Gas-Solid Reactions:
The Kinetics of the Decomposition of
Silver Carbonate

by

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A study has been made of the general non-catalytic gas-solid reaction,
\[ a^A_{\text{gas}} + b^B_{\text{solid}} \rightleftharpoons g^G_{\text{gas}} + s^S_{\text{solid}} \]
while the decomposition of silver carbonate has been investigated experimentally.

The equations for non-isothermal reaction in a porous pellet are presented, with solutions for the simple isothermal case for reaction at initial times.

The receding interface theory of reaction in an impervious solid is described, with particular attention paid to the problem of thermal instability in exothermic reactions. It is shown that inclusion of a transient term in the energy balance equation, accounting for the changing enthalpy of the reacting solid, radically changes the analysis and gives a more realistic representation of practical situations.

The decomposition of silver carbonate has been studied by measuring the rate of carbon dioxide evolution and by following the temperature of the pellet during reaction. In the presence of water vapour the reaction exhibits an activation energy of 30 Cals/gm.mole and it is found that the presence of water vapour enhances diffusion rates by creating a more porous oxide lattice. The rate of decomposition of carbonate pellets is partly controlled by the rate of heat transfer to the pellet, resulting in a lowering of the reaction temperature. Application of the
theoretical considerations to the results is successful.

Full use was made of a KDF9 computer in connection with both the theoretical and experimental work.
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CHAPTER 1

INTRODUCTION AND SUMMARY

The general subject of non-catalytic gas-solid reactions has been studied, and particular attention paid to the thermal decomposition of silver carbonate. The report is divided into two main sections, theoretical and experimental, preceded by a discussion and literature survey in Chapter 2 pertaining to the subject of study.

The theoretical section of the report is to be found in Chapters 3-6. Chapter 3 is distinguished from the others as being concerned with reaction within porous solids, where reaction proceeds throughout a zone in the solid at varying rates. This has had limited treatment in the literature, and although only simplified solutions of the general equations presented are given, it is recommended that further research in this field is undertaken.

The rest of the theoretical section is devoted to expansion of the well-established sharp-interface or "shell-progressive" mechanism of reaction in impervious solids. Chapter 4 is restricted to isothermal cases, but the theory already in existence is taken further to include various geometries, while the effect of a distribution of particle sizes is also considered. General solutions of the resulting dimensionless equations are presented showing the effect of diffusion on the course of the reaction. In Chapter 5 the equations are modified to include heat transfer effects so that the theory is then applicable to non-isothermal situations.
The problems of reaction instability, including both geometrical and thermal instability, are described, the theory of thermal instability being presented in a new and simplified light. Criteria for instability are developed and presented graphically. While Chapters 4 and 5 are restricted to purely steady-state analyses in both mass and heat balances, the heat balance is made transient in Chapter 6 by the inclusion of an accumulation term related to the heat capacity of the solid. This modification puts the whole of the non-isothermal theory of gas-solid reactions in quite a different light and highlights the shortcomings of the steady-state approach, particularly in regard to thermal instability in exothermic reactions. In this respect, Chapter 6 represents a completely new approach to the theoretical study of gas-solid reactions.

A large part of Chapters 4–6 has been accepted for publication in "Chemical Engineering Science" (Beveridge and Goldie) under the title "Effectiveness factors and instability in non-catalytic gas-solid reactions: the effect of solid heat capacity".

Work on the thermal decomposition of silver carbonate, and to a lesser extent on the recombination reaction, is described in Chapters 7–9. The previous work on silver carbonate and the resulting problems regarding its decomposition to the oxide are described in Chapter 7 and the relation to the present work shown. The apparatus and technique used in the present work is described in Chapter 8, as well as the material used for the decomposition experiments. The results and discussion of these experiments are given in Chapter 9. A novel technique of following the reactions
by measuring the reaction temperature is shown to simplify the analyses of the experimental system. The effect of water vapour and carbon dioxide on the reaction can be evaluated by this method, which was also used to measure the equilibrium pressure of carbon dioxide at various temperatures. The decomposition reaction was studied both by this technique and by following the carbon dioxide concentration of the exit gases from the reactor in a katharometer over the range 160–220°C. It was found that the reaction shows, in the presence of water vapour, an activation energy of about 30 Cals/g.mole, somewhat in excess of previously recorded values. When following the reaction of a moulded sphere of carbonate, the decomposition rate was found to be seriously affected by heat transfer to the sphere from the surroundings. The non-isothermal character of these reactions was overcome by decomposing the carbonate in a more finely divided form. Correlation with theory was found, when attempted, to be good. The effect of water vapour on the reaction was found to be due, at least in part, to its effect on the subsequent structure of the silver oxide formed by decomposition. Photographic evidence of this effect is presented.

In Chapter 10, brief conclusions and suggestions relating to all the work are presented.

Experimental results are presented in tabular form in Appendix A.

The diffusibility of the moulded silver carbonate was determined by a novel method, which is described in Appendix B. It is recommended that further work on the application of this method to the general measurement of diffusion coefficients in porous
solids is undertaken.

Boundary layer heat and mass transfer coefficients and rates related to the $\frac{1}{4}$" spheres used in the experimental study are given in Appendix C. The theories of non-equimolar counterdiffusion and thermodynamic equilibrium pressures, together with some particular results of the latter, are described in Appendices D and E respectively.

The theories developed in Chapters 4-6 were applied mainly to the sphere. Further results for the infinite cylinder and the slab or thin plate are given in Appendix F.

Appendix G describes the computer programs used in the research. The programs themselves are given in Atlas Autocode.

Notes At the foot of each page is given the number of the last section, Figure (F), Table (T) or Plate (P) presented on that page, together with the page number. All graphical, diagrammatic or photographic illustrations associated with the text are presented separately after the Appendices, and before the nomenclature and references. On these Figures and Plates are given both the number of the Figure and the section of text to which it refers. For example, Fig. 4(8.4).8 indicates that the figure presented, i.e. Fig. 4.8, was referred to in Section 4.8.4. The page number of the first Figure associated with each Chapter or Appendix is given in the Contents list.
CHAPTER 2

REVIEW OF GAS—SOLID REACTION LITERATURE

2.1 Introduction. Non-catalytic gas-solid reaction systems involve solid and gaseous phases with the solid phase participating in the chemical reaction and undergoing a conversion. These reactions occur at a well-defined boundary or interface. Cases of solid solutions being formed have been encountered (e.g. Sosman) but are rare and will not be discussed.

Most non-catalytic gas-solid reactions can be represented by the general equation

\[ aA_{\text{gas}} + B_{\text{solid}} \rightleftharpoons gG_{\text{gas}} + sS_{\text{solid}} \quad (2.1) \]

Binary gaseous systems are the most usual, with either two gases, A and G, participating in the reaction or only one, with the other present in the system as an inert. Important examples of such reactions which are of industrial importance are the oxidation of zinc sulphide,

\[ \text{ZnS} + \frac{3}{2}O_2 \rightleftharpoons \text{ZnO} + \text{SO}_2 \]

the calcination of limestone,

\[ \text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2 \]

and the reduction of iron ore,

\[ \text{FeO} + \text{H}_2 \rightleftharpoons \text{Fe} + \text{H}_2\text{O} \]

All these examples have received a great deal of attention in the literature, both from a theoretical and industrial point of view, and together with a wealth of information on many other examples, make up a subject which is of growing importance. The industrial
importance of many gas-solid reactions, e.g. the combustion of fuels and extraction metallurgy has led to a deeper understanding of the governing factors in determining their workings. The various factors which are involved in assessing a situation will be discussed, and although in many cases theoretical and experimental knowledge of a system is lacking the guidance contained in this report may help in the proper direction of effort towards a fuller knowledge. Many existing systems may be better understood if approached with wider appreciation of the various factors involved.

The main difference between non-catalytic and catalytic gas-solid reactions is the normally steady-state nature of catalytic reactions as opposed to the time dependent solid-exhaustion peculiar to non-catalytic reactions. Various other obvious differences also exist such as the absence of most solids-handling problems in catalytic reactions when looked at from an industrial point of view. Various similarities between the two systems obviously exist and recent progress in the catalytic has been reviewed in the articles of Mukherjee and Doraiswamy.

2.2 Summary of factors influencing progress of reaction.

The overall rate of the reaction represented by the general reaction equation above will not always be equivalent to the potential chemical rate determined at the ambient or bulk reactor conditions. For example, in a furnace with the inner wall maintained at a constant temperature and with a steady throughflow of gas of known composition substantial temperature and concentration gradients may occur within and around the solid in the
furnace such that a specific knowledge of the kinetic behaviour of the system may be of little use in determining the actual progress of the reaction. Obviously the "overall" rate of reaction will be influenced by mass and heat transfer to the reaction site from the controlled boundaries. Serious errors can result if mass and heat transfer limitations are ignored. This aspect of gas-solid reactions is well described by Hills.

2.2.1 Reactor systems. The solid may be present in a fixed or moving bed, or in a fluidised bed. Fluidised or fixed beds are commonly encountered in catalytic reactions, and in laboratory-scale non-catalytic reactions, while the moving bed (e.g. the chain grate or sinter strand) is limited to non-catalytic reactions, such as the combustion of coal or the oxidation of zinc sulphide. Moving bed systems are equivalent to fixed beds in which a reaction zone moves through the solid phase.

Bulk physical properties of the solid arrangement affect regional results, for example in determining the rate of movement of reaction zones, heat and mass transfer coefficients, and resultant temperatures and pressure profiles. Radiational effects can also be important.

2.2.2 Solid form. This may be a fine powder, as in fluidised beds, or coarse lumps and rocks (reduction of ores, calcination), or crystals, or regular shapes fashioned artificially such as spheres and cylinders, found commonly in experimental studies, and in industrial applications where the required uniform solid size necessitates pelletisation. Local effects caused by solid may be important, such as gas velocity and temperature changes.
These and other effects will be dependent on the various physical properties of the solid, which must be determined, such as voidage, pore size distribution, density, specific heat etc. Specialised techniques have been developed for the measurement of certain of these properties such as that of Powell for the measurement of thermal conductivity.

2.2.3 Bulk gas: Apart from being often an essential participant in the reaction itself, a flow of gas through the solid interstices is essential for the provision and removal of the reactant and product gases, and in many cases for the supply or removal of the heat of reaction. Preheating or subsequent cooling of the solid phase may also be a function of the bulk gas. Again properties such as viscosity, density etc. must be determined.

The above considerations will therefore affect the relative values of local mass and heat transfer limitations, which can now be mentioned.

2.2.4. a Boundary layer mass and heat transfer. Each solid particle exposed to the flow of bulk gas will develop a low velocity boundary layer through which reacting gases must be transferred. Temperature gradients in this layer will also be set up. In extreme cases of high kinetic rate and low gas velocities the boundary layer effect may control the overall rate.

2.2.4. b Pore diffusion. When the solid particles in the gas stream are porous, or when the solid product of the reaction forms a porous coating on an impervious reactant, total utilisation of the solid interior or of the product/reactant boundary may be restricted by the rate of diffusion of the gaseous species through
the pores. Depending on the size of the pores, normal diffusion, Knudsen or surface diffusion may occur.

2.2.4.c Conduction of heat through the solid. Mass transfer through the boundary layer and through the pores are comparable processes as both are controlled by diffusion coefficients in the gas phase. However, heat transfer in the solid depends on the solid thermal conductivity, so that in certain cases of low voidage temperature gradients can be ignored, whereas concentration gradients will be very high.

2.2.4.d Reaction kinetics. Although this would perhaps seem to be the most important factor in overall rate considerations, in certain situations it might be quite insignificant. However, it is frequently attempted in experimental investigations to create conditions such that only the kinetics of the reaction are important. Relatively high gas velocities, low temperatures, and temperature-controlled furnaces or reactors are the usual means of achieving this.

The above idea of mixed control of overall rate has been studied by Bircumshaw and Riddiford who limit their study to mass or "transport" control, and describe the history of a reaction as transport to the site, adsorption at the site, reaction, and desorption and removal of the gaseous products. The authors discuss the serious errors of assuming control by either mass transfer or kinetics. Isothermal situations are also treated by Levenspiel who develops simple equations for cases of specific control. Carter developed a simple similar model for the sphere with application to both solid/solid and gas-solid reactions. Bischoff (1962) stresses the errors which can result by assuming
overall control by a single factor.

2.3 Reaction mechanism and kinetics. A knowledge of the chemical rate of the reaction is essential, and also of the possible side-reactions, be they similar gas-solid reactions or vapour phase reactions.

A good example of the possibility of many complicating side reactions is the oxidation of zinc sulphide (Beveridge, 1960). Ideal systems with only a single reaction are rare. Even in the thermal decomposition of silver carbonate, a reaction reputed for approach to ideality, the further decomposition of silver oxide to silver is possible,

\[ \text{Ag}_2\text{CO}_3 \rightarrow \text{Ag}_2\text{O} + \text{CO}_2 \]

\[ 2\text{Ag}_2\text{O} \rightarrow 4\text{Ag} + \text{O}_2 \]

In some reactions the solid reactant may be completely used up, as in the combustion of carbon, and the number of moles of reactant and product gases may be different. In general the reaction equation is of the form given in equation (2.1). The non-equimolar nature of the diffusional processes in some systems is usually ignored, though where the diffusion process governs the rate, this leads to errors in the systems analyses. Particular cases of the above equation, Eq. (2.1), are

\[ a\text{A} + B = g\text{G} \quad \text{e.g. carbon combustion} \]

\[ a\text{A} + B = g\text{G} + s\text{S} \quad \text{zinc sulphide oxidation} \]

\[ a\text{A} + B = s\text{S} \quad \text{calcination} \]

In such reactions a certain surface rather than quantity of solid is involved in the reaction, and solid concentrations are unimportant. The fact that non-catalytic gas-solid reactions occur
at a definite boundary or surface was shown by Langmuir.

The unidirectional rate would normally be defined as a function of temperature and pressure by

$$\text{rate} \propto f(T) \cdot f(P)$$

where $T$ is the temperature of the solid surface and $P$ is the partial pressure of the reactant gas, $A$. $f(T)$ is normally defined by the Arrhenius equation as

$$f(T) = A \exp\left(-\frac{E_c}{R'T}\right)$$

where $A$ is a frequency factor and $E_c$ is the activation energy of the reaction. Most actual reactions are found to fit simple rate expressions over small ranges of gas concentrations. For example, McKewan (1961a) shows that the reduction of hematite by hydrogen is governed by a first order law, such that the chemical rate can be expressed as

$$\text{rate} \propto f(T) \cdot P_{H_2}$$

Similarly, Cannon and Denbigh (1957a) have shown that the rate of oxidation of zinc sulphide is governed by $(P_{O_2})^\frac{3}{2}$ over a small range of oxygen pressures. The rate of decomposition of calcium carbonate is a constant for a given temperature, if the partial pressure of carbon dioxide is zero, and for low carbon dioxide concentrations Zawadski and Bretsznajder show that the rate at a given temperature is proportional to $(P_e - P_{CO_2})$ where $P_e$ is the equilibrium pressure.

Often the rate of the forward reaction can be reduced to zero by moderate pressures of product gas, so that a practical equilibrium can be achieved. Consequently any true rate expression
must include a negative element to allow for the reverse reaction. Both irreversible and reversible rate expressions can usually be evaluated by consideration of a Langmuir adsorption. For an irreversible reaction the rate of adsorption is proportional to the number of vacant sites for adsorption.

\[
\text{rate of adsorption} = k_1(1-\beta)P, \quad \text{rate of desorption} = k_2\beta
\]

so that reaction rate is \( k_2P(a-P)^{-1} \) where \( a = \frac{k_1}{k_2} \), \( k_1 \) and \( k_2 \) are temperature dependent adsorption coefficients and \( \beta \) is the fraction of the surface of the solid covered in adsorbed molecules of \( A \). For a reversible reaction the theory can be further extended (see Moore).

Equilibrium between forward and reverse reactions is achieved when the chemical potentials of reactants and products become equal. Hence for the general reaction we have,

\[
\sum \mu^G_i + \sum \mu^S_i = \mu^o_A + \mu^o_B + \sum \mu^S_i
\]

where \( \mu \) is the chemical potential and

\[
\mu_1^o = \mu_1^o + RT \ln P_i
\]

giving,

\[
-R'T \ln P_i^{V_1} = v_1 \mu_1^o
\]

so that,

\[
-R'T \ln \frac{P_i^A}{P_i^G} = -(\sum \mu^o_A + \mu^o_B - \mu^o_S)
\]

and \( \frac{P_i^A}{P_i^G} \) is the equilibrium constant, \( K_p \). A lucid account of the thermodynamics of gas-solid reactions is given by Denbigh (1961). This application of thermodynamics to equilibrium to be best understood will be applied to the decomposition of carbonates. For the reaction

\[
\text{MCO}_3 ^\rightleftharpoons \text{MO} + \text{CO}_2
\]
we have, from the above considerations, \( K_P = \frac{P_{MO}P_{CO_2}}{P_{MCO_3}} \) where \( P_{MO} \) and \( P_{MCO_3} \) are the vapour pressures of the solids at given temperatures which are therefore constants, so that a new equilibrium constant can be defined as,

\[
K'_P = \frac{P_{CO_2}}{P_P} = \frac{P_{MCO_3}}{P_{MO}}
\]

The Van't Hoff equation will then give actual values for the equilibrium pressure of carbon dioxide at given temperatures.

The above discussion enables the potential kinetic rate or the overall rate of reaction defined at specific conditions of temperature and partial pressure. When these conditions cannot be specified directly, formulation of a reaction model is essential to the analysis.

2.4 Reaction model. In heterogeneous catalysis the reaction occurs on the solid surface, and this surface remains constant, while the reaction itself and the associated diffusional processes are essentially steady-state. For non-catalytic reactions, however, the prediction of reaction rates as a function of time is necessary. As the solid is used up, a new area is exposed, and this area will usually decrease with time. For systems in which the overall rate is controlled by kinetics, and where the reactant B is impervious to A, prediction of the rate/time relationship is simple for simple geometry. The reaction process is initiated through "nucleation" on the surface and thereafter the process is essentially one of uncovering subsequent molecular layers to produce porous product S. Hence the velocity of propagation of the reaction "interface" is a constant, so that if the
solid is in the form of, say, a thin sheet or flake, the reaction rate per solid particle is also constant. For the sphere, Fig. 2.1 we may write
\[ \frac{d r_1}{d t} = \text{constant}, \quad \text{rate} \propto r_1^2 \]
where \( r_1 \) is the interfacial radius and \( t \) is time. Hence \( r_1 \) and \( t \) are equivalent parameters and a plot of rate/initial rate versus fractional penetration, \( \alpha \), i.e. \( 1 - r_1/R \), where \( R \) is the outside radius of the sphere, is as shown in Fig. 2.2. For the cylinder of radius \( R \) and of infinite length, we have rate \( \propto r_1 \), giving a rate versus penetration plot which is a straight line (Fig. 2.2). It is interesting to note that the shape of this rate vs penetration curve for a cube is the same as that for a sphere, showing that the spherical model is a good fit for many geometries. A cylinder with a length to diameter ratio of unity exhibits the same curve.

This "shell progressive" mechanism (White) is the one in most common use. Spencer and Topley (1929) used the model for the decomposition of silver carbonate and obtained good correlation with experiment. Levenspiel, Shen and Smith and others (Ishida, Suguyama) also used the same technique but without the limiting assumption of kinetic control.

Many experimental investigations are so organised as to rule out interference by mass and heat transfer limitations. This is usually simple in the case of mass transfer, but temperature gradients are more troublesome. Keeping reaction samples as small as possible aids isothermal operation. Alexander and Tollefsen have developed a novel technique for mounting a catalyst used in a highly exothermic reaction. Further techniques are also...
available for reducing the labour involved in obtaining kinetic data such as differential thermal analyses (Reed). Ingraham and Marier (1963, 1964) have shown that a linearly increased reaction temperature technique can be used to evaluate activation energies more simply. On the one hand, then, heat transfer effects are artificially introduced to enable simple measurement of a temperature difference which can be related theoretically to the kinetics of the reaction via a heat balance, and on the other a system which excludes heat and mass transfer has been further modified to provide a variety of conditions in a single experiment.

In the reactions discussed so far it has been assumed that reaction occurs at a well-defined interface between reactant and product solids. This has been shown by visual examination of specimens and by the fact that the equilibrium constant is independent of the degree of reaction, showing that the solids in question exert their full vapour pressure and do not form solutions. Such a reasoning is presented by Langmuir.

In porous, however, analysis of the reaction system becomes more difficult, as through nucleation an interface will develop at all points within the solid, to a greater or lesser degree depending on concentration and temperature gradients. The theory of nucleation is discussed by Jacobs and Tompkins, Bradley, and Macdonald. This "diffuse" interface may arise in compacted pellets of amorphous solids such as zinc sulphide and silver carbonate. Previous theoretical work on such systems is limited to that of Lacey et al, although they assumed in their analyses that the local reaction rate was proportional to solid concentration.
Further work along these lines is obviously required.

In porous solids, then, a different approach is required, something similar to that of heterogeneous reactions in porous catalysts except that the steady-state can no longer be assumed. The porous solid can be visualised, say, as a mass of spheres of uniform size, with the interface theory being applied to the individual spheres, and the total effect of the spheres integrated throughout the whole pellet. Depending on the mass and heat transfer characteristics of the pellet, so a reaction zone will move through the solid till conversion is complete.

Some analyses of such systems can be carried out by analogy with heterogeneous catalysis but this is limited to steady-state conditions. However, assuming mass accumulation to be negligible, a worth while result can be obtained for initial times, i.e. at times when solid surface is available equally throughout the pellet. For isothermal cases and 'infinite' times, equivalent to zero time if mass accumulation can be ignored, solutions have been obtained by Damkohler (1950, 51) based on solutions for diffusion without reaction, for the sphere, cylinder, parallelepiped and semi-infinite slab. Solutions can be obtained in the form of effectiveness factors, as introduced by Thiele and taken further e.g. for non-isothermal cases by Petersen (1962, 65) and Roberts and Satterfield. For further information on this subject, see also Bischoff (1967), Wicke, Weisz and Prater, and for general diffusion effects, Satterfield and Sherwood.

2.5 Rate control
2.5.1 Boundary layer. The flow of gas past a pellet of solid
creates a low velocity boundary layer which can form a resistance to mass transfer to or from the solid. This effect is most noticeable at low gas velocities and at initial times when the potential kinetic rate is at its highest on the outside surface of the solid. If the chemical rate is extremely fast compared to the potential boundary layer rate, the latter will control the process. For an irreversible reaction, experimental observation of such a control is simple as the effect of temperature on the two rates is so different. The potential boundary layer rate is evaluated on the assumption of such rapid utilisation of reactant gas that if the value of \( P_A \) at the interface, is zero and the boundary layer rate is given by \( k_B P_A^{\text{G}} \) where \( k_B \) is the mass transfer coefficient and \( P_A^{\text{G}} \) is the partial pressure of \( A \) in the bulk gas. The potential chemical rate evaluated on the assumption of no boundary layer mass transfer resistance may be written as \( k_C P_A^{\text{G}} \) where \( k_C \) is the reaction velocity constant, which is highly dependent on temperature. A simple comparison of the effect of temperature on the rate is shown in Fig. 2.3. \( k_B \) is proportional to \( T^n \) where \( n = \frac{1}{2} - 1 \), whereas \( k_C \) can double for a 10°C temperature rise. At low temperatures the kinetic rate will control the process. As temperature increases the kinetic rate will approach the potential boundary layer rate and the control will be shared by the two processes. The resistances of the two processes will be additive as the steps are consecutive. As temperature rises even further, chemical reaction rates are very high and the overall rate is equivalent to that of the limiting boundary layer rate.

The overall rate can be evaluated by equating the
individual rates, \[ \text{rate} = k_c P_i^A = k_B (P_i^A - P_i^A) \]. Note that the rates are determined for the simple case of, say, an impervious sphere of solid, so that at initial times the reaction surface and the area for diffusion can be taken as equal. Eliminating \( P_i \) from the above equations we have that

\[ \text{rate} = P_G \left( \frac{1}{k_c} - \frac{1}{k_B} \right)^{-1} \]

which shows the resistance form of the equations. Change in control from kinetics to boundary layer diffusion has been observed by Beveridge (1961).

For reversible reactions the distinction between the two potential rates, by their dependence on temperature, is not as easily observed. This is because the boundary layer rate must be expressed as a function of an equilibrium pressure, which is a distinct function of temperature.

2.52 Internal Transfer. In reactions in impervious solids, for further reaction to occur after reaction at the surface, a porous product must be created. Thereafter reactant gas must pass through this layer to the interface for reaction to occur. In a reaction with no inerts and no product gases this will be achieved by a "bulk" or pressure flow into the solid. In general though, a diffusion process occurs in which a counter-transfer of reactant and product gases occurs by either free, Knudsen or surface diffusion. Free diffusion predominates when pores are large, Knudsen when pores are of the order of the mean free paths of the gases. Surface diffusion is less common, occurring in cases where reactants or products are vapours near their boiling points. A knowledge of the pore sizes and their distribution, and the
resulting diffusibility of the solid are therefore essential.

As mentioned above, the reactant solid can itself be porous, in which case reaction and diffusion will no longer be consecutive steps, but will be occurring in parallel. Hence the approach to the study of the truly sharp interface case and the diffuse case will be quite different. Whereas the sharp interface theory involves the equating of many different steps, which are assumed equal by the steady-state assumption (see Bischoff (1963)), the diffuse case is more difficult and involves the setting up of an elemental balance which must include a reaction term. This has been done by Lacey et al but the subject requires more attention.

2.5.3 Heat transfer. Obviously the boundary layer will affect the transfer of heat to or from the pellet in the same way as mass transfer. The transfer coefficients can be evaluated from empirical relations such as described by Yoshida et al. Reaction rates will also be affected by the conduction of heat through the solid product. For the sharp interface approach, heat transfer resistances can again be set in series as with mass transfer, and equated to the heat of reaction.

Unlike mass transfer resistances, those of heat transfer may either reduce or promote the rate depending on whether the reaction is endothermic or exothermic. For the former, heat and mass transfer effects are the same in that both reduce the overall rate. Furthermore for given conditions a unique solution to steady-state theory is obtained. For exothermic reactions, however, more than one solution to the steady-state equations can be obtained (Cannon (1957b), Shen). This gives the well known
effect of thermal instability. Ishida and Wen, Aris and others (Regenass, Van Heerden) have discussed this phenomenon and shown how rapid transitions can occur between the non-unique solutions, either when perturbations affect a system or due to the time effect of solid exhaustion. These theories have, however, assumed that the heat capacity of the solid is negligible, whereas the sensible heat will actually act as a brake on transitions. This point has been thoroughly examined quantitatively, and will be described in Chapter 6. (see also Beveridge and Goldie).

2.6 Specific examples.

2.6.1 Oxidation of zinc sulphide. This reaction is of importance in the production of zinc, and over a wide range of conditions can be represented by the equation

\[ \text{ZnS} + \frac{3}{2}O_2 \rightarrow \text{Zn} + \text{SO}_2 \]

Cannon and Denbigh (1957a) measured the rate of reaction of the 110 faces of zinc sulphide crystals by suspending single crystals a few millimetres in size in a vertical tubular furnace and continuously recording their weight. Gas flows were chosen so as to avoid any boundary layer effects. Below 830°C it was found that the rate of penetration of the interface was essentially a constant. The activation energy was found to be 50 Cals/g.mole, and by varying the composition of the purging gas it was found that the rate was approximately proportional to the square root of the oxygen partial pressure. At temperatures greater than 830 °C however, the rate of penetration was no longer constant and this was thought to be due to the influence of diffusion through the product. Visual evidence of this was given by the rounding
off of formerly sharp corners on the receding interface. Also as a result of their work on zinc sulphide, Cannon and Denbigh put forward their theory of thermal instability (1957b), which depends on the assumption of the solid specific heat being zero, as discussed above. This work on zinc sulphide was continued by Beveridge (1960, '61) (see also Denbigh (1962)), who measured the reaction rate of pelleted spheres of powdered sulphide. Rates were measured by absorbing the $\text{SO}_2$ off-gas. It was found that the reaction followed a sharp interface mechanism, despite the fact that the pellets were porous. However, the interface was not well-defined. It was also found that higher temperatures caused a sintering process whereby the solid became more dense, and the area available for reaction was greatly reduced. To achieve results which bore a relation to one another it was necessary to presinter all the spheres. Initial reaction rates were found to rise with temperature exponentially over the lower range of temperatures, giving an activation energy which agreed with that of Cannon and Denbigh. As the temperature rose so diffusion through the pores began to be of importance and the temperature coefficient fell off. This showed up for unsintered spheres, but not for spheres presintered at 1150°C, as the surface area for reaction was so small that diffusion processes could always cope without becoming controlling. At relatively high temperatures it was found that the rate fell off rapidly with time due to the blocking action of the impervious oxide layer on the surface of the sphere. Theoretical considerations showed some degree of agreement with experiment and use was made of
Thiele-type effectiveness factors. At very high temperatures it was found that the oxidation took place via the vapourisation of zinc sulphide, so that the oxide product was formed as a shell round the sulphide core, and quite separate from it.

2.6.2 The decomposition of carbonates. This subject has probably received the greatest attention in the literature, although much of the earlier work has been directly concerned only with industrial application, with empirical rather than fundamental results. Garner et al. (1955) have given an excellent review of earlier work on carbonates within a study concerned with all aspects of gas-solid reactions, including the subject of nucleation. Garner distinguishes between endothermic and exothermic reactions in order to achieve a classification, while Cutler in his review paper on the decomposition of minerals makes the distinction between reactions which depend on an interface between the reactant and product solids, and those which do not. The distinction is a difficult one to make unless it is emphasised that the first category describes systems which depend on an interface of a chemical nature, whereas the second category might include cases where an interface is set up as a natural result of a diffusion process. It may be, in fact, that the two categories are the extremes set up by operation of systems with vastly different relationships between the kinetic and diffusional processes.

The first significant study on silver carbonate decomposition was that of Spencer and Topley (1929) who measured the rate of decomposition of prepared crystals in vacuum, at various temperatures and as a function of time. Considering the crystal
as a sphere and knowing that for kinetic control the rate of penetration of the interface is constant, a simple expression relating rate to time can be obtained. Spencer and Topley used the equation \[ \frac{v}{R} = \frac{1-(1-x)^{\frac{1}{2}}}{t} \]
where \( v \) is the velocity of propagation of the interface, \( R \) is the radius of the sphere, and \( x \) is the fractional conversion of carbonate to oxide at time \( t \). They found the rate of reaction and the energy of activation to be dependent on the method of preparation of the crystals, with values of \( E_0 \) of approximately 23 Cals/g.mole. It was found that in order to retain this velocity of propagation constant, it was necessary to have a certain pressure of water vapour in the reactor. This was thought to be due to some assistance provided by the water vapour to the diffusion of carbon dioxide through the product shell, or to the necessity for water vapour to be present at the interface.

The works of Spencer and Topley and others on silver carbonate are discussed more fully in Chapter 7.

Studies of the decomposition of calcium carbonate yield very similar results. No differentiation has yet been made, however, between the interface associated with the reaction of a crystal and that which penetrates a porous lump of a mineral, which is quite different from the chemical interface. However, from the point of view of analysing a system this distinction may be unnecessary. Cutler discusses the adsorption theory behind the kinetics of the decomposition of carbonates with special reference to calcium and shows a good correlation between theory and experiment, both for calcium and silver, for varying carbon
dioxide pressures. Cutler points out the importance of water vapour on the course of the reaction, but this feature has not yet been adequately explained. Berger found no significant chemical or "mechanical" effect of water vapour on the decomposition of limestone between 600°C and 1000°C, any slight differences in rates being ascribed to varying gaseous physical properties. Whereas in this study and in most others, not much attention is paid to the limitations imposed on the endothermic reaction by heat transfer processes, Haslam and Smith attempted to describe their experimental conditions, in which they used blocks of limestone $1\frac{1}{2}\"x2\"x4\", by equations for heat transfer for a semi-infinite slab. Furnas found a constant rate of advance of the interface through a limestone lump, and attempted an explanation for the lack of reaction within this interface. Although accepting that calcination can occur at temperatures such as were measured at the centre of the reaction cores, it was not appreciated that it was a question of mass transfer through a virtually impervious stone which excluded reaction in the interior. The results tend to suggest a kinetically controlled reaction, corresponding to a constant velocity of propagation of the interface. Wakefield and Tyner, on the other hand, found that the rate of diffusion of CO$_2$ through the reaction product was the controlling factor. They developed an empirical relation which described the effects of particle size, 0.02" to 0.08", temperature, 760-930°C, and carbon dioxide level. The question of removal of carbon dioxide by diffusion through the product solid is discussed by Cunningham in a qualitative paper devoted to lime-kiln practice.
Both mass and heat transfer effects on the rate were considered by Britton et al in extensive studies of the thermal decomposition of calcite, magnesite and dolomite. Deviations from kinetic control were encountered, and put down to effects of self-cooling due to the endothermic reaction, and to the difficulty of removal of carbon dioxide from the interface, which would proceed by a mechanism involving both diffusion and recombination both at the interface and throughout the product shell. The effect of nucleation was also mentioned. The study of dolomite was further complicated by the presence of the two oxides. It was shown that for rapid calcination the two behaved as one in producing a single interface, but no obvious interface was present when calcination was carried out slowly, due the solution of (MgCa)O giving way to the possibility of recombination to CaCO₃. Mitchell had previously concluded that the reaction could be described by

\[
\text{CaCO}_3,\text{MgCO}_3 = \text{CaO},\text{MgO} + 2\text{CO}_2
\]

but could not conclude whether \( \text{CaO},\text{MgO} \) was a solution or a compound. The question as to whether dolomite decomposes as a whole has been the subject of argument. MacIntyre and Stansel discuss this, and also show that steam can be used as a catalyst, contrary to the findings of others. Satterfield and Feakes (1959a) studied the decomposition of compacted spheres and cylinders of calcium carbonate and found heat transfer to play an important role. Ingraham and Marier (1963) ruled out heat and mass transfer effects in their experiments on calcium carbonate pellets, and developed a method of determining accurately the activation energy for the forward reaction, so as to disprove the theory that the activation
energy and heat of reaction were equal, and that the reverse reaction had no activation energy, as discussed by Garner (1955).

For other useful works on carbonates see also Bijawat, Gilkey, Knibbs, Narsimhan (1961), Rao et al, and Satterfield and Feakes (1959b).

2.6.3 The reduction of iron ore. This is a very important industrial process, and is at the same time a system of some complexity. Wetherill and Furnas consider the complete reduction by carbon monoxide to proceed by two stages, the first being reduction to ferrous oxide via two reactions, and the second being the metalisation process. These stages are represented by the reactions,

\[
\begin{align*}
3\text{Fe}_2\text{O}_3 + \text{CO} &= 2\text{Fe}_3\text{O}_4 + \text{CO}_2 \\
\text{Fe}_3\text{O}_4 + \text{CO} &= 3\text{FeO} + \text{CO}_2 \\
\text{FeO} + \text{CO} &= \text{Fe} + \text{CO}_2
\end{align*}
\]

Wetherill and Furnas studied various ores, with particle sizes up to 1cm. dia. to find that the more porous ores reacted more quickly, thus indicating a diffusion effect. Data was obtained on the effect of particle size, bulk gas composition, and boundary layer, while the theory of constant velocity of propagation of the interface is confirmed. Ralston gives a critical review of the reduction equilibrium from a thermodynamic viewpoint. A thorough earlier study of the reduction of iron ore was that of Britsianes and co-workers (see also Edstrom, and Schluter). The topochemical nature of the reaction is visually demonstrated (Bitsianes (1953)), and the existence of three interfaces shown to separate distinct regions of unreduced hematite ore, magnetite, wustite, and in the outermost layer iron. These regions were
identified by partial reduction of a piece of dense hematite ore at 850°C by hydrogen. High power micrographs showed up the fact that the interface was to some extent diffuse, depending on the porosity of the ore. The topochemical nature of the reaction was less definite at 500°C where extensive cracking caused reaction to occur prematurely at the interior surfaces of the specimen. The wustite phase was not detectable. In a later work (1954) to investigate more fully the wustite layer obtained in the high temperature reduction it was found that the oxygen content of the wustite, FeO_x, increased with depth. A more detailed study of the topochemical processes (1955) showed up the effects of porosity, cracking caused by thermal effects and also by impurities and of trapping of wustite within sintered iron causing a minimum rate at about 800°C for some ores. Concerned more with the actual control of the formation of wustite (Edstrom), the rate was shown to be determined by the migration of iron through the wustite the wustite layers, as identified through the parabolic law, which defines the product thickness as proportional to the square root of the reaction time. Schluter and Bitsianes develop the study further by investigating the effect of a bed of ore and reproducing an iron ore sintering system.

McKewan (1960) showed the overall rate of reduction of small pellets of iron ore by hydrogen to be kinetically controlled at the interface FeO/Fe, except under certain low temperature conditions, where the cracking noticed by Bitsianes et al was confirmed. McKewan also found the reaction rate to be dependent on the hydrogen partial pressure, i.e. \( f(P) = P_{H_2} \). The belief that
the velocity of propagation of the interface was constant was shared by Feinman and Drexler in their work on reduction in fluidised beds. Narsimhan (1962, '63) extends the theory to include diffusion effects. Kawasaki et al found that the control of the process was by counterdiffusion of reactant and product gases through the product layers. Care was taken to ensure that boundary layer effects were absent. Warner (1964b) shows that diffusion effects exist in both the boundary layer and the product pores, and that solid state diffusion does not control the formation of wustite. Warner (1964a) reviews the earlier work and points out a number of flaws. His findings showed the existence of mixed control between kinetics and diffusion. Diffusion effects were also noted by Feinman et al (1965).

For further information see also Mokewan (1958, 1961b) and Themelis.

2.6.4 The combustion of carbon. This subject covers both the burning of solid fuel and the regeneration of porous catalysts such as are used in the oil industry in catalytic cracking units.

Walker et al point out a control by gas flows through a coke bed, although some doubt was expressed as to whether the limitation was caused by a boundary layer diffusion effect or the changing partial pressures within the gas phase. Smith and Godmundsen studied the process of the combustion of fixed carbon in solid fuels with the emphasis on the factors influencing the combustion rate in a furnace, including particle size, relative velocities of particles and gas, the temperatures of the furnace walls, and the humidity and temperatures of the furnace gases. Spherical particles made from electrode carbon were suspended on
wires, and their temperatures measured by an optical pyrometer. Reaction rates and surface temperatures were found to be much higher for small than for large particles. In common with many other typical gas–solid reactions, the rate was found to increase with gas flow when this was low, but not when high, indicative of the effect of the boundary layer. Tu et al. found a similar effect of gas flow in their study of the combustion of brush carbon, such that the reaction rate was proportional to $T^n$ where $n = 0.6$ to $1.1$, while at low flows, whereas in the kinetic region the rate doubled for every $15^\circ C$, at $1050^\circ C$. Consideration was also given to the actual reactions involved. A further study (Davis) was aimed at providing a more geometrically certain diffusion path by placing carbon discs at the base of a parallel-sided cup. The results, which were liable to errors due to eddy currents, were found to be within the limits imposed by the theory presented by the authors. Concentration gradients within the diffusion path adjacent to the carbon surface were measured by Parker and Hottel in order to understand the mechanism of diffusion of gas through this film. A great deal of work is carried out by the British Coal Utilisation Research Association. For example, Bangham and Townend outlined the work of the Association during the period 1939–49.

The combustion of carbon during regeneration of a porous catalyst pellet has been studied by Ausman and Watson, who have obtained expressions for overall carbon burning rate, taking into account the surrounding gas film, and oxygen and carbon concentration gradients within the pellets. Mickley et al (1965)
successfully fitted a model to their experimental results in a similar study in which they showed control both by the kinetics of the process and by the rate of diffusion of $O_2$ through the catalyst pores.

2.6.5 Miscellaneous reactions. The thermal decomposition of silver oxide has been studied by Garner and Reeves, and Herley and Prout. Ganguly and Mukherjee investigated the oxidation of copper sulphide in both fixed and moving beds. Diffusion effects were shown by Rigg to exist in the reduction of ferrous chloride. Explosive reactions have been the subject of studies of Bowden and Singh, (decomposition of azides) and Garner and Hailes, (decomposition of mercury fulminate).

Other examples are the thermal decomposition of ferric and aluminium sulphates (Warner and Ingraham), the dehydration of chrome alum (Anous et al, Cooper), and the reaction between oxygen and thorium (Levesque).
3.1 Introduction. In this section is described a theory of reaction in porous solids as introduced in Section 2.4. The subject has received little attention in the literature, perhaps mainly due to the difficulty of achieving a simple mathematical analysis. Solutions which include time as a parameter are necessary numerical, while certain of the steady-state approximations can be solved analytically. Although the bulk of experimental evidence shows that most gas-solid reactions can be described by a sharp interface theory, certain situations demand an approach similar to that used in heterogeneous catalysis, where reaction is known to occur throughout a porous solid at varying rates, dependent on mass and heat transfer. In heterogeneous catalysis reaction occurs at a surface of constant area, whereas in non-catalytic reactions the interface at which reaction is taking place penetrates discrete particles of solid, with the area for reaction changing dependent on the geometry of the solid. Reaction in the discrete particle occurs at a "sharp" interface, while the overall reaction occurs in a zone within the larger porous pellet.

The theory is applied to pellets shaped as spheres, infinite cylinders and slabs of finite thickness, and the generalised time-dependent equations for each geometry are presented for both isothermal and non-isothermal situations. Steady-state
solutions to these equations are given, and recommendations are made for future work. Time–dependent diffusion in a sphere with no reaction is also discussed and solutions presented to illustrate the insignificance of mass "accumulation" in most cases.

3.2 Model  The theory is applied to the general reaction

\[ aA_{\text{gas}} + B_{\text{solid}} \rightleftharpoons gG_{\text{gas}} + sS_{\text{solid}} \]

The reactant solid B is in the form of a porous pellet of specific geometry. The lump of solid is immersed in a flowing gas made up of A and G, resulting in a boundary layer which contributes resistance both to mass and heat transfer. Reaction of A and B to give G and S occurs within a zone in the lump such that discrete particles at the outermost boundary of the zone are completely reacted whereas those at the inside of the zone are unreacted. This model is shown in simplified form in Fig. 3.1 for a slab, infinite in two dimensions, and finite in a third, made up of irregularly shaped discrete particles. The zones can extend, of course, throughout the whole of the solid, should mass transfer resistances be relatively low. Reactant gas A diffuses through the boundary layer counter to product gas G, then through the micro–pores of the pellet of B, followed by diffusion, probably of a Knudsen–type or surface diffusion, through the interstices of the outer shell of S on a discrete particle, and thus to the reaction interface. Here A reacts with B to give an increasing layer of S and gives rise to gas G which counterdiffuses into the surrounding bulk gas.

The pellet of B can have several geometrical forms. The useful ones from the point of view of a mathematical analysis are
the sphere, the cylinder of infinite length and finite diameter, and the slab, infinite in two dimensions and finite in a third. These three shapes can also be achieved easily in practice. The sphere is the simplest, and many naturally occurring solids, which represent an approximate to this shape. Compacted solids can be fashioned into infinite cylinders by capping the ends of a finite cylinder with an impervious coating. Similarly the infinite slab can be made by compacting a powdered solid into a hole in an impervious plate. However, whereas a mass transfer model is satisfied by these experimentally obtained conditions, the model is not fully representative of heat transfer because of conduction through the surrounding material to the ends of the cylinder or the sides of the slab. These experimental cases are shown in Figs. 3.2 a,b,c. Models for the sphere or infinite cylinder are shown in Fig. 3.3a and for the infinite slab in Fig. 3.3b. The solids are characterised by the distance of their surface from their centres, R, while pressures and temperatures corresponding to various points within the solids are indicated.

For the purposes of this analysis diffusion in the small interstices of the discrete particles is assumed to be rapid due to the small distances involved, with a corresponding assumption regarding heat transfer. The isothermal case will be considered first.

3.3 Isothermal reaction in a porous sphere. The mathematical model is set up by carrying out a mass balance over the elemental volume represented in Fig. 3.3a.

Diffusion of G into the element in the direction of
Increasing $r$ can be written (see also Appendix D),

$$-4\pi r^2 \frac{D_e P_T}{R'T_G} \frac{\partial P}{\partial r} \frac{P_T}{P_T-(1-a/g)P}$$

where $D_e$ is the effective binary diffusion coefficient for the porous solid as defined in Appendix B, which necessitates an average between the coefficient for the unreacted solid B and the reaction product S. $P_T$ is the total pressure (i.e. the sum of the partial pressures of A and G), and $P$ is the partial pressure of G at a distance $r$ from the centre of the solid. $R'$ is the gas constant, $T_G$ is the temperature of the bulk gas surrounding the solid and it is at this temperature that concentrations and diffusion coefficients are taken. The above expression can be written

$$\frac{4\pi r^2}{(1-a/g)} \frac{D_e P_T}{R'T_G} \frac{\partial}{\partial r} \left( \ln \left( \frac{P_T-(1-a/g)P}{P_T} \right) \right)$$

The diffusion of G out of the element in the same direction can be similarly as

$$\frac{4\pi (r-dr)^2}{(1-a/g)} \frac{D_e P_T}{R'T_G} \frac{\partial}{\partial r} \left[ \ln \left( \frac{P_T-(1-a/g)P}{P_T} \right) - \frac{\partial}{\partial r} \ln \left( \frac{P_T-(1-a/g)P}{P_T} \right) dr \right]$$

Accumulation of G within the element is given by

$$4\pi r^2 dr \frac{\sigma}{R'T_G} \frac{\partial P}{\partial t}$$

where $\sigma$ is the voidage of the solid B, again an average between those of B and S, assuming no shrinkage, and $t$ is time.

The expression for the amount of G produced by reaction is obtained by the product of an expression dependent on the kinetics of the reaction and the surface area available for reaction.

For a reversible reaction with first order kinetics we have that
the amount of G produced by reaction in the element is

\[ 4\pi r^2 \rho_m S f(X) \frac{1}{RT} \left( k_c (P_K - P) - k_c' P \right) \]

or

\[ 4\pi r^2 \rho_m S f(X) \frac{1}{RT} \left( k_c' (P_K - (1 - 1/K) P) \right) \]

where \( \rho_m \) is the molar bulk density of the solid B, \( S \) is the molar surface area and \( k_c \) and \( k_c' \) are the rate constants of the forward and reverse reactions, with equilibrium constant \( K \). \( P_K \) would normally be \( P_T \) but is written as such to allow for carbonate decomposition reactions where \( P_K \) would be the equilibrium pressure of \( \text{CO}_2 \). \( P_0 \). \( f(X) \) is a term which is a measure of the degree of reaction which has already taken place within discrete particles, and is independent of concentration but dependent on the shape of the discrete particles. It must be stressed that the reaction rate will depend on the surface area of the interface available for reaction and not on the amount of unreacted solid still present within the interface.

### 3.4 Gas phase mass balance

The above expressions can be related in the usual way to give

\[
\frac{D e P_T}{(1 - a/g)} \left[ r^2 \frac{\partial^2}{\partial r^2} \ln \left( \frac{P_T - (1 - a/g) P}{P_T} \right) + 2r \frac{\partial}{\partial r} \ln \left( \frac{P_T - (1 - a/g) P}{P_T} \right) \right]
\]

and hence,

\[
\frac{\partial P}{\partial t} = \frac{g \rho_m S f(X) k_c}{(1 - \frac{1}{K})} \frac{D e P_T}{(1 - \frac{a}{g})} \left( 2 \frac{\partial}{\partial r} \ln \left( \frac{P_T - (1 - \frac{a}{g}) P}{P_T} \right) \right)
\]

This equation can be rewritten,

\[
\frac{\partial P}{\partial t} = K_1 \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \ln p \right) + K_2 f(X)(p_0 - p)
\]
where the substitutions have been made that

\[ p = \frac{(P_T - (1-a/g)P)}{P_T} \quad \text{and} \quad p_0 = 1 - \frac{P_K (1-a/g)}{P_T (1+ \frac{1}{K})} \]

and where \( K_1 = \frac{D_o}{\sigma} \) and \( K_2 = \frac{g_o m Sk_c (1+1/K)}{\sigma} \)

3.5 Solid phase mass balance. The depletion of the solid can now be brought into the analyses. The change in conversion is given by the rate of reaction as a fraction of the total amount of B originally present, so that

\[ \frac{\partial X}{\partial t} = \frac{S_k c f(X)P_T}{R_T G} \left[ \frac{P_K}{P_T} \left( \frac{1+1/K}{1-a/g} (1-p) \right) \right] \]

= \[ -K_3 f(X) (p_0 - p) \] (3.4)

where \( K_3 = \frac{S_k c P_T}{R_T G} \frac{(1+1/K)}{(1-a/g)} \)

3.6 Boundary conditions. Initially the reaction would be inhibited by the total absence of A, so that \( P = P_T \) at \( t = 0 \) for all positions. Also we can assume that \( P(r) \) is in the form of a reflection at the centre of the solid so that \( \frac{\partial P}{\partial r} = 0 \) at \( r = 0 \), for all time. Lastly we must define conditions at the surface of the sphere. For relatively high gas velocities we may write \( P = P_G \) at \( r = R \), for all time. Otherwise we must equate the rate of diffusion in the solid pores at the surface of the sphere to the rate of diffusion through the boundary layer. Hence the boundary conditions are,

1) \( P = P_T, 0 \leq r \leq R, t = 0 \) \hspace{1cm} i.e. \( p = a/g \)

2) \( \frac{\partial P}{\partial r} = 0, r = 0, t > 0 \) \hspace{1cm} i.e. \( \frac{\partial P}{\partial r} = 0 \)

3) a. \( P = P_G, R = R, t > 0 \) \hspace{1cm} i.e. \( p = p_G \)

3.6. : 36
or
\[
\frac{D_{e}P_{T}}{(1-a/g)} \left[ \frac{\partial}{\partial r} \ln \left( \frac{P_{T}-(1-a/g)P}{P_{T}} \right) \right]_{r=R} = k_{B}(P_{S}-P_{G})
\]

i.e.
\[
\frac{D_{e}P_{T}}{(1-a/g)} \left[ \frac{\partial}{\partial r} (\ln p) \right]_{r=R} = k_{B}(P_{G}-P_{S})
\]

3.7 Corresponding equations for the cylinder and the slab.

Gas phase mass balance for the cylinder -
\[
\frac{\partial P}{\partial t} = K_{1} \frac{1}{r} \frac{\partial}{\partial r} (r \frac{\partial}{\partial r} \ln p) + K_{2} f(X)(p_{0}-p)
\]

Gas phase mass balance for the slab -
\[
\frac{\partial P}{\partial t} = K_{1} \frac{\partial^{2}}{\partial r^{2}} \ln p + K_{2} f(X)(p_{0}-p)
\]

The solid phase mass balances and the boundary conditions for the cylinder and the slab are the same as those for the sphere.

3.8 Equimolar counterdiffusion: the sphere - steady state.

In cases where \(a=g\), i.e. equimolar counterdiffusion, and in cases where diffusional resistances are relatively low, Eq. (3.2) becomes
\[
\frac{\partial P}{\partial t} = \frac{g_{m} S f(X)k_{o}}{c} (P_{K}-(1+\frac{1}{K})P) + \frac{D_{e}}{c} \frac{1}{r^{2}} \frac{\partial}{\partial r} (r^{2} \frac{\partial P}{\partial r})
\]

Substituting \(v = \frac{P_{K}}{1+1/K} - P\) gives
\[
\frac{\partial v}{\partial t} = K_{1} \frac{1}{r^{2}} \frac{\partial}{\partial r} (r^{2} \frac{\partial v}{\partial r}) - K_{2} f(X)v
\]

In all gas-solid reactions it is reasonable to assume that the accumulation term is negligible. This is also discussed later in this Chapter. Eq. (3.6) then becomes, with \(K' = K_{2}/K_{1}\)
\[
\frac{1}{r^{2}} \frac{d}{dr} (r^{2} \frac{dv}{dr}) - K' f(X)v = 0
\]

Solution of this equation and the simultaneous solid phase mass
balance, with suitable boundary conditions, would be a complicated numerical solution, and the problem was dropped in favour of further study of the sharp interface theory in Chapters 4–6. However it is interesting and useful to study the steady state solution to the above equations. This solution is obtained by setting \( f(X) = \text{constant} = 1 \), and corresponds to the steady-state solution of a heterogeneous catalysis situation. For a non-catalytic reaction it represents the initial stages of the reaction when no solid has been used up and its availability is the same throughout the sphere.

Putting \( v = u/r \) Eq. (3.7) becomes

\[
\frac{d^2u}{dr^2} - K'u = 0
\]

which has a subsidiary \( D = \frac{1}{2} (K')^{\frac{1}{2}} \), giving the solution

\[
v = \frac{C_1}{r} \exp(r(K')^{\frac{1}{2}}) + \frac{C_2}{r} \exp(-r(K')^{\frac{1}{2}})
\]

where \( C_1 \) and \( C_2 \) are constants. The boundary conditions for this case are

\[
\left( \frac{dv}{dr} \right)_{r=R} = \frac{k_B (v_g - v_s)}{D_e} \quad \text{and} \quad \left( \frac{dv}{dr} \right)_{r=0} = 0
\]

Hence, \( \frac{dv}{dr} = \frac{C_1}{r} (K')^{\frac{1}{2}} e^{r(K')^{\frac{1}{2}}} - \frac{C_1}{r^2} e^{-r(K')^{\frac{1}{2}}} - \frac{C_2}{r^2} e^{-r(K')^{\frac{1}{2}}} \)

and applying the boundary conditions gives

\[
v = \frac{h_B P_0 R^2}{D_e r} \frac{\sinh(Y_2 (r/R)^2)^{\frac{1}{2}}}{(Y_2)^{\frac{3}{2}} \cosh(Y_2)^{\frac{1}{2}} - (1 - 1/Y_1) \sinh(Y_2)^{\frac{1}{2}}}
\]

where \( Y_1 = D_e / k_B R \) and \( Y_2 = K' R^2 \)
Now the reaction rate per sphere can be written as

\[ 4\pi R^2 \frac{D_e}{R'T_G} \frac{dY}{dr} \left|_{r=R} \right. \]

while the maximum rate, or the rate which would obtain in the absence of diffusional resistance is

\[ \frac{1}{3} R^3 \gamma \frac{k_e}{R'T_G} f(X)(1+1/K) v_G \]

It is convenient to represent the solutions to such equations by a factor which indicates the degree of utilisation of the internal surface of the solid. This concept was introduced by Thiele. The effectiveness factor, \( \gamma_e \), is defined as the ratio of the actual rate to that which would obtain in the absence of diffusional resistances. Hence

\[ \gamma_e = \frac{(Y_1^2)^{1/3} \cosh(Y_2^1)^{1/3} - \sinh(Y_2^1)^{1/3}}{(Y_2^2)^{1/3} \cosh(Y_2^2)^{1/3} - (1-1/Y_1^2) \sinh(Y_2^2)^{1/3}} \]

Values of \( \gamma_e \) for various values of \( Y_1 \) and \( Y_2 \) are displayed graphically in Fig.3.4. The equation was solved via Computer program 1, Section 3.1.

In the absence of diffusional resistances Eq.(3.11) becomes \( \gamma_e = 1 \) on substitution of \( \tanh(Y_2^1)^{1/3} = (Y_2^1)^{1/3} - \frac{1}{3}(Y_2^1)^{3/2} \), as \( Y_2 \) is small.

3.9 Equimolar counterdiffusion: the cylinder - steady-state.

For the cylinder, the corresponding equation to Eq.(3.7) is

\[ r^2 \frac{d^2 Y}{dr^2} + r \frac{dY}{dr} - K'R^2 Y = 0 \quad (3.12) \]

which is a special case of the Bessel equation, whose solution (see Mickley et al) is
\[ v = C_1 I_0(r(|K'|)^{\frac{1}{2}}) + C_2 K_0(r(|K'|)^{\frac{1}{2}}) \]

where \( I_0 \) is a modified Bessel function of zero order and first kind, \( K_0 \) is a modified Bessel function of zero order and second kind, and \( C_1 \) and \( C_2 \) are constants.

The boundary conditions are the same as those for the sphere. Hence

\[ \frac{dv}{dr} = C_1 \left( \frac{1}{2} \right) I_1(r(K')) - C_2 K_1(r(K')) \]

where \( I_1 \) and \( K_1 \) are modified Bessel functions of the first order and of first and second kinds respectively.

Inserting the boundary conditions gives

\[ \frac{v}{v_G} = \frac{h_B}{D_e} \frac{I_0(r(K'))}{(K')^{\frac{1}{2}} I_1(R(K')) + h_B I_0(R(K'))} \]

The rate of reaction per unit length of cylinder can be represented as \( 2\pi R \frac{D_e}{R' T_G} \left( \frac{dv}{dr} \right) r = R \) and the maximum rate as

\[ \pi R^2 \rho_m S_g \frac{k_e}{R' T_G} f(X)(1+\frac{1}{K})v_G \]

so that the effectiveness factor is

\[ \eta_e = \frac{2}{Y_2 Y_1} \frac{(Y_2)^{\frac{1}{2}} I_1(Y_2)^{\frac{1}{2}}}{(Y_2)^{\frac{1}{2}} I_1(Y_2)^{\frac{1}{2}} + (Y_1)^{-1} I_0(Y_2)^{\frac{1}{2}}} \] \hspace{1cm} (3.13)

The solutions to this equation are presented in Fig.3.5, being obtained via Computer program 3, Section G.3. In the absence of diffusional resistances, \( Y_2 \to 0 \), \( I_1(Y_2)^{\frac{1}{2}} \to (Y_2)^{\frac{1}{2}}/2 \) and \( I_0(Y_2)^{\frac{1}{2}} \to 1 \) so that \( \eta_e = 1 \).

3.10 Equimolar counterdiffusion: the slab – steady-state.

For the slab the corresponding equation to Eq.(3.7) is

\[ \frac{d^2v}{dr^2} - K'v = 0 \] \hspace{1cm} (3.14)
which has the subsidiary equation \( D = \pm (K')^{\frac{1}{2}} \), so that
\[
v = C_1 \exp(r(K')^{\frac{1}{2}}) + C_2 \exp(-r(K')^{\frac{1}{2}})
\]
The boundary conditions are the same as those for the sphere,
\[
\text{so that} \quad v = \frac{h_B}{D_e} v_G \frac{\cosh(R(K')^{\frac{1}{2}})}{(K')^{\frac{1}{2}} \sinh(R(K')^{\frac{1}{2}}) + \frac{h_B \cosh(R(K')^{\frac{1}{2}})}{D_e}}
\]
The reaction rate can be written as
\[
\frac{D_e (dv)}{R' T_G} \frac{1}{r-R}
\]
and the maximum rate as
\[
R_{m} \frac{k c}{R' T_G} (1+1/K)f(X) v_G
\]
so that the effectiveness factor is,
\[
\eta_0 = \frac{1}{Y_1 Y_2} \frac{(Y_2')^{\frac{1}{2}} \sinh(Y_2')^{\frac{1}{2}}}{(Y_2')^{\frac{1}{2}} \sinh(Y_2')^{\frac{1}{2}} + (Y_1')^{-\frac{1}{2}} \cosh(Y_2')^{\frac{1}{2}}}
\]
The solutions to this equation are presented in Fig.3.6, being obtained via Computer program 2, Section 2.2. In the absence of diffusional resistances, \((Y_2')^{\frac{1}{2}} \to 0\), and \(\tanh(Y_2')^{\frac{1}{2}} \to (Y_2')^{\frac{1}{2}} - (Y_2')^{3/2}\), so that \(\eta_0 = 1\).

3.11 Non-isothermal reaction in a porous sphere. In most gas-solid reactions, appreciable temperature gradients exist both in the boundary layer and throughout the solid, so that a heat balance similar to the mass balance in Section 3.4 must be employed.

The heat conducted into the element of solid in the direction of increasing \( r \) is
\[
-4\pi r^2 k_e \frac{\partial T}{\partial r}
\]
where \( k_e \) is the effective thermal conductivity of the solid.
Similarly, the heat conducted out of the element is
\[
-4\pi (r-dr)^2 k_e \frac{\partial T}{\partial r} (T- \frac{\partial T}{\partial dr})
\]
The accumulation within the element is

\[ 4\pi r^2 \rho_m C_P \frac{dT}{dt} \]

where \( C_P \) is the average molar specific heat of the two solids.

Because the elemental temperature is no longer equal to that of the bulk gas the reaction term used in Section 3.3 must be modified to

\[ 4\pi r^2 \rho_m \frac{S k_c^0}{R'T_G} f(X)(P_K - \left(1 + \frac{1}{K}\right) P) \exp\left(\frac{-E_c}{R'T}\right) \]

where \( k_c^0 \) is \( k_c / \exp(-E_c / R'T) \) and \( E_c \) is the activation energy of the reaction less that of \( P_K \), and where \( K \) is also a function of temperature. The heat absorbed by the reaction is obtained by multiplying the above expression by \( \Delta H / g \) where \( \Delta H \) is the heat of reaction per mole of solid B. The gas and solid phase mass balances must also be modified to take account of the temperature dependence of \( k_c \) and \( K \).

### 3.12 Heat balance.

The above items are related to give

\[ \frac{dT}{dt} = K_4 \frac{1}{r^2} \frac{\delta}{\delta r} \left( r^2 \frac{\delta T}{\delta r} \right) - K_5 V \exp\left(\frac{-E_c}{R'T}\right) \]  

(3.16)

where \( K_4 = k_c / (\rho_m C_P) \) and \( K_5 = \frac{S k_c^0 f(X) \Delta H}{R'T_G C_P} \).

Eq. (3.16) must be solved simultaneously with the modified gas and solid phase mass balances, with the appropriate boundary conditions. In the absence of diffusional effects the problems become solely those of heat transfer, and Eq. (3.16) becomes

\[ \frac{dT}{dt} = K_4 \frac{1}{r^2} \frac{\delta}{\delta r} \left( r^2 \frac{\delta T}{\delta r} \right) - K_5 V_G \exp\left(\frac{-E_c}{R'T}\right) \]  

(3.17)

with the boundary conditions \( \frac{dT}{dt} = 0 \) at \( r = 0, \ t > 0 \), and either

\[ T = T_G \] at \( r = R, \ t > 0 \) for high gas velocities, or
\[ k_e \left( \frac{\partial T}{\partial r} \right)_{r=R} = h_B (T_S - T_G) \]

where \( h_B \) is the boundary layer heat transfer coefficient.

Eq. (3.17) can be further simplified by ignoring the accumulation term, although this is less valid than the mass accumulation assumption. However, this gives, on putting \( K_6 = K_5/K_4 \),

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T}{\partial r} \right) = K_6 \exp\left( \frac{-E_6}{RT} \right) v_G \quad (3.18)
\]

Eq. (3.18) can then be used to obtain diffusion-free non-isothermal effectiveness factors.

3.13 Mass transfer in a porous sphere in the absence of reaction.

It is common in reactions of the type being discussed for the term representing the accumulation of the gas within the pores to be ignored, i.e., to assume steady-state in the gas phase mass balance. It is interesting to study the case of mass transfer without reaction to illustrate the rapid attainment of essentially steady-state.

Hence in the absence of chemical reaction, Eq. (3.5) becomes, for equimolar counterdiffusion in a sphere, with no boundary layer resistance,

\[
\frac{\partial P}{\partial t} = \frac{D_e}{r^2} \frac{1}{r^2} \frac{\partial }{\partial r} \left( r^2 \frac{\partial P}{\partial r} \right)
\]

This has been solved by Crank for the boundary conditions

\[
P = P_K, \quad 0 < r < R, \quad t = 0
\]
\[
P = P_G, \quad r = R, \quad t > 0
\]
\[
\frac{\partial P}{\partial r} = 0, \quad r = 0, \quad t > 0
\]

to give,
\[
\frac{P-P_k}{P_G-P_k} = 1 + \frac{2R}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \left( \frac{n \pi r}{R} \right) \exp \left( -\frac{D_n^2 \pi^2 t}{\sigma R^2} \right) \tag{3.19}
\]

Eq. (3.19) has been solved via Computer program 4, Section G.4, and the solutions presented in Fig. 3.7, which gives \( \frac{P_k-P}{P_G-P_k} \) as a function of \( r/R \) for various values of \( \left( \frac{e_e}{R} \right) \).

If we define the amount of gas present within the porous sphere at time \( t \) as \( M_t \), then

\[
\frac{dM_t}{dt} = 4\pi R^2 \frac{D e}{R T_G} \left( \frac{dP}{dr} \right)_{r=R} = 4\pi R^2 \left( \frac{2D e}{R T_G} \frac{P_k-P}{P_G-P_k} \right) \sum_{n=1}^{\infty} \frac{n \pi^2 \sigma}{n} \exp \left( -\frac{D_n^2 \pi^2 t}{\sigma R^2} \right)
\]

or more generally,

\[
\frac{M_t}{M_K} = \frac{\int \frac{D e}{\sigma R^2} \frac{d}{dt} \left( \frac{D e}{\sigma R^2} \right) d\left( \frac{D e}{\sigma R^2} \right)}{1 - \frac{\int \frac{D e}{\sigma R^2} \frac{d}{dt} \left( \frac{D e}{\sigma R^2} \right) d\left( \frac{D e}{\sigma R^2} \right)}{1 - \frac{\int \frac{D e}{\sigma R^2} \frac{d}{dt} d\left( \frac{D e}{\sigma R^2} \right)}{1 - \frac{\int \frac{D e}{\sigma R^2} d\left( \frac{D e}{\sigma R^2} \right)}}}
\tag{3.20}
\]

where \( M_t/M_K \) is the ratio of the gas present in the sphere at time \( t \) to that present at \( t=0 \). Eq. (3.20) was also solved by Computer program 4, and the results are shown in Fig. 3.8.

3.14 Example of rapid depletion of mass. The porous silver carbonate used in the experimental study described in this work had a voidage of about 0.65 after decomposition, and were \( \frac{1}{4} \) in diameter. The effective diffusion coefficient of \( \text{CO}_2 \) in air was measured (see Appendix B) as 0.3 ft\(^2\)/hr. at 25°C. Hence

\[
\frac{D e}{\sigma R^2} = \frac{0.3 t}{0.65(1/48)^2} \approx t \times 10^3
\]

Examination of Fig. 3.7 shows that for \( D e t/(\sigma R^2) = 0.5 \), even the concentration at the centre of the sphere has been reduced by 98%. This has been achieved, then, within \( t = 0.5 \times 10^{-3} \times 3600 \),
i.e. a time of 1.8 seconds.

The majority of reactions followed in experimental studies would involve a time scale many orders of magnitude greater than this, so that it is obvious that it is justifiable to assume that mass accumulation is negligible. Another method of showing this is to compare the total possible accumulation of gas within a porous sphere with the amount which can be produced or absorbed by reaction. Taking the same example then, the \(\frac{1}{4}\)" sphere can hold, in the gaseous phase, 0.09ccs. of carbon dioxide whereas the amount which is evolved by decomposition of the carbonate, whose specific gravity is 6.077 (Perry), is about 25ccs.

Although the assumption of negligible mass accumulation can be made it will be shown in Chapter 6, in relation to the sharp interface theory, that the same assumption cannot always be made regarding the "accumulation" of heat.
CHAPTER 4

SHARP INTERFACE THEORY: BASIC ISOTHERMAL EQUATIONS AND SOLUTIONS.

4.1 Introduction. The subject of the sharp interface reaction was introduced in Section 2.4. The interface is the boundary separating a reacting solid and the solid reaction product. In certain cases this interface may be of finite width so that a gradient of solid concentration exists between pure reactant and pure product. Indeed this finite width may be the total width of a solid particle under conditions of relatively high porosity. This situation can then be termed a "diffuse" interface, and has been dealt with in Chapter 3. The term sharp interface can be applied, then, to situations where a reactant and a product solid are separated by a narrow reaction zone, or indeed by a zone which defines the distance separating two molecules, where this zone is relative to the overall particle which is reacting, and not to a discrete particle within a reacting pellet, made up of many discrete particles which themselves may have associated interfaces.

It is assumed, therefore, that a pellet or crystal of a solid which is reacting with a gas contains a single interface separating reactant and product, and that the solid particle is immersed in a flowing gas stream, and can be considered in isolation, i.e. it represents a single particle suspended in a gas stream or, if it is associated with other similar pellets in a "bed", that consideration of the single pellet in isolation can be incorporated in a study of the mass of pellets. The
application of single particle data to packed beds has not been attempted, but the implications are obvious.

The case of a sharp interface reaction in a sphere will be considered in detail and solutions obtained which account for reaction kinetics, boundary layer mass transfer limitations, pore diffusion, and also the effect of solid shape and a distribution of particle sizes.

4.2 Model of the system. The analysis is based upon the usual model of sharp interface reactions in a sphere as shown in Fig. 4.1, and for the general equation given previously, Eq. (2.1), with obvious changes, as indicated later, the model also applies to the infinite cylinder and the slab of finite thickness. Reaction takes place at an interface situated at time $t$ at a distance $r_1$ from the centre of the solid. The solid reactant is assumed to lie within the interface ($r_1 > r > 0$) while the solid product forms a surrounding shell ($R > r > r_1$). $R$, the radius of the sphere, is assumed constant although shrinkage or expansion of the sphere can also be taken into account, as shown by Shen and Smith. The sharp interface assumption requires that the reactant solid is impervious to $A$, or that the reaction velocity is relatively high compared to the rate of diffusion. The interface is assumed to retain the shape of the outside surface as it penetrates the solid, with a velocity assumed negligible for the purposes of obtaining a steady-state gas phase mass balances (this point is shown to be valid by Bischoff (1963)). The solid is assumed to lie immersed in a flowing binary gas mixture composed of $A$ and $G$, so that a boundary layer, assumed of constant thick-

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ness round the solid is set up and through which gases must be transferred. Note that the retention by the interface of the original external shape of the solid depends both on the uniformity of the boundary layer thickness and on the fact that the solid is symmetrical in three dimensions, or only two if one is infinite, or even only one if two are infinite, as in the cases of the infinite cylinder and the slab respectively. In certain cases a or g may be zero, where A or G would respectively be considered as the inert species.

As the impervious reactant B becomes porous product S so the reaction gases A and G must be transferred to and from the reaction site or interface through the pores as well as through the boundary layer.

4.3 Conservation equations.

4.3.1 Gas phase mass balance. This can be derived by considering mass transfer within the solid product shell shown in Fig. 4.1. The non-equimolar counterdiffusional transfer (this is explained in Appendix D) of gas G into the element of width dr in the direction of increasing r is given by

\[-4\pi r^2 \frac{D_e}{R'T_G} \frac{\partial P}{\partial r} \frac{P_T}{P_T - (1-a/g)P}\]

where P is the partial pressure of G at r, R' is the gas constant, P_T is the sum of the partial pressures of G and A and is assumed constant, with the effective binary diffusion coefficient, D_e, evaluated at the constant temperature, T_G, of the bulk gas flowing past the solid (for a definition and fuller discussion of D_e see Appendix B). It is assumed that the transport of gases through the product shell is by "free" diffusion,
and not by Knudsen or surface diffusion. The above term can be re-expressed as,

$$4\pi r^2 \frac{D e P_T}{R' T_G (1- \frac{a}{g})} \frac{\partial}{\partial r} \ln\left(\frac{P_T-(1-\frac{a}{g})P}{P_T}\right)$$

Similarly, the transport of G out of the element is given by

$$4\pi (r-dr)^2 \frac{D e P_T}{R' T_G (1- \frac{a}{g})} \frac{\partial}{\partial r} \left[\ln\left(\frac{P_T-(1-\frac{a}{g})P}{P_T}\right) + \frac{\partial}{\partial r} \ln\left(\frac{P_T-(1-\frac{a}{g})P}{P_T}\right)dr\right]$$

while the accumulation of G within the element is given by

$$4\pi r^2 dr \frac{e}{R' T_G} \frac{\partial P}{\partial t}$$

where $\sigma$ is the voidage of the solid product $S$ and $t$ is time.

Assuming there is no gas phase reaction, the net diffusion into the element can then be equated to the accumulation, giving

$$\frac{\partial P}{\partial t} = - \frac{D e P_T}{\sigma (1- \frac{a}{g})} \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial}{\partial r} \ln\left(\frac{P_T-(1-\frac{a}{g})P}{P_T}\right)\right]$$

(4.1)

The accumulation term is always extremely small and can be ignored, giving the steady-state mass transfer equation for a sphere,

$$\frac{d}{dr}\left[r^2 \frac{d}{dr} \ln\left(\frac{P_T-(1-\frac{a}{g})P}{P_T}\right)\right] = 0$$

(4.2)

Integration of equation (4.2) then gives

$$\ln\left(\frac{P_T-(1-\frac{a}{g})P}{P_T-(1-\frac{a}{g})P_S}\right) = \frac{1}{r} - \frac{1}{r_1} - \frac{1}{1/R - 1/R_1} \ln\left(\frac{P_T-(1-\frac{a}{g})P_1}{P_T-(1-\frac{a}{g})P_S}\right)$$

(4.3)

after insertion of the boundary conditions that $P_S$ and $P_1$ are the values of $P$ at $R$ and $r_1$ respectively.

A similar expression can be obtained for the mass transfer...
of $G$ in the boundary layer, namely

$$\ln\left(\frac{P_T - (1 - \frac{a}{g}) P_G}{P_T - (1 - \frac{a}{g}) P_B}\right) = \frac{1}{1/R - 1/R_B} \ln\left(\frac{P_T - (1 - \frac{a}{g}) P_S}{P_T - (1 - \frac{a}{g}) P_G}\right)$$

where $(R_B - R)$ is fictitious boundary layer thickness, and the further boundary condition has been used that $P_G$ is the value of $P$ at $r = R_B$.

By considering mass transfer of $G$ on either side of the external surface we can express the rate of production of $G$ as both,

$$N = -4\pi R^2 \frac{D e}{R'T_G} \left(\frac{dP}{dr}\right)_{r=R^-} - \left(\frac{P_T}{P_T - (1 - \frac{a}{g}) P_G}\right)$$  \hspace{1cm} (4.5)

and

$$N = -4\pi R^2 \frac{D}{R'T_G} \left(\frac{dP}{dr}\right)_{r=R^+} + \left(\frac{P_T}{P_T - (1 - \frac{a}{g}) P_S}\right)$$  \hspace{1cm} (4.6)

where $D$ is the free binary diffusion coefficient of $G$ in $A$. On differentiating Eqs. (4.3) and (4.4), evaluating $(dP/dr)_{r=R^-}$ and $(dP/dr)_{r=R^+}$, substitution in Eqs. (4.5) and (4.6) gives

$$N = 4\pi \frac{D e P_T}{R'T_G (1 - \frac{a}{g})} \ln\left(\frac{P_T - (1 - \frac{a}{g}) P_i}{P_T - (1 - \frac{a}{g}) P_S}\right) \frac{1}{1/R - 1/r_i}$$  \hspace{1cm} (4.7)

$$N = 4\pi \frac{D P_T}{R'T_G (1 - \frac{a}{g})} \ln\left(\frac{P_T - (1 - \frac{a}{g}) P_S}{P_T - (1 - \frac{a}{g}) P_G}\right) \frac{1}{1/R_B - 1/R}$$  \hspace{1cm} (4.8)

Eliminating $P_S$ from Eqs. (4.7) and (4.8), then gives

$$N = -4\pi \frac{D P_T}{R'T_G (1 - \frac{a}{g})} \ln\left(\frac{P_T - (1 - \frac{a}{g}) P_S}{P_T - (1 - \frac{a}{g}) P_G}\right) \left(\frac{1}{R' e} \frac{1 - \frac{r_i}{R}}{\frac{r_i}{R} / k_B R^2}\right)^{-1}$$  \hspace{1cm} (4.9)

where the boundary layer mass transfer coefficient $k_B$ has been equated in the usual manner to $(D/(R_B - R))/(R_B/R)$

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The unknown in this equation, Eq. (4.9), $P_i$, can now be evaluated from the chemical kinetics of the system.

In general, the rate of production of G by reaction is adequately expressed as

$$N = 4\pi r_1^2 g \frac{k_c}{R'T_G} (P_K - (1 + \frac{1}{K})P_i) \quad (4.10)$$

where $k_c$ is the velocity constant of the forward reaction, based on one mole of B, and at temperature $T_G$. $K$ is the thermodynamic equilibrium constant and $P_K$, normally $P_T$, is so written to allow for the analyses of carbonate decomposition type reactions. In such reactions $P_K = P_e$, where $P_e$ is the equilibrium pressure of carbon dioxide, and $f(P) = (P_e - P_i)$ at small values of $P_i$. In such cases $K$ would be $\infty$. In general the forward reaction is proportional to $(P_T - P_i)$ and the reverse to $P_i$.

Elimination of $P_i$ from Eqs. (4.9) and (4.10) then gives,

$$N = \frac{R'T_G(1 - \frac{a}{E})}{4\pi RD_e P_T} \left[ \frac{D_e}{Rk_B} + \frac{1-r_1/R}{r_1/R} \right] = -\ln \left[ \frac{P_T - \frac{1-a/E}{1+1/K} \left( \frac{NRT_G}{NRT_G + 2gk_c} \right)}{P_T - (1-a/g)P_G} \right] \quad (4.11)$$

This is the gas phase mass balance on the system.

4.3.2 Solid phase mass balance. The overall rate of production of G can also be defined in terms of the velocity of propagation of the interface, $-dr_i/dt$, as

$$N = -4\pi r_1^2 \rho_m g \frac{dr_i}{dt} \quad (4.12)$$

where $\rho_m$ is the molar bulk density of the reactant solid, B.
Eq. (4.12) can be written as

\[ t_{r_1} = 4\pi R^3 \rho_m g \int_{r_1/R}^{1} \frac{(r_1/R)^2}{N} \, d(r_1/R) \] (4.13)

where \( t_{r_1} \) is the time required for the interface to travel from the surface of the sphere to the interface, through a distance \((R-r_1)\). Eq. (4.13) is the solid phase mass balance.

4.4 Dimensionless form of equations. Eqs. (4.11) and (4.13), which represent the gas and solid phase mass balances respectively, can be rendered in a dimensionless form which allows solutions to be presented in a more useful form. The method was used by Shen and Smith and is again used here, with essentially the same nomenclature. Thus grouping terms in Eq. (4.11) gives

\[ \eta_d (1- \frac{a}{g}) Y_2 (Y_1 + \frac{1- r_1}{R}) (Y_9 - Y_6 Y_7) = -\ln \left[ 1 - \frac{(1- \frac{a}{g}) (Y_9 - Y_6 Y_7)}{Y_7 (1-(1- \frac{a}{g}) Y_6)} \left( 1 - \frac{\eta_d}{r_1/R} \right) \right] \] (4.14)

and in Eq. (4.13) gives,

\[ \theta_{r_1} = \int_{r_1/R}^{1} \frac{(r_1/R)^2}{\eta_d} \, d(r_1/R) \] (4.15)

where \( \eta_d \) is a decay factor and is evaluated as the ratio of the overall rate of reaction at any time to that which would obtain at the surface of the solid if diffusional resistances were absent, so that

\[ \eta_d = \frac{NRT_G}{4\pi R^2 \rho c P_{T} (Y_9 - Y_6 Y_7)} \]

4.4 : 52
Other dimensionless groups used are,

\[ \Theta_{r_i} = \frac{t_{r_i} \frac{P_T k_c}{R_m R'T_g}}{Y_6 Y_7} \], a dimensionless time

\[ Y_1 = \frac{D_e}{Rk_B}, \quad Y_1^{-1} \] being a modified Sherwood no.

\[ Y_2 = \frac{Rgk_c}{D_e}, \] a modified Thiele modulus

\[ Y_6 = \frac{P_G}{P_T} \]

\[ Y_7 = 1 + \frac{1}{K} \]

and \[ Y_9 = \frac{P_K}{P_T} \]

Eqs. (4.14) and (4.15) define the isothermal system for the sphere completely, and will be considered for solution in general form later.

4.5 The infinite cylinder and the slab. Although the sphere is perhaps the most commonly encountered case in experimental studies, two other simple forms are also practical, namely the infinite cylinder, of infinite length and finite radius, and the slab, infinite in two dimensions and finite in one, as used in Chapter 3. The models for the cylinder and the slab are the same as that for the sphere in that the distance from the centre of the solid to the surface is \( R \), and from the centre to the interface, is \( r_i \).

The equations for the cylinder and the slab are developed in a similar manner to those for the sphere, bearing in mind that
the equivalent diffusion equations to Eq. (4.2) for the sphere are

\[ \frac{d}{dr} \left[ r \frac{d}{dr} \ln \left( \frac{P_T - (1 - \frac{a}{g})P}{P_T} \right) \right] = 0 \] (4.2. Cylinder)

and

\[ \frac{d^2}{dr^2} \ln \left( \frac{P_T - (1 - \frac{a}{g})P}{P_T} \right) = 0 \] (4.2. Slab)

Eqs. (4.14) and (4.15) can now be written in the geometrically general form,

\[ \eta_d (1 - \frac{a}{g}) Y_2 (Y_1 + B) (Y_9 - Y_6 Y_7) = - \ln \left[ 1 - \frac{(1 - \frac{a}{g}) (Y_9 - Y_6 Y_7)}{Y_7 (1 - (1 - \frac{a}{g}) Y_6)} \left( 1 - \frac{\eta_d}{(r_1/R)^C} \right) \right] \] (4.14. General)

and

\[ \theta_{r_1} = \int_{r_1/R}^{1} (r_1/R)^C \frac{r_1}{\eta_d} \, d(r_1/R) \] (4.15. General)

where \( \eta_d \) is defined as

\[ \frac{N R' T_G}{A g k_0 P_T (Y_9 - Y_6 Y_7)} \]

and, for the sphere \( A = 4 \pi R^2 \), \( B = \frac{1 - r_1/R}{r_1/R} \) and \( C = 2 \)

for the cylinder \( A = 2 \pi R \), \( B = \ln(R/r_1) \) and \( C = 1 \)

and for the slab \( A = 1 \), \( B = 1 - r_1/R \) and \( C = 0 \)

Solutions to the equations for the cylinder and the slab are presented in Appendix F.

4.6 Kinetic control of reactions. When mass transfer resistances are low, the overall rate of reaction will be controlled by the kinetics of the system. As defined by the sharp interface
theory, the rate must then be a constant per unit interfacial area, assuming isothermal conditions, so that the change in rate with time will be dependent solely on the geometry of the solid, which governs the way the interfacial area changes with time. For example, for the slab described earlier, the area of the interface will be constant so that the rate of reaction will be constant with time. For the sphere the interfacial area, and hence the rate, is proportional to \( r_1^2 \) as described briefly in Chapter 2. Similarly the rate for the cylinder is proportional to \( r_1 \). If the solid were in cubic form the rate would be proportional to the receding cubical interface, and hence to \( r_1^2 \), giving the same result as for the sphere. Note that for kinetic control, the time of reaction is equivalent to the fractional penetration, as the velocity of penetration is a constant.

Results can therefore be conveniently be represented as a plot of the ratio of the reaction interface area and the external area of the solid, which is in fact the effectiveness factor \( \eta_d \) defined above, against the fractional penetration, \( \alpha \), i.e. \( 1-r_1/R \).

These results are shown in Fig. (4.2) for these geometries and also for the finite cylinder, defined below.

4.6.1 Further geometries. (1) Another common form is the finite cylinder, radius \( R \) and length \( 2L \). The interface will proceed into the solid, retaining the external shape, so that the thickness of the reaction product is constant all round the cylinder, and at any time the new dimensions of the reactant core will be radius \( r_1 \) and length \( 2(L-R-r_1) \), so that the decay factor
can be written as

\[
\frac{\text{area of interface}}{\text{external area}} = \frac{(r_1/R)^2 + 2r_1(L/R - 1 + r_1/R)}{1 + 2L/R}
\]

(4.16)

i.e.

\[
\eta_d = \frac{(1-\alpha)^2 + 2(1-\alpha)(L/R - \alpha)}{1 + 2L/R}, \quad \frac{L}{R} \geq 1
\]

(4.17)

and

\[
\eta_d = \frac{(1-\alpha L/R)^2 + 2(1-\alpha)(L/R - \alpha L/R)}{1 + 2L/R}, \quad \frac{L}{R} < 1
\]

(4.18)

where \( \alpha = 1 - \frac{r_1}{R}, \quad \frac{L}{R} \geq 1 \) or \( \alpha = (1 - \frac{r_1}{R})/\frac{L}{R}, \quad \frac{L}{R} < 1 \)

It can be noticed that the length to diameter ratio, when unity, gives \( \eta_d = (r_1/R)^2 \), so that this special case of the finite cylinder is identical to the sphere. The results for the finite cylinder are also shown in Fig.4.2 for various values of \( L/R \). It can also be seen that as \( L/R \to \infty \) the solution for the infinite cylinder is approached, and at low values, i.e. \( L/R \to 0 \), that for the slab.

(ii) Another interesting shape is the bar-shaped solid, with sides \( 2R \) (shortest side), \( 2L \) and \( 2Z \). The dimensions of the reactant core at any time will have the corresponding values \( 2r_1 \), \( 2(L-R+r_1) \) and \( 2(Z-R+r_1) \), so that

\[
\eta_d = \frac{r_1(L-R+r_1) + r_1(Z-R+r_1) + (Z-R+r_1)(L-R+r_1)}{RL + RZ + ZL}
\]

4.6.2 Alternative representation. In some cases the histories of the reactions may be better represented by plotting conversion or fractional decomposition \( X \), against fractional penetration. These are related as follows:
Sphere or cube: \[ X = 1 - \left(\frac{r_1}{R}\right)^3 = 1 - (1 - \alpha)^3 \]

Cylinder (infinite): \[ X = 1 - \left(\frac{r_1}{R}\right)^2 = 1 - (1 - \alpha)^2 \]

Slab: \[ X = 1 - \frac{r_1}{R} = 1 - (1 - \alpha) \]

Cylinder (finite): \[ X = 1 - \frac{\frac{r_1^2(L-R+r_1)}{R^2L}}{1 - (1 - \alpha)^2(L/R - \alpha)} \]

Bar-shape: \[ X = 1 - \frac{\frac{r_1(L-R+r_1)(Z-R+r_1)}{RLZ}}{1 - (1 - \alpha)(L/R - \alpha)(Z/R - \alpha)} \]

The conversion/penetration relationships for certain of these cases is shown in Fig. 4.3.

4.7 Effect of particle size distribution on kinetic control.

If reaction in a powdered mass of solid is being studied wrong conclusions may be drawn regarding the nature of the reaction if the distribution of particles is ignored. The significance of this error has been studied using a normal distribution.

The normal or Gaussian distribution is defined by the equation

\[ n_x = \frac{1}{\sigma \sqrt{2\pi}} \exp\left(-\frac{1}{2}\left(\frac{x-\bar{x}}{\sigma}\right)^2\right) \]

where \( n_x \) is the probability of a particle of size less than \( x \), where the average particle radius is \( \bar{x} \) and the standard deviation from the average size is \( \sigma \). The relative number of particles within a range, say between \( x_1 \) and \( x_2 \), is given by
\[
\begin{align*}
n &= \frac{1}{\sigma'(2\pi)^{\frac{3}{2}}} \int_{-\infty}^{\infty} \frac{x^2}{2} \exp\left(-\frac{1}{2} \left(\frac{x-\bar{x}}{\sigma'}\right)^2\right) \, dx \\
&= \frac{1}{2} \left(\frac{2}{\pi}\right)^{\frac{3}{2}} \int_{-\infty}^{\infty} \frac{x^2}{2} \exp\left(-\frac{1}{2} t^2\right) \, dt
\end{align*}
\]

where \( t = (x-\bar{x})/\sigma' \). This can be expressed alternatively as,

\[
\begin{align*}
n &= \frac{1}{2} \left[ \left(\frac{2}{\pi}\right)^{\frac{3}{2}} \int_{-\infty}^{\infty} \frac{t^2}{2} \exp\left(-\frac{1}{2} t^2\right) \, dt - \left(\frac{2}{\pi}\right)^{\frac{3}{2}} \int_{-\infty}^{\infty} \frac{1}{2} \exp\left(-\frac{1}{2} t^2\right) \right] \\
&= \frac{1}{2} \left[ \left(\frac{2}{\pi}\right)^{\frac{3}{2}} \int_{0}^{t} \frac{t^2}{2} \exp\left(-\frac{1}{2} t^2\right) \, dt - \left(\frac{2}{\pi}\right)^{\frac{3}{2}} \int_{0}^{t} \exp\left(-\frac{1}{2} t^2\right) \right] \\
&= \frac{1}{2} \left[ \left(\frac{2}{\pi}\right)^{\frac{3}{2}} \int_{0}^{t} \frac{t^2}{2} \exp\left(-\frac{1}{2} t^2\right) \, dt - \left(\frac{2}{\pi}\right)^{\frac{3}{2}} \int_{0}^{t} \exp\left(-\frac{1}{2} t^2\right) \right]
\end{align*}
\]

where the bracketed terms in Eq. (4.19) can be readily evaluated from standard tables such as those of Comrie.

For simplicity we may redefine the size as the ratio of size to average, so that the mean particle size \( \bar{x} \) becomes unity. This leaves \( \sigma' \) as the only remaining variable, apart from the extremes of particles chosen to give the distribution band.

The distribution can now be broken up into equal size intervals, and the relative frequencies of particles in these intervals calculated from Eq. (4.19). Dividing the range arbitrarily into 40 divisions, where \( \Delta x = 0.05 \), a choice of standard deviation of 0.25 ensures that the integration of the probability function over all the particles is 0.999637, so that a full normal distribution is being studied. The relative frequency of occurrence of particles within a given range, where the size of particle in a given range is taken as \((x_1-x_2)/2\), is given in Table 4.1. This distribution is also shown graphically in Fig. 4.4.

A similar distribution for \( \sigma' = 0.125 \), with \( \Delta x = 0.025 \) so that \( \Sigma n \) still equals 0.999637, has also been used and is shown in Fig. 4.4 also.
To obtain results for $\eta_d$ against penetration, as above for single particles, it is necessary to define the fractional penetration in terms of the largest particle, so that when the reaction has penetrated the largest particle the fractional penetration becomes unity and the reaction is complete. Similarly $\eta_d$ is defined as the ratio of the sum of the interfacial areas available for reaction in all the particles to the total external surfaces of all the particles. Initially $\eta_d$ is obviously unity, and thereafter equal amounts must be subtracted from the radius of each particle to correspond to the penetration of the interface equal distances into each particle, the new total area calculated and divided by the initial area. Hence $\eta_d$ is obtained as a function of $\alpha$.

Table 4.1 Normal distribution.

<table>
<thead>
<tr>
<th>$\frac{1}{2}(x_1+x_2)$</th>
<th>1.975</th>
<th>1.925</th>
<th>1.875</th>
<th>1.825</th>
<th>1.775</th>
<th>1.725</th>
<th>1.675</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2}(x_1+x_2)$</td>
<td>0.025</td>
<td>0.075</td>
<td>0.125</td>
<td>0.175</td>
<td>0.225</td>
<td>0.275</td>
<td>0.325</td>
</tr>
<tr>
<td>$n \times 10^4$</td>
<td>0.385</td>
<td>0.800</td>
<td>1.750</td>
<td>3.500</td>
<td>6.650</td>
<td>12.05</td>
<td>21.05</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\frac{1}{2}(x_1+x_2)$</th>
<th>1.625</th>
<th>1.575</th>
<th>1.525</th>
<th>1.475</th>
<th>1.425</th>
<th>1.375</th>
<th>1.325</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2}(x_1+x_2)$</td>
<td>0.375</td>
<td>0.425</td>
<td>0.475</td>
<td>0.525</td>
<td>0.575</td>
<td>0.625</td>
<td>0.675</td>
</tr>
<tr>
<td>$n \times 10^4$</td>
<td>35.4</td>
<td>57.0</td>
<td>88.5</td>
<td>132.0</td>
<td>188.5</td>
<td>259.5</td>
<td>343.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\frac{1}{2}(x_1+x_2)$</th>
<th>1.275</th>
<th>1.225</th>
<th>1.175</th>
<th>1.125</th>
<th>1.075</th>
<th>1.025</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2}(x_1+x_2)$</td>
<td>0.725</td>
<td>0.775</td>
<td>0.825</td>
<td>0.875</td>
<td>0.925</td>
<td>0.975</td>
</tr>
<tr>
<td>$n \times 10^4$</td>
<td>436.0</td>
<td>532.0</td>
<td>624.0</td>
<td>703.5</td>
<td>761.5</td>
<td>792.5</td>
</tr>
</tbody>
</table>

This arithmetic procedure has been followed in Computer program 5, Appendix G. As well as calculating $\eta_d$ as a function of $\alpha$.
the program also supplied information regarding the relative areas available for reaction by evaluating the square of the interfacial radius for each chosen value of \( \alpha \). In Fig. 4.5 the results for \( \sigma' = 0.25 \) and \( \sigma' = 0.125 \) are shown, as \( \gamma_d \) versus \( \alpha \), and compared with that for the single sphere. The result for the single sphere, of course, represents a single particle of diameter equal to that of the largest sphere in the distribution, i.e. 1.975.

Also included in Fig. 4.5 is the history a single particle equal in size to the mean particle of the distribution. Note that we must define \( \alpha \) as \( (1 - x_1/1.975) \) for \( \sigma' = 0.25 \) and as \( (1 - x_1/1.4875) \) for \( \sigma' = 0.125 \). The correspondence between the distribution and single particle solutions can be seen to be good, especially at the lower value of \( \sigma' \). The conclusion may be drawn then, that for kinetic control, approximation to the true solution for a distribution by assuming an average particle size can be valid, certainly for the type of distribution chosen.

In Fig. 4.6 the distribution of areas (actually the parameter plotted is \( nx_1^2 \)) is shown for progressive values of fractional penetration of the largest particle. From the point of view of area the distribution is seen to be initially skew. As the reaction proceeds so the smaller particles contribute less and less. The final tail on the reaction, as can be identified in Fig. 4.5, is formed by the very few large particles, when the contribution to the amount of reaction is very small.

Two further distributions can be postulated by taking \( n \) to be either relative surface area or relative amount of particle within a given size range, and assuming the same distribution as
in Table 4.1, i.e. making no change in $\bar{X}$ (-1). The $\gamma_d$ versus fractional penetration relations for these cases have been evaluated by simple modification of program 5 as outlined in Appendix G, and are shown in Fig.4.7, again being compared with the relevant result for a single sphere. Again correspondence is good especially, as would be expected, at the lower value of $\sigma^t$.

4.8 Diffusion effects - equimolar counterdiffusion. In many reactions, e.g. the reduction of iron ore, the stoichiometric coefficients of A and G, the reactant and product gases, are equal. Hence $a=g$ and the transfer of A and G through the porous product solid and through the boundary layer can be termed equimolar counterdiffusion. This special case has been treated also by Shen and Smith.

Substituting $a=g$ in Eq.(4.14) we obtain, by correct manipulation of $(1-a/g)$, and assuming irreversible reactions,

$$\eta_d = \left[ Y_2(Y_1 + \frac{1-r_1}{r_1/R}) + \frac{1}{(r_1/R)^2} \right]^{-1} \tag{4.20}$$

Substitution of $\eta_d$ from Eq.(4.20) in Eq.(4.15) gives the equation for shared control of the overall rate,

$$\theta = (1-r_1/R)^{-2} \left[ \frac{Y_1}{3} \left(1+ \frac{r_1}{R} + \left(\frac{r_1}{R}\right)^2\right) + \frac{1}{6} \left(1+ \frac{r_1}{R} - 2\left(\frac{r_1}{R}\right)^2\right) \right]$$

which is the equation obtained by Shen and Smith.

4.8.1 Kinetic control. If diffusional resistances are relatively low, then $Y_2 \to 0$ and we obtain from Eq.(4.20)

$$\eta_d = (r_1/R)^2$$

4.8.1 : 61
Following the example of Ishida and Wen we may define an effectiveness factor \( \eta_e \), which represents the ratio of the actual rate of reaction at the interface to that which would obtain on the same area under conditions of chemical control. Hence

\[
\eta_e = \eta_d/(r_1/R)^2 = \frac{1}{1 - (1 - X)^{\frac{3}{2}}}
\]

Hence the effective utilisation of the interface under conditions of chemical control is described as being 100%. Values of \( \eta_e \) in excess of 1 are possible under non-isothermal conditions, as will be shown in Chapters 5 and 6. Integration of Eq. (4.15) with this value of \( \eta_e \) leads to

\[
\theta_{r_1} = 1 - \frac{r_1}{R} = 1 - (1 - X)^{\frac{3}{2}}
\]

where \( X \) is fractional conversion.

### 4.8.2 Pore diffusion control.

In this case, \( Y_1 \rightarrow 0 \) and \( Y_2 \) is large, so that

\[
\eta_e = \frac{(r_1/R)}{Y_2/(1-r_1/R)}
\]

and

\[
\theta_{r_1} = (1 - \frac{r_1}{R}) \left[ \frac{Y_2}{6(1-(1-X)^{\frac{3}{2}})-2X} \right]
\]

This case is partially fictitious in that at small values of \( \theta_{r_1} \) or at \( r_1/R = 1 \), we have \( \eta_d \rightarrow \infty \). Kinetic effects must be included for small values of time, so that

\[
\theta_{r_1} = (1 - \frac{r_1}{R}) \left[ \frac{Y_2}{6(1+\frac{r_1}{R}-2(\frac{r_1}{R})^2)+1} \right]
\] (4.22)
4.8.3 Boundary layer diffusion control. In this case \( Y_1 \) is large so that Eq. (4.20) becomes

\[
\eta_d = 1/(Y_1 Y_2)
\]

and

\[
\theta_{r_1} = \frac{Y_1 Y_2}{3} \left[ (1-(\frac{r_1}{R})^3) \right] = \frac{Y_1 Y_2 X}{3}
\]

Hence for boundary layer control, as expected, the overall rate is a constant with time, as long as the control persists.

4.8.4 Mixed control with size distribution. The effect of a distribution of particle sizes when "mixed" control by pore diffusion and kinetics occurs was studied using the number frequency distributions used earlier and shown in Table 4.1. To study this effect a special program, No.6, had to be developed. Quite a different technique was necessary to that used in program 5 because of the non-interchangability of the parameters time and distance, as the velocity of penetration is no longer a constant. A description of the technique used in the simultaneous solution of Eq. (4.22) for a number of particle sizes is given in Appendix G, Section G.6.

The results for \( \sigma' = 0.25 \) and 0.125 for two values of \( Y_2 \) are shown in Fig.4.8 with \( \eta_d \) plotted as a function of \( \theta_{x_1} \). For this case \( Y_2 \) is defined in terms of the mean particle size so that the corresponding result for the single sphere can be superimposed directly on the solutions for both \( \sigma' = 0.25 \) and 0.125. Again a remarkable correspondence can be seen between the distribution solutions and that for the single sphere, even at the higher value of \( Y_2 \), and again especially for \( \sigma' = 0.125 \). This
illustrates the point that, experimentally, a distribution can be ignored and all observed results, except for the long tails on $\eta_d$ versus $e_{r_1}$, based on the mean particle size.

4.9 Solution of the general equations of the isothermal case.

Eq. (4.14), the general equation describing non-equimolar counter-diffusion with reversible reactions, has been solved using Newton Raphson iteration, and Eq. (4.15) by numerical integration, by means of Computer program 8 for the sphere, 9 for the infinite cylinder and 10 for the slab. The method of solution is described with the program in Section 38. The program was also used to evaluate the equimolar situations, and some of the results were compared with the analytical solutions from the equations given in Section 4.8. For the case of kinetic control of the reaction in a sphere ($Y_2 = 0.00001$), with equimolar counterdiffusion, agreement of $e_{r_1}$ obtained from Eq. (4.21) and from the numerical integration performed by the program was found to be exact to at least six significant figures. This was also true no matter what the values of $Y_1$, $Y_2$ and $r_1/R$. It is impossible to compare computer results for non-equimolar cases with analytical results as the latter are unattainable. However, the criterion for choice of solution via the Newton Raphson technique was chosen such that a more precise criterion gave no different results.

Also as the integration procedure was adequate for the equimolar case it would also be adequate for the non-equimolar case.

4.9.1 Boundary layer diffusional resistances absent. (i.e. $Y_1 = 0$)

Solutions for this case have been obtained for values of $Y_2$.
ranging from $0.00001$ to $1000$, some of which are presented in Fig. 4.9 as $\eta_d$ and $\eta_e$, the decay and effectiveness factors respectively, versus conversion, $X$, and in Fig. 4.10 as $\eta_d$ versus the dimensionless time, $\theta_{ri}$. It can be seen that $\eta_d$ and $\eta_e$ always assume an initial value of unity, indicating the absence of a resistance to diffusion in the boundary layer, so that initially the reaction is purely dependent on the chemical kinetics. A more important point to notice is that $\eta_e$ increases at large values of $X$, showing that the reaction rate per unit area of interface increases as the interface penetrates deeper into the sphere. This will be discussed in greater detail in Chapter 5, under the title "geometrical instability".

4.9.2 Mixed control. When diffusional resistances in the boundary layer become important the initial rate is no longer equal to the potential chemical rate and $\eta_d$ and $\eta_e$ are less than unity at $X = 0$ ($\theta_{ri} = 0$), being smaller at higher values of $Y_1$. Solutions for this case for various combinations of $Y_1$ and $Y_2$ are shown in Fig. 4.11 as $\eta_d$ versus $X$, with $\eta_e$ versus $X$ included for the curves $Y_2 = 1$. It can be seen that on the introduction of boundary layer resistances the occurrence of a rise of $\eta_e$ with conversion appears progressively earlier as $Y_1$ increases. This is a further effect of geometrical instability. In Fig. 4.12 are given the $\eta_d$ versus $\theta_{ri}$ results.

4.9.3 Non-equimolar counterdiffusion. It has been commonly assumed that the equimolar counterdiffusion equations adequately represent gas-solid reactions, but this is obviously untrue for
such reactions as the decomposition of carbonates. The equations for non-equimolar counterdiffusion have been developed earlier and solutions are given in Fig. 4.13. It can be seen from these results that serious errors can result especially at higher values of \( Y_2 \) and values of \((1-a/g)\) more remote from 0. The results presented have taken no account of boundary layer resistance, although this would only add to the errors. As diffusional effects become less important it can be seen that the equimolar counterdiffusion case becomes a good approximation. For example, at \( Y_2 = 1 \), all values of \( a \) and \( g \) give approximately the same result, as can be seen in Fig. 4.13. The difference in the value of \( \theta \) at \( r_1 = 0.05 \) (essentially complete reaction) for \((1-a/g) = 1\) and \((1-a/g) = -1\) (the two extremes shown for \( Y_2 = 10 \) and \( Y_2 = 50 \)) is only 2%, whereas for \( Y_2 = 10 \) it is 52% and for \( Y_2 = 50 \) it is 158%. Inclusion of the effect of non-equimolar counterdiffusion involves the use of numerical techniques to replace analytical results, as used in programs 8-10. This may be responsible for its being ignored previously.

4.10 The cylinder and the slab. The above results have also been obtained for the cylinder and slab and are reported in Appendix F.
5.1 Introduction. The controlling equations for reactions occurring in isothermal conditions were given in Chapter 4. Such conditions can be maintained by special experimental techniques which preclude the possibility of temperature gradients, or in cases where the heat of reaction is small, gas velocities high, and where the thermal conductivity of the solid is high. Generally, however, significant temperature gradients will exist in the reacting solid and the boundary layer in order to transfer the heat of reaction to or from the reaction site. Hence it is necessary to develop equations which will truly represent a non-isothermal reaction. These have been obtained and are presented here with the usual steady-state assumptions regarding accumulation of heat within the solid, and the phenomenon of thermal instability is studied in detail. In Chapter 6 a transient term which includes the changing solid enthalpy is introduced, and its effect on nonisothermal reactions studied.

5.2 The energy balance. The heat required by the reaction, \( Q \), is defined as \( \Delta H / g \), using the convention that \( \Delta H \), the molar heat of reaction based on B, is positive for endothermic and negative for exothermic reactions. All conditions are as in Chapter 4, and reference may be made to Fig.4.1 for the distribution of temperatures in and around the reacting sphere.

The heat of reaction, \( Q \), can be written in terms of both
the heat transferred to the surface of the sphere, and in terms of the heat conducted through the product solid. Hence we have,

\[ Q = \frac{N\Delta H}{g} = 4\pi R^2 (h_B (T_G - T_s) + h_R (T_G - T_s)) \quad (5.1) \]

and

\[ = 4R^2 k_e \left( \frac{dT}{dr} \right)_{r=R} \quad (5.2) \]

where the sensible heats of the gases transferred into and out of the sphere have been ignored, and the surfaces which radiate to the particle are assumed to be at the bulk gas temperature, \( T_G \). \( h_B \) is the boundary layer heat transfer coefficient and \( k_e \) is the effective thermal conductivity of the solid product. The effect of radiational heat transfer has not yet been included in such an analysis and is again ignored here, although its importance in conditions of thermal instability is mentioned later.

The equation for heat conduction in a sphere is

\[ \frac{d}{dr} \left( r^2 \frac{dT}{dr} \right) = 0 \quad (5.3) \]

Integrating Eq. (5.3) gives

\[ T = T_1 + (T_S - T_1) \frac{(1/r_1 - 1/r)}{(1/r_1 - 1/R)} \quad r_1 \leq r \leq R \quad (5.4) \]

using the boundary conditions that \( T_1 \) and \( T_S \) are the values of \( T \) at \( r_1 \) and \( R \) respectively.

Evaluating \( (dT/dr) \) at \( r=R^- \) from Eq. (5.4) and substituting in Eq. (5.2) gives

\[ Q = 4\pi Rk_e (T_S - T_1) \frac{r_1/R}{1-r_1/R} \quad (5.5) \]
Eliminating $T_S$ from Eqs. (5.1) and (5.5), and ignoring $h_R$ gives

$$Q = 4\pi R k_0 (T_0 - T_1) \left( \frac{k_0}{R h_B} + \frac{1-r_1/R}{r_1/R} \right)^{-1}$$  \hspace{1cm} (5.6)$$

which is the heat balance equation.

5.3 The mass balance. The equations of the mass balance must be adjusted to allow for temperature gradients within the solid. The chemical rate expression, Eq. (4.10), now becomes

$$N = 4\pi r_1^2 \frac{k_0}{R' T_1} \exp\left(- \frac{E_c}{R' T_1}\right) \left( P_K^{T_1} - (1+1/K)P_i \right)$$  \hspace{1cm} (5.7)$$

where $k_0 \exp\left(- \frac{E_c}{R' T_1}\right)$ is the velocity constant of the reaction at the temperature of the interface, $T_1$, and $P_K^{T_1}$ is the value of $P_K$ also at the interfacial temperature. When $P_K$ represents the equilibrium pressure of carbon dioxide in the decomposition of carbonates, we have

$$P_K^{T_1} = P_e = P_0^{T_1} \exp\left(- \frac{E_c}{R' T_1}\right)$$  \hspace{1cm} (5.8)$$

where $P_0^{T_1}$ is a frequency factor, and $E_c$ is a constant which has been arranged in the same form as the temperature coefficient of the reaction velocity constant. In circumstances where $P_K$ does represent $P_e$ then $E_c$ must be redefined as the activation energy of the reaction less that of the equilibrium pressure, $E_e$. $K$ is the thermodynamic equilibrium constant whose temperature dependence can be included in any numerical analysis.

Eq. (4.11) can now be re-expressed as

5.3 : 69
Note that the rate of diffusion has been evaluated at a constant value of $D_e$, which is evaluated at $T_G$, the bulk gas temperature. Correction for the variation of $D_e$ with temperature could easily be applied as the solutions are necessarily numerical. The same also applies to $k_B$.

5.4 The dimensionless form of the equations. Eqs. (5.9) and (5.6) can be rendered in dimensionless form to give, as in Chapter 4,

$$\eta_d \left(1 - \frac{a}{g}\right) Y_2 \left(Y_1 - \frac{1 - r_1/R}{r_1/R}\right) (Y_9 - Y_6 Y_7)$$

$$= -\ln \left[ 1 - \frac{1-a/g}{Y_7 \left(1 - \left(1 - \frac{a}{g}\right) Y_6 \right)} \left[ Y_9 \exp(Y_{10} \left(1 - \frac{T_G}{T_1}\right) - Y_6 Y_7 - \frac{\eta_d (Y_9 - Y_6 Y_7)}{(r_1/R) \exp(Y_5 \left(1 - \frac{T_G}{T_1}\right))} \right] \right]$$

and

$$\frac{T_1}{T_G} = 1 - Y_2 Y_4 \eta_d \left(Y_3 + \frac{1 - r_1/R}{r_1/R}\right)$$

while the time integration equation, Eq. (4.15) remains the same, and

$$\eta_d = \frac{N R' T_G}{4 \pi R D e P_T} \frac{\exp(-Y_5) (Y_9 - Y_6 Y_7)}{g k_e P_T}$$

$$\theta_{r_1} = \frac{t_{r_1} P_T k_e \exp(-Y_5) (Y_9 - Y_6 Y_7)}{R m R' T_G}$$

5.4 : 70
\[
Y_4 = \frac{\Delta H \tau_{PT} (Y_0 - Y_6 Y_7)}{g k_e R^2 T_G^2}
\]
\[
Y_2 = R g k_e^0 \exp(-Y_2)/D_e
\]
\[
Y_3 = k_e/R h_B
\]
\[
Y_5 = E_c/R^2 T_G
\]
\[
Y_{10} = E_e/R^2 T_G
\]

5.5 The infinite cylinder and the slab. As with the mass transfer equations, the heat balance for these cases is evolved in a similar manner to that for the sphere, with the equivalent equations for the cylinder and the slab to Eq. (5.3) for the sphere being,

\[
d(r \frac{dT}{dr}) = 0 \quad \text{for the cylinder} \quad (5.3 \text{Cyl})
\]
\[
\frac{d^2 T}{dr^2} = 0 \quad \text{for the slab} \quad (5.3 \text{Slab})
\]

Eqs. (5.10) and (5.11) can be written in the general form

\[
\gamma_d (1 - \frac{a}{g}) Y_2 (Y_1 - B) (Y_9 - Y_6 Y_7)
\]
\[
= -\ln \left[ 1 - \frac{1 - a/g}{Y_7 (1 - (1 - a/g) Y_6)} \left( Y_9 \exp \left( 10 \left( 1 - \frac{T_G}{T_1} \right) - Y_6 Y_7 - \frac{\gamma_d (Y_9 - Y_6 Y_7)}{\left( \frac{T_1}{R} \right)^c \exp (Y_5 (1 - \frac{T_G}{T_1}))} \right) \right) \right]
\]

and \[
\frac{T_1}{T_G} = 1 - Y_2 Y_4 \gamma_d (Y_3 + B)
\]

5.5 : 71
where
\[ \eta_d = \frac{\frac{NRT_G}{Agk_0F_T\exp(-Y_5)(Y_9-Y_6y_7)}}{\frac{r_1}{R}} \]

and A, B and C are as defined in Section 4.5. The time integration equation, Eq. (4.15) remains the same, for the definition of \( \theta_{r_1} \) given in Section 5.4.

These are the general equations for non-isothermal reactions, with the usual steady-state assumptions, and will be considered for solution in Chapter 6.

5.6 Geometrical instability. To illustrate the effects of geometrical and thermal instability it is useful to consider equimolar reactions, i.e. \( a = g \), so that Eqs. (5.10) and (5.11) become,

\[ \eta_d(F_1 + \exp(-Y_5(1-\frac{T_G}{T_1}))) = (r_1/R)^2 \]  \hspace{1cm} (5.12)

\[ \eta_dF_2 = (\frac{T_1}{T_G} - 1)(r_1/R)^2 \]  \hspace{1cm} (5.13)

where relative mass and heat transfer characteristics have been grouped as \( F_1 \) and \( F_2 \) respectively such that,

\[ F_1 = Y_2(\frac{r_1}{R}) - (1-Y_1)(\frac{r_1}{R})^2 \]  \hspace{1cm} (5.14)

and \[ F_2 = -Y_2Y_4(\frac{r_1}{R}) - (1-Y_3)(\frac{r_1}{R})^2 \]  \hspace{1cm} (5.15)

Instability in non-catalytic gas-solid reactions is of two kinds, geometrical and thermal. A third kind has been suggested (Ishida and Wen) in which sudden transitions occur in the...
the control of the reaction rate. This transitional instability will be mentioned later.

The term geometrical instability describes the situations in which deeper penetration of the interface into the solid favours higher reaction rates, defined on a unit interfacial area basis. This rate may increase with penetration depending on the geometry of the solid, and is represented by \( \eta_e \), even although the overall rate, represented by \( \eta_d \), is decaying. Any tendency for uneven growth of product layer thickness due to, for example, crystal defects, can be amplified to produce rapid propagation of the interface in such a region. This effect, recognised by Cannon and Denbigh (1957a,b) in the oxidation of zinc sulphide crystals, is most noticeable when heat transfer resistances are high. Geometrical instability can occur in isothermal as well as exothermic and endothermic reactions.

For the sphere,

\[
\eta_e = \frac{\eta_d}{(\frac{r_i}{R})^2}
\]

and the general criterion for geometrical instability is, then,

\[
\frac{d \eta_e}{d(\frac{r_i}{R})} < 0
\]

### 5.6.1 Isothermal reactions

The mass balance for the isothermal irreversible case can be written from Eq. (4.20) as,

\[
\eta_e = \frac{1}{\frac{r_i}{R} - (1-Y_1)(\frac{r_i}{R})^2 + 1}
\]

(5.16)
so that

$$\frac{d\eta_e}{d\left(\frac{r_1}{R}\right)} = -\frac{Y_2(1-2(1-Y_1)\frac{r_1}{R})}{(F_1+1)^2}$$

yielding the criterion for isothermal instability as $(1-Y_1)\frac{r_1}{R} < 0.5$. Instability will occur at all penetrations if $Y_1 < 0.5$ and at all $\frac{r_1}{R} < 0.5$ for all values of $Y_1$. The point of onset of instability can be found from,

$$\frac{d\eta_e}{d\left(\frac{r_1}{R}\right)} = 0$$

to be

$$(1-Y_1)\frac{r_1}{R} = 0.5$$

The description of geometrical instability in isothermal reactions with a steady-state analysis since all accumulation terms are negligible. Such a simple analysis is not usually possible in non-isothermal reactions, although this will be presented as a basis for comparison.

5.6.2 Non-isothermal reactions. $(T_1/T_G)$ from Eq. (5.13) can be substituted in Eq. (5.12) to give the effectiveness factor

$$\eta_e = \left[ F_1 + \exp(-Y_5(1-\frac{1}{1+F_2\eta_e})) \right]^{-1} \tag{5.17}$$

Differentiation of Eq. (5.17) yields

$$\frac{1}{\eta_e^2} \frac{d\eta_e}{d\left(\frac{r_1}{R}\right)} \left[ 1+ \frac{Y_5\eta_e(1-\frac{T_1}{T_G})}{\exp(Y_5(1-\frac{T_G}{T_1}))(\frac{T_1}{T_G})^2} \right] = -\frac{dF_1}{r_1/R} + \frac{Y_5\eta_e \frac{dF_2}{d\left(\frac{r_1}{R}\right)}}{\exp(Y_5(1-\frac{T_G}{T_1}))(\frac{T_1}{T_G})^2} \tag{5.18}$$
When $T_1/T_G = 1$ Eq. (5.18) reduces to the isothermal result. If diffusional resistances are low, $F_1 = 0$, and geometrical instability will exist if,

$$\frac{dF_2}{d\left(\frac{r_i}{R}\right)} \left[ 1 + Y_3 \frac{1 - \frac{T_1}{T_G}}{(\frac{T_1}{T_G})^2} \right]^{-1} < 0$$

Cannon and Denbigh (1957b) obtained a similar result and concluded for the exothermic case that $dF_2/d\left(\frac{r_i}{R}\right) < 0$ for instability as the denominator is normally positive. In fact it can be shown that the denominator is positive when $T_1$ is less than the minimum ignition temperature or greater than the maximum extinction temperature. For a system obeying the steady-state equations this is always true, but on introducing a transient term in the heat balance, as in Chapter 6, $T_1$ can assume values which lie between these limits, thus invalidating the reduced criterion. For endothermic reactions, of course, the denominator (i.e. the inverted bracketed term in the above equation) is always positive. If the denominator is positive then $dF_2/d\left(\frac{r_i}{R}\right)$ for instability, so that the criterion is $(1 - Y_3)\frac{r_i}{R} > 0.5$ for exothermic reactions and $< 0.5$ for endothermic reactions. In the absence of diffusional resistances, geometrical instability is thus always present in endothermic reactions when $r_i/R < 0.5$ or for all values of $r_i/R$ when $Y_3 > 0.5$, it being absent in exothermic reactions under the same conditions. The similarity to the criterion for instability in isothermal reactions can be noticed.
5.6.3 Illustrations of geometrical instability. Examples of geometrical instability can be seen in the solutions obtained in Chapter 4. For example in Fig.4.9 it can be seen that geometrical instability occurs at values of conversion greater than 0.875, corresponding to $\frac{r_i}{R} = 0.5$ (i.e. $X = 1 - 0.5^2$). This is in agreement with the relation obtained above.

Again, in Fig.4.11 geometrical instability can be seen to exist in some cases for all values of $X$, such as for $Y_2 = 1$ and $Y_1 = 1$. For $Y_2 = 1$ and $Y_1 = 0.25$ we have from the criterion above that $\frac{r_i}{R} = 0.667$ at the onset of instability. It can also be seen from the criterion that for $Y_1 = 1$, instability will occur for any value of $\frac{r_i}{R}$.

Ishida and Wen have stated that use of the sharp inter- surface theory as defined in Chapters 4 and 5 should not be made in conditions where geometrical instability exists, on the grounds that this instability may cause a sudden increase in local reaction rate at some point on the interface. However, this presupposes some inconsistency in the solid such as a crystal defect to initiate this sudden increase. It is probable that where geometrical instability exists but is not serious the theory can be applied, but not when the instability persists, say throughout the reaction, or when the value of $\frac{d\eta}{dR}$ is high.

5.7 Thermal instability. Thermal instability occurs only in exothermic reactions and is really a mathematical term used to describe the existence of multiple solutions to the two simultaneous equations arising from the conservation balances. The
term loses much of its significance in practice where situations may not be well represented by the usual steady-state equations.

In a steady-state analysis the interfacial temperature, $T_1$, is determined by the simultaneous solution of Eqs. (5.12) and (5.13). More than one solution, however, sometimes exists in the steady-state case for exothermic reactions. Such solutions are often depicted on a plot of heat generation and heat loss against $T_1$ as in Fig. 5.1. As can be seen, slightly modified dimensionless co-ordinates have been used. The heat generation and heat loss curves are represented by the equivalent effectiveness factors, $\eta_{e_g}$ and $\eta_{e_1}$ respectively. $\eta_{e_g}$ represents the effectiveness factor which one obtains by evaluating the mass balance equation, Eq. (5.12), at a given value of $T_1/T_G$, whereas $\eta_{e_1}$ is the effectiveness factor obtained by evaluating the heat balance equation, Eq. (5.13), also at $T_1/T_G$. Hence we have,

$$\eta_{e_g} = \left[ \frac{F_1}{1 + \exp(-Y_5(1 - T_G/T_1))} \right]^{-1} \quad (5.19)$$

$$\eta_{e_1} = \frac{T_1}{T_G - 1}/F_2 \quad (5.20)$$

As can be seen $\eta_{e_1}$ is a linear function of temperature, indicating the absence of radiational effects. The existence of multiple solutions to Eqs. (5.19) and (5.20) when $\eta_{e_g}$ is equated to $\eta_{e_1}$ depends on the values of $F_1$, $F_2$ and $Y_5$, which represent the fundamental characteristics of the system.

In Fig. 5.1 the loss lines A and C intersect the generation curve to give unique stable solutions respectively in the
"kinetic" and "diffusion" regimes. The "kinetic" regime corresponds to situations where $\eta_g$ is near to unity, i.e. with $\frac{T_i}{T_G} \approx 1$ also, and the "diffusion" regime to cases where $\frac{T_i}{T_G}$ is remote from unity and the heat loss line intersects that part of the generation curve where the dependence of $\eta_g$ on temperature is greatly reduced due to the predominance of mass transfer control.

On the other hand the loss line B intersects the generation curve at three points, the centre crossing point being unstable, while the other two intersections constitute stable solutions in the kinetic and diffusion regimes. If the unstable solution were achieved, any increase in the temperature above this critical value causes the upper solution to be achieved instantaneously, due to the respective gradients of the loss and generation curves. Similarly a slight decrease in temperature would cause instantaneous achievement of the lower stable solution. It must be appreciated, of course, that such instantaneous transitions are a result of the steady-state assumption in the analysis. Thus the existence of unstable solutions is possible within the shaded area bounded by the tangents to the generation curve, as depicted in Fig.5.1. These tangential points I and E represent the points of minimum ignition and maximum extinction (minimum combustion) temperature respectively, as mentioned earlier in the discussion of geometrical instability. Because the tangents at I and E are linear loss curves, the unstable region is not determined by heat transfer, but depends
only on the mass transfer and kinetic characteristics. This is not necessarily so, however, when radiational heat transfer is included. The points I and E are defined by

\[ \eta_{eg} = \eta_{e1} \quad \text{and} \quad \frac{d \eta_{eg}}{d T_G} = \frac{d \eta_{e1}}{d T_G} \]

so that

\[ \left[ F_1 + \exp(-Y_5(1- \frac{T_G}{T_1})) \right]^{-1} = \frac{T_1 - 1}{T_G} \frac{T_1}{F_2} \] (5.21)

\[ \frac{Y_5 \exp(-Y_5(1- \frac{T_G}{T_1}))}{(\frac{T_1}{T_G})^2 \left[ F_1 + \exp(-Y_5(1- \frac{T_G}{T_1})) \right]^2} = \frac{1}{F_2} \] (5.22)

Dividing Eq. (5.21) and (5.22) and rearranging gives

\[ \frac{T_1}{T_G} - 1 = \frac{1}{Y_5} \left[ F_1 \exp(Y_5(1- \frac{T_G}{T_1})) + 1 \right] \] (5.23)

which defines the minimum ignition and maximum extinction temperatures. In the absence of diffusional resistances, \( F_1 = 0 \) and Eq. (5.23) can be solved to give

\[ \left( \frac{T_1}{T_G} \right)_I = \frac{1}{2} \left( Y_5 - \sqrt{\left( Y_5^2 - 4Y_5 \right)} \right) \] (5.24a)

and

\[ \left( \frac{T_1}{T_G} \right)_E = \frac{1}{2} \left( Y_5 + \sqrt{\left( Y_5^2 - 4Y_5 \right)} \right) \] (5.24b)

Examination of these solutions shows that no thermal instability
can exist for \( Y_5 = 4 \), the point at which the limiting ignition
and extinction temperatures are equal.

Eq. (5.23) is most easily solved by evaluating \( P_1 \) in
terms of \( T'_1/T_G \) and \( Y_5 \). This has been carried out for values of
\( Y_5 \) from 4 to 40 and the results presented in Fig. 5.2. For given
values of \( P_1 \) and \( Y_5 \) there are two corresponding temperature
ratios, one of which corresponds to the minimum ignition temp-
erature and the other to maximum extinction. A steady-state
solution is unstable if the current interfacial temperature lies
within these limits. Eq. (5.23) was solved by Computer program 7,
Section G.7.

Inclusion of radiation in the analysis would reduce the
occurrence of instability, as the minimum ignition and maximum
extinction temperatures are closer. Fig. 5.3 shows how the
tangential points are altered and the area of the unstable region
reduced due to the resulting curvature of the loss lines.

Whether a loss line of type B in Fig. 5.1 lies within the
unstable region depends on the heat transfer characteristics of
the system, as represented by \( P_2 \). Instability will occur if the
gradient of the loss line is greater than that of the tangent at
I and less than that of the tangent at E. Referring to Fig. 5.4, the
criteria for this situation are therefore,

\[
\frac{(\eta_{eG})_I}{(T'_1/T_G)_I - 1} < \frac{1}{P_2} < \frac{(\eta_{eG})_E}{(T'_1/T_G)_E - 1}
\]

Limiting values of \( P_2 \) may then be defined from these inequalities
as/
as

\[(F_2)_j = \left[ \frac{T_1}{T_G} \right]_j - 1 \left[ F_1 + \exp(-Y_5(1-(\frac{T_G}{T_1})_j)) \right] \quad (5.25)\]

where \(j = I \) or \(E\) so that the range of values of \(F_2\) which give loss lines within the unstable region is

\[(F_2)_I > F_2 > (F_2)_E \quad (5.26)\]

In the absence of diffusional resistances, Eq. (5.25) becomes, on substitution of \(Y_5\) from Eq. (5.23)

\[(F_2)_j = \left[ \frac{T_1}{T_G} \right]_j - 1 \exp(-\frac{T_1}{T_G}) \quad (5.25)\]

The limiting values of \(F_2\) are shown in Fig. 5.5 for a range of values of \(F_1\) and \(Y_5\). In a steady-state analysis this diagram is an important guide to the prediction of instability from the basic heat, mass and kinetic data. The bounds on \(F_2\) were evaluated whilst computing the results for Fig. 5.2, and the resulting map of arbitrary values converted to the plot of lines of constant \(F_2\) in Fig. 5.5 by first difference interpolation.

The use of Figs. 5.2 and 5.5 in the analysis of a given case will be illustrated in greater detail in Chapter 6 where the significance of thermal instability is illustrated by examples.

Figs. 5.2 and 5.5 can also apply to the cylinder and the slab, with the modifications that, for the cylinder,

\[F_1 = \frac{Y_2}{2R} \left( Y_1 + \frac{\ln R}{R_1} \right) \quad \text{and} \quad F_2 = -\frac{Y_2}{4R} \left( Y_3 + \frac{\ln R}{R_1} \right)\]

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and for the slab,

\[ F_1 = Y_2(Y_1 + 1 - \frac{r_1}{R}) \quad \text{and} \quad F_2 = -Y_2Y_4(Y_3 + 1 - \frac{r_4}{R^2}) \]

as Eqs. (5.19) and (5.20) for all cases are a function only of \( F_1, F_2, Y_5 \) and \( T_1/T_0 \).

5.8 The instability envelope. The curves in both Figs. 5.2 and 5.5 can be seen to be bounded by an enveloping curve which represents the point at which \( (T_1/T_G)_I \) and \( (T_1/T_G)_E \) become equal for specific values of \( F_1 \) and \( Y_5 \).

In this situation, then, the generation curve is such that no loss line can intersect the curve in more than one discrete point, so that instability becomes impossible. Hence at a given value of \( Y_5 \) there is a limiting value of \( F_1 \) beyond which instability cannot occur, despite the heat transfer characteristics of the system. Outside the envelope, tangents to the generation curve no longer exist. This maximum value of \( F_1 \) at constant \( Y_5 \) is obtained by differentiation of Eq. (5.23) with respect to \( T_1/T_G \) so that

\[ 1 - 2(1 - \frac{T_G}{T_1}) = F_1 \exp(Y_5(1 - \frac{T_G}{T_1})) \]

which on resubstitution from Eq. (5.23) gives the solutions,

\[ 1 - \frac{T_G}{T_1} = \frac{2}{Y_5} \quad \text{or} \quad 1 \]

Since the latter solution is unattainable the limiting value of \( F_1 \) is \( (Y_5-4)/(Y_5-2) \) which defines the envelope shown in Fig. 5.5.
For high values of $Y_5$, stable solutions occur when $F_1 > \exp(-2)$. Similarly, instability occurs for values of $F_2 > \exp(-2)$. The limiting equality arises when $Y_5 = 4$ and $F_1 = 0$.

5.9 Conclusions. The fundamental theory behind the problems of geometrical and thermal instability has been presented. Figs. 5.2 and 5.5 give a guide to the likelihood of thermal instability in gas–solid reactions, as will be illustrated by examples in Chapter 6. Again it must be realised that this theory is dependent on the steady-state nature of the heat balance, which together with the steady-state mass balance allows the conditions at any conversion to be evaluated independently of the previous history of the reaction. This assumption is invalid in cases where the solid heat capacity is significant, thus rendering the theory invalid for most situations other than those where temperatures do not deviate markedly from the furnace temperature and where the initial temperature of the solid is equal to that of the gas. Hence it can be concluded that as the cases in which thermal instability occur involve reaction temperatures far removed from gas temperatures the thermal instability theory can only be approximate, giving only an indication of the time history of the reaction, and indeed will be quite inaccurate in some circumstances, as will also be seen in Chapter 6.
6.1 Introduction. The significant shortcoming of the equations presented in Chapter 5, i.e. Eqs. (5.10) and (5.11), is their pseudo-steady-state nature. Although this is of little importance in the mass balance equation, Eq. (5.10), in that the mass accumulation in the solid pores is always very small, it will be shown that the same assumption cannot satisfactorily be made in the energy balance, as the accumulation term can be of the same order as the heat of reaction. Inclusion of such a term in the energy balance makes the solution of the equations only slightly more difficult, as they are numerical anyway, and the solutions throw quite a new light on the problems of thermal instability. In certain cases it will be seen that inclusion of the transient term has little effect on the result.

6.2 The enthalpy of the solid particle. The enthalpy of the reacting sphere, $H$, can be defined with reference to $T_G$ as

$$H = \int_0^R 4\pi r^2 \rho_m c_p (T - T_G) dr$$

$$= \frac{4}{3} \pi r_1^3 \rho_m c_p (T_1 - T_G) + \int_{r_1}^R 4\pi r^2 \rho_m c_p (T - T_G) dr \quad (6.1)$$

where the molar densities, $\rho_m$, are taken for the two solids B and S to be the same since the change in the number of moles of B and
S on reaction is usually the same. An average value, \( C_p \), of the molar heat capacities of the two solids is taken, although it would be simple to specify two different specific heats for the reaction core, whose enthalpy is represented by the first term on the right hand side of Eq. (6.1) and for the product shell, represented by the second term in Eq. (6.1). Note that it has been assumed that the temperature of the reactant core is everywhere equal to the interfacial temperature, \( T_i \), and that the temperature at any point within the product solid shell is given by the steady-state heat conduction equation for a sphere,

\[
\frac{d}{dr}(r^2 \frac{dT}{dr}) = 0
\]

(6.2)

This equation can be integrated as in Chapter 5 and the resulting value for \( T_i \) substituted in Eq. (6.1) to give,

\[
H = \frac{4}{3} \pi r_3^3 \rho_m C_p \left( (T_i-T_0) + (T_S-T_i) \right) \left( \frac{2-r_i^2}{R} + \frac{R r_i^3}{2(1-r_i/R)} \right)
\]

(6.3)

In contrast to Chapter 5, Eqs. (5.1) and (5.2), the heat transferred to the reaction site must now be written as

\[
Q + \frac{dH}{dt} = 4\pi R^2 h_B(T_G-T_S)
\]

(6.4)

\[
= 4\pi R^2 k_e \left( \frac{dT}{dr} \right)_{r=R}
\]

(6.5)

Evaluating \( \left( \frac{dT}{dr} \right)_{r=R} \) from Eq. (6.2) and substituting in Eq. (6.5), the resulting expression for \( T_S \) on equating Eqs. (6.4) and (6.5) can be substituted in Eq. (6.3) to give,
$$H = \frac{4}{3} \pi R^3 \rho_m c_p (T_1 - T_G) \left[ 1 - \frac{1 - r_i / R}{r_i / R} \left( \frac{2 - r_i / R - (r_i / R)^2}{2 \left( \frac{k_e}{R h_B} + \frac{1 - r_i / R}{r_i / R} \right)} \right) \right]$$  \hspace{1cm} (6.6)

$$= \frac{4}{3} \pi R^3 \rho_m c_p (T_1 - T_G) F_C$$  \hspace{1cm} (6.7)

For the purposes of evaluating a simple accumulation term it was originally assumed that the whole sphere was at the interfacial temperature, $T_1$, rather than only the reactant core, an assumption valid only if the resistance to heat conduction in the product shell is low. Hence the bracketted term in Eq. (6.6), $F_C$, could therefore be called the "conduction" factor.

The new energy balance is now,

$$Q = h \pi R k_e (T_G - T_i) \left( \frac{k_e}{R h_B} + \frac{1 - r_i / R}{r_i / R} \right) - \frac{\partial H}{\partial t}$$  \hspace{1cm} (6.8)

6.3 The final general dimensionless equation form.

The generalised form of Eq. (5.10Gen) remains the same as,

$$\eta_d (1 - \frac{a}{g}) Y_2 (Y_1 + B) (Y_9 - Y_6 Y_7)$$

$$= -\ln \left[ 1 - \frac{1 - a / g}{Y_7 (1 - (1 - a / g) Y_6)} \left[ Y_9 \exp (Y_10 (1 - \frac{T_G}{T_1}) - Y_6 Y_7 - \eta_d \frac{Y_9 - Y_6 Y_7}{(r_i / R)^2} \exp (Y_6 (1 - \frac{T_G}{T_1}) \right) \right]$$  \hspace{1cm} (6.9)

and the energy balance, Eq. (6.8), can be written as,

6.3 : 86
\[ \frac{T_1}{T_G} = 1 - Y_2 Y_4 (Y_3 + B) \left[ \eta_d + \frac{Y_8}{c+1} \frac{d}{dS} \left( F_c \left( \frac{T_1}{T_G} - 1 \right) \right) \right] \] (6.10)

and the time integration equation is

\[ \theta_{r_1} = \int_{r_1}^{1} \frac{\left( r_1/R \right)^C}{\eta_d} \frac{d}{dS} \left( \frac{r_1}{R} \right) \] (6.11)

where A, B and C are defined for the sphere, cylinder and slab as previously, in Section 4.5, and where,

\[ Y_8 = \frac{C_p T_G}{\Delta H} \]

so that \( Y_8 \) is the ratio of the absolute molar enthalpy of the solid to the heat of reaction, and where,

\[ F_c = 1 - \frac{2B + (r_1/R)^2 - 1}{2(Y_3 + B)} \] (6.12)

Eqs. (6.9), (6.10) and (6.11) are therefore the complete general description of sharp interface reactions.

6.4 Solution of the general equations. Simultaneous solution of Eqs. (6.9), (6.10) and (6.11) has been achieved by Computer program 8 for the sphere, and by programs 9 and 10 for the cylinder and slab respectively. Further details of the method of solution are given in Section 6.8.

The method of solution involves evaluating a value of \( T_1/T_G \) at a given value of \( r_1/R \), using the value of \( \eta_d \) obtained at
the previous interfacial position. Hence is obtained a value of \( \eta_d \) at the new interfacial position which in turn gives a better approximation to \( T_i/T_G \), and so on until \( \eta_d \) and \( T_i/T_G \) cease to change. For equimolar counterdiffusion \( \eta_d \) is of course obtained from the correctly simplified form of Eq. (6.9), using \( \alpha = \gamma \). However, if \( \alpha = \gamma \) Eq. (6.9) must be written in the form

\[
fn = a_1 \eta_d + \ln(a_2 + a_3 \eta_d) \quad (6.13)
\]

and guess a value of \( \eta_d \) to give \( fn = 0 \), \( a_1, a_2 \) and \( a_3 \) being taken as constants. The choice of the \( \eta_d \) guess is made simpler by Newton Raphson iteration. Differentiating Eq. (6.13) gives,

\[
fn' = a_1 + \frac{a_3}{a_2 + a_3 \eta_d}
\]

A better choice of \( \eta_d \) may now be made from the relation,

\[
\eta_d\text{new} = \eta_d\text{previous} - \frac{fn}{fn'}
\]

and this procedure repeated until \( \eta_d \) no longer changes. In Eq. (6.13) \( a_1, a_2 \) and \( a_3 \) are assumed to be independent of \( \eta_d \), which is not strictly true, as these constants incorporate \( (T_i/T_G) \), which is dependent on \( \eta_d \) as given by Eq. (6.10). However it was found that the iterative procedure adopted still caused rapid and accurate convergence. Hence \( \eta_d \) is evaluated by iteration until it no longer changes, at a constant value of \( T_i/T_G \), then \( T_i/T_G \) is corrected and a new value of \( \eta_d \) obtained until \( \eta_d \) and \( T_i/T_G \) no longer change significantly.
6.4 Endothermic reactions. It will be shown later that, generally speaking, the transient and steady-state solutions for endothermic reactions are similar. Hence only transient solutions will be indicated.

As thermal instability cannot occur in endothermic reactions, only unique solutions are obtained which renders analysis of such systems simpler than exothermic cases. However, as with isothermal reactions, it is not possible to illustrate all the various solutions as these are legion. Thus only those solutions will be presented which refer to systems with negligible diffusional resistances, by choosing \( Y_1 = 0 \) and \( Y_2 = 0.001 \). As in the exothermic examples given later, an arbitrary though representative value of \( Y_5 \) is taken, namely 20. Other values held constant for the endothermic examples are \( Y_6 = 0 \), \( Y_7 = 1 \), \( Y_9 = 1 \), and \( Y_{10} = 0 \). Thus we are describing a reaction which is irreversible, with virtually no diffusional resistance, with no product gas \( G \) in the bulk gas, and with \( P_K = P_T \). Also \( Y_8 = (C_P T_0 / \Delta H) \) has been chosen as 1.0, again an arbitrary though representative value. Note that for the pseudo-steady-state result \( Y_8 \) would be taken as zero.

Three endothermic situations have been considered with the above limitations. 1)– Figs. 6.1 and 6.2 give the results for negligible heat transfer in the boundary layer, i.e. \( Y_3 = 0 \). 2)– Figs. 6.3 and 6.4 give the results for negligible heat transfer resistance in the solid product shell, with \( Y_4 = 0.1 \), and the main resistance to heat transfer being in the boundary layer.
3) Figs. 6.5 and 6.6 give an intermediate case in which shell heat conduction resistance is significant, with \( Y_4 = 10 \), while \( Y_3 \) is varied.

6.4.1 This case is partly artificial in that it is fairly unlikely in practice. Where resistance to heat transfer exists in both boundary layer and product shell, the latter is likely to provide less resistance than the boundary layer because the conduction is by conduction through a solid rather than a gas. However, if the product is highly porous, and if the particle is receiving radiational heat transfer, and also if the solid thickness is great, case 1) is approached, especially at high values of conversion. It can be seen in Figs. 6.1 and 6.2 that as reaction proceeds \( T_1/T_0 \) and \( \eta_e \) gradually fall. As the reaction approaches completion the temperature begins to fall off again rapidly, with a corresponding drop in \( \eta_e \). It can be seen, however, that this drop only occurs at higher values of conversion when the particle reaction rate would be very small so that in practice this aspect of the results would not be important. The effect arises from the rapid absorption by the reaction of local sensible heat, while the heat being transferred to the solid from the exterior is being used to bring the whole sphere back to the same temperature as the surroundings. In fact, then, the sensible heat of the whole sphere is increasing while the interfacial and core temperature is falling. The result shows another interesting feature in the almost complete absence of geometrical instability, which is a characteristic of endothermic reactions of this type.
6.4.2 When a significant degree of resistance to heat transfer through the solid product is introduced, the effectiveness factor is at its lowest at the beginning of the reaction once the initial drop in temperature occurs. Note that this drop in temperature occurs over a significant change in conversion, whereas, as will be seen later, in the pseudo-steady-state result the initial temperature drop occurs instantaneously. The drop in temperature at the end of the reaction noticed in case 1) is now absent due to the different distribution of temperatures throughout the solid. However, geometrical instability can be seen in Fig. 6.4 to exist throughout the reaction. It can also be seen in Fig. 6.4 that when heat transfer through the boundary layer is more of a limitation, i.e. for $\gamma_3 = 5000$, $\eta_d$, representing the actual particle rate of reaction, remains virtually constant for a considerable time. In these circumstances the boundary layer supports a constant heat transfer rate, resulting in a constant reaction rate.

6.4.3 This intermediate case has been created by setting $\gamma_4 = 10$. It can be seen in Fig. 6.5 and Fig. 6.6 that results similar to case 2) are obtained although for lower values of $\gamma_3$. Again geometrical instability is prevalent.

Unfortunately, then, the cases in which geometrical instability does not occur, and therefore those which the theory is liable to represent more accurately, are those which are least liable to be met with in practice.

6.5 Exothermic reactions:
6.5 Exothermic reactions: Transient solutions and comparison with pseudo-steady-state. Because of the existence of thermal instability in many exothermic reactions it is difficult to present general solutions as were given for isothermal reactions and in a more restricted manner for endothermic reactions. This point will be brought out in example 1 of the several examples which will now be given. These examples illustrate the difference between transient solutions, i.e. solutions which take into account the heat capacity of the solid, and pseudo-steady-state solutions, and show the shortcomings of the latter. The effect of introducing the solid at a temperature different to that of the gas is shown, and also the effect of a change in the specific heat of the solid.

In all examples \( Y_5 \) is taken as 20, \( a \) and \( g \) are 1, \( Y_6 = 0 \), \( Y_7 = 1 \), \( Y_9 = 1 \), and \( Y_{10} = 0 \), as before.

6.5.1 The difficulty of presenting general solutions.

An attempt was made to obtain fairly general results for the exothermic case similar to those for endothermic reactions. The \( \eta \) versus \( X \) history of one of these sets of results was obtained and is shown in Fig. 6.7. The case represents one of low diffusional resistances, with \( Y_1 = 0 \) and \( Y_2 = 0.001 \), and with \( Y_4 \) set at -0.1 and \( Y_3 \) varied. The solutions given in Fig. 6.7 are transient, with \( Y_0 = -1.0 \), and in all cases the initial temperature of the solid, \( \frac{T_4}{T_G} \), is equal to 1.000.

At low values of \( Y_3 \) when boundary layer resistance to heat transfer is significantly reduced the reaction proceeds in a
fairly straightforward manner with a distinct absence of geometrical instability. Note that values of \( \eta_e \) are all \( > 1 \), due to the exothermic nature of the reaction, although values of \( \eta_e < 1 \) can of course be obtained in such reactions but only if \( Y_1 \) and/or \( Y_2 \) are significantly large so that diffusion effects inhibit the reaction. Whereas in endothermic reactions any limitations in heat transfer resulted in a reduction in \( \eta_e \), such limitations produce an increase in \( \eta_e \) in exothermic reactions due to the higher interfacial temperatures.

As \( Y_3 \) increases there is a tendency for \( \eta_e \) to accelerate as reaction proceeds, because the heat generation is in excess of the loss of heat by the particle to the surroundings. The history of the \( Y_3 = 250 \) curve shows that the tendency for \( \eta_e \) to go on increasing has been overcome at an intermediate value of conversion. This is because the heat generated at the reaction interface, although greater than the rate of heat loss from the particle, is not sufficient to continue raising the heat content of the sphere itself, so that the temperature and \( \eta_e \) begin to fall. However, at very high values of \( Y_3 \), because of the severe heat transfer limitation, the reaction once started is seen to accelerate rapidly, and in fact \( \eta_e \) continues to increase to higher and higher values as the reaction proceeds. These high values of \( \eta_e \) correspond to extremely high values of \( T_i/T_G \), values of approximately 5 being typical. At these extreme temperatures, of course, radiation would assume such an important role in heat transfer that the present theory, which ignores radiational heat
The pseudo-steady-state solutions to these cases will now be considered, and in particular, as an illustration of the general method of obtaining such solutions, the case where $Y_3 = 100$. The $\eta_e$ versus $X$ history of the reaction is obtained by simultaneous solution of Eqs. (5.12) and (5.13). As diffusional effects are relatively unimportant $F_1$ can be taken as zero, so that from these equations we have,

$$\eta_{eG} = \exp(Y_5(1-\frac{T_G}{T_1}))$$  \hspace{1cm} (6.14) $$

and

$$\eta_{e1} = \frac{T_1}{T_G} - 1)/F_2$$  \hspace{1cm} (6.15) $$

Due to the absence of diffusion effects the generation curve is independent of $r_1/R$, and hence $X$, and is shown in Fig. 6.8 over a small portion of the kinetic regime, corresponding to the lower end of the generation curve in Fig. 5.1. Also shown in Fig. 6.8 are the heat loss lines for various values of $r_1/R$, and for $Y_3 = 100$. The intersections of the loss and generation curves give the values of $\eta_e$ and $T_1/T_G$ for different values of $r_1/R$ or conversion for the steady-state case. The $\eta_e$ versus $X$ histories for $Y_3 = 100$ are shown together in Fig. 6.9, the transient result having been obtained by computer solution and the steady-state from Fig. 6.8. The difference between the two is slight, the most significant point being that a steady-state solution assumes that the solid temperature will rise instantaneously at $X = 0$ without any heat being required. However if the two solutions
were compared for $Y_3 = 250$ they would be found to be quite different. This is because the initial intersection of the loss curve for $r_1/R = 1$ and the generation curve is in the diffusion regime of the reaction, because the gradient of this line is less than that of the tangent to the generation curve at the minimum ignition point. For the transient solution, however, which must start with $(T_1/T_G)_0 = 1$ and with $\eta_e = 1$ in the absence of boundary layer diffusional limitations, the heat-absorbing capacity of the solid is such that the diffusion regime solution cannot be approached. This point will be illustrated in a later example.

As can be seen, therefore, each exothermic case requires detailed attention and provides a wealth of information so that none but the most general conclusions can be made from each. One important generalisation from example 1) is that the steady-state result is a good approximation to the transient result if the former lies well within the kinetic regime, so that the reaction is almost solely controlled by kinetics.

6.5.2 Steady-state "diffusion regime" solutions and the corresponding transient solutions. This example is again confined to the parameter limitations of example 1), the main one being the absence of diffusional resistances.

A system with moderate heat transfer resistances might be described by line C in Fig 5.1 at initial times, i.e. $r_1/R = 1$. Due to the low mass transfer limitation an extremely high value of $\eta_e$ would result, this value being a unique solution in the diffusion regime with a correspondingly high value of $T_1/T_G$. Note
that Fig. 5.1 only applies to steady-state analyses. In the steady-state this implies an instantaneous rise in $T_1/T_0$ at $t=0$ on the assumption that the solid undergoes no change in enthalpy, i.e. $Y_3=0$. In this case the steady-state theory gives the minimum ignition and maximum extinction temperature ratios as 1.0555 and 18.9445, the latter obviously having little practical meaning. Evaluation of Eqs. (5.25) and (5.26) with $F_1=0$ shows that $F_2$ must lie within the limits $1.1 \times 10^{-7}$ and 0.0193 for the loss line to lie within the unstable region. As in example 1), because $F_1=0$ the generation curve is essentially the same for all values of $r_1/R$, and part of the curve, again a small part of the kinetic regime, is shown in Fig. 6.10 together with the loss lines, with the heat transfer characteristics $Y_3=2.2$ and $Y_4=-10$, at various values of $r_1/R$. The initial value of $F_2$, i.e. at $r_1/R=1.0$ is found to be 0.022 and because this is higher than the upper instability bound on $F_2$ the steady-state solution originates in the diffusion regime, as with the $Y_3=250$ example given earlier in example 1), Section 6.5.1. Furthermore $F_2$ essentially never falls below the lower instability limit ($F_2$ only falls below $1.1 \times 10^{-7}$ when the reaction is virtually complete) so that the reaction will continue in this regime except for negligibly small values of $r_1/R$. In fact, none of the steady-state solution can be represented on Fig. 6.10 due to the large values of $\eta_e$.

Transient solutions derived from Eqs. (6.9), (6.10) and (6.11) do not, however, achieve the diffusion regime solution
except at low values of $|Y_8|$, at which values, of course, the two solutions are the same. Transient solutions for various values of $Y_8$ are shown in Fig. (6.10), with $\eta_0$ plotted against $r_1/R$ as a parameter, these curves bearing no relation to the $T_1/T_0$ axis. Again in all cases $(T_1/T_0) = 1.00$ so that because $F_1 = 0$, $\eta_0 = 1$ at $r_1/R = 1$. It can be seen that as $|Y_8|$ is reduced the transient solutions accelerate towards the steady-state solutions described above. For higher values of $|Y_8|$ the solutions remain in the kinetic regime, with the transition towards the diffusion regime occurring for a value of $Y_8$ between -0.4 and -0.3. The rate of change of $\eta_0$ with $r_1/R$ can be seen to be negative for small values of $X$, showing the existence of geometrical instability up to and not beyond the peak value of $\eta_0$ in the solutions obtained with the transient analysis.

It is obvious that the transient solution is in no way equivalent to the steady-state solution for comparatively large values of $|Y_8|$, in cases where the steady-state solution would lie in the diffusion regime. In fact, in circumstances where the steady-state solution does lie in the diffusion regime, the transient solution may remain permanently a kinetically controlled reaction, thus giving reaction times which are many orders of magnitude different to the steady-state. It is also obvious that interfacial temperatures which lie between the minimum ignition and maximum extinction temperatures, as obtained from a steady-state analysis, need no longer be considered as unstable, due to the stabilising effect of the solid heat capacity. A steady-
stat. analysis is therefore quite unrealistic unless \( Y_8 \neq 0 \), or in
cases where the thermal conductivity of the solid is so low that
thermal instability can occur locally.

6.5.3 The effect of variations in initial solid temperature.

Two steady-state solutions exist only when the value of \( F_2 \) at
\( r_1/R = 1 \) lies within the instability limits given by Eqs. (5.25)
and (5.26), when the loss line would be similar to line B in Fig.
5.1. The attainment of one of these solutions depends on the
initial temperature of the solid or on anomalous perturbations
which are outside the scope of any theory. If this lies above
the unstable temperature a diffusional regime result is obtained,
and if below the result lies in the kinetic regime. When \( F_2 \)
falls below its lower instability limit as the reaction proceeds,
the upper solution disappears and the loss line corresponds to
line A in Fig. 5.1, giving a solution in the kinetic regime. If
\( F_2 \) is initially greater than the upper instability limit only one
solution exists as was found in example 2.

A system will now be considered in which two steady-state
solutions exist, becoming equivalent at some subsequent value of
\( r_1/R \). When solutions are said to be the same it is meant that \( \gamma_e \)
has the same value at a given value of \( r_1/R \), and hence \( X \),
although the time taken to achieve this interfacial radius will
be different, due to the previous history of the reaction. Such
a system is achieved by choosing \( Y_1 = 0 \) (no boundary layer
diffusion resistance), \( Y_2 = 0.1 \), \( Y_3 = 1 \) and \( Y_4 = -0.18 \) with \( Y_5 = 20 \).
The two possible steady-state solutions for this case are shown
as the broken lines in Fig. 6.11 where $\eta_e$ is plotted as a function of conversion, $X$. Part of the diffusion regime solution lies outside the range of the graph. Note that these steady-state solutions were achieved by Computer program 8, setting $Y_8 = 0$, and not by graphical solution as in example 1), Section 6.5.1. Achievement of either of these solutions depends on the initial temperature of the solid, and it can be shown by evaluation of the unstable intersection of the relevant loss and generation curves that the upper solution will be achieved only if $(T_1/T_G)_0 > 1.082$. It can be seen from Fig. 6.11 that the two steady-state solutions coincide instantaneously at a conversion of about 0.812. This occurs when $F_2$ becomes equal to its lower bound, i.e. 0.0103, given in Fig. 5.5, or by Eqs. (5.25) and (5.26) at the current value of $F_1$, i.e. 0.0245. This instantaneous drop in $\eta_e$ from the diffusion regime solution represents a sudden change in the control of the overall reaction rate. This transitional instability was recognised by Ishida and Wen, but while rapid changes in $\eta_e$ are practically possible as seen in a transient analysis, change in rate control always occurs over a finite time period.

Transient solutions for this system for various values of $(T_1/T_G)_0$ are shown in Fig. 6.11 for $Y_8 = -1.0$ and in Fig. 6.12 for $Y_8 = -0.5$. As stated, steady-state considerations show a critical initial temperature ratio of 1.082, separating the two unique solutions. In a transient analysis one can only expect $(d\eta_e/dX)_0$ to be positive if $(T_1/T_G)_0 > 1.082$ and negative if $(T_1/T_G)_0$
This effect is illustrated in Figs. 6.11 and 6.12, being more obvious for the smaller value of $|Y_G|$. It can also be seen that larger values of $(T_i/T_G)_0$ do not necessarily yield results in the diffusion regime. Subsequent falling off of $\eta_\infty$ towards the steady-state kinetic solution is due to the constantly changing intersections of the loss lines and generation curves as the interface moves through the solid, but mainly due to the quenching action of the solid. It can be seen that all the transient solutions tend to approach one or other of the steady-state solutions, except at high values of $X$, when $\eta_\infty$ rises rapidly in one set of transient histories. Thus in Fig. 6.11 the unsteady-state variation of $\eta_\infty$ with $X$ is shown, the upper state being attained for initial temperature ratios of 1.107 and greater, and the lower for 1.106 and less. The use of intermediate values of $(T_i/T_G)_0$ yields a similar separation, to the degree of accuracy required in $(T_i/T_G)_0$. Thus to the next order of magnitude, the separation occurs between values of $(T_i/T_G)_0$ of 1.10645 and 1.10650. The separation of the two sets of transient solutions with increasing conversion is more clearly defined as $|Y_G|$ decreases, representing a reduced effect of the heat accumulation term. This separation occurs at lower values of $(T_i/T_G)_0$ as $|Y_G|$ decreases, approaching the limiting steady-state value of 1.082 when $Y_G=0$. As the interface approaches the centre of the solid the interfacial temperature can rise even although the enthalpy of the sphere is decreasing, and the product $(T_i/T_G - 1)P_c$ may reduce as $T_i/T_G$ increases. The
additional heat which must be removed from the sphere to account for the reduction in enthalpy then necessitates a higher interfacial temperature. This explains the noted rapid rise in \( \eta_e \) at high values of \( X \).

It can be seen from Figs. 6.11 and 6.12 that there exists an infinite number of solutions of the transient equations, depending on the initial temperature of the solid, given by \( (T_1/T_G)_0 \). Under some experimental conditions, however, as when the solid is heated by a gas, the initial temperature is usually equal to the temperature of the gas, so that \( (T_1/T_G)_0 = 1.00 \). The solution then remains in the kinetic regime and the steady-state analysis is a fair approximation, improving as \( Y_0 \to 0 \). For larger values of \( (T_1/T_G)_0 \) as obtained by an external ignition source a close agreement between the transient and steady-state solutions is only found if \( (T_1/T_G)_0 \) is very large, so large that in practice it would not normally be attained.

No geometrical instability exists in the steady-state solutions in this example as \( d\eta_e/dX \) is always negative. Geometrical instability, however, can be seen in the transient solutions. In some cases this occurs to quite an appreciable extent; for example, when \( (T_1/T_G)_0 = 1.11 \) in Fig. 6.11, \( d\eta_e/dX \) is positive throughout the whole of the reaction history for this case.

6.6 Close agreement between the two methods of solution in endothermic reactions. The steady-state analysis can also be shown to be a reasonable approximation when considering endothermic reactions.
endothermic reactions. For \( Y_1 = 0, Y_2 = 0.01, Y_3 = 1 \) and \( Y_4 = 10 \) (note that \( Y_4 \) and \( Y_8 \) are always positive for endothermic reactions but negative for exothermic reactions, because of the heat of reaction sign convention), the steady-state solution and the transient solution for \( Y_8 = 1.0 \) are shown in Fig. 6.13, in terms of \( \eta_d \), the decay factor, plotted as a function of \( \theta_{ri} \) for, in both cases, \( (T_i/T_0) = 1.00 \). The close agreement is easily seen.

It can be shown that the interfacial temperature and the enthalpy of the sphere rise steadily during intermediate stages of the reaction. The higher reaction rate at initial times in the transient solution is then compensated by the lower later rate to give good agreement with the steady-state solution. Such a solution could well be used to calculate the expected exit concentration of carbon dioxide from a furnace in which the endothermic decomposition of a carbonate was taking place. A steady-state analysis would be justified in this case, and in all cases where only moderate heats of reaction are involved. It can also be seen, on examination of Fig. 6.13, that no geometrical instability occurs in either solution.

6.7 Conclusions. A theory has been developed for a sharp interface reaction which shows that the currently accepted steady-state analysis of thermal instability in gas-solid reactions has limited applicability in a practical situation, unless a transient energy balance is included. In cases where only moderate temperature changes occur, as for example in endothermic reactions the transient and steady-state approaches give comparable results.
This is true of any results which lie within the kinetic regime. For histories in the diffusion regime, however, which necessarily involve large changes in solid enthalpy, the normal steady-state analysis of thermal instability, such as that of Shen and Smith, Aris or Ishida and Wen, is unsatisfactory.
CHAPTER 7

THE EXPERIMENTAL SYSTEM: SILVER CARBONATE - SILVER OXIDE.

7.1 Introduction. The first chapters of this report have been concerned with general aspects of gas-solid reactions. A survey of many such reactions was presented, followed by general theories of reaction for both isothermal and non-isothermal reactions, in both porous and non-porous solid reactants. Running currently with this research, a programme of experimental work was carried out, in which a typical gas-solid reaction was studied, particularly in the light of some of the findings in the theoretical section. It is not suggested that the theoretical section directed the course of experiments completely. On the contrary, most of the theories concerned with non-isothermal situations resulted from consideration of certain of the experimental results.

Initially a typical but simple example of a gas-solid reaction was required. The criteria for simplicity were mainly moderate reaction conditions, that is moderate reaction temperatures, and the absence of complicating side reactions. A similar decision was made by Spencer and Topley (1929) who arrived at the same conclusion, namely that such a reaction was the reversible decomposition of silver carbonate to silver oxide, represented by the equation,

\[ \text{Ag}_2\text{CO}_3 \rightleftharpoons \text{Ag}_2\text{O} + \text{CO}_2 \]
The decomposition reaction can be studied at temperatures below 250°C, the dissociation pressure of carbon dioxide being one atmosphere at 216°C, while the only side reaction is the further decomposition of silver oxide to silver,

\[ 2\text{Ag}_2\text{O} \rightarrow 4\text{Ag} + \text{O}_2 \]

However the rate of this reaction is very low (see Basael, and Hood and Murphy), and is noticable only slightly at the higher temperatures at which the carbonate decomposition is studied, even although the thermodynamic dissociation temperatures are lower than those of the carbonate (see Benton and Drake). The decomposition reaction, in common with all other practical reactions, is by no means ideal in a simplified theoretical sense, but forms a close approach to ideality, unlike, for example, the oxidation of zinc sulphide mentioned in Chapter 2 with its many side reactions. Hence it was decided to use the thermal decomposition of silver carbonate as the basis for an experimental programme into a typical gas–solid reaction. Previous work on this system has been studied and details presented here. To some extent the objects of the present research were of a different nature to those of the work previously reported, but many of the conclusions of the latter were relevant as will be seen.

### 7.2 Previous work on silver carbonate decomposition

Early work at about the turn of the century was found to be of little relevance, and is reported by Centnerszwer and Bruzs and by Spencer and Topley (1929). In the course of a
study of the decomposition of carbonates in general, Centnerszwer and Bruza investigated the decomposition of "amorphous" silver carbonate and found it to be analogous to the results of radiation from plates exposed for a short time to radium emanation. The first major work was that of Spencer and Topley (1929, 1931) on both crystalline and "amorphous" silver carbonate. Not only was the decomposition studied but also the recombination reaction and cycled operation between decomposition and recombination. Cutler reviewed Spencer and Topley's work as part of a general review on carbonate decomposition, in which he also put forward further theories regarding the kinetics of such reactions. Attention in more recent years has centred on the use of silver oxide as an absorbent for carbon dioxide from the air or oxygen atmospheres in space capsules. This work has been reported by Roach and Culbertson, although the aims of the work were quite different from the aims followed in this investigation.

7.3 The kinetics of the reversible decomposition reaction. In its simplest form the reaction can be represented by the equation,

\[ \text{Ag}_2\text{CO}_3 \rightleftharpoons \text{Ag}_2\text{O} + \text{CO}_2 \]

It is assumed in this case that the carbonate and oxide solids are immersed in an atmosphere which is made up of carbon dioxide alone, or with some inert species present also. The mechanism of the reaction involves an interface between sections of carbonate and oxide lattices, with an associated transfer of carbon dioxide between the two lattices. This type of reaction has been
discussed by Langmuir, who points out that if the equilibrium pressure of carbon dioxide at a given temperature, i.e. the pressure of carbon dioxide which just prevents the forward or the reverse reactions taking place, is independent of the extent of reaction, as has indeed been shown to be the case, then the areas, rather than the amounts, of both carbonate and oxide available for reaction are equal, so that an interfacial or topochemical reaction is postulated. Spencer and Topley (1929) describe their concept of this interfacial reaction. The two crystalline lattices are removed from each other by a distance no greater than that of a single molecular dimension such that vibration of ions from the carbonate towards the oxide lattice, with the associated loss of bond stability, results in the rearrangement of the molecules to suit the oxide lattice, while a carbon dioxide molecule is set free. This would occur only if certain controlling conditions were favourable, and if the oxide lattice were free from absorbed carbon dioxide molecules. The simpler equation can now be rewritten in the form,

\[ \text{Ag}_2\text{CO}_3 \leftrightarrow \text{Ag}_2\text{O(CO}_2) \leftrightarrow \text{Ag}_2\text{O} + \text{CO}_2 \]

Thus the decomposition rate is proportional to the area of oxide lattice associated with the interface which is covered in absorbed carbon dioxide while the reverse reaction is proportional to the free oxide interfacial surface. The overall rate of decomposition is therefore the difference, i.e.,

\[ \text{rate} = K_k (1-\beta) - K_l \delta \]

\[ 7.3 : 107 \]
where \( \beta \) is the fraction of oxide interfacial surface covered in carbon dioxide and \( K_k \) and \( K_l \) are velocity constants. The dependence of \( \beta \) on the pressure of carbon dioxide can be obtained by assuming a Langmuir adsorption equilibrium, such that,

\[
k_1 \beta = k_2 (1-\beta)P
\]

where \( P \) is the partial pressure of carbon dioxide at the interface and \( k_1 \) and \( k_2 \) are constants dependent on adsorption characteristics. Hence Spencer and Topley obtained the equation,

\[
\frac{\text{rate}}{\text{maximum rate}} = \frac{P_e - P}{P_e + K_{kl} P} = \eta_e
\]

where \( K_{kl} = K_k/K_l \) and the maximum rate is that at \( P = 0 \), while the rate is zero at \( P = P_e \), the equilibrium pressure.

Cutler proposes a somewhat similar reaction equation,

\[
\begin{align*}
\text{Ag}_2\text{CO}_3 & \overset{k_1}{\underset{k_2}{\rightarrow}} \text{Ag}_2\text{O}^{\text{**}} + \text{CO}_2 \\
\text{Ag}_2\text{O}^{\text{**}} & \overset{k_3}{\underset{k_4}{\rightarrow}} \text{Ag}_2\text{O}
\end{align*}
\]

with an active intermediate \( \text{Ag}_2\text{O}^{\text{**}} \) which comprises a fraction of the interface, denoted by \( \beta^{**} \). Silver carbonate comprises the remaining portion of this interface. Hence we have,

\[
\text{rate} \propto k_1 (1-\beta^{**}) - k_2 \beta^{**} P
\]

\( \beta^{**} \) can be obtained from the equilibrium condition set up in the
second reaction, where

\[ k_1(1-\beta^*) - k_2P - k_3P + k_4(1-\beta^*) = 0 \]

on the assumption that \( \beta^* \) remains a constant. From these equations Cutler obtains the relation

\[ \frac{\text{rate}}{\text{maximum rate}} = \frac{P_e - P}{P_e + K_{ld}P} \]

which is the same as that of Spencer and Topley.

Cutler goes on to show that the inclusion of the effect of water vapour on the reaction, which is known to be significant, can be described by the reaction,

\[ \text{MCO}_3 + \text{H}_2\text{O} \xrightarrow{k_5} \text{H}_2\text{O}^* + \text{CO}_2 + \text{H}_2\text{O} \]

and results in the kinetic description,

\[ \frac{\text{rate}}{\text{maximum rate}} = \frac{P_e - P + K'P_{\text{H}_2\text{O}}}{P_e + K_{ld}P} \]

where \( K' \) is a further equilibrium constant.

Culbertson proposes two possible mechanisms for this water vapour catalysis of the recombination reaction,

\[ \text{Ag}_2\text{O} + \text{H}_2\text{O} + \text{CO}_2 \rightarrow 2\text{AgHCO}_3 \]

followed by

\[ 2\text{AgHCO}_3 \rightarrow \text{Ag}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \]

and

\[ \text{Ag}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{AgOH} \]

followed by

\[ 2\text{AgOH} + \text{CO}_2 \rightarrow \text{Ag}_2\text{CO}_3 + \text{H}_2\text{O} \]

7.3 : 109
The possibility of the existence of the hydroxide has been shown by Riley, who found that the oxide can become covered in a surface film of hydroxide, which would account for the difficulty of drying the oxide.

7.4 The decomposition reaction. Centnerszwer and Bruzs studied the decomposition of "amorphous" silver carbonate and contrasted it with the decomposition of the crystalline variety. Of the latter, they reported that it conformed to a unimolecular rate law such that,

\[
\text{rate of reaction} = \text{initial reaction rate} \times \exp(-kt)
\]

where \( k \) is a constant and \( t \) time, and quoted a temperature coefficient of 2.14 per 10°C. The "amorphous" carbonate, which term can only describe a material which is merely less coarse than the obviously crystalline variety, was prepared from a silver nitrate/potassium bicarbonate solution, then dried at 50-60°C. This was found to decompose less rapidly than the crystalline carbonate, and to follow a course which could in no way be represented wholly by the unimolecular law equation. An example of one such decomposition, carried out in an atmosphere of carbon dioxide, is shown in Fig. 7.1, where the reaction rate is in ccs. CO₂ evolved/min./gm. Ag₂CO₃. After an initial rapid decrease in reaction rate a constant rate is maintained for some time, followed thereafter by an exponentially decreasing rate which did in fact follow the unimolecular law equation. Centnerszwer and Bruzs proposed that the reaction proceeded
through an intermediate oxycarbonate, which in turn decomposed to the oxide, both steps following a unimolecular law in themselves, but when combined, and taking into account the changing concentration of the intermediate oxycarbonate, resulting in a reaction history such as that depicted in Fig. 7.1. For a component of concentration \( c \) following the unimolecular law,

\[
\text{rate of reaction} = \frac{dc}{dt} = -kc
\]

i.e.

\[
\ln c = -kt + \text{constant}
\]

Now at \( t = 0 \), \( c = c_0 \) so that initial rate \( = -kc_0 \) and,

\[
\text{reaction rate} = -kc_0 \exp(-kt)
\]

\[
= \text{initial rate} \times \exp(-kt)
\]

as before.

Such a rate theory is consistent with homogeneous reactions but in the case of interfacial gas-solid reactions account should be taken of the areas involved rather than the concentrations. This has been the approach used in the theoretical work carried out in this research. The unimolecular approach assumes that each silver carbonate molecule has the same probability of reaction as any other, which is not the case in an interfacial reaction. Although the experimental conditions for the reaction are not given in detail, it is possible that non-isothermal conditions may have partly the cause of the shape of the rate/time curve. This will be obvious after presentation of some of the results of this research. It is interesting to
compare the expected shapes of the reaction histories for both the unimolecular law and the kinetic control equation obtained in Chapter 4 for the sphere. The unimolecular law derives that \( \ln(\text{rate/initial rate}) \) versus time is a straight line, so the same plot has been obtained for the interfacial theory and is shown in Fig. 7.2 (note that \( \alpha \), the fractional penetration, which for the interfacial theory is the equivalent of time, has been used). It can be seen by comparison of the resultant curve with the broken arbitrary reference line that the interfacial theory line is approximately a straight line for some 70-80% conversion, so that in fact the two theories are very similar and could easily be confused, one for the other.

Centnerszwer and Bruza found the same shape of curve occurred if a previous reaction had been interrupted when half complete and the solid cooled and stored before again attempting decomposition. It was suggested that this might show that the postulated oxy-carbonate reverted to the carbonate on cooling. They also found that the reaction exhibited a much reduced rate at a temperature of about 260°C, and obtained a negative temperature coefficient in this region. A similar effect was noticed by Culbertson but at a somewhat reduced temperature (185°C), and in vacuo. The decrease in rate could perhaps be due to a sintering effect such as has been found by Beveridge (1960) in the oxidation of zinc sulphide. Some of the experimental evidence for the conclusion of Centnerszwer and Bruzas is shown in Fig. 7.3 as the time required to achieve a
certain conversion at a given temperature.

A considerably more methodical approach to the problem was made by Spencer and Topley (1929) dealing with carbonate crystals, prepared in a variety of ways, of about 0.003 cm. dia., assumed spherical. The carbonate was brought to reaction temperature in an atmosphere of dry carbon dioxide, and the reaction then followed, in vacuo, by continuous weighing. Spencer and Topley analysed their results in the light of the equation,

\[ \frac{u}{R} = \frac{1-(1-\alpha)^{\frac{1}{3}}}{t} \]

which can be derived from the basic theory of constant velocity of penetration of the interface into a spherical crystal, i.e.,

\[ u = -\frac{dr_1}{dt} \text{ or } ut = -r_1 + \text{constant} \]

and knowing that \( r - R \) at \( t = 0 \) and that \( \alpha = 1-(r_1/R)^3 \) the above equation is obtained. Spencer and Topley found that certain of their results followed such an equation but that others (termed "abnormal") did not. In the abnormal reactions the velocity of propagation of the interface was found to fall off with time, but it was found that this situation could be corrected by admitting a certain pressure of water vapour, up to 15 mm. Hg, into the reactor. This pressure increased with temperature and was also a function of the method of preparation of the carbonate, which quite markedly affected the results even in the absence of water vapour. It was concluded therefore that the reaction was
of the topochemical type, but that the constant propagation velocity was affected when the diffusion of carbon dioxide out through the oxide product became hindered, and that this diffusion rate, and perhaps also the interfacial reaction itself, were both affected by the presence of water vapour. The possibility of a silver hydroxide intermediate, shown to exist by Riley, was suggested, via the reaction:

\[
\text{Ag}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{AgOH} + \text{CO}_2 \rightarrow \text{Ag}_2\text{O} + \text{H}_2\text{O} + \text{CO}_2
\]

Various factors affected the reproducibility of the results, such as the method of preparation of the crystalline carbonate, the duration of the warm-up period in carbon dioxide, but not, as might be expected, the retention of foreign ions in the crystal lattice.

Spencer and Topley obtained activation energies of 23.4, 22.8 and 22.5 Cal/g.mole for their three preparations.

The work of Cutler was confined to a review of previous work and to a discussion of the reaction mechanism. An attempt was made, as mentioned in Chapter 2, to categorise gas-solid reactions into those which are dependent on an interface and those which are not, the decomposition of carbonates being rightly placed in the former category.

Culbertson studied the decomposition of 0.08" extruded worms of "amorphous" silver carbonate by a similar technique to that of Spencer and Topley, and also by differential thermal analysis. The main aim of the work was to achieve a system for
the removal of carbon dioxide from air, which was lightweight, compact and economic to run in the light of its use in space capsules, and as a result the findings were not all applicable to the present research. However an important aspect of any such absorption system would be its ability to regenerate itself, so that Culbertson's research included the decomposition reaction. The work showed up a peculiar transition in the silver carbonate at a temperature of about 185°C which resulted in a reduced rate of decomposition above this temperature. This transition was found to be reversible so that higher decomposition rates resulted if the temperature was returned to less than 185°C, although the change was slow. The "low temperature" reaction was governed by an activation energy of 20.2 Cals/g.mole, and the "high temperature" reaction by 26.3 to 31.2 Cals/g.mole, these activation energies being measured by a "split run" method where conditions were suddenly changed to new levels during a single reaction for a short period before returning to previous conditions. This technique therefore obviated the necessity to take into account the changing interfacial area with time.

The results of Culbertson relating to the transition at 185°C reflect the similar results of Centnerszwer and Buzs, but the hypothesis of the sintering of carbonate could not be considered a reversible transition.

One of the most interesting conclusions from Culbertson's research was that the decomposition rate could be markedly improved by coprecipitating the silver carbonate with one of a
variety of catalysts, notably an Yttrium salt. The "catalyst" was found not to affect the equilibrium pressure but to greatly increase the decomposition rate, and to nullify the effect of water vapour. In fact, water vapour was found to inhibit the decomposition. Rare earths with ionic radii similar to that of silver were found generally to increase decomposition rates.

Table 7.1 Decomposition reactions of Spencer and Topley.

a) "Normal" reaction: Temperature, 147°C, H₂O pressure 0mm.Hg.

<table>
<thead>
<tr>
<th>t mins</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>50</th>
<th>80</th>
<th>120</th>
<th>160</th>
<th>200</th>
<th>250</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>.002</td>
<td>.036</td>
<td>.110</td>
<td>.274</td>
<td>.424</td>
<td>.580</td>
<td>.716</td>
<td>.817</td>
<td>.894</td>
<td>.940</td>
</tr>
<tr>
<td>rate</td>
<td>.018</td>
<td>.211</td>
<td>.300</td>
<td>.290</td>
<td>.262</td>
<td>.212</td>
<td>.163</td>
<td>.128</td>
<td>.085</td>
<td>.055</td>
</tr>
</tbody>
</table>

b) "Abnormal" reaction: Temperature, 172.8°C, H₂O 1mm.Hg.

<table>
<thead>
<tr>
<th>t mins</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>.021</td>
<td>.038</td>
<td>.067</td>
<td>.087</td>
<td>.104</td>
<td>.121</td>
<td>.137</td>
<td>.150</td>
</tr>
<tr>
<td>rate</td>
<td>.248</td>
<td>.228</td>
<td>.206</td>
<td>.170</td>
<td>.167</td>
<td>.132</td>
<td>.114</td>
<td>.129</td>
</tr>
</tbody>
</table>

Note: rates quoted in moles CO₂/mole Ag₂CO₃/hr.

The phenomenon of nucleation, which is of course necessary for the initiation of an interfacial reaction, has been generally found to be unimportant in the decomposition reaction, indicating that the interfacial reaction process is quickly developed and that the subsequent reaction is dependent on the propagation process. Spencer and Topley found an initial acceleration in the rate, indicative of the nucleation process. The nucleation stage
is aided at high temperatures by the fact that slight decomposition of the carbonate can occur at structural defects in the crystalline lattice, even if the prevailing carbon dioxide pressure is higher than the dissociation pressure of the bulk of the material at that temperature. This was shown to occur by Spencer and Topley (1929).

Examples of the "normal" and "abnormal" results of Spencer and Topley are given in Table 7.1.

7.5 The recombination reaction. The most apparent finding of Spencer and Topley when they studied the recombination reaction (1931), and one which could be predicted, is the early blocking of the porous silver oxide, obtained by previous decomposition of the crystalline and essentially impervious carbonate, by silver carbonate with its larger molecular dimensions. This synthetically prepared oxide would retain some structural regularity, but would be of a more open nature than a more directly prepared sample of silver oxide. The extent of reaction was restricted to some 25% of complete absorption, this being achieved only after some days of exposure. Spencer and Topley also concluded that the rate of surface diffusion of the carbon dioxide over the carbonate surface was the reaction rate limitation, unlike in the decomposition reaction where the surface diffusion on the silver oxide was rapid. In keeping with this theory of carbon dioxide starvation in the inside of oxide particles, the amount of reaction was found to be less at high carbon dioxide pressures, when the increase in potential reaction
rate would greatly outweigh any increase in the diffusion rate so that the surface of the oxide would soon become blocked with carbonate. At the same time and in keeping with this theory, increase in carbon dioxide pressure caused an increase in the initial rate of reaction. It was concluded that there must exist an optimum carbon dioxide pressure which would permit the required nucleation at an acceptable rate but which would be low enough not to block the oxide surface prematurely.

Culbertson also used decomposed carbonate as the starting point for the recombination reaction, in the same extruded form as for the decomposition reaction. It was shown that these relatively large particles did not introduce a diffusion effect, and Culbertson also concluded that there was no boundary layer effect, although the evidence for this seemed dubious. Low concentrations of carbon dioxide were used and it was found that the rate dropped with rising temperature, reaching a minimum at about 50°C, and rose again thereafter. The effect was noticeable at greater conversions although the rates were much reduced. The activation energy varied from 2 to 12 Cals/g.mole. It was postulated that at lower temperatures the reaction was aided by physically adsorbed water which was driven off at higher temperatures, while at higher temperatures chemically adsorbed water catalysed the reaction. Again, addition of certain co-precipitants, such as Yttrium, caused significant improvements, such that the absorption capacity of the silver oxide was increased, even to 100%.
Roach studied the recombination reaction using the "break-through" technique, whereby a stream of nitrogen containing 3% carbon dioxide was passed through a column containing silver oxide and the time at which break-through of carbon dioxide in the off-gas was noted. Using pure silver oxide break-through was immediate, and a similar rapid termination of an initially high rate was noticed. Thereafter the rate became slower until the reaction terminated short of complete conversion. By co-precipitation and subsequent decomposition of silver carbonate and aluminium hydroxide, 20% aluminium oxide (Al$_2$O$_3$) was obtained and used in place of the pure oxide. This resulted in a much improved performance, with over 90% conversion of the silver oxide to carbonate. An increase in the Al$_2$O$_3$ content was found to reduce the effectiveness of the absorption, although conversion was still high. The possibility of the formation of a bicarbonate was suggested, as carbon dioxide absorption was greater than 100% based on the formation of Ag$_2$CO$_3$ rather than AgHCO$_3$. The theory of diffusion controlled reaction in a slab-shaped solid is applied to the results, although the validity of the application seems doubtful.

7.6 Cyclic operation. In the application of carbon dioxide absorption to space travel the importance of the ability to cycle between absorption and regeneration of the absorption medium is obvious, in order to reduce the mass of material which must be carried. However cyclic operation was used prior to such considerations by Spencer and Topley (1931) mainly in order to
produce a sample of material which would give stable and repeatable results. It was found that if conditions were kept identical from one regeneration to another, and the regenerations were followed to completion, the results were identical. However, if the regeneration were terminated during the rapid section of the reaction, it was found that in the next regeneration, after intermediate complete decomposition, the initial rapid section accounted for less of the reaction. Cycled operation was also found to affect the dissociation pressure as will be mentioned later.

The main restriction on cycled operation is gradual decomposition of silver oxide to silver, although this is only important at high temperatures. In certain circumstances Spencer and Topley noticed complete decomposition to silver.

7.7 The effect of carbon dioxide. Spencer and Topley (1929) investigated the effect of carbon dioxide on the decomposition reaction using the "split run" method which was later used by Culbertson, as described in Section 7.4. The results were compared with the equation for the kinetics given in Section 7.3 and found to give a fair agreement. Experimental results at three temperatures are shown in Fig. 7.4, together with a theoretical prediction from the kinetic equation, using the value of the dissociation pressure, $P_e$, at the relevant temperature ($193.6^\circ C$) and an average value of $K$ obtained from the values deduced from the experimental results.

The effect of carbon dioxide on the reverse reaction was
found by Spencer and Topley (1931) to be more curious and is illustrated qualitatively in Fig. 7.5. As explained earlier the changing shape of the curves is due to the effect of diffusion of the carbon dioxide to the interior of the oxide. As the carbon dioxide pressure is increased, although the initial rate is higher, the final degree of conversion is less.

Culbertson also studied this effect and showed that there was a saturation effect such that above a certain pressure of carbon dioxide no increase in rate resulted.

7.8 The effect of water vapour. Spencer and Topley (1929) suggested that above a certain pressure of water vapour, at a given temperature, no increase in decomposition rate occurred, and that the water vapour pressure required increased with temperature. The absence of water vapour in some cases resulted in "abnormal" reactions, resulting from poor diffusion of the carbon dioxide from the reaction site, and possibly also from a catalytic effect at the interface itself. It was also concluded that the effect of water vapour was more pronounced at high values of conversion. Spencer and Topley's results are depicted in Fig. 7.6.

The saturation effect was also found by Culbertson but only for the low temperature reaction. At high temperatures the rate increased linearly with water vapour pressure, although the upper limit of pressure was only the vapour pressure at 25°C. The effect is shown qualitatively in Fig. 7.7.

For the recombination reaction Spencer and Topley (1931) found that water vapour had a greater effect on the second slower
section of the reaction than on the first, in that the former was faster and accounted for a greater degree of conversion. This was put down to the increase in the rate of surface diffusion of carbon dioxide on the silver carbonate rather than catalysis.

7.9 The equilibrium pressure. The subject of the equilibrium pressure is discussed in greater detail in Chapter 9 and in Appendix E.

Spencer and Topley (1929) correlated the results of dissociation pressures of other workers and obtained results over a wider temperature range, these results being shown in Table 7.2.

<table>
<thead>
<tr>
<th>T°C</th>
<th>130</th>
<th>140</th>
<th>150</th>
<th>160</th>
<th>170</th>
<th>180</th>
<th>190</th>
<th>200</th>
<th>210</th>
<th>216.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_e, ats.</td>
<td>0.0272</td>
<td>0.0444</td>
<td>0.0697</td>
<td>0.107</td>
<td>0.162</td>
<td>0.252</td>
<td>0.374</td>
<td>0.548</td>
<td>0.794</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Spencer and Topley noticed that a certain amount of decomposition would occur even in the presence of a pressure of carbon dioxide higher than the equilibrium value from Table 7.2. This was said to be due to crystal defects, edges etc., at which the carbonate would decompose more readily. If such defects were to be predominant, it would be expected that the equilibrium decomposition pressure would increase. This was indeed found by Spencer and Topley, who repeatedly decomposed and regenerated silver carbonate in order to obtain what has been described as "amorphous" material. Thus at 158°C, with an equilibrium pressure of 75 mm Hg. for the crystalline material, repeated decomposition
gave a material with an equilibrium pressure of 115 mm Hg.

Culbertson measured equilibrium pressures by two methods and obtained quite different results. This point will be discussed in Chapter 9.

7.10 Conclusions - directives to the present research.

As can be appreciated from the above summary, previous findings on the silver carbonate/silver oxide system are such that the system can in no way be termed simple, although in all probability it is more simple than the majority of non-catalytic gas-solid reactions. However it will be appreciated that in certain circumstances the decomposition reaction at least follows a predictable course, so that it could be considered an "ideal" reaction, while the system as a whole provides many challenges, as many of the points covered partly by previous workers are as yet unresolved.

Notable among the omissions of previous reports was the question of the possibility of non-isothermal conditions during the reaction. Although Culbertson used the differential thermal analysis technique for some of his work, little information is given as to precise details. This lack of attention to the possibility of temperature gradients both in the solid and in the surrounding gas in the furnace is common to almost all previous work on any gas-solid systems. From the considerations of a theoretical nature presented in Chapter 6 it can be seen that such gradients can significantly affect the validity of analysis of experimental results, if isothermal conditions are assumed.
This point was therefore given considerable attention in the experimental study, both in its own right, but also because it was found to be a useful experimental tool for the general analysis of the gas–solid system. The non-isothermal nature of the decomposition reaction as studied in this work was found useful particularly in studying the effect of water vapour and in determining the equilibrium pressure of the reaction.

The apparatus and procedure used in the experimental study are described in Chapter 8, and the results presented and discussed in Chapter 9.
8.1 Introduction. The experimental study of the decomposition of silver carbonate was undertaken both as a "grass roots" investigation and in the light of previous studies of the same reaction. Thus, as it was previously found (see Culbertson, Spencer and Topley (1929)) that the most successful application of this reaction to a practical situation, such as the space capsule application, involved the use of "amorphous" silver carbonate and oxide prepared by decomposition of the "amorphous" carbonate, this material was used for the study.

The material and the form in which it was used is described in this Chapter. Also described are the experimental apparatus and the technique used.

8.2 Silver carbonate study material. Two proprietary makes of silver carbonate were used in the investigation, those of Johnson, Matthey & Co. Ltd., and British Drug Houses Ltd. The former is made by the addition of sodium carbonate/sodium bicarbonate to a solution of silver nitrate, the solution being violently agitated while the silver carbonate precipitates. The carbonate is then washed, and finally dried at about 70°C. Details of impurities were not available (private communication, Johnson & Sons' Smelting Works Ltd., 20th March, 1967). The B.D.H. carbonate (private communication, The British Drug Houses Ltd., 17th November, 1964, and 17th October, 1967) is made in a similar
manner, and has the following specification of purity,

Minimum assay (ex Ag) \( 98\% \)

Maximum limits of impurities—

alkalis (sulphated) \( 0.3\% \)
nitrate \( (NO_2) \) \( 0.05\% \)

This carbonate, however, was not used to any great extent during the study. Further reference to silver carbonate will indicate the Johnson, Matthey carbonate. The other carbonate was used mainly for initial qualitative work.

No exact specification regarding particle size was available although it was said that this should be within 0.5 to 5 microns \( (\mu) \). An attempt to measure the particle size distribution on a Coulter Counter was made but unfortunately particle agglomeration took place, as the technique involves forming a suspension in water. The phenomenon can also be observed when trying to dry the carbonate at too high a temperature (Johnson & Sons' Smelting Works Ltd., private communication, 20th March, 1967). The two Coulter results are shown in Fig. 8.1, giving a range of particle sizes between 7 and 70 \( \mu \). Microscopic examination undertaken in conjunction with these measurements showed the basic particle size to be about 2 \( \mu \).

Examination of the carbonate powder by an optical microscope did not give a satisfactory picture of the size or of the distribution. It was therefore decided to examine the powder on an electron microscope. This was carried out on an Akashi (TRS-50E1) Transcope and also by a Stereoscan, the former giving an
electron transmission photograph and the latter a reflection photograph.

The first transmission pictures were taken of a sample of silver carbonate brought to suspension in water by sonic mixing then dropped onto a carbon background. The micrographs were taken at a magnification of x1200, being later further magnified photographically to either x5000 or x10000. One such preliminary photograph is shown in Plate 1a. It can be seen that the particles are cylindrical or capsule-shaped with dimensions of 0.5-1 \( \mu \) in diameter, and 1-4 \( \mu \) long, although it is apparent that some degree of agglomeration has taken place. A similar picture of the B.D.H. carbonate is shown in Plate 1b. The individual particles seem to be of a more regular size, and nearer to a spherical shape.

Other photographs were taken of carbonate deposited on a glass slide by "dusting". An example of these photographs is given in Plate 2. It is immediately obvious that a greater degree of minute "fines" has been retained in the preparation, but the general shape and size of the bulk of the particles is the same as in Plate 1a.

In general the photographs were found to show that the average ratio of length to diameter was about 2.5:1, although quite large variation from this value occurred. It can also be seen from Plate 2 that some of the particles are slightly barrel-shaped, while others, especially the smaller ones, are irregular and do not conform to the general shape of the larger particles.
The density of the carbonate was measured roughly by the conventional method of immersion in water within a container of known volume, and found to be 5.9 gm./cc., compared with a literature value (Perry) of the crystalline material of 6.077. An attempt to obtain an X-ray powder diagram of the sample was unsuccessful. However it is certain that the term "amorphous" can only be descriptive of the very small size of the particles rather than of their chemical structure, which was crystalline.

The powder was yellow in colour, darkening on exposure to light or heat, especially when moist.

The B.E.T. (see Brunauer et al) surface area of the carbonate was measured on the earlier batch of silver carbonate used in the study and found to be 0.5 μm²/gm. The equivalent spherical diameter to give this B.E.T. area is 1.828μm.

8.3 Kinetic control of reaction in the carbonate powder.

In Fig. 8.2 are diagrams of a capsule-shaped (model 1) and a cylindrical-shaped (model 2) model of the powder particles described above. The length to diameter ratio of 2.5:1 is retained, and the capsule model is taken to have hemi-spherical ends, while model 2 is a flat-ended cylinder. In a similar manner to that which was used in Chapter 4, the history of an interfacial reaction occurring in these models can be obtained.

**Model 1** The external surface area and the volume of the capsule are,

\[
\begin{align*}
\text{surface area} &= 4\pi R^2 + \pi R \cdot 3R = 10\pi R^2 \\
\text{volume} &= 4/3\pi R^3 + \pi R^2 \cdot 3R = 13/3\pi R^3
\end{align*}
\]

8.3 : 128
Hence the surface area to volume ratio is $\frac{30}{13R}$, compared with $\frac{3}{R}$ for the sphere.

The area of an interface penetrating the capsule-shaped model is, as indicated on Fig. 8.2,

$$\text{interfacial area} = 4\pi r_1^2 + 6\pi R r_1$$

Thus the decay factor, defined as above, can be written as,

$$\eta_d = \frac{2}{5} (\frac{r_1}{R})^2 + \frac{3}{5} (\frac{r_1}{R})^4$$

A plot of $\eta_d$ versus $r_1/R$ (note- $(1-r_1/R)$ is directly proportional to $\theta_{r_1}$ for a kinetically controlled reaction) from Eq. (8.1) is shown in Fig. 8.3. It can be seen that the result lies between those for the sphere and cylinder, also depicted in Fig. 8.3.

Model 2 The external surface area and the volume of the cylindrical-shaped model are,

$$\text{surface area} = 2\pi R^2 + 2\pi R(2R - r_1) = 2\pi R^2$$

$$\text{volume} = 5\pi R^3$$

Hence the surface area to volume ratio is $\frac{12}{5R}$, compared with $\frac{3}{R}$ for the sphere and $\frac{30}{13R}$ for model 1.

The area of the interface penetrating the cylindrical-shaped model is, as indicated in Fig. 8.2,

$$\text{interfacial area} = 2\pi r_1^2 + 2 r_1(5R - 2(R - r_1))$$

Thus the decay factor, defined as above, can be written as,

$$\eta_d = \frac{2}{5} (\frac{r_1}{R})^2 + \frac{3}{5} (\frac{r_1}{R})^4$$

\[8.2\]
A plot of $\eta_d$ versus $r_1/R$ from Eq.(8.2) is shown in Fig. 8.3. The resulting curve is little different from that of model 1, and again lies between that for the sphere and that for the cylinder.

### 8.4 The relation of B.E.T. surface area to particle size.

The surface area to volume ratios of the two models above and of the sphere are,

- model 1: $30/(13R)$
- model 2: $12/(5R)$
- sphere: $3/R$

For silver carbonate, with a density of 6.077 gm./cc., this gives B.E.T. surface areas for the three cases of,

- model 1: $0.380/R \text{ m}^2/\text{gm.}$
- model 2: $0.395/R \text{ m}^2/\text{gm.}$
- sphere: $0.494/R \text{ m}^2/\text{gm.}$

where $R$ is the radius of the particle in microns. As mentioned, the B.E.T. area of the carbonate was determined as $0.54 \mu m^2/gm.$, so that to give this value the particle size for each of the models would be 1.41, 1.46 and $1.83 \mu$ dia. respectively. These values are all somewhat higher than those which were obtained from the electron micrographs. Later photographs taken with the Stereoscan confirmed that the particles were indeed smaller than given in this calculation. It is thought, however, that measurement of the B.E.T. area by the method used, when this area is of the order of $1.1^2$, then the measurement is liable to considerable error. The later Stereoscan photographs also show that the
particle size is fairly regular. If the particle size is taken as $1\mu$, then the B.E.T. surface areas become, for model 1, 0.76 $m^2/gm$, and for model 2, 0.79 $m^2/gm$, which areas are probably within the experimental error of the B.E.T. area method.

8.5 The effect of a size distribution on the B.E.T. surface area.

As mentioned earlier, Plate 2 shows a considerable number of very small particles, and it could be argued that this would contribute highly to the B.E.T. surface of the bulk material. To test this effect it was decided to make further use of the normal distribution used in Chapter 4, and thereby obtain a measure of the change of B.E.T. area with standard deviation, $\sigma'$. The relative frequencies or amounts were chosen as listed in Table 4.1 with the size interval of $\Delta x$ again chosen such that 99.9637% of the distributed variable was accounted for. This gave $\sigma'/5\Delta x$. Computer program 11 was designed to provide this information and is described in Appendix G, Section G.11. All three distributions namely area, number and volume as used in Chapter 4 were studied.

The distribution of area contributions makes no difference to the B.E.T. area, this being $3/\sqrt{\sigma'}$ for all values of $\sigma'$ (note— these considerations are confined to the spherical particle). The effects of all three types of distribution are shown in Fig. 8.4. Although the choice of a normal distribution has been made for this study, and although as described in Chapter 4 the area and volume distributions are partly artificial, it can be seen from Fig. 8.4 that the effect of a distribution of particle sizes is remarkably slight, which was also found in Chapter 4 in
relation to the $d$ versus $x_i/x$ histories of kinetically controlled reactions and the $d$ versus $\theta_{r_1}$ curves for reactions with control shared between kinetics and pore diffusion. Hence it can be said with qualifications due to the restricted distributions studied, that experimental results are unlikely to be seriously influenced by the lack of uniformity of particle size, as was in fact suggested by Culbertson.

The results given in Fig. 8.4 indicate the effect of $\theta_1$ on the quantity $3\Sigma nx^2/(\Sigma nx^3)$ where it will be remembered from Chapter 4 that $x$ is a dimensionless quantity. The B.E.T. area is obtained by dividing this quantity by $R\rho$. Thus for a $1\mu$ dia. spherical particle of silver carbonate the B.E.T. area is 0.987 m$^2$/gm.

8.6 Moulded particles used for the experimental study.

Many experimental studies, such as those of Spencer and Topley and Culbertson, have been undertaken primarily to obtain kinetic data on the particular system studied, and not to study the influence of extraneous factors which might be introduced in circumstances where the reaction studied might be put to practical use. In certain reactions, however, such as the calcination of limestone, the combustion of limestone and the reduction of iron ore, the practical aspects have been considered to a much greater extent, so that knowledge grows of such effects as those of the boundary layer and of pore diffusion. It is noticeable, however, that the effects of heat transfer have not been studied to such an extent. It was decided, then, to study the silver carbonate
decomposition with these aspects not only in mind but also built into the reaction system. It was thought that a convenient way of doing this would be to form the carbonate powder described earlier into spherical pellets. A size of $\frac{1}{4}''$ was chosen for these spheres, not larger for reasons both of economy of the expensive material and of size of apparatus, and not smaller as the sphere moulding process employed, although still possible, would have been more difficult. The possibility of resorting to another particle size at a later date was not excluded.

The $\frac{1}{4}''$ spheres were moulded rather than compressed pellets of silver carbonate. The procedure for moulding was similar to that used earlier by Beveridge (1960). The carbonate was made into a semi-stiff paste by adding the powder slowly to a quantity of water and slowly mixing until the desired consistency was obtained. Small quantities of this paste, slightly greater than was required for a single $\frac{1}{4}''$ sphere, were shaped roughly into spheres by rolling in the palm. This ball of paste was then placed in one half of a perspex sphere mould, the other half being placed on top and the two squeezed together, the excess material being expelled through the holes provided.

The perspex moulds used for the process are shown in Fig. 8.5 and in Plate 3a. Originally brass was used, as was used by Beveridge, but this was found to discolour the carbonate while moist, due to oxide formation. The original design of the perspex mould did not incorporate the land which can be seen in Fig. 8.5. This tended to allow the two halves of the mould to
rock on each other and as a consequence break up the carbonate sphere. The final moulds, nineteen in all, were made to more exacting specifications. The \( \frac{1}{4} \)" hemispherical holes were turned on a lathe using, at first, a specially made tool, but this was found to leave burrs on the inside of the mould. Later the holes were bored using a ball-ended mill. A very smooth interior to the holes was obtained which was further improved by polishing. The excess material escaped both through the small central hole in one half of the mould and at the circumference of the junction between the two halves. Hand pressure was applied to the two halves to ensure that not a significant amount of material was left between the two halves. A "blow-hole" was added later to allow air, trapped within the exactly fitting halves, to escape. Care was taken not to rotate the halves relative to each other as this broke up the pellets.

The spheres were dried for some hours within their moulds as any attempt to open the moulds before the material was dry split them in two. The water in the material tended to condense in minute droplets on the inside of the mould, but the material became reasonably dry and could be removed intact quite easily. Drying was carried out at about 60°C in a dark oven to avoid darkening the carbonate by light. Further drying with the carbonate removed from the moulds rendered the carbonate quite dry, as determined by successive weighings. The resulting spheres were very regular, their weights from a single batch of carbonate paste being within ±7%. Table 8.1 shows the weights of

8.6 : 134
18 spheres obtained from each of two batches.

Table 8.1 Weights of single moulded particles.

<table>
<thead>
<tr>
<th>Batch 1:</th>
<th>0.2830 0.2680 0.2863</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2806 0.2989 0.2778</td>
</tr>
<tr>
<td></td>
<td>0.2742 0.2675 0.2948</td>
</tr>
<tr>
<td></td>
<td>0.2808 0.2908 0.2742</td>
</tr>
<tr>
<td></td>
<td>0.2873 0.2882 0.2829</td>
</tr>
<tr>
<td></td>
<td>0.2743 0.2943 0.2796</td>
</tr>
</tbody>
</table>

Average weight, 0.282gm., deviation within ±6%.

<table>
<thead>
<tr>
<th>Batch 2:</th>
<th>0.2641 0.2810 0.3019</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2637 0.2772 0.2747</td>
</tr>
<tr>
<td></td>
<td>0.2705 0.2847 0.2755</td>
</tr>
<tr>
<td></td>
<td>0.2833 0.2836 0.2560</td>
</tr>
<tr>
<td></td>
<td>0.2853 0.2865 0.2868</td>
</tr>
<tr>
<td></td>
<td>0.2842 0.2945 0.2814</td>
</tr>
</tbody>
</table>

Average weight, 0.280gm., deviation within ±8%.

The moulded spheres were highly fragile, and had to be handled gently. Powder was easily removed by touch. The deviations from the average were found later not to be critical. Small hair cracks on the surface of the spheres were also found, but again because of the nature of the reaction these were also unimportant.

8.7 Carbonate-coated celite particles. As will be discussed later, it became necessary to provide carbonate for decomposition in a form which would rule out any question of mass or heat transfer limitations. This was achieved by coating 1/8" dia. by
3/16" long porous particles of celite catalyst carrier with the carbonate. A similar though wetter paste to that used for the moulded spheres was used and some 400 to 600 celite particles were rolled in this paste to pick up some 6gm. of the carbonate. A similar drying method to that used above was employed. Microscopic examination of a split celite particle showed that the thin layer of carbonate on the surface of the celite had not penetrated the pores. No attempt was made to ensure that the carbonate layer was of uniform thickness, as the layer was only required to be thin relative to the 3/4" sphere.

8.8 Miscellaneous reaction forms. A limited amount of material was used in the study in the form of dia. cylinders of highly compressed powder. These were made in a simple die press, achieving voidages of about 0.2 (compare with the high voidages of the spheres, given in Section 8.9.). Unfortunately, due to a mechanical fault introduced into the pellets during compression, no reliable results with this material were obtained. Further work with such pellets would be useful.

Other systems included brass blocks both blind and through-drilled, the holes being filled with carbonate.

8.9 Voidage and pore size of the moulded material. From the figures in Table 8.1 an average voidage, \( \varepsilon \), for the carbonate of 66.5% is obtained. It was found difficult to maintain this figure from batch to batch, and in fact the voidage varied from 63 to 75%, and an average figure of 65% was generally used.

From this value of the voidage one can obtain a value for
the average pore size from,

\[
\frac{2 \times \text{Pore volume per unit mass}}{\text{Surface area per unit mass}}
\]

of the order of \(10^4\), which is obviously outwith the realms of Knudsen diffusion, which has a significance on the reaction.

Values of the effective diffusivity of the carbonate and also of the oxide obtained by decomposition of the carbonate were obtained and are presented in Appendix B.

8.10 The reaction apparatus. In keeping with the suggestion of Warner (1964a) that one of the ways in which a reaction should be studied is an investigation of the reaction of single particles in a bed of inert material, and also because of the expense of the reaction material, the \(\frac{1}{4}\)" spheres were placed within a large inert bed of \(\frac{1}{3}\)" steel spheres. Originally ceramic balls were used, but these were replaced by steel in order to improve the heat transfer within the bed. A number of "live" spheres were placed among the steel spheres so that contact was always with steel and not with other live particles. Such an arrangement is shown in Plate 3b. The reactor bed had a diameter of \(2\frac{1}{2}\)", i.e. 10 times that of the spheres to minimise wall effects, although this was later found to be unimportant. The spheres were supported on a \(3/16\)" plate bored with \(1/8\)" holes. The \(1/8\)" walled reactor bed, as well as all other parts of the reactor, were made of aluminium. A schematic diagram of the reaction set-up is shown in Fig. 8.6.

The bed was held within an electrically heated aluminium
tube, 15" long, $8\frac{1}{2}$" o.d., and $2\frac{3}{8}$" bore. Although other furnace designs were considered this was chosen because of its simplicity and because of previous success with such designs in the department. The furnace had been found to give very uniform temperatures along its length. The outside of the furnace block was covered with a sheet of miconite, then wound in a lathe with resistance wire (Gilby Brunton, Tophet A, SWG 19) at 4 tpi to give a loading of 1Kw at 240V, being finally insulated with refractory cement.

The furnace current was manually set by a 0-260V, 5 amp. variable transformer, and controlled by a Smiths two-position proportional and electrical anticipatory controller (Series 5) with a supplementary 15 amp. relay, via a Pyrotenax pre-assembled sheathed chromel/alumel thermocouple, 41thou. o.d., set in the body of the furnace, half-way along its length and half-way between the inside and outside diameters. The bore of the aluminium furnace was extended at each end by 3" i.d., 5" long flanged tubes, these tubes extending the furnace outside the main lagging box. The whole furnace was contained within a 16" dia. asbestos cement pipe, the annulus being filled with vermiculite. As a result, only a small fraction of the full furnace loading was required to maintain operating temperatures. These were up to 250°C, although the furnace would be capable of reaching over 500°C.

The reactor bed had a spiggotted lower end which was a push fit over the bed carrier, the inner diameter of which was
smoothly reduced to \( \frac{1}{3} \)". This pipe then led the reaction gases, which passed downwards through the bed, out through the main furnace flange. Two thermocouples, similar to that used for the furnace temperature control, passed through holes in this flange, into which they were secured with araldite to provide a seal. The sheathed thermocouples then passed up through slots on the side of the bed carrier, through the seal between the carrier and the bed, and then into the midst of the inert spheres via the reactor bed base plate. The exit gas pipe and the reactor bed were integral with the main flange so that the whole could be removed as a unit for recharging the bed with carbonate. The lower extension tube was provided with a vent valve so that the dead zone below the reactor bed could be purged.

The top 5" of the axial hole through the furnace, as well as the upper extension tube, were filled with \( \frac{1}{2} \)" ceramic balls, to act as a preheater for the incoming gas.

The whole reactor assembly was mounted to allow easy withdrawal of the reactor bed from the furnace.

8.11 The gas system. Fig. 8.7 shows the flow diagram for the reaction gas system. Air was pumped by a Speedivac Model RB4 compressor (70 l/min. capacity) with a controlled suction, through either a humidifier or a Si-gel drier, or direct, to a rotameter with integral needle valve. The drier and the humidifier were made from a 2' long by 4" i.d. section of Q.V.F. glassware filled either with Si-gel or with water and \( \frac{1}{2} \)" Raschig rings. After the rotameter, the air could either be fed to a
common inlet to the reactor or through a further humidifier made up of two 1" diameter glass tubes filled with moist celite particles, the first tube being heated, the second being at ambient temperature, humidification being assumed 100% at the temperature at the top of the second tube. On occasion this humidifier was used in conjunction with a separate rotameter so that dry and humidified air could be mixed to give intermediate humidities. Dry nitrogen from a cylinder could also be admitted to the reactor through the same rotameter. A separate carbon dioxide supply (cylinder) and rotameter were also used. On occasion this flow was diverted through the second humidifier.

The mixed gases were then passed through a preheater consisting of three 1" dia. brass tubes, down the centre of which were held standard 0.5Kw radiant heating elements. Two of the elements were supplied directly while the third was controlled manually by a 2 amp. variable transformer. The temperature of the gas was sensed by a chromel/alumel thermocouple wired in opposition to a similar thermocouple placed in the same thermocouple pocket as the furnace temperature control couple. The output from this double couple system was fed to a twin-sensitivity d.c. galvanometer. The galvanometer current was brought to zero by adjustment of the preheater variac, indicating that the furnace temperature and the temperature of the preheated gas were equal. This preheater was actually by-passed for most experiments as the preheating section at the top of the reactor itself was found to be sufficient for the low flows generally used.
The gases leaving the reactor pass through a further rotameter before being discharged to atmosphere. In the majority of experiments the vent valve in the extension tube on the exit end of the furnace was left slightly open to ensure constant purging of the dead zone, so that the flow which actually passed through the bed had to be measured by rotameter downstream of the furnace.

A small sidestream was taken from the exit gases before the rotameter to the gas analysis system. A similar stream for comparative purposes was taken either from the inlet to the reactor or directly from the nitrogen/air system. Both flows were measured by rotameters with integral needle valves.

Pipework was run in polythene and copper. All rotameters were calibrated against a standard gas meter. Thermocouples used for measuring reaction temperatures were calibrated against NPL mercury-in-glass thermometers.

A general view of the whole apparatus showing the control panel is shown in Plate 4, with a closer view in Plate 5.

8.12 Gas analysis by thermal conductivity. A variety of methods were considered for following the reaction rate. This can be carried out by following in particular either the solid or the gas. For a reaction like the decomposition of a carbonate, continuous monitoring of the weight of the reacting solid, as used by Spencer and Topley (1929, 1931), and described by Topley and Whytlaw-Gray, can be used. Alternatively, the solid can be quenched at intermediate points during the reaction and the extent
of reaction identified by examination and measurement, or again by weighing. Both methods were discarded, the former because of the large size of the reactor bed, and the latter both because no definite conclusions could be reached by examination of the reacted carbonate, and because of the uncertainty involved in the quenching procedures.

It was therefore decided to concentrate on gas analysis. Absorption by caustic solution of the reaction gases was tried but found to be of limited accuracy and to suffer from non-continuous operation. Of the physical methods available, both infra-red absorption and thermal conductivity are suitable, the former being more expensive but capable of greater sensitivity. Finally it was decided to use the most obvious method, i.e. thermal conductivity (see Daynes).

The katharometer constructed was based on a Gow-Mac "Pretzel" cell, Type GM 9285/SS with "W2" filaments. This is a highly sensitive cell, with a response time of less than 1 sec., using a 4-filament (0.001 thou dia. tungsten) system shown in the wiring diagram in Fig. 8.8. The gas to be analysed is passed over filaments 1 and 3, while a reference gas for comparison is passed over filaments 2 and 4. The "out of balance" of the bridge caused by variation of composition of the analysis sample can be measured on a galvanometer or voltmeter. (The variation in thermal conductivity affects the temperature of the filaments and hence their resistance. The flow of gas through each half of the cell is recommended 50 ± 2 ccs/min., while the bridge current for
a nitrogen carrier with the cell at ambient temperature is normally 100 mA, maximum 160 mA. Bridge currents for a helium carrier are much higher because of its very high thermal conductivity; normally 250 mA, maximum 375 mA.

Because of the sensitivity of the instrument a constant current circuit was designed to supply the katharometer bridge, so that fluctuations such as those in mains voltage would not affect the calibration. This circuit is shown in Fig 8.8. The mains voltage was rendered steady at 230V by a 30w, 50 c/s constant voltage transformer. This voltage was then transformed to 20V and rectified, to supply a d.c. transistorised control circuit, based on a constant voltage Zener diode (Zd). The current range is set by the control fixed resistor $R_1$, while a limited variation of current is available via $R_2$. A constant current, actually set at 91 mA, was used as the bridge current.

The bridge out-of-balance potential was zeroed by a 3 ohm, 3-turn precision potentiometer, while the sensitivity of the output, i.e. the fraction of the potential output of the bridge taken by the recording device, was controlled by a 200 ohm, 10-turn precision potentiometer.

The out-of-balance voltage of the bridge was recorded on a Smiths Servoscribe multi-range recorder. The bridge was calibrated by mixing known flows of air and carbon dioxide, and passing 49 ccs/min. of this composite gas through the sample cell of the katharometer. This was compared with the same flow of "pure" air, and a plot made of the katharometer output at full
sensitivity versus carbon dioxide concentration. This is shown in Fig. 8.9.

The analyser was housed in a polystyrene-lined cabinet. The cabinet, made of sheet aluminium, was held at a constant temperature of $35 \pm 0.5 \, ^\circ\text{C}$ by a 15w bulb, with an additional 40w boost heater for bringing the cabinet to temperature quickly. The temperature was controlled by a bi-metallic thermostat, the temperature being kept uniform by a circulating fan. The control panel for the katharometer analyser can be seen in Plate 5.

The katharometer was highly sensitive to fluctuations in flow rate, to the extent that any increase in bridge current produced no greater sensitivity, due the proportionate rise in flow rate "noise".

The control circuit, control panel and cabinet were entirely constructed by the author.

8.13 Measurement of variables. As mentioned, the output from the katharometer was recorded on a Smiths Servoscribe recorder. This had an infinitely variable range from 0 to 0.8 mV to 0 to 20 V, with provision for zero suppression, and a choice of six chart speeds. A switch was incorporated in the recorder input so that two variables could be followed at once. Thus it was possible to follow the reaction or furnace temperatures as well as the concentration of carbon dioxide in the reaction gases. Most experimental results were obtained on the 10 mV range, with chart speeds of 120 or 600 mm/hr.

The compensating cables on the pre-assembled thermo-
couples were welded to copper leads, the junctions being immersed in melting ice. Measurement of furnace and reaction temperature was to the nearest $\frac{1}{4}^\circ\text{C}$.

All flow rates, including those of the katharometer samples, were measured by rotameters calibrated against wet gas meters.

3.14 Experimental procedure. A variety of slightly different procedures were used, but only the final variation will be described. Any deviation from this procedure associated with any of the results presented in the next Chapter will be noted with them.

Spheres of silver carbonate were made up in the manner described in Section 8.6, weighed when dry and placed singly into the reactor bed, being so distributed as to be in contact only with steel spheres. Also, the spheres were set in a single layer or two if the number of spheres used was too large, at a point mid-way through the bed, so that carbon dioxide produced by any particle should not affect the rate of reaction of any other particle, and so that any bed-end effects, especially heat transfer effects, would be minimised. A top view of the arrangement of particles in the bed is shown in Plate 3b. Otherwise, "rolled" coated celite particles were dispersed throughout almost the whole bed, a top view being shown in Plate 3c. In either case the weight of carbonate placed in the bed was known.

The bed was then raised into the reactor, through which carbon dioxide had already been passing for some minutes, the
furnace flange then secured, and the carbon dioxide flow main-
tained during the period in which the bed was warming up. This
period was from 60 to 90 minutes, the delay being caused partly
by the large heat capacity of the bed, but mainly because of the
lack of contact between the reactor bed wall and the inner wall
of the furnace block. Although the warm-up delay was inconvenient
the capacity of the bed for heat was so high that after starting
the reaction, the effect of poor contact between these two
surfaces was unimportant. Furthermore, not only did it provide
an opportunity to stabilise the katharometer before starting the
reaction, but it provided something of a standardisation of
"heat treatment" of the particles before reaction, which was
shown to be of importance by Spencer and Topley (1929). Once on
temperature, a further 5 to 10 mins. was allowed before starting
the reaction.

About 30 mins. before the start of the reaction, flows of
either nitrogen or air, whichever was to be used for the reaction,
were started through both cells of the katharometer, and the
current switched on, the bridge output being found to stabilise
in this period.

In certain experiments the temperature of the centre of a
live sphere was followed throughout the reaction. Early work
showed that merely allowing a thermocouple to pass into the centre
of a single particle was unsatisfactory due to heat transfer
along the thermocouple itself, so that for the majority of these
experiments four or five particles were beaded onto the thermo-
couple, the centre of the final particle being sensed by the hot junction. The particles were not moulded onto the thermocouple, but were bored delicately by hand with a No. 56 drill and slipped onto the sheath. In these experiments, both the particle temperature and the temperature within the bed about 1" from this particle were measured. For the latter measurement, a thermocouple was terminated in a short 1/8" dia. cylinder of brass. In these temperature experiments the reaction gases were not analysed.

When the bed temperature had steadied, the carbon dioxide flow was discontinued, and the reaction gas immediately admitted to the reactor at the required flow rate, measured on the rotameter after the furnace, as a small purge was allowed to leak through the furnace vent valve mentioned earlier. The control valve on the exit rotameter was left fully open to ensure that the reaction pressure was almost atmospheric. One minute after start-up the flow of reaction product gas to the katharometer was started, this to ensure that a shock load of 100% carbon dioxide did not reach the cell. The exit gas carbon dioxide concentration, and the temperature of the inert section of the bed were monitored throughout the reaction, which lasted from 5 to 180 mins.

When the reaction was complete, the bed was removed, and in certain "sphere" reactions the product solid was weighed.

In experiments to determine the equilibrium pressure of silver carbonate, the decomposition was allowed to continue at a high rate for a few minutes. While measuring the live sphere
temperature, successive mixtures of carbon dioxide/air were then introduced to the reactor so that the particle temperature cycled above and below the bed temperature, above if the CO\textsubscript{2} concentration was high enough to enable the reverse exothermic reaction to occur, and below otherwise. The CO\textsubscript{2} concentration, at which the particle and bed temperatures became equal, was taken as the equilibrium pressure. A special "bomb" was designed and made in order to measure the equilibrium pressure by direct measurement of developed CO\textsubscript{2} pressure, but no experiments were carried out with this equipment. A similar cycling technique was used in certain experiments to determine the effect of water vapour on the reaction, wherein successive changes in water vapour content were made throughout a single reaction. All such experiments in which changes were introduced during the reaction were followed by means of particle temperature, and never by exit gas composition.

Note: All apparatus other than intricate machined parts were designed and constructed by the author, with the useful guidance of academic and workshop staffs of the University of Edinburgh and Heriot-Watt University.
CHAPTER 9

EXPERIMENTAL SYSTEM: RESULTS AND DISCUSSION.

9.1 Introduction. In Chapter 7 the findings of other works on the decomposition of silver carbonate were discussed, while in Chapter 8 the material and apparatus used for this study were described together with the procedure used for experimentation. The results of these experiments will now be presented and discussed.

The experimental work is divided into three obvious sections. Firstly, the reaction rate experiments carried out initially to obtain a guide towards future work; secondly a collection of experiments of various types which did not involve direct measurement of the reaction rate, but which made use of a temperature-following technique; and finally, reaction rate experiments carried out under various conditions to study further the nature of the decomposition. Both before and during this work some purely qualitative work was also undertaken. This involved mainly physical examination of reacted and partially reacted specimens. The results will be pursued under the above three headings, preceded by a short discussion on general aspects of the reaction.

9.2 Qualitative observations. The silver carbonate used was a pale yellow powder. This powder darkened slowly on exposure to sunlight, especially when moist, and very markedly when moist and in contact with steel and even more so brass. Drying the moulded
spheres or the coated celite particles in sunlight resulted in a very thin dark layer on the surface which could be removed simply by touch. Consequently most drying was accomplished in a darkened oven, and below 60°C to avoid decomposition. Warming the carbonate powder in an atmosphere containing a pressure of carbon dioxide higher than its equilibrium pressure caused a small amount of decomposition. This is due to premature decomposition at unstable localities in the crystal lattice such as edges and fissures, and has been reported by Spencer and Topley (1929). The B.E.T. surface areas of the fresh carbonate and carbonate which had been heated to 200°C and cooled to ambient again in an atmosphere of CO₂ were found to be 0.54 and 0.69 m²/gm., respectively. When fully decomposed to silver oxide via the reversible reaction,

\[
\text{Ag}_2\text{CO}_3 \quad \text{Ag}_2\text{O} \; - \; \text{CO}_2
\]

the B.E.T. surface area was found to be 1.11 m²/gm., although further measurements will be discussed later. During decomposition an exceedingly thin white layer was sometimes formed on the surface of the carbonate particles. This layer was taken to be metallic silver from thermal decomposition of the oxide as shown by Culbertson, and also noticed by, although not identified by, Baasel. Attempts to identify the carbonate, oxide and pure silver by X-ray powder diagrams proved unsuccessful. On one occasion, carbonate was decomposed in the furnace and allowed to remain there at about 200°C for some days. On removing the specimen it was found to be pure white throughout. Normally,
however, the extent of decomposition to silver was very slight and often completely absent. Decomposition to silver, which as has been said was normally confined to a very thin surface layer, seemed more apparent when the original carbonate sample had been exposed to light before decomposition. This would explain the thinness of the surface layer, which could not be put down to diffusion limitations in the carbonate/oxide as this was a very open structure.

Many experiments were conducted towards identifying the possible presence of separate reacted and unreacted zones within the $\frac{1}{8}$" spheres by interrupting decomposition reactions and splitting the particles. This procedure gave confusing results which in the main were attributed to unrepresentative or artificial conditions during the trials in question. On occasion, fairly distinct gradations in colour could be identified while at other times partially decomposed specimens were uniform in colour. Furthermore, fully decomposed specimens sometimes showed variation in internal colouring. It was thought that this was due to varying temperature histories within the particles, and it was also noted that fully decomposed particles were blacker when decomposed at higher temperatures than would be expected of pure oxide, which is a dark brown powder. This dark brown colour was obtained at lower temperatures.

On the basis of these observations it was obvious that an interfacial reaction in respect of the $\frac{1}{8}$" pellet, such as is found commonly in reactions in densely packed and crystalline
materials, did not occur, but that it was possible that due to either mass or heat transfer limitations the reaction rate throughout a carbonate pellet might not be constant. This absence of an interface within the large pellets was also confirmed by consideration of the mass transfer rates within pellets compared to actual reaction rates. This will be discussed later.

Transmission electron microscope photographs of the decomposed material are shown in Plate 6a,b.

9.3 Section 1 - Preliminary measurements of reaction rate.

These first experiments were carried out using 1/4" moulded spheres distributed in a bed of inert steel spheres, and using a carrier gas of air drawn from the surroundings by the compressor and left untreated. Thus a gas partially saturated with water vapour was passed through the reactor. The procedure for these trials was slightly different to that outlined in Chapter 8 in that the warm-up in carbon dioxide was followed by a period of 2 mins. during which a high flow, 1-2 cu.ft./min., of air was blown through the reactor to remove the carbon dioxide. The temperature of this high flow of air was maintained by the external gas preheater. The experiments were in two sections, the first being carried out in a less controlled manner using carbonate moulded in inaccurate moulds, although this was later seen to be of no significance, while the later experiments were more carefully carried out, using accurately machined moulds. The concentration of carbon dioxide leaving the furnace was followed on the katharometer, and with a knowledge of the flow
rate and the amount of carbonate in the bed, the reaction rate could be obtained. The resulting rate histories are shown graphically in Figs. 9.1 for the first set and 9.2 for the second. Reaction conditions and other information are given in Tables A.1 and A.2 respectively.

If the reactions were occurring under isothermal conditions and in the absence of concentration gradients, the reaction rates at equal conversions would follow the Arrhenius law in regard to temperature, so that,

\[ \text{rate} \propto \exp\left(-\frac{E_c}{R' T_G}\right) \]

so that \( \ln(\text{rate}) \) versus \( 1/T_G \) is a straight line with a slope of \( -E_c/R' \) where \( E_c \) is the activation energy for the reaction, and \( T_G \) is the furnace temperature. The initial reaction rates, obtained by extrapolation to zero time of the katharometer output are given in Tables A.1 and A.2, and shown in the above form in Fig. 9.3. The rates at 50\% and 75\% conversion have been obtained for the second set of experiments by square counting and are given in Table A.3, and plotted in Fig. 9.3.

The most obvious result, especially from the second set of experiments, is the convex rather than concave shape of some of the rate/time curves. As was shown in Chapter 4 the interfacial theory of reaction predicts that for solids of a spherical or cylinder-type shape the rate/time curve is usually concave. Thus it was concluded that either the reaction did not follow the model proposed in Chapter 4 or that the reaction was influenced
by other considerations such as heat or mass transfer.

Mass transfer limitations associated with the \( \frac{1}{4} \)" sphere can be ruled out on consideration of diffusion rates in the boundary layer and in the macro-pores of the pellets. Mass transfer rates are discussed in Appendix C for the boundary layer where the rates have been calculated specifically for the \( \frac{1}{4} \)" spheres, as a function of flow rate and temperature and are given in Fig. C.2 and in Table C.2. The rates are evaluated as the maximum potential rates of mass transfer if this step was to be controlling, i.e. the reaction step is potentially very fast. In such circumstances the mass transfer driving force is highly dependent on temperature, to the extent of the temperature dependence of the equilibrium carbon dioxide pressure. As an example of the results it can be seen that at \( 150^\circ \text{C} \) and a flow rate of 1 l/min. through the reactor bed, the mass transfer rate is \( 8.8 \times 10^{-4} \) lbs. CO\(_2\)/hr. whereas in Run 19 (Fig. 9.2 and Table A.2) the maximum rate is less than \( 1 \times 10^{-4} \), and this at a temperature of about \( 165^\circ \text{C} \). Hence it can be said that any boundary layer limitation on the overall rate is negligible.

Diffusion rates within the macro-pores of the pellets can be easily shown to be rapid by reference to Sections 3.13 and 3.14, and to Figs. 3.7 and 3.8. The example quoted in Section 3.14 is at \( 25^\circ \text{C} \) so that the rates would be very much increased at \( >150^\circ \text{C} \). Although the example considers diffusion without reaction it is obvious that even the shortest reaction times measured in this work are very much greater than the mass
depletion times, so that again it can be assumed that diffusion rates within the solid macropores do not play an important role in determining the overall reaction rate. Note that it was only possible to obtain quantitative information on this constraint by examining the effective diffusion coefficient within the moulded carbonate both before and after reaction. This was carried out by a novel technique described in Appendix B. The diffusibilities, i.e. the factors by which the free diffusion coefficient of CO₂ in air must be reduced, of the two solids were found to be 0.44 and 0.47 respectively, which are not considerable reductions.

If mass transfer limitations can be ruled out, and assuming that the reaction should follow the proposed model, then the observed departure from kinetic control must be explained by heat transfer effects. Boundary layer heat transfer rates have also been obtained in Appendix C and are presented as a function of flow rate in Fig. C.2 and Table C.2. The fact that heat transfer has a considerable influence on the reaction rate will be considered in Section 2 of the results, associated with the measurement of the solid temperature during reaction.

Further evidence that the overall rate of reaction is not solely dependent on kinetics is obtained from the plot of ln(rate) versus 1/T₀, Fig. 9.3, where rates at X = 0, 0.5, and 0.75 have been plotted. For kinetic control these curves should be straight lines, but it can be seen that at high temperatures the rates fall below the hypothetical straight line at each of the values of conversion. At low temperatures the points can be
seen to approach a straight line corresponding to an activation energy of about 23 Cals/gm.mole, similar to the values obtained by Spencer and Topley (1929). Fig. 9.3 will be referred to later in connection with boundary layer heat transfer effects on the rate at $X=0$.

9.4 Section 2 - Reaction temperature measurements. The actual temperature within the reacting spheres was measured primarily to ensure that conditions within the bed were isothermal, although this was far from what was found. In nearly all the cases in which reaction temperature was measured the thermocouple was "beaded" with a number of spheres as described in Section 8.13, and in most cases departure of reaction temperature from furnace or gas temperature was found to be significant. The solid temperature fell rapidly on removing the carbon dioxide from the bed, then climbed back to furnace temperature throughout the run.

9.4.1 Preliminary experiments. The first experiments of this kind were done under conditions similar to those used in the rate measurements in Section 9.3. Flow rate through the bed was found not to affect the results so this was not noted but was kept below 2 l/min. The runs were carried out at five temperature levels and a simplified illustration of the results is given in Fig. 9.4. More complete details of Runs 28 to 54 are given in Fig. 9.6 and Tables A.4 and A.5. Runs 28 and 29 were carried out with only a single live sphere on the thermocouple and can be seen from Fig. 9.7 to give quite different results, caused by excessive heat conduction along the thermocouple into the solid.
The initial maximum temperature drops for each of the experiments are shown in Fig. 9.5 as a function of furnace temperature, and can be seen to follow a regular pattern. The experiments carried out with only one particle on the thermocouple are seen to give quite different results.

The explanation for the temperature drop can quickly be appreciated. Taking Run 16 as an example, it can be seen from Fig. 9.2 that at 6.5 mins. the reaction rate is \(2.4 \times 10^{-4}\) lbs. CO\(_2\) per hr. Comparing this run with the temperature profiles in Fig. 9.4 (e.g. set 4) a corresponding temperature drop of \(8.0^\circ C\) is obtained. This point condition has been chosen because at this time during the reaction the temperature of the solid is virtually constant, so that all the reaction heat is being supplied by an identical heat flow through the boundary layer. Assuming the whole \(\frac{1}{4}\)" sphere to be at the same temperature, i.e. there is no conduction limitation within the particles themselves, a heat transfer coefficient can be obtained as

\[
h_B = \frac{0.00024 \times 454 \times 19.6 \times 0.9}{44 \times 4 \times \left(\frac{2.54}{8}\right)^2 \times 8.5}
\]

\[
= 0.004 \text{ Cals/hr.cm}^2 \cdot ^\circ \text{C}
\]

\[
= 15 \text{ Btu/hr.ft}^2 \cdot ^\circ \text{C}
\]

where 19.6 Cals/gm.mole is the heat of reaction and a factor of 0.9 has been introduced to allow for the material displaced by the thermocouple. On comparing this value with the calculated heat transfer coefficients from Appendix C, Table C.1, i.e. 3.1 Btu/hr.ft\(^2\cdot^\circ\)C, it is obvious that the majority of the heat
required for reaction is obtained by the point contact of the live spheres with the steel spheres. Any inclusion of temperature gradients within the solid would increase the required boundary layer coefficient and thereby increase the discrepancy between the actual and calculated coefficients. Examination of reacted particles revealed small circular indentations, normally slightly darker than the bulk of the solid, about 1mm. dia., and numbering 6 or 7. Thus the contacts constituted approximately 16% of the live sphere surface.

From these considerations, which are typical of all the results and not just of the example given, it can be argued that the likelihood of temperature gradients within the particles is small except in the vicinity of the point contacts. Thus it was deduced that the control of the overall rate was shared between kinetics and "boundary layer" (including point contact) heat transfer, certainly in the intermediate and lower temperatures.

9.4.2 Application of temperature runs to rate measurement.

It can now be seen why the \( \ln(\text{rate}) \) versus \( \frac{1}{T} \) plots in Fig. 9.3 did not give straight lines. Reaction temperatures should have been used. These temperatures can be found from Fig. 9.5 and are listed in Table A.3. Re-plotting \( \ln(\text{rate}) \) at \( X = 0 \) using these reduced temperatures greatly alters the position and slope of the line, which now becomes straight, also in Fig. 9.3, with an activation energy of about 30 Cals/gm. mole. This is quite conclusive evidence that the reaction is mainly controlled by boundary layer heat transfer. The high activation
energy, compared with that of Spencer and Topley is thought to be caused by the presence of water vapour, as will also be seen later.

9.4.3 Reaction rates from temperature measurements. If the reaction is controlled by boundary layer heat transfer then the difference in temperature between the furnace and the reacting particle is an indirect but proportional measure of the reaction rate. Thus the temperature profile curves are simply inverted versions of the reaction rate histories. Hence the same convex rather than concave shape can be detected in the temperature histories as for the rate histories. The same general shape of curve can be seen also in the endothermic examples given in Chapter 6, and will be seen again in later discussions.

The areas enclosed between the temperature history curves and the constant furnace temperature should obviously always be equal. The areas have been obtained by square counting and can be seen to reduce to smaller integrals with increasing temperature, but not appreciably. The small change could probably be explained by the greater importance of heat conduction within the particle at higher reaction rates. From the integrated areas the temperature difference, $\Delta T$, at conversions of 0.25, 0.5 and 0.75 have been obtained and are shown in table A.5. From the above argument $\ln(\Delta T)$ versus $1/T_i$, should give identical results to those obtained from rate measurements. These results, taken from Fig. 9.4, are shown in Fig. 9.8, with results at $X=0$ shown against both furnace and reaction temperature. Again the same
result as with the rate plot in Fig. 9.3 is obtained. The lowering of the activation energy at high conversions is thought to be due both to experimental error and perhaps to a diffusion limitation within the discrete particles of carbonate.

9.4.4 Temperature measurements with controlled humidity.

Further temperature experiments were carried out with dry and humidified nitrogen as the reaction product carrier gas, at similar flows and conditions to those carried out above. A slightly modified procedure was used, corresponding to that outlined in Section 8.14. The results of the tests carried out in an atmosphere of N₂ are given in Table A.6 with some of the temperature profiles plotted in Fig. 9.9. The results for humidified tests are given in Table A.7 and Fig. 9.10. Plots of \( \ln(\Delta T) \) at \( X = 0 \) against both reaction and furnace temperatures are given in Fig. 9.11 corresponding to Fig. 9.8 for the previous results. The initial temperature drops are shown as a function of temperature in Fig. 9.12.

The most interesting results from Fig. 9.11 are the differences between the activation energies for the dry and wet Runs when plotted against the reaction temperature. For the dry Runs an activation energy of approximately 23 Cals/gm.mole is obtained whereas for the wet Runs, again a value of 30 Cals/gm.mole pertains. The only explanation for this lies in the presence of water vapour, although the exact reasons are not obvious.

One other significant feature of these results can be seen by comparison of Fig. 9.10 with Figs. 9.9 and 9.4. The
temperature histories of the humidified Runs show a characteristic "square" shape compared to the triangular nature of the other two sets. This is again due to the increased water vapour content of the reaction gas.

9.4.5 The dissociation pressure of carbon dioxide.

The facility to measure the reacting solid temperature opened up further possibilities regarding investigation of the decomposition reaction. Obviously, if the solid temperature is lower than that of the furnace the decomposition reaction must be taking place, while if higher then the recombination (exo-thermic) reaction is occurring. By the same reasoning, if the solid and furnace temperatures are equal then the reactions have ceased. The only reasons for the reaction to stop are if the solid is completely converted to either oxide or carbonate during decomposition or recombination respectively, or if the pressure of carbon dioxide in the vicinity of the solid sample is equal to the thermodynamic equilibrium pressure. This provides an extremely simple method of measuring the equilibrium pressure. The procedure for the measurement has been described in Chapter 8.

The results of the equilibrium pressure measurements are given in Table A.8 and plotted as a function of $1/T_G^0 K$ in Fig. 9.15, being compared with the values obtained theoretically in Appendix E. Also shown in Fig. 9.15 are the results of Spencer and Topley (see Table 7.2), Watanabe (see Eq. (9.1) below), and Culbertson.

Watanabe: $\log_{10}(P_e)'ats. = 7.904 - \frac{3855.9}{T_G^0 K} \quad (9.1)$
Although most results were obtained by the "static" procedure described previously, three results were obtained by the more "dynamic" method of holding the CO\textsubscript{2} pressure constant and allowing the furnace temperature to change, at the same time observing whether the solid temperature is greater than or less than that of the furnace. The point at which the two become equal give the temperature associated with the particular CO\textsubscript{2} pressure. The results of these three experiments can be seen in Fig. 9.15 to be little different from the static experiments, which is very significant in throwing doubt on the results of Culbertson which were also obtained by a "dynamic" method. Culbertson did not measure the reaction temperature, i.e. the actual temperature of the reacting solid, so that it is possible that there was a large difference between the temperature of the solid and that of the furnace. For example, for a dissociation pressure of 1 atmosphere of carbon dioxide, the dissociation temperature measured by Culbertson is some 35\textdegree{}C lower than the results obtained in this work. Static experiments carried out by Culbertson did conform more closely to the values obtained in this work.

The results in Fig. 9.9 indicate a degree of scatter, but do tend to follow the thermodynamic line rather than that of Spencer and Topley. This is partially fortuitous as a different source of thermodynamic data would give different results.

9.4.6 The effects of water vapour. It was shown earlier that water vapour has a significant effect on the apparent activation energy of the reaction. Further information on the effect of
water vapour was obtained using the technique of changing reaction conditions during the reaction, i.e. specifically to alter the composition of the gas passing through the reactor.

The first significant reaction of this kind was Run 95, the history of which is shown in Fig. 9.13. The reaction was begun in an atmosphere of dry air (dried by Si-gel). After about 5 mins. this flow was replaced by 100% R.H. air (room temperature humidification) and after a further 5 mins. by air drawn directly from the surroundings, i.e. of an intermediate R.H. This was then replaced by dry air, then again by 100% R.H. air, and finally by dry air once again. The effect of these changes can be seen in Fig. 9.13. After the first change the difference in temperature, $\Delta T$, between furnace and solid changes from 7 to 11°C, i.e. the reaction rate has increased by a factor of 11:7. However, purely on the basis of temperature, and the Arrhenius effect on the reaction rate, the rate should have fallen by a factor given by,

$$\exp(-\frac{E_c}{R'T_2}) / \exp(-\frac{E_c}{R'T_1}) \quad \text{or} \quad \exp(\frac{E_c}{R'} \cdot \frac{T_1-T_2}{T_1T_2})$$

where $T_1$ and $T_2$ are the temperatures of the solid before and after the change respectively. Using $E_c=23$ Cals/gm.mole, this can be evaluated as 1:1.25, so that in effect the rate has increased on addition of water vapour by a factor of $(11/7) \times 1.25$ or about 2. The second time that the dry gas is replaced by the humidified gas the rate increases by an apparent factor of 9.75:7 but on taking the temperature effect into consideration, by a
real factor of about 1.6, i.e. the effect persists but to a lesser degree. A further point to observe from Fig. 9.13 is that the rate remains constant from the first section at 0% R.H. to the second, whereas considerations of solid depletion would indicate that the rate should be less. Thus it can be argued that an intermediate "boost" of water vapour during an otherwise "dry" Run causes a subsequent increase in the reaction rate under dry conditions.

The very pronounced effect of water vapour on the decomposition reaction can be seen more vividly from Run 96, Fig. 9.14. This result has been copied directly from the recorder chart, and due to an electrical fault no quantitative values can be placed on the drops in temperature. It can be seen that water vapour has a slightly diminishing effect as reaction proceeds.

The effect of the intermediate boost of water vapour on an otherwise dry reaction is shown in Runs 121 and 222, Fig. 9.16. It can clearly be seen that the subsequent rate in dry conditions is higher than would have obtained if the reaction had continued with the water vapour boost (note: Run 121 is qualitative only, having been copied direct from the recorder chart while electrical trouble was being experienced).

An example of humid reaction with an intermediate dry "brake" on the rate was obtained in Run 223, Fig. 9.19. No significant conclusions can be drawn.

Spencer and Topley (1929) found that water vapour had a saturation effect, in that beyond a certain level of water vapour,
this level being a function of temperature, no rise in reaction rate was obtained. This point was investigated in Run 152, Fig. 9.18, by changing between various levels of water vapour and following the solid temperature. It can be seen from the diagram that increases in water vapour concentration produce a gradually diminishing increase in reaction rate. Other experiments showed that this "saturation" level of water vapour was indeed of the same order as 100% R.H. at room temperatures.

The results of Run 121, Fig. 9.16, suggested that had the Run continued without the 100% R.H. boost the reaction may not have reached completion. Run 140, Fig. 9.17, shows that this is indeed the case. When the reaction appeared to be virtually complete water vapour was introduced and a further endothermic peak obtained. This point can also be seen by comparing the encompassed areas of the curves in Fig. 9.9 (dry Runs) with the larger areas (i.e. more extensive reaction) in Fig. 9.10 (humid Runs). The extent of the dry reactions appears to diminish at higher temperatures.

9.4.7 The reverse reaction. Any attempts to recarbonate the oxide formed by decomposition resulted in a restricted conversion, limited to less than 30% conversion. Such reverse reaction temperature histories are shown in Fig. 9.20. The area enclosed by the curves was integrated and compared with that obtained for the decomposition runs, giving the extent of reaction, which was found to increase with temperature, but was always incomplete. The conditions of the reactions are given in Table A.9. This
conversion restriction was also noticed by Spencer and Topley (1931). Recarbonation of the oxide was carried out always with 1 atm. CO₂ in the reactor so that at higher temperatures the driving force \((P-P₀)\) became less. Hence the pore blocking action of the surface carbonate is reduced when diffusion limitations are reduced at higher temperatures. The extent of the reaction was also found to be increased, reversibly, in the presence of water vapour and to be extended after apparent completion on the introduction of water vapour. The reverse reaction was not initiated in some cases when the CO₂ pressure was only slightly above the dissociation pressure. It can be seen from Table A.9 that in fact the difference between these two pressures can be quite large. The effect can be put down to the difficulty of nucleation without a high driving force.

9.4.8 Cycling operation. Repeated decomposition and recarbonisation of the silver compounds were necessary for the space application of Culbertson. Spencer and Topley found that cycled operation of this kind finally gave a product with reproducible properties. Experiments of this kind were found to give immediately reproducible cycled operation with the "amorphous" carbonate used. An example of this type is given in Fig. 9.21. The effect of water vapour was also investigated in this test by carrying out the first sets of reaction in the presence of water vapour, and then excluding it. A reduction in the rate and extent of reaction can be noticed.

9.5/
Section 3 - Reaction rates with controlled humidity.

As a result of the distinct divergence from isothermal conditions in the reacting spheres, the reaction rate was measured by coating celite particles as described in Section 8.7, on the assumption that the heat capacity of the celite and the close contact of the small amount of carbonate with the celite would obviate self-cooling. Also a few Runs in which the weight of the samples, originally 1 gm. \( \text{Ag}_2\text{CO}_3 \), was measured throughout the reaction, were carried out and the results shown in Fig. 9.22. After a short initiation section, probably caused by the delay in flushing carbon dioxide out of the reactor, the reactions proceed along lines similar to those corresponding to kinetic control of reaction in a sphere. The exact details of the trials, carried out in the Warren Spring Laboratories, were not known but the important conditions are noted in Fig. 9.22. At the higher temperature, 190°C, it can be seen that the reaction is faster in an atmosphere saturated with water vapour at room temperature. The rates for these reactions at initial times, taken from the initial slope, were 2.10 and 1.27 moles \( \text{CO}_2 \)/mole \( \text{Ag}_2\text{CO}_3 \) hr. For the Runs at a lower temperature, 170°C, the two results are almost the same. If the first section of the "dry" Run is ignored, then the two rates are this time 0.67 and 0.49 for the wet and dry cases respectively. These rates represent activation energies of 23.9 and 19.9 Cals/gm.mole respectively, with the ratio of rates as 1.65 and 1.37 at 190 and 170°C respectively. The extent to which self-cooling occurred in these Runs, in which
the carbonate powder was present only as a powdered mass, was not measured, but it is evident from the low activation energies.

9.5.1 Rate runs under humid conditions. The rate of decomposition of the carbonate was followed by exit gas analysis, while passing air humidified at about 22°C through the reactor bed at a flow rate of about 1 l/min. for both carbonate present on celite particles and as 1\(\frac{1}{4}\)" spheres. The conditions and histories of these Runs are given in Tables A.10 and A.11, and A.12 and A.13 respectively. The time zero of these reactions related to the output of the katharometer was determined by following the normal procedure for a reaction but without any carbonate in the bed. This was repeated several times at various flow rates and allowed the flush-out and sample residence time delays to be subtracted from the reaction history. This left a period of 1 to 1\(\frac{1}{2}\) mins. at the beginning of each reaction in which the reaction rate was not known. Consequently, for high temperature Runs of short duration accurate results were not obtained, and extrapolation of the reaction history back to zero time was difficult.

The usual plot of ln(initial rate) versus 1/\(T^0\)K was plotted for furnace temperature, and in the case of the spheres also for reaction temperature, this temperature being obtained using Fig. 9.12 (humid Runs). This plot is shown in Fig. 9.23. For the celite Runs an activation energy of the order of 30 Cals/gm.mole is again seen. For the spheres the activation energy is much reduced when using furnace temperature, and the
reaction rates are also much less at all temperatures. When the plot is corrected for reaction temperature, although an activation energy cannot reliably be obtained from the points, it can be seen that the majority of the results virtually coincide with those obtained for the celite. This is significant evidence of the absence of diffusional resistances in the control of the reaction. Examination of the celite histories in Table A.11 also shows the typical kinetic control as shown in Fig. 8.3.

9.5.2 Computer simulation of humid Runs. On the assumption of no boundary layer diffusional limitations, and that the only important factors other than kinetics are heat transfer to the \( \frac{1}{4} \)" sphere via a "boundary layer" coefficient, and diffusion within the discrete particles within the pellet, a model of the reaction can be set up on the same lines as program 8, but this time of a dimensional nature, giving actual values of reaction rates and temperatures. Thus it is assumed that the reaction rate is a constant throughout a \( \frac{1}{4} \)" sphere but that the reaction is not isothermal.

The rate of reaction of a discrete particle, modelled as a sphere of radius 0.9142\( \mu \) as described in Section 8.2, is given by the equation,

\[
\text{rate} = \frac{4\pi x^2 \left( P_K - P_G \right)}{R'T_G} \left[ \frac{P_T - P_G}{P_T - P_D} \frac{1 - \frac{x_1}{x}}{x_1^2} + \left( \frac{x_1}{x} \right)^2 \kappa \epsilon \exp\left( -\frac{E_c}{R'T_1} \right) \right]^{-1}
\]

(9.2)

where \( x \) is the radius of a discrete particle of silver carbonate within the pellet, and the kinetic rate has been defined as,
\[
\text{rate} = 4\pi x_1^2 \frac{k_c \rho}{R'T_G} \exp\left(-\frac{E_c}{R'T_1}\right) \left(\frac{P_T - P_i}{P_K}\right)
\]  

so that \(E_c\) is the observed activation energy of the reaction when \(P_i\) is zero, less the activation energy of the equilibrium pressure, \(P_e = P_K\), taken from the results of Watanabe given in Eq. (9.1). Ignoring heat conduction resistance in the solid, the value of \(T_1\) can be obtained by the equations given in Chapter 6, using the same numerical techniques. Other details of the model included; a specific heat of 25 cal/gm.mole°C (average of carbonate and oxide); an allowance for CO\(_2\) in the gas round the 1" sphere, evaluated by assuming that each of the 80 (approx.) spheres in each layer in the bed are associated with 1/80th of the gas flow, so that the CO\(_2\) evolved into this gas flow results in an average CO\(_2\) concentration round the sphere; although the model can be applied also to celite runs, the program used for the model, Computer program 12, Appendix G, also calculates the rate of reaction of a 1/4" sphere, taking into account the voidage of this material.

Using this model simulation an attempt was made to reproduce the results of the humid reactions, it being assumed that the diffusion in the discrete particles was rapid. The results were very encouraging, although tediously achieved. An example of the degree of achievement is shown in Fig. 9.24. The continuous lines represent the results of Runs 247 (celite) and 239 (spheres) carried out at almost the same furnace temperature.
The difference between the rate histories is extreme. The broken lines are the results of Computer program 12 using a value of $k_c^0$ of $\exp(15.5)$, and an activation energy of 32 Cals/gm.mole, and using the same heat transfer coefficient for the sphere as obtained in Section 9.4.1. For the celite Run, of course, isothermal operation was assumed. Agreement with the celite Run was achieved by adjusting $k_c^0$, using this value subsequently to evaluate the sphere result. As can be seen the degree of agreement is good. Again, this is evidence of the boundary layer heat transfer control of the overall rate of reaction in the sphere.

The temperature history of the sphere at a furnace temperature of 189.8°C, as obtained by the simulation, is shown in Fig. 9.25, to be compared with those in Fig. 9.10.

9.5.3 Rate Runs under dry conditions. Many experiments were carried out in a similar manner to those above but with dry gases passing through the furnace; either air or nitrogen. The conditions and histories for these runs are given in Tables A.14 and A.15 for celite and in Tables A.16 and A.17 for spheres. Other runs carried out using the brass blocks mentioned in Section 8.8 were also carried out but are not reported.

It was found impossible to usefully compare these runs with those carried out in humid conditions in a quantitative manner. However, it was obvious from the tests that the absence of water vapour seriously hindered the progress of the reaction. This effect can be seen by comparing the histories of the two humid examples from Section 9.5.2 with two results at similar
temperatures obtained in the absence of water vapour. All four histories are shown in Fig. 9.26. The initial rates of reaction for the dry runs were impossible to obtain, as the rate fell very rapidly initially. Hence an activation energy could not be obtained. This rapid fall off in rate can be seen for the dry celite run in Fig. 9.26. Similar results were obtained for the spheres, especially at higher temperatures. Activation energies at later values of conversion again could not be achieved as it was evident from many, though not all, of the results in dry conditions, that the degree of decomposition when the reaction appeared to be complete was not 100%. In some cases conversions of <50% were obtained. This effect was not reproducible and followed no logical pattern.

The initial rapid fall-off in rate and the generally lower rates, indicated a diffusion limitation caused by the absence of water vapour. Whether the water vapour also had a catalytic effect could not be determined because of the possibility of determining whether the initial rates were the same as those obtained in humid conditions.

9.6 Photographic examination. Plate 6a,b shows Transcope transmission micrographs of the oxide obtained on decomposition. It was noticed from these pictures that the surface of the particles was no longer smooth. Obviously, in the decomposition the resulting oxide is more "open" than the carbonate, this being evident also from the higher B.E.T. surface area (Section 9.2). Thus the open structure of the oxide allowed further carbon
dioxide to escape from the inside of the particles. This "furry" appearance was much more clearly seen in the reflection photographs taken on the stereoscan microscope. The smooth carbonate and the furry oxide are compared at different magnifications in Plate 7. These photographs again show that the process of decomposition results in the formation of an oxide structure made up of much smaller crystal units than the carbonate, thus allowing free exit of carbon dioxide from the undecomposed interior of the particles.

If water vapour has a chemical effect on the decomposition reaction, it is possible that at the same time the water vapour would affect the oxide lattice formation. This was tested by photographically comparing the oxide obtained by decomposition of carbonate in dry conditions with that obtained in humid conditions. Both of the decompositions were carried out at 200°C and the results of the photographs are given in Plate 8. A most striking difference was found between the two cases. The broken surface of the oxide is much less obvious for the oxide obtained by dry decomposition than that obtained in humid conditions. This indicates that the presence of water vapour does affect the resulting structure of the oxide. B.E.T. area measurements of the two materials gave further evidence of this, from an area of 1.65 m²/gm. for the dry oxide to an area of 1.98 m²/gm. for the other.

Thus it would appear that water vapour so affects the subsequent structure of the oxide lattice or crust surrounding
the undecomposed carbonate that carbon dioxide can escape freely from the core in cases where water vapour is present during the reaction, but is restricted by a tighter oxide formation when water vapour is absent. This point will be further discussed in Chapter 10.
10.1 Theoretical section. The most obvious and important conclusion which can be drawn from the theoretical section of this study is the effect of the inclusion of a transient heat capacity term in the energy balance of the sharp interface theory. This has shown that for exothermic reactions the previous concepts of thermal instability were at best only a rough indication of the possibility of practical existence. The present work has shown also that the problem of theoretical simulation of an exothermic reaction must be approached with specific regard to the circumstances of the particular system. The transient theory still needs further sophistication, especially to take into account the effects of radiation from the particle, this important point having been mentioned in Chapter 5. A specific exothermic reaction should be selected for comparison with this new theory. From such a study the transient and purely steady-state theories could be further compared.

Solution of the general equations relating to the diffuse theory outlined in Chapter 3 would add to the work of Lacey et al and open out the theory of reactions in porous solids, which is as yet in its infancy, due perhaps to previous concentration on the sharp interface theory.

No theory, of course, is of any use unless applied to practical examples. Although this was attempted with the silver
carbonate decomposition system, the comparison could be taken further, particularly in the respect of the effects of diffusion limitations. Other experimental systems could also be used for the comparison.

10.2 Experimental system. The results of the experimental system illustrated two main points.

Firstly, a general point relating to any endothermic reaction, the extent of control of the reaction by heat transfer to the decomposing moulded spheres of silver carbonate. This control resulted in a greater emphasis on heat transfer considerations than on considerations of diffusion. This represents a significant change in the approach to such studies, which have in the past tended to ignore temperature effects, perhaps resulting in mistaken conclusions. Significant among studies of this kind were those of Centnerszwer and Bruzs, and Culbertson, and it may be that certain of the anomalous results obtained in these studies could be put down to lack of attention to heat transfer. The degree of correspondence between experimental and theoretical results in this work showed that the theoretical approach which was used for non-isothermal reactions was worth while.

Secondly, the effect of water vapour on the decomposition of silver carbonate was taken further. Spencer and Topley found that it was probable that water vapour had a dual effect in assisting the reaction. These were assistance to the rate of diffusion of carbon dioxide from the reaction site, and a
catalytic effect associated with the reaction itself. Both these effects were confirmed in the present work, but the results also suggest that the two effects are in fact one. The distinct difference between the initial temperature drops for the dry and humid results with the $\frac{1}{4}$" spheres showed that even the initial rate of reaction is increased by the presence of water vapour, which suggests a catalytic effect. This difference between the experiments carried out in which the reaction rate was measured in dry and in humid conditions also emphasises an effect of water vapour but does not differentiate between catalytic and diffusion effects. Even the temperature Runs in which dry gas was humidified at a later point in the reaction points only to an effect of water vapour which could be catalytic and could be diffusional.

Perhaps the most significant results on the effect of water vapour was the photographic evidence obtained in Plate 8. This suggests that the presence of water vapour at the reaction site results in a different oxide lattice formation, giving perhaps integral structures with a lesser number of molecules. This would result in a more open structure, allowing higher diffusion rates, but the basic reason for the higher rate would be a chemical one. The fact that the extent of reaction in dry runs is sometimes less than 100% at apparent completion again could be explained by the tighter oxide formation in the absence of water vapour, due to a chemical effect. However, the temperature Run in which the carbonate was decomposed to apparent completion but was then boosted by humidifying the gas in the furnace suggests
about this case that a definite diffusional effect pertained. It can therefore only be concluded that water vapour has a possible dual effect but that this effect is probably more due to a chemical effect than was proposed by Spencer and Topley.

The activation energy of the reaction, found to be about 30 Cals/gm.mole, is significantly higher than that of Spencer and Topley, i.e. 23. It is possible that their experimental set-up resulted in a sufficient degree of self-cooling to produce this low value.

A value of $k^0_c$ of $\exp(15.5)$ was obtained, but this has little significance due to the doubt about the surface area available for reaction. The figure is based on the spherical model of the carbonate particles.

The use of the reaction temperature-following technique greatly added to the rapidity with which the effect of certain variables could be studied. This technique could probably be improved to the point where the temperature measured is known to be represented as the temperature of a whole reacting particle. If this were so, actual reaction rates could be measured accurately by this method.

The facility to measure the initial rate of reaction accurately would greatly aid work of this nature. The technique most likely to allow this would be a continuous weighing method such as was used for certain of the Runs in this work. With this method, further information regarding the effect of water vapour would be obtained.
The technique of measuring effective diffusivities which is developed and described in Appendix B should be further tested on a variety of materials to prove its reliability and accuracy, and to ensure the development of an apparatus which can be used to measure the diffusibilities of porous catalysts and reactants.
APPENDIX A

EXPERIMENTAL RESULTS.

Table A.(9.3)1 Preliminary rate measurements (old moulds).

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Ag₂CO₃ gms·(Nd)</th>
<th>Flow l/min</th>
<th>T₀°K</th>
<th>(\frac{1}{T₀°K}) x 10³</th>
<th>Rate, X=0 lbs/hr x 10⁴</th>
<th>(\ln(\text{rate x 10}^{14}), @X=0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5.260(13)</td>
<td>1.46</td>
<td>469.3</td>
<td>2.135</td>
<td>3.68</td>
<td>1.303</td>
</tr>
<tr>
<td>6</td>
<td>3.233(10)</td>
<td>1.20</td>
<td>470.3</td>
<td>2.125</td>
<td>4.06</td>
<td>1.401</td>
</tr>
<tr>
<td>7</td>
<td>3.368(10)</td>
<td>1.25</td>
<td>477.3</td>
<td>2.100</td>
<td>4.57</td>
<td>1.520</td>
</tr>
<tr>
<td>8</td>
<td>4.059(12)</td>
<td>1.17</td>
<td>464.3</td>
<td>2.155</td>
<td>3.12</td>
<td>1.138</td>
</tr>
<tr>
<td>9</td>
<td>4.645(14)</td>
<td>1.17</td>
<td>458.3</td>
<td>2.180</td>
<td>2.14</td>
<td>0.761</td>
</tr>
<tr>
<td>10</td>
<td>5.924(19)</td>
<td>1.17</td>
<td>448.3</td>
<td>2.230</td>
<td>1.31</td>
<td>0.273</td>
</tr>
<tr>
<td>11</td>
<td>4.347(14)</td>
<td>1.84</td>
<td>481.5</td>
<td>2.075</td>
<td>5.32</td>
<td>1.672</td>
</tr>
</tbody>
</table>

Table A.(9.3)2 Preliminary rate measurements (new moulds).

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Ag₂CO₃ gms·(Nd)</th>
<th>Flow l/min</th>
<th>T₀°K</th>
<th>(\frac{1}{T₀°K}) x 10³</th>
<th>Rate, X=0 lbs/hr x 10⁴</th>
<th>(\ln(\text{rate x 10}^{14}), @X=0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>4.361(15)</td>
<td>1.28</td>
<td>472.3</td>
<td>2.120</td>
<td>3.70</td>
<td>1.308</td>
</tr>
<tr>
<td>15</td>
<td>4.463(15)</td>
<td>1.27</td>
<td>464.3</td>
<td>2.155</td>
<td>2.99</td>
<td>1.095</td>
</tr>
<tr>
<td>16</td>
<td>4.234(15)</td>
<td>1.21</td>
<td>460.3</td>
<td>2.175</td>
<td>2.43</td>
<td>0.886</td>
</tr>
<tr>
<td>17</td>
<td>4.092(15)</td>
<td>1.09</td>
<td>449.5</td>
<td>2.225</td>
<td>1.56</td>
<td>0.445</td>
</tr>
<tr>
<td>18</td>
<td>5.517(20)</td>
<td>1.14</td>
<td>445.8</td>
<td>2.245</td>
<td>1.21</td>
<td>0.191</td>
</tr>
<tr>
<td>19</td>
<td>5.462(20)</td>
<td>1.10</td>
<td>441.0</td>
<td>2.265</td>
<td>0.99</td>
<td>-0.010</td>
</tr>
<tr>
<td>20</td>
<td>4.237(16)</td>
<td>1.17</td>
<td>463.0</td>
<td>2.160</td>
<td>2.84</td>
<td>1.044</td>
</tr>
<tr>
<td>21</td>
<td>4.557(16)</td>
<td>1.23</td>
<td>475.5</td>
<td>2.185</td>
<td>2.25</td>
<td>0.811</td>
</tr>
<tr>
<td>22</td>
<td>4.142(16)</td>
<td>1.17</td>
<td>452.3</td>
<td>2.210</td>
<td>1.72</td>
<td>0.542</td>
</tr>
<tr>
<td>24</td>
<td>4.611(16)</td>
<td>1.14</td>
<td>453.8</td>
<td>2.205</td>
<td>1.68</td>
<td>0.519</td>
</tr>
<tr>
<td>25</td>
<td>4.518(16)</td>
<td>1.18</td>
<td>455.3</td>
<td>2.195</td>
<td>1.72</td>
<td>0.542</td>
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<tr>
<td>26</td>
<td>3.454(12)</td>
<td>1.30</td>
<td>473.0</td>
<td>2.115</td>
<td>3.91</td>
<td>1.364</td>
</tr>
</tbody>
</table>

See also Figs. 9.1 and 9.2
Table A. (9.3 & 9.4.2)3 Initial reaction temperatures and reaction rates at subsequent conversions.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>( T_{i0} @ x=0 )</th>
<th>( \frac{1}{T} \times 10^3 )</th>
<th>( \text{rate, } x=0.5 )</th>
<th>( \ln(\text{rate}) )</th>
<th>( \text{rate, } x=0.75 )</th>
<th>( \ln(\text{rate}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>456.3</td>
<td>2.190</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>456.7</td>
<td>2.185</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>459.3</td>
<td>2.180</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>454.0</td>
<td>2.200</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>450.5</td>
<td>2.220</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>443.3</td>
<td>2.255</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>462.5</td>
<td>2.160</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>458.0</td>
<td>2.180</td>
<td>2.55</td>
<td>0.936</td>
<td>1.78</td>
<td>0.574</td>
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<tr>
<td>15</td>
<td>453.8</td>
<td>2.205</td>
<td>2.10</td>
<td>0.742</td>
<td>1.38</td>
<td>0.318</td>
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<tr>
<td>16</td>
<td>451.3</td>
<td>2.215</td>
<td>1.80</td>
<td>0.588</td>
<td>1.20</td>
<td>0.182</td>
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<td>17</td>
<td>444.0</td>
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<td>1.33</td>
<td>0.281</td>
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<td>441.5</td>
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<td>19</td>
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<td>0.668</td>
<td>1.40</td>
<td>0.337</td>
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<tr>
<td>21</td>
<td>449.5</td>
<td>2.225</td>
<td>1.58</td>
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<td>0.072</td>
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<td>22</td>
<td>446.0</td>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>24</td>
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<td>0.372</td>
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<td>0.049</td>
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<td>2.175</td>
<td>2.30</td>
<td>0.833</td>
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<td>0.412</td>
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See also Figs. 9.1, 9.2 and 9.3.
Table A(9.4.1)4

Initial (i.e. X=0) drops, ΔT, in reaction temperature.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>28*</th>
<th>29*</th>
<th>30</th>
<th>31</th>
<th>32</th>
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<tbody>
<tr>
<td>T&lt;sub&gt;G&lt;/sub&gt;, °C</td>
<td>212.5</td>
<td>205.75</td>
<td>204.75</td>
<td>205.75</td>
<td>204.25</td>
</tr>
<tr>
<td>ΔT, °C</td>
<td>11.5</td>
<td>8.0</td>
<td>16.5</td>
<td>17.25</td>
<td>14.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run No.</th>
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<th>35</th>
<th>36</th>
<th>37</th>
<th>38</th>
</tr>
</thead>
<tbody>
<tr>
<td>T&lt;sub&gt;G&lt;/sub&gt;, °C</td>
<td>198.5</td>
<td>198.25</td>
<td>191.5</td>
<td>189.5</td>
<td>183.25</td>
</tr>
<tr>
<td>ΔT, °C</td>
<td>11.5</td>
<td>11.0</td>
<td>10.5</td>
<td>8.5</td>
<td>6.25</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Run No.</th>
<th>40</th>
<th>41</th>
<th>42</th>
<th>43</th>
<th>44</th>
</tr>
</thead>
<tbody>
<tr>
<td>T&lt;sub&gt;G&lt;/sub&gt;, °C</td>
<td>203.5</td>
<td>204.5</td>
<td>216.0</td>
<td>218.5</td>
<td>215.25</td>
</tr>
<tr>
<td>ΔT, °C</td>
<td>17.0</td>
<td>18.0</td>
<td>23.0</td>
<td>24.25</td>
<td>21.25</td>
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</table>

<table>
<thead>
<tr>
<th>Run No.</th>
<th>45</th>
<th>46</th>
<th>47</th>
<th>48</th>
<th>49</th>
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</thead>
<tbody>
<tr>
<td>T&lt;sub&gt;G&lt;/sub&gt;, °C</td>
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<td>194.5</td>
<td>194.5</td>
<td>194.5</td>
<td>185.75</td>
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<tr>
<td>ΔT, °C</td>
<td>17.5</td>
<td>11.75</td>
<td>11.75</td>
<td>12.25</td>
<td>8.75</td>
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</table>

<table>
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<tr>
<th>Run No.</th>
<th>50</th>
<th>51</th>
<th>52</th>
<th>53</th>
<th>54</th>
</tr>
</thead>
<tbody>
<tr>
<td>T&lt;sub&gt;G&lt;/sub&gt;, °C</td>
<td>184.75</td>
<td>185.75</td>
<td>175.75</td>
<td>175.75</td>
<td>175.0</td>
</tr>
<tr>
<td>ΔT, °C</td>
<td>7.75</td>
<td>8.25</td>
<td>5.25</td>
<td>5.75</td>
<td>4.5</td>
</tr>
</tbody>
</table>

See also Figs. 9.4, 9.5, 9.6 and 9.7.

* Runs with only one sphere on thermocouple.
Table A. (9.4.3) 5

Temperature drops and reaction temperatures at various conversions, temperature Runs, sets 1 to 5.

<table>
<thead>
<tr>
<th>Set No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_G$, °K</td>
<td>489.0</td>
<td>477.0</td>
<td>467.5</td>
<td>458.75</td>
<td>448.75</td>
</tr>
<tr>
<td>$\Delta T @ X=0$, °C</td>
<td>22.5</td>
<td>17.25</td>
<td>12.0</td>
<td>8.5</td>
<td>5.25</td>
</tr>
<tr>
<td>$\ln(\Delta T)$, $X=0$</td>
<td>3.1135</td>
<td>2.8478</td>
<td>2.4849</td>
<td>2.1401</td>
<td>1.6582</td>
</tr>
<tr>
<td>$T_1$, °K, $X=0$</td>
<td>466.5</td>
<td>459.75</td>
<td>455.5</td>
<td>450.25</td>
<td>443.5</td>
</tr>
<tr>
<td>$1/T_1$, $X=0$, $x10^3$</td>
<td>2.145</td>
<td>2.175</td>
<td>2.195</td>
<td>2.220</td>
<td>2.255</td>
</tr>
<tr>
<td>$1/T_G$, $X=0$, $x10^3$</td>
<td>2.045</td>
<td>2.095</td>
<td>2.140</td>
<td>2.180</td>
<td>2.230</td>
</tr>
<tr>
<td>$\Delta T @ X=0.25$, °C</td>
<td>21.0</td>
<td>14.5</td>
<td>11.5</td>
<td>7.75</td>
<td>5.25</td>
</tr>
<tr>
<td>$\ln(\Delta T)$, $X=0.25$</td>
<td>3.0445</td>
<td>2.6742</td>
<td>2.4424</td>
<td>2.0477</td>
<td>1.6582</td>
</tr>
<tr>
<td>$1/T_1$, $X=0.25$, $x10^3$</td>
<td>2.137</td>
<td>2.162</td>
<td>2.193</td>
<td>2.217</td>
<td>2.255</td>
</tr>
<tr>
<td>$\Delta T @ X=0.5$, °C</td>
<td>16.25</td>
<td>11.5</td>
<td>9.75</td>
<td>6.75</td>
<td>5.0</td>
</tr>
<tr>
<td>$\ln(\Delta T)$, $X=0.5$</td>
<td>2.7881</td>
<td>2.4424</td>
<td>2.2773</td>
<td>1.9095</td>
<td>1.6094</td>
</tr>
<tr>
<td>$1/T_1$, $X=0.5$, $x10^3$</td>
<td>2.115</td>
<td>2.148</td>
<td>2.185</td>
<td>2.212</td>
<td>2.254</td>
</tr>
<tr>
<td>$\Delta T @ X=0.75$, °C</td>
<td>11.5</td>
<td>8.75</td>
<td>7.25</td>
<td>5.25</td>
<td>3.75</td>
</tr>
<tr>
<td>$\ln(\Delta T)$, $X=0.75$</td>
<td>2.4424</td>
<td>2.1691</td>
<td>1.9810</td>
<td>1.6582</td>
<td>1.3218</td>
</tr>
<tr>
<td>$1/T_1$, $X=0.75$, $x10^3$</td>
<td>2.094</td>
<td>2.136</td>
<td>2.173</td>
<td>2.205</td>
<td>2.247</td>
</tr>
<tr>
<td>Area under curve °C.min</td>
<td>304.13</td>
<td>309.17</td>
<td>320.23</td>
<td>326.32</td>
<td>361.50</td>
</tr>
</tbody>
</table>

See also Fig. 9.8.
Table A(9.4.4). 6

Temperature drops and reaction temperatures for reaction in dry nitrogen.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$T_G ^{\circ C}$</th>
<th>$\Delta T @ X=0, ^{\circ C}$</th>
<th>ln($\Delta T$)$_{X=0}$</th>
<th>$1/T_G ^{o K} x10^3$</th>
<th>$1/T_1 ^{o K} x10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>136</td>
<td>184.25</td>
<td>4.5</td>
<td>1.6094</td>
<td>2.185</td>
<td>2.210</td>
</tr>
<tr>
<td>139</td>
<td>211.75</td>
<td>13.25</td>
<td>2.5840</td>
<td>2.065</td>
<td>2.120</td>
</tr>
<tr>
<td>140</td>
<td>210.75</td>
<td>14.25</td>
<td>2.6568</td>
<td>2.070</td>
<td>2.130</td>
</tr>
<tr>
<td>141</td>
<td>213.75</td>
<td>17.25</td>
<td>2.8478</td>
<td>2.055</td>
<td>2.130</td>
</tr>
<tr>
<td>142</td>
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<td>15.75</td>
<td>2.7569</td>
<td>2.045</td>
<td>2.115</td>
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<tr>
<td>143</td>
<td>212.25</td>
<td>16.25</td>
<td>2.7881</td>
<td>2.060</td>
<td>2.135</td>
</tr>
<tr>
<td>144*</td>
<td>213.25</td>
<td>19.0</td>
<td></td>
<td></td>
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<tr>
<td>145**</td>
<td>213.5</td>
<td>23.75</td>
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<td>2.1401</td>
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<td>2.6742</td>
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</tr>
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<td>2.6211</td>
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<tr>
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<tr>
<td>218</td>
<td>222.0</td>
<td>18.5</td>
<td>2.9178</td>
<td>2.020</td>
<td>2.095</td>
</tr>
<tr>
<td>221</td>
<td>218.25</td>
<td>19.5</td>
<td>2.9704</td>
<td>2.035</td>
<td>2.115</td>
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<tr>
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<tr>
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<td>2.3979</td>
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<td>2.155</td>
</tr>
<tr>
<td>226</td>
<td>208.75</td>
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<td>2.5650</td>
<td>2.075</td>
<td>2.135</td>
</tr>
<tr>
<td>230</td>
<td>192.75</td>
<td>7.5</td>
<td>2.0149</td>
<td>2.145</td>
<td>2.180</td>
</tr>
<tr>
<td>231</td>
<td>195.5</td>
<td>10.25</td>
<td>2.3275</td>
<td>2.135</td>
<td>2.180</td>
</tr>
</tbody>
</table>

See also Figs. 9.9, 9.11 and 9.12. *no inerts in bed, only one sphere on t/c; **no inerts in bed, string of spheres on t/c.
**Table A(9.4.4).7**

Temperature drops and reaction temperatures for reaction in humidified nitrogen. (Humidification temperature indicated as $T_H$).

<table>
<thead>
<tr>
<th>Run</th>
<th>$T_G{^\circ}C$</th>
<th>$\Delta\theta@X=0{^\circ}C$</th>
<th>ln($\Delta T$),$X=0$</th>
<th>$1/T_G{^\circ}K, x10^3$</th>
<th>$1/T_1{^\circ}K, x10^3$</th>
<th>$T_H{^\circ}C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>137*</td>
<td>183.5</td>
<td>10.0</td>
<td>2.2513</td>
<td>2.190</td>
<td>2.235</td>
<td>19.5</td>
</tr>
<tr>
<td>138*</td>
<td>210.0</td>
<td>20.25</td>
<td>3.0082</td>
<td>2.070</td>
<td>2.160</td>
<td>20</td>
</tr>
<tr>
<td>148*</td>
<td>193.25</td>
<td>12.5</td>
<td>2.5257</td>
<td>2.145</td>
<td>2.205</td>
<td>30</td>
</tr>
<tr>
<td>216*</td>
<td>211.0</td>
<td>22.0</td>
<td>3.0911</td>
<td>2.065</td>
<td>2.165</td>
<td>23.5</td>
</tr>
<tr>
<td>219*</td>
<td>223.25</td>
<td>29.0</td>
<td>3.3673</td>
<td>2.015</td>
<td>2.140</td>
<td>22.75</td>
</tr>
<tr>
<td>220*</td>
<td>219.0</td>
<td>25.5</td>
<td>3.2387</td>
<td>2.035</td>
<td>2.145</td>
<td>23</td>
</tr>
<tr>
<td>223</td>
<td>222.25</td>
<td>26.0</td>
<td>3.2581</td>
<td>2.020</td>
<td>2.135</td>
<td>24</td>
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<tr>
<td>224</td>
<td>207.0</td>
<td>19.5</td>
<td>2.9704</td>
<td>2.090</td>
<td>2.175</td>
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</tr>
<tr>
<td>227</td>
<td>203.25</td>
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<td>2.8904</td>
<td>2.100</td>
<td>2.180</td>
<td>22.75</td>
</tr>
<tr>
<td>228</td>
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<td>12.5</td>
<td>2.5257</td>
<td>2.135</td>
<td>2.190</td>
<td>23.5</td>
</tr>
<tr>
<td>229</td>
<td>191.75</td>
<td>12.75</td>
<td>2.5456</td>
<td>2.155</td>
<td>2.215</td>
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<td>233</td>
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<td>2.0149</td>
<td>2.200</td>
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<tr>
<td>234</td>
<td>175.0</td>
<td>4.5</td>
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<td>2.230</td>
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<td>235</td>
<td>164.25</td>
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<td>2.285</td>
<td>2.305</td>
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<td>2.6742</td>
<td>2.120</td>
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See also Figs. 9.10, 9.11 and 9.12.

*Dry air used in these Runs.*
Table A.(9.4.3)8

Equilibrium pressure measurements.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>99</th>
<th>100</th>
<th>100</th>
<th>100</th>
<th>101</th>
<th>101</th>
<th>101</th>
</tr>
</thead>
<tbody>
<tr>
<td>T&lt;sub&gt;G&lt;/sub&gt;, °C</td>
<td>186.75</td>
<td>212.5</td>
<td>202.5</td>
<td>201.25</td>
<td>211.5</td>
<td>213.0</td>
<td>211.75</td>
</tr>
<tr>
<td>( \frac{1}{T_G} \times 10^3 )</td>
<td>2.174</td>
<td>2.059</td>
<td>2.102</td>
<td>2.108</td>
<td>2.065</td>
<td>2.055</td>
<td>2.060</td>
</tr>
<tr>
<td>P&lt;sub&gt;e&lt;/sub&gt;, ats.</td>
<td>0.272</td>
<td>0.830</td>
<td>0.588</td>
<td>0.572</td>
<td>0.779</td>
<td>0.867</td>
<td>0.827</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run No.</th>
<th>102*</th>
<th>102*</th>
<th>102*</th>
<th>103</th>
<th>103</th>
<th>105</th>
<th>106</th>
</tr>
</thead>
<tbody>
<tr>
<td>T&lt;sub&gt;G&lt;/sub&gt;, °C</td>
<td>219.5</td>
<td>214.25</td>
<td>211.25</td>
<td>178.75</td>
<td>177.0</td>
<td>168.25</td>
<td>174.25</td>
</tr>
<tr>
<td>( \frac{1}{T_G} \times 10^3 )</td>
<td>2.030</td>
<td>2.052</td>
<td>2.064</td>
<td>2.213</td>
<td>2.221</td>
<td>2.266</td>
<td>2.235</td>
</tr>
<tr>
<td>P&lt;sub&gt;e&lt;/sub&gt;, ats.</td>
<td>1.33</td>
<td>1.13</td>
<td>1.00</td>
<td>0.183</td>
<td>0.164</td>
<td>0.101</td>
<td>0.138</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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<th>108</th>
<th>109</th>
<th>110</th>
<th>111</th>
<th>112</th>
<th>113</th>
</tr>
</thead>
<tbody>
<tr>
<td>T&lt;sub&gt;G&lt;/sub&gt;, °C</td>
<td>178.25</td>
<td>187.5</td>
<td>187.75</td>
<td>187.5</td>
<td>186.0</td>
<td>193.25</td>
<td>195.25</td>
</tr>
<tr>
<td>( \frac{1}{T_G} \times 10^3 )</td>
<td>2.215</td>
<td>2.171</td>
<td>2.170</td>
<td>2.171</td>
<td>2.178</td>
<td>2.144</td>
<td>2.135</td>
</tr>
<tr>
<td>P&lt;sub&gt;e&lt;/sub&gt;, ats.</td>
<td>0.142</td>
<td>0.198</td>
<td>0.187</td>
<td>0.205</td>
<td>0.195</td>
<td>0.317</td>
<td>0.425</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Run No.</th>
<th>115</th>
<th>116</th>
<th>117</th>
<th>118</th>
<th>119</th>
<th>120</th>
<th>172</th>
</tr>
</thead>
<tbody>
<tr>
<td>T&lt;sub&gt;G&lt;/sub&gt;, °C</td>
<td>201.0</td>
<td>208.75</td>
<td>204.75</td>
<td>221.0</td>
<td>186.75</td>
<td>182.75</td>
<td>185.25</td>
</tr>
<tr>
<td>( \frac{1}{T_G} \times 10^3 )</td>
<td>2.109</td>
<td>2.075</td>
<td>2.092</td>
<td>2.024</td>
<td>2.174</td>
<td>2.193</td>
<td>2.182</td>
</tr>
<tr>
<td>P&lt;sub&gt;e&lt;/sub&gt;, ats.</td>
<td>0.486</td>
<td>0.800</td>
<td>0.640</td>
<td>1.19</td>
<td>0.273</td>
<td>0.240</td>
<td>0.309</td>
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</table>

continued overleaf—
<table>
<thead>
<tr>
<th>Run No.</th>
<th>173</th>
<th>174</th>
<th>175</th>
<th>176</th>
<th>177</th>
<th>177</th>
<th>178</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_G, ^\circ C$</td>
<td>182.5</td>
<td>176.25</td>
<td>178.75</td>
<td>171.0</td>
<td>163.0</td>
<td>166.0</td>
<td>164.5</td>
</tr>
<tr>
<td>$\frac{1}{T_G} \times 10^3$</td>
<td>2.195</td>
<td>2.225</td>
<td>2.213</td>
<td>2.251</td>
<td>2.293</td>
<td>2.277</td>
<td>2.285</td>
</tr>
<tr>
<td>$P_e$, ats.</td>
<td>0.266</td>
<td>0.220</td>
<td>0.225</td>
<td>0.161</td>
<td>0.115</td>
<td>0.122</td>
<td>0.116</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Run No.</th>
<th>179</th>
<th>179</th>
<th>179</th>
<th>180</th>
<th>181</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_G, ^\circ C$</td>
<td>158.5</td>
<td>156.75</td>
<td>156.0</td>
<td>154.25</td>
<td>150.5</td>
</tr>
<tr>
<td>$\frac{1}{T_G} \times 10^3$</td>
<td>2.317</td>
<td>2.326</td>
<td>2.330</td>
<td>2.337</td>
<td>2.360</td>
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<tr>
<td>$P_e$, ats.</td>
<td>0.067</td>
<td>0.058</td>
<td>0.059</td>
<td>0.061</td>
<td>0.045</td>
</tr>
</tbody>
</table>

*These Runs performed using "dynamic" technique described in Section 9.4.5. See also Fig. 9.15.

**Table A(9.4.7)**

Reverse reaction temperature Runs.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>56</th>
<th>57*</th>
<th>58</th>
<th>59</th>
<th>60</th>
<th>61</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_G, ^\circ C$</td>
<td>176.5</td>
<td>156.75</td>
<td>146.75</td>
<td>164.25</td>
<td>188.25</td>
<td>186.75</td>
</tr>
<tr>
<td>$P_e$, ats.</td>
<td>0.212</td>
<td>0.096</td>
<td>0.060</td>
<td>0.128</td>
<td>0.348</td>
<td>0.326</td>
</tr>
<tr>
<td>$X$, final</td>
<td>0.15</td>
<td>0.06</td>
<td>0.07</td>
<td>0.13</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>$P_{CO_2}$ $#$</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>0.5</td>
<td>0.5</td>
<td>-</td>
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</table>

* Same particles used for this Run as for Run 56.

$\#$ At this $CO_2$ pressure (ats.), no reaction occurred even although the pressure is higher is much higher than the equilibrium pressure, $P_e$. See also Fig. 9.20.
### Table A.9.5.10

Reaction rate measurements in humidified nitrogen/air and carbonate-coated celite particles. (rates in mole CO₂/mole Ag₂CO₃ hr⁻¹)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>242</th>
<th>243</th>
<th>244</th>
<th>245</th>
<th>246</th>
<th>247</th>
<th>248</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag₂CO₃, gm.</td>
<td>5.635</td>
<td>5.20</td>
<td>5.87</td>
<td>2.66</td>
<td>2.785</td>
<td>2.55</td>
<td>2.955</td>
</tr>
<tr>
<td>T_H, °C</td>
<td>21.5</td>
<td>22</td>
<td>22</td>
<td>22.5</td>
<td>22</td>
<td>22.5</td>
<td>22.5</td>
</tr>
<tr>
<td>Flow, l/min</td>
<td>1.24</td>
<td>1.07</td>
<td>0.94</td>
<td>1.96</td>
<td>1.56</td>
<td>1.58</td>
<td>1.35</td>
</tr>
<tr>
<td>T_G, °C, t=0</td>
<td>174.75</td>
<td>162.5</td>
<td>151.5</td>
<td>208.5</td>
<td>197.5</td>
<td>189.25</td>
<td>177.5</td>
</tr>
<tr>
<td>T_G, °C, Av.</td>
<td>171.0</td>
<td>161.5</td>
<td>151.0</td>
<td>208.5</td>
<td>194.75</td>
<td>187.40</td>
<td>175.25</td>
</tr>
<tr>
<td>ln(rate)</td>
<td>1.250</td>
<td>0.432</td>
<td>7.601</td>
<td>3.395</td>
<td>2.857</td>
<td>2.569</td>
<td>1.534</td>
</tr>
<tr>
<td>1/T_G x10³</td>
<td>2.235</td>
<td>2.290</td>
<td>2.355</td>
<td>2.075</td>
<td>2.125</td>
<td>2.160</td>
<td>2.220</td>
</tr>
</tbody>
</table>

See also Fig. 9.23 and Table A.12
Table A.(9.5.1)11

Reaction rate measurements in humidified air using carbonate spheres. (rates in moles CO₂/mole. Ag₂CO₃·hr.)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>236</th>
<th>237</th>
<th>238</th>
<th>239</th>
<th>240</th>
<th>241</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag₂CO₃, gms.</td>
<td>2.34</td>
<td>1.705</td>
<td>2.48</td>
<td>2.79</td>
<td>4.215</td>
<td>5.035</td>
</tr>
<tr>
<td>No. of pellets</td>
<td>9</td>
<td>7</td>
<td>10</td>
<td>12</td>
<td>18</td>
<td>21</td>
</tr>
<tr>
<td>T_H, °C</td>
<td>20</td>
<td>20.5</td>
<td>21</td>
<td>22</td>
<td>22.5</td>
<td>21.5</td>
</tr>
<tr>
<td>Flow, l/min.</td>
<td>0.94</td>
<td>0.90</td>
<td>1.21</td>
<td>1.20</td>
<td>1.16</td>
<td>1.00</td>
</tr>
<tr>
<td>T_G, °C, t=0</td>
<td>210.5</td>
<td>198.75</td>
<td>193.25</td>
<td>188.75</td>
<td>175.75</td>
<td>173.5</td>
</tr>
<tr>
<td>T_G, °C, Av.</td>
<td>210.5</td>
<td>200.0</td>
<td>192.0</td>
<td>187.75</td>
<td>175.75</td>
<td>173.25</td>
</tr>
<tr>
<td>Rate, t=0</td>
<td>8.44</td>
<td>5.32</td>
<td>4.57</td>
<td>4.10</td>
<td>1.45</td>
<td>1.29</td>
</tr>
<tr>
<td>ln(rate)</td>
<td>2.133</td>
<td>1.672</td>
<td>1.5195</td>
<td>1.4110</td>
<td>0.3716</td>
<td>0.2546</td>
</tr>
<tr>
<td>1/T_G°Kx10³</td>
<td>2.070</td>
<td>2.115</td>
<td>2.145</td>
<td>2.165</td>
<td>2.230</td>
<td>2.226</td>
</tr>
<tr>
<td>1/T_G°Kx10³</td>
<td>2.160</td>
<td>2.190</td>
<td>2.205</td>
<td>2.220</td>
<td>2.255</td>
<td>2.240</td>
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See also Table A.13 and Fig. 9.23.
Table A.12.

Reaction rate histories; celite, humidified air. (Rates given in moles CO$_2$/mole Ag$_2$CO$_3$·hr, time in mins.)

<table>
<thead>
<tr>
<th>Run No.</th>
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</thead>
<tbody>
<tr>
<td>time</td>
<td>0</td>
</tr>
<tr>
<td>rate</td>
<td>3.49</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>time</td>
<td>0</td>
</tr>
<tr>
<td>rate</td>
<td>1.54</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run No.</th>
<th>244</th>
</tr>
</thead>
<tbody>
<tr>
<td>time</td>
<td>0</td>
</tr>
<tr>
<td>rate</td>
<td>0.671</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>time</td>
<td>0</td>
</tr>
<tr>
<td>rate</td>
<td>29.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>time</td>
<td>0</td>
</tr>
<tr>
<td>rate</td>
<td>17.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>time</td>
<td>0</td>
</tr>
<tr>
<td>rate</td>
<td>13.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run No.</th>
<th>248</th>
</tr>
</thead>
<tbody>
<tr>
<td>time</td>
<td>0</td>
</tr>
<tr>
<td>rate</td>
<td>4.73</td>
</tr>
</tbody>
</table>

See also Table A.10.
Table A. (9.5.1) 13.

Reaction rate histories; spheres, humidified air. (Rates given in moles CO₂/mole Ag₂CO₃.hr, time in minutes.)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>236</th>
<th>time</th>
<th>0</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>14</th>
<th>15</th>
<th>17</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>rate</td>
<td>8.44</td>
<td>7.15</td>
<td>5.27</td>
<td>2.78</td>
<td>0.40</td>
<td>0.17</td>
<td>0.04</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run No.</th>
<th>237</th>
<th>time</th>
<th>0</th>
<th>2</th>
<th>3</th>
<th>5</th>
<th>7.5</th>
<th>10</th>
<th>12.5</th>
<th>15</th>
<th>17.5</th>
<th>20</th>
<th>22</th>
</tr>
</thead>
<tbody>
<tr>
<td>rate</td>
<td>5.32</td>
<td>4.72</td>
<td>4.47</td>
<td>4.13</td>
<td>3.76</td>
<td>3.27</td>
<td>2.66</td>
<td>1.88</td>
<td>1.09</td>
<td>0.42</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run No.</th>
<th>238</th>
<th>time</th>
<th>0</th>
<th>2</th>
<th>3</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>29</th>
</tr>
</thead>
<tbody>
<tr>
<td>rate</td>
<td>4.57</td>
<td>3.92</td>
<td>3.64</td>
<td>3.28</td>
<td>2.86</td>
<td>2.32</td>
<td>1.65</td>
<td>0.70</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run No.</th>
<th>239</th>
<th>time</th>
<th>0</th>
<th>2</th>
<th>3</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>36</th>
</tr>
</thead>
<tbody>
<tr>
<td>rate</td>
<td>4.10</td>
<td>3.50</td>
<td>3.32</td>
<td>3.01</td>
<td>2.46</td>
<td>2.11</td>
<td>1.76</td>
<td>1.12</td>
<td>0.52</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Run No. | 240 | time | 0 | 2 | 5 | 10 | 15 | -   | -   | -   |
|---------|-----|------|---|---|---|----|----|-----|-----|
| rate    | 1.45| 1.36 | 1.34| 1.29| 0.88| -   | -   | -   | -   |

<table>
<thead>
<tr>
<th>Run No.</th>
<th>241</th>
<th>time</th>
<th>0</th>
<th>2</th>
<th>3.5</th>
<th>8.5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>rate</td>
<td>1.29</td>
<td>1.13</td>
<td>1.12</td>
<td>1.16</td>
<td>1.18</td>
<td>1.15</td>
<td>1.09</td>
<td>0.97</td>
<td>0.78</td>
<td>0.38</td>
<td>0.06</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

See also Table A.11
Table A. (9.5.3) 14.

Reactions rate measurements in dry nitrogen using carbonate-coated celite. (Rates in moles CO₂/mole Ag₂CO₃/hr).

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ag₂CO₃, gms.</th>
<th>Flow, l/min</th>
<th>T_G °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>158*</td>
<td>6.0005</td>
<td>0.9</td>
<td>166.5</td>
</tr>
<tr>
<td>159</td>
<td>4.6221</td>
<td>0.81</td>
<td>171.0</td>
</tr>
<tr>
<td>160</td>
<td>6.6308</td>
<td>0.95</td>
<td>174.0</td>
</tr>
<tr>
<td>161</td>
<td>6.8852</td>
<td>1.15</td>
<td>186.0</td>
</tr>
<tr>
<td>163</td>
<td>4.0838</td>
<td>0.85</td>
<td>190.0</td>
</tr>
<tr>
<td>164</td>
<td>3.4350</td>
<td>1.08</td>
<td>190.0</td>
</tr>
<tr>
<td>165</td>
<td>3.8190</td>
<td>1.43</td>
<td>193.5</td>
</tr>
<tr>
<td>184</td>
<td>3.6211</td>
<td>1.22</td>
<td>179.5</td>
</tr>
<tr>
<td>185</td>
<td>3.2892</td>
<td>1.10</td>
<td>193.5</td>
</tr>
<tr>
<td>187</td>
<td>3.5210</td>
<td>1.19</td>
<td>191.75</td>
</tr>
<tr>
<td>193</td>
<td>4.4097</td>
<td>1.40</td>
<td>191.0</td>
</tr>
<tr>
<td>197</td>
<td>3.1591</td>
<td>1.30</td>
<td>202.75</td>
</tr>
<tr>
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<td>2.1878</td>
<td>1.25</td>
<td>201.0</td>
</tr>
<tr>
<td>202</td>
<td>3.33</td>
<td>1.06</td>
<td>187.0</td>
</tr>
<tr>
<td>204</td>
<td>3.62</td>
<td>1.18</td>
<td>178.5</td>
</tr>
<tr>
<td>205</td>
<td>2.895</td>
<td>1.04</td>
<td>178.5</td>
</tr>
<tr>
<td>206</td>
<td>3.87</td>
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</tr>
<tr>
<td>208</td>
<td>3.88</td>
<td>1.12</td>
<td>179.0</td>
</tr>
<tr>
<td>210</td>
<td>3.72</td>
<td>1.80</td>
<td>215.5</td>
</tr>
<tr>
<td>212</td>
<td>2.135</td>
<td>1.85</td>
<td>205.25</td>
</tr>
</tbody>
</table>

See also Table A.15

*This run carried out in air dried by Si-gel.
### Table A. (9.5.3)15.
Reaction rate histories; celite, dry nitrogen. (Rates given in moles CO$_2$/mole Ag$_2$CO$_3$.hr, time in mins).

<table>
<thead>
<tr>
<th>Run No. 158 (dry air)</th>
<th>time</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>7</th>
<th>9</th>
<th>11</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>rate</td>
<td>0.93</td>
<td>0.82</td>
<td>0.76</td>
<td>0.72</td>
<td>0.69</td>
<td>0.62</td>
<td>0.57</td>
<td>0.54</td>
<td>0.52</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run No. 159</th>
<th>time</th>
<th>1</th>
<th>3</th>
<th>7</th>
<th>14</th>
<th>19</th>
<th>29</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>rate</td>
<td>1.58</td>
<td>1.42</td>
<td>1.24</td>
<td>1.04</td>
<td>1.00</td>
<td>0.78</td>
<td>0.63</td>
<td>0.48</td>
<td>0.33</td>
<td>0.21</td>
<td>0.11</td>
<td>0.04</td>
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</table>

<table>
<thead>
<tr>
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<th>1.5</th>
<th>4</th>
<th>9</th>
<th>19</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>rate</td>
<td>1.96</td>
<td>1.66</td>
<td>1.52</td>
<td>1.22</td>
<td>0.99</td>
<td>0.79</td>
<td>0.63</td>
<td>0.48</td>
<td>0.31</td>
<td>0.17</td>
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<table>
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<th>2</th>
<th>4</th>
<th>9</th>
<th>14</th>
<th>19</th>
<th>24</th>
<th>29</th>
<th>34</th>
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<tbody>
<tr>
<td></td>
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<td>0.46</td>
<td>0.13</td>
<td>0.04</td>
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<table>
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<th>1.5</th>
<th>4</th>
<th>6.5</th>
<th>9</th>
<th>14</th>
<th>19</th>
<th>24</th>
</tr>
</thead>
<tbody>
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<td>3.65</td>
<td>2.84</td>
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<th>2</th>
<th>3</th>
<th>5</th>
<th>7</th>
<th>9</th>
<th>11</th>
<th>13</th>
<th>15</th>
<th>17</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>rate</td>
<td>8.19</td>
<td>6.66</td>
<td>5.75</td>
<td>4.56</td>
<td>3.62</td>
<td>2.56</td>
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<table>
<thead>
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<th>time</th>
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<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>16</th>
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</thead>
<tbody>
<tr>
<td></td>
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<td>6.27</td>
<td>4.42</td>
<td>2.47</td>
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<td>0.31</td>
<td>0.13</td>
<td>0.03</td>
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<table>
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<th>9</th>
<th>14</th>
<th>19</th>
<th>24</th>
<th>29</th>
<th>34</th>
<th>40</th>
<th>45</th>
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<tbody>
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<td>2.73</td>
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<td>1.75</td>
<td>1.33</td>
<td>0.96</td>
<td>0.53</td>
<td>0.26</td>
<td>0.12</td>
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<table>
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<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>16</th>
<th>18</th>
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<td>4.34</td>
<td>3.34</td>
<td>2.21</td>
<td>1.16</td>
<td>0.51</td>
<td>0.16</td>
<td>0.03</td>
</tr>
</tbody>
</table>

TA.15 : 193
<table>
<thead>
<tr>
<th>Run No.</th>
<th>time</th>
<th>rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>187</td>
<td>1</td>
<td>9.46</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>7.05</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>5.66</td>
</tr>
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<td></td>
<td>5</td>
<td>4.40</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>3.47</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>2.51</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>0.63</td>
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<tr>
<td></td>
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<td>0.14</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>0.00</td>
</tr>
<tr>
<td>193</td>
<td>1</td>
<td>8.58</td>
</tr>
<tr>
<td></td>
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See also Table A.14.
Table A.(9.5.3)16.

Reaction rate measurements in dry nitrogen using carbonate spheres. (Rates in moles CO₂/mole Ag₂CO₃ hr).

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See also Table A.17
Table A.(9.5.3)17.

Reaction rate histories; spheres, dry nitrogen/air. (rates in moles $\text{CO}_2$/mole $\text{Ag}_2\text{CO}_3$.hr, time in mins.).

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See also Table A.16
APPENDIX B

THE EFFECTIVE DIFFUSIVITY OF MOULDED SILVER CARBONATE
AND OXIDE SPHERES.

B.1 Introduction. As was mentioned in the main text of this work, it became necessary to measure the diffusibility of the spheres of silver carbonate being used in the investigation. Initially, and briefly, it was suspected that the reaction would proceed according to a sharp interface mechanism in the usually accepted sense of the term, in other words that on splitting a particle before complete reaction had occurred, a definite boundary would be observed between the oxide product and the undecomposed carbonate. This, however, did not occur and it was quickly realised that this was due to the very high porosity of the moulded spheres and the relatively slow reaction rate. It was therefore decided that the effect of this high voidage on diffusion within the pores should be investigated.

Various methods have been used in the literature to measure diffusibilities, all of which are complicated and necessitate expensive and very accurately made equipment as well as cautious procedure. A novel technique has been developed which requires very simple and cheap equipment, and which gives quick and reliable results.

The importance of the diffusion coefficients of gases within solids will be appreciated after reference to the earlier theoretical Chapters of this report, notably Chapters 2 and 3.
Note that the discussions presented here, as in the rest of the report, are restricted to binary diffusion.

3.2 Definitions. A porous solid may be visualised as a number of parallel tubes, the walls of which represent the material and the holes the pores of the solid. The rate of diffusion through the solid, or rather through the tubes, based on the area of the porous solid (i.e. solid plus pores) is proportional to

\[ D \times \frac{\text{area of holes perpendicular to direction of diffusion}}{\text{total area in same plane}} \]

where \( D \) is the free binary diffusion coefficient of the gas in question. Now the area of "holes" per unit cross-sectional area is the same as the voidage, \( \sigma \), of the solid (see Pirie) so that the rate of diffusion is proportional to \( D\sigma \).

It is only realistic to visualise the tubes as tortuous, so that a further factor has to be introduced, so that diffusion is now proportional to \( D\sigma/z \) where \( z \) is the tortuosity factor. The term \( D\sigma/z \) is known as the effective diffusion coefficient, \( D_e \), and the ratio of this coefficient to the free coefficient is known as the diffusibility (see Hoogschagen) of the solid, \( \sigma/z \), and is obviously, at least for free as opposed to Knudsen diffusion, independent of the gases in question.

B.3 The nature of the problem. To carry out any calculations concerning the overall rate of reaction in a porous solid it is false to use the binary diffusion coefficient of gases A and G without any further restricting factor. As noted above the correction factor is the diffusibility of the solid, which for
free or normal diffusion is purely a function of the solid. This can only be determined by analogy with other similar systems or by direct measurement by a method such as that presented here. For a system in which free diffusion predominates the effect of temperature is easy to predict so that diffusibility experiments can be performed at other temperatures than those at which the property must be known.

B.4 Previous work. The first significant work on diffusion in loose porous solids was concerned mainly with soils (Buckingham). Measurement of the diffusion coefficients in solids began mainly with the work of Wicke and Kallenbach, who measured the rate of diffusion of nitrogen and carbon dioxide in porous glasses and carbons.

Hoogschagen introduced the term "diffusibility" and also a novel method of measuring this for various porous samples. The plugs were connected by rubber tubing to a closed tubular glass loop, one bulbous section of which contained activated copper heated to $400^\circ$C in an aluminium block furnace. This caused convection currents to circulate the gases in the loop and so allowed the copper to react with oxygen which had diffused from the surrounding air through the open end of the plug. Nitrogen was supplied to the loop to replace that which had been removed by diffusion through the plug, and this amount could be measured volumetrically. Alternatively the quantity of oxygen absorbed by the copper could be weighed.

Dye and Dallavalle used the most usual method for their measurements of diffusion rates through compressed pellets of
potassium perchlorate with voidages from 0.2 to 0.4. Carbon
dioxide and nitrogen were supplied continuously past the opposite
faces of a 1½" plug whose length varied from 1 to 8". The
concentrations of both gases could be measured on a katharometer.
The whole system was maintained at a carefully controlled temp-
erature and circulation of the gases through the thermal
conductivity cells ensured a constant concentration on each face
of the plug. The method is suggested for the measurement of
diffusion coefficients of catalysts but the size of the plugs
used would be rather large for this purpose, while the whole
apparatus was unnecessarily complicated. No mention is made of
the sealing of the edges of the pellets parallel to the proposed
direction of diffusion, although the pellets were reported as held
within tubing of a similar diameter. Also, although carbon
dioxide was used in the tests no account was taken of the
possibility of surface diffusion which was found to be important
at low voidages by Kammermeyer and Rutz.

Currie uses an unsteady-state method to measure the
diffusion coefficient of hydrogen/air mixtures in a variety of
loose materials. The apparatus was of precise mechanical
construction, but permitted rapid changing of samples. Gas
analysis was by katharometer.

Scott and Cox used a steady-state method to study the
temperature dependence of the binary diffusion coefficients of
gases, using standard microporous porcelains with average pore
sizes of 1.52 and 2.33 µ. The sides of the cylindrical samples
were sealed either by rubber tubing or by epoxy cement. The gas pairs \( \text{N}_2/\text{H}_2 \) and \( \text{NH}_3/\text{H}_2 \) were studied. The more ideal \( \text{N}_2/\text{H}_2 \) system gave better results.

The effect of compacting stress on compressed pellets of silver catalysts was investigated by Amberg and Echigoya using the same kind of apparatus as Wicke and Kallenbach. No evidence of Knudsen diffusion was found using nitrogen and hydrogen. The effect of voidage on diffusibility was also determined.

Weisz and Schwartz measured the effective diffusivity of 49 different samples of gel-derived catalysts by the normal steady state method, and satisfactorily developed a model for the prediction of diffusivities from pore volume and specific surface area which agreed with experiment. The method was also used by Wakao and Smith for the same reason, to compare experimental evidence with a pore volume/pore radius model of diffusibility, with bidisperse media, that is media which have a pore size distribution such that part of the diffusion occurs in macro-pores, and part in micro-pores. The steady-state method was again used by Henry et al to measure diffusion of gases through porous solids over a large pressure range so that both free and Knudsen diffusion were encountered. Villet and Wilhelm, and Gilliland et al used a forced flow technique to measure Knudsen diffusion. The influence of diffusion processes in chemical reactions is discussed by Scott, who also discusses various methods of measuring diffusion coefficients.

**B.5 The steady-state method.** The steady-state method, which has been used predominantly in the past, can be represented by
Fig. B.1. As the system is unconfined or "open", the diffusional fluxes of the two gases are not equal. Pure gases A and B are passed through the open volumes on either side of the plug so that the concentration of each gas at the surfaces of the plug are equal to those in the main flow. Pressures in the two volumes are maintained equal so that transfer through the plug is by diffusion alone. Beek stresses that in order to analyse such a case, both diffusional fluxes must be measured as they are not equal as in equimolar counterdiffusion due to the open nature of the system. In fact, Wicke and Kallenbach measured only a single flux, as did Weisz, although in this case transport was by Knudsen diffusion.

It has been shown (Hoogschagen) that the ratio of fluxes of A and B is approximately equal to the square root of the inverse ratio of the molecular weights of A and B. Beek also recommends that, rather than maintain pressures on either side of the plug equal, pressures should be adjusted such that diffusional fluxes are the same. A further work on the analysis of similar diffusion situations is that of Spiegler.

Comprehensive works on diffusion through solids are those of Jost, and Barrer, mainly concerned with permeability and hence Knudsen diffusion, and Carman. Recent works on the prediction of effective diffusivities are those of Scott and Dullien, and Steisel and Butt.

B.6 The unsteady-state method. Beek's proposal that the two fluxes should be made equal is very simply achieved by making one of the gas volumes in Fig. B.1 a closed system, as shown in
Fig. B.2. Hence pure gas A is originally placed in the closed finite "source", and is restricted from diffusing into the other infinite "sink", that is the other volume through which B is passed continuously. This volume is unnecessary as such, and can be considered as infinite. At time zero, the intervening stop or restriction is removed and gas A is allowed to diffuse out of the source volume into the sink, while B will counterdiffuse and take the place of A within the finite volume. The system will initially tend to proceed in the same manner as the steady-state system in that the rates of diffusion of A and B will not be equal. This will therefore result in a change in pressure within the source, which will be a drop or a rise depending on whether A is the lighter or heavier molecule. A bulk flow will then occur such that the transfer of A out will equal the transfer of B in, thus resulting in what is generally termed equimolar counterdiffusion, but which should probably be called equimolar countertransfer.

Initially, therefore, a cover is placed on the porous plug at \( t = 0 \) (or alternatively at \( t_0 \), to give different boundary conditions and probably an impractical system). The cover is removed at \( t = 0 \) and after a short initial period equilibrium is established such that counterdiffusion or countertransfer of A and B is equimolar. Diffusion through the pores of the plug is governed by,

\[
\frac{\partial y}{\partial t} = \frac{D}{\sigma} \frac{\partial^2 y}{\partial x^2} \\
0 < 1 < 1_0
\]
and the relevant boundary conditions are,

\[
y = 0, \; l = 0, \; t \geq 0 \\
y = 1, \; l > 0, \; t = 0
\]

and on the assumption that the source and sink are perfectly stirred, the boundary condition at \( l = l_o \) becomes,

\[
\frac{\partial y}{\partial t} = -\frac{A_d D_e}{V} \frac{\partial y}{\partial l}, \; l = l_o, \; t \geq 0
\]

where \( A_d \) is the cross-sectional area of the porous plug, and \( V \) is the volume of the finite source.

Similar equations for heat transfer in a rod have been solved by Carslaw and Jaeger. By analogy, then, we obtain the solution,

\[
y(l, t) = \sum_{n=1}^{\infty} \frac{2(a_n^2 + h^2)\sin(a_n l_o)\exp(-\frac{D a_n^2 t}{\sigma})}{a_n(l_o(a_n^2 + h^2) + h)}
\]

where the \( a_n \)'s are the solutions of the equation,

\[
a_n \tan(a_n l_o) = h = \frac{A_d \sigma}{V}
\]

where \( \sigma \) is the voidage of the porous plug. In practice the mole fraction of \( A \), given by \( y \), would be measured in the finite source so that Eq. (B.1) reduces to,

\[
y(l_o, t) = \sum_{n=1}^{\infty} \frac{2(a_n^2 + h^2)\sin(a_n l_o)\exp(-\frac{D a_n^2 t}{\sigma})}{a_n(l_o(a_n^2 + h^2) + h)}
\]

This solution assumes that the total pressure \( P_T \) remains everywhere constant. In fact this will not be so, but changes in pressure within the source will always be small and can be
B.7 The pseudo-steady-state solution. When the ratio of the volume of the pores in the plug to the volume of the source is small it is found that only the first of the roots of the subsidiary equation, Eq. (B.2) need be considered. Solutions of this equation when in the form,

\[ \frac{a_1 \tan(a_1 \ell_0)}{\ell_0} = \frac{A_d \sigma_0}{V} = \frac{\text{pore volume}}{\text{source volume}} \]

are listed in Carslaw and Jaeger. If \( \ell_0 \) itself is small then \( \tan(a_1 \ell_0) \approx a_1 \ell_0 \) so that \( a_1^2 = (A_d \sigma)/(V \ell_0) \) and the solution becomes,

\[ y(1_0, t) = \frac{2(a_1^2 + h^2)\exp\left(-\frac{D e A_d}{V \ell_0}\right)}{2a_1^2 + h^2} \]

As \( h^2 \) is small in comparison to \( a_1^2 \) then,

\[ y(1_0, t) = \exp\left(-\frac{D e A_d}{V \ell_0}\right) \quad (B.4) \]

This equation can be more simply obtained by equating the change in the A content of the source to the rate of transfer of A through the plug, assuming the plug to be very thin, i.e.,

\[ \frac{d}{dt} y = \frac{D e A_d}{1_0} y \]

and hence we obtain Eq. (B.4) by integration. Solutions to Eq. (B.4) are shown graphically in Fig. B.3 for various values of \( \frac{D e A_d}{V \ell_0} \), (min\(^{-1}\)).

It is found that the true solution need only be used for extremely small times, or for very large values of the ratio of pore to source volume. These would never be used in practice, so
that the simple solution is always sufficient.

**B.8 A simple apparatus for the measurement of D**

A simple apparatus based on the above model was made and found to be quite satisfactory (see Fig. B.4). The source was fabricated in perspex with a volume of about 1l, and was cylindrical in shape, approximately 5" in diameter and 3½" long. In one of the flat ends was a hole larger than the plug over which could be clamped a perspex plate carrying the porous plug, which was of a much smaller diameter than the end of the source vessel. Over the plug carrier a further small plate could be clamped to act as a cover plate.

At the opposite end of the source vessel from the plug was a connection which could be used to admit gas A, or an analysis liquid, as will be shown later. Also on this end, and situated centrally, was an "O-ring" gland through which the spindle of a stirrer passed. On the plug end, another connection was available to allow purging of the vessel. The inner edge of the large hole on this end was chamfered to allow the plug to "see" as much of the inside of the vessel as possible. Care was taken to ensure that the vessel and connections were leak-proof, as both the diffusion experiment itself, and more especially the subsequent analysis of the source contents depended on this.

The plug carrier plate was circular and of the same thickness as the plug to be used, with a chamfer at one end of the plug hole to facilitate sealing the edges of the plug. The side of the perspex cover plate adjacent to the plug was partly
hollowed to ensure that the plug was not damaged when the cover was in place.

The stirrer spindle, 3/16" dia., and the two blades, each 1" x 4", were made of brass as was the body of the gland and the two connections. A perspex pulley wheel was attached to the outer end of the stirrer spindle, this pulley being driven by a rubber band which was wrapped round the rubber-sleeved spindle of an ordinary variable-speed stirrer motor.

On removing the cover plate, the plug is exposed to the surrounding ambient air (gas B), thus providing an infinite sink into which gas A can diffuse.

B.9 The material to be tested. The plugs used for the determinations were made in a similar manner to the spheres used for reaction studies. A stiff paste of the silver carbonate was made and then pressed gently into a shallow open-ended cylindrical mould. The top of the paste was then smoothed over. After drying at only moderate temperatures, 30-40°C, the majority of the plugs were then removed from the moulds and decomposed to silver oxide in the reaction furnace. A few were used for measurement of the diffusibility of the carbonate.

As the resulting plug was mechanically fragile, it was difficult to make them very thin, so that 1/8" and 1/4" plugs were made, of 1" and 7/8" dia. respectively. Hence the ratio $\frac{A_d \sigma l_o}{V}$ was always less than 0.004. Negligible shrinkage of the plugs took place on drying or decomposition.

After the decomposed plugs had cooled the outer edges were coated with an ordinary rubber solution so that the diffusion
out through the edges was prevented. Various other coatings were tried and found to be unsuitable. For example, polystyrene cement contracted to such an extent on setting that the resultant band round the plug pulled the plug apart. The plugs were then slipped into the hole in the plug carrier plate, which was slightly larger than the plug diameter, and rubber solution was then applied in a number of coats to the chamfer in the carrier plate, such that the gap between the plate and the plug was closed. Gas A was carbon dioxide, and B air.

B.10 Method of measurement. The carrier plate and plug assembly was attached to the source vessel and sealed against a thin cork gasket. Carbon dioxide was then purged through the vessel for some time, until the source was 100% carbon dioxide, this time being set by blank trials. The outlet connection was then closed, followed by the inlet, so that the apparatus was slightly pressurised. Carbon dioxide was then periodically vented off until it was assumed that the contents had reached room temperature, and the pressure in the vessel was atmospheric. The vessel was then placed with the plug facing either upwards into the surroundings, or in other experiments downwards, and the stirrer switched on and set to the required r.p.m. The cover plate was then removed and left off for the duration of the diffusion period, 0.5 to 1.5 hrs. This time was controlled to ensure that a reasonable partial pressure of carbon dioxide was left within the source. The cover plate was then replaced and the apparatus placed in the "plug upwards" position. The gland
on the stirrer was also tightened to ensure that the apparatus was leak-proof.

The inlet to the vessel was then opened and a small amount of 0.3N caustic soda admitted to the source under slight pressure. The levels of solution in the supply vessel and the apparatus were equalised and the vessel shaken gently so that carbon dioxide was absorbed and a slight vacuum created in the gas space, thereby introducing more caustic into the vessel. This procedure was then continued for some 15-20 mins. until all the carbon dioxide was absorbed. The levels in the caustic supply vessel and in the apparatus were again equalised and the inlet valve closed.

The diffusion apparatus was then weighed, having been previously weighed both empty and full, to determine its weight and internal volume respectively. Knowing the specific gravity of the solution, each volume of solution was equivalent to a volume of carbon dioxide, so that the partial pressure of carbon dioxide within the source could be estimated easily to the nearest 0.1% (i.e. = 1gm. caustic solution).

Initial experiments were carried out with the 1" dia. \(\frac{1}{4}\)" thick plugs, both with and without stirring. Oblique impingement of air on the outside surface of the plug was also tried. Stirring speeds were 30-120 r.p.m. Further experiments were done using the \(\frac{3}{8}\)" dia. \(\frac{1}{8}\)" thick plugs.

B.11 Results. A summary of the experiments carried out is shown in Table B.1 with the results also shown in Fig. B.3 as a plot of the final mole fraction of carbon dioxide in the vessel.
asa function of time.

Experiments carried out with the plugs facing upwards, and the carbon dioxide therefore diffusing upwards, gave consistently lower results than with the plug facing downwards, as the carbon dioxide in the latter case would create gravitational convection currents, it being on top of the air on both sides of the plug. This effect was more noticeable for the thin plugs. The use of the stirrer and the air jet caused a significant increase in the diffusion coefficient obtained. For the thicker plugs the diffusion coefficient obtained from the plug downwards experiments without stirring was the same as that for the stirred "upwards" experiments with the thin plugs.. Upwards experiments with the thick plugs caused only a slight decrease in the diffusion coefficient.

Experiments carried out without stirring were highly reproducible, both for similar runs done with the same plug and for runs done with different plugs under the same conditions. With stirring, however, a 3% spread in the results was obtained.

During some experiments the pressure in the finite source was followed by a micromanometer. As the carbon dioxide was diffusing out of the source, and has a higher molecular weight than air, a bulk flow outwards was required to maintain the transfer equimolar. Hence the source pressure was slightly higher than that of the surroundings. If this pressure was large the mathematical approach used would be invalid. However the pressure never exceeded 15 mm H₂O, less than 0.2% of the total pressure. The highest pressure occurred at about 5 mins. after
### Table B.1  Diffusion experimental results. (oxide)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Exposure mins.</th>
<th>Plug ins.</th>
<th>$y_{CO_2}$</th>
<th>$T^\circ C$</th>
<th>Direction &quot;up&quot; &quot;down&quot;</th>
<th>Stirring</th>
<th>$D_{\text{ft}^2/\text{hr.}}^#$</th>
</tr>
</thead>
<tbody>
<tr>
<td>68</td>
<td>60</td>
<td>1/2</td>
<td>0.255</td>
<td>23</td>
<td>x</td>
<td>-</td>
<td>0.1745</td>
</tr>
<tr>
<td>69</td>
<td>60</td>
<td></td>
<td>0.260</td>
<td>22</td>
<td>x</td>
<td>-</td>
<td>0.1725</td>
</tr>
<tr>
<td>70</td>
<td>33.5</td>
<td></td>
<td>0.475</td>
<td>22</td>
<td>x</td>
<td>-</td>
<td>0.1710</td>
</tr>
<tr>
<td>71</td>
<td>30</td>
<td></td>
<td>0.571</td>
<td>22</td>
<td>x</td>
<td>-</td>
<td>0.1715</td>
</tr>
<tr>
<td>72</td>
<td>45</td>
<td></td>
<td>0.275</td>
<td>22.5</td>
<td>-</td>
<td>x</td>
<td>0.2205</td>
</tr>
<tr>
<td>73</td>
<td>46</td>
<td></td>
<td>0.270</td>
<td>24</td>
<td>-</td>
<td>x</td>
<td>0.218</td>
</tr>
<tr>
<td>74</td>
<td>30</td>
<td></td>
<td>0.417</td>
<td>24</td>
<td>-</td>
<td>x</td>
<td>0.223</td>
</tr>
<tr>
<td>75</td>
<td>30</td>
<td></td>
<td>0.420</td>
<td>23.5</td>
<td>-</td>
<td>x</td>
<td>0.221</td>
</tr>
<tr>
<td>80</td>
<td>30</td>
<td></td>
<td>0.300</td>
<td>24</td>
<td>x</td>
<td>-</td>
<td>0.305</td>
</tr>
<tr>
<td>81</td>
<td>30</td>
<td></td>
<td>0.317</td>
<td>23.5</td>
<td>x</td>
<td>-</td>
<td>0.2915</td>
</tr>
<tr>
<td>82</td>
<td>30</td>
<td></td>
<td>0.320</td>
<td>24.5</td>
<td>x</td>
<td>-</td>
<td>0.288</td>
</tr>
<tr>
<td>83</td>
<td>30</td>
<td></td>
<td>0.315</td>
<td>22</td>
<td>x</td>
<td>-</td>
<td>0.2945</td>
</tr>
<tr>
<td>85</td>
<td>90</td>
<td>5/16</td>
<td>0.390</td>
<td>22.5</td>
<td>-</td>
<td>x</td>
<td>0.294</td>
</tr>
<tr>
<td>86</td>
<td>90</td>
<td></td>
<td>0.381</td>
<td>23</td>
<td>-</td>
<td>x</td>
<td>0.301</td>
</tr>
<tr>
<td>87</td>
<td>90</td>
<td></td>
<td>0.384</td>
<td>23</td>
<td>-</td>
<td>x</td>
<td>0.299</td>
</tr>
<tr>
<td>88</td>
<td>92</td>
<td></td>
<td>0.399</td>
<td>22</td>
<td>x</td>
<td>-</td>
<td>0.281</td>
</tr>
<tr>
<td>89</td>
<td>95</td>
<td></td>
<td>0.386</td>
<td>22</td>
<td>x</td>
<td>-</td>
<td>0.283</td>
</tr>
<tr>
<td>90</td>
<td>90</td>
<td></td>
<td>0.383</td>
<td>22</td>
<td>x</td>
<td>-</td>
<td>0.301</td>
</tr>
<tr>
<td>91</td>
<td>90</td>
<td></td>
<td>0.387</td>
<td>21.5</td>
<td>-</td>
<td>x</td>
<td>0.297</td>
</tr>
<tr>
<td>92*</td>
<td>90</td>
<td></td>
<td>0.422</td>
<td>23</td>
<td>-</td>
<td>x</td>
<td>0.270</td>
</tr>
<tr>
<td>93*</td>
<td>90</td>
<td></td>
<td>0.423</td>
<td>23</td>
<td>-</td>
<td>x</td>
<td>0.269</td>
</tr>
</tbody>
</table>

*denotes carbonate plugs. See also Fig. B.3. ($V = 1002ccs., 996$ with stirrer)

$^\# @ 25^\circ C.$
the cover plate was removed, the pressure thereafter falling off exponentially to atmospheric throughout the run. An example, Run 94, of the pressure history within the source volume is given in Fig. B.6.

The technique of following the source pressure was used to determine the effects of internal stirring and the air jet. When using the thinner plug oblique impingement of air on the outside of the plug caused an increase in pressure within the vessel. This effect was hardly noticeable with the thicker plug. When testing the internal stirring, however, a slight increase in the source pressure in the vicinity of the plug face caused an additional bulk flow through the plug. The exact effect of stirring could not be determined, but it seemed obvious that best results would be achieved if stirring were unnecessary.

B.12 Discussion. The finally accepted values of the diffusion coefficient were 0.300 ft²/hr. for the oxide, and 0.282 ft²/hr. for the carbonate. These were obtained with the thicker plugs with the plugs facing downwards, and without stirring. It was thought that the slightly higher diffusivity obtained with the thicker plugs when stirring was used was artificially high due to pressure disturbances in the vessel. Using a value of 0.636 ft²/hr. (Coulson and Richardson) for the free diffusion coefficient of carbon dioxide in air at 25°C the values of the diffusibility are 0.47 and 0.44 respectively. The porosities of the oxide and carbonate plugs were found to be 0.75 and 0.65 respectively, giving tortuosity factors of 1.59 and 1.71.

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The values of diffusibility found agree well with those obtained by Currie. For a number of loose materials, Currie's results are shown in Fig. B.5 with the results for the oxide and carbonate plugs also shown. Currie used unconsolidated media, and it is interesting to find that the diffusibility of a semi-consolidated mass such as the plugs used can be predicted from Currie's results with some accuracy. Also shown in Fig. B.5 are the results of Dye and Dallavalle on $N_2/CO_2$ diffusion in porous solid samples of varying porosity. The compacted samples were either 1, 2, 4 or 8" long, and were saturated initially with either $CO_2$ or $N_2$. The average diffusibility of the $CO_2$ saturated plugs is shown in Fig. B.5 as a function of voidage. The results can be seen to diverge from those of Currie at high voidage, which is opposite to what would be expected. Buckingham says that the rate of diffusion is proportional to the square of the porosity. If we assume that $D_e = D$ when $\sigma = 1$, and that $D_e/D = 0$ at $\sigma = 0$, then Buckingham's results are as shown in Fig. B.5 and can be seen to fit modestly only at high values of $\sigma$. Further examples of attempts to estimate diffusibility are given by Currie.

In view of the good agreement obtained between the measured diffusibilities in this work and those of Currie it is thought that the method proposed for their measurement is an accurate one, as well as being simple and reliable. One suggested source of error is that ambient temperature fluctuations will cause similar fluctuations in the internal pressure of the source and hence cause forced flow into and/or out of the source.
Although it is thought that such fluctuations would be damped out by the comparatively high heat capacity of the perspex walls, actual ambient temperatures changed by only $\frac{1}{2}^\circ\text{C}$ at most, and this by a gradual drift.

As the "diffusibility" of a solid is a property of the solid alone, and not a function of the gases used in the determination, at least over the "free" diffusion range, the above method is suitable for diffusibility measurements on all solids such as porous catalysts. Better results would obviously be obtained by operating the system with thicker plugs, or better still with plugs of various thicknesses by means of which an extrapolated result would be obtained. However it is of interest to note that Satterfield and Saraf found that the diffusibility of compressed pellets varies with depth, being obviously a function of the method of preparation.
C.1 Introduction. It was necessary during the course of the experimental work on the decomposition of silver carbonate to determine whether the boundary layer diffusional and heat transfer resistances were significant. The evaluation of the rates of these processes is given here, but discussion and conclusion regarding the results will be found in the main text.

C.2 Boundary layer coefficients; definition. Boundary layer coefficients within a particular range of conditions and specifically for flow of gases through beds of particles rather than past single particles were required. These were taken from the work of Yoshida et al, who gave them in the form,

\[ j_D = \frac{k'_B (Sc)^{0.8}}{G_m} \frac{(P_S - P_G)}{\ln \left( \frac{P_T - P_G}{P_T - P_S} \right)} = 0.84(Re)^{-0.51} \] (C.1)

\[ j_H = \frac{h_B (Pr)^{0.8}}{G C_p} = 1.076 j_D \] (C.2)

for the range of Reynolds numbers, 0.01<Re<50, within which the experimental flow rates of this work lay, and where \( j_D \) and \( j_H \) are the Chilton-Colburn mass and heat transfer factors respectively, \( G_m \) and \( G \) are the molar and mass fluxes through the bed of particles, \( k'_B \) is a boundary layer mass transfer coefficient, \( h_B \) a heat transfer coefficient, and \( C_p \) is the specific heat of the flowing gas. The dimensionless groups used are
\[ Sc = \frac{\mu}{\rho
abla} \quad Pr = \frac{C_p}{k} \quad \text{and} \quad Re = \frac{G}{\nu \mu} \]

where \( \mu \) is the viscosity, \( \rho \) the density, and \( k \) the thermal conductivity of the flowing gas, and \( D \) is the binary diffusion coefficient of the diffusing species in the bulk gas. \( a_v \) is the surface area of the particles per unit volume of bed.

From Eq. (C.1) we have,

\[ k_B' = \frac{0.84 m}{Sc \cdot Re \cdot 0.51} \ln \left( \frac{P_T - P_G}{P_T - P_S} \right) \left( \frac{1}{P_T - P_S} \right) \] (C.3)

and the rate of transfer per particle of the diffusing species through the boundary layer is given by,

\[ 4\pi R^2 k_B' (P_S - P_G) \] (C.4)

However in Chapter 4 we have defined this rate as,

\[ -4\pi R^2 \frac{k_B P_T}{R' T_G} \ln \left( \frac{P_T - P_G}{P_T - P_S} \right) \] (C.5)

so that the coefficient \( k_B \) may be defined as

\[ k_B = \frac{0.84 m}{Sc \cdot Re \cdot 0.51 \cdot P_T} \] (C.6)

and this coefficient is independent of the partial pressures in the boundary layer. Also from Eq. (C.2),

\[ h_B = \frac{0.90 \mu C_p G}{Pr \cdot Re \cdot 0.51} \] (C.7)
C.3 Boundary layer coefficients; evaluation. The units used for the calculations are lbs., ft., atmos., °C and Btu. The results are specific for the reaction system of this work, namely for random packed 1/4" spheres in a 2.5" dia. bed, and for carbon dioxide diffusing from the spheres into a stream of nitrogen at atmospheric pressure. Mass transfer figures are obtained for 150, 175 and 200°C and both mass and heat transfer figures for flow rates through the bed of 0.1, 0.5, 1, 5 and 10 l/min. (Note: flow rates are quoted, for convenience, in l/min, as in the actual reaction Runs). All physical data was obtained from Perry.

a). Mass transfer. Values of Sc for the three temperatures above were found to be approximately constant at 0.95. Hence Eq.(C.6) becomes

\[ k_B = 1.151 \frac{G \cdot T}{Re^{0.51}} \text{ ft/hr.} \quad (C.8) \]

\( a_v \) was obtained from the voidages of packed spheres given by Leva, in this case for a particle to tube diameter ratio of 0.1. From the voidage of 0.37, \( a_v = 181 \text{ ft}^2/\text{ft}^3 \). \( a_v \) was also found by a simple experiment to be 154 ft\(^2\)/ft\(^3\), but unfortunately the apparatus did not conform strictly to the 0.1 ratio. A value of 170 ft\(^2\)/ft\(^3\) was chosen for the calculations. Eq.(C.8) was evaluated for the conditions listed above and the results are shown in Table C.1 and Fig. C.1. It can be seen that the values of Re lie within the specified range.

b). Heat transfer. \( Pr \) was found to be approximately constant at 0.86. Hence Eq.(C.7) becomes,
\[ h_B = 0.453 \frac{G}{Re^{0.51}} \text{ Btu/hr}\cdot\text{ft}^2\text{C} \quad (C.9) \]

Hence \( h_B \) is hereafter assumed to be independent of temperature, being evaluated at 175°C as representative of the range 175-200°C. The results of Eq. (C.9) are also shown in Table C.1 and Fig. C.1.

Note: The temperature dependence of \( D \) for \( \text{CO}_2 / \text{air} \) was taken from Reid and Sherwood.

C.4 Boundary layer rates. The potential boundary layer mass transfer rate obtains if the reaction is so rapid that equilibrium is established on the surface of the sphere. This means that the decomposition equilibrium pressure will obtain on the surface, so that \( P_S = P_e \). It will be assumed that \( \text{CO}_2 \) is absent in the bulk gas, so that \( P_G = 0 \). Values of \( P_e \) at 150, 175 and 200°C are taken from the results of Spencer and Topley in Table 7.2 as 0.07, 0.20 and 0.548 atm, respectively.

Hence the rate of diffusion through the boundary layer as given by Eq. (C.5) can now be written as

\[ N = -4\pi R^2 c \frac{k_B P_T}{R^T G} \ln(1-P_e) \quad (C.10) \]

Eq. (C.10) becomes for the particular system,

\[ N = -0.105 \frac{k_B}{T_G} \ln(1-P_e) \text{ lbs/hr.} \quad (C.11) \]

Eq. (C.11) has been evaluated and the results are shown in Table C.2 and in Fig. C.2.
Similarly the rate of transfer of heat through the boundary layer to the sphere is given by,

\[ Q = 4\pi R^2 k_B (T_G - T_S) \]  \hspace{1cm} (C.12)

so that the heat transfer rate per particle per unit temperature difference is,

\[ \frac{Q}{\Delta T} = 1.36 \times 10^{-3} h_b \text{ Btu/hr.} \]  \hspace{1cm} (C.13)

The results of Eq. (C.13) are depicted in Table C.2 and Fig. C.2.

Tables C.1 and C.2 over.
Table C.1  Boundary layer mass and heat transfer coefficients.

<table>
<thead>
<tr>
<th>$T_G$ °C</th>
<th>F l/min</th>
<th>0.1</th>
<th>0.5</th>
<th>1.0</th>
<th>5.0</th>
<th>10.0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G lbs/hr. ft$^2$</td>
<td>0.455</td>
<td>2.275</td>
<td>4.55</td>
<td>22.75</td>
<td>45.5</td>
</tr>
<tr>
<td>200</td>
<td>Re</td>
<td>0.0443</td>
<td>0.222</td>
<td>0.443</td>
<td>2.22</td>
<td>4.43</td>
</tr>
<tr>
<td></td>
<td>$k_B$ ft/hr.</td>
<td>43</td>
<td>94.5</td>
<td>133</td>
<td>292</td>
<td>410</td>
</tr>
<tr>
<td>175</td>
<td>Re</td>
<td>0.046</td>
<td>0.23</td>
<td>0.46</td>
<td>2.3</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>$k_B$ ft/hr.</td>
<td>40</td>
<td>88</td>
<td>124</td>
<td>276</td>
<td>382</td>
</tr>
<tr>
<td>150</td>
<td>Re</td>
<td>0.048</td>
<td>0.24</td>
<td>0.48</td>
<td>2.4</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>$k_B$ ft/hr.</td>
<td>37.8</td>
<td>81.4</td>
<td>114</td>
<td>251</td>
<td>352</td>
</tr>
<tr>
<td>all</td>
<td>$h_B$ Btu/hr. ft$^2$ °C</td>
<td>0.99</td>
<td>2.18</td>
<td>3.11</td>
<td>6.83</td>
<td>9.45</td>
</tr>
</tbody>
</table>

Table C.2  Boundary layer mass and heat flows.

<table>
<thead>
<tr>
<th>$T_G$ °C</th>
<th>F l/min</th>
<th>0.1</th>
<th>0.5</th>
<th>1.0</th>
<th>5.0</th>
<th>10.0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G lbs/hr. ft$^2$</td>
<td>0.455</td>
<td>2.275</td>
<td>4.55</td>
<td>22.75</td>
<td>45.5</td>
</tr>
<tr>
<td>200</td>
<td>Re</td>
<td>32.8</td>
<td>72.1</td>
<td>101.5</td>
<td>223</td>
<td>313</td>
</tr>
<tr>
<td>175</td>
<td>$N_B$ lbs/hr. x10$^4$</td>
<td>9.09</td>
<td>20.0</td>
<td>28.2</td>
<td>62.6</td>
<td>86.7</td>
</tr>
<tr>
<td>150</td>
<td>$Q/°$C Btu/hrx10$^4$</td>
<td>13.46</td>
<td>29.65</td>
<td>42.3</td>
<td>92.8</td>
<td>128.5</td>
</tr>
</tbody>
</table>

See also Figs. C.1 and C.2
D.1 Introduction. This appendix develops the diffusion equation for non-equimolar counterdiffusion for a sphere, as used in Chapter 4. Previous work on gas-solid reactions has been limited to equimolar counterdiffusion, and the resulting simpler diffusion equation.

D.2 The diffusion equation for non-equimolar counterdiffusion.

Referring to Fig. 4.1 the total transfer of G into the element in the direction of increasing r can be written as,

\[-4\pi r^2 \frac{D_e}{R'T_G} \frac{dP}{dr} + (\frac{F}{P - P_T}) \cdot F\]

where F is the bulk flow of gas A into the element in the same direction. The total transfer of A into the element in the same direction is,

\[-4\pi r^2 \frac{D_e}{R'T_G} \frac{d(P_T - P)}{dr} + F\]

and also, \[-\frac{a}{g}(-4\pi r^2 \frac{D_e}{R'T_G} \frac{dP}{dr} + (\frac{P}{P_T - P}) \cdot F)\]

Hence,

\[F(1 + \frac{a}{g} \frac{P}{P_T - P}) = 4\pi r^2 \frac{D_e}{R'T_G} \frac{dP}{dr} \left(\frac{a}{g} - 1\right)\]

so that the total transfer of product gas G into the element is
\[-4\pi r^2 \frac{D_e}{R'T_G} \left(1 + \frac{(1-\frac{a}{g})\left(\frac{P}{P_T}\right)}{1 + \frac{a}{g}\frac{P}{P_T - P}}\right)\]

or,

\[-4\pi r^2 \frac{D_e}{R'T_G} \frac{dP}{dT} \left(\frac{P_T}{P_T - (1-\frac{a}{g})P}\right)\]
E.1 General thermodynamic considerations. The thermal
decomposition of a carbonate can be represented by the reaction,

\[ \text{MCO}_3 \rightarrow \text{MO} + \text{CO}_2 \]

This reaction is brought to equilibrium by applying a certain
pressure of CO$_2$ at a given temperature. The condition for
equilibrium can be written as,

\[ \mu_{\text{MCO}_3} = \mu_{\text{MO}} + \mu_{\text{CO}_2} \]

Denbigh explains that as phase equilibrium must also attain, the
chemical potential of the solids and their vapours must also be
equal, so that the equilibrium constant can be written in the
form,

\[ -RT \ln \frac{P_{\text{MO}}P_{\text{CO}_2}}{P_{\text{MCO}_3}} = \mu_{\text{MO}}^\circ_{\text{gas}} + \mu_{\text{CO}_2}^\circ_{\text{gas}} - \mu_{\text{MCO}_3}^\circ_{\text{gas}} \quad (E.1) \]

so that the thermodynamic equilibrium constant is,

\[ K_p = \frac{P_{\text{MO}}P_{\text{CO}_2}}{P_{\text{MCO}_3}} = f(T) \text{ only} \]

As $P_{\text{MCO}_3}$ and $P_{\text{MO}}$ must be saturation vapour pressures, as phase
equilibrium must attain, a new partial equilibrium constant can
be defined as
\[
\frac{K'_p}{K_p} = \frac{P_{\text{MCO}_3}}{P_{\text{MO}}} = P_{\text{CO}_2}
\]

Denbigh also shows that Eq. (E.1) can then be rewritten, with sufficient accuracy, as

\[
-R'T \ln \frac{K'_p}{K_p} = \mu_{\text{MO}}^{\circ} \text{solid} + \mu_{\text{CO}_2}^{\circ} - \mu_{\text{MCO}_3}^{\circ} \text{solid}
\]

where the chemical potentials can be replaced by the standard free energies of formation, to give,

\[
-R'T \ln \frac{K'_p}{K_p} \times 298.16 = \Delta G_{fMO}^{\circ} + \Delta G_{f\text{CO}_2}^{\circ} - \Delta G_{f\text{MCO}_3}^{\circ}
\]

where the free energies are evaluated at 25°C.

The dependence of the enthalpy of reaction on temperature can then be defined as a function of the specific heats of the reactants and products by,

\[
\frac{d\Delta H_T}{dT} = C_{\text{PMO}} + C_{\text{PCO}_2} - C_{\text{PMCO}_3}
\]

where \(\Delta H_T\) is the enthalpy of reaction and \(C_p\) is the molar specific heat at constant pressure. \(C_p\) is normally expressed in a form such as,

\[
C_p = a' + b'T - c'T^2
\]

where \(a', b',\) and \(c'\) are constants, so that Eq. (E.3) can be integrated to give,

\[
\Delta H_T = \Delta H_0 + \int_0^T C_{p_1} \, dT
\]

E.1 : 227
where $\Delta H_0$ is a constant of integration and can be visualised as the enthalpy change on reaction at $0^\circ K$. This constant is obtained from the above equation by evaluation at $25^\circ C$, using the relation,

$$H_T @ 25^\circ C = \Delta H_{f_0}^0 + \Delta H_{f_{CO2}}^0 - \Delta H_{f_{MO}}^0$$

where $\Delta H_{f}^0$ is the standard enthalpy of formation at $25^\circ C$.

**E.2 Calculation of $K_p'$ for silver carbonate/silver oxide.**

Table E.1 gives thermodynamic properties of some carbonates for use in the above calculations. From the Table is obtained, $\Sigma \Delta G_f^0$ is $7.6342 \times 10^3$ cals/gm.mole, and $\Sigma \Delta H_f^0$ as $19.6122 \times 10^3$ cals/gm.mole. Hence,

$$-(R' \ln K_p')_{25^\circ C} = \frac{7.6342 \times 10^3}{298.16} = 25.6044 \text{cals/gm.mole}^\circ C$$

(E.6)

Now Eq. (E.4) can be used to determine the integration constant $\Delta H_0$ using the specific heat data from Table E.1, where $C_p$ is given as a function of temperature. Hence,

$$\Delta H_T - \Delta H_0 = -2.5543T + 4.13665 \times 10^{-3} \frac{T^2}{2} - 5.6111 \times 10^{-6} \frac{T^3}{3}$$

(E.7)

Evaluating at $298.16^\circ K$, using $\Delta H_{298.16} = \Sigma \Delta H_f^0$, gives $\Delta H_0$ as $20154.77$, which can be resubstituted in Eq. (E.4) for recalculation of $\Delta H_T$. Substituting this expression for $\Delta H_T$ in Eq. (E.5), and also the value for $(R' \ln K_p')_{298.16}$ obtained above in Eq. (E.6) gives, over/
(R¹ lnK'ₚ)ₜ = -2.5543ln(T/298.16) + 4.13665 x 10⁻³T - 2.80505 x 10⁻⁶T²
\[- \frac{20154.77}{T} + 41.0091\]  
(E.8)

From this equation can be evaluated K'ₚ in atmospheres for various values of T °K (R = 1.9872). These values are shown in Table E.2 and also in Fig. E.1. The analysis of K'ₚ has also been carried out for other carbonates, namely Mn, Mg, Ca, Sr and Ba, and the results for these are included in Table E.2 and Fig. E.1.

By comparing the temperatures at which the equilibrium pressures of each carbonate are one atmosphere it can be seen from the results that the kinetics of the decomposition of silver carbonate can be studied at lower temperatures than the others. Also in Fig. E.1 are shown some experimental values of the equilibrium pressures such as those of Spencer and Topley (1929) (see Table 7.2), and Watanabe on silver carbonate, and Smyth and Adams on calcium carbonate. Any discrepancies which exist between the results are likely to be explained by the lack of accuracy in the thermodynamic data rather than in the experimental work.

Data for the calculations on equilibrium pressures were obtained from Kubaschewski and Evans, Spencer and Justice, and Rossini.
Table E.1  Thermodynamic data

<table>
<thead>
<tr>
<th></th>
<th>$-\Delta G_f^0$</th>
<th>$\xi \Delta G_f^0$</th>
<th>$-\Delta H_f^0$</th>
<th>$\xi \Delta H_f^0$</th>
<th>$a'$</th>
<th>$b' \times 10^3$</th>
<th>$c' \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$_2$CO$_3$</td>
<td>104.48</td>
<td>7.63</td>
<td>120.97</td>
<td>19.61</td>
<td>18.97</td>
<td>25.85</td>
<td>-</td>
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<tr>
<td>Ag$_2$O</td>
<td>2.586</td>
<td></td>
<td>7.306</td>
<td></td>
<td>10.02*</td>
<td>23.93*</td>
<td>13.3*</td>
</tr>
<tr>
<td>MnCO$_3$</td>
<td>195.4</td>
<td>14.34</td>
<td>213.90</td>
<td>27.85</td>
<td>21.99</td>
<td>9.30</td>
<td>4.69</td>
</tr>
<tr>
<td>MnO</td>
<td>86.8</td>
<td></td>
<td>92.0</td>
<td></td>
<td>11.11</td>
<td>1.94</td>
<td>0.88</td>
</tr>
<tr>
<td>MgCO$_3$</td>
<td>24.6</td>
<td>15.61</td>
<td>266</td>
<td>28.11</td>
<td>18.62</td>
<td>13.80</td>
<td>4.16</td>
</tr>
<tr>
<td>MgO</td>
<td>136.13</td>
<td></td>
<td>143.84</td>
<td></td>
<td>10.18</td>
<td>1.74</td>
<td>1.48</td>
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<tr>
<td>CaCO$_3$</td>
<td>269.78</td>
<td>31.12</td>
<td>288.45</td>
<td>42.50</td>
<td>24.98</td>
<td>5.24</td>
<td>6.20</td>
</tr>
<tr>
<td>CaO</td>
<td>144.4</td>
<td></td>
<td>151.9</td>
<td></td>
<td>11.86</td>
<td>1.08</td>
<td>1.66</td>
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<tr>
<td>SrCO$_3$</td>
<td>271.9</td>
<td>43.84</td>
<td>291.2</td>
<td>56.05</td>
<td>21.42</td>
<td>8.56</td>
<td>3.396</td>
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<tr>
<td>SrO</td>
<td>133.8</td>
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<td>141.1</td>
<td></td>
<td>12.34</td>
<td>1.12</td>
<td>1.806</td>
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<td>BaCO$_3$</td>
<td>272.2</td>
<td>51.64</td>
<td>291.3</td>
<td>63.85</td>
<td>20.77</td>
<td>11.70</td>
<td>2.86</td>
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<td>BaO</td>
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<td>12.74</td>
<td>1.04</td>
<td>1.984</td>
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<tr>
<td>CO$_2$</td>
<td>94.26</td>
<td>94.05</td>
<td>6.3957*</td>
<td>10.1933*</td>
<td>3.5333*</td>
<td></td>
<td></td>
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</table>

See also Table E.2. Free energies and heats of formation given in Cals/gm.mole.

*a', b' and c' are constants in the equation,

$$C_p = a' + b'T - c'/T^2$$

*a', b' and c' are constants in the equation,

$$C_p = a' + b'T - c'T^2$$, with c' given as $c' \times 10^6$
Table E.2 Thermodynamic equilibrium pressures.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \log K'_{p} )</th>
<th>( K'_{p}, \text{ats.} )</th>
<th>( T^0K )</th>
<th>( 1/T^0K \times 10^4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ag}_2\text{CO}_3/\text{Ag}_2\text{O} )</td>
<td>-1.9498</td>
<td>0.01122</td>
<td>400</td>
<td>25.0</td>
</tr>
<tr>
<td></td>
<td>-0.7730</td>
<td>0.1687</td>
<td>450</td>
<td>22.22</td>
</tr>
<tr>
<td></td>
<td>0.1630</td>
<td>1.455</td>
<td>500</td>
<td>20.0</td>
</tr>
<tr>
<td>( \text{MnCO}_3/\text{MnO} )</td>
<td>-0.2822</td>
<td>0.5222</td>
<td>600</td>
<td>16.67</td>
</tr>
<tr>
<td></td>
<td>0.4805</td>
<td>3.023</td>
<td>650</td>
<td>15.38</td>
</tr>
<tr>
<td></td>
<td>-1.1885</td>
<td>0.06479</td>
<td>550</td>
<td>18.18</td>
</tr>
<tr>
<td>( \text{MgCO}_3/\text{MgO} )</td>
<td>-1.7978</td>
<td>0.01593</td>
<td>550</td>
<td>18.18</td>
</tr>
<tr>
<td></td>
<td>-0.8606</td>
<td>0.1378</td>
<td>600</td>
<td>16.67</td>
</tr>
<tr>
<td></td>
<td>-0.0728</td>
<td>0.8459</td>
<td>650</td>
<td>15.38</td>
</tr>
<tr>
<td>( \text{CaCO}_3/\text{CaO} )</td>
<td>-1.6626</td>
<td>0.02175</td>
<td>950</td>
<td>10.53</td>
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<td></td>
<td>-0.3964</td>
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<td></td>
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</tr>
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<td>( \text{SrCO}_3/\text{SrO} )</td>
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<td>0.01244</td>
<td>1150</td>
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<td></td>
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<td>0.1879</td>
<td>1300</td>
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<td>0.4598</td>
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<td>-0.3645</td>
<td>0.4320</td>
<td>1600</td>
<td>6.25</td>
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<tr>
<td></td>
<td>0.0858</td>
<td>1.218</td>
<td>1700</td>
<td>5.88</td>
</tr>
</tbody>
</table>

See also Fig. E.1
APPENDIX F

THE INFINITE CYLINDER AND THE SLAB.

F.1 Introduction. The sharp interface theory of gas–solid reactions has been presented in Chapters 4, 5 and 6 together with many isothermal and non-isothermal solutions of the controlling equations, evaluated by a Computer program (No. 8). These solutions were restricted to the sphere. Many of these solutions have also been obtained for the infinite cylinder and the slab, by Computer programs 9 and 10, Appendix G, and are presented here. The geometry and equations of these cases are described in Chapters 4–6.

F.2 Geometrical instability.

a) The cylinder:— For isothermal, irreversible reactions

\[
\eta_e = \left[1 - Y_2(Y_1 - \ln \frac{R}{r_1})\frac{r_1}{R}\right]^{-1}
\]

so that the criterion for geometrical instability is that

\[
(1-Y_1) + \ln \frac{r_1}{R} < 0
\]

with instability initiating at \(r_1/R = \exp(Y_1-1)\).

b) The slab:— For the slab,

\[
\eta_e = (Y_2(Y_1 + 1 - \frac{r_1}{R}) + 1)^{-1}
\]

F.2 : 232
so that

\[ \frac{d \eta_e}{d \frac{r_1}{R}} = \frac{Y_2}{(Y_2(Y_1+1-\frac{r_1}{R})+1)^2} \]

It can be seen from this equation that geometrical instability can never be achieved.

F.3 Isothermal solutions. The solutions for the cylinder and the slab given here correspond to those given for the sphere in Section 4.9.

a) Equimolar counterdiffusion:- Boundary layer diffusional resistances absent (i.e. \( Y_1 = 0 \)). These solutions are shown in Figs. F.1 and F.2 for the cylinder and F.3 and F.4 for the slab. Noticeable are the onset of geometrical instability at \( X = 0.865 \) for the cylinder compared to 0.875 for the sphere, and the absence of this instability in the results for the slab. It can also be seen that similar diffusion effects, as represented by the value of \( Y_2 \), produce greater reductions in reaction rate for the cylinder than for the sphere, purely because of the geometrical difference, and even greater reductions for the slab. The solutions should be compared with those for the sphere in Figs. 4.9 and 4.10.

b) Equimolar counterdiffusion:- Mixed diffusion control. These solutions are shown in Figs. F.5 and F.6 for the cylinder and Figs. F.7 and F.8 for the slab, and correspond to the solutions for the sphere given in Figs. 4.11 and 4.12. For the cylinder, geometrical instability initiates at \( \frac{r_1}{R} = \exp(Y_1-1) \), but for the slab instability is absent. Again it can be noticed that similar diffusion effects, as represented by \( Y_1 \) and \( Y_2 \), produce longer
reaction times for the cylinder and longer still for the slab, than for the sphere.

F.4 Non-isothermal reactions.

a) Endothermic:— The solutions obtained correspond to those obtained for the sphere, for intermediate cases, described in Section 6.4, case 3, and depicted in Figs. 6.5 and 6.6. The results are shown in Figs. F.9 and F.10 for the cylinder and Figs. F.11 and F.12 for the slab. The effect of heat transfer limitations is the same as that of mass transfer, in that reaction times are increased for the cylinder, and even more so for the slab. For the cylinder geometrical instability can be seen to predominate, whereas it is absent for the slab.

b) Exothermic:— It was pointed out during discussions on the sphere that no general presentation of results is possible, this being illustrated by example 1, Section 6.5. This example has been repeated for the cylinder and the slab, and the results shown in Figs. F.13 and F.14 respectively. Whereas diffusional effects and heat transfer effects associated with endothermic reactions produce progressively slower reactions for the cylinder and for the slab than for the sphere, heat transfer effects associated with exothermic reactions produce the opposite effect. This is obvious from the results, especially in the case of $Y_3$ 250. $\eta_e$ is higher for the cylinder than for the sphere, and obviously there is a tendency to accelerate into the diffusion regime. For the slab this break-away occurs, resulting in a very rapid reaction.
APPENDIX G

COMPUTER PROGRAMS.

The computer programs described in this appendix are presented after the appendix in Atlas Autocode, having been compiled with the aid of the report of Schofield and Osbourne.

G.1 Program 1 - Effectiveness factors in a porous sphere.

This program evaluates $\eta_e$ in terms of $Y_2$ and $Y_1$ as defined in Eq. (3.11), which can be rewritten,

$$\eta_e = \frac{3}{Y_1 Y_2} \frac{(Y_2)^{\frac{1}{3}} - \tanh(Y_1)^{\frac{1}{3}}}{(Y_2)^{\frac{1}{3}} - (1-1/Y_1)\tanh(Y_2)^{\frac{1}{3}}}$$ (G.1)

At each of the set values of $Y_1$, i.e. 1.00 to 0.00 in steps of 0.05, $\eta_e$ is calculated at the values of $Y_2$,

0.1 0.36 1 3.6 10 36 100 360 1000 3600 10000

The program prints the current value of $Y_1$ followed by a series of values of $Y_2$ and the corresponding value of $\eta_e$. No "data" is required. The results have been presented in Fig. 3.4.

Symbol in main text - Program symbol

\begin{align*}
\eta_e & \quad \text{n} \\
Y_1 & \quad \text{y} \\
\frac{Y_2}{Y_1} & \quad \text{y}'' \\
\frac{1}{3} \ln(Y_2) & \quad \text{x} \\
\tanh(Y_2)^{1/3} & \quad \text{tanh}
\end{align*}

Running time (full result), 3 secs.

G.1 : 235
G.2 Program 2 - Effectiveness factors in a porous slab.

This program evaluates $\eta_e$ in terms of $Y_2^1$ and $Y_1$ as defined by Eq. (3.15), which can be rewritten,

$$\eta_e = \frac{1}{Y_1 Y_2^1} \frac{(Y_2^1)^{1/3} \tanh(Y_2^1)^{1/3}}{(Y_2^1)^{2/3} \tanh(Y_2^1)^{2/3} + Y_1^{-1}}$$

$\eta_e$ is calculated for the same range of values of $Y_2^1$ and $Y_1$ as in Program 1 for the sphere, and gives the same print out. Symbols are as for Program 1, and no "data" is required. The results have been presented in Fig. 3.6. Running time (full results) 2 secs.

G.3 Program 3 - Effectiveness Factors in a porous cylinder.

This Program evaluates $\eta_e$ in terms of $Y_2^1$ and $Y_1$ as defined in Eq. (3.13) for the same range of values as in Programs 1 and 2. The procedure of calculation is slightly different in that for each of the set values of $Y_2^1$, $\eta_e$ is calculated for the range of values of $Y_1$. The program prints out the current value of $Y_2^1$, followed by a series of values of $Y_1$ and the corresponding values of $\eta_e$. Data required for the program are the values from tables of $I_0$ and $I_1$ for the values of $(Y_2^1)^{1/3}$ where $Y_2^1$ has the values 0.1, 0.36, 1.0, 3.6 and 10, while the remaining values of $I_0$ and $I_1$ for the higher values of $Y_2^1$ are obtained in the program from the formulae,

$$I_0(x) = \frac{e^x}{(2\pi x)^{1/2}} \left[ 1 + \frac{1^2}{1! 8x} + \frac{2^2 3^3}{2! (8x)^2} + \frac{3^2 2^2 2^2}{3! (8x)^3} + \frac{4^2 3^2 5^2 7^2}{4! (8x)^4} \right]$$

$$I_1(x) = \frac{e^x}{(2\pi x)^{1/2}} \left[ 1 - \frac{1.3}{1! 8x} - \frac{2.3 5}{2! (8x)^2} - \frac{3.2 5 7}{3! (8x)^3} - \frac{4.3 5 7 9}{4! (8x)^4} \right]$$

G.3 : 236
These formulae are accurate for large values of $x$. Results have been presented in Fig. 3.5. Symbols used were as for Programs 1 and 2, with the additions,

Symbols in main text - Program symbol

\[
I_0(Y_2)^\frac{1}{2} \quad b(j) = b(x)
\]

\[
I_1(Y_2)^\frac{1}{2} \quad b'(j) = b'(x)
\]

Data for certain values of $I_0$ and $I_1$ are required as shown in the program. Running time (full results), 2 secs.

G.4 Program - Diffusion in a porous sphere; concentration distribution.

This program calculates $1 - \frac{P-P_K}{P-G-P_K}$ in terms of $\frac{D_t}{\sigma R^2}$ and $r/R$,

as defined by Eq. (3.19), and $d(\frac{M_t}{P_K})/d(\frac{\epsilon}{\sigma R^2})$ in terms of $\frac{\epsilon}{\sigma R^2}$ as defined by Eq. (3.20). At a fixed value of $\frac{\epsilon}{\sigma R^2}$ (printed), ranging from 0.002 in steps of 0.001 to 0.600, the program calculates

$1 - \frac{P-P_K}{P-G-P_K}$ (printed) and a series of values (printed) of

\[ d(\frac{M_t}{P_K})/d(\frac{\epsilon}{\sigma R^2}) \]

at values of $r/R$ ranging from 1.0 to 0.05 in steps of 0.05. Results are shown in Fig. 3.7 and Fig. 3.8. No "data" is required.

Symbol in main text - Program symbol

\[
1 - \frac{P-P_K}{P-G-P_K} \quad pp
\]

\[
\frac{D_t}{\sigma R^2} \quad dta
\]

\[
\frac{M_t}{P_K} \quad D_t
\]

\[
d(\frac{M_t}{P_K})/d(\frac{\epsilon}{\sigma R^2}) \quad rate
\]
Criteria: In Eq.(3.19) the modulus of (series term minus subsequent series term) must not exceed 0.0001 before completion of the series, and in Eq.(3.20) the same criterion applies.

Running time, 2 mins.

G.5 Program 5 – Kinetic control of overall rate in a normal distribution of particle sizes. This Program evaluates \( \eta_d \) as a function of fractional penetration, \( \alpha \), where \( \eta_d \) is defined as

\[
\eta_d = \frac{\sum n(x - \alpha x_{\max})^2}{\sum nx^2}
\]

where all negative values of \( x - \alpha x_{\max} \) are treated as zero and where \( x_{\max} \) is the radius of the largest particle in the distribution, and \( \alpha \) is defined as the fractional penetration of the largest particle.

For given values of \( \sigma' \), the standard deviation, and \( \Delta x \), the difference in size between two adjacent particle sizes, chosen as equal to \( \sigma'/5 \) for the distribution in Table 4.1 so that \( \Delta n = 0.999637 \), and for the distribution given in Table 4.1, the program sets \( \alpha' \), calculates and prints \( n(x - \alpha x_{\max})^2 \) for each particle unless \( x - \alpha x_{\max} \) is negative, then sums \( n(x - \alpha x_{\max})^2 \) for the current value of \( \alpha \) and prints \( \alpha \) and \( n(x - \alpha x_{\max})^2 \). A new value of \( \alpha \) is then chosen such that \( |\Delta x| = 0.025 \) and the calculations repeated.

The data required are \( \sigma', \Delta x \) and values of \( n \) for one half of the particle size range (because the distribution is
symmetrical) starting from an extreme value of \( x \) and working towards the mean. Some of the results have been presented in Figs. 4.5 and 4.6.

Symbol in main text - Program symbol

\[
\begin{align*}
\sigma' & \quad \text{sigma} \\
\Delta x & \quad \text{int} \\
n & \quad n(i), n(41-i) \\
x-\Delta x/2 & \quad x(i), x(41-i) \\
|\Delta x| = x_{\text{max}}/40 & \quad dx' \\
\alpha x_{\text{max}} & \quad dx \\
\alpha & \quad j/40 \\
\leq nx^2 & \quad a' \\
n(x-\alpha x_{\text{max}})^2 & \quad da \\
\leq n(x-\alpha x_{\text{max}})^2 & \quad a
\end{align*}
\]

Running time, 6 secs.

G.6 Program 6 - Pore diffusion/kinetic control of the overall rate in a normal distribution of particle sizes.

This Program calculates the \( \eta_d \) versus \( \theta_{r_1} \) profiles for the particle distributions described in the text and also shown in Fig. 4.4 and used in Program 5. In terms of a single particle,

\[
\theta_{r_1} = \left(1 - \frac{r_1}{R}\right)\left(Y_2(1 + \frac{r_1}{R} - 2\left(\frac{r_1}{R}\right)^2) + 1\right) \quad (G.6)
\]

\[
\eta_d = \left(Y_2\left(\frac{1-r_1/R}{r_1/R}\right) + \left(\frac{r_1}{R}\right)^2 \right)^{-1} \quad (G.7)
\]

where \( r_1/R, Y_2 \) and \( \theta_{r_1} \) refer to a specific size of particle.

In terms of a variable particle size Eqs. (G.6) and (G.7) must be
rewritten as

\[ \theta_{r_1/x} = (1 - \frac{r_1}{R})(1 + \frac{r_1}{R} - 2(\frac{r_1}{R})^2 + 1) \tag{G.8} \]

and

\[ \eta_d = (Y_2 \frac{x}{X}(\frac{1-r_1/R}{r_1/R}) + (\frac{r_1}{R})^{-2})^{-1} \tag{G.9} \]

where in this case \( x \) and \( X \) are the radii of a particle and the mean particle respectively and \( r_1/R \) refers to the particle of radius \( x \). The point of this modification is to take account of particle size, so that for any particle its history may be defined in terms of a commonly defined value of \( \theta_{r_1} \). Hence \( \theta_{r_1} \) and \( Y_2 \) are defined relative to the mean particle.

First of all, then, the Program calculates the history of the largest particle and stores the values of \( \theta_{r_1} \) and \( \eta_d \) for values of \( r_1/R \) from 1.00 to 0.01 in steps of 0.01. The Program then goes on to the next smallest particle and begins its history starting at \( \theta_{r_1} = 0 \) and \( \eta_d = 1 \) for \( r_1/R = 1 \). When \( r_1/R = 0.99 \) the Program then evaluates \( \eta_d \) and \( \theta_{r_1} \) and continues to do so for subsequent \( r_1/R \) until \( \theta_{r_1} \) at a particular \( r_1/R \) is greater than \( \theta_{r_1} \) at \( r_1/R \) for the largest particle, 0.99. Linear interpolation is then used between the value of \( \theta_{r_1} \) and the preceding one to give \( \eta_d \) for the second largest particle at the same value of \( \theta_{r_1} \) as was obtained for the largest particle for \( r_1/R = 0.99 \). This value of \( \eta_d \), or rather \( n\eta_d \), where \( n \) is the relative frequency of the second particle, is then added to a cumulative total of \( n\eta_d \). The Program then proceeds with the history of the second largest particle until it finds two subsequent values of \( \theta_{r_1} \) for this
particle which "surround" the value of $\theta_{r_1}$ obtained for the largest particle when $r_1/R$ was 0.98, and so on until the reaction in the second largest particle is complete, thus giving an accumulative total of weighted values of $\eta_d$ for all the values of $\theta_{r_1}$ obtained for the largest particle at the 100 values of $r_1/R$. The Program then continues in the same manner with the next particle size, again comparing new values of $\theta_{r_1}$ with those for the largest particle, with the $(n\eta_d)$ totals accumulating as before. Hence $\eta_d$ is obtained as a function of $\theta_{r_1}$ for the whole distribution.

The Program prints the values of $\sigma'$ and $x$ used for the program followed by a chosen value of $Y_2$ for the largest particle and a list of 100 values of $\eta_d$ and the corresponding values of $\theta_{r_1}$. The data required are $\sigma'$, $x$, the size distribution as required also in Program 5, followed by the values of $Y_2$ for which results are required, these values being preceded by a number equal to the number of values of $Y_2$ to be used.

Symbol used in main text - Program symbol

- $\sigma' \quad \text{sigma}$
- $\Delta x \quad \text{int}$
- stored values of $\theta_{r_1}$ for $x_{\text{max}}$ t(k)
- current and preceding $\theta_{r_1}$ t', t''
- for other particles
- current and preceding $\eta_d$ n', n''
- for other particles
- n freq

G.6 : 241
current extrapolated value, \( \eta_d \)  
accumulating value of \( (n\eta_d) \)  
Running time (10 values of \( Y_2 \)), 1 min. 10 secs.

G.7 Program 7 - Thermal instability criteria and the instability envelope

From Eq. (5.23),

\[
F_1 = \left[ \frac{Y_5(T_1/T_G - 1)}{(T_1/T_G)^2 - 1} \right] \exp(-Y_5(1 - \frac{T_G}{T_1})) \]  \hspace{1cm} (G.10)

When \( F_1 = 0 \), i.e. no diffusional resistance, we have,

\[
Y_5 = \left[ \frac{(T_1/T_G)^2}{T_1/T_G - 1} \right] = \frac{1}{m(1-m)} \]  \hspace{1cm} (G.11)

where \( m = 1 - T_G/T_1 \). The limiting values of \( F_1 \) are given in terms of \( Y_5 \) by,

\[
F_1 = \frac{(Y_5 - 4)}{Y_5 \exp(2)}
\]

while \( Y_5 = \frac{2}{1 - T_G/T_1} = \frac{2}{m} \) \hspace{1cm} (G.12)

so that \( F_1 = m(\frac{2}{m} - 4)/(2\exp(2)) \) \hspace{1cm} (G.13)

The limiting values of \( F_2 \) are defined by Eq. (5.25). If \( F_1 = 0 \) then from Eq. (5.25),

\[
(F_2)_j = \left( \frac{T_1}{T_G} - 1 \right) \exp(-Y_5(1 - \frac{T_G}{T_1}))
\]

\hspace{1cm} (G.7 : 242)
i.e. \((F_2)_j = \frac{m}{1 - m} \exp(-Y_5m)\) \hspace{1cm} (G.14)

The program selects and prints a value of \(m = 1 - \frac{T_G}{T_1}\), where \(\frac{T_i}{T_G} = (\frac{T_i}{T_G})_I\) or \((\frac{T_i}{T_G})_E\) then calculates and prints the value of \(Y_5\) corresponding to \(F_1 = 0\) from Eq. (G.11). Then the Program calculates and prints the value of \(F_1\) when \(\frac{T_i}{T_G} = (\frac{T_i}{T_G})_E\) at the selected value of \(m\), i.e. on the instability envelope, from Eq. (G.13) as well as the value of \(Y_5\) for this value of \(F_1\), from Eq. (G.12). This is followed by the value of \(F_2\) for \(F_1 = 0\) at the selected value of \(m\) and at the value of \(Y_5\) when \(F_1 = 0\), obtained above. This is calculated from Eq. (G.14).

At the chosen value of \(m\), the Program then calculates \(F_1\) from Eq. (G.10) and \(F_2\) from Eq. (5.25) for a series of values of \(Y_5\) between 4 and 50 in steps of 0.5, printing in the order \(Y_5\), \(F_1\) and \(F_2\), and always with \(F_1\) positive.

The Program is arranged to perform the calculations for values of \(m\) from 0.020 to 0.100 in steps of 0.001, 0.105 to 0.5 in steps of 0.005 and from 0.52 to 0.80 in steps of 0.02. No "data" is required. The results have been depicted in Figs. 5.2 and 5.5.

Symbol in main text - Program symbols

1. \(1 - \frac{T_G}{T_1} = m\) \hspace{1cm} x
2. \(Y_5\) \hspace{1cm} y

G.7 : 243
Running time (Full results), 2 mins. 27 secs.

G.8 Program 8 - Sharp interface theory, sphere. This was the main Program used in connection with the theoretical section of this work, and was also the most difficult, so that more attention will be given to its workings.

The Program solves the simultaneous transient equations given by Eqs. (6.9) and (6.10) and integrates for \( \theta_{r_1} \) via Eq. (6.11) giving values of \( \eta_d, \eta_e, T_i/T_G \) and \( \theta_{r_1} \) throughout a reaction.

The solid is initially at a temperature \( (T_i/T_G)_0 \) this value being fed in as data. The whole reactant core is at this temperature so that \( \eta_d \) can be immediately evaluated, no transience having developed as yet. Initially \( r_1/R = 1 \). A new value of \( r_1/R \), actually 0.999, is then chosen. Assuming that \( \eta_d \) is constant over the time taken for the interface to move to this new value of \( r_1/R \), the time interval can be obtained, thus allowing a new more correct value of \( T_i/T_G \) for \( r_1/R = 0.999 \) to be calculated. This new but approximate value of \( T_i/T_G \) gives a more correct value for \( \eta_d \), which in turn gives a more correct value for the time interval for the interfacial movement. The "loop" is repeated until no further significant change in \( \eta_d \) is detected. An exact value of \( \theta_{r_1} \) is obtained, and the Program then moves on to the next value of \( r_1/R \), these values going from 1.000 to 0.050 in steps of 0.001.

Values of \( \eta_d \) are obtained from Eq. (6.9) at current values
of $T_i/T_G$ either by Newton Raphson iteration if diffusion is non-equlimolar, or directly if $a = g$. $T_i/T_G$ is obtained from Eq. (6.10) in the form,

$$
\frac{T_i}{T_G} \approx 1 - Y_2 Y_4 \left( Y_3 \frac{1 - \frac{r_i}{R}}{r_i/R} + \frac{Y_8}{3 \Delta \theta_{r_i}} \left( F_{c_2} \left( \frac{T_i}{T_G} - 1 \right) - F_{c_1} \left( \frac{T_i}{T_G} - 1 \right) \right) \right)
$$

where $2$ and $1$ refer to present and previous values of variables at present and previous values of the $r_i/R$ choice, $\Delta \theta_{r_i}$ being obtained from Eq. (6.11) in the form,

$$
\Delta \theta_{r_i} = \frac{1}{3} \left( \frac{r_i}{R} \right)^3 - \frac{\left( \frac{r_i}{R} \right)^3}{2}
$$

while $F_c$ is obtained from Eq. (6.12).

A simplified flow diagram of the Program is given in Fig. G.1. The Program evaluates $\eta_d$, $\eta_r$, and $\theta_{r_i}$ at all values of $r_i/R$ from 1.000 to 0.050 in steps of 0.001; these steps were found to be small enough to give highly accurate values of $\theta_{r_i}$. The Newton Raphson iteration for non-equlimolar counterdiffusion was continued until the correction was less than 0.00001. The routine for evaluating $T_i/T_G$ was continued until $\text{mod}(\eta_{d_2}/\eta_{d_1} - 1)$ was less than 0.00001.

The data required for the Program are the number of sets of "data", the stoichiometric coefficients $a$ and $g$, and $Y_1$ to $Y_{10}$, with finally the value $(T_i/T_G)_0$. With the exception of the latter, all these are printed out at the head of each result, the first number being the number of the "data" set. There then
follows the main result in column form, the columns being $\eta_d$, $\eta_e$, $T_1/T_G$, $\theta r_1$, $\rho_1/R$, $X$, the number of times the Newton Raphson cycle was used before correcting $\eta_d$ sufficiently (this is printed as 1 for $a = g$) and finally the number of times a new try was made at evaluating $T_1/T_G$ correctly. The above items are printed for values of $\rho_1/R$ of 1.000 to 0.850 in steps of 0.005, and from 0.80 to 0.05 in steps of 0.05, this arrangement being used as changes are more rapid towards the beginning of the reaction in most cases. Special print-out procedures were used on occasion to give more results in certain ranges of $\rho_1/R$, for example the exact point at which $\eta_d$ suddenly changes in the non-transient diffusion regime solutions in Figs. 6.11 and 6.12 was obtained in this way.

An example of a result of the Program is given in part in Table G.1, captions having been added for clarity. This example corresponds to one of the endothermic reaction examples given in Section 6.4.2 and Figs. 6.3 and 6.4, i.e. for $Y_3 = 1000$.

Symbol in main text - Program symbol

| $a, g$ | $a, g$ |
| $Y_1$ to $Y_{10}$ | $y(1)$ to $y(10)$ |
| $\eta_d$ | $n(dr)$ |
| $\rho_1/R$ | $r r(dr)$ |
| $T_1/T_G$ | $t r(dr)$ |
| $\theta r_1$ | $t l(dr)$ |
| $f n, f n'$ | $f n, f n'$ |

Running time (single result), $\frac{1}{2}$ min. approx.

---

G.8 : 246
Fig. G.1  Flow diagram, Program 8. (Also Programs 9, 10)

start  

read new data

set new value of $r_1/R$

evaluate $\theta_{r_1}$ interval at current $\eta_d$

evaluate $F_c$ and $\frac{T_1}{T_G}$ at current $\eta_d$ with $\left(\frac{T_1}{T_G}\right)_1$ and current interval in $\theta_{r_1}$

is diffusion equimolar?

evaluate new $\eta_d$ by N-R iteration

is new $\eta_d$ much diff. from previous?

is $r_1/R = 1$?

is $d$ much different to $\eta_d$ calculated at previous $T_1/T_G$?

evaluate $\theta_{r_1}$ and add to $\theta_{r_1}$

print results at certain $r_1/R$

is $r_1/R = 0.05$?

stop

any more data?
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<th>( \theta_{r_1} )</th>
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<th>( X )</th>
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Table G.1: Example of result of program 8
G.9 Program 9 - Sharp interface theory, cylinder. This is exactly the same as for the sphere, except for obvious minor alterations to allow for the different geometry.

G.10 Program 10 - Sharp interface theory, slab. This is exactly the same as for the sphere, except for obvious minor alterations to allow for the different geometry. Also, as for the slab $\eta_d = \eta_e$, only one is printed. Similarly, as $r_1/R = 1 - X$, only $r_1/R$ is printed.

G.11 Program 11 - Surface area to volume ratio, normal distribution.

This program was used to study the effect of a distribution of particle sizes on the B.E.T. surface area of a porous solid made up of spherical particles. The same frequency or relative amount distribution was used as given in Chapter 4, Table 4.1. A variety of values of $\sigma^r$ were used and the divisions of the particle size range were such as to account for 99.9637% of the quantity distributed. The mean particle size is again taken as a dimensionless ratio of unity.

The data required for the program are the forty frequency values of the distribution, the number of sets of $\sigma^r$ and $\Delta x$ following, then these values. To achieve the frequency summation given above, $\Delta x = \sigma^r/5$. The program gives the values of the following quantities for each data set:

- Distribution by number,
  \[ 3 \xi (nx^2) \quad \xi (nx^2) \quad (3 \xi (nx^2)) \xi (nx^2) \]

- Distribution by volume,
  \[ 3 \xi (n/x) \quad \xi n \quad (3 \xi (n/x))/\xi n \]

Running time 1 sec.
Program 12 - Theoretical fit of experiments. This Program was a dimensional equivalent of Program 8, modified to give specific results for direct comparison of experimental results for the decomposition of silver carbonate. The program assumes that the only resistance to heat transfer is through the boundary layer surrounding a \( \frac{1}{4}'' \) sphere, while from a diffusional point of view the concentration of carbon dioxide throughout the carbonate sphere is assumed constant, while concentration gradients are possible within the discrete pellets making up the \( \frac{1}{4}'' \) sphere. The interfacial theory, therefore, was applied to the discrete particles while reaction rates were taken as constant throughout the \( \frac{1}{4}'' \) sphere, as was the temperature of reaction, with a temperature gradient but no concentration gradient in the boundary layer surrounding the sphere. The equations governing the model were mentioned in Section 9.5.2.

The program can also be applied to the coated celite Runs, if an excessively high heat transfer coefficient is used to ensure an isothermal reaction. The flow diagram for the Program is essentially the same as for the diagram in Fig. G.1.

The data required form the program are; the number of calculations to be done; \( \ln k^0_c \) where \( k^0_c \) has been defined by Eq. (9.3); the effective diffusivity of \( CO_2 \) in air within the pores of the discrete particle, \( \text{cm}^2/\text{hr.} \); the boundary layer heat transfer coefficient \( h_B \), \( \text{Cals/hr.cm}^2.\text{O}° \text{C} \); a factor to multiply the reaction rate by to evaluate the average concentration of \( CO_2 \) surrounding the pellet, given by \( 15.6/F \) where \( F \) is the flow in \( 1/\text{min} \) through
the reactor bed; the voidage of the \( \frac{1}{4} \)" spheres (this value is unimportant for celite reactions); the number of simulations to be carried out under the above conditions; and the furnace temperature corresponding to each of the simulations to be performed at the above conditions.

The print-out gives: the variables fed in as data; the number of the simulation within the set dependent on these variables; the relevant furnace temperature; then in tabular form similar to Program 8; the rate of reaction per pellet, gms. CO\(_2\)/hr; the reaction rate, moles CO\(_2\)/mole Ag\(_2\)CO\(_3\).hr; the interfacial temperature, \( ^{\circ}\)K; the reaction time, mins; \( 1-\alpha \), \( X \); the number of iterative cycles necessary to evaluate the correct results; the decay factor, \( \eta_d \); the effectiveness factor, \( \eta_e \).

The differences between the Program and Program 8 are the larger steps in penetration (0.002 compared with 0.001) and the absence of Newton Raphson iteration.

The nomenclature used in the program is similar to that used in Program 8, with the additions,

Symbol in main text - Symbol in Program

\( \ln k_0^0 \) and \( k_0^0 \) & \( kc \),
\( D_e \) & \( de \),
\( h_B \) & \( hg \),
\( T_G \) & \( tg \),
\( 15.6/F \) & \( \text{factor} \),
\( \sigma \) & \( \sigma \),

Running time, 8 secs per simulation approx.
Errata:— In Program 12, where the numbers 7.904 and 3856 appear, these should be multiplied by 2.303.
Program 1 - Effectiveness factors in a porous sphere.

BEGIN
REAL y', y'', x, tanh, n
INTEGER i, j

CYCLE i=0,1,20
y'=1-0.05i ; print(y',1,2) ; newline

CYCLE j=1,1,11
y''=0.01*(10^((int pt(j/2)+1)))
IF frac pt (j/2)=0 THEN y''=0.36y''
x=sqrt(y'') ; IF x>10 THEN ->1
tanh=(exp(2x)-1)/(exp(2x)+1) ; ->2
1: tanh=1
2: n=(3*(x-tanh))/((x^2*(y'*x)-(y'-1)*tanh))
IF n<0.001 THEN ->3
print (y'',5,4) ; print (n,1,5)
REPEAT
newline
3: REPEAT
END OF PROGRAM

Program 2 - Effectiveness factors in a porous slab.

BEGIN
REAL y', y'', x, tanh, n
INTEGER i, j

CYCLE i=0,1,20
y'=1-0.05i ; print(y',1,2) ; newline

CYCLE j=1,1,11
y''=0.01*(10^((int pt(j/2)+1)))
IF frac pt (j/2)=0 THEN y''=0.36y''
x=sqrt(y'') ; IF x>10 THEN ->1
z=(exp(2x)-1)/(exp(2x)+1) ; ->2
1: tanh=1
2: n=(3*(x-tanh))/((x^2*(y'*x)-(y'-1)*tanh))
IF n<0.001 THEN ->3
print (y'',5,4) ; print (n,1,5)
REPEAT
newline
3: REPEAT
END OF PROGRAM
Program 3 - Effectiveness factors in a porous cylinder.

BEGIN
REAL y', y'', x, tanh, n
ARRAY b, b' (1:12)
INTEGER i, j, k

CYCLE j=1, 1, 11
y' = 0.01*(10^(int pt(j/2)+1))
IF frac pt(j/2)=0 THEN y'' = 0.36y'
print (y'', 5, 4)
x=sqrt(y')
IF x > 5 THEN ->1
read (b(j)); read (b'(j)); ->2
1: b(j) = 1 + 0.125/x - 0.07031/x
   b'(j) = 1 - 0.375/x - 0.11715/x^2
k = 0

2: CYCLE i = 0, 1, 20
y' = 0.05*i
k = k+1
IF frac pt ((k-1)/5) = 0 THEN newline
n = (2x*b'(j))/(x^2*(x*y'*b'(j)+b(j)))
IF n < 0.001 THEN ->3
print (y', 1, 2); print (n, 1, 5)
REPEAT

3: newlines(2)
REPEAT

END OF PROGRAM

1.02515709 0.16009973
1.09204535 0.31370403
1.255965533 0.56515910
2.1239795 1.4469311
5.57172491 4.57607325

C P 3 : 254
Program 4 - Diffusion in a porous sphere; concentration distribution.

BEGIN
REAL dta, dta', radrat, sum, sum', pp, rate
ARRAY fn(1:100), fn'(1:100)
INTEGER data, ndr, n, m

dta'=0.001

CYCLE data=1,1,599
dta=dta'+0.001*data
newline
print(data,4,o)
print(dta,1,3)
m=0
sum'=0
3: m=m+1
fn'(m)=exp(-m^2*π^2*dta)
sum'=sum'+fn'(m)
IF m=1 THEN ->3
IF mod(fn'(m)-fn'(m-1))<0.0001 THEN ->4
->3
4: rate=6*sum'
print(rate,5,5)
newline
CYCLE ndr=1,1,20
radrat=1-(ndr-1)/20
n=0; sum=0
1:n=n+1
fn(n)=parity(n)/n*(sin(n*π*radrat)*exp(-n^2*π^2*dta))
sum=sum+fn(n)
IF n=1 THEN ->1
IF mod(fn(n)-fn(n-1))<0.0001 THEN ->2
->1
2: pp=1+(2/(π*radrat))*sum
print(1-pp,1,3)
REPEAT
REPEAT
END OF PROGRAM
Program 5 - Kinetic control of overall rate in a normal
distribution of particle sizes.

BEGIN
REAL sigma, int, x', dx, dx', a, a', da
ARRAY n, x(1:40)
INTEGER i, j

read (sigma) ; print (sigma,1,4)
read (int) ; print (int,1,3) ; newline

CYCLE i=1,1,20
read (n(i)) ; n(41-i)=n(i)
x(i)=1+(20.5_i)*int
x(41-i)=1-(20.5_i)*int
REPEAT

dx'=x(1)/40

CYCLE j=0,1,39
dx=j*dx' ; a=0

CYCLE i=1,1,40
IF dx>x(i) THEN ->1
da=(x(i)-dx)^2*n(i) ; print(da,1,10) **
a=a+da
REPEAT

1: newline
IF j=0 THEN a'=a ; IF j=0 THEN print (a',2,5)
print(1-0.025j,1,3) ; spaces(4)
print(a/a',1,5) ; newline

REPEAT

END OF PROGRAM

0.25 0.05
0.0000385 0.000009 0.000175 0.00035 0.000665
0.001205 0.002105 0.00354 0.0057 0.00885
0.0132 0.01885 0.02595 0.0343 0.0436
0.0532 0.0624 0.07035 0.07615 0.07925

** For Distribution By Area Line 17 Becomes
da=(x(i)-dx)^2*n(i)/x(i)^2 ; print(da,1,10)
For Distribution By Volume Line 17 Becomes
da=(x(i)-dx)^2*n(i)/(x(i)^3) ; print(da,1,10)

CP 5 : 256
Program 6 - Pore diffusion/kinetic control of the overall rate in a normal distribution of particle sizes.

upper case delimiters
BEGIN
REAL  n', t', n'', t'', int, sigma, y', r, r', extrapn
ARRAY  t, totaln(1:100), freq(1:40)
INTEGER a, b, i, j, k, l, m

read (sigma); print (sigma, 1, 4)
read (int); print (int, 1, 4)

CYCLE a=1, 1, 20
read (freq(a)); freq(41-a)=freq(a)
REPEAT
read (1); CYCLE m=1, 1, 1
read (y''); print (y'', 3, 3)

CYCLE i=1, 1, 40
r' = 1+4*sigma-(i-1)*int
k=2; t'=0; n'=0

CYCLE j=1, 1, 100
r = 0.01-0.01*j
n''=(r**2)/(y''*r'(1-r)/r+1/(r**2))
t''=r*(1-r*((y''*r''/6)*(1+r-2*(r**2))+1)
IF i=1 THEN ->1
IF j=1 THEN ->2
IF t''<t(k)<t' THEN ->3; ->4
1: t(j)=t''
totaln(j)=n'*freq(i); ->4
2: totaln(1)=totaln(1)+n'*freq(i); ->4
3: extrapn=n''-(t'-t(k))*(n''-n''')/(t'-t''')
totaln(k)=totaln(k)+extrapn*freq(i)
k=k+1
4: REPEAT
REPEAT
print (totaln(1), 5, 5); newline

CYCLE b=1, 1, 100
IF frac pt((b-1)/5)=0 THEN newline
print (totaln(b)/totaln(1), 1, 4)
print (t(b), 4, 4)
REPEAT; newlines(2)
REPEAT
END OF PROGRAM

0.25 0.05
0.0000385 0.00009 0.000175 0.00035 0.000665
0.001205 0.002105 0.00354 0.0057 0.00885
0.0132 0.02595 0.0343 0.0436 0.0532 0.0624 0.07035 0.07615 0.07925

C P 6 : 257
Program 7 - Thermal instability criteria and the instability envelope.

Upper case delimiters

BEGIN
REAL x, frn, fh, c, d, y
INTEGER a, b, i, j, k

a = 0 ; b = 30 ; c = 0.02 ; d = 0.001 ; -> 3
1: a = 1 ; c = 0.1 ; d = 0.005 ; -> 3
2: b = 15 ; c = 0.5 ; d = 0.02

3: CYCLE i = a, b
   x = c + i * d
   print (x, 1, 3)
   y = 1 / (x * (1 - x))
   print (y, 2, 2)
   | value of y at current x for fm = o
   IF (2/x - 4) > 0 THEN print ((2/x - 4) / (exp(2) * (2/x))^1000, 3, 3)
   | value of fm at current x, on stability envelope
   print (2/x, 2, 2)
   | value of yApp at current x corr to envel value = current fm
   IF y * x < 15 THEN print (((1/(1-x)-1)/exp(y*x))^1000, 3, 3)
   | min value of fh for fm = 0 at value of y above
   k = 0

CYCLE j = 8, 1, 100
   y = j / 2
   IF y * x > 15 THEN -> 5
   fm = (y * x * (1 - x) - 1) / exp(y * x)
   IF fm < 0 THEN -> 4
   fh = (1/(1-x)-1)*((fm+1/exp(y*x))
   k = k + 1
   IF frac pt((k-1)/5) = 0 THEN newline
   print (y, 2, 1)
   print (fm*1000, 3, 3)
   print (fh*1000, 3, 3)
   spaces(2)
   4: REPEAT

5: newlines(2)
REPEAT

IF c = 0.02 THEN -> 1
IF c = 0.1 THEN -> 2
END OF PROGRAM
Program 8 - Sharp interface theory, sphere.

upper case delimiters

BEGIN
REAL a,g,a',b',c',a'',b'',c'',dt',dt,fn,fn',corr,n'
ARRAY n,rr,tr,t,cf(0:1000),y(1:10)
INTEGER dr,f,no',tries,count
read (no'); CYCLE no=1,1,no'; print(no,3,0); newline
read (a); print(a,1,1); read (g); print(g,1,1)
CYCLE f=1,1,10; read(y(f)); print(y(f),3,3); REPEAT
read(tr(0)); newline; n(0)=1; t(0)=0; cf(0)=1
a'=(g-a)*y(2)*(y(9)-y(6)*y(7))/g
b'=((g-a)*y(7)*(g-a)*y(6))
c'=((g-a)*(g(9)-y(6)*y(7))/y(7)*(g-a)*y(6))
IF (g-a)=0 THEN a'=1/y(7)*(y(9)-y(6)*y(7))
CYCLE dr=0,1,950
rr(dr)=1-0.001*dr; tries=0; count=0
IF dr=0 THEN ->2; n(dr)=n(dr-1)
1: count=count+1; n'=n(dr)
dt'=((rr(dr-1))*3-(rr(dr))*3)/((3/2)*(n(dr-1)+n(dr)))
ct(dr)=0.5*(1-rr(dr))/rr(dr)*((2-3*rr(dr)-rr(dr))^2)
cf(dr)=1-of(dr)/y(3)+(1-rr(dr))/rr(dr))
tr(dr)=y(2)*y(4)*(n'(dr)-cf(dr)+ct(dr-1)-ct(dr-1))*y(8)/(3*dt')
tr(dr)=tr(dr)*y(3)+(1-rr(dr))/rr(dr))
tr(dr)=tr(dr)/y(2)*y(4)*y(3)*cf(dr)*y(3)+(1-rr(dr))/rr(dr))
2: IF (g-a)=0 THEN ->0
a''=a'*y(1)+(1-rr(dr))/rr(dr))
b''=-b'*y(7)*exp(y(10)*(1-1/tr(dr)))-y(5)*y(7)
c''=1/(rr(dr))^2*exp(y(5)*(1-1/tr(dr)))
3: tries=tries+1
fn=a'*n(dr)+log(b'+c'*n(dr))
fn'=a'*c'/b'*c'*n(dr))
corr=fn/fn'; IF corr<-n(dr) THEN ->4; ->5
4: n(dr)=a'*n(dr); ->3
5: n(dr)=n(dr)+corr
IF mod(corr)<0.00001 THEN ->7; ->3
6: a''=a'*y(9)*exp(y(10)*(1-1/tr(dr)))-y(5)*y(7)
b''=y(2)*y(1)+(1-rr(dr))/rr(dr))
c''=1/(rr(dr))^2*exp(y(5)*(1-1/tr(dr)))
n(dr)=a''/(b''+c'') ; tries=1
7: IF dr=0 THEN ->10 ; IF count=1 THEN ->1
IF mod(n(dr)/n'-1)<0.0001 THEN ->8 ; ->1
8: dt=(2/3)*((rr(dr-1))*3-(rr(dr))*3)/(n(dr-1)+n(dr))
t(dr)=t(dr-1)+dt
IF dr>50 THEN ->9 ; IF frac pt (dr/5)=0 THEN ->10 ; ->11
9: IF frac pt (dr/50)=0 THEN ->10 ; ->11
10: print (n(dr),4,6); print ((n(dr)/rr(dr))^2,4,6)
print (tr(dr),3,6); print (t(dr),3,6)
print (rr(dr),3,3); print ((1-rr(dr))^3,3,4)
print (tries,3,0); print (count,3,0)
newline
11: REPEAT ; newlines(2) ; REPEAT
END OF PROGRAM

CP8 : 259
Program 9 - Sharp interface theory, cylinder.

upper case delimiters
BEGIN
REAL a,g,a',b',c',a'',b'',c'',dt',dt,fn,fn',corr,n'
ARRAY n,rr,tn,cf(0:1000),y(1:10)

INTEGER dr,f,no,no',tries,count

read (no') ; CYCLE no=1,1,no' ; print(no,3,0) ; newline
read (a) ; print(a,1,i) ; read (g) ; print(g,1,i)

CYCLE f=1,1,10 ; read(y(f)) ; print(y(f),3,3) ; REPEAT
read(tr(o)) ; newline ; n(0)=1 ; t(0)=0 ; cf(0)=1

a'=(g-a)*(y(2)*(y(9)-y(6)*y(7)))/g
b'=((g-a)/(y(7)*(g-(g-a)*y(6))))
c'=((g-a)*(y(9)-y(6)*y(7)))/(y(7)*(g-(g-a)*y(6)))

IF (g-a)=0 THEN a'=1/(y(7)*(y(9)-y(6)*y(7)))

CYCLE dr=0,1,950

rr(dr)=1+0.001*dr ; tries=0 ; count=0

IF dr=0 THEN ->2 ; n(dr)=n(dr-1)
1: count=count+1 ; n'=n(dr)
dt'=((rr(dr-1))^2-(rr(dr))^2)/(n(dr-1)+n(dr))
cf(dr)=0.5(2log(1/rr(dr))-(1-rr(dr))^2)
cf(dr)=1-cf(dr)/(y(3)+log(1/rr(dr)))
tr(dr)=y(2)*y(4)*(n(dr)-((cf(dr)+tr(dr-1)-1)*cf(dr-1)*y(8))/(2*dt'))

tr(dr)=tr(dr)/(1+y(2)*y(4)*y(5)*cf(dr)*y(3)+log(1/rr(dr)))/(2*dt'))

2: IF (g-a)=0 THEN ->6

a'=a'*(y(1)+log(1/rr(dr)))
b'=(1-b'*exp(y(10)*(1-1/tr(dr))))-y(6)*y(7))
c'=(rr(dr)*exp(y(5)*(1-1/tr(dr))))

3: tries=tries+1

fn'=n(dr)+log(b'+c'*n(dr))
fn'=a'*/(b'+c'*n(dr))
corr=fn/fn' ; IF corr<-n(dr) THEN ->4 ; ->5
4: n(dr)=9*n(dr) ; ->3
5: n(dr)=n(dr)+corr

IF mod(corr)<0.0001 THEN ->7 ; ->3
6: a'=a'*(y(9)*exp(y(10)*(1-1/tr(dr))))-y(6)*y(7))
b'=y(2)*(y(1)+log(1/rr(dr)))
c'=(1/(y(7)*exp(y(5)*(1-1/tr(dr))))

n(dr)=a'*/(b'+c') ; tries=1

7: IF dr=0 THEN ->10 ; IF count=1 THEN ->1

8: dt=((rr(dr-1))^2-(rr(dr))^2)/(n(dr-1)+n(dr))
t(dr)=t(dr-1)+dt

IF dr>50 THEN ->9 ; IF frac pt (dr/5)=0 THEN ->10 ; ->11
9: IF frac pt (dr/50)=0 THEN ->10 ; ->11
10: print (n(dr),4,6) ; print ((n(dr)/rr(dr)),4,6)
print (tr(dr),3,6) ; print (t(dr),3,6)
print (rr(dr),3,3) ; print ((1-rr(dr))^2),3,4)
print (tries,3,0) ; print (count,3,0)

IF count=1 THEN ->1

END OF PROGRAM

CP9 : 260
Program 10 - Sharp interface theory, slab.

**upper case delimiters**

```
BEGIN
REAL a, b, c, d, e, f, g, h, i, j, k, l, m, n, o, p, q, r, s, t, u, v, w, x, y, z,
     a', b', c', d', e', f', g', h', i', j', k', l', m', n', o', p', q', r', s', t', u', v', w',
     x', y', z', a'', b'', c'', d'', e'', f'', g'', h'', i'', j'', k'', l'', m'', n'', o'', p'',
     q'', r'', s'', t'', u'', v'', w'', x'', y'', z''
ARRAY n, r, t, v, w, x, y, z, a', b', c', d', e', f', g', h', i', j', k', l', m', n', o',
     p', q', r', s', t', u', v', w', x', y', z', a'', b'', c'', d'', e'', f'', g'', h'', i'',
     j'', k'', l'', m'', n'', o'', p'', q'', r'', s'', t'', u'', v'', w'', x'', y'', z''
INTEGER d, f, h, i, j, k, l, m, n, o, p, q, r, s, t, u, v, w, x, y, z, d', f',
     h', i', j', k', l', m', n', o', p', q', r', s', t', u', v', w', x', y', z', d'',
     f'', h'', i'', j'', k'', l'', m'', n'', o'', p'', q'', r'', s'', t'', u'', v'', w'',
     x'', y'', z'', d'''
read (no) ; CYCLE no=1,1,no' ; print(no,3,0) ; newline
read (a) ; print(a,1,1) ; read (b) ; print(b,1,1)
CYCLE f=1,1,10 ; read(y(f)) ; print(y(f),3,3) ; REPEAT
read(tr(0)) ; newline ; n(0)=1 ; t(0)=0 ; cf(0)=1
a'=(g-a)*y(2)*y(3)*y(4)*y(5)*y(6)
(b'=((g-a)*y(2)*y(3)*y(4)*y(5)*y(6))
   n(2)=n(1)
   t(2)=t(1)+dt(2)
   IF g-a<0 THEN ->6
   a'=(g-a)*y(2)*y(3)*y(4)*y(5)*y(6)
   b'=(g-a)*y(2)*y(3)*y(4)*y(5)*y(6)
   c'=exp(y(5)*(1-1/tr(2)))-y(6)*y(7)
   c'=(exp(y(5)*(1-1/tr(2)))-y(6)*y(7))
   n(2)=n(2)+1
   t(2)=t(2)+dt(2)
   IF g-a<0 THEN ->6
   a'=(g-a)*y(2)*y(3)*y(4)*y(5)*y(6)
   b'=(g-a)*y(2)*y(3)*y(4)*y(5)*y(6)
   c'=exp(y(5)*(1-1/tr(2)))-y(6)*y(7)
   c'=(exp(y(5)*(1-1/tr(2)))-y(6)*y(7))
   n(2)=n(2)+1
   t(2)=t(2)+dt(2)
   IF g-a<0 THEN ->6
   a'=(g-a)*y(2)*y(3)*y(4)*y(5)*y(6)
   b'=(g-a)*y(2)*y(3)*y(4)*y(5)*y(6)
   c'=exp(y(5)*(1-1/tr(2)))-y(6)*y(7)
   c'=(exp(y(5)*(1-1/tr(2)))-y(6)*y(7))
   n(2)=n(2)+1
   t(2)=t(2)+dt(2)
   IF g-a<0 THEN ->6
   a'=(g-a)*y(2)*y(3)*y(4)*y(5)*y(6)
   b'=(g-a)*y(2)*y(3)*y(4)*y(5)*y(6)
   c'=exp(y(5)*(1-1/tr(2)))-y(6)*y(7)
   c'=(exp(y(5)*(1-1/tr(2)))-y(6)*y(7))
   n(2)=n(2)+1
   t(2)=t(2)+dt(2)
   IF g-a<0 THEN ->6
   a'=(g-a)*y(2)*y(3)*y(4)*y(5)*y(6)
   b'=(g-a)*y(2)*y(3)*y(4)*y(5)*y(6)
   c'=exp(y(5)*(1-1/tr(2)))-y(6)*y(7)
   c'=(exp(y(5)*(1-1/tr(2)))-y(6)*y(7))
   n(2)=n(2)+1
   t(2)=t(2)+dt(2)
```

END OF PROGRAM
Program 11 - Surface area to volume ratio, normal distribution.

upper case delimiters
BEGIN
REAL  sigma, int, a, da, v
ARRAY  x, n(1:40)
INTEGER i, j, k

CYCLE i=1,1,20
read (n(i)) ; n(41-i)=n(i)
REPEAT

read (j)
CYCLE k=1,1,j
read (sigma) ; print (sigma,1,10)
read (int) ; print (int,1,10)
newline

CYCLE i=1,1,20
x(i)=1+(20.5-i)*int
x(41-i)=1-(20.5-i)*int
REPEAT

| NUMBER DISTRIBUTION
a=0 ; v=0
CYCLE i=1,1,40
da=n(i)*(x(i)^2)
a=a+da ; v=v+da*x(i)
REPEAT
print (4*pi*a,2,10) ; print ((4/3)*pi*v,2,10)
print (3*a/v,5,5) ; newline

| VOLUME DISTRIBUTION
a=0 ; v=0
CYCLE i=1,1,40
a=a+n(i)/x(i) ; v=v+n(i)
REPEAT
print (3*a,2,10) ; print (v,2,10)
print (3*a/v,5,5)
newlines(2)
REPEAT

END OF PROGRAM

0.0000385 0.00009  0.000175 0.00035  0.000665
0.001205 0.002105 0.00354 0.0057  0.00885
0.0132  0.01885  0.02595 0.0343  0.0436
0.0532  0.0624  0.07035 0.07615  0.07925
Program 12 - Theoretical fit of experiments.

upper case delimiters
BEGIN
REAL  
ARRAY 
INTEGER 
BEGIN
READ
CYCLE
READ
CYCLE
READ
NEWLINE
K = EXP(K)
READ
CYCLE
NEWLINE
NEWLINE
IF
IF
IF
IF
IF
IF
IF
IF
IF
IF
NEWLINE
NEWLINE
NEWLINE
END OF PROGRAM
Fig. 2(.4).1
Interfacial reaction model.

Fig. 2(.4).2
Reaction histories for various geometries.

Fig. 2(.5.1).3
The effect of temperature on potential and resultant rates.
Fig. 3.2.1 Model of reaction in a porous slab.

Fig. 3.2.2 Experimental achievement of various reaction models.
a) Sphere, cylinder.

b) Slab.

Fig. 3(2.3) Mathematical models for various geometries.
Fig. 3.4 Effectiveness factors in a porous sphere.

F 3.4 : 267
Fig. 3(9).5 Effectiveness factors in a porous cylinder.
Fig. 3.6 Effectiveness factors in a porous slab.
Fig. 3.7 Concentration distributions in a sphere for diffusion without reaction.
Fig. 3(13).8 Mass transfer rates at the surface of a sphere for diffusion without reaction.
Model of System

Fig. 4.2.1  Model of sharp interface reaction in a sphere.
Fig. 4.6.2 Decay factor histories for kinetic control in various geometries.

Fig. 4.6.3 Effect of geometry on reaction histories.

F4.3 : 273
Fig. 4(7.4) Normal Distribution.

Fig. 4(7.5) Kinetic control of reaction in a distribution of particle sizes.
Contribution to interfacial area as a function of penetration.
(Normal distribution.

\[ x_{i}/x \text{ for largest sphere} \]

Particle size

Kinetic control, distribution by area, volume.
Fig. 4(8.4).8 Effect of pore diffusion on reaction in a distribution of particle sizes.
Fig. 49. The effect of pore diffusion on the decay and effectiveness factor histories. ($Y_1 = 0$)

F 49 : 277
Fig. 4(.9.1).10  The effect of pore diffusion on the conversion history. \((Y_1 = 0)\)
The effect of mixed control on the decay factor.
Fig. 4(.9.2).12 The effect of mixed control on the conversion history.
Fig. 4.9.3.13 The effect of non-equimolar counterdiffusion.

\( \eta_2 = 0 \)
Fig. 5(7.1) Thermal instability - Heat loss and heat generation.

- **Unstable Region**
- **Generation**
- **Loss**

- **Stable**
- **Unstable**

\[ \frac{T_i}{T_g} \]
MINIMUM IGNITION & COMBUSTION TEMPERATURES

INSTABILITY ENVELOPE

Fig. 5(2).
Minimum ignition and combustion temperatures from $F_{1}$ and $Y_{5}$
Fig. 5(7).3 The effect of radiation on thermal instability.

Fig. 5(7).4 Instability Limits of $F_2$.
Fig. 5.7.5  Instability criteria - Limits of $F_2$ in terms of $F_1$ and $Y_5$.  

In the figure, the plot represents the instability envelope for given criteria. The axes are labeled as $F_1$ and $Y_5$, with specific scales for each axis. The diagram illustrates the relation between the criteria values and the instability envelope, indicating the limits of $F_2$ for various $F_1$ and $Y_5$ values.
Fig. 6.4.1.1 Endothermic example 1). $Y_3 = 0$.

Fig. 6.4.1.2 Endothermic example 1).
$Y_3 = 0$. 
Fig. 6(4.2.3) Endothermic example 2). $Y_4 = 0.1$

Fig. 6(4.2.4) As above.
Fig. 6(4.3.5) Endothermic example 3). $Y_a = 10$

Fig. 6(4.3.6) As above.
Fig. 6.(5.1).7 Exothermic example 1). Transient solution.

\[ Y_4 = -0.1, \quad Y_3 \text{ varied.} \]
Fig. 6(.5.1).8 Graphical solution of the steady-state solution to exothermic example 1), when \( Y_3 = 100 \).

Fig. 6(.5.1).9 Comparison of transient and steady-state solutions for exothermic example 1), when \( Y_3 = 100 \).
Fig. 6(5.2).10 Exothermic example 2). Effect of change in solid heat capacity on the comparison between transient and steady state solutions.
Fig. 6(5.3).11 Exothermic example 3). Effect of change in initial solid temperature on achievement of diffusion regime. $X_b = 1$
Fig. 6. Exothermic example 3. Effect of changing initial solid temperature on achievement of diffusion regime. $Y_8 = -0.5$.

$Y_8 = -0.5$

$[T_i/T_G]_0$ Varied

Transient Reaction Histories

Steady State

X, Conversion
Fig. 6.13 Close agreement between transient and steady-state solutions for endothermic reactions.

ENDOTHERMIC REACTION

\[ Y_1 = 0 \quad Y_2 = 0.01 \quad Y_3 = 1 \quad Y_4 = 10 \]

\[ \Theta_{ji} \]

Transient

Steady State
Fig. 7.4.1 Decomposition history, Centnerszwer and Bruzs.

Fig. 7.4.2 Comparison of interfacial theory with uni-molecular law.
Fig. 7.4. Time required to achieve certain conversions as a function of temperature, by Centnerszwer and Bruzs.

Fig. 7.7.4
The effect of CO₂ on the rate of decomposition, compared with theory. (Spencer and Topley)

Fig. 7.7.5
The effect of CO₂ pressure, P, on the reverse reaction.
Fig. 7(.8).6 The effect of water vapour on the decomposition reaction. (Spencer and Topley).

Fig. 7(.8).7 The effect of water vapour on the low and high temperature decomposition reaction. (Centnerszwer and Bruzs).
Fig. 8(.2).1 Two Coulter Counter measurements of the particle size distribution of silver carbonate.
Fig. 8.3.2 Simple models of the powdered silver carbonate.

Fig. 8.3.3 Kinetic control of reaction in models of the powdered silver carbonate.
Fig. 8(.5).4 The effect of a particle size (or area, or volume) distribution on the B.E.T. surface area.

Fig. 8(.6).5 Perspex sphere mould.
1  Gas inlet pipe  
2  Extension tubes  
3  Sindanyo cover  
4  Asbestos cement tube  
5  Vermiculite insulation  
6  Refractory cement  
7  Sindanyo support plate  
8  Thermocouples  
9  Gas exit pipe  
10 Reactor end flange  
11 Firebrick  
12 Reactor bed carrier  
13 Perforated plates  
14 Thermocouple pocket  
15 Electrical winding  
16 Aluminium furnace block  
17 Terminals  
18 Ceramic balls  

scale : 5:1

Fig. 8(.10).6 Diagram of apparatus – reactor.
Fig. 8(11.7) Diagram of apparatus - Gas flow.
Fig. 8.12.9 calibration of katharometer.
Fig. 9(.3).1 Preliminary measurement of reaction rates. (old moulds)

Fig. 9(.3).2 Preliminary measurement of reaction rates. (New moulds).
Fig. 9(.3).3 "Activation energy" plot of reaction rates at various conversion; Correction for reaction temperature drop.

Fig. 9.3: 305
Fig. 9(.4.1).4 Reaction temperature profiles, arbitrary humidity.

Fig. 9(.4.1).5 Temperature runs - initial temperature drop.
(Arbitrary humidity).
Fig. 9.1.6 Details of temperature history Runs.

(Arbitrary humidity).

Fig. 9.1.7 Temperature Runs with heat conduction along thermocouple.
Fig. 9(4.3.8) "Activation energy" plot of temperature drops, correction for reaction temperature drop.
Fig. 9. Details of temperature histories, dry nitrogen.

Fig. 9. Details of temperature histories, humidified air.
Fig. "Activation energy" plot of temperature drops, correction for reaction temperature drop. (Controlled humidities).
Fig. 9.4.12 Initial temperature drops, controlled humidity Runs.

Fig. 9.4.6.13 The effect of water vapour, Run 95.

Fig. 9.4.6.14 The effect of water vapour, Run 96.
**Fig. 9.4.5.15** Thermodynamic equilibrium pressures; experimental measurements; the results of previous workers.
**Fig. 9.4.6.16** The effect of humidification at 23°C temperature. Runs 121 & 222

**Fig. 9.4.6.17** The effect of water vapour. Run 140.

**Fig. 9.4.6.18** The saturation effect of water vapour, Run 152.
Fig. 9(.4.6).19
The effect of water vapour, Run 223.

Fig. 9(.4.7).20
Reverse reaction temperature histories.
Fig. 9.4.8.21 Cylced operation and the effect of water vapour.
Fig. 9(5).22 Measurement of decomposition rate in dry and humid N₂, by continuous weighing.
Fig. 9.23: "Activation energy plot for humid sphere and celite rate runs."
Fig. 9(5.2).24 Theoretical fit of reaction rates, celite and spheres, humid runs.

Fig. 9(5.2).25 Theoretical prediction of temperature history in a sphere.

Fig. 9(5.3).26 Comparison of both dry and humid Runs in celite and spheres.
Fig. B(.5).1 Steady-state apparatus for measurement of diffusivity in porous solids.

Fig. B(.6).2 Unsteady-state apparatus for measurement of diffusivity in porous solids.
Fig. B.7.3 Unsteady-state diffusivity measurements; theory.

F B.3 : 320
Fig. B(8.4) Simple apparatus for the measurement of diffusivities.
Steel wool
+ Celite
△ Kaolin
○ Woburn soil crumbs
▼ Sodium chloride
• Carborundum
○ Sand
○ Glass spheres
△ Dye & Dallavalle
--- Buckingham
○ Present work

Fig. B(.12).5  Comparison of results with those of Currie.

Fig. B(.11).6  Finite source pressure during diffusion experiment.
Fig. C(3.1) Boundary layer heat and mass transfer coefficients.

Fig. C(4.2) Boundary layer heat and mass transfer rates.
Fig. E(.2). Thermodynamic equilibrium pressures for various carbonates.
Fig. F(3).1 The effect of pore diffusion on the decay and effectiveness factor histories. ($Y_1 = 0$) (Cylinder)

FF.1 : 325
Fig. F(3).2 The effect of pore diffusion on the conversion history. ($Y_1 = 0$) (Cylinder)
Fig. F(.3).3 The effect of pore diffusion on the decay and effectiveness factors histories. \((Y_1 = 0)\) (Slab)

\[ \eta_e = \eta_d \]
Fig. F(3.4) The effect of pore diffusion on the conversion history. ($Y_1 = 0$) (Slab)
Fig. F(3.5) The effect of mixed control on the decay factor.
(Cylinder)

FF.5 : 329
Fig. F(3).6 The effect of mixed control on the conversion history. (Cylinder)
Fig. F(3).7 The effect of mixed control on the decay factor.
(Slab)

FF.7 331
Fig. F(.3).8 The effect of mixed control on the conversion history. (Slab)
Fig. F(0.4).9 Intermediate endothermic example (cylinder). $Y_4 = 10$

Fig. F(0.4).10 As above.

Fig. F(0.4).10: 333
Fig. F.11 Intermediate endothermic example (slab). \( Y_4 = 10 \)

Fig. F.12 As above.
Fig. F(4).13 Exothermic example. (Cylinder).

Fig. F(4).14 Exothermic example. (Slab).
a) Silver carbonate powder (Johnson Matthey) x5000

Plate 1. Transmission Electron Micrographs.

b) Silver carbonate powder (B.D.H.) x5000
Plate 2. Transmission Electron Micrograph.

(Johnson Matthey) x10000
a) Sphere moulds - carbonate and decomposed spheres.

Plate 3

b) Arrangement of spheres in bed    c) Arrangement of celite in bed.
Plate 4. General view of apparatus and control panel.
Plate 5. View of control panel and reactor unit.
a) Silver oxide, formed by decomposition at less than 200°C.


b) Oxide, decomposition at 230°C.
Plate 7. Reflection Electron Micrographs - carbonate, and oxide from decomposition of carbonate in air of arbitrary humidity.

a) Carbonate, x 14500
b) Carbonate, x 4400
c) Carbonate, x 14500

d) Oxide, x 1500

e) Oxide, x 4500
f) Oxide, x 15000
Plate 8. Reflection Electron Micrographs - oxide from decomposition of carbonate in dry and moist atmospheres, at 200°C.
NOMENCLATURE

\( a, g, s \)  stoichiometric coefficients
\( a', b', c' \)  coefficients, specific heat equation
\( a_v \)  surface area of spheres per unit volume of bed
\( A, B, C \)  see page 54
\( A_d \)  cross-sectional area of porous plug
\( c \)  concentration of reacting solid
\( C_p \)  molar specific heat
\( D \)  binary diffusion coefficient
\( e, \exp \)  exponential
\( E_c \)  activation energy of reaction
\( E_e \)  "activation energy" of equilibrium pressure
\( F_1, F_2 \)  Dimensionless mass and heat transfer groups
\( F_c \)  Conduction factor
\( G \)  mass velocity
\( \Delta G_f \)  free energy of formation
\( h_B \)  boundary layer heat transfer coefficient
\( H \)  enthalpy of reacting solid
\( \Delta H \)  heat of reaction
\( \Delta H_f \)  enthalpy of formation
\( I_0 \)  modified Bessel function of 0 order and 1st kind
\( I_1 \)  modified Bessel function of 1st order and 1st kind
\( J_D, J_H \)  mass and heat transfer factors
\( k_c, k_c' \)  velocity constants, forward and reverse reactions
\( k_c^0 \)  velocity constant at infinite temperature
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_B$</td>
<td>boundary layer mass transfer coefficient</td>
</tr>
<tr>
<td>$k_e$</td>
<td>thermal conductivity of solid</td>
</tr>
<tr>
<td>$k$</td>
<td>thermal conductivity of gas</td>
</tr>
<tr>
<td>$K$</td>
<td>$k_C/k_C'$</td>
</tr>
<tr>
<td>$K_p$</td>
<td>Thermodynamic equilibrium constant</td>
</tr>
<tr>
<td>$K'_p$</td>
<td>partial equilibrium constant, $P_e$</td>
</tr>
<tr>
<td>$K_0$</td>
<td>modified Bessel function of 0 order and 2nd kind</td>
</tr>
<tr>
<td>$K_1$</td>
<td>modified Bessel function of 1st order and 2nd kind</td>
</tr>
<tr>
<td>$l$</td>
<td>distance through porous plug</td>
</tr>
<tr>
<td>$l_0$</td>
<td>thickness of porous plug</td>
</tr>
<tr>
<td>$L$</td>
<td>$\frac{1}{2}$-length of cylinder or bar</td>
</tr>
<tr>
<td>$M_t, M_K$</td>
<td>contents of pores at time $t$ and time 0</td>
</tr>
<tr>
<td>$m$</td>
<td>$1-T_G/T_1$</td>
</tr>
<tr>
<td>$n$</td>
<td>relative frequency of particle in fixed range</td>
</tr>
<tr>
<td>$n_X$</td>
<td>probability of particle smaller than $x$</td>
</tr>
<tr>
<td>$N$</td>
<td>overall rate of reaction per pellet</td>
</tr>
<tr>
<td>$P$</td>
<td>partial pressure of component $G$</td>
</tr>
<tr>
<td>$P_e$</td>
<td>equilibrium pressure of $CO_2$</td>
</tr>
<tr>
<td>$P_K$</td>
<td>total, or equilibrium, pressure</td>
</tr>
<tr>
<td>$P_T$</td>
<td>total pressure</td>
</tr>
<tr>
<td>$Pr$</td>
<td>Prandtl number</td>
</tr>
<tr>
<td>$Q$</td>
<td>heat transferred to reaction site</td>
</tr>
<tr>
<td>$r$</td>
<td>distance from centre of solid</td>
</tr>
<tr>
<td>$R$</td>
<td>distance from centre of solid to surface</td>
</tr>
<tr>
<td>$R'$</td>
<td>gas law constant</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynolds number</td>
</tr>
</tbody>
</table>
S  molar surface area
Sc  Schmidt number
t  time
t_{r_i}  time taken for interface to penetrate to r_i
T  temperature at distance r from centre of solid
\Delta T  T_G - T_i
(T_i)_I  minimum ignition temperature
(T_i)_E  minimum combustion (maximum extinction) temperature
u  velocity of interfacial penetration
V  volume of finite source
x  radius of discrete particle
X  fractional conversion
y  mole fraction of diffusing species
Y_{1-10}  Dimensionless groups, pages 53 and 71
Y_2  Dimensionless group, page 38
z  tortuosity factor
Z  \frac{1}{2}-width of bar

\alpha  fractional penetration
\beta  fractional covering of surface area
\mu  chemical potential
\theta_{r_i}, \theta_{x_i}  dimensionless time for interfacial penetration
\eta_d, \eta_e  decay and effectiveness factors
\sigma  voidage
\sigma'  standard deviation
\rho  mass density
SUBSCRIPTS

B  boundary layer
e  effective
E  minimum combustion or maximum extinction
f  formation
g  generation
G  in bulk gas
i  at the interface
I  minimum ignition
j  I or E
l  loss
m  molar
T  total

SUPERSCRIPT

o  standard
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