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Problems of Combustion in Chemical Technology and in Metallurgy

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Combustion processes leading to the formation of valuable products of chemical technology and metallurgy—acetylene, carbon black, starting materials for acid manufacture, metal oxides, ferro-alloys, refractory compounds, etc.—are surveyed with emphasis on the possibilities and the advantages of combustion as a technical chemical procedure. Prospects for the widespread utilisation of combustion processes in chemical technology and metallurgy are examined on the basis of specific examples. Certain aspects of the development of combustion theory in connection with technical problems are discussed. A list of 78 references is included.

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I. INTRODUCTION

The term *combustion* is usually applied to a strongly exothermic chemical reaction occurring at temperatures resulting from the evolution of the heat of reaction. Two fundamentally different combustion regimes can be established: in the layered (wave) process reaction occurs in a narrow zone separating the reactants from the heated reaction products and moving spontaneously through the material at a definite speed in the form of a combustion wave; in the homogeneous process the reaction occurs in a combustion chamber to which reactants are continuously supplied and from which reaction products are continuously removed, while reactants and products are mixed. A characteristic feature in both cases is the high temperature arising during the reaction from the liberation of the chemical energy of the initial system, unconnected with an external supply of energy. Other forms of combustion include, for instance, the diffusion combustion of gases, in which the reactants are not mixed but are fed from different sides to a flame front whose position is stabilised in space.

The theoretical foundations were laid during the 1930 to 1940s by the fundamental investigations of Semenov and his school[1-3]. He examined the laws of the evolution and removal of heat in the reacting material[4], and calculated for the first time the critical conditions for thermal explosion. Subsequently Frank-Kamenetskii[5,6] and Todes[7-10] made important advances in the theory of the thermal explosion of gases. The theory of flame propagation was established by Zel'dovich and Frank-Kamenetskii[11]. Zel'dovich worked out the theories of combustion limits[12] and the combustion of unmixed gases[13], and also discussed the thermal conditions of exothermic reactions in a flow-type reaction vessel[14,15]. Several theoretical investigations of thermal explosion, ignition, and the propagation of a combustion wave in a condensed system have been undertaken by the Reviewer[16-20].

Two broad uses of combustion can be distinguished. Firstly the generation of power utilises the heat of reaction and very often, but not always, the energy of the expanding gaseous products. In the second use a product of combustion is itself of interest, as the desired result of a technical process.

The generation of power has been hugely developed and has exerted a strong influence on the theory of combustion. Almost all problems in the theory arose from the utilisation of chemical energy. Combustion theoreticians on their part have made an important contribution to energetics. The joint efforts of scientists and designers have developed such fields as engine manufacture, heat and power engineering, and rocket technology.

The second use has been developed mainly by technical chemists and metallurgists in isolation from combustion theory, and has reduced to working out the technology of individual products. Unfortunately, the extent and the level of investigations have been inadequate, and do not correspond to the great importance of this problem for the national economy.

This Review is an attempt to systematise the main combustion processes employed to obtain useful substances (gaseous and condensed products of chemical industry, metals and alloys, refractory inorganic compounds, etc.), to formulate specific features of combustion as a process of chemical technology, and to discuss certain problems associated with its development. Other aspects of combustion are also of interest to chemical technology and metallurgy, among them security from fire and explosion in chemical industries (the theoretical foundations of safety techniques), the production of technical furnaces burning natural fuels, and the organisation of thermal processes in flames. Here, however, we shall discuss only problems on synthesis, which are the most urgent and the least investigated.

II. MAIN TYPES OF TECHNICAL COMBUSTION PROCESSES

We shall discuss briefly the most widely used technical combustion processes.

1. Combustion of Hydrocarbons

The combustion of hydrocarbons is used in chemical industry to obtain various products (process gas, ethylene and acetylene, carbon black, etc.). Many variants of the process are used, distinguished by the starting material

(usually natural gas and air), the concentration ratio of combustible and oxidant, the design of burners or combustion chambers, and methods of removing the required products.

Process gas is manufactured by the combustion of a hydrocarbon according to the equation

$$C_nH_{2n+2} + \frac{n}{2} O_2 = n\,CO + (n+1)\,H_2.$$

The products are in thermodynamic equilibrium, and are used for the synthesis of ammonia and methanol[21].

Acetylene and carbon black are obtained by combustion that is kept incomplete[22–26]. Excess of a hydrocarbon is pyrolysed in the flame formed by burning the major part of the hydrocarbon:

$$C_nH_{2n+2} \rightarrow C_2H_4 \rightarrow C_2H_2 \rightarrow C.$$

This process has been termed *oxidative pyrolysis*. Sometimes different hydrocarbons are used for combustion and pyrolysis, the latter being introduced directly into the flow of combustion products. Acetylene is an intermediate product of pyrolysis. It is therefore obtained by quenching (water is usually sprayed into the reacting mixture). The duration of the pyrolysis stage (which should be optimum) and the intensity of quenching (which should be great) determine the yield of acetylene — the chief index of the efficiency of a particular technical scheme.

Carbon black is the final product of pyrolysis, which is made as complete as possible in manufacture. A specific design feature of the plant is the presence of collectors for the condensed phase (soot collectors). Important characteristics of carbon black are its degree of dispersion and its impurity content, which depend on the conditions of pyrolysis and the starting material.

Because of variation in these parameters many brands of carbon black are available for particular purposes.

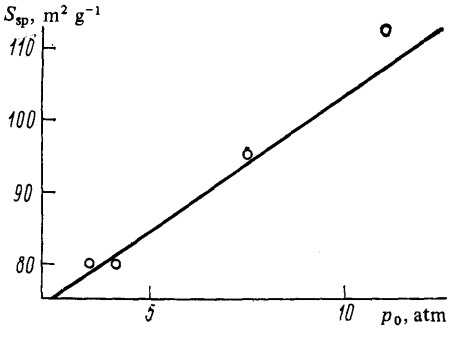


Figure 1. Dependence of specific surface of carbon black on initial pressure of acetylene[28].

In the above method the combustion itself does not lead to the formation of acetylene and carbon black, but has the ancillary role of providing a high temperature. Carbon black is produced not only by oxidative pyrolysis but also by other processes, e.g. the burning and detonation of acetylene (acetylene black)[27,28]. Fig. 1 illustrates the effect of the conditions on the characteristics of the product, showing the dependence of the specific surface of the carbon black on the initial pressure of acetylene[28].

A new method for the production of ethylene and acetylene is the so called immersion combustion of hydrocarbons[29,30]. Oxygen preheated to ~ 600°C is blown into a liquid hydrocarbon (e.g. kerosene), which vaporises and burns in the bubbles thus formed. After the oxygen has been used up, the hydrocarbon vapour is pyrolysed to ethylene and acetylene. Contact with the liquid phase results in effective quenching. The exhaust gases contain a substantial quantity of the required products.

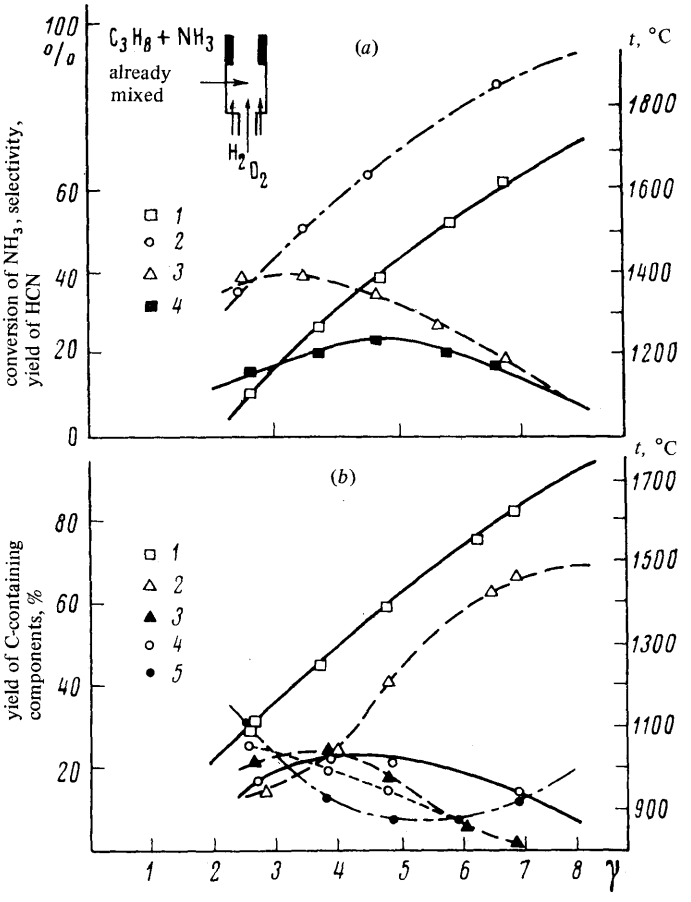


Figure 2. Dependence of combustion temperature and yield of carbon-containing products on ratio γ of space velocities of H_2–O_2 and C_3H_8–NH_3 mixtures[33]: (*a*) *1*) temperature; *2*) conversion; *3*) selectivity; *4*) yield of HCN (based on N); (*b*) *1*) temperature; and yields based on carbon of: *2*) CO; *3*) $C_2H_4 + C_2H_2$; *4*) CH_4; *5*) CO_2.

The combustion of hydrocarbons is used also for the production of hydrogen cyanide (manufacture of hydrocyanic acid). For this purpose ammonia is introduced either into the initial mixture or into the flow of combustion products[31–33]. The process can be represented empirically as

$$C_nH_{2n+2} + O_2 + NH_3 \rightarrow HCN + \ldots .$$

The yield of hydrogen cyanide (based on nitrogen) is high. The processes differ according to the raw material (e.g. with n = 1 [31] or 3 [33]) and the conditions of mixing of the reactants. The chief results obtained[33] for the synthesis of hydrogen cyanide are illustrated in Fig. 2.

2. Gas-flame Synthesis of Gaseous Products from the Elements

The reaction can be written

$$\underset{\text{fuel}}{X_{L,G}} + \underset{\text{oxidant}}{Y_G} = \underset{\text{required product}}{Z_G}$$

element

where X and Y are the reactants and Z the reaction product. Combustion is easily conducted in burners or combustion chambers to a very high degree of completion: there are no fundamental difficulties in controlling the combustion. Further developments on these lines involve mainly intensification of the process and utilisation of the heat of combustion. In this respect a furnace technique, based on the solution of heat-engineering problems, has proved very effective[34].

The gas-flame synthesis of gaseous compounds from the elements has found widespread application in acid manufacture for the production of (*a*) hydrogen chloride (manufacture of hydrochloric acid)

$$H_2 + Cl_2 = 2HCl;$$

(*b*) sulphur trioxide (sulphuric acid)

$$S + O_2 = SO_2;$$

(*c*) phosphorus pentoxide (phosphoric acid)

$$2P + 2.5O_2 = P_2O_5.$$

3. Roasting of Sulphide Raw Material

This process[35–37] is interesting in giving simultaneously two required products having completely different purposes:

$$\underset{\text{fuel}}{MS_m} + \underset{\text{oxidant}}{\left(m + \frac{n}{2}\right)O_2} = \underset{\text{product I}}{MO_n} + \underset{\text{product II}}{m\,SO_2},$$

Metal oxides are used in metallurgy for the production of metals, and sulphur dioxide serves for the manufacture of sulphuric acid. Sulphide minerals are widely distributed in Nature (M = Fe, Mo, Cu, Ni, Zn, etc.).

Roasting is usually conducted in combustion reactors having a fluidised bed with an air blast. Particles of concentrate are continuously introduced, and the cinders (particles of oxide) are removed. Water is sometimes sprayed in to control the temperature. The variations in design of fluidised-bed vessels for the roasting of sulphide raw material have been discussed in detail[37]. The main difficulty is to achieve completeness of reaction. The process is characterised by comparatively low temperatures: for example, pyrites (FeS_2) is roasted at 800–900 and molybdenite at 600°C. Higher temperatures involve the formation of nodules, fusion, impaired access of air to the inner layers of particles, and lowered efficiency. It is interesting that the adiabatic temperatures for the combustion of sulphides are far higher than the roasting temperatures. For example, the combustion of molybdenum sulphide develops temperatures of ~ 1500°C in air, but above 3000°C in oxygen. Such a large difference between the maximum possible and the actual temperatures suggests that use of a fluidised bed is not the best method of organising combustion in roasting and that there are many opportunities for intensifying the process. Strictly speaking, the existing process of roasting bears little resemblance to combustion. Although it is close to homogeneous combustion, the considerable artifical lowering of temperature causes marked degeneration of the combustion. It is not by chance that the term "combustion" is not used in relation to this technique in the technical literature, and the combustion vessels are termed *furnaces*.

However, successful attempts have been made to organise the combustion of sulphides in a different manner. Thus the combustion of pyrites in a cyclone chamber with tangential feed gave a temperature of 1400°C, at which the oxide was molten, which made separation of the products more convenient[38]. The possibilities of using cyclone furnaces for the roasting of sulphides have been examined[39].

At the present time the two products are not manufactured together. In chemical industry the process is directed to the production of sulphur dioxide, while the metal oxides constitute low-quality by-products; the opposite situation occurs in metallurgy. This is also an indication of inadequate organisation of the process.

4. Blast-furnace Process

The blast-furnace process is one of the oldest and most important in metallurgy. It is based on the incomplete combustion of carbon, and can be represented schematically as

$$C + \underset{\text{reducible cpd.}}{MO_m} + Q \rightarrow M + \ldots.$$

$$C + O_2 \rightarrow CO + Q;$$

Carbon acts as both fuel and reducing agent. The burning of part of the carbon evolves heat, which raises the temperature of the mixture of the metal oxide with the rest of the carbon to values at which reduction to the metal takes place. At moderate temperatures carbon monoxide, formed by the combustion of carbon, also takes part in the reduction. The reduced metal is the desired product of the blast-furnace process.

The scheme of the process resembles oxidative pyrolysis: incomplete combustion also takes place here, and combustion has an ancillary role as a source of heat. However, the chemistry of the main reaction, leading to formation of the product, is essentially different.

The blast-furnace process is most widely used for the production of cast iron from iron ores:

$$\underset{\text{ore}}{\text{Iron}} + \underset{\text{(coke)}}{\text{Carbon fuel}} + \underset{\text{dolomite)}}{\text{Fluxes (limestone,}} + \text{Air} = \underset{\text{iron}}{\text{Cast}} + \text{Slags} + \underset{\text{gas}}{\text{Blast-furnace}}$$

A blast furnace (combustion chamber) consists of a hearth, in which the fuel burns and the charge melts, together with a shaft containing the melting material being fed to the hearth. The temperature in the hearth during the production of cast iron is 1300–1900°C.

Other metallurgical products, e.g. ferromanganese from manganese ores, are obtained by the blast-furnace method.

5. "Ex-furnace" Thermite Process

The main purpose of the thermite process[40–42] is to obtain metals from their oxides (or other compounds) by redox reactions in the condensed phase with the use of chemical

elements as reductants. The chemical equation of the process is

$$\underset{\text{reducible cpd.}}{MX_m} + \underset{\text{reducing element}}{\frac{m}{n}M'} = \underset{\text{product}}{M} + \underset{\text{by-product (slag)}}{\frac{m}{n}M'X_n},$$

where M = Fe, Mn, V, Co, etc.; M′ = Ca, Al, Si, Mg, etc.; and X = O, Cl, etc.

Thermite processes have been known for a long time; the first experiments were made by Beketov during the nineteenth century.

If much heat is evolved in the thermite reduction, the process may take place under conditions of combustion. This case is referred to in metallurgical literature as an "ex-furnace" † thermite process. The example best known in the theory of combustion is the iron-aluminothermic process[43–45]

$$Fe_2O_3+2Al=2Fe+Al_2O_3.$$

An important practical task of the thermite process — the smelting of metals or alloys ‡ — can be achieved only if the metallic and slag phases in the combustion products separate out. For this it is necessary and sufficient that the temperature of combustion should be higher than the melting point of the products §, while the time of phase separation at the combustion temperature should be less than the thermal relaxation (cooling) time of the system.

The efficiency of extraction depends on the completeness of the redox reactions and the phase separation. Fig. 3 shows as example the dependence of the yield of metal on the particle sizes of iron oxide and of aluminium in the smelting of a ferroaluminium master alloy (80% Fe + 18% Al + 2% Si). The charge comprised 10 kg of iron oxide (98% Fe_2O_3) and 4.9 kg of aluminium powder (97% Al) with 0.8 kg of lime (90% CaO).[41] Study of ways for controlling thermite processes in order to ensure completeness in the main task of research in this field. One of the most effective methods is to introduce addivites for various purposes (slag-forming, preheating, etc.). The temperature of the thermite process is high, usually 2000–3000°C. The main charge and an ignition charge (primer) are placed in very simple open vessels with refractory walls and a hole for removal of the metal.

The thermite process has been most widely employed in ferrous metallurgy for the production of ferro-alloys and master alloys[41–46], most often with aluminium as reducing element.

Combined processes are also known, in which combustion is accomplished with an additional source of heat (preheating additives, raising the initial temperature of the charge by heating in a furnace). This extends considerably the range of systems in which combustion can be accomplished. The blast-furnace process can also be regarded as involving thermite reduction, with carbon as reducing element. However, the distinctive additional source of heat (the combustion of carbon in air) is responsible for a different, more complicated organisation of production.

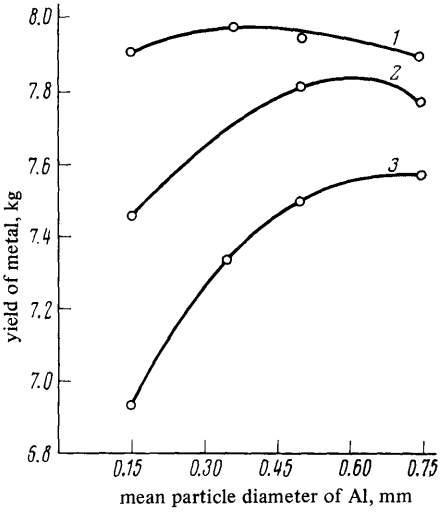


Figure 3. Effect of mean particle diameter of aluminium on yield of metal for different mean particle diameters of iron oxide (mm): *1*) 0.36; *2*) 0.55; *3*) 0.76.[41]

Thermite processes are used also to obtain non-ferrous metals[42]. However, the exploitation of combustion is less efficient than in the production of ferro-alloys and master alloys.

6. Self-propagating High-temperature Synthesis of Refractory Inorganic Compounds

This is the "youngest" technical combustion process[47–50]. Work in this field began in 1967, after discovery of the propagation of a combustion front in powdered mixtures of high-melting chemical elements, resulting in the formation of refractory compounds. Later other elements (of low melting point, liquid, and gaseous) were used for the synthesis. The general chemical scheme of the process, which has been termed *self-propagating high-temperature synthesis*, can be written.

$$\underset{\text{fuel elements}}{\sum_{i=1}^{m} a_i X_i} + \underset{\text{oxidising elements}}{\sum_{j=1}^{n} b_j Y_j} = \underset{\text{product}}{Z},$$

where X = Ti, Zr, Hf, V, Nb, Ta, Mo, W, etc.; Y = B, C, N, Si, S, Se, Al, etc.; and Z represents borides, carbides, nitrides, silicides, etc.

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† The term "ex-furnace" is unfortunate, firstly, because it is terminologically inexact. The word "ex-furnace" implies that a furnace exists but that the process is for some reason conducted outside it, somewhere at its side. The sense would have been conveyed more accurately by "non-furnace" or "furnaceless". Secondly—perhaps the most important—the term indicates not the essential nature of the process but a technical consequence (absence of a furnace). In this sense it is more correct to speak of self-propagating thermite processes.

‡ Alloys are obtained by reducing two (or more) compounds together.

§ Very often the combustion temperature is higher also than the melting points of the reactants, and the reduction accompanying combustion occurs entirely in the liquid phase.

The elements X are in the form of powdered metals, the Y elements are used in powdered, liquid, or gaseous states, and the product Z is refractory and usually solid at the combustion temperature. The first group of elements (metals) act as fuels, and the latter group (non-metals) as oxidising agents. Chemical reaction between the elements takes place in the condensed phase, even if one of the reactants is a gas. In most of the processes the reaction is accompanied by the evolution of a large quantity of heat, which is responsible for the possibility of combustion. Thus this process involves a strongly exothermic reaction between chemical elements in a condensed phase taking place under combustion conditions.

The usual forms of the process with $m = 1$ and $n = 1$ have now been supplemented by other variants ($m \neq 1$ and $n \neq 1$), leading to the production of more complicated compounds:

(*a*) $m = 1$, $n = 2$ (carbonitrides MC_xN_y, where M = Ti, Zr, Nb, Ta);[51]

(*b*) $m = 2$, $n = 1$ ($Nb_xZr_{1-x}N$,[51] $Mo_xNb_{1-x}S_2$, $Ti_xCr_{1-x}B_2$, $Ti_xW_{1-x}C$);[52,53]

(*c*) $m = 2$, $n = 2$ (mixed carbonitride $Nb_xZr_{1-x}C_yN_z$).[51]

This process entails some of the highest combustion temperatures (~2500–4000°C).

Three types of processes can occur depending on the state of aggregation of the elements—(1) combustion of mixtures of X and Y powders in a vacuum of an inert gas (e.g. production of carbides, borides, and silicides), (2) combustion of powdered X in the gaseous oxidant Y (e.g. production of nitrides by burning metals in gaseous nitrogen), and (3) combustion of powdered X in a liquid oxidant Y (e.g. production of nitrides by burning metals in liquid nitrogen). The powders may first have been compressed or may be used in a loose state.

Special reaction vessels are used, different for each of the above three modifications of the process. The most common at present are gas-free synthesis vessels for processes of type (1).[54] A characteristic feature of the self-propagating high-temperature processes is the absence of by-products. Together with the possibility of complete conversion of the reactants (theoretical yields), this enables high-quality refractory products to be obtained, satisfying the most rigorous modern requirements with respect to materials behavour.

An example is the production of titanium carbide, which is effectively used in the compositions of solid alloys, high-temperature materials, and abrasive pastes. Investigation of the mechanism of the combustion of mixtures of powdered titanium and carbon blacks[55] has helped to establish the main factors controlling the rate and the completeness of synthesis, among them the particle size of the titanium, the density of the pellets and the proportions of reactants in the charge, and the removal of heat from the combustion products. The experimental linear burning velocity varied[55] over the range 0.5–5 cm s^{-1} depending on the parameters of the initial mixture. The calculated adiabatic temperature was 3200 K, and the experimental temperature ~ 3000 K.[56]

Research on the mechanism of combustion of the titanium–carbon sytem has led to the development of the efficient technical production of titanium carbide[53] by a batch process in vessels of capacity 4–10 litres. This technology permitted the experimental production of high-quality titanium carbide powders. The product obtained from PTS (or PTM) titanium powder and Pm-15TS carbon black under optimum conditions contained (% by weight) 19.6–19.8 combined carbon, 0.1 uncombined carbon, 0.1 oxygen, and traces of nitrogen.

Various combined processes are now being developed, one of them involving the self-propagating high-temperature synthesis and thermite processes. A possible scheme is

$$\underset{\text{reducible product}}{MX_m} + \underset{\substack{\text{element (reductant and oxidant)}}}{Y} \rightarrow \underset{\text{product}}{MY_n} + \underset{\text{by-product}}{YX_k},$$

An example is the reaction[57]

$$WO_3 + 3B = WB + B_2O_3.$$

The essence of this combined process is that the metal—one of the reactants in the self-propagating process—is formed by a prior thermite reaction. The combined process is cheaper than the self-propagating process alone, but gives products of poorer quality.

The self-propagating high-temperature method has at present found its widest application for the production of powdered refractory compounds, although other applications may be of interest (the manufacture of solid articles, the deposition of coatings, and the synthesis of single crystals). The general scheme of utilisation of these processes and products is shown diagrammatically in Fig. 4.

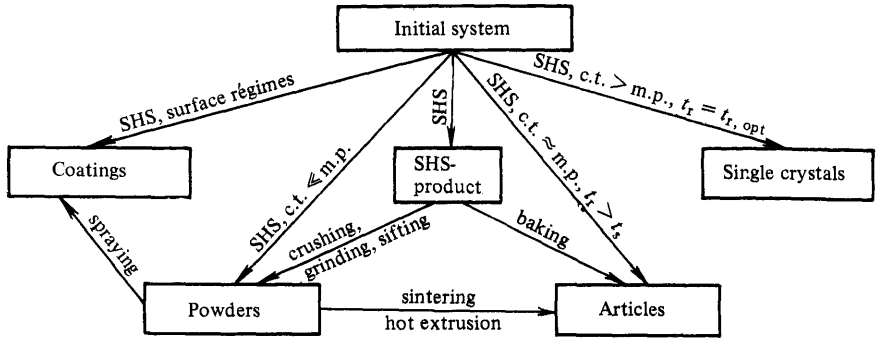


Figure 4. Diagram of uses of self-propagating high-temperature synthesis (SHS) processes and products: c.t. = combustion temperature; m.p. = melting point of product; t_r = thermal relaxation (cooling) time of product; $t_{r,opt}$ = optimum value of t_r; and t_s = duration of sintering.

Principal indices of technical combustion processes.

Process	Raw material	Product	State of aggregation of product under normal conditions	Principal applications	Combustion régime	Combustion temp., °C	State of aggregation of reactants in combustion zone	Chemical nature of combustion
Combustion of C_xH_y	natural gas	unsat. C_xH_y, process gas, carbon black	gas, solid	organic synthesis	layer, homogeneous	1300–1700	gas	oxidation, pyrolysis
Gas-flame synthesis	S, P	oxides	gas	acid production	layer, homogeneous	1000–2500	gas	synthesis from elements
Oxidising roast	sulphides	oxides	gas, solid	acid production, metallurgy	homogeneous	600–900	gas, solid	oxidation
Blast-furnace process	iron ore	cast iron	solid	metallurgy	homogeneous	1600–1900	solid, liquid	redox
Thermite	oxide, Al	ferro-alloys, master alloys	solid	metallurgy	layer	2000–3000	liquid	redox
SHS	powdered metals and non-metals	refractory compounds	solid	inorganic materials	layer	2500–4000	gas, liquid solid	synthesis from elements

The most common technical combustion processes have been outlined above. They differ in many characteristics—the raw material used, the state of aggregation and purpose of the products, the chemistry of the reaction, the conditions and temperature of combustion, etc. Their main unifying feature is that the products of combustion contain a useful substance, which provides the reason for carrying out the process. The Table compares the main features of the processes that have been described.

III. COMBUSTION AS A TECHNICAL CHEMICAL PROCEDURE

1. Technical Features of Combustion

We shall now examine the chief specific features of combustion that permit its use in chemical technology, drawing where possible a comparison with the most widely used furnace and rapidly developing plasma processes. Almost all the peculiarities of combustion are due to its strongly exothermic character. This is responsible for the high temperatures of burning and the absence of external supplies of energy. The high temperatures in turn produce high reaction velocities and complete conversion of starting materials into end-products ¶.

When the reaction goes to completion, condensed products are of high quality and gaseous products are obtained in high yields †. The extremely high reaction velocities lead to high outputs. Since an external supply of energy is unnecessary, the equipment is simple and reliable. These factors are responsible for the favourable economics of the process. In chemical technology combustion is thus a highly efficient method for obtaining high-quality products cheaply.

Combustion is intermediate between furnace and plasma processes with respect to physical parameters (temperature ‡ and rate), but surpasses them considerably in certain technical parameters, primarily the consumption of electrical energy and the equipment. An almost negligible quantity of energy is required to initiate combustion, and the process itself takes place entirely on the basis of the intrinsic energetic possibilities of the system. Furnace and especially plasma processes require an immense consumption of electrical energy to produce the high temperatures involved. Simple equipment — combustion vessels, burners — is used for combustion, it is reliable in operation, with an almost unlimited life. High-temperature furnaces and especially plasmatrons are less reliable, with a short life, since the heating elements often deteriorate because of the high energy intensity. Thus the development of plasmachemistry is held back at the present time largely by the absence of improved plasmatrons.

¶ At high temperatures the reversibility of combustion may become evident (e.g. in dissociation of the product), with consequent thermodynamic incompleteness of conversion. On cooling, however, the thermodynamic equilibrium of the combustion products is usually displaced towards formation of the required product, and by controlling (if necessary diminishing) the rate of cooling we can eliminate the incompleteness of reaction due to thermodynamic factors. The equilibrium can be influenced also by varying the pressure and the temperature of combustion.

† When the required product is an intermediate the situation is more complicated.

‡ For various systems the temperature of combustion usually lies in the range 1000–4000°C; the temperature of furnace processes does not exceed 2500°C, and the mass-average temperature of the jet in plasmachemical processes reaches 10 000°C.

Combustion has wide possibilities when technical processes are conducted in large plant units. The fundamental difficulties associated with the change in scale from laboratory apparatus to industrial plant do not usually exist for combustion processes: very often combustion takes place more easily and more completely in large than in small volumes.

The possibility of accomplishing combustion at high and ultrahigh pressures is of great importance. In many cases fundamentally new constructions are not required, and modern high-pressure apparatus can be used. The combination of high pressures with high temperatures in furnace processes involves great difficulties, and high-pressure plasmatrons do not exist at all.

The erroneous opinion is held among technologists that technical processes based on combustion are difficult to control. An understanding of the factors governing the rate and the completeness of the chemical reactions involved will enable effective methods of control to be established. Particular combustion régimes can be deliberately maintained by regulating the temperature by the introduction of an additional source of energy or dilution of the initial reactants with the products, by varying the pressure and the concentrations in the reaction zone, by establishing a definite disperse composition when condensed phases are involved, and by other methods.

From a survey of the above considerations it may be concluded that combustion is one of the most ideal processes of chemical technology. It is therefore desirable to obtain products where possible under conditions of combustion.

2. Conditions for the Accomplishment of Processes of Chemical Technology under a Combustion Régime

In considering the possibility of conducting technical processes under combustion conditions we must pose two questions: (i) when can combustion be accomplished at all; and (ii) when can combustion be used for technical purposes.

The first question is answered by combustion theory[12]. The precise quantitative solution depends on many factors—the kinetic character of the combustion (simple or stepwise reactions, slight or marked kinetic inhibition by reaction products), the state of aggregation of the reactants, the combustion régime (homogeneous or layered steady state or oscillatory), etc. Fundamentally, however, the solution is common to all cases. We shall therefore examine for simplicity the propagation of a combustion wave during a first-order reaction in the gas phase.

In theory there exist necessary and sufficient conditions for a combustion wave to be propagated. The necessary conditions are

$$\beta = \frac{R(CT_0+Q)}{CE} \ll 1;$$
$$\gamma = \frac{R(CT_0+Q)^2}{CEQ} \ll 1,$$

where Q is the heat of reaction, E the activation energy, C the heat capacity at constant pressure § (molar or specific depending on the units in which Q has been expressed), T_0 the initial temperature of the reactants, and R the gas constant. These conditions evidently include the reaction parameters of combustion Q, E, and C, together with T_0 characterising the initial state of the system.

The sufficient condition is determined from the relation between the evolution of heat in the combustion wave and the loss of heat to the surrounding medium. In order that a combustion wave shall be propagated, it is sufficient that the heat losses should be less than a critical value: $\eta < \eta_{cr}$. The quantity η can be determined from the formula

$$\eta = \frac{T_{adb} - T_c}{T_{adb} - T_0},$$

where T_c is the temperature of combustion in the presence of heat losses. For the present example

$$T_{adb} - \frac{RT_{adb}}{E} \leqslant T_c \leqslant T_{adb}$$

so that

$$\eta_{cr} = \gamma.$$

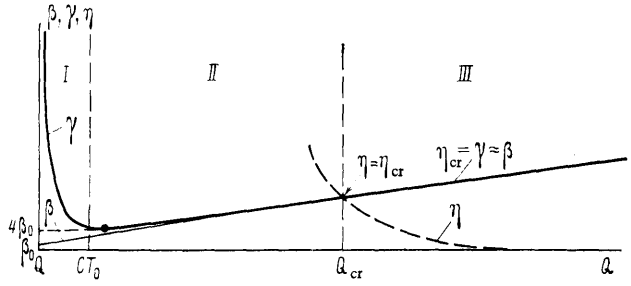


Figure 5. Necessary and sufficient conditions for propagation of combustion waves.

For clarity the necessary and sufficient conditions can be shown graphically. Fig. 5 illustrates the dependence of β, γ, and η on Q for constant T_0 and E with $\beta_0 = RT_0/E \ll 1$¶. The heat of reaction is chosen as variable on this graph, since it is the most important characteristic of the combustion. In most cases, when the composition of the products is known or can readily be assumed, the heat of reaction can be determined from thermochemical considerations. Three characteristic ranges (I)–(III) can be distinguished in Fig. 5, characterised by small, medium, and large heats of reaction.

(I) A combustion wave cannot be propagated, since the necessary conditions cannot be observed because of the large value of γ. Rates of reaction at T_{adb} and T_0 are comparable, and the pattern of propagation of a reaction zone through the substance, which is characteristic of combustion, is impossible.

§ In the theory of combustion we use the mean heat capacity determined by means of the formula

$$C = \frac{1}{T_{adb} - T_0} \int_{T_0}^{T_{adb}} C_p(T)\,dT,$$

where T_{adb} is the adiabatic (thermodynamically calculable) temperature of combustion.

¶ Strictly speaking, such a relation with a constant activation energy can be obtained only by diluting the initial reactants with inert products, but qualitatively it represents a more general rule. Special effects, not considered in the theory, arise when the heat of reaction is very large.

(II) The necessary conditions are observed, but the sufficient condition is not satisfied. A combustion wave cannot be propagated, since heat losses from the reaction zone are large. If combustion is initiated by special means, it is unable to develop, and dies out.

(III) Both necessary and sufficient conditions are observed, and the process has all the characteristic features of combustion. Usually $Q \gg CT_0$ and $\beta \simeq \gamma$.

A similar situation occurs in other, more complicated cases. There is no definite boundary between ranges (I) and (II). The critical heat of reaction Q_{cr}, separating ranges (II) and (III), is quite specific, and is determined in the theory of combustion limits[12] from the critical condition for propagation of a combustion wave. It depends both on the kinetic factors characterising the rate of evolution of heat in the combustion wave and on the geometric and thermophysical factors characterising the conditions of combustion. The latter include the geometrical scale of the burning system (the diameter of the specimen, tube, or jet) and the effective heat-transfer coefficient from the reaction zone to the surrounding medium. Even under the same conditions the critical heat of reaction may vary greatly on passing from one system to another. Whether or not a given system will burn cannot be predicted merely on the basis of information on the heat of reaction. The various classifications of the ability of exothermic systems to burn, based on values of this parameter and detached from the kinetic characteristics of the system and the thermophysical circumstances, are therefore untenable. Furthermore, determination of the critical conditions of combustion in any specific case is unreal—despite the theoretical possibilities—both because methods of calculation have been inadequately developed and because the data necessary for the calculation are lacking.

In such a situation a preliminary analysis can most reasonably be made by calculating thermodynamically the adiabatic temperature of combustion. Although the result will not give an unambiguous answer to the question, it is always useful, since some experience of working with a given class of systems enables a correct appraisal to be made of the possibility of combustion in a particular system. For example, experimental studies of the self-propagating high-temperature synthesis of four classes of refractory compounds—carbides, borides, nitrides and silicides — show that combustion does not occur when $T_{adb} < 1500$ K, systems always burn when $T_{adb} > 2500$ K, and additional investigations are required for intermediate values.

The answer to the second question — when combustion can be used for technical purposes—depends on the technical demands made. Here the main indicators are the yield and the possibility of isolating the product, its quality (for condensed substances), and the cost of the starting material. Detailed discussion of these criteria is innecessary, so that we shall merely examine a few examples.

It has already been noted that metal and slag phases should separate in the thermite production of ferro-alloys and master alloys. If such separation does not take place, the combustion cannot be used for the preparation, because of the difficulty of isolating the product. Phase separation is clearly possible when the combustion temperature is higher than the melting points of all the combustion products. For it to be complete, however, the operating conditions must ensure long thermal relaxation times, so that the system does not cool before complete phase separation can occur. The theory of the thermite process[41] has established criteria indicating the possibility of metal extraction in any specific case, and has suggested methods for controlling the process (preheating or slag-forming additives, the combination of combustion and furnace methods, etc.).

Complete conversion is very important to self-propagating high-temperature processes, in order to avoid contamination of the product with unchanged reactants, as isolation (i.e. purification) of the product is almost impossible. For the same reason single-phase products should be obtained.

The production of acetylene and ethylene by incomplete combustion of a hydrocarbon is possible only if adequate quantities of intermediate products of the pyrolysis of hydrocarbons are formed and if effective quenching is ensured.

It must be remarked, however, that the conditions of technical combustion depend on how the process is organised, and with correct organisation are very often feasible. It is therefore more important to satisfy conditions under which combustion can in general be accomplished (in systems whose use is economically justified).

IV. SOME PROMISING LINES OF ADVANCE IN THE USE OF COMBUSTION PROCESSES IN CHEMISTRY AND TECHNOLOGY

Analysis of the possibilities for applying combustion to chemical production suggests that only a small proportion of useful processes have yet been exploited. For this reason the development of research on combustion towards technical objectives offers great promise.

Firstly, we may note that the application of combustion processes to the chemistry and technology of inorganic materials is a novel and little investigated problem. Great prospects are opened up, whose full scope is at present difficult to envisage. The variety of factors characterising the composition and structure of powdered inorganic compounds and materials based on them leads to difficulties in establishing the scientific foundations of control for ensuring that quite definite products are obtained. The use of combustion methods for these purposes presents a difficult and fascinating scientific problem, whose solution is closely connected with the need to develop the theory of combustion.

Among promising tasks is firstly expansion of the range of inorganic compounds formed by interaction of the elements under conditions of combustion (it is the easiest). Here we may have in mind the synthesis of semiconducting compounds (sulphides, selenides, tellurides, phosphides, etc.), refractory compounds based on rare-earth metals, refractory one-phase composite compounds (mainly multicomponent solid solutions), and new modifications of binary compounds under conditions of combustion at high and ultrahigh pressures, etc.

It is of interest to apply self-propagating high-temperature processes to compounds of metals (e.g. chlorides and oxides), firstly because the use of a cheaper material than powdered metals will lower the cost of refractory compounds and secondly because the volatile components (chlorides) will permit combustion in the gas phase yielding the products as with homogeneous gas-phase deposition) in the form of powders of high specific surface, which is important for certain applications. It is tempting to try to transfer gas-phase precipitation to combustion conditions (by analogy with the transfer of certain furnace processes in the self-propagating high-temperature method). However, systems with chlorides or oxides as components are in most cases insufficiently exothermic, so that the main problem is to compound (select) high exothermic combinations. Here a thermodynamic approach may prove very effective. A thermodynamic analysis of the combustion of several systems

involving chlorides has been made[58]. As an example[40], the reaction

$$BCl_3 + NH_3 = BN + 3HCl$$

is weakly exothermic and leads to an adiabatic temperature rise of only 500–600 deg. Nevertheless, the introduction of a gaseous mixture of hydrogen and chlorine into the initial mixture may raise the adiabatic temperature considerably and make possible the establishment of a combustion régime. The consequent decrease in the yield of the nitride from the boron is not very great. Analogous methods can be used in other cases.

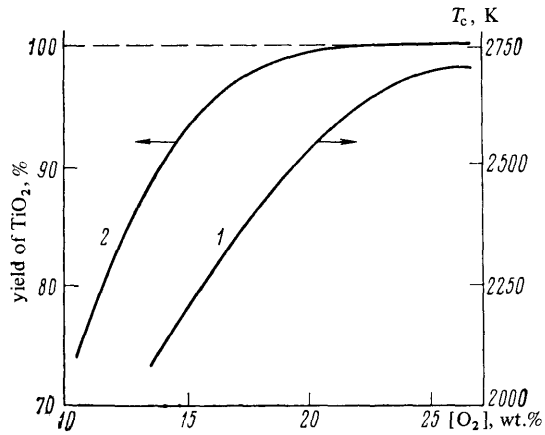


Figure 6. Thermodynamic calculation for $TiCl_4 + O_2 + H_2$ system with H : Cl ≃ 2 and p = 1 atm: *1*) combustion temperature; *2*) yield of TiO_2.

An important practical task is to obtain titanium dioxide pigment from the tetrachloride:

$$TiCl_4 + O_2 = TiO_2 + 2Cl_2 .$$

This reaction is at present accomplished in the jet of an oxygen plasma, which is one of the greatest achievements of plasmachemistry[59]. It is therefore especially interesting to examine the possibilities of combustion for solving this problem. The temperature of adiabatic reaction between titanium tetrachloride and oxygen is ~ 1200 K,[60] which may be too low for combustion. However, the introduction of hydrogen into the initial mixture (giving titanium dioxide together with hydrogen chloride) will establish quite good thermodynamic conditions for combustion to occur (Fig. 6). The main difficulty in the experimental investigation will evidently be to control the degree of dispersion and the phase constitution of the dioxide with the aim of satisfying technical requirements.

Zel'dovich has put forward the interesting idea that cyanogen and its decomposition products might be used as reductants. Mixtures of cyanogen and oxygen develop very high temperatures on combustion, so that the excess of cyanogen could efficiently be used for gas-phase reduction (and probably for nitriding).

An important practical problem is to make solid articles from refractory compounds or composite materials by combustion. Its solution will lead to the introduction of combustion methods into powder metallurgy, which will undoubtedly aid progress. At present combustion methods yield refractory compounds in the form of powders, from which articles are produced by the usual sintering processes of powder metallurgy. However, sintering often takes place during combustion. It would be useful to study the completeness of sintering as a function of the combustion conditions and to learn how to control the process. Articles may then be obtained directly from the initial components under a combustion régime in a single technical stage. Compositions occupy a special position in the problem, and attempts have been reported[61] to obtain solid mixtures by combustion.

Several other types of use of combustion processes in the chemistry and technology of inorganic materials are of interest — the employment of surface combustion for the application of coatings for various purposes, the growing of single crystals by cooling liquid or condensing gaseous combustion products, etc.

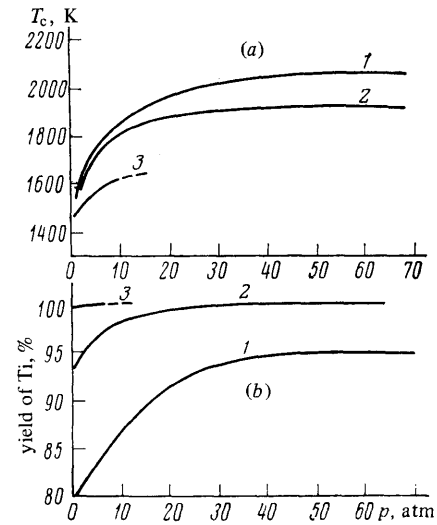


Figure 7. Pressure dependence of: *a*) combustion temperature; *b*) yield of titanium for $TiCl_4$ + Mg system containing different proportions (%) of magnesium: *1*) 20 (stoichiometric); *2*) 22; *3*) 24.

There are also several important but little developed uses of combustion in metallurgy and chemical technology. The production of non-ferrous metal powders, e.g. titanium, offers great possibilities. One of the most familiar methods for obtaining titanium is based on the thermite reaction[62]

$$TiCl_4 + 2Mg = Ti + 2MgCl_2 .$$

In industry it is accomplished by molten magnesium with a spray of titanium tetrachloride by a furnance method (to give so called titanium sponge). However, this reaction is sufficiently exothermic to be of interest from the viewpoint of combustion. The results of special thermodynamic calculations[58] illustrated in Fig. 7, together with some preliminary experiments, show that magnesium is able to reduce the tetrachloride to titanium under a combustion régime, and this process should be of industrial importance. The main task is evidently to examine the quality of the titanium

obtained in this way. It can readily be shown that several other metals may be produced by analogous processes. An interesting problem is to obtain metal powders of different degrees of dispersion, as well as powdered alloys.

The oxidation of sulphides offers great opportunities for the application of combustion methods. As already remarked, existing processes for roasting sulphide ores in a fluidised bed are inefficient, since the energy reserves of the system itself are by no means fully utilised (the working temperatures in the technical process are far lower than the combustion temperatures actually obtainable). It appears useful to examine the possibilities of combustion in a stream of a highly dispersed sulphide and oxygen (or air greatly enriched with oxygen). Very high temperatures will develop, and lead to a qualitatively different mechanism of oxidation. It can be regarded[39] as involving two stages, in the first of which sulphur burns to form its oxides. Combustion takes place in the vapour phase. The thermal flux from the combustion front heats a particle to a high temperature and causes thermal dissociation of the sulphide. Thus the first stage involves the burning of sulphur vapour, and the metal plays no part in the reaction. This mechanism recalls the burning of a hydrocarbon drop as described by Varshavskii[63]. In the second stage the residue, consisting of the metal (or a lower sulphide) burns away, by either vapour-phase or heterogeneous combustion depending on the relation between the combustion temperature and boiling point of the metal (see theory of combustion of metal particles[64]). By this mechanism oxidation processes should go to completion.

The use of combustion methods to obtain chemical reagents shows promise. The self-propagating high-temperature method, for example, is able to yield chemically pure specimens of many inorganic compounds. Borovinskaya et al. [65] have recently produced salts of certain inorganic acids by combustion processes:

$$NH_3 + H_2 + Cl_2 \rightarrow NH_4Cl;$$
$$V_2O_5 + Mg \rightarrow MgVO_4;$$
$$CaO + C + O_2 \rightarrow CaCO_3.$$

Simple and mixed gases have been obtained[66] by the combustion of pyrotechnic compositions, which may be of practical value under specific conditions.

The above is a by no means complete list of promising lines of research on combustion processes in chemical technology.

V. TECHNICAL PROCESSES AND COMBUSTION THEORY

We shall now consider the relation between problems of chemical technology and combustion theory. We have already noted in the Introduction the extremely small contribution made by chemical technology to the general theory of combustion, whose development was stimulated mainly by energetic problems. Indeed, the development of such processes as the blast-furnace production of cast iron, the roasting of sulphide ores, and the manufacture of acetylene did not present to the science of combustion a single major problem of general theoretical importance.

An exception is the work by Tesner and his colleagues[24] on the formation of soot in flames, in connection with the problem of obtaining carbon black. The importance of this work extends beyond the specific problem, since the burning of gases accompanied by the formation of condensed products is very widespread and is met in various applied processes. An understanding of the mechanism of formation of a condensed phase in the circumstances will permit not only control of the state of dispersion of condensed combustion products (which is of direct practical importance) but also development of the theory of the combustion of gases to take into account the influence of the kinetics and the thermodynamics of condensation processes on the rate of burning (establishment of a theory of so called "condensation" combustion).

However, it would be erroneous to assume that known technical combustion processes do not contain interesting theoretical problems: such problems exist, and are by no means few. We shall discuss some of them.

The immersion preparation of acetylene and ethylene involves the combustion of a gas bubble. This type of combustion of heterogeneous systems (in contrast to that of drops of fuel suspended in a gaseous oxidant) remains almost uninvestigated. The limited volume of oxidant, the intense heat transfer from the combustion zone to the liquid phase, the continuously increasing volume of the hot hearth, the stepwise chemical reaction, and other features may be responsible for several interesting effects of theoretical importance.

It is no less important to extend the theory[67] of the stepwise combustion of gases to exothermic oxidation accompanied by endothermic pyrolysis as in the incomplete combustion of hydrocarbons. Such a theory should reveal the factors primarily responsible for the structure of the combustion zone, in order to indicate ways of establishing high concentrations of intermediate products and of obtaining them in high yield by the optimum application of quenching media (when an intermediate is the required product) or of ensuring completeness of combustion (when a final product is required). Attempts have been made to give a detailed mathematical description of the process taking into account all possible reactions. However, it would be more useful to formalise the description[67] and consider only the most important stages.

The above account indicates that the problem of stepwise combustion arises also in the roasting of sulphides. Here, however, it extends to the diffusion combustion of heterogeneous systems. The stepwise burning of particles and their aggregates is an almost undeveloped branch of combustion theory.

Interesting theoretical problems of combustion are connected also with the thermite extraction of ferro-alloys and master alloys. One of these is to develop a theory of liquid-phase gas-free combustion allowing for diffusion processes. Interest in this arises from the use under industrial conditions of coarse granules of reactants and the fact that the limiting kinetic régimes of theory are not realised in liquid-phase combustion. A diffusion-kinetic theory of liquid-phase processes of gas-free combustion should indicate ways of diminishing the incompleteness of thermite reactions caused by diffusion hindrances. Another problem[46] is the possibility of explosion in the combustion of highly exothermic compositions (such as molybdenum trioxide with aluminium) in large quantities owing to gas formation resulting from partial vaporisation of the reactants.

The development of self-propagating high-temperature processes was from the very beginning closely connected with combustion theory. The peculiar forms of conversion of the reactants has led to the development of new trends in combustion theory, and the large range of new substances to the discovery of hitherto unknown phenomena. The mechanism of gas-free[20,55,68-71] and filtration[72-74] combustion has been investigated, the phenomena of spin[75,76] and oscillatory[20,68,75-77] combustion have been observed, régimes of surface and layer-by-layer combustion[72-74], the propagation of a combustion front, and burning down[55,70-72] have been studied, and methods have been worked out for

calculating the rate of propagation of a combustion wave with broad zones of chemical reaction[71,78].

Although the survey in this section is incomplete, it indicates that not only energetics but also technology has given rise to many interesting problems in combustion theory.

* * *

Combustion can occupy an important position in modern chemistry, with its tendency to intensify processes and accomplish new reactions by establishing so called "extreme" conditions. The purpose of this Review was to direct attention to this. Highly intensive technical chemical processes have already been organised on the basis of combustion, and there are clear prospects for the further development of this trend. Problems in chemical technology may be expected to give a new impetus to the development of combustion theory.

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