

**The Engineering of
Gas—Solid
Reactions**



I.Chem.E.—VTG/VDI Joint Meeting—Brighton, 1968

The Engineering of Gas-Solid Reactions

Proceedings of the Symposium

held on 24—26 April 1968

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PHYSICO-CHEMICAL ASPECTS OF
GAS-SOLID REACTIONS

Papers presented

at the

First Symposium on

The Characteristics of
Solid Particles which are
Relevant to Gas-Solid
Reactions

and a

Report on the Discussion

By R. M. DELL, B.Sc., Ph.D., C.Eng., F.R.S.

This paper reviews the basic reaction characteristics of reactions in dispersed systems. These are classified under four categories:

- (1) Decomposition of solids and liquids
- (2) Gas-solid reactions involving solid particles
- (3) Oxidation and reduction processes
- (4) Reaction of the general type

For each reaction discussed the various physical and chemical factors which influence the reaction rate and the nature of the process are described. The paper concludes that a clear understanding of the physical chemistry of the reaction is an essential prerequisite for engineering the process on a large scale.

The symposium was held at the University of Cambridge, England, on 10-11 November 1961. The papers were presented by the following authors:

Introduction

The engineering of a gas-solid reaction in the large scale requires a knowledge of the basic reaction characteristics of the reaction. These reactions are generally so complex that varying a number of influencing operational variables has to be appreciated with care. The design of the reactor and the characteristics of the chemical engineering equipment employed. This paper sets out to discuss the various chemical factors which are important in gas-solid reactions and to indicate how these factors should be taken into account when engineering the reaction on a large scale. The approach adopted is essentially that of the solid state chemist interested in reaction mechanisms and kinetics. Some typical reactions are considered in outline to illustrate the principles involved; many of these are drawn from the field of nuclear chemical engineering.

The term "gas-solid reaction" is very broad and includes, for example, such diverse types of chemical process as the decomposition of solids, the oxidation and reduction of metals, the reaction of metals with acids, and the reaction of metals with gases. The approach adopted is essentially that of the solid state chemist interested in reaction mechanisms and kinetics. Some typical reactions are considered in outline to illustrate the principles involved; many of these are drawn from the field of nuclear chemical engineering.

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Joint Chairmen Professor Dr. rer. nat. E. Wicke, and Professor P. N. Rowe, C.Eng.

Decomposition reactions

The decomposition of solids, like other chemical reactions, may be either exothermic or endothermic. Some decomposition reactions involve only a single reactant species, their rates are rate supply-limited although removal of gaseous products may be the limiting step. Unless an exothermic decomposition reaction is carried out at a low enough temperature for the heat of the reaction to be dissipated, local hot spots may develop and the reaction will accelerate rapidly, sometimes leading to explosion, as in the case of heavy metal oxides of

PHYSICO-CHEMICAL ASPECTS OF GAS-SOLID REACTIONS

By R. M. DELL, B.Sc., Ph.D., F.Chem. Soc.*

SYNOPSIS

This paper reviews the basic physico-chemical concepts underlying gas-solid reactions of various types. A selection of reactions is discussed, many of them drawn from the field of nuclear chemical engineering, and these are considered under four categories:

- (1). Decompositions of hydroxides and salts.
- (2). Reactions between solids leading to a solid and gaseous product.
- (3). Oxidation and ignition processes in oxygen or fluorine.
- (4). Reactions of the general type $\text{Solid}_I + \text{Gas}_I \rightleftharpoons \text{Solid}_{II} + \text{Gas}_{II}$.

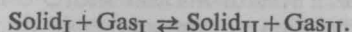
For each reaction discussed the various chemical and physical factors which influence the mechanism and kinetics of the process are described. The complexity of gas-solid reactions is emphasised and it is argued that a clear understanding of the physical chemistry of the reaction is an essential preliminary to engineering the process on a large scale.

Introduction

The engineering of a gas-solid reaction on the basis of data acquired in laboratory-scale reactors is well known to be fraught with difficulty. These reactions are generally so complex that scaling-up a process or introducing operational variables has to be approached with extreme caution unless one has a clear understanding of both the physical chemistry of the reaction and the dynamics of the chemical engineering equipment employed. This paper sets out to discuss the various chemical factors which are important in solid-gas reactions and to indicate how these factors should be taken into account when engineering the reaction on a large scale. The approach adopted is essentially that of the solid state chemist interested in reaction mechanisms and kinetics. Some typical reactions are considered in outline to illustrate the principles involved; many of these are drawn from the field of nuclear chemical engineering.

The term "gas-solid reaction" is very broad and includes, for example, such diverse types of chemical process as the decomposition of salts, the oxidation and corrosion of metals, and reaction of oxides with such gases as hydrogen or sulphur dioxide. There are several possible ways in which these reactions may be classified: they may be subdivided according to the nature of the solid phase involved (salt, metal, oxide, etc), the temperature range of the reaction, or the type of chemical reactor employed. In this paper we shall adopt a physico-chemical classification in which reactions are considered under four major headings as follows:

- (1). Decomposition reactions (hydroxides, carbonates, salts).
- (2). Reactions between two solid phases leading to a gaseous product.
- (3). Oxidation and ignition processes wherein a solid reacts exothermically with oxygen or fluorine.
- (4). Reactions of the general type:



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Each of these groups includes reactions which are important in industry or technology. For some selected processes we describe how the reaction kinetics and the textural properties of the product solid (grain size, surface area, porosity, etc) are influenced by the physico-chemical conditions prevailing in the reaction system.

Decomposition Reactions

The decomposition of salts, like other chemical reactions, may be either exothermic or endothermic. Since decompositions involve only a single reactant species their rates are not supply-limited although removal of gaseous products may be the limiting step. Unless an exothermic decomposition reaction is carried out at a low enough temperature for the heat of the reaction to be dissipated, local "hot spots" may develop and the reaction will accelerate rapidly, sometimes leading to explosion, as in the case of heavy metal azides or fulminates. Most decomposition reactions of interest to chemical engineers, however, are endothermic in nature and it is necessary to supply heat to the reactor. Examples are the preparation of magnesia from magnesium hydroxide, lime from limestone, and the decomposition of nitrates to metallic oxides.

Alkaline earth hydroxides

Magnesium oxide and beryllium oxide are commonly prepared by decomposition of the hydroxides. Magnesium oxide finds widespread use as an adsorbent, for the manufacture of other magnesium chemicals and as a refractory; beryllium oxide is normally employed as a ceramic. According to the application the oxide may be required in a stated particle size range (powder or granules) or with a specified surface area. Low surface area magnesium oxide (periclase) is produced by calcining at temperatures above 1000°C, while reactive magnesia ("light burn" grades) is prepared at lower temperatures and may have a surface area in excess of 200 m²/g. (Fig. 1).

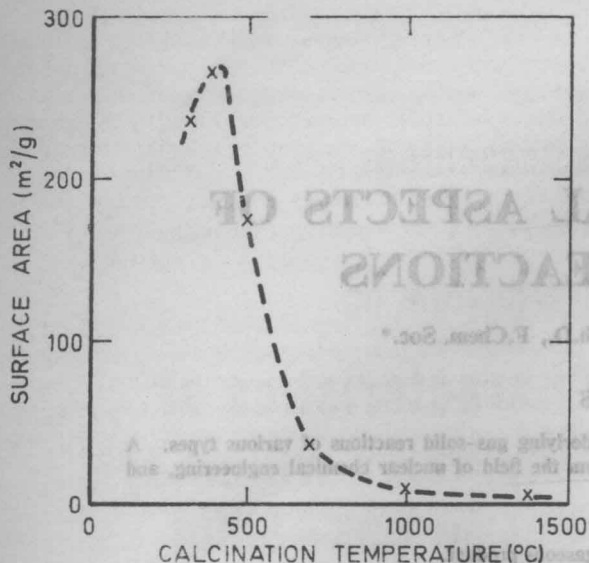


Fig. 1.—Surface area of magnesium oxide prepared from magnesium hydroxide as a function of calcining temperature in air

Electron microscope studies have shown that the magnesia particles consist of agglomerates of micro-crystallites aggregated into a relic structure which is pseudomorphic after the hexagonal platelets of the parent magnesium hydroxide.¹ At low temperatures, crystallite growth and sintering take place within the individual pseudomorphs and only at high temperatures is there appreciable interparticulate sintering and grain growth. The surface area of the magnesium oxide is very much dependent upon the prevailing water vapour pressure; below 400°C the presence of water vapour facilitates nucleation and leads to smaller MgO crystallites with a higher specific surface area than when decomposition is carried out in high vacuum. At high temperatures (800°C) the converse holds true and water vapour facilitates the sintering of magnesium oxide and the loss of surface area. Water vapour appears to exert a catalytic role in surface diffusion processes, thereby enhancing sintering. The surface area of the final magnesia is therefore a complex function of the rate of heating, the prevailing water vapour pressure at the interface, and the final temperature reached.

The decomposition of beryllium hydroxide also leads to particles of beryllium oxide which are pseudomorphic after the parent hydroxide crystals.² This system is of interest in that vacuum decomposition produces a microporous aggregate in which ~70% of the pores are < 6Å wide. The presence of such fine pores in high concentration is quite unusual and invalidates surface area measurements by gas adsorption. When beryllium hydroxide is decomposed in the presence of water vapour both the total pore volume (~50% of the aggregate volume) and the beryllia crystallite size (~30Å) are essentially unchanged, yet the average pore radius is now very much larger. Subtle distinctions such as this may profoundly influence the sintering behaviour of the powder when preparing dense oxide compacts. These examples show that it is important to control the gas atmosphere during decomposition reactions when preparing oxide powders for ceramic applications.

Alumina hydrates

The dehydration of alumina hydrates, studied in detail by de Boer and co-workers,³ reveals several interesting facets. Alumina forms two crystallographically distinct trihydrates (gibbsite and bayerite) and two monohydrates (boehmite and diaspore). The decomposition scheme of these hydrates to yield various forms of anhydrous alumina is outlined in Table I.

While certain details of this scheme are still open to question, the salient features to be noted are

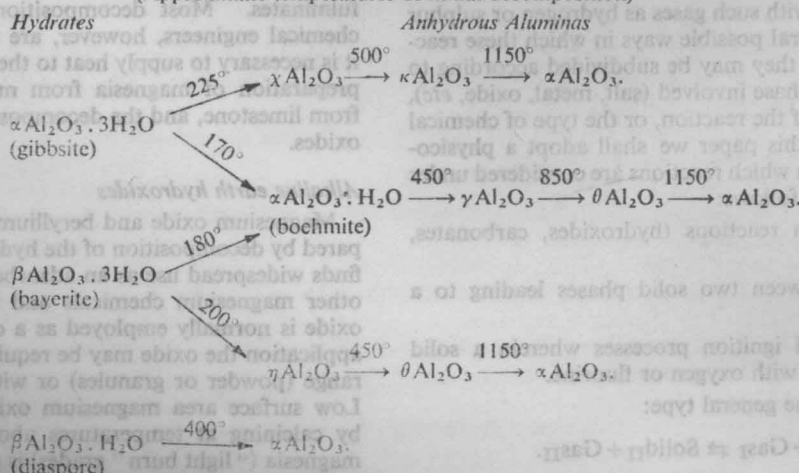
(1). Gibbsite and bayerite may each undergo decomposition by two distinct paths, one of which is common to both substances.

(2). In the characteristic decomposition mode, gibbsite forms first χ -Al₂O₃ whereas bayerite yields η -Al₂O₃; these crystallographic modifications possess quite distinct properties and the distinction has practical importance, for example in catalyst manufacture.

(3). Diaspore decomposes directly to α -Al₂O₃ at a low temperature.

Experiments have revealed that finely divided gibbsite and bayerite decompose directly to anhydrous alumina (χ or η respectively) with no formation of boehmite whereas larger crystallites decompose simultaneously by both routes. This is made clear by the differential thermal analysis curves for gibbsite (Fig. 2), in which it is seen that small crystallites

TABLE I.—Decomposition Scheme for Alumina Hydrates heated in Dry Air.
(Approximate temperatures of initial decomposition)



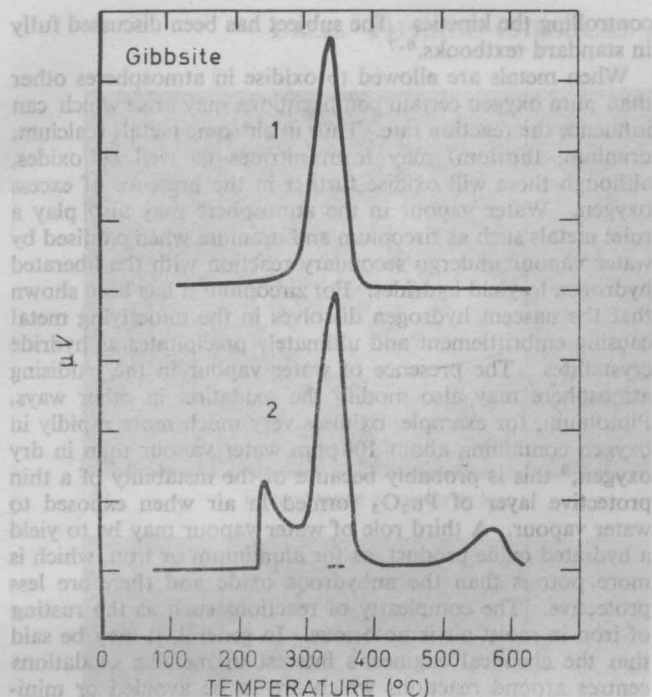


Fig. 2.—Differential thermal analysis of gibbsite (1) small crystallites (2) large crystallites

decompose in a single endothermic process while large crystallites decompose in three steps; the first endotherm at 240°C corresponds to partial conversion to boehmite, the second at 300°C to direct decomposition of gibbsite to χ Al_2O_3 and the third at 500°C to decomposition of the boehmite. The reason for this behaviour is that boehmite is formed from the trihydrate only under hydrothermal conditions by heating in pressurized steam or water. When large crystallites of gibbsite are heated rapidly, the decomposition pressure developed internally gives rise to hydrothermal conditions and partial conversion to boehmite. By contrast, the water vapour can escape more readily from small crystals and hydrothermal conditions are not developed. Thus the decomposition path depends not only upon the crystallographic modifications of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ employed, but also on the crystallite size and the heating rate. The end product is thus conditioned by the hydroxide precipitation conditions (which determine the phase formed), the ageing time of the gibbsite or bayerite precipitate, and the design of the dehydration equipment.

Uranyl nitrate (see p. 7)

The decomposition of uranyl nitrate to uranium trioxide is a primary process in the manufacture of uranium metal and uranium hexafluoride. In the past this reaction has been carried out batchwise in a stainless steel vessel heated by gas ("pot-denitration") although in recent years continuous fluidised-bed denitrators have been employed. The complexity of the reactions involved in the decomposition of uranyl nitrate [$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] has been demonstrated by simple laboratory experiments. Thus Fig. 3 shows a sequence of photo-micrographs of a crystal of the hexahydrate heated at a steady rate in still air. The yellow crystal first effloresces as water is lost (Figs 3A and B), then melts at 60°C to a solution containing suspended $\text{UO}_3(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ crystals (Figs 3c and D). At about 185°C these melt also to leave a clear droplet (Fig. 3E) from which water progressively boils off, followed by nitrogen oxides (Fig. 3F). Crystals of anhydrous uranyl nitrate and basic nitrates then form (Fig. 3G), the remaining

liquid evaporates to leave a solid which finally denitrates to orange UO_3 (Fig. 3H). By varying the reaction conditions, the sequence of chemical steps followed may be quite different: for example, in vacuum the reactions occur entirely in the solid state. Indeed, it has been found that by changing the experimental conditions the product uranium trioxide may consist of any one of six crystallographic forms (α , β , γ , ϵ , ζ , or amorphous). The primary variables appear to be:

- the mass and geometry of the reaction bed,
- the rate of gas flow past the decomposing solid, and
- the rate of temperature rise.

These factors together determine the kinetics of water and nitrate loss and the relative stability of various intermediate phases. The dependence of the reaction mechanism, and even of the product formed, on extensive factors such as these makes it extremely difficult to extrapolate laboratory experiments to plant scale operation.

In the fluidised-bed process a concentrated solution of uranyl nitrate is sprayed into an air-fluidised bed of uranium trioxide held at about 320°C. Decomposition is rapid to give approximately spherical particles of γ UO_3 , of varying size depending upon the conditions (Figs 4A–C). The particles are essentially non-porous and of low surface area and many exhibit a characteristic "core and shell" texture, a friable core being surrounded by a harder shell both of which consist of γ UO_3 . The detailed mechanism of this decomposition in a fluidised bed is not well understood, although the texture of the uranium trioxide particles is of paramount importance in determining their subsequent chemical reactivity (see below).

From the above three examples we see that the principal physico-chemical factors which may be important in a decomposition reaction are crystal size and crystal structure of the decomposing solid, mass and geometry of the bed, heating rate and rate of removal of product gases from the reaction zone. These factors may influence the kinetics of the reaction and the pore structure, or even the crystal structure, of the product.

Solid-state Reactions

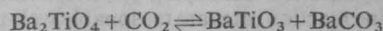
Reactions between two solids in which a gaseous product is formed may be included under the general heading of gas-solid reactions. Two technically significant processes of this type are the preparation of barium titanate and the carbothermic reduction of uranium dioxide.

Barium titanate formation

Barium metatitanate (BaTiO_3) has assumed commercial importance as a ferroelectric material, both in single crystal form and as a polycrystalline ceramic. Its piezo-electric properties find application in a wide range of devices, for example ultrasonic drills, depth sounders, sonar, gramophone pickups, etc. The powder is prepared conventionally by reacting barium carbonate (witherite) and titanium dioxide (rutile):



This reaction proceeds quantitatively to completion provided that the carbon dioxide product is not removed too rapidly. However, if the reaction is carried out in flowing air the rate of decomposition of barium carbonate exceeds the rate of solid-solid reaction and free BaO is formed. This then reacts further to yield Ba_2TiO_4 as a side product. By carrying out the reaction in flowing carbon dioxide below 1100°C the formation of orthotitanates is repressed according to:

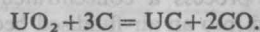


leaving BaTiO_3 as the sole reaction product. It may be noted that the crystallisation of an intermediate phase is by no means

uncommon in solid-solid reactions if the wrong experimental conditions are employed. Such phases, once formed, may be difficult to remove but their formation can often be avoided by a prior study of the thermodynamics of the system and a choice of the appropriate reaction conditions. Thermodynamic investigation of the present system showed that the equilibrium pressure of carbon dioxide over $\text{TiO}_2/\text{BaTiO}_3/\text{BaCO}_3$ is one atmosphere at 1100°C .⁴ Therefore at higher temperatures the reaction product is Ba_2TiO_4 even in flowing carbon dioxide. This sets a ceiling to the reaction temperature at 1 atm pressure.

Carbothermic reduction of uranium oxide

The most economically attractive route for the preparation of uranium monocarbide, a potential nuclear fuel, is by reduction of uranium oxide with graphite.⁵ In its simplest terms this reaction may be represented:



Strictly speaking UC is not in equilibrium with carbon. At all ordinary temperatures the reaction lies well to the left, and even at 1300°C the "equilibrium" pressure of the carbon monoxide is only 10^{-1} mm. These circumstances dictate that the preparation of UC be carried out above 1400°C and that the product carbon monoxide be removed rapidly from the reaction zone by pumping. Even higher temperatures are necessary if the use of a sweep gas such as argon is contemplated to avoid the difficulties of high temperature vacuum engineering on a production basis. These high temperatures lead to the use of graphite reactors, heated electrically or inductively.

Conventionally, the uranium oxide powder is mechanically mixed with a fine grade of graphite and pelleted. The pellets are reacted at $1400\text{--}1450^\circ\text{C}$ in vacuo or at 1500°C in flowing argon. It is found that *in vacuo*:

- (1) loose powders react faster than pellets but are less convenient to handle,
- (2) for pellets, the rate is independent of the oxide and carbon particle size over a wide range,
- (3) very coarse particles of oxide ($> 100\mu$) only react slowly with carbon: thorough mixing is therefore important to avoid agglomerates of oxide.

The only intermediate reaction product is an oxycarbide, $\text{UC}_{1-x}\text{O}_x$, and the rate-determining step is thought to be diffusion through a layer of this oxycarbide. The reaction *in flowing argon* can be carried out using granulated reactants in a spouting bed, contained in a conical shaped reactor, to ensure thorough purging of the carbon monoxide. Alternatively, a counter-current moving-bed reactor may be employed.

Under the optimised conditions both the vacuum and argon processes are capable of giving single phase UC with oxygen contents as low as 0.2 wt%. However, careful control of stoichiometry is essential if the product is not to contain needle-like precipitates of UC_2 . The reaction has been extended to include the preparation of $(\text{U}_{1-x}\text{Pu}_x)\text{C}$ from $\text{UO}_2\text{--PuO}_2$. According to whether the oxides are mechanically mixed or in solid solution, the reaction mechanism, and therefore the optimum conditions, are quite different.

Oxidation and Ignition Processes

The oxidation of metals is a topic which has been studied very extensively and the underlying physico-chemical factors which determine reaction rates are reasonably well-understood. Thus the existence of a lower oxide which may form a protective layer, the volume expansion which occurs during oxidation and the possibilities for epitaxy are all important factors

controlling the kinetics. The subject has been discussed fully in standard textbooks.^{6,7}

When metals are allowed to oxidise in atmospheres other than pure oxygen certain complications may arise which can influence the reaction rate. Thus in air some metals (calcium, uranium, thorium) may form nitrides as well as oxides, although these will oxidise further in the presence of excess oxygen. Water vapour in the atmosphere may also play a role: metals such as zirconium and uranium when oxidised by water vapour undergo secondary reaction with the liberated hydrogen to yield hydrides. For zirconium it has been shown that the nascent hydrogen dissolves in the underlying metal causing embrittlement and ultimately precipitates as hydride crystallites. The presence of water vapour in the oxidising atmosphere may also modify the oxidation in other ways. Plutonium, for example, oxidises very much more rapidly in oxygen containing about 100 ppm water vapour than in dry oxygen;⁸ this is probably because of the instability of a thin protective layer of Pu_2O_3 formed in air when exposed to water vapour. A third role of water vapour may be to yield a hydrated oxide product, as for aluminium or iron, which is more porous than the anhydrous oxide and therefore less protective. The complexity of reactions such as the rusting of iron in moist air is notorious. In general, it may be said that the chemical engineer's interest in metallic oxidations centres around reactions which are to be avoided or minimised, for example, the corrosion of heat exchangers, chemical reactors, or cladding materials for nuclear fuel elements. For such undesirable reactions an understanding of the physical chemistry and reaction mechanism is often a first step towards alleviating the problem by expedients such as alloying the metal or controlling the impurity content of the gas phase.

A rather different type of oxidation reaction is that involving the semi-metallic (or "interstitial") compounds such as the metallic carbides, nitrides, borides, silicides, etc. Typically a metallic oxide is formed as well as an oxide of the non-metal, which may be either gaseous (CO_2 , N_2) or solid (B_2O_3 , SiO_2). In some cases a single solid phase may result as in the oxidation of a metallic phosphide to a phosphate. These reactions are characteristically more complex than the oxidation of a simple metal as may be illustrated by a comparison of the oxidation behaviour of uranium and plutonium mononitrides.

Uranium mononitride (UN) and plutonium mononitride (PuN) are semi-metallic compounds crystallising in the rock-salt structure. These compounds are technically important as potential fast reactor fuels and the nuclear chemical engineer is interested in their oxidation behaviour from two points of view:

- (1) the control of the atmosphere which must be exercised during the preparation, handling and fabrication of the powders, and
- (2) the consequences of accidental ingress of air or water vapour to the fuel element.

Although UN and PuN are superficially very similar their oxidation behaviour, particularly in respect of water, is quite different.⁹ Thus UN is virtually unattacked by boiling water at 100°C and is only slowly hydrolysed by water vapour at 300°C . By contrast, PuN is rapidly hydrolysed to form a hydrated oxide $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ even at 50°C . This difference in behaviour is to be ascribed to the protection afforded by an epitaxially oriented film of U_2N_{3+x} present on the surface of UN; plutonium does not form a higher nitride and therefore is unprotected from hydrolysis. Observations such as this are pertinent to the design of glove boxes and inert gas facilities for handling powdered nitrides, particularly in specifying the permissible moisture impurity level in the box.

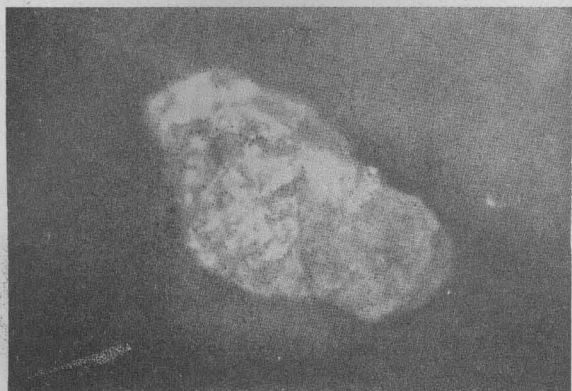
When a metal or semi-metallic compound is exposed to



(A) Efflorescence as water is lost



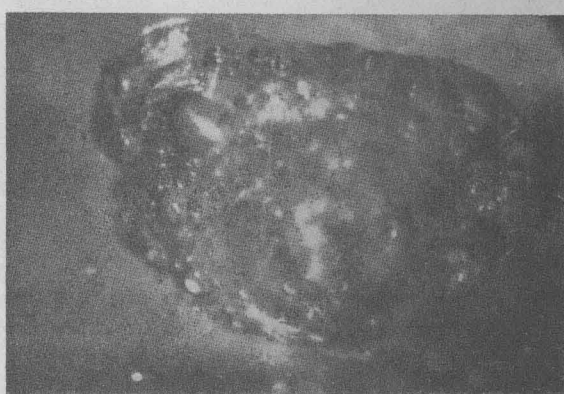
(E) Melts to clear droplet at 185°C



(B) Efflorescence as water is lost

(F) Boiling, with loss of NO_2 

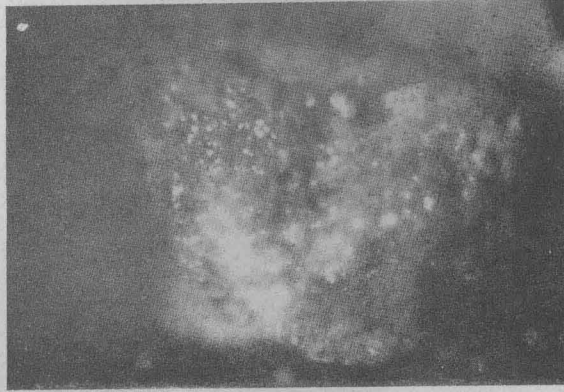
(C) Melts at 60°C; trihydrate crystals in suspension



(G) Crystals of anhydrous and basic nitrate form



(D) Boiling

(H) Final denitration to UO_3 Fig. 3A-H.—Successive stages in the decomposition of a crystal of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ heated at a steady rate in still air

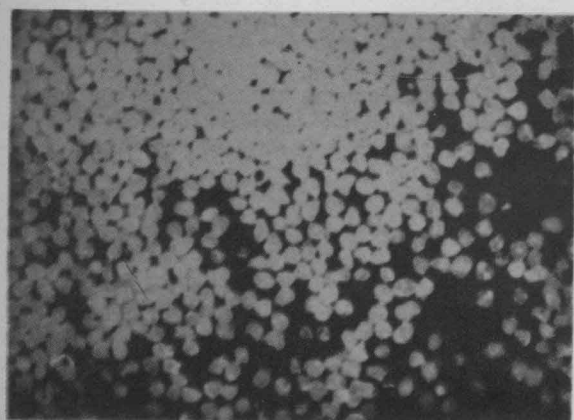
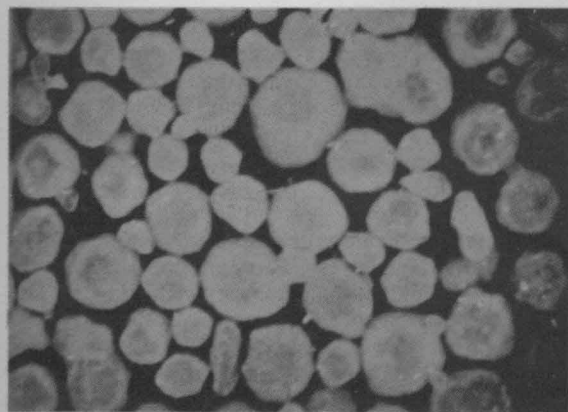
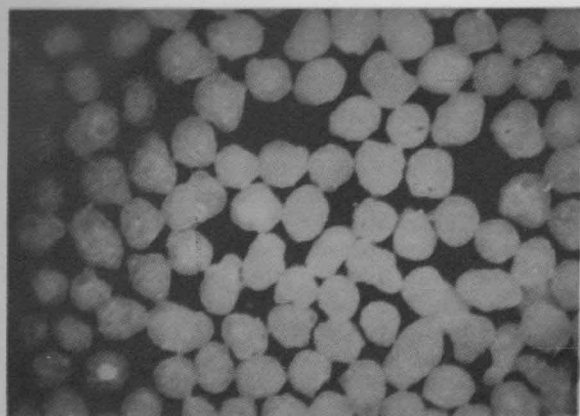


Fig. 4A-C.—Particles of γUO_3 formed in a fluidised-bed reactor. (Note the particles are mounted and sectioned to reveal their internal texture)



Fig. 5.—Photomicrograph of Fe_2O_3 specimen partially reduced in hydrogen at 590°C ($\times 200$); white phase iron metal, dark grey phase Fe_3O_4 , light grey phase Fe_2O_3

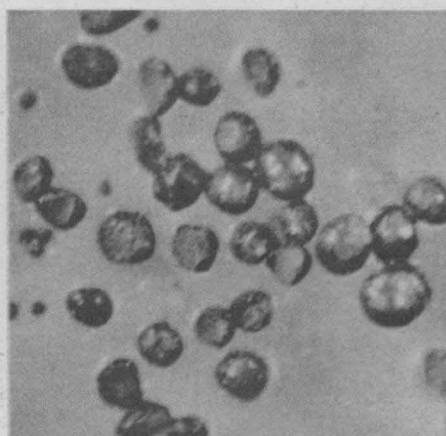


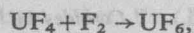
Fig. 6.—Photomicrograph of partially reduced UO_3 . (Particles are mounted and sectioned.) Yellow cores are unreacted UO_3 , black surfaces are UO_2 .

oxygen at a sufficiently high temperature and pressure it is liable to ignite and burn. The conditions under which ignition occurs may be of interest to the engineer either because he wishes to prevent the process (e.g. during missile re-entry or the storage of reactive metal powder) or to promote it (design of swarf burning facilities, pyroprocessing of nuclear fuels). Ignition takes place when the rate of heat liberation in a chemical reaction exceeds the rate of heat dissipation and when as a consequence the reaction accelerates rapidly. There are many different factors which determine the ignition temperature of a solid for a particular reaction, chief among which are the specific surface area of the solid and its particle size. Other factors which influence either the rate of heat liberation or dissipation (or both) are: the oxygen partial pressure, the gas circulation rate, the mass and geometry of the specimen under study and its thermal conductivity.¹⁰ Any circumstance which introduces local "hot spots", such as abrasion of the specimen or rapid rate of heat-up of the reaction furnace, may lead to ignition at an anomalously low temperature. An extreme instance of this is the ignition of bars of titanium or zirconium at room temperature when fractured under oxygen at high pressure.¹¹

The burning of a metal in pure oxygen or pure fluorine is possibly the simplest of ignition processes provided there is no gaseous product to blanket the reaction. Once started the reaction generally proceeds to completion. Pure oxygen, even at low partial pressures, is very much more effective than air or diluted oxygen in supporting combustion; in air the local depletion of oxygen at the reaction interface frequently causes the ignition to be extinguished.

The combustion of metallic carbides or nitrides is more complex than the combustion of metals in that there is a gaseous product (CO, CO₂, or N₂) which tends to blanket the reaction. The factors then governing the ignition temperature are too complex for mathematical analysis and an empirical approach must be adopted.¹⁰ It is interesting that the ignition temperature of cast uranium carbide falls with increasing age of the specimen. Apparently atmospheric attack (hydrolysis) along the grain boundaries causes an increase in chemical reactivity and a concomitant decrease in thermal conductivity; both of these factors facilitate ignition. Some compounds which are very readily hydrolysed, for example PuN, will ignite and burn even in pure steam.

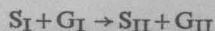
Finally in this section we mention oxidation reactions in fluorine which give rise to a gaseous higher fluoride. Of prime industrial significance is the reaction:



which is employed in the preparation of UF₆ as feed for the gaseous diffusion (U₂₃₅ enrichment) plant. As the UF₆ product is a gas and the reaction is exothermic, it is an ideal process for fluid-bed operation. UF₄ is mixed with CaF₂ (diluent) and fluidised with fluorine. The concentration of UF₄ in the bed and the feed rate of fluorine are adjusted to maintain the reaction temperature with little input of heat. UF₆ is condensed from the exit gas and fluorine is recycled, with appropriate make-up from an electrolytic cell. Some care is necessary to ensure that no moisture is introduced as this produces solid UO₂F₂ which blocks the gas distributor. Again, the engineering of the process must guard against the formation of UF₅ as this intermediate fluoride is molten at the bed temperature and will cause agglomeration of the solids, resulting in localised defluidisation of the bed. This process is now operated on an industrial scale.

Reactions of the Type S_I + G_I → S_{II} + G_{II}

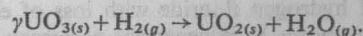
Reactions of the type:



constitute possibly the largest class of interest to the production chemical engineer. Particularly important are reduction reactions for the preparation of metals, lower oxides, or halides. We may distinguish between those reactions which are reversible, in the temperature range of interest, and those which are essentially irreversible. As an example of the first type, the photomicrograph of Fig. 5 shows Fe₂O₃ which has been partially reduced in hydrogen at 590°C to metallic iron.¹² The reaction is seen to proceed via an intermediate phase, Fe₃O₄, and there is a tendency for the reduction to propagate preferentially down grain boundaries ahead of the main reaction front. The unreacted Fe₂O₃ accumulates in isolated regions. As the reaction involves an overall decrease in molar volume (contraction of the solid) the pores do not become blocked and there is free access to hydrogen gas. However, the production of water vapour leads to the gas composition in the pores being very different from that of the external gas phase; in fact the gas will tend to the equilibrium composition at that temperature. The rate of reduction will then be limited by the rate of gas diffusion into and out of pores which, in turn, will be controlled by such factors as particle size, pore size, temperature and external gas velocity. It is evident that the kinetics are likely to be quite variable depending upon the grade of Fe₂O₃ employed and the reduction conditions. This will be true for all reduction reactions where the value of P[H₂O]/P[H₂] at equilibrium is greater than about 1/10. Considerable care is necessary when designing chemical plant for reversible gas-solid reactions on the basis of kinetic data obtained in bench-scale experiments.

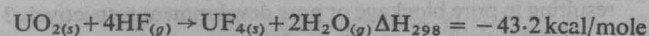
UO₃-UO₂-UF₄ reaction¹³

The industrial production of both uranium metal and uranium hexafluoride involves UF₄ as an intermediate. This is prepared from fluidised-bed UO₃ by reduction to UO₂ followed by reaction with HF gas ("hydrofluorination"); both reactions are carried out in fluidised-bed reactors, sequentially after the denitration step in which the UO₃ is formed. The reduction reactor is fluidised with hydrogen and operated at 500°C. This reaction, which is exothermic to the extent of 25 kcal/mole, is essentially irreversible:



Examination of partly reduced UO₃ particles under the microscope reveals that the reaction propagates by an interface reaction from the exteriors of the particles towards the centre. (Fig. 6). There is a significant increase in crystal density (UO₃ = 7.3 g/cm³, UO₂ = 10.97 g/cm³) but rather little contraction in the particle volume. The result is that the UO₂ product is porous and freely accessible to hydrogen gas. For reactions such as this which are irreversible and where there is a molar volume decrease the kinetics are generally chemically controlled and the design of the reactor is not critical. However, in the present instance, the solid product is required to undergo a further gas-solid reaction (hydrofluorination) for which its texture, in particular its surface area, is critical. It is necessary therefore to exercise careful control over the reduction reaction to ensure that the UO₂ meets product specification for conversion to UF₄.

The hydrofluorination reaction is also exothermic:



but in this case the reaction is reversible and there is a molar volume increase. These factors, together with the ease of sintering of UF₄ resulting from its low melting point, all militate against easy reaction. The forward reaction proceeds at a reasonable rate at 500°C, at which temperature the equilibrium constant of the back reaction is significant. Particularly in the early stages of the reaction, where the intrinsic

rates are high, the pores will be filled with steam and an equilibrium set up. Gas diffusion problems in the UO_2 then assume some importance. As reaction proceeds, the increase in molar volume on passing from UO_2 to UF_4 (90%) results in progressive blocking of the pores in the UO_2 . Because of this blocking, and also because of the ease of sintering of UF_4 , there is a marked drop in surface area during the reaction and the product UF_4 consists of non-porous particles, pseudo-morphic after the original UO_3 particles. The extent of the reaction is critically dependent upon the particle texture of the UO_2 ; for some oxides the hydrofluorination reaction may virtually cease as the pores become blocked and further reaction is possible only by diffusion of gas through the UF_4 product. This difficulty is avoided by using fluidised-bed UO_2 of specific surface area greater than $2\text{ m}^2/\text{g}$ when reaction proceeds to completion before all the pores are sealed. The surface area of the UO_2 is determined by the parameters of the UO_3 reduction process and also by the UO_3 particle texture as determined in the denitration reaction; here we have an instance of sequential gas-solid reactions in which the kinetics of the last reaction (hydrofluorination) are influenced by all the steps which have gone before. This is a common phenomenon when a solid undergoes a series of reactions in sequence.

Not all gas-solid reactions in which there is an expansion of the solid phase behave in this fashion. As we have seen, the hydrolysis of UC or PuN, in which there is a large volume expansion, proceeds readily to completion. In these reactions the product phase exfoliates and breaks away from the reactant solid, exposing fresh surface. By contrast, the UF_4 is adherent to the UO_2 , sinters together readily at 500°C and blocks off the oxide from further reaction.

In addition to these essentially chemical aspects of UF_4 formation there is also the engineering to be considered. When hydrofluorination is carried out in a fluidised-bed reactor, it is essential to dissipate the heat of reaction and avoid overheating and sintering of the UF_4 . This necessitates the use of a dilute hydrogen fluoride in nitrogen mixture. The formation of bubbles in the fluidised bed is necessary for thorough mixing, but must not be allowed to lead to "break through" of hydrogen fluoride with loss of efficiency. For reasons of economy it is generally necessary to feed dilute hydrogen fluoride in the early stages of the reaction. Aside from the corrosion problems this introduces, the reaction is now supply-limited and therefore prolonged compared to that in a small laboratory reactor, giving the UF_4 more opportunity to sinter and trap unreacted UO_2 . These and inter-related problems make the task of the chemical engineer so much more complex than that of the research chemist.

To summarise, the purely chemical features which are important in determining the kinetics of a reaction of the type $\text{S}_I + \text{G}_I = \text{S}_{II} + \text{G}_{II}$ are contained in the following questions:

- (1) is the reaction reversible or irreversible at the temperature employed?
- (2) is there a decrease or increase in density of the solid phase during the reaction?
- (3) do the particles expand/contract to follow the density changes or, alternatively, do they remain the same size resulting in pore blockage or pore development respectively?
- (4) does the product solid exfoliate, breaking away from the reactant phase, or is it adherent and easily sintered?

These are fundamental questions of physical chemistry which should be asked by any chemical engineer wishing to

exploit a gas-solids reaction of this type. An understanding of these factors, together with kinetic data obtained in laboratory scale reactors should permit at least semi-quantitative predictions of the behaviour of full-scale equipment. However, as stated at the beginning of this paper, gas-solid reactions are invariably complex and in making extrapolations, one must bear in mind that the physical chemistry, engineering and economics of the process are all closely inter-related. If the reaction is to be optimised, a clear understanding of these inter-relationships must be established.

Conclusion

In this paper we have explored some of the chemical factors which are important in determining the intrinsic reaction rate and mechanism of a wide variety of gas-solid reactions. Little attempt has been made to consider essentially chemical engineering concepts which arise when implementing the reaction on a practical scale, for example solids residence time, gas flow patterns or heat transfer coefficients. These topics will be the subject of other papers in this symposium. There is little doubt that many of the chemical research papers published in this field are vitiated by failure to ensure satisfactory design of specimen holder and to appreciate the importance of gas-contacting conditions and heat transfer coefficients. Conversely, many chemical engineering plants have failed to live up to design expectation because of inadequate understanding of the influence of scale-up parameters on the physical chemistry of the reaction. It is to be hoped that this symposium will serve to draw together those working on both the basic chemistry and the engineering of gas-solid reactions and will lead to a wider appreciation of each other's point of view.

References

- 1 Anderson, P. J. and Livey, D. T. *Powder Metall.*, 1961, 7, 189.
- 2 Horlock, R. F. and Anderson, P. J. *Trans. Faraday Soc.*, 1967, 63, 717.
- 3 de Boer, J. H., Fortuin, J. M. H., and Steggerda, J. J. *Koninkl. Nederl. Akademie van Wetenschappen (Amsterdam)*, 1954, B57, 170; *Idem ibid*, 434.
- 4 Templeton, L. K. and Pask, J. A. *J. Am. Ceram. Soc.*, 1959, 42, 212.
- 5 Russell, L. E. (Ed.). "*Carbides in Nuclear Energy*", 1964. (London: McMillan & Co. Ltd.)
- 6 Hauffe, K. "*Oxidation of Metals*", 1965. (New York: Plenum Press.)
- 7 Kubachewski, O. and Hopkins, B. E. "*Oxidation of Metals and Alloys*", 1967, *Second Edition* (London: Butterworths.)
- 8 Schnizlein, J. G. and Fischer, D. F. *J. electrochem. Soc.*, 1967, 114, 23.
- 9 Dell, R. M., Wheeler, V. J., and Bridger, N. J. *Trans. Faraday Soc.*, 1967, 63, 1286.
- 10 Dell, R. M. and Wheeler, V. J. *J. nucl. Mater.*, 1967, 21, 328.
- 11 Littman, F. E., Church, F. M., and Kinderman, E. W. *J. less-common Metals*, 1961, 3, 367; *Idem ibid*, 379.
- 12 Endom, A., Hedden, K., and Lehmann, G. in "*Reactivity of Solids*", 1964. (Amsterdam: Elsevier Publications.)
- 13 Dell, R. M. and Wheeler, V. J. *Trans. Faraday Soc.*, 1962, 58, 1590.

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