMPOSITION TUBE
COLD TRAP
MANOMETER
OIL BATH

FIGURE 7.1

The weight of the sample was kept constant (232 mg) in each experiment with pure A.C. In the case of A.C. and metal oxide mixtures an amount of the mixture was taken such as to contain the same amount of A.C. as that used with A.C. on its own.

Method of investigating the first stage of the reaction

The apparatus used in this experiment is shown in FIGURE 7.1. It was very similar to that described for the study of the complete decomposition, except that the mercury manometer was replaced with a n-butylphthalate manometer of slightly different design, to achieve a better accuracy in the measurement of pressure.

The procedure for the decomposition and the measurement of pressure were the same as described before.

The mixtures were prepared by grinding the two solids in a ball mill for a known length of time.

RESULTS AND INTERPRETATIONS

7.1. THE INFLUENCE OF ZINC OXIDE

Plots of pressure as a function of time for the isothermal decomposition of A.C. and for that of mixtures of A.C. and zinc oxide (4 : 1) are shown in FIGURE 7.2. The A.C. was ground with zinc oxide for eight hours. To check the reproducibility of the grinding and of the experimental result in general duplicate runs were carried out. These are shown in the FIGURE 7.2 and can be seen to agree closely.

A.C. has a sigmoid shaped curve similar to those reported by the other workers[10,72]. The mixture of A.C. with zinc oxide exhibits an initial steep curve corresponding to a rapid process which is then

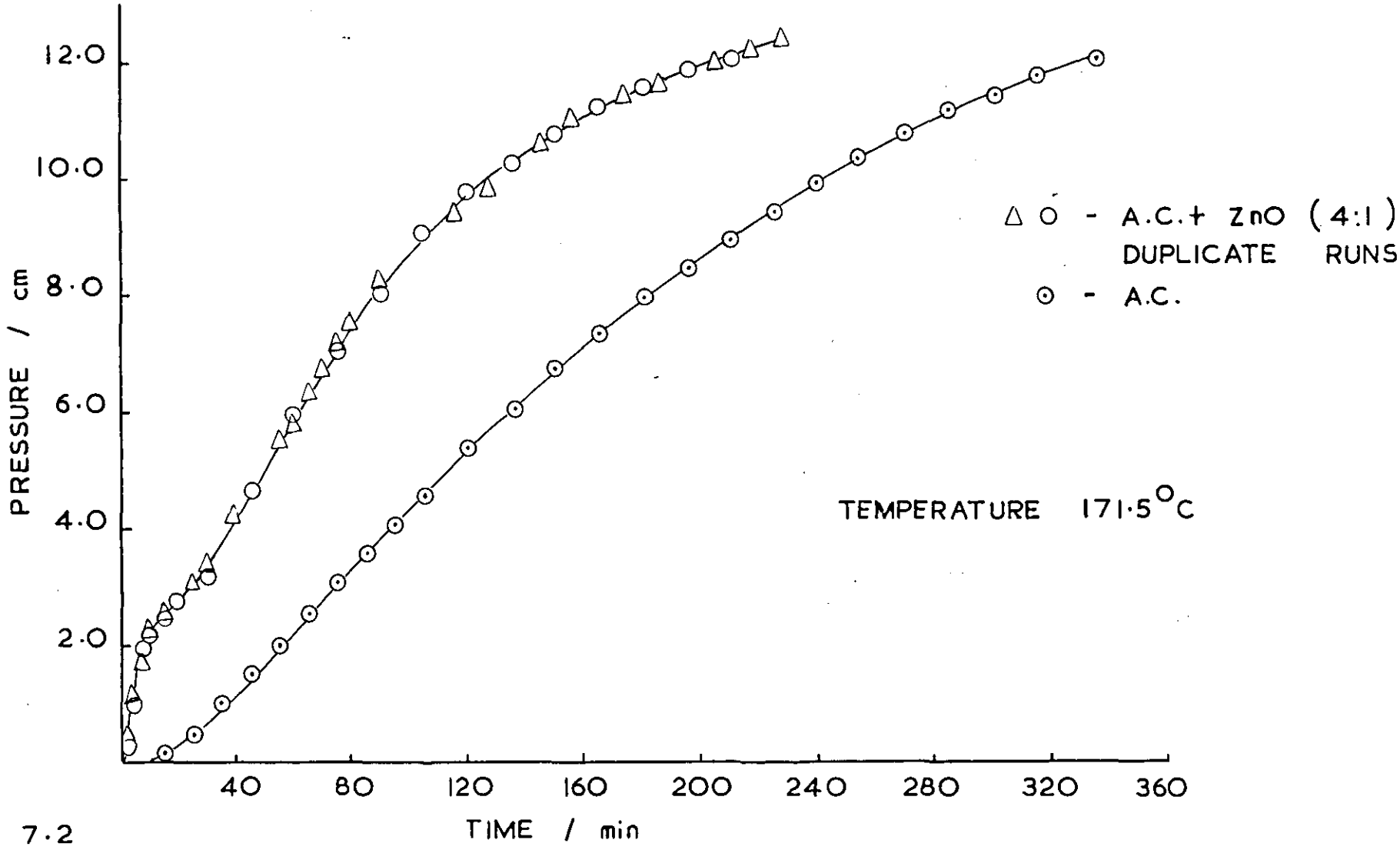

ISOTHERMAL DECOMPOSITION OF A.C. AND
A.C. + ZnO MIXTURES
PRESSURE / cm
12·0
10·0
8·0
6·0
4·0
2·0
40
80
120
160
200
240
280
320
360
TIME / min
△ ○ - A.C.+ ZnO (4:1)
DUPLICATE RUNS
⊙ - A.C.
TEMPERATURE 171·5°C

FIGURE 7·2

followed by a more gentle curve similar to that obtained from pure A.C. It appears that the mixture decomposes in two steps, the initial step representing about 10% of the decomposition.

It is found that neither with A.C., nor with the mixture does the pressure become constant even after prolonged heating. This behaviour was also observed by Swann[10] in the study of the isothermal decomposition of A.C., both by thermogravimetric and gaseous volume measurement methods. In the former, no constant weight was obtained, and in the latter the gaseous volume never reached a constant level even after prolonged heating. This behaviour may be either because a certain portion of the A.C. is still undecomposed, or because one of the solid products is decomposing slowly. Owing to the difficulties in assessing the final pressure, an accurate determination of the extent of decomposition at a given time is not possible and therefore a detailed analysis of the kinetic data cannot be made.

The effects of two factors on the pressure time plot for the isothermal decompositions of A.C. and zinc oxide mixtures have been studied.

(i) The effect of grinding

FIGURE 7.3 shows a plot of the gaseous pressure as a function of time when a 4:1 mixture of A.C.and zinc oxide, ground for different lengths of time, is decomposed at 171.5°C. It is observed that the first stage of the decomposition reaction is greatly influenced by the length of grinding time. As the grinding time increases the first step constitutes a higher percentage of decomposition.

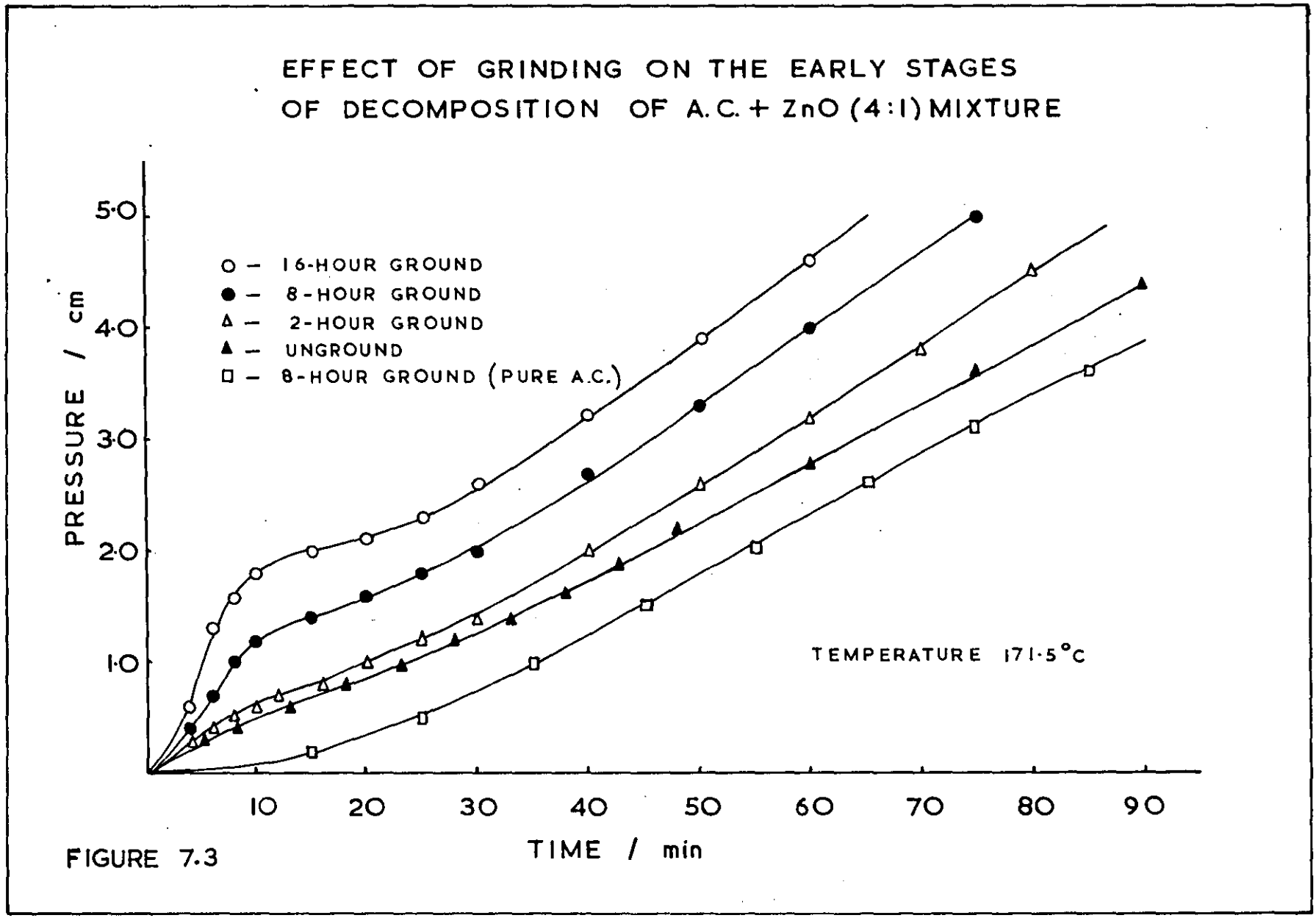

EFFECT OF GRINDING ON THE EARLY STAGES
OF DECOMPOSITION OF A.C. + ZnO (4:1) MIXTURE
PRESSURE / cm
5·0
4·0
3·0
2·0
1·0
O — 16-HOUR GROUND
● — 8-HOUR GROUND
Δ — 2-HOUR GROUND
▲ — UNGROUND
□ — 8-HOUR GROUND (PURE A.C.)
TEMPERATURE 171·5°C
10
20
30
40
50
60
70
80
90
TIME / min

FIGURE 7.3

The curve with the unground mixture shows very little sign of the reaction taking place in two steps. It appears that the first step is a surface reaction because more grinding almost certainly results in a greater interfacial contact area between the A.C. and zinc oxide particles. It is difficult to compare quantitatively the different percentages constituting the first step of the reaction resulting from different lengths of grinding because the termination of the first step and the start of the second are not sharply defined.

(ii) The effect of temperature

A plot of the gaseous pressure as a function of time during the isothermal decomposition of the same 4:1 mixture of A.C. and zinc oxide is shown in FIGURE 7.4. The rate of the first step of the decomposition increases with temperature and at 180°C the rate is too fast to be measured and behaves as though an explosion has occurred. This behaviour resembles that observed during the determination of the decomposition temperature of the ground mixture of A.C. and zinc oxide (CHAPTER 6). At 180°C the reaction is so violent that it is impossible to say whether it occurs in two steps. The curve at 171.5°C shows an intermediate rate of decomposition in which the two steps are clearly defined.

For comparison, the initial stages of the decomposition of pure A.C. have been investigated under the same conditions. The results are shown in FIGURE 7.5. The induction period, in this case, decreases as the temperature increases but there is no indication that the decomposition occurs in two steps. Furthermore, there is no explosive type of fast reaction at 180°C as is

EFFECT OF TEMPERATURE ON THE EARLY STAGES OF DECOMPOSITION OF A.C. + ZnO (4:1) MIXTURE

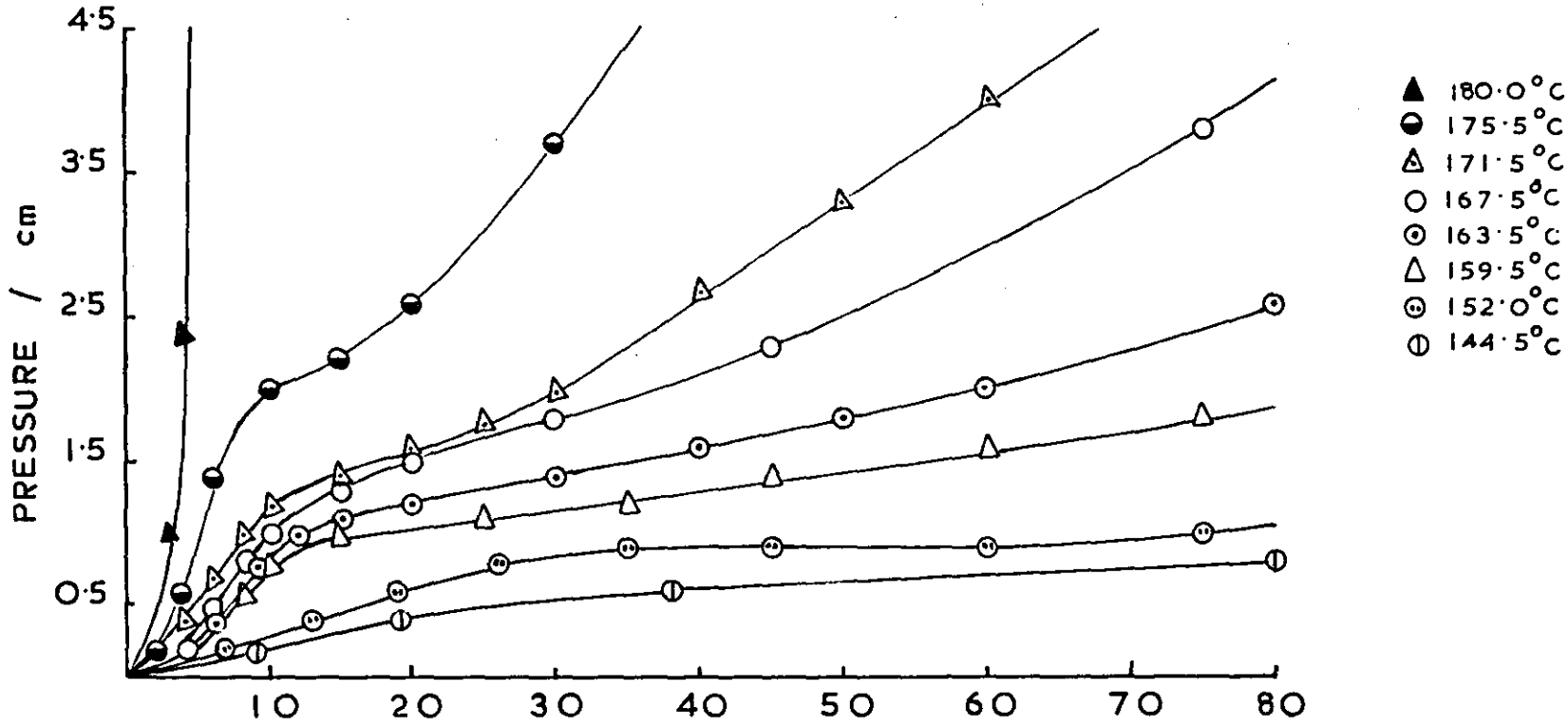


FIGURE 7.4

EFFECT OF TEMPERATURE ON THE EARLY STAGES OF DECOMPOSITION OF GROUND A.C.

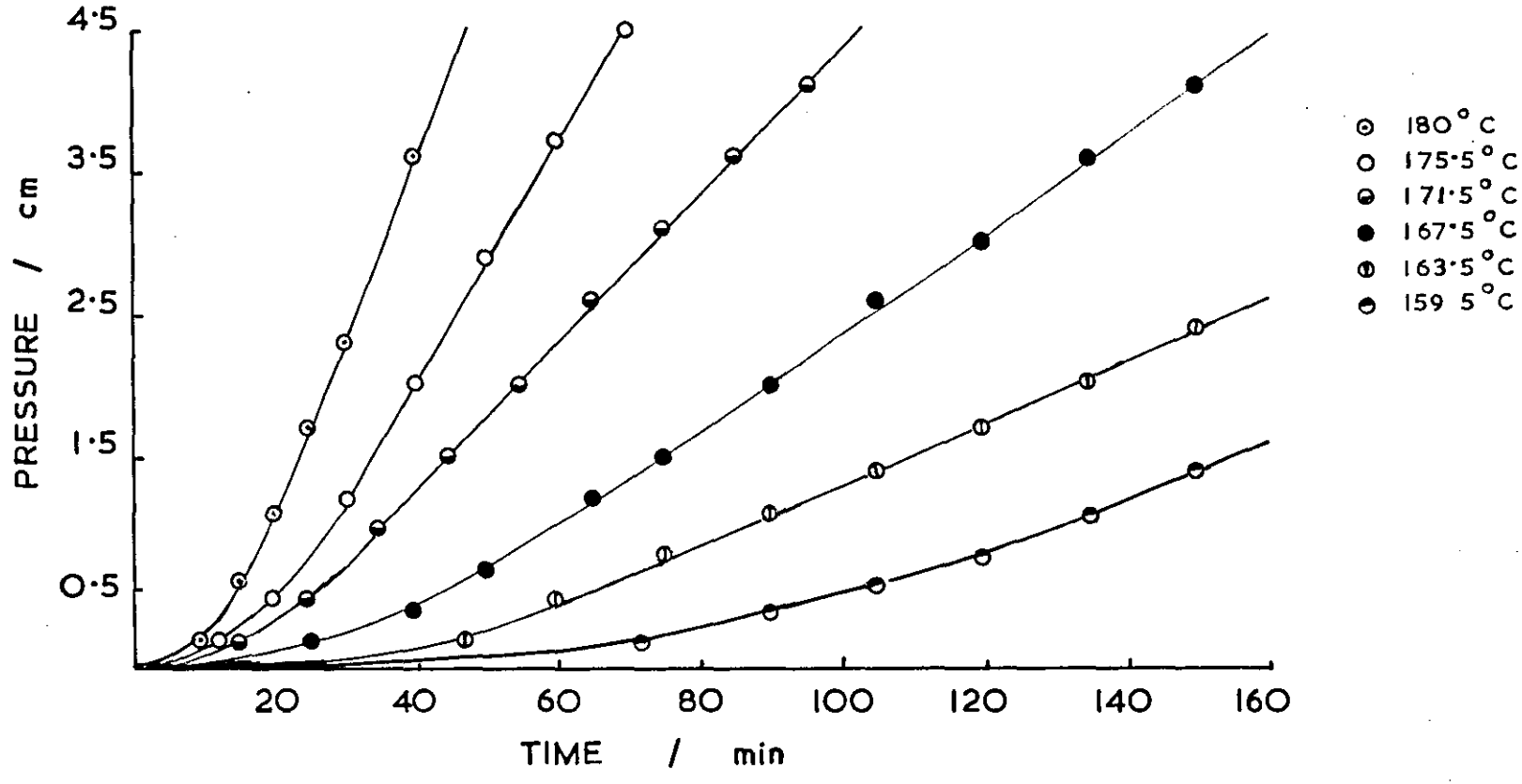


FIGURE 7·5

observed with the A.C. and zinc oxide mixture.

From the evidence available, it seems more than probable that the first step in the decomposition of a mixture of A.C. with zinc oxide is a surface reaction. The surface reaction at the early stages of the decomposition produces some solid products and possibly some gaseous products. The solid products cover the A.C. particles and the interfacial contact between the A.C. particles and the zinc oxide particles is lost. This makes the zinc oxide thereafter ineffective and during the later stages of the decomposition the A.C. decomposes uncatalysed on its own.

If this theory is correct, then on pre-heating the mixture of A.C. with zinc oxide at a lower temperature to complete the first step of the reaction without involving the second step, and then carrying out the remaining decomposition at a higher temperature, the explosion should be avoided. In addition, if the pre-heated material is reground to create fresh surfaces, the explosion should again occur. In an attempt to confirm this experimentally, a mixture of A.C. and zinc oxide was heated at 144.5°C at which temperature the second stage of the decomposition does not take place to any significant extent. FIGURE 7.6 shows that on subsequent heating at a higher temperature (180°C), although a certain amount of the first step reaction occurs, the explosion is prevented. The first step may be still appearing for two reasons. Firstly, the reaction may be incomplete at the lower temperature and secondly, some fresh surfaces may be created during handling. However, when the pre-heated material is reground, the explosion does occur. It is, therefore, clear that the explosion is related to the interfacial

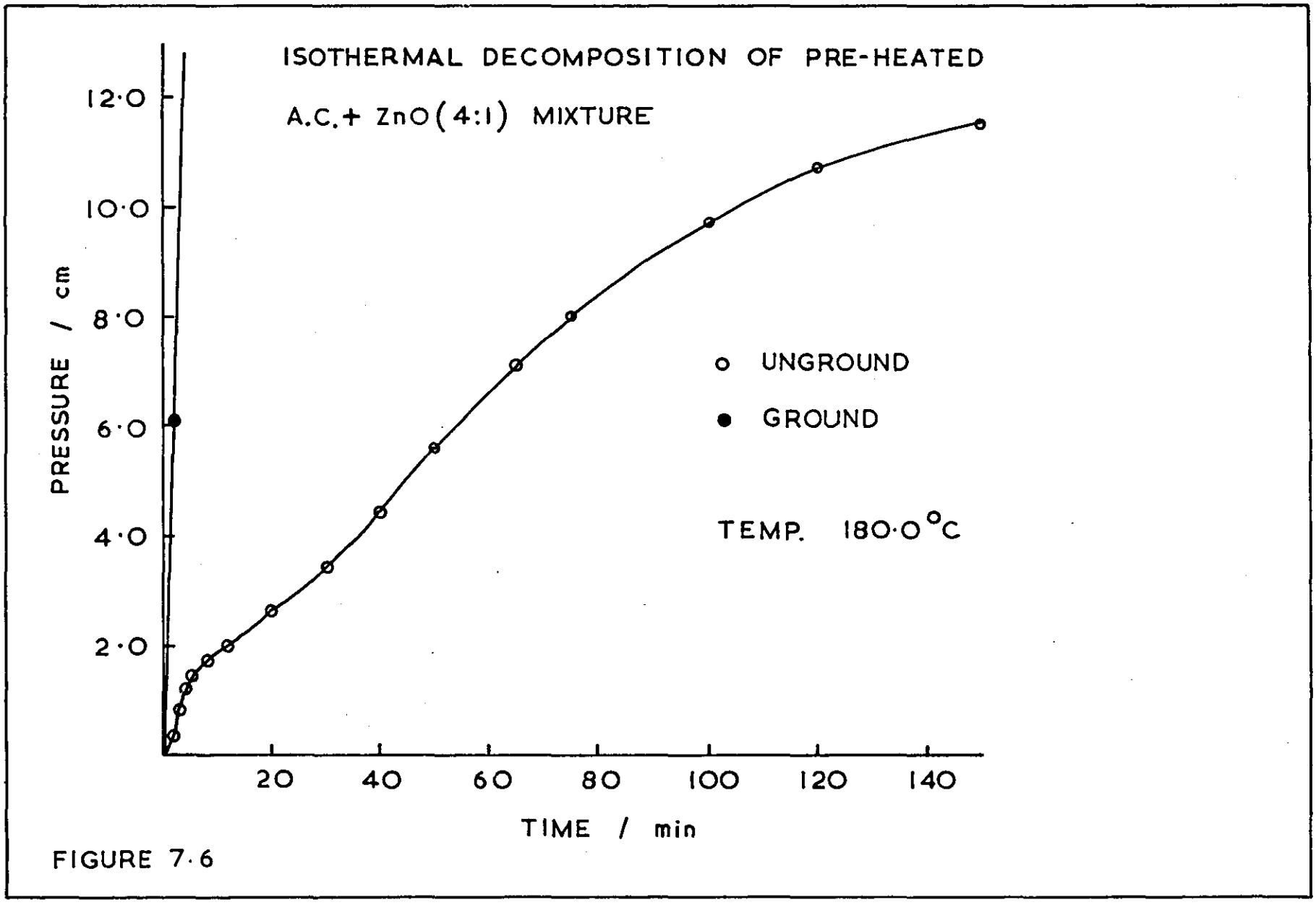

ISOTHERMAL DECOMPOSITION OF PRE-HEATED
A.C.+ ZnO (4:1) MIXTURE
PRESSURE / cm
12·0
10·0
8·0
6·0
4·0
2·0
20
40
60
80
100
120
140
TIME / min
o UNGROUND
● GROUND
TEMP. 180·0 °C

FIGURE 7·6

contact area between the A.C. and zinc oxide particles.

In an attempt to confirm whether the second step of the decomposition resembles the normal decomposition of A.C. on its own, the two curves were compared. Owing to the difficulties in eliminating the first step quantitatively from the former, the two curves are not superimposable, but the shapes of the two curves are very similar. In another attempt it was decided to compare the activation energy of the reaction of A.C. with zinc oxide (4:1) taking place during the second stage with that of pure A.C.

The energy of activation of a 4:1 A.C. and zinc oxide mixture during the second stage has been calculated by plotting $\log_{10}(\frac{1}{t})$ against $\frac{1}{T}$, where t is the time taken for the pressure to increase from 3.5 cm to 5.0 cm in the linear portion of the curve. FIGURE 7.7 shows the plot of the data which are tabulated in TABLE 7.1.

TABLE 7.1

Data for the determination of the activation energy during the second stage of the decomposition of an A.C. and zinc oxide (4:1) mixture

Temperature T K	$\frac{1}{T} \times 10^3$	Time (t) min	$\frac{1}{t} \times 10^2$	$\log_{10}(\frac{1}{t})$
448.5	2.2296	15.0	6.6667	- 1.8694
444.5	2.2497	22.5	4.4444	- 1.6946
440.5	2.2701	32.0	3.1250	- 1.5052
436.5	2.2909	49.5	2.0202	- 1.3522
432.5	2.3121	74.0	1.3514	- 1.1761

The energy of activation calculated from the slope of the linear curve is found to be 38.0 k cal mol^{-1} (see APPENDIX I for the calculation).

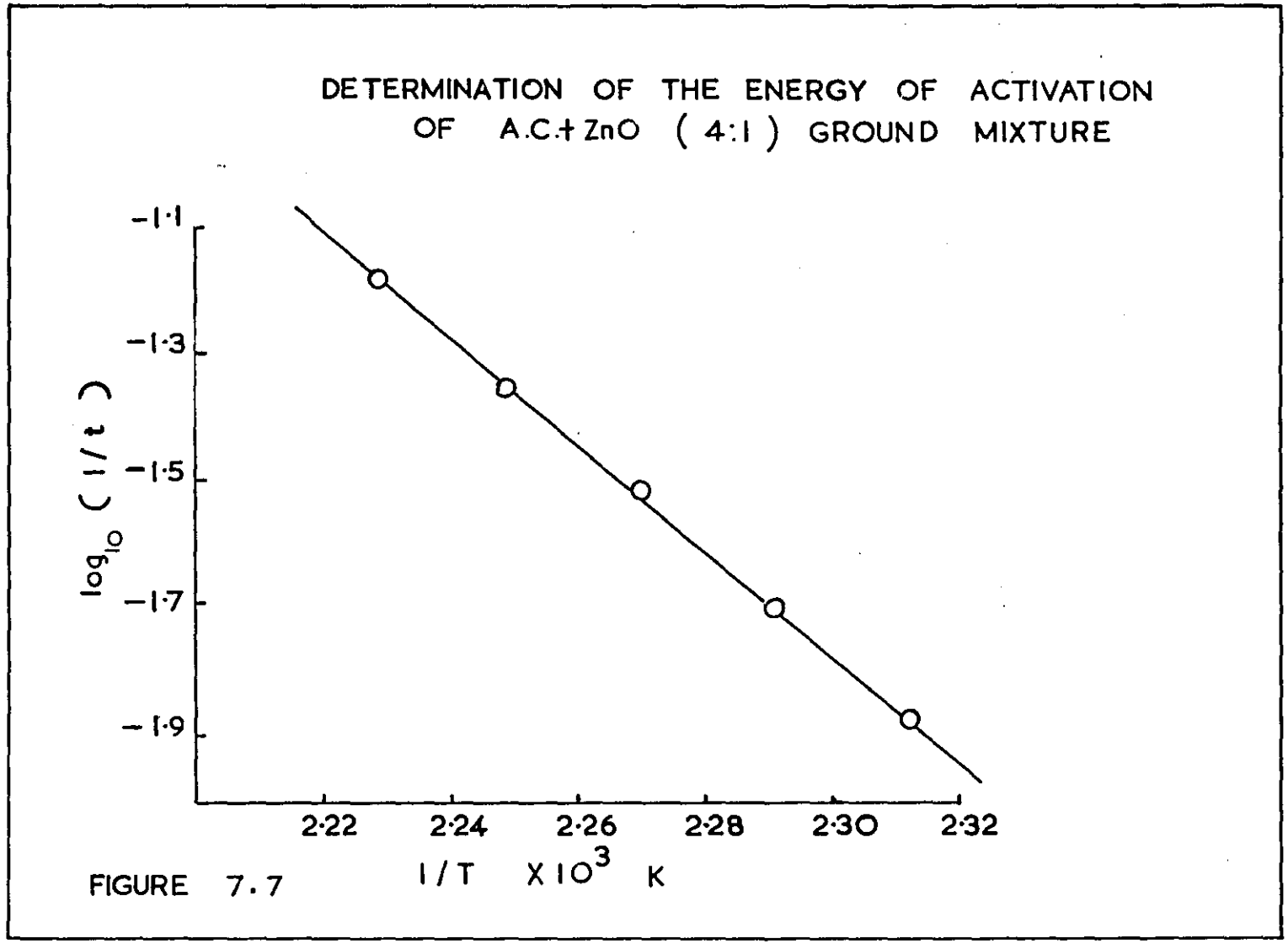

DETERMINATION OF THE ENERGY OF ACTIVATION
OF A.C.+ ZnO (4:1) GROUND MIXTURE
-1·1
-1·3
-1·5
-1·7
-1·9
log10 (1/t)
2·22
2·24
2·26
2·28
2·30
2·32
1/T X 10^3 K

FIGURE 7.7

The energy of activation of the pure ground A.C. has been estimated by the same method, and likewise using the linear portion of the graph and is found to be 37.0 k cal mol^{-1}. The plot of $\log_{10}(\frac{1}{t})$ against $(\frac{1}{T})$ is shown in FIGURE 7.8, and the data are tabulated in TABLE 7.2.

TABLE 7.2

Data for the determination of the activation energy of the decomposition of ground A.C.

Temperature T K	$\frac{1}{T} \times 10^3$	Time (t) min	$(\frac{1}{t}) \times 10^3$	$\log_{10}(\frac{1}{t})$
453.0	2.2075	12	8.3333	- 1.0792
448.5	2.2296	17	5.5882	- 1.2527
444.5	2.2497	29	3.4483	- 1.4624
440.5	2.2701	42	2.3810	- 1.6232
436.5	2.2909	55	1.8182	- 1.7405
432.5	2.3121	72	1.3889	- 1.8576

It is noticed that the energies of activation in the two cases are very close to each other, which suggests that the second stage is very similar to the normal decomposition of A.C.

The method used in the study of the complete decomposition of an A.C. and zinc oxide mixture does not reveal adequate information regarding the reaction involved in the first step. It was, therefore, decided to carry out a detailed investigation of the first step reaction separately.

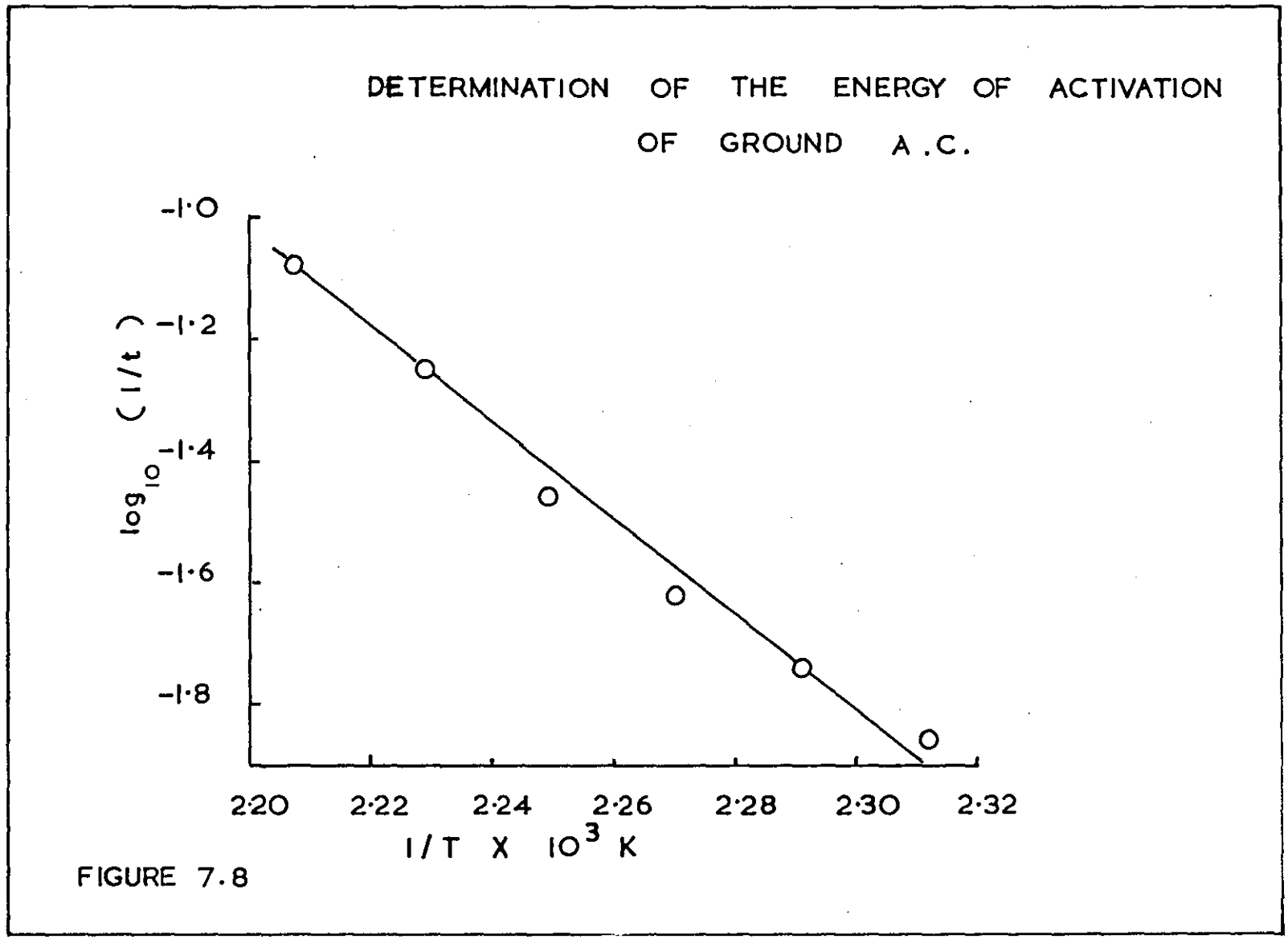

DETERMINATION OF THE ENERGY OF ACTIVATION
OF GROUND A.C.
-1·0
-1·2
-1·4
-1·6
-1·8
log10 (1/t)
2·20
2·22
2·24
2·26
2·28
2·30
2·32
1/T X 10³ K

FIGURE 7.8

The investigation of the early stages of the decomposition

With the help of an accurate pressure measuring device it has been possible to investigate the nature of the reaction between A.C. and zinc oxide occurring during the early stages. A typical plot of pressure as a function of time for this part of the reaction is shown in FIGURE 7.9. The curve is deceleratory throughout until there is a sign of the start of the second stage. The shape of the curve indicates that a surface reaction has occurred. This type of reaction is normally dependent on the interfacial contact area between the two reactants. As the reaction progresses the interfacial contact area diminishes due to the formation of the product, thus the curve shows a deceleratory shape.

Before carrying out further investigation, A.C. and zinc oxide were heated separately in the apparatus attached to the accurate pressure measuring device to see whether they liberate any gas. In the case of zinc oxide alone no measurable pressure developed. The A.C., however, started decomposing as soon as the heating started. This phenomenon was also observed by Swann[10]. FIGURE 7.10 shows the early stages of the decomposition of pure A.C. The grinding has very little effect on the rate of the decomposition. The actual extent of decomposition is not high enough to cause serious error in the investigation of the reaction of A.C. with zinc oxide (or other oxides which will be discussed later) during the early stages.

An attempt has been made to study the kinetics of the reaction of A.C. with zinc oxide during the early stages of the decomposition.

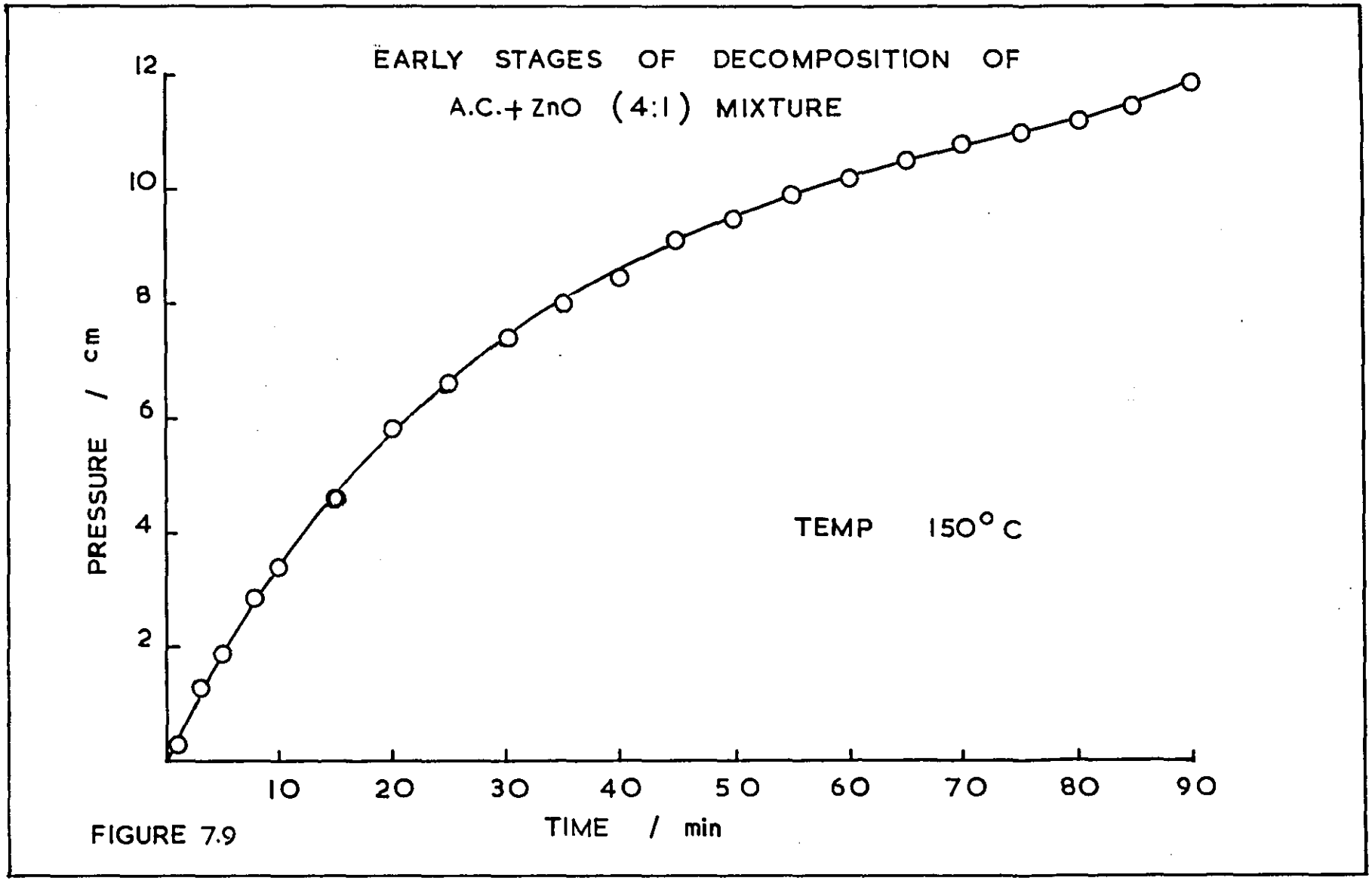

EARLY STAGES OF DECOMPOSITION OF
A.C.+ ZnO (4:1) MIXTURE
TEMP 150° C
PRESSURE / cm
TIME / min
2
4
6
8
10
12
10
20
30
40
50
60
70
80
90

FIGURE 7.9

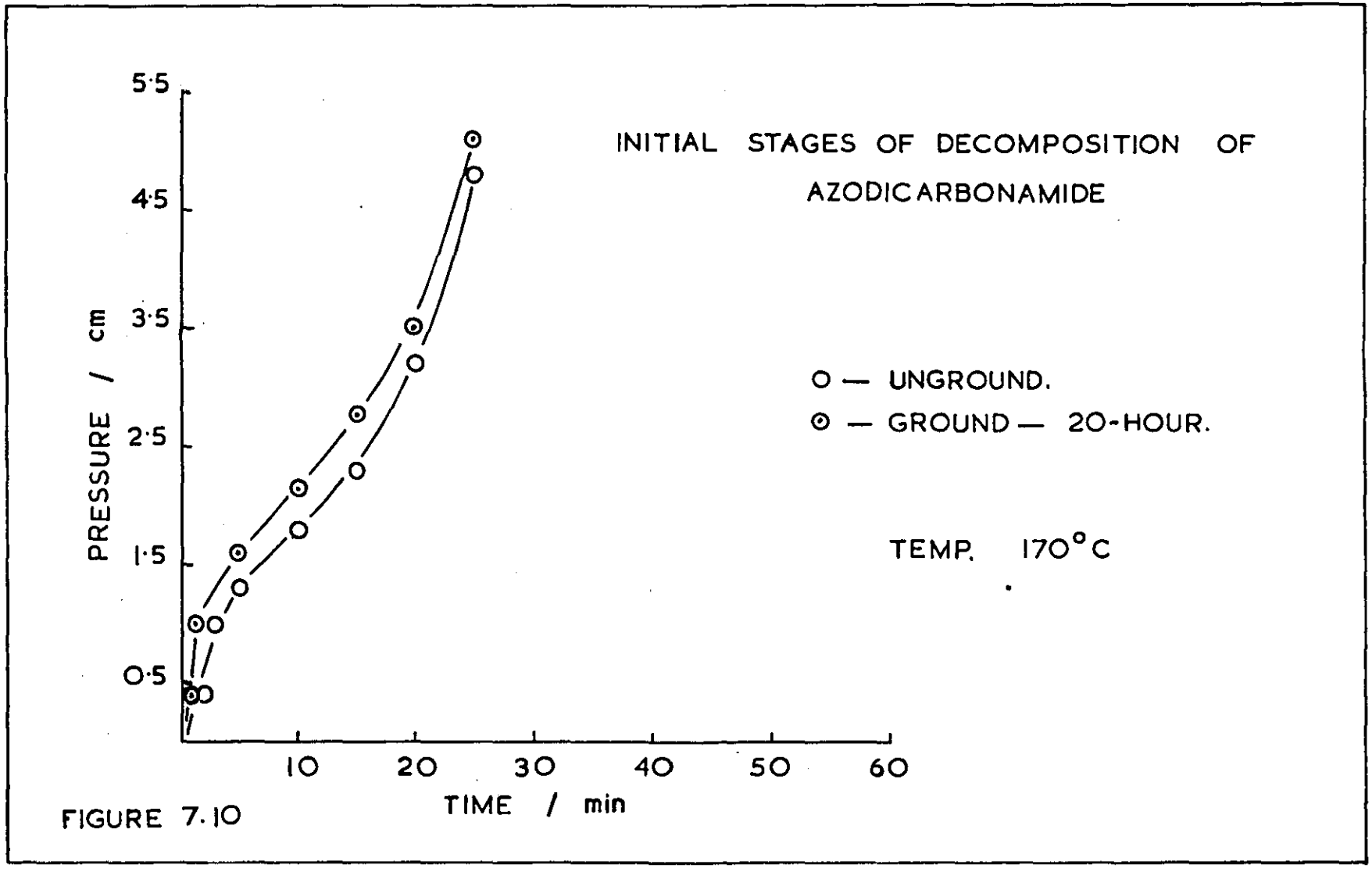

INITIAL STAGES OF DECOMPOSITION OF AZODICARBONAMIDE
O — UNGROUND.
⊙ — GROUND — 20-HOUR.
TEMP. 170°C
PRESSURE / cm
5·5
4·5
3·5
2·5
1·5
0·5
10
20
30
40
50
60
TIME / min

FIGURE 7.10

From the pressure-time plot it is difficult to determine the exact pressure at the end of the first stage because the second step appears to commence before the first step is complete. Guggenheim's[75] method has therefore been used for the analysis of the results. In this particular method it is not necessary to know the value of the final pressure.

For a first order reaction the procedure is to take a series of readings of the pressure P_1 at intervals of time t. A second set of readings P_2 is also taken, each at time $t + t^1$, where t^1 is a constant interval after the time of the corresponding reading P_1. The period t^1 must be at least two or three times the half life of the reaction. If P_∞ is the final pressure at the end of the first stage and k is the rate constant, the first order rate equation can be written as:

$$kt + \ln (P_2 - P_1) = P_\infty \left[P_\infty \left(1 - e^{-kt^1}\right) \right] \qquad (1)$$

The right hand side of the equation is constant.

Therefore

$$kt + \ln (P_2 - P_1) = \text{constant} \qquad (2)$$

A plot of $\ln (P_2 - P_1)$ against t will therefore give a straight line of slope $-k$.

FIGURE 7.11 shows such a plot for the data obtained from the decomposition of an A.C. and zinc oxide mixture at 150°C. The data are tabulated in TABLE 7.3.

It is observed that a good straight line is obtained indicating that the reaction is first order.

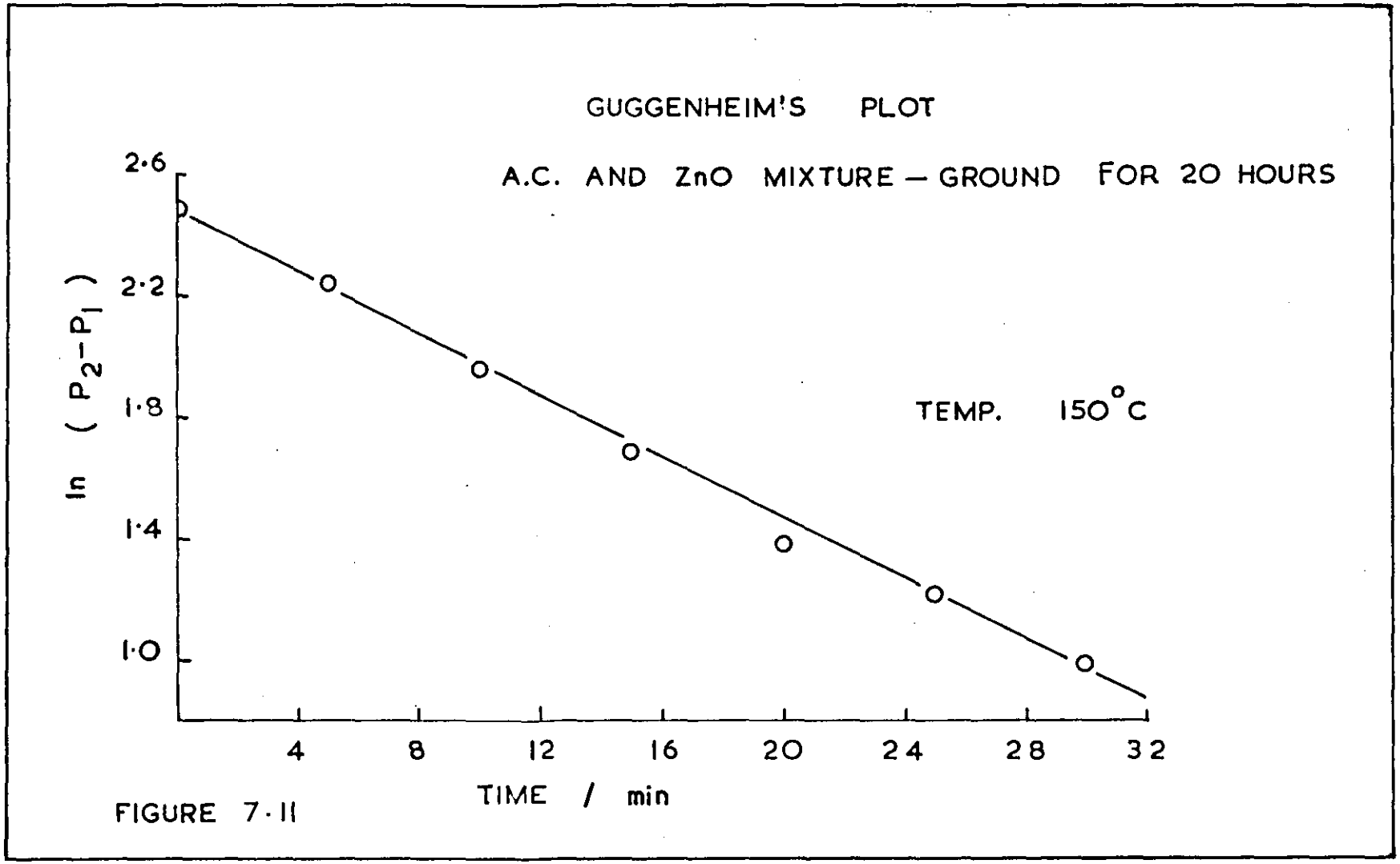

GUGGENHEIM'S PLOT
A.C. AND ZnO MIXTURE – GROUND FOR 20 HOURS
TEMP. 150°C
ln (P2−P1)
2·6
2·2
1·8
1·4
1·0
4
8
12
16
20
24
28
32
TIME / min

FIGURE 7·11

TABLE 7.3

A.C. and zinc oxide (4:1) mixture - ground for 20 hours

Data for Guggenheim's plot

First set		Second set		$(P_2 - P_1)$ / cm	$\ln (P_2 - P_1)$	Time (t) /min
Time /min	P_1 /cm	Time /min	P_2 /cm			
0	0	40	12.10	12.10	2.4932	0
5	3.15	45	12.60	9.45	2.2460	5
10	5.90	50	13.00	7.10	1.9601	10
15	8.08	55	13.50	5.42	1.6901	15
20	9.70	60	13.70	4.00	1.3863	20
25	10.60	65	14.00	3.40	1.2238	25
30	11.50	70	14.20	2.70	0.9933	30

The value of P_∞, the pressure at the end of the first stage, can be calculated from equation (1). With the calculated value of P_∞ the validity of the first order reaction is further confirmed by applying the normal first order rate equation:-

$$k = \frac{1}{t} \ln P_\infty / (P_\infty - P) \qquad (3)$$

A straight line is obtained by plotting t against $\ln P_\infty/(P_\infty - P)$ which is shown in FIGURE 7.12.

The data are tabulated in TABLE 7.4.

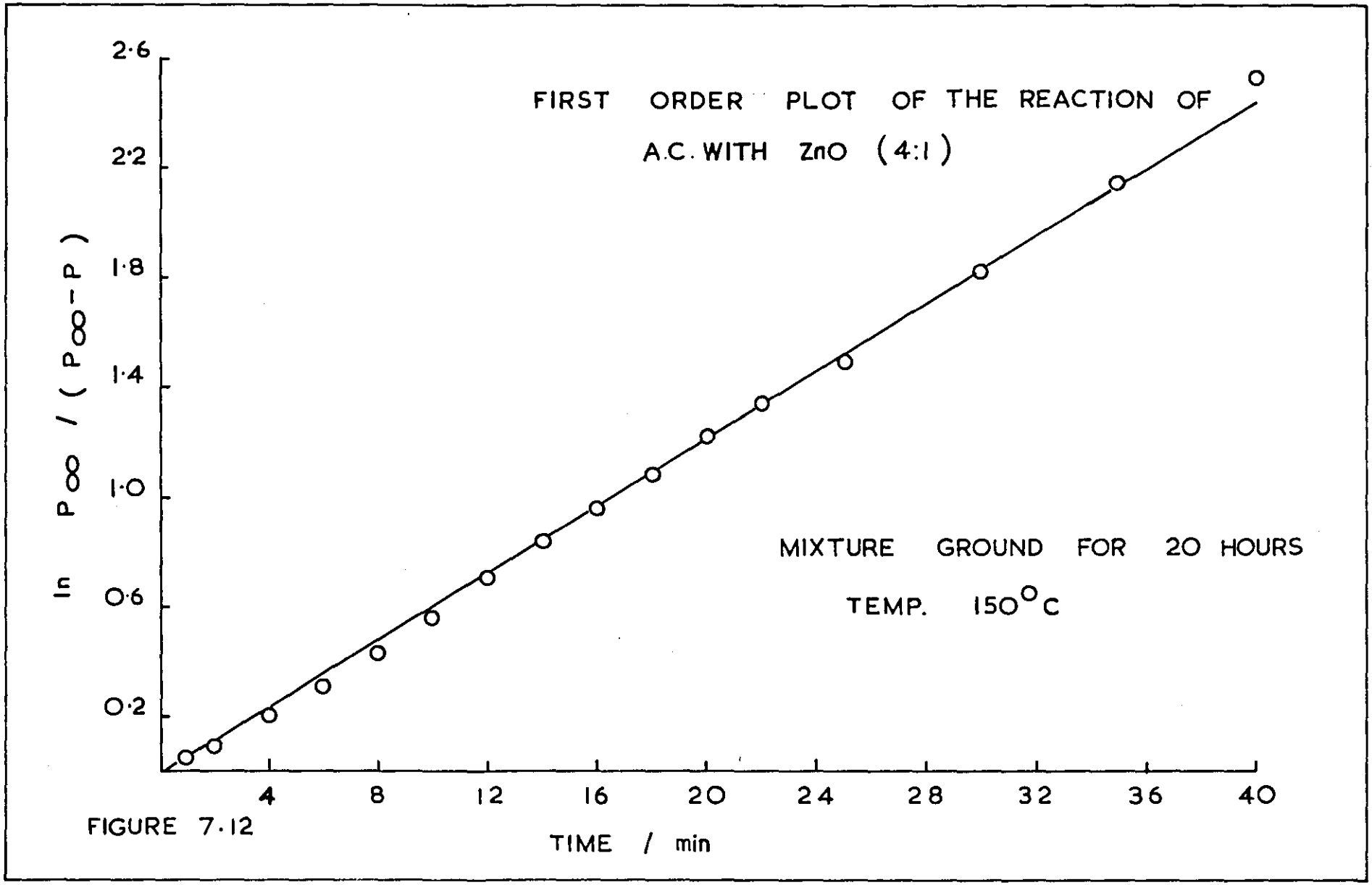

FIRST ORDER PLOT OF THE REACTION OF
A.C. WITH ZnO (4:1)
MIXTURE GROUND FOR 20 HOURS
TEMP. 150°C
ln P∞ / (P∞ - P)
2·6
2·2
1·8
1·4
1·0
0·6
0·2
4
8
12
16
20
24
28
32
36
40
TIME / min

FIGURE 7·12

TABLE 7.4

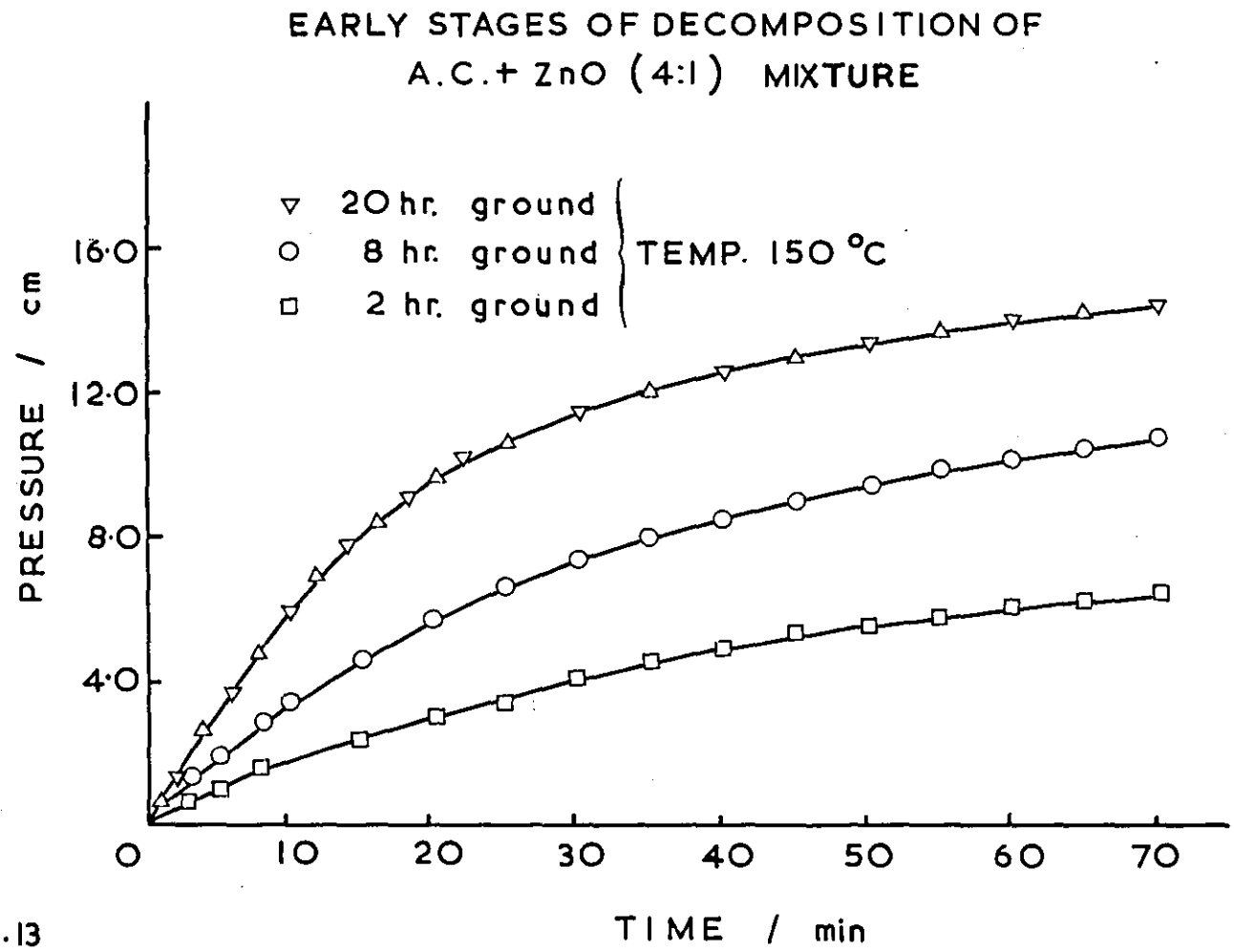
A.C. and zinc oxide (4:1) mixture - ground for 20 hours

Data for the first order plot

Temperature - 150°C, P_∞ = 13.68 cm

Time / min	P / cm	$(P_\infty - P)$ / cm	$P_\infty / (P_\infty - P)$	$\ln P_\infty / (P_\infty - P)$
1	0.7	12.98	1.054	0.0525
2	1.3	12.38	1.105	0.0999
4	2.6	11.08	1.235	0.2108
6	3.7	9.98	1.371	0.3154
8	4.8	8.88	1.541	0.4321
10	5.9	7.78	1.758	0.5644
12	6.9	6.78	2.018	0.7019
14	7.8	5.88	2.327	0.8444
16	8.5	5.18	2.641	0.9711
18	9.1	4.58	2.987	1.0942
20	9.7	3.98	3.437	1.2346
22	10.1	3.58	3.821	1.3406
25	10.6	3.08	4.442	1.4910
30	11.5	2.18	6.275	1.8366
35	12.1	1.58	8.658	2.1585
40	12.6	1.08	12.67	2.5390
45	13.0	0.68	20.12	3.0016

It has been found that the value of P_∞ depends on the extent of grinding. By grinding the two particles together the particles become smaller and thus the interfacial contact area increases. It is, therefore, expected that prolonged grinding would increase the proportion of the first step. This agrees well with the experimental results shown in FIGURE 7.13. The Guggenheim's equation fits well for all three curves. The value of P_∞ increases as the grinding time increases (see TABLE 7.5).


EARLY STAGES OF DECOMPOSITION OF
A.C.+ ZnO (4:1) MIXTURE
20 hr. ground
8 hr. ground
2 hr. ground
TEMP. 150 °C
PRESSURE / cm
16·0
12·0
8·0
4·0
0
10
20
30
40
50
60
70
TIME / min

FIGURRE 7·13

TABLE 7.5

Calculated values of P_∞ , the pressure at the completion of the first stage of the reaction between A.C. and zinc oxide (4 : 1).

Temperature / K	Grinding Time /hour	P_∞ /cm
423.0	2	8.08
423.0	8	11.85
423.0	20	13.68
420.0	20	12.54
418.0	20	10.78
414.0	20	9.20
410.0	20	11.10

The value of P_∞ appears to vary also with temperature. There is a tendency for the value to decrease as the temperature decreases, but the data are scattered and it is not possible to draw any definite conclusions.

The value of the rate constant obtained from Guggenheim's plot at different temperatures can be used for the determination of the activation energy of the first stage. For a 4:1 A.C. and zinc oxide mixture the activation energy is found to be 26.2 k cal mol^{-1}. The values of ln k as a function of $(\frac{1}{T})$ are plotted in FIGURE 7.14 and the data are shown in TABLE 7.6.

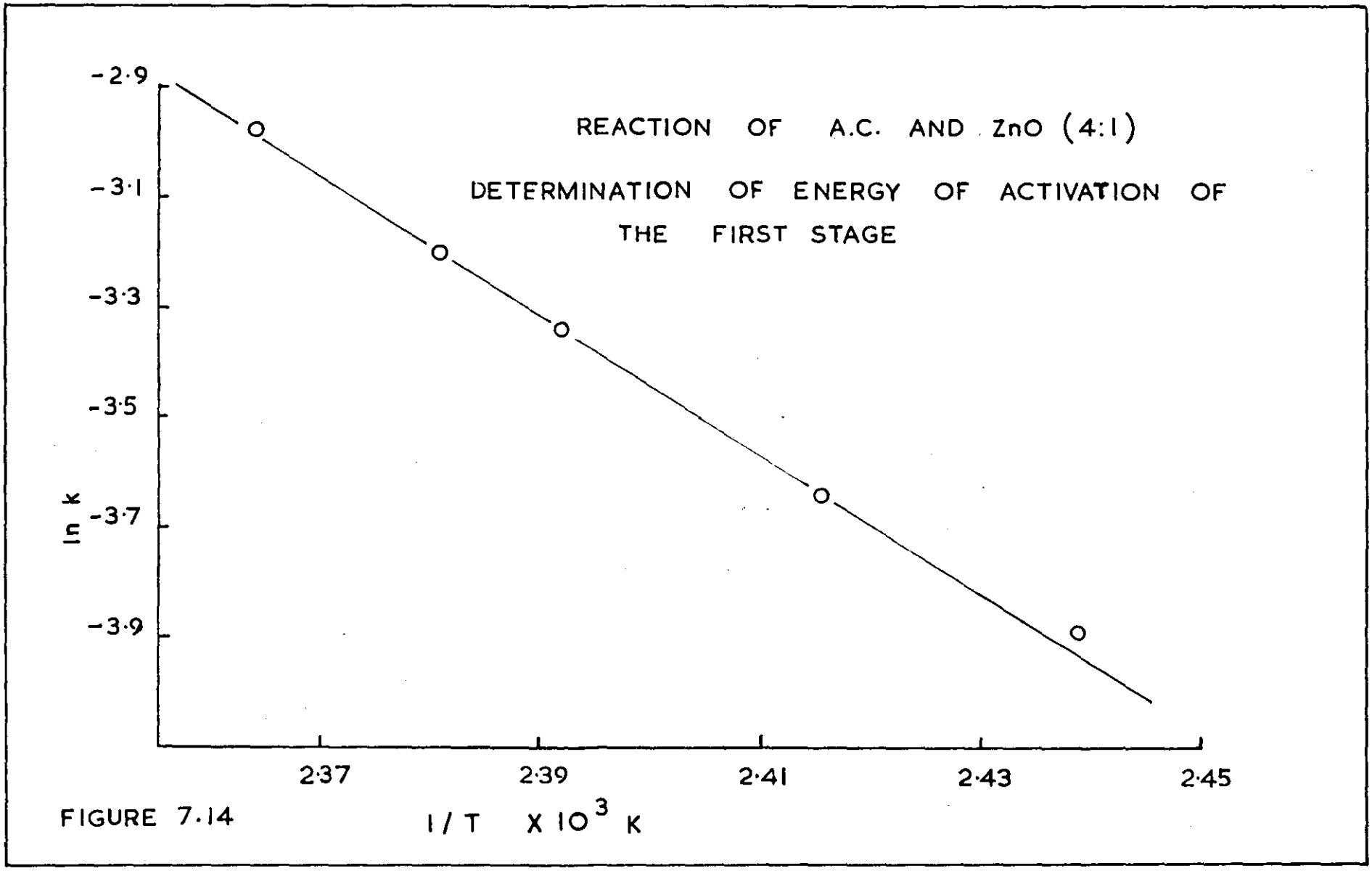

REACTION OF A.C. AND ZnO (4:1)
DETERMINATION OF ENERGY OF ACTIVATION OF THE FIRST STAGE
-2·9
-3·1
-3·3
-3·5
-3·7
-3·9
ln k
2·37
2·39
2·41
2·43
2·45
1 / T X 10 3 K

FIGURE 7.14

TABLE 7.6

Data for the determination of the activation energy for the first stage of decomposition of a 4:1 A.C. + zinc oxide mixture.

Temperature T / K	$\frac{1}{T} \times 10^3$	$k \times 10^2$ /min	ln k
423	2.364	5.084	- 2.979
420	2.381	4.076	- 3.200
418	2.392	3.516	- 3.348
414	2.415	2.625	- 3.640
410	2.439	1.880	- 3.974

The kinetic equation for a first order reaction encountered frequently in homogeneous systems, as mentioned earlier, is rarely followed in a solid phase reaction. It is only followed when physical phenomena such as internal diffusion, sublimation, etc., have no effect on the process rate[74]. Furthermore, the equation derived for homogeneous reactions is valid for a reaction taking place in a heterogeneous system only for a constant surface of contact between the reactants. Therefore, for a reaction of the first order expressed by equation (3) taking place in a solid mixture, it is more correct to write:-

$$k F = \frac{1}{t} \ln P_\infty / (P_\infty - P) \qquad (4)$$

where F is the surface contact area between the reactants. The value of F is dependent on the shape and size of the particles. Owing to the lack of information regarding the latter, a quantitative analysis of the data is impossible. However, it has been found that progressive grinding increases the magnitude of the rate

constant which is most likely to be due to the influence of grinding on the contact area between the two particles. The variation of the rate constant with grinding time in the reaction of A.C. with zinc oxide is shown in TABLE 7.7.

TABLE 7.7

Variation of the rate constant with grinding time for A.C. + ZnO (4:1) mixture at 150°C

Grinding time / hour	Rate constant k / min
2	2.38×10^{-2}
8	3.07×10^{-2}
20	5.08×10^{-2}

7.2. THE INFLUENCE OF THE OXIDES OF LEAD, CADMIUM, BARIUM AND MAGNESIUM

The pressure of the gas evolved as a function of time when different metal oxides react with A.C. at 171.5°C in a 1:4 ratio, is shown in FIGURE 7.15. The oxide of lead reacts with A.C. in two steps similar to that of zinc oxide. In the case of magnesium oxide, however, it is difficult to say whether the reaction has occurred in two steps. If the reaction has taken place in two steps, the first step is extremely small in comparison with the second step. Barium oxide gives a curve very similar to the oxides of lead and cadmium indicating a two step reaction. But a further investigation revealed that when barium oxide is heated on its own,

EFFECT OF DIFFERENT OXIDES ON THE ISOTHERMAL DECOMPOSITION OF A.C.

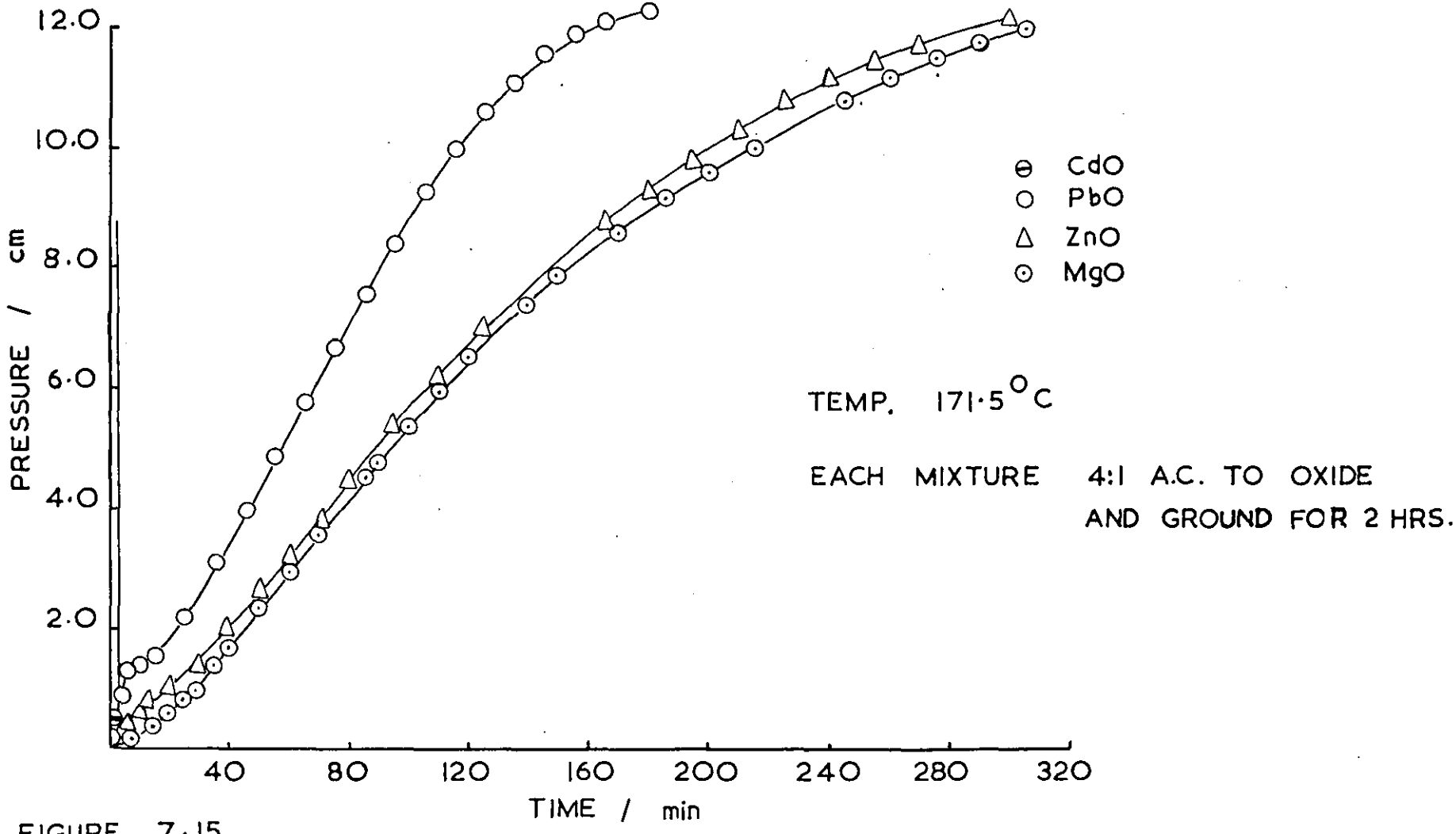


FIGURE 7·15

a small but rapid initial evolution of gas occurs in exactly the same way as when a mixture of barium oxide and A.C. is heated. It appears that barium oxide gets moist during grinding and handling because of the ease with which it absorbs moisture from the atmosphere. It is most likely, therefore, that the first stage of the barium oxide and A.C. reaction is due to this cause. In contrast on heating the other oxides on their own there was no rapid gas evolution.

The reaction of A.C. with cadmium oxide is so fast as to appear as though an explosion has occurred. It is impossible to say from the curve at 171.5°C whether the reaction has occurred in two steps. However, studies at lower temperatures have confirmed that the cadmium oxide also reacts with A.C. in two steps similar to the oxides of lead and zinc.

The explosion type reaction between A.C. and cadmium oxide is found to occur at a much lower temperature than the reaction of A.C. with zinc oxide. It was, therefore, decided to check whether the explosion is prevented by pre-heating the mixture, as was found in the case of zinc oxide. FIGURE 7.16 shows that pre-heating a mixture of A.C. and cadmium oxide at 144.5°C prevents the explosion at a higher temperature. There is a slight indication with the preheated mixture of the reaction taking place in two steps, but the major portion of the reaction is very similar to the decomposition of pure A.C.

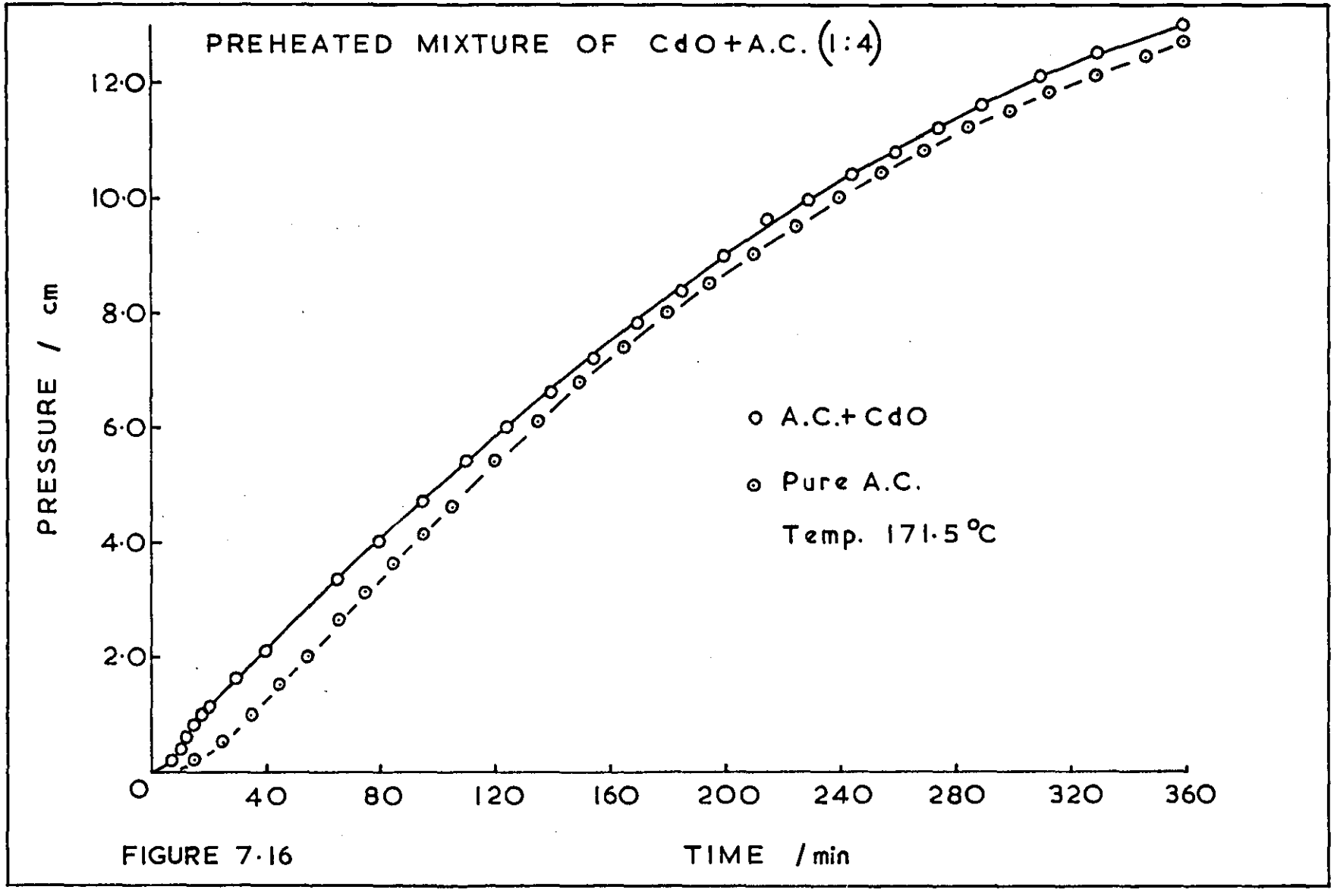

PREHEATED MIXTURE OF CdO+A.C. (1:4)
PRESSURE / cm
12·0
10·0
8·0
6·0
4·0
2·0
0
40
80
120
160
200
240
280
320
360
TIME / min
o A.C.+CdO
o Pure A.C.
Temp. 171·5 °C

FIGURE 7·16

The investigation of the early stages of the decomposition

Lead oxide reacts with A.C. in a similar manner to zinc oxide during the early stages and the pressure-time plot fits Guggenheim's equation for a first order reaction quite well. The activation energy for the first step of the reaction, in this case, is found to be 22.1 k cal mol^{-1}. The data are plotted in FIGURE 7.17 and tabulated in TABLE 7.8.

Cadmium oxide also reacts with A.C. in a similar manner to zinc and lead, during the early stages of decomposition, but it is only possible to obtain data below 145°C. Above 145°C the reaction is explosive and it is impossible to measure the rise in pressure as a function of time. The activation energy for the reaction of A.C. with cadmium oxide during the early stages is estimated to be 8.1 k cal mol^{-1}. The data are plotted in FIGURE 7.18 and tabulated in TABLE 7.8.

TABLE 7.8

Data for the determination of the activation energy for the first step in the decomposition of an A.C. + oxide (4:1) mixture

Temperature T / K	$\frac{1}{T} \times 10^3$	Lead Oxide		Cadmium oxide	
		k x 10^2 /min	ln k	k x 10^2 /min	ln k
423	2.364	15.210	-1.883	-	-
420	2.381	13.870	-1.975	-	-
418	2.392	11.320	-2.179	3.244	-3.428
414	2.415	8.951	-2.413	2.932	-3.530
410	2.439	6.778	-2.692	2.624	-3.641
406.5	2.460	-	-	2.380	-3.738
404.5	2.472	-	-	2.389	-3.734

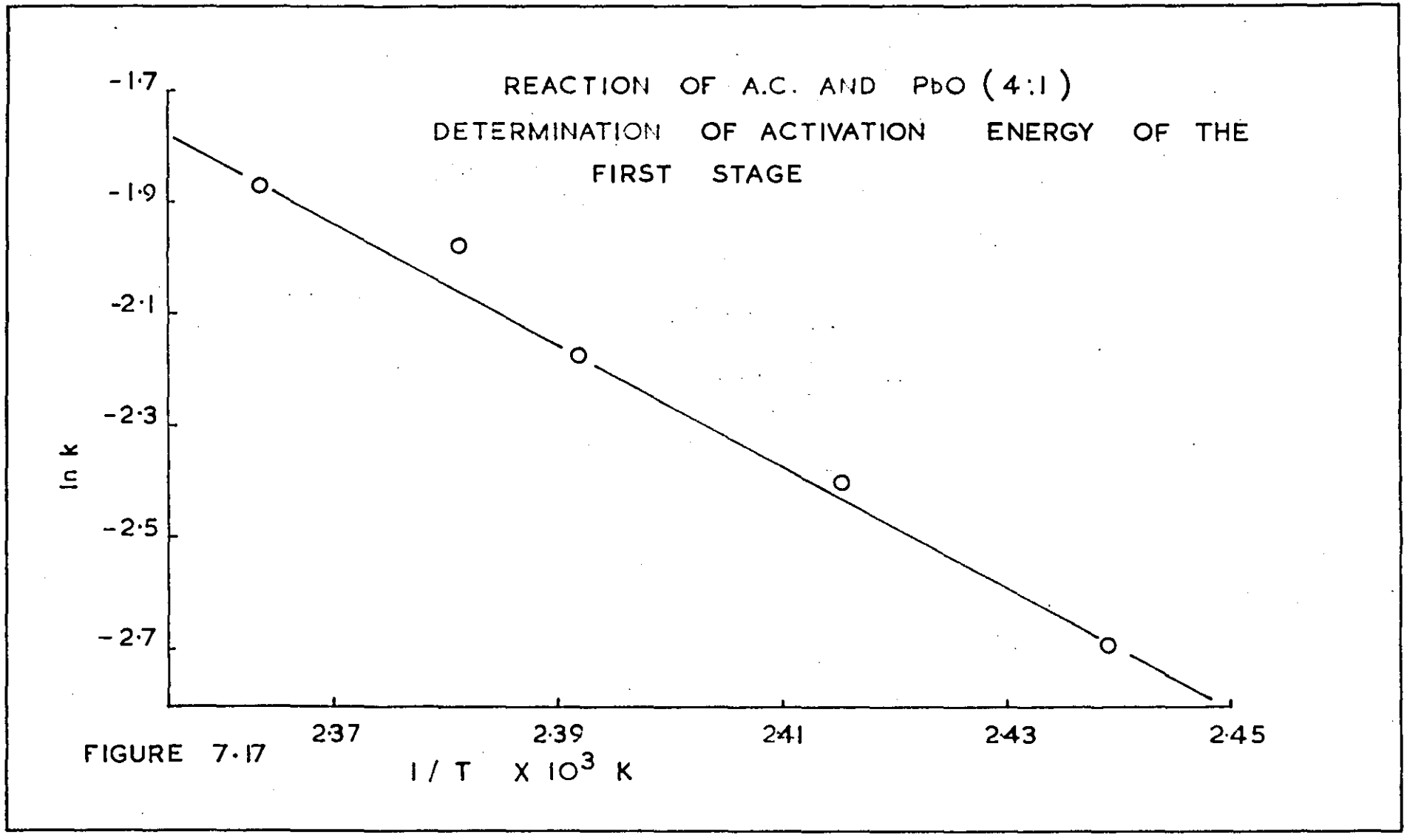

REACTION OF A.C. AND PbO (4:1)
DETERMINATION OF ACTIVATION ENERGY OF THE FIRST STAGE
-1·7
-1·9
-2·1
-2·3
-2·5
-2·7
ln k
2·37
2·39
2·41
2·43
2·45
1 / T X 10³ K

FIGURE 7·17

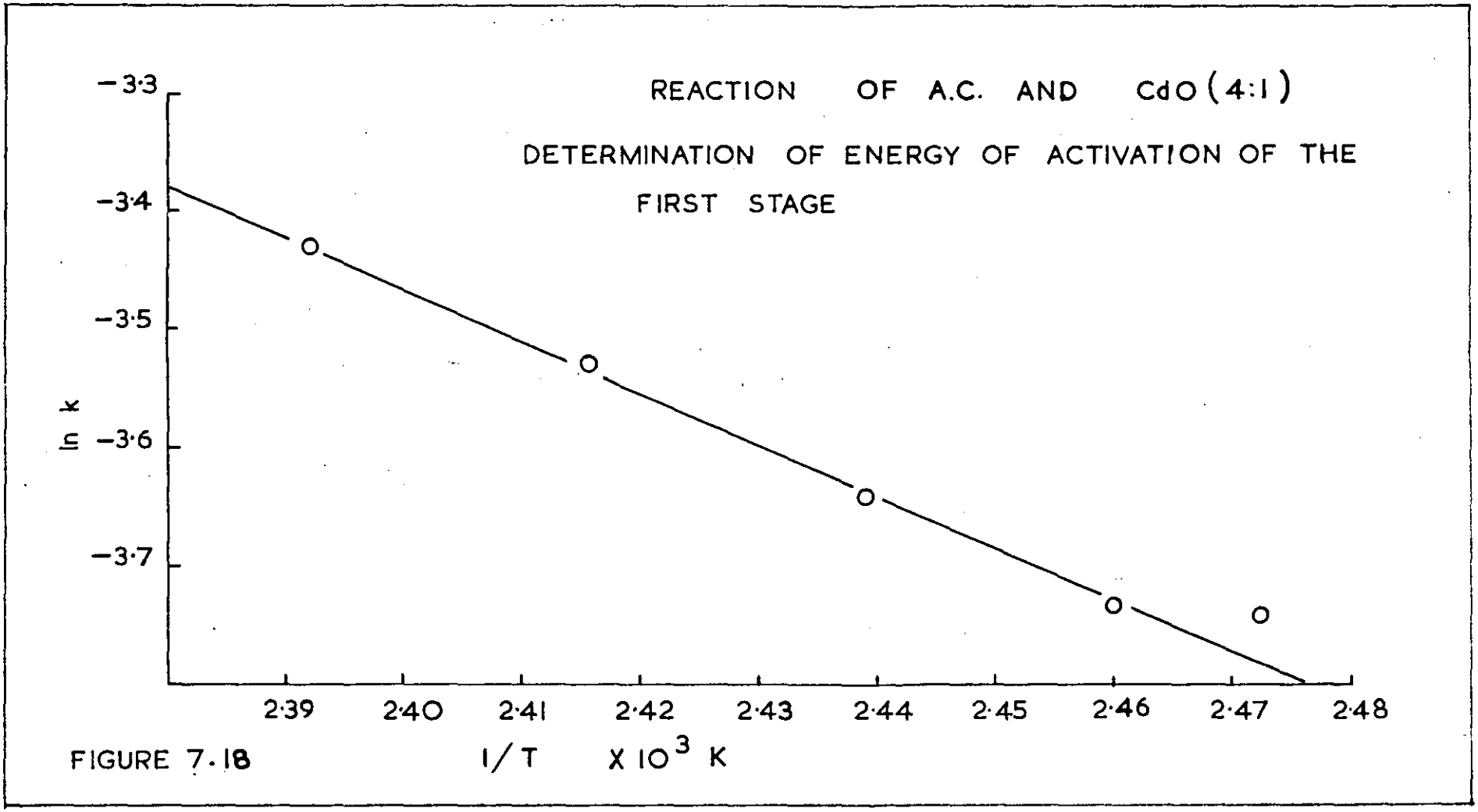

REACTION OF A.C. AND CdO (4:1)
DETERMINATION OF ENERGY OF ACTIVATION OF THE FIRST STAGE
−3·3
−3·4
−3·5
−3·6
−3·7
ln k
2·39
2·40
2·41
2·42
2·43
2·44
2·45
2·46
2·47
2·48
1/T X 10³ K

FIGURE 7.18

The value of P_∞ appears to vary with temperature in the reaction of A.C. with the oxides of lead and cadmium during the early stages of the decomposition, in a similar way to that observed with zinc oxide. TABLE 7.9 shows the variation of P_∞ with temperature, but the data again is not consistent enough to draw any definite conclusions.

TABLE 7.9

Calculated values of P_∞, the pressure at the completion of the first stage of the reaction between A.C. and the oxides of lead and cadmium

Temperature / K	Lead Oxide		Cadmium Oxide	
	Grinding time /hour	P_∞ /cm	Grinding time /hour	P_∞ /cm
423.0	2	9.03	-	-
420.0	2	7.53	-	-
418.0	2	7.88	2	20.68
414.0	2	7.32	2	33.65
410.0	2	6.36	2	9.54
406.5	2	-	2	12.02
404.5	2	-	2	4.13

DISCUSSION

In the present investigation the effects of two types of oxides on the decomposition of A.C. have been studied. The n-type of oxides such as zinc oxide, lead oxide and cadmium oxide are found to be more effective than the insulator type oxides such as barium and magnesium oxides. It is clear that all the n-type oxides investigated react with A.C. in two steps in which the second step

represents the major bulk of the decomposition. TABLE 7.10 shows the rate of increase in pressure during the second stage of the reaction, when a mixture of A.C. with different oxides is heated at 171.5°C.

TABLE 7.10

Rates of pressure increase during the second stage of reaction of an A.C. and oxide (4:1) mixture

Catalyst	Temperature / °C	Rate /cm min^{-1}
Cadmium oxide	171.5°C	1.500
Lead oxide	171.5°C	0.095
Zinc oxide	171.5°C	0.059
Barium oxide	171.5°C	0.047
Magnesium oxide	171.5°C	0.060
None	171.5°C	0.052

Although magnesium oxide, an insulator type oxide, shows a similar rate to the n-type zinc oxide during the second stage, the former does not develop an explosion at higher temperatures.

The rate of most reactions between solid substances is limited by diffusion of the reagent through the layer of the product. In general, one substance reacts with the other, forming a product, the thickness of whose layer continuously increases during the process. Under these conditions one of the substances (or the product of its decomposition) diffuses to the surface of the other

through the product layer at a rate much less than the rate of the chemical reaction between the two materials, so that diffusion totally determines the kinetics of the process[74]. Since the reaction of A.C. with metal oxides follows first order reaction kinetics during the early stages, it would appear that this reaction is not influenced by the diffusion process. Instead, it is dependent on the interfacial contact area between the two particles.

The conclusion that the reaction during the early stages is a surface reaction is based on two observations. Firstly, the proportion of the first stage of the reaction increases with grinding time. Secondly, the explosion occurring at higher temperatures is prevented by pre-heating the mixture of the reactants.

It also appears that electronic factors have some influence on the mechanism of the catalysis by metal oxides of the decomposition of A.C. It is probable that during the early stages a surface reaction occurs between the oxides and the A.C. in which electrons are transferred from the oxide catalyst to the A.C. Owing to the absence of electron donating properties insulator-type oxides are incapable of catalysing the decomposition of A.C.

An interesting feature is apparent in the rates of gas evolution during the second stage of the reaction between A.C. and an oxide, shown in TABLE 7.10. Zinc oxide has a similar activation energy during the second stage to that of pure A.C. and the rates of gas evolution in the two cases are not greatly different. But the rate with lead oxide is significantly higher and with cadmium oxide it is explosive. It appears that although the shape of the curve

obtained during the second stage is the same in all the cases and resembles closely that of pure A.C., the rate is higher. This increase in the rate appears to be dependent on the reaction occurring in the first stage. There could be two reasons for this. Either the three oxides form entirely different products and these catalyse the second stage reaction to different extents. Alternatively, there is a production of heat during the early stages the magnitude of which varies from one oxide to another, and this increases the local temperature. The first possibility is ruled out by the evidence from the pre-heated mixtures that the products have practically no effect on the second stage decomposition.

The heat evolution factor appears the more likely explanation since the thermogram of the decomposition of an A.C. and zinc oxide mixture (CHAPTER 6) showed an exothermic peak, indicating that a certain amount of heat is given out. It is found that P_{∞} , the pressure at the completion of the first stage, is dependent on the grinding time (TABLE 7.5). The greater the contact area between the two particles, the higher the value of P_{∞} . In equation (4) F represents the contact area between the two reactant particles. If one supposes that P_{∞} is a measure of F, then

$$\text{the rate of heat production} \propto k \; P \; (-\Delta H)$$

where k is the rate constant at a particular temperature, and ΔH the heat of the surface reaction. The value of ΔH is unlikely to vary greatly from one oxide to another.

The product of k and P_{∞} , therefore, will be proportional to the rate of heat production during the early stages. The data

obtained at 414 K with the three oxides are shown below:-

	CdO	PbO	ZnO
$k P_{\infty}$	98.6	65.5	24.2

It shows that cadmium oxide at this temperature has the highest and zinc oxide the lowest rate of heat production. The data at 418 K and 410 K also show that zinc oxide has a lower rate of heat production than either the oxides of cadmium or lead but the figures for cadmium oxide are not higher than those for lead at these two temperatures. This may be due to experimental errors in the P_{∞} values for cadmium oxide which show a much wider variation than those for either zinc or lead oxide.

It is believed that the different rates of heat production during the early stages increase the local temperature to different extents. The highest rate of heat production in the case of cadmium oxide brings about explosion at the lowest temperature. This hypothesis also explains why the second stage of the reaction shows a similar rate to that of A.C. on its own when the first stage is eliminated.

CHAPTER 8

THE INFLUENCE OF ACTIVATORS OTHER THAN METAL OXIDES ON THE DECOMPOSITION OF AZODICARBONAMIDE

There are several different types of activators other than metal oxides which have been used successfully for catalysing the azodicarbonamide (A.C.) decomposition. A general outline of these activators and the available information regarding the mechanism of catalysis have been given in CHAPTER 5.

In this chapter the isothermal decomposition of A.C. in the presence of the stearates of cadmium, zinc, lead and barium, zinc octoate, zinc acetate, urea and zinc dust has been studied by measuring the pressure of the gas evolved as a function of time. An attempt has been made to contaminate the A.C. with zinc acetate at the time of crystallization to increase the rate of decomposition, and the degree of contamination has been determined by chemical analysis of the contaminated sample.

EXPERIMENTAL

The Materials and the Preparation of Mixtures

The sample of zinc acetate (Analytical Reagent grade) was dried to a constant weight at 110°C. The metal stearates and zinc octoate were dried for two hours at the same temperature prior to mixing with A.C.

All the mixtures, except zinc-octoate, were prepared by grinding the two solids together in a ball mill as described in CHAPTER 6. The grinding time was two hours in each case and the proportion of activator was 20% by weight of A.C.

The sample of zinc octoate (supplied by Fisons Industrial Chemicals Ltd., Loughborough) was in the form of a thick liquid at room temperature. The mixture in this case was prepared by the method used for the preparation of an unground mixture described earlier. The A.C. used in this preparation was preground for two hours in a ball mill.

The Preparation of A.C. Contaminated with Zinc Acetate

A purified sample of A.C. was dissolved in a minimum quantity of dimethylsulphoxide. The solution was filtered and the A.C. precipitated by adding ten per cent aqueous solution of zinc acetate. The temperature was not allowed to rise above room temperature during the addition. The precipitate was washed with alcohol, and then with ether. The material was dried under vacuum and stored in a dark coloured bottle.

The Decomposition and The Measurement of Pressure

The decomposition and the measurement of the pressure of the gas evolved were carried out as described earlier (CHAPTER 7).

The Determination of Zn^{++} in A.C. Contaminated with Zinc Acetate

A 250 mg quantity of the contaminated sample was decomposed at 171.5°C. The solid products were dissolved in warm 2 N hydrochloric acid and filtered. The solution was neutralised with 2 N sodium hydroxide and diluted to 100 ml. The determination of Zn^{++} was carried out by titrating the above solution with 0.01 M E.D.T.A. solution using Erio-chrome black-T as indicator.

Identification of the Gaseous Products

The gaseous products other than nitrogen were identified by infra-red spectroscopy as described earlier.

RESULTS AND INTERPRETATION

8.1 THE EFFECT OF ZINC ACETATE

It has been found that zinc acetate reacts with A.C. in two steps in a similar way to the metal oxides. The second step, which represents a major portion of the pressure-time plot, is similar in shape to that of pure A.C. Swann[10], who studied the reaction of zinc acetate with A.C. by measuring the gaseous volume as a function of time did not find any evidence that the reaction occurs in two steps. This may be due to the difference in the extent of grinding or due to the lack of sensitivity of the technique employed. The general shape of the curve, however, resembles closely the one obtained in the present investigation.

The catalytic effect of zinc acetate on the early stages of the decomposition of A.C. at different temperatures is shown in FIGURE 8.1. The rate of the first step increases as the temperature increases and at 171.5°C it develops into an explosion. At this temperature the two steps no longer remain distinct. At lower temperatures the curve during the first step appears to be 'S' shaped most probably because some time is taken for the reactants to heat up. But if an allowance is made for this time lag, the curve becomes deceleratory as was found with metal oxides (CHAPTER 7).

EFFECT OF TEMPERATURE ON THE EARLY STAGES OF DECOMPOSITION OF A.C.+ZINC ACETATE (4:1) MIXTURE

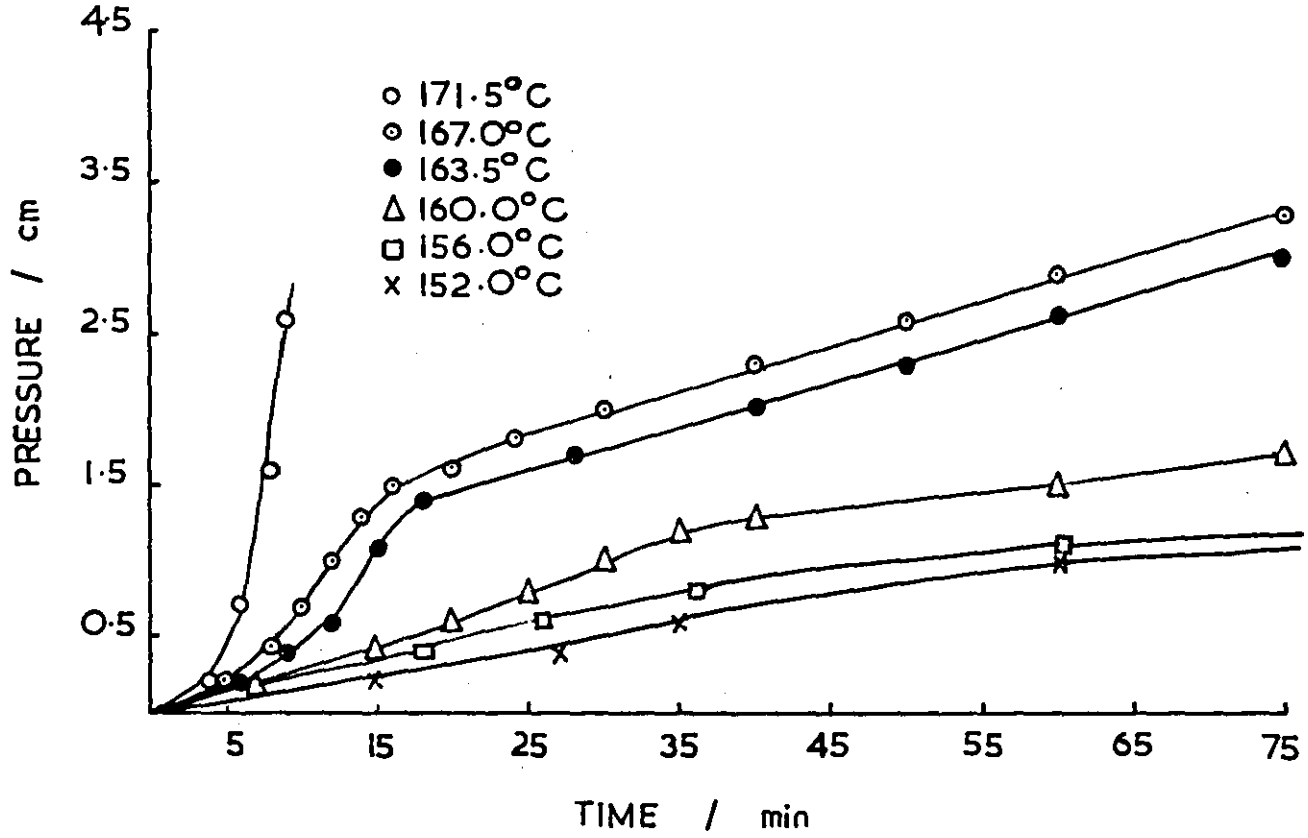


FIGURE 8.1

At the lowest temperatures (below 160°C), the second stage of the reaction is so slow as to be hardly detectable.

8.2 THE EFFECT OF METAL STEARATES

The effect of different metal stearates on the decomposition of A.C. at 163.5°C is shown in FIGURE 8.2. Although the two stages of the reaction are not well defined, there is a clear indication that the reaction has occurred in two steps. The curves are similar in shape to each other, but they differ from those of the oxides. After the completion of the first stage, the curve becomes slightly acceleratory. The acceleratory period of the curve is difficult to explain unless the full mechanism of the reaction during the first stage is established. It is possible that during the first stage of the reaction some water is formed, which reacts with the iso-cyanic acid vapour to produce ammonia and carbon dioxide.

$$H - N = C = O + H_2O \longrightarrow CO_2 + NH_3$$

The occurrence of this reaction is supported by the fact that the gaseous products contain carbon dioxide, and also by the fact that the total pressure of gas evolved is found to be considerably higher than normally obtained. Ammonia formed in this reaction is not detected in the gas phase. This is undoubtedly because it reacts with iso-cyanic acid to form urea.

Owing to its poor definition, the exact shape of the curve during the first step of the decomposition is not known. In an attempt to resolve the first stage, the effect of temperature on the early stages of the decomposition of an A.C. and zinc stearate

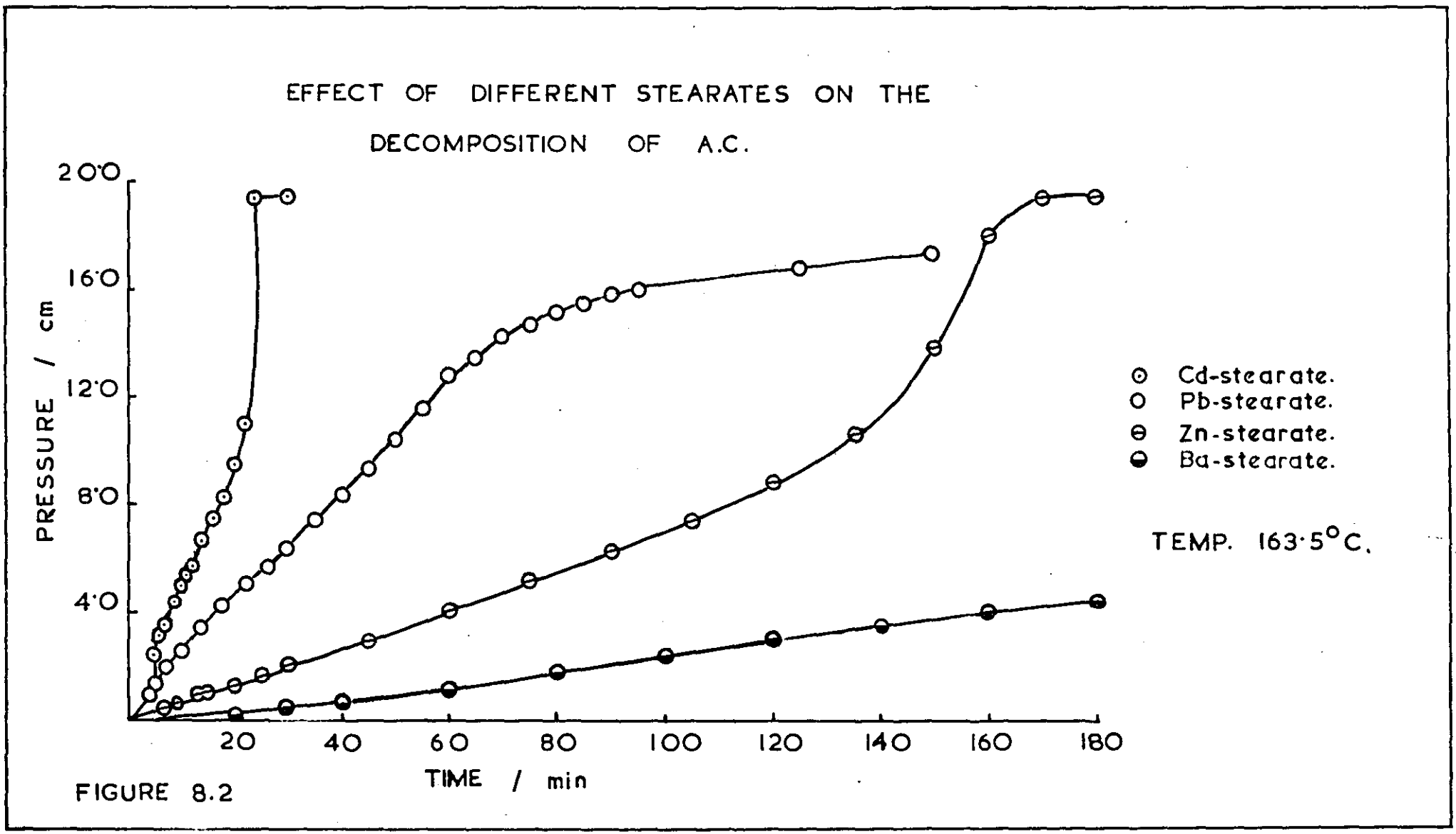

EFFECT OF DIFFERENT STEARATES ON THE
DECOMPOSITION OF A.C.
PRESSURE / cm
20·0
16·0
12·0
8·0
4·0
20
40
60
80
100
120
140
160
180
TIME / min
Cd-stearate.
Pb-stearate.
Zn-stearate.
Ba-stearate.
TEMP. 163·5°C.

FIGURE 8.2

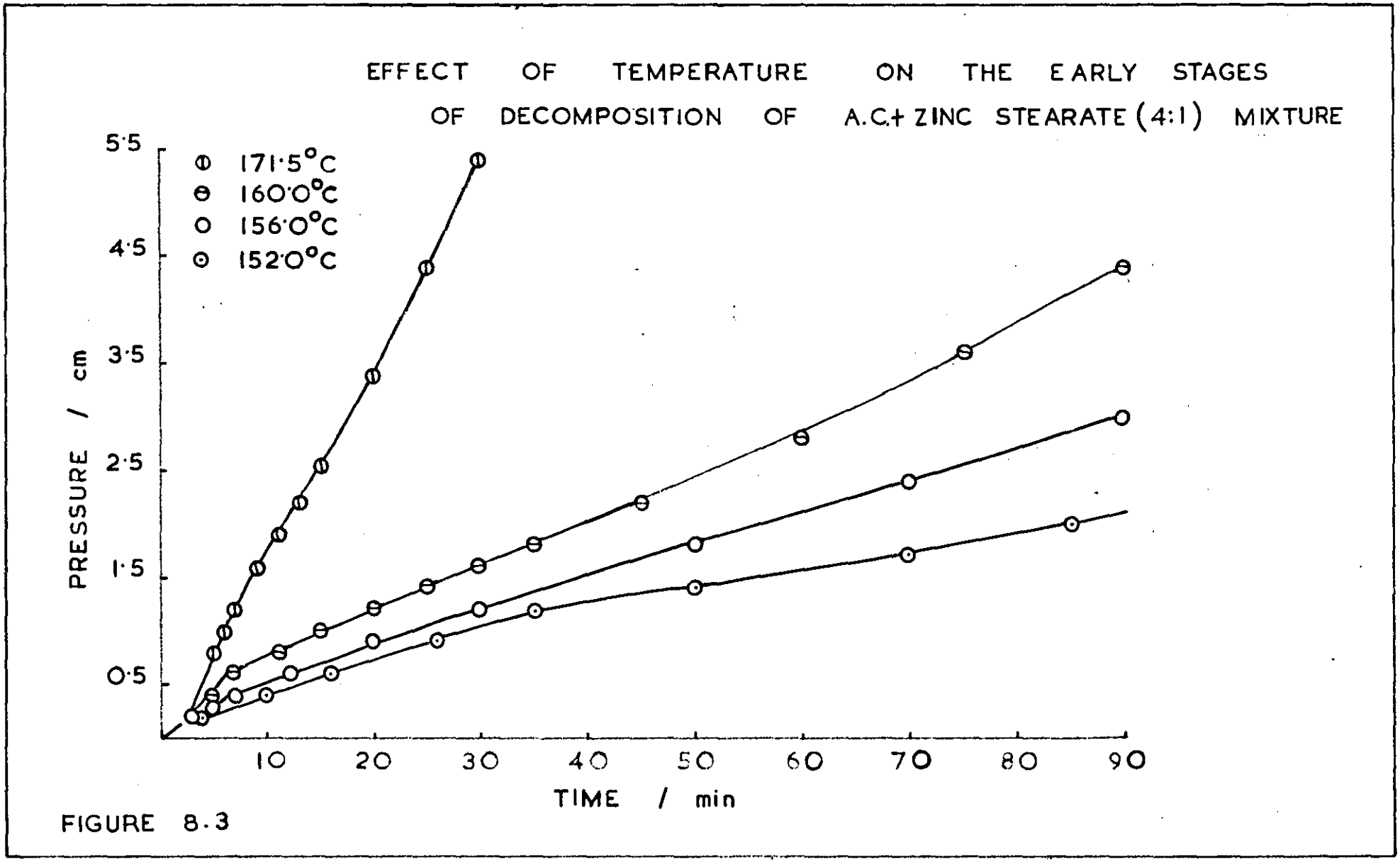

EFFECT OF TEMPERATURE ON THE EARLY STAGES
OF DECOMPOSITION OF A.C.+ ZINC STEARATE (4:1) MIXTURE
171·5°C
160·0°C
156·0°C
152·0°C
PRESSURE / cm
5·5
4·5
3·5
2·5
1·5
0·5
10
20
30
40
50
60
70
80
90
TIME / min

FIGURE 8.3

mixture has been studied. The results are shown in FIGURE 8.3. The rate of the reaction during the first stage increases as the temperature increases, but the shape is still ill defined at all the temperatures. It is believed that the second stage of the reaction starts before the first stage terminates, thus preventing the first step from being observed separately.

8.3 THE EFFECT OF ZINC OCTOATE

The working range of a mixture of zinc octoate and A.C. is found to be much lower than that of a mixture of any of the other materials with A.C. At a temperature higher than 144°C, the gas evolution is so fast that it appears as though an explosion has occurred. A plot of gaseous pressure as a function of time at three temperatures is shown in FIGURE 8.4. The decomposition curve shows that the reaction occurs in two stages, but a major portion of the curve differs in shape from the curves obtained with the oxides. It is similar to those obtained with the stearates and therefore can be explained similarly. The gaseous products, in this case, also contain carbon dioxide in the same way as with the stearates.

8.4 THE EFFECT OF UREA

The catalytic effect of urea on the decomposition of A.C. is shown in FIGURE 8.5. From the curves it appears that the reaction takes place in two steps. Urea itself decomposes at 132°C and liberates iso-cyanic acid and ammonia.

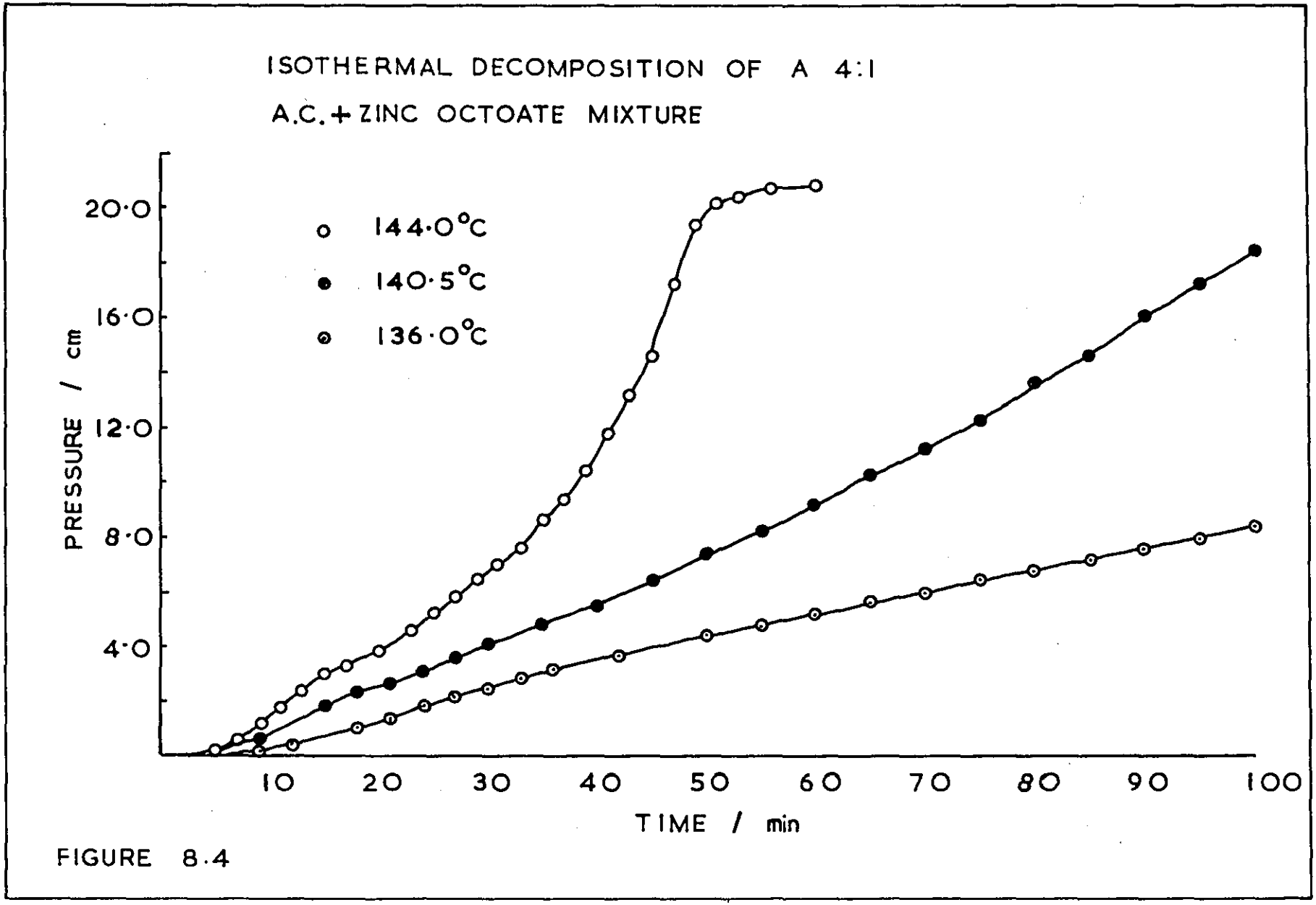

ISOTHERMAL DECOMPOSITION OF A 4:1
A.C. + ZINC OCTOATE MIXTURE
144·0°C
140·5°C
136·0°C
PRESSURE / cm
20·0
16·0
12·0
8·0
4·0
10
20
30
40
50
60
70
80
90
100
TIME / min

FIGURE 8.4

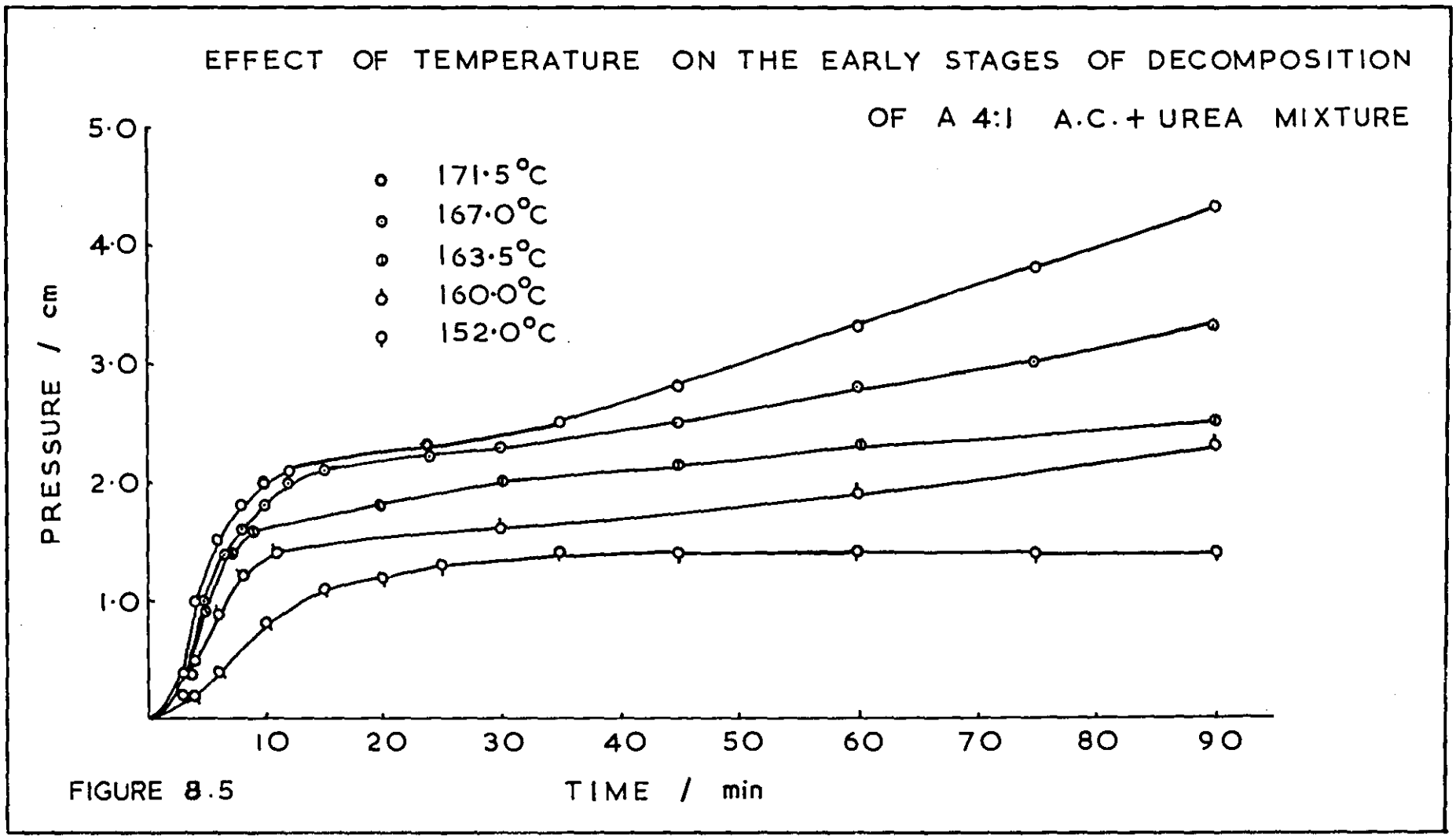

EFFECT OF TEMPERATURE ON THE EARLY STAGES OF DECOMPOSITION
OF A 4:1 A.C.+ UREA MIXTURE
171·5°C
167·0°C
163·5°C
160·0°C
152·0°C
PRESSURE / cm
5·0
4·0
3·0
2·0
1·0
10
20
30
40
50
60
70
80
90
TIME / min

FIGURE 8.5

$$H_2N.\ CO.\ NH_2 \rightleftharpoons H - N = C = O + NH_3$$

Some of the iso-cyanic acid may polymerize to form cyanuric acid and cyamelide, leaving free ammonia in the system. It is, therefore, difficult to decide how much pressure has been developed in the first stage from the gaseous products of the urea and A.C. reaction, because a significant proportion of the total gas must have been contributed by the gaseous products from the decomposition of urea itself. The percentage of the first stage is temperature dependent. This may partly be due to the difference in the extent of the decomposition of urea at different temperatures, and partly due to the reaction of urea with A.C.

It has been found that although the shape of the second stage of the A.C. and urea reaction is similar to that of the second stage of the A.C. and metal oxide reaction, the rate in the former is even slower than that of pure A.C. This suggests that under the present experimental conditions the overall reaction is not accelerated by urea.

8.5 THE EFFECT OF ZINC DUST

FIGURE 8.6 shows the effect of pure zinc dust on the decomposition of A.C. at 171.5°C. The reaction proceeds in a very similar manner to that of pure A.C. and there is no indication that the reaction has occurred in two steps. The main part of the curve has a very similar shape and rate to that of pure A.C. It is concluded that zinc dust does not react with A.C. and thus shows no catalytic effect.

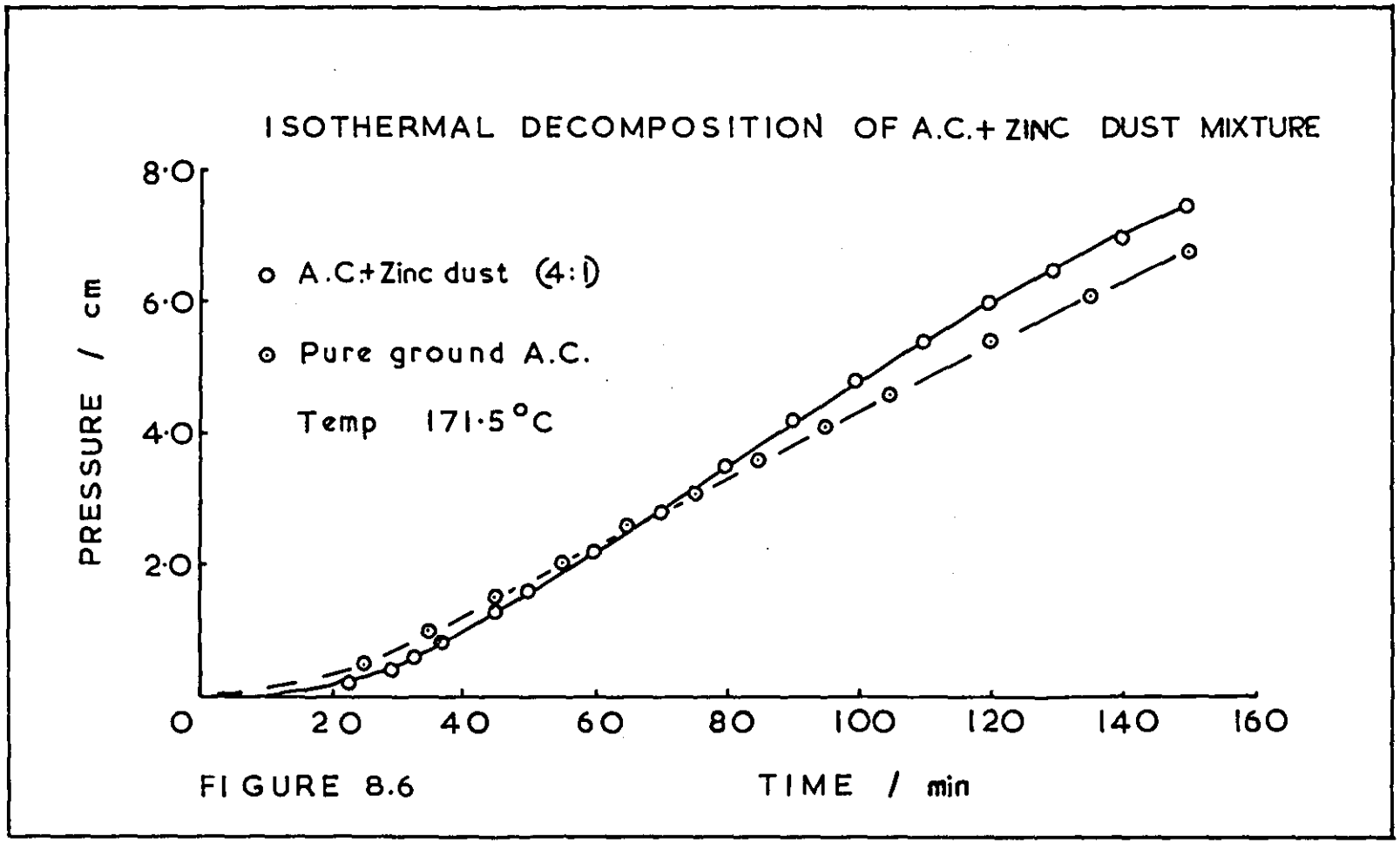

ISOTHERMAL DECOMPOSITION OF A.C.+ ZINC DUST MIXTURE
PRESSURE / cm
8·0
6·0
4·0
2·0
o A.C+Zinc dust (4:1)
⊙ Pure ground A.C.
Temp 171·5 °C
0
20
40
60
80
100
120
140
160
TIME / min

FIGURE 8.6

8.6 THE EFFECT OF CONTAMINATING A.C. WITH ZINC ACETATE

During the preparation of A.C. contaminated with zinc acetate, it was observed that the colour of the solution became dark. It was thought that some chemical reaction might have occurred. The infra-red spectrum of the precipitated material was found to be identical to that of pure A.C., suggesting no change in the chemical character.

The decomposition curve of the contaminated sample is shown in FIGURE 8.7. It is found that the rate of the decomposition at 171.5°C is significantly higher than that of pure A.C. but there is no indication that the reaction has occurred in two steps. The shape of the curve is similar to that of pure A.C.

Owing to the higher rate of decomposition at 171.5°C, it was thought that at a high enough temperature an explosion might occur, as was observed when the other activators were mechanically mixed with A.C. It was found that no explosion occurs at 180°C. Only an increase in the rate is observed.

The degree of contamination was assessed by determining Zn^{++} ion content in the contaminated sample. This was found to be 0.51 and 0.49% by weight in duplicate determinations. This indicates that the sample was only slightly contaminated with zinc acetate and that the increase in the rate of decomposition at 171.5°C was probably due as much to the change in the method of preparing the sample and the consequent change in the particle size, as to the contamination itself.

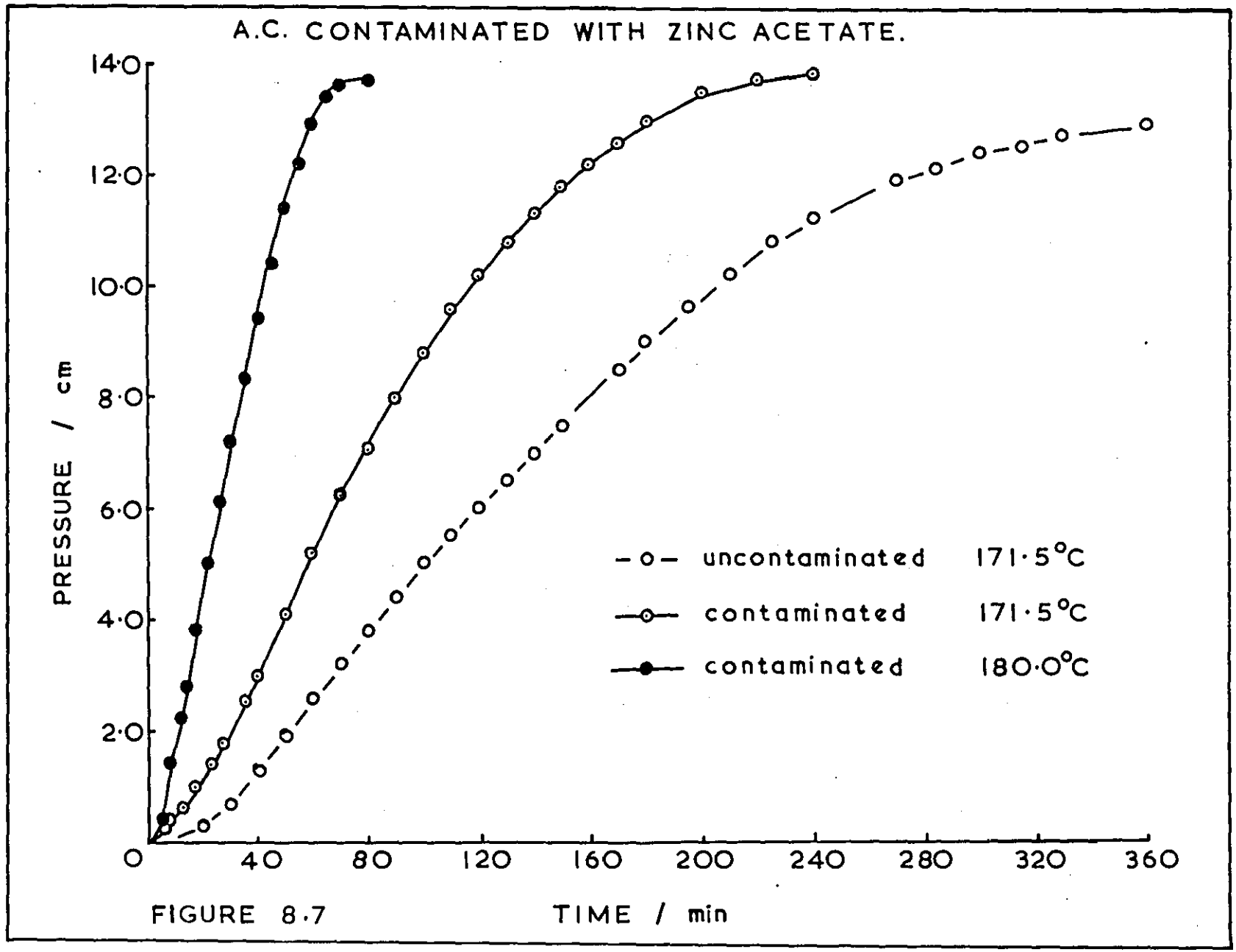

A.C. CONTAMINATED WITH ZINC ACETATE.
PRESSURE / cm
14·0
12·0
10·0
8·0
6·0
4·0
2·0
0
40
80
120
160
200
240
280
320
360
TIME / min
uncontaminated 171·5°C
contaminated 171·5°C
contaminated 180·0°C

FIGURE 8.7

8.7 GENERAL DISCUSSION

The observations indicate that the decomposition of A.C. in the presence of activators takes place in two steps. This phenomenon is common to all the activators investigated.

The first stage reaction in some of the cases is not well defined. This first stage includes reactant heat-up time, and if allowance is made for this factor, the shapes of all the curves are believed to be similar to those obtained with A.C. and metal oxides, indicating a surface reaction.

The overall activation of A.C. most probably depends on the nature of the reaction taking place between A.C. and an activator during the early stages. The second stage represents the major portion of the reaction between A.C. and an activator, but the exact rate of decomposition during the second stage is difficult to determine because the shapes of curves are different for different reactions, and the kinetic mechanism of the decomposition is unknown. TABLE 8.1 shows the rate of the pressure increase from 3.5 to 5.0 cm during the second stage of the reaction for A.C. and different activators.

TABLE 8.1

Rate of pressure increase in the second stage of the reaction

Catalyst	Temperature °C	Rate cm / min
Cd-stearate	163.5	0.500
Pb-stearate	163.5	0.200
Zn-stearate	163.5	0.070
Ba-stearate	163.5	0.023
Zn-octoate	163.5	1.500
Zn-acetate	163.5	0.027
Zn-dust	163.5	0.027
Urea	163.5	0.003
None	163.5	0.027

Zinc octoate is the most effective catalyst of all the materials studied. Its mixture with A.C. has the highest rate of gas evolution and explodes at the lowest temperature.

It has been found that urea has practically no catalytic effect on the decomposition of A.C. The reason may be that the urea decomposes fast and forms iso-cyanic acid as one of the products. The latter polymerises into cyanuric acid and cyamelide, which cover the surface of the A.C. so that the interfacial contact between A.C. and the remaining portion of the urea particles is lost, thus making the urea ineffective.

If one compares the activities of different stearates, the

metal ions are in the following order of activity

$$Cd > Pb > Zn > Ba$$

Nass[60] also found that cadmium salts are the most effective and barium the least, when he compared the catalytic activities of the salts of different metals. His theory for this order of activity, that the activating effect by these metals proceeds via the formation of the intermediate metallic azodicarboxylates, does not seem likely in this case because it supposes alkaline hydrolysis of A.C. as the first step in the mechanism (CHAPTER 5). Other workers[62,63,64] have also found that the salts of cadmium and lead are comparatively better catalysts in the decomposition of A.C. than the salts of other metals.

The reason for this order of activity is not yet clear. When the reaction takes place at the interface between the A.C. and the activator, a barrier of solid product is set up between the two during the early stages of the reaction. The rate of the second stage may depend on the nature of the barrier and the diffusion of the reactant through the barrier. But the work on the metal oxides suggests that the first step follows first order reaction kinetics, which indicates that the reaction is not influenced by the diffusion process. An alternative explanation may be that the amount of heat production during the first step reaction between A.C. and cadmium stearate is higher than that with A.C. and any of the other stearates. The liberation of a greater amount of heat raises the local temperature and accelerates the reaction to a greater extent. The rate of heat production depends mainly on two factors - the rate constant

of the surface reaction occurring during the early stages and the interfacial contact between A.C. and activator particles (see CHAPTER 7). The reason for cadmium stearate being more effective than others may be that either the rate constant is higher, or the interfacial contact area is greater. In the case of metal oxides it has been found that the increase in the grinding time increases the proportion of the first stage, or in other words, the magnitude of the first stage is proportional to the interfacial contact area between A.C. and activator particles. In the reaction of A.C. with metal stearates, the two steps are not well defined (see FIGURE 8.2) so the relative magnitude of the first stage reaction in the case of different stearates is difficult to compare. But zinc octoate being a liquid, for example, almost certainly has a higher interfacial contact area with A.C. than do any of the solids and this could explain why it shows great effectiveness as a catalyst.

CHAPTER 9

CONCLUSIONS AND RECOMMENDATION FOR FUTURE WORK

The overall picture which emerges from the present investigation is as follows:

PART I

On decomposition azodicarbonamide (A.C.) forms four major solid products, namely, urazole, biurea, cyanuric acid and urea, and a small quantity of cyamelide. The gaseous product consists of nitrogen, carbon monoxide, iso-cyanic acid and ammonia. Whether iso-cyanic acid or ammonia remain at the end of the reaction depends on whichever is formed in excess, which in turn depends on the temperature of decomposition.

A.C. decomposes by the following two primary processes:

(1) $2\ NH_2.CO.N:N.CO.NH_2 \longrightarrow \underset{\text{Biurea}}{NH_2.CO.NH.NH.CO.NH_2} + N_2 + 2\ HNCO$

(2) $2\ NH_2.CO.N:N.CO.NH_2 \longrightarrow \underset{\text{Urazole}}{\text{H-N(-C(=O)-NH-C(=O)-)-N-H}} + N_2 + [HNCO + NH_3 \rightleftharpoons \underset{\text{Urea}}{NH_2.CO.NH_2}] + HNCO$

Major portions of the iso-cyanic acid, biurea, urazole, urea and nitrogen are formed via these two processes. In addition, the following secondary reactions occur in which either new secondary

products or the same products as result from the primary processes, are formed.

(i) Iso-cyanic acid polymerises to form cyanuric acid and cyamelide.

(ii) Iso-cyanic acid reduces undecomposed A.C. to form carbon monoxide along with biurea and nitrogen.

(iii) At higher temperatures (above ~180°C), biurea decomposes to form urazole and ammonia. The ammonia, produced in this reaction, reacts with iso-cyanic acid to produce urea.

PART 2

The activation of A.C. occurs by way of an initial surface reaction between A.C. and the activator. This initial step occurs more readily and has a lower activation energy than the decomposition of pure A.C. In the decomposition of an A.C. and zinc oxide mixture the first step represents only a small fraction of the total reaction. The exact magnitude of the first step depends on the extent of the grinding and compression together of the two components.

The decomposition of an A.C. and activator mixture is an exothermic process. The heat liberated in the first step increases the local temperature and accelerates the decomposition rate. The rate of heat production varies from one activator to another and different degrees of activation result. This rate is dependent on two main factors - the rate constant of the surface reaction

occurring during the early stages, and the interfacial contact area between the two reactant particles.

The catalytic efficiencies of the oxides and the stearates of four metals investigated are in the order

$$Cd > Pb > Zn > Ba$$

The estimated rate of heat production during the first step reaction of A.C. with the oxides of the first three metals is in the same order (with barum oxide, the rate of heat production was impossible to estimate). This suggests that the rate of heat production in the first step of the reaction of A.C. with an activator determines the catalytic efficiency of the activator.

RECOMMENDATION FOR FUTURE WORK

1. The present knowledge of the mechanism of the catalytic decomposition of azodicarbonamide (A.C.) is inadequate. An attempt should be made to learn more about the nature of the first step reaction between A.C. and an activator. To investigate the first step of the reaction, the following methods are recommended:-

   (i) A complete analysis of the gaseous and possibly the solid products, formed during the early stages of the reaction of A.C. with an activator, should be carried out.

   The gaseous products could be analysed by the method employed in this investigation by using an increased sample weight. Alternatively, the analysis could be conducted by vapour phase

chromatography, using a 'silicone' column, on which isocyanic acid can be resolved successfully.

(ii) An electronmicrograph of the partially decomposed material obtained during the early stages should be taken. This would provide the information regarding the physical state of the reactant and product particles.

2. The catalytic effects of n-type and insulator type oxides have been studied in the present investigation. To learn whether the electronic factor has an influence on the mechanism of catalysis by metal oxides, the effects of other types of oxides should be studied. An investigation of the effect of nickel oxide, and zinc oxide doped with the oxides of gallium and lithium would provide some instructive information.

APPENDIX I

The 'slope' has been calculated by using the following equation:

$$\text{Slope} = \frac{\Sigma XY - \frac{\Sigma X \Sigma Y}{N}}{\Sigma X^2 - \frac{(\Sigma X)^2}{N}}$$

Where X and Y are the two variables along the two axes.

REFERENCES

1. R. A. REED, 'The Chemistry of Modern Blowing Agents', Plastics Progress, Iliffe and Sons Ltd., London (1955).

2. L. I. NATURMAN, Plast. Tech., 15 (10), 41-47 (1969).

3. Chem. Abs., 71, 125880 j, (1969).

4. Chem. Abs., 71, 125651 k, (1969).

5. Chem. Abs., 71, 31037 n, (1969).

6. R. A. REED, Brit. Plast., 33, 468 (1968). (1960)

7. M.M. WILLIAMS, W. S. McEVAN and R. A. HENRY, J. Phys. Chem., 61, 261-7 (1957).

8. Chem. Abs., 64, 9601 f, (1966).

9. Chem. Abs., 60, 5342 g, (1964).

10. W. A. SWANN, M.Sc. Thesis, Loughborough University of Technology, (1967).

11. J. H. BRYDEN, Acta. Cryst., 14, 61, (1961).

12. J. ARMAND, Bull. Chim. Soc. (France), 1658-1667, (1966).

13. J. P. PICARD and J. L. BOIVIN, Canad. J. Chem., 29, 223-7, (1951).

14. H. R. LASMAN and J. C. BLACKWOOD, Plast. Tech. 9 (9), 37-39, (1963).

15. R. GLICKSMAN and C. K. MOREHOUSE, J. Electrochem. Soc., 108, 303 - 306, (1961).

16. C. M. KRAEBEL and S. M. DAVIS, J. Org. Chem., 34 (7), 2226-2229, (1969).

17. R. JOINER, F. VIDAL and H. MARKS, Tech. Molitoria, 17 (10), 234-45, (1966). (Chem. Abs., 65, 19215^{g}, (1966))

18. G. S. HAMMOND, J. N. SEN and C. E. BOOZER, J. Am. Chem. Soc., 77, 3244, (1955).

19. C. H. S. WU, G. S. HAMMOND and J. WRIGHT, J. Am. Chem. Soc., 82, 5386, (1960).

20. A. M. HYSON, J. K. BEASLEY, P. F. HOLUB, S. C. OVERBAUGH and R. C. SCHREYER, Polychemicals Department, Du Pont Experimental Station, Wilmington, Delaware, Unpublished work.

21. J. THIELE, Am., 271, 127, (1892). (Chem. Abs., 1298, 1430, (1892))

22. H. ITO, Japan Plast. Age, 7 (5), 46-48, (1969).

23. H. ITO, Japan Plast. Age, 7 (6), 25-30, (1969).

24. J. THIELE and O. STANGE, Ann, 283, 1, (1894).

25. E. A. WERNER and W. R. FEARON, J. Chem. Soc. 117, 1356, (1920).

26. G. HERZBERG and C. REID, Disc. Farad. Soc., 9, 92, (1950).

27. I. L. FINAR, 'Organic Chemistry', 4th Edition, 299, (1963).

28. W. E. GARNER (Ed.), 'Chemistry of The Solid State', Butterworths and Co. Ltd., London, Chapter 7, (1955).

29. W. GOMES, Nature, 192, 865, (1961).

30. J. H. TOPLIN, Nature, 194, 471, (1962).

31. J. H. SHARP, G. W. BRINDLEY, B. N. NARAHARI ACHAR, J. Am. Ceram. Soc., 49, 379, (1966).

32. M. AVRAMI, J. Chem. Phy., 7, 1103, (1939).
8, 212, (1940).
9, 177, (1941).

33. B. V. EROFE'EV, Comp. Rend. Sci., URSS, 52, 511-514, (1946).

34. A. K. GALWEY, Chemistry of Solids, Science Paperbacks, London, (1967).

35. E. STAHL (Ed.), 'Thin-layer Chromatography', Academic Press Ltd., London, (1965).

36. 'Dyeing Reagents for Thin-layer and Paper Chromatography', Published by E. Merck A.G. - Darmstadt, Germany.

37. J. H. WILLIAMS and I. FLEMING, 'Spectroscopic Methods in Organic Chemistry', McGraw-Hill and Co., London, (1966).

38. A. I. FINKELSHTEIN, E. N. BOITSOV and Y. I. MUSHKIN, State Sci. Res. and Dev. Inst., U.S.S.R., Zavod. Lab., 38, 1, (1964).
(Anal. Abs. 12, 1792, (1965))

39. E. N. BOITSOV and A. I. FINKELSHTEIN, Zhur. Anal. Khim., 17 (6), 748-750, (1962).
(Anal. Abs. 10, 2775, (1962))

40. H. H. BROWN, Anal. Chem., 31, 1844, (1959).

41. R. E. CLINE and R. M. FINK, Anal. Chem., 28, 47, (1956).

42. G. C. ELLIS and R. L. FORMAINI, J. Agr. Food Chem., 3, 615, (1955).

43. F. W. HOOVER, H.B. STEVENSON and H. S. ROTHROCK, J. Org. Chem., 28 (7), 1825-1830, (1963).

44. J. Y. P. MUI and R. A. BACK, Canad. J. Chem., 41, 826, (1963).

45. S. R. SMITH and H. B. JONASSEN, J. Inorg. Nucl. Chem., 29, 860, (1967).

46. A. YAMAGUCHI, J. Chem. Soc. (Japan), Pure Chem. Sec., 78, 1467, (1957).

47. R. MECKE and F. LANGENBUCHER, 'Infra-red Spectra of Selected Chemical Compounds', Published by Heyden and Son Ltd., London, (1965).

48. W. M. PADGETT, J. M. TALBERT and W. F. HAMMER, J. Chem. Phys., 26, 959, (1957).

49. R. NEWMAN and R. M. BADGER, J.A.C.S., 74, 3545, (1952).

50. W. M. PADGETT II and W. F. HAMMER, J. Am. Chem. Soc., 80, 803, (1958).

51. C. J. POUCHERT, 'The Aldrich Library of Infra-red Spectra', Published by Aldrich Chem. Co., U.S.A.

52. M. MASHIMA, Bull. Chem. Soc. (Japan), 37, 974, (1964).

53. T. A. SCOTT, Jr., and E. L. WAGNER, J. Chem. Phy., 30, 465, (1959).

54. R. H. PIERSON, A. N. FLETCHER and E. St. C. GANTZ, Anal. Chem., 28, 1218, (1956).

55. F. J. SCHILTKNECHT, Promotionsarbeit, 3403 (Zurich), (1963).

56. Chem. Abs., 69, 107374^{b}, (1968).

57. Chem. Abs., 67, 44410^{w}, (1967).

58. Chem. Abs., 66, 38479^{p}, (1967).

59. Chem. Abs., 63, 5867^{d}, (1965).

60. L. I. NASS, Mod. Plast., 40 (7), 151-237, (March 1963).

61. C. J. BENNING, Plastic Foams - The Physics and Chemistry of Product Performance and Process Technology, Volume 1, Published by John Wiley and Sons, Inc. (1969).

62. R. A. LALLY and L. M. ATLER, S. P. E. Journal, 23 (11), 69-74, (1967).

63. Chem. Abs., 71, 39922^{t}, (1969).

64. Chem. Abs., 71, 4159^{x}, (1969).

65. Brit. Patent, 1221 153, (1971).

66. Chem. Abs., 64, 11410^{e}, (1966).

67. Chem. Abs., 57, 1679^{c}, (1962).

68. J. M. THOMAS and W. J. THOMAS, 'Introduction to the Principles of Heterogeneous Catalysis', Academic Press, Inc. (London) Ltd., (1967).

69. G. M. SCHWAB, 'Semiconductor Surface Physics', 283, University of Pennsylvania Press, Philadelphia, (1957).

70. M. O. KEEFFE and F. S. STONE, Proc. Roy. Soc., A267, 501, (1962).

71. A. I. VOGEL, 'Text Book of Quantitative Inorganic Analysis', Third Edition, 433, (1964).

72. V. I. ALESEENKO and V. E. DENISENKO, Kozh. Obur., Prom., 10 (10), 41-44, (1968).

73. H. TAKAHASHI and K. TSUTSUMI, DECHEMA (Monogr.), 57, 475-494, (1966).

74. P. P. BUDNIKOV and A. M. GINSTLING, 'Principles of Solid State Chemistry', Elsevier Publishing Company, Amsterdam, (1968).

75. K. LAIDLER, 'Chemical Kinetics', Second Edition, McGraw-Hill Book Company Inc., 14, (1965).