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ON THE CONSIDERATION OF CHEMICAL KINETICS IN COMBUSTION CALCULATIONS

Summary. The present contribution is a brief review of the problems associated with the modelling of the chemical aspects of the combustion process and some of the approaches that are being followed, including the consideration of chemical kinetics. A number of examples are then cited where this approach has been applied to consider some common engineering problems.

Introduction

Combustion processes, as they take place in the wide range of engineering devices and application, comprise exothermic systems that react chemically and are usually accompanied by a flame. The phenomenon has long been recognized as a complex one requiring intimate knowledge in many fields including physical chemistry, fluid mechanics, heat and mass transfer and thermodynamics.

The majority of past attempts to construct a mathematical model for combustion in engineering systems have been of limited utility because of the difficulty of relating reliably the time independent thermodynamic quantities to the time dependent kinetic considerations.These limitations become particularly serious and inhibiting when considering phenomena such as autoignition, rate of heat release, and the nature and extent of exhaust emissions where time dependent chemical rather than merely thermodynamic or physical considerations predominate.

A particularly troublesome feature in the consideration of combustion is the realization that in no instance of practical engineering importance does the reaction process proceed in a direct step from fuel and air to combustion products. The conversion of reactants into the products proceeds usually though a large number of intermediate and overlapping simpler steps that have widely different rates and involve the production, sequentially, of a very large number of both stable and unstable species of varying composition. These only ultimately produce the expected products. Often, some of the reacting molecules may not proceed through these steps to completion allowing the survival of some of the intermediate products to the final stage of combustion, thus contributing towards increased pollution.

Accordingly, it is not surprising that the combustion process has been treated in the past in a very simplified manner, invariably implying either an infinite reaction rate that leads to completion and the release of the energy of the reaction suddenly or that chemical equilibrium conditions are achieved throughout.Even occasionally when finite reaction rates are considered, it is normally simplified by assuming that a single step reaction prevails converting the reactant fuel and air directly to the assumed products. Obviously, these approaches can serve our needs only in a limited number of cases and will fail completely when considering the air pollution problem. Ideally the conversion of reactants to products need to be described fully in terms of the multitude of steps that may take place with different individual rates and the numerous intermediate species involved. Such an accurate description can very soon, even for the simplest of reactive systems, involve extremely complex array of reaction steps and species requiring a wealth of information about reaction kinetic data that may be lacking and may remain so for the near future.

The present contribution is a brief review of the problems associated with the modelling of the chemical aspects of the combustion process and some of the approaches that are being followed including the consideration of detailed chemical kinetics. Throughout this treatment which obviously is not meant to be exhaustive, reference will be made primarily to work the author and his co-workers have been involved with.

Overall combustion kinetics

It is well recognized that our present knowledge of chemical kinetics is incomplete and does not permit us to present a reliable detailed description of all the kinetic schemes and associated steps for the combustion reactions of common fuels. Therefore, gross simplifications in the course of these processes are made to relate the initial reactants directly to the final products. A resort to this overall chemical kinetic approach implies the whole combustion process is represented as a single overall reaction. The fuel and oxidant is considered to be converted directly to products without due considerations being given to the multitude of reaction steps and products that are involved intermediately.

The overall combustion reaction rate may be represented adequately for most of the common hydrocarbons by the following form of a single step reaction:

$$\dot{m}_f''' = K(m_f)^a (m_{ox})^b p^{(a+b)} e^{-E/RT} \qquad (1)$$

This simplified reaction rate of the fuel $\dot{m}_f'''$ $\left[\text{i.e. } \frac{d(M_f/v)}{dt}\right]$ implies that the rate of change of the specific mass of the fuel with time is a function of the instantaneous mass concentration of the fuel m_f, (i.e. $M_f/\Sigma M$) and oxygen m_{ox}, (i.e. $M_{ox}/\Sigma M$) and of an exponential relationship with respect to the mixture thermodynamic temperature (T) which is commonly known as being of the Arrhenius form K and E are constants, the latter being the activation energy of the reaction.

This form of the reaction indicates that the reaction rate is initially slow and would increase rapidly as the temperature of the system increases reaching a maximum value at relatively high temperature. The reaction rate then decreases rapidly as either the fuel or oxygen becomes nearly exhausted. Moreover, it will be expected that this limited and approximate approach will provide agreement with experiment only over a limited range of operating conditions.

The success of overall chemical kinetics suggests that over the opperating range considered a reaction step may exercise a dominant role in the overall conversion rate and at the same time bear some quantitative relationship to the major reacting constituents. Such a possible step, if it does exist, would vary from one fuel to another and the temperature and concentration ranges.

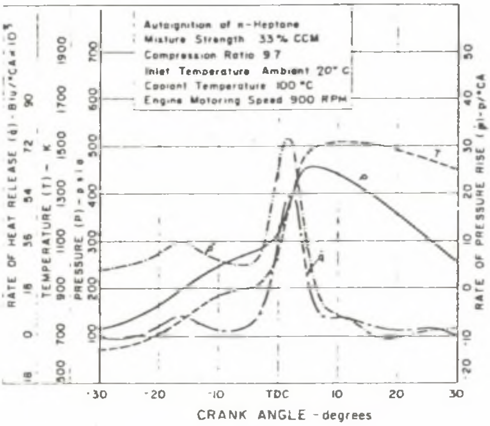

Fig. 1. Typical calculated variations of the effective rate of heat release $\dot{q}$, pressure P, rate of pressure rise $\dot{P}$, temperature T and cumulative energy release during a cycle in a compression ignition engine when using n-heptane as a fuel and employing gross reaction kinetics

For example when considering the autoignition of a homogeneous mixture of a fuel and air in a compression ignition piston engine, the rate of change of the mass of the fuel can be evaluated as the reaction proceeds due to increasingly higher temperature and pressure. This means that the appropriate constants of the overall reaction rate of equation (1) be made available and a computer programme is developed to carry out the necessary calculations step by step [1]. Accordingly, the instantaneous relative concentrations of the fuel and oxidant together with the rate of energy release and temperature are established.

Figure 1 shows the calculated rate of heat release $\dot{q}$, pressure P and temperature T; the point of ignition, peak temperature and rate of pressure and temperature rise can thus be evaluated. However, the relative success od such a prediction will be primarily dependent on the reliability of the kinetic constants chosen in the reaction rate equation and to what extent a gross reaction rate equation can adequately describe the reactions involved. Moreover, with such an approach it is impossible to predict the concentrations of the reacting species, making the gross reaction approach even when successful of limited utility.

By examining the combustion reactions of lean mixtures of methane and air at atmospheric pressure in a flat flame burner, the following gross reaction rate can be suggested for the combustion of methane [2]:

$$-\frac{d\left[CH_4\right]}{dt} = 7,8 \times 10^{21}\left[CH_4\right]^{1,0}\left[O_2\right]^{1,5} \exp(-56,900/RT) \qquad (2)$$

where the concentrations are in mol/cm^3, R in cal/(mol K) and E in cal/mol.

In view of the limitations of the gross kinetic approach in describing the whole combustion process from the stage of reactants to final products, it has been customary in the literature to quote the reaction rate equation in terms of the initial concentrations of the fuel and oxidant. This would make the reaction rate equation much simpler to use,though primarily suitable for the ignition phase of the reactions where no significant changes in the concentrations of the fuel and oxidant have taken place. However, unfortunately the literature is full of cases where such formulations have been used or derived because of their simplicity with the implied indiscriminate assumption that changes in the concentrations of the reactants are only of second order to that of temperature. This practice alone has contributed significantly to the chaotic nature of the gross reaction rates data that are present in the literature. In any case it should always be remembered that considering the high complexity of the combustion process, it is evident that a formula such as that of equation (1) can hardly represent completely the combustion process over a wide range of operating conditions, particularly when only the initial values of the concentrations are employed. Accordingly, ideally detailed chemical kinetics if available need to be considered.

Some detailed chemical kinetic schemes

As far as common combustion reactions are concerned, currently, there are only a few fuel systems that can be described fully kinetically in terms of the many likely reaction steps and intermediate species that take part to yield the final products. This list though at the moment may appear to be very limited, it includes however the oxidation reactions of some very important fuels such as hydrogen, carbon monoxide and methane representing natural gas. Moreover, the reactions that take part in the formation of the pollutants, oxides of nitrogen can also be described fully. Some other fuel systems can be incorporated in such an exclusive list. However, the reliability and completeness of their detailed kinetic schematic formulation will diminish as more complex fuel molecules are considered.

Despite, these limitations much modelling work can be made, particularly, in the consideration of the reactions that proceed within the products of combustion at high temperature. Some attempts have been made to consider the highly simplified gross reaction rate kinetics for the oxidation of common fuels followed by more comprehensive detailed description of the reactions of the partial oxidation and final products. Examples, will be given of some cases where the detailed kinetic approach has been utilized by the author and his co-workers.

Considering the results of the numerous kinetic investigations reported in the literature on the oxidation of methane, hydrogen and carbon monoxide, an adequate reaction scheme can be formulated involving some 32 reaction steps and at least 14 chemical species that will describe the gradual degradation of the methane and its oxidation through intermediate species such as CH_3, CH_2O and CHO to the final products [3]. Table 1, lists these reaction steps for methane, hydrogen and carbon monoxide oxidation. The relevant kinetic constants associated with every reaction step are usually obtained from the chemical literature.

Table 1

Reaction scheme employed for the oxidation of methane

$CH_4 + OH \rightleftharpoons CH_3 + H_2O$

$CH_4 + H \rightleftharpoons CH_3 + H_2$

$CH_4 + O \rightleftharpoons CH_3 + OH$

$CH_4 + HO_2 \rightleftharpoons CH_3 + H_2O_2$

$CH_4 + O_2 \rightleftharpoons CH_3 + HO_2$

$CH_4 \rightleftharpoons CH_3 + H$

$CH_3 + O \rightleftharpoons CH_2O + H$

$CH_3 + O \rightleftharpoons CHO + H_2$

$CH_3 + O_2 \rightleftharpoons CH_2O + OH$

$CH_2O + OH \rightleftharpoons CHO + H_2O$

$CH_2O + H \rightleftharpoons CHO + H_2$

$CH_2O + O \rightleftharpoons CHO + OH$

$CH_2O + O_2 \rightleftharpoons CHO + HO_2$

$CHO + OH \rightleftharpoons CO + H_2O$

$CHO + O_2 \rightleftharpoons CO + HO_2$

$CO + OH \rightleftharpoons CO_2 + H$

$$\begin{array}{lcl}
CO + O_2 & \rightleftharpoons & CO_2 + O \\
H_2 + OH & \rightleftharpoons & H_2O + H \\
H + O_2 & \rightleftharpoons & O + OH \\
H_2 + O & \rightleftharpoons & H + OH \\
H_2O + O & \rightleftharpoons & OH + OH \\
H_2O_2 + O_2 & \rightleftharpoons & HO_2 + HO_2 \\
H_2O_2 + H & \rightleftharpoons & H_2O + OH \\
H_2 + O_2 & \rightleftharpoons & OH + OH \\
H_2 + HO_2 & \rightleftharpoons & H_2O_2 + H \\
HO_2 + H & \rightleftharpoons & OH + OH \\
H + H + M & \rightleftharpoons & H_2 + M \\
O + O + M & \rightleftharpoons & O_2 + M \\
H + OH + M & \rightleftharpoons & H_2O + M \\
OH + OH + M & \rightleftharpoons & H_2O_2 + M \\
H + O_2 + M & \rightleftharpoons & HO_2 + M \\
HO_2 + OH & \rightleftharpoons & H_2O + O_2
\end{array}$$

Similarly, the reactions that bring about the reaction of the nitrogen in the air with oxygen to produce the oxides of nitrogen can be equally formulated and shown in Table 2 [4].

Table 2

$$\begin{array}{lcl}
NO + O_2 & \rightleftharpoons & NO_2 + O \\
NO + N & \rightleftharpoons & N_2 + O \\
O_2 + N & \rightleftharpoons & NO + O \\
N + O + M & \rightleftharpoons & NO + M \\
N_2 + O_2 & \rightleftharpoons & NO + NO \\
N_2O + O & \rightleftharpoons & NO + NO \\
NO_2 + N & \rightleftharpoons & NO + NO \\
2N + M & \rightleftharpoons & N_2 + M \\
O_2 + N_2 + M & \rightleftharpoons & N_2O + M \\
O + NO + M & \rightleftharpoons & NO_2 + M
\end{array}$$

An analytical model for detailed chemical kinetics

The change in the composition of a homogeneous reacting system under constant temperature and pressure over a known short residence time, can be considered in terms of a steady mass flow rate of the mixture, allowing the reactants to reside within a reaction zone at an assumed uniform and constant temperature T and pressure P for a time Δt. All the intermediate reactions necessary to represent adequately the combustion process, are assumed to take place simultaneously, both in the forward and backward directions before leaving this zone. Accordingly, the conservation of species equation is:

$$\frac{\rho}{\Delta t}\left(s_i^* - s_i\right) = \sum_{\text{all } j} \left(x_{ij}' - x_{ij}''\right)\left(R_{jf} - R_{jb}\right) \tag{3}$$

where s_i^* and s_i are the concentrations of a specie "i" in the input and output mixtures respectively in (mol/g); x_{ij}' and x_{ij}'' are the stoichiometric constants in the chemical equation of the j^{th} reaction:

$$x_{ij}' \; F + \ldots . = x_{ij}'' \; F + \ldots . \tag{4}$$

where F is the chemical formula of specie i . If R_{jf} and R_{jb} represent reaction rates for the forward and backward reactions respectively for a j^{th} reaction then:

$$R_{jf} = \left[\prod_{\text{all } i} (\rho s_i)^{x_{ij}}\right] K_{jf} \tag{5}$$

$$R_{jb} = \left[\prod_{\text{all } i} (\rho s_i)^{x_{ij}''}\right] K_{jb} \tag{6}$$

$$K_{jf} = A_{jf} \, e^{-\frac{E_f}{RT}} \tag{7}$$

$$K_{jb} = A_{jb} \, e^{-\frac{E_b}{RT}} \tag{8}$$

$$\rho = P/RT \sum_{\text{all } i} (s_i) \tag{9}$$

where A_{jf}, E_{jf} and A_{jb}, E_{jb} are the kinetic parameters of the j^{th} reaction for the forward and backward reactions respectively. The above non-linear simultaneous equations can be solved to determine the concentration of each specie s_i in the output, when the values of P, T, $\frac{\rho}{t}$ and s_i^* together with the relevant kinetic and thermodynamic data are given.

The set of kinetic species equations represented by equation (3) can be made an integral part of any group of simultaneous equations that are formulated to describe the behaviour of an engineering system or device. This normally will add a significant degree of complexity to the model as it will demand the solution of a large number of nonlinear simultaneous reaction equations. However, there are now efficient computer programmes developed to cope specifically with the solution of these equations. They can be made subroutines within the main computer programme directed at the solution of any engineering problems. A number of simple examples will be cited where this approach has been applied to consider a number of engineering problems.

Examination of the extent of approach of a reactive system towards equilibrium

The extent of approach of a reactive system to equilibrium conditions at constant temperature and pressure can be viewed in terms of the value of the equilibrium constant function in terms of the observed relevant instantaneous concentrations rather than the corresponding ultimate equilibrium concentrations. Accordingly an apparent equilibrium constant function K_p can be calculated for the reacting system to be termed K_{pcal} as a function of time which will approach at equilibrium conditions the accepted tabulated thermodynamic value K_{ptab} and will remain subsequenly at that value. The ratio (K_{pcal}/K_{ptab}) can be viewed in general as an indication of the extent of approach of the Gibbs function change for the reaction to its minimum value when equilibrium conditions are achieved, i.e.,

$$(K_p)_{cal}/(K_p)_{tab} = e^{\frac{\Delta G}{RT}} \qquad (10)$$

where $\Delta G \rightarrow 0$ as the equilibrium state is approached.

The time required for a reaction to reach effective equilibrium, τ, under isothermal and isobaric conditions will depend upon initial conditions and the temperature and pressure involved. This time also depends upon the initial concentrations of the species involved within the reacting mixture and the definition of what constitutes in practice an effective equilibrium state.

It can be shown that τ is given by the following relationship:

$$\rho \tau A_j \, e^{-\frac{E}{RT}} \cong Z \qquad (11)$$

where Z is largely a function of the initial composition of the mixture and A_j and E are the kinetic data of the reaction being considered[5]. Hence, the time to achieve effective equilibrium for a reaction can be established for any initial composition when the kinetics of the reactions are known.

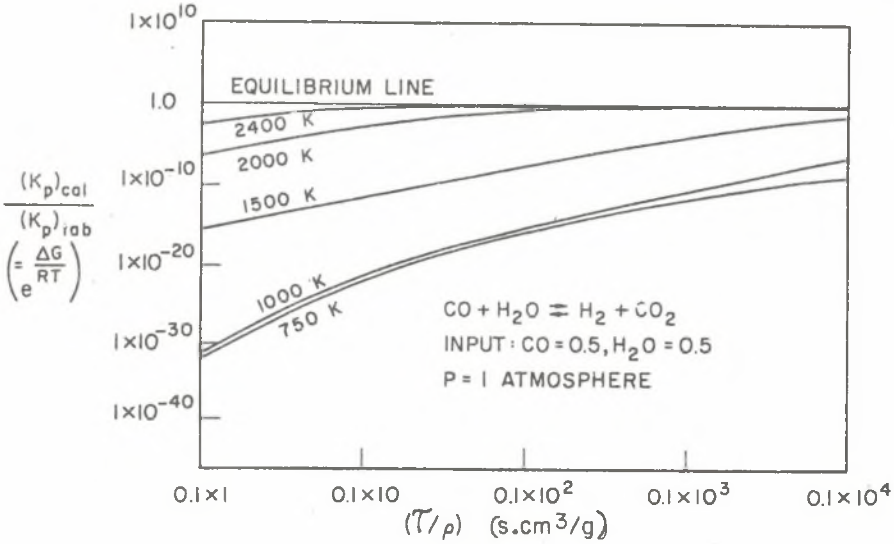

Fig. 2. The effect of temperature and time on the progress of the water gas shift reaction for a initial mixture of 50% CO and 50% H_2O by volume at atmospheric pressure

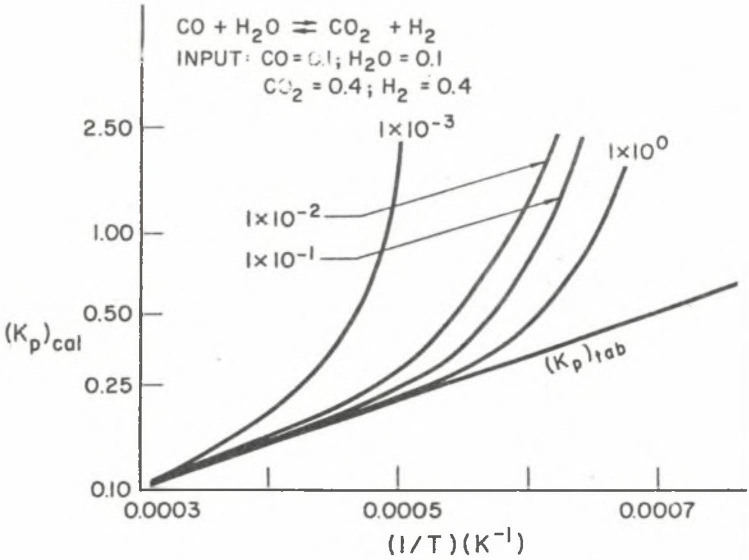

Fig. 3. Variation of the function $(K_p)_{cal}$ for the water gas shift reaction i.e. $[CO_2].[H_2]/[CO].[H_2O]$ versus $\frac{1}{T}$ for various constant values of residence time in seconds for a typical input mixture of H_2, H_2O, CO and CO_2

Figure 2 shows typically the progress of the conversion of a homogeneous mixture of CO and H_2O towards equilibrium at various constant temperature values extending from 750 K up to 2400 K when employing detailed chemical kinetic calculations. It can be seen for example, that the time period required to achieve near equilibrium conditions appears to increase by about an order of magnitude as the temperature is reduced from 2400 K to 2000 K. Moreover, equilibrium conditions cannot be assumed to be achieved within reasonable residence time for the two cases shown involving temperatures of 1000 K or 750 K. Thus the reaction would appear to reach "frozen" conditions at around such temperatures.

Figure (3) shows typical variations with $(\frac{1}{T})$ of the apparent values of the function $(K_p)_{cal}$ for the water gas shift reaction involving the instantaneous concentrations after a specified period of reaction time for two initial mixture conditions. From such plots for example, the temperature at which approximately equilibrium conditions are achieved after a certain residence time can be determined.

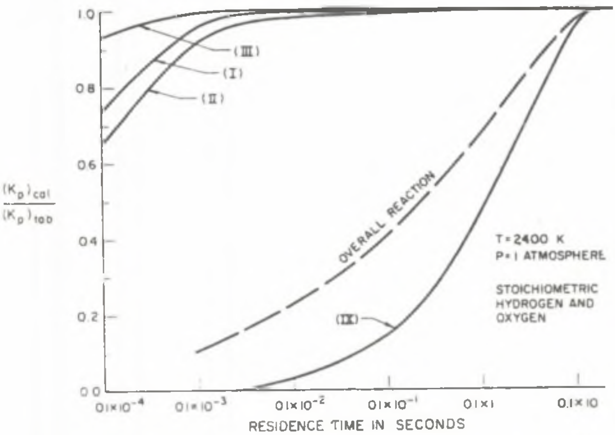

Fig. 4. Progress of four intermediate elementary reaction steps towards equilibrium in relation to the overall reaction of a stoichiometric mixture of hydrogen and oxygen at a typical temperature of 2400 K and 1 atmosphere

I. $(H_2 + O_2 = 2\ OH)$, II. $(H_2 + OH = H_2O + H)$
III. $(O_2 + H = O + OH)$, IV. $(H + OH + M = = H_2O + M)$

An overall reaction will appear to come to equilibrium only when all the intermediate single step reactions involved have approached a similar state themselves. It is evident from the typical case of Figure 4 for example that the intermediate reaction III is some four orders of magnitude faster than the overall combustion reaction of hydrogen. Moreover, the reaction IX appears to be one of the controlling steps. Thus it is possible to demonstrate the basis of the relative success of overall kinetics of combustion reactions and provide pointers as to whether simplifications can be made to complex reaction schemes describing these reactions (5).

Analytical considerations of the formation of oxides of nitrogen in combustion processes

When examining the problem of air pollution from combustion processes, mainly two oxides of nitrogen, NO and NO_2, are considered to be important. Furthermore, experimental evidence indicates that engines normally produce oxides of nitrogen almost entirely in the form of nitric oxide, NO. In the presence of oxygen and at relatively low temperature, the nitric oxide is converted to nitrogen dioxide (NO_2), the essential ingredient in the formation of atmospheric smog. Usually, the conversion is relatively slow and takes place in the atmosphere, though it can commence within the exhaust system. Customarily, the oxides of nitrogen produced from combustion processes are referred to as NO_x.

The concentration of NO_x in the exhaust gas of various combustion devices, are usually present at levels that are much greater than those established by chemical equilibrium considerations relating to exhaust temperature conditions. The quantities measured normally indicate that the oxides of nitrogen may be considered frozen at some relatively high temperature within the combustion zone. The mode and extent of oxides of nitrogen formation has therefore been an area of active interest and research both analytically and experimentally [6]. Accordingly detailed chemical kinetics can be employed to consider the formation of oxides of nitrogen and their rate of survival in the exhaust products. It can then be shown how most operating and design variables influence the concentration of NO_x in the exhaust and means for its reduction may be pointed out.

A survey of the literature indicates that the reactions appearing in Table 2 are of importance when considering the production of NO_x. Suggestions, however, have been made that for fuel rich mixture yet further additional reactions may become necessary [7]. Moreover, it has been widely suggested that the simplified mechanism proposed by Zeldovitch involving only the reactions:

$$N_2 + O \rightleftarrows NO + N$$

$$N + O_2 \rightleftarrows NO + O$$

is adequate for predicting NO formation. In this simplified mechanism, it is assumed that the chain reactions are initiated by the atomic oxygen which is formed from the dissociation of oxygen molecules at high temperature. Thereby the formation of NO is closely related to the local oxygen atom concentration and temperature values. Furthermore, it has been suggested that the concentrations of the species N, at the typical temperature encountered in combustion phenomena, are normally much smaller than those of atomic oxygen and the N concentrations can be approximated by the corresponding values. Clearly, this approach though tends to simplify the calculations appreciably, can yield significant deviation from experimental observations.

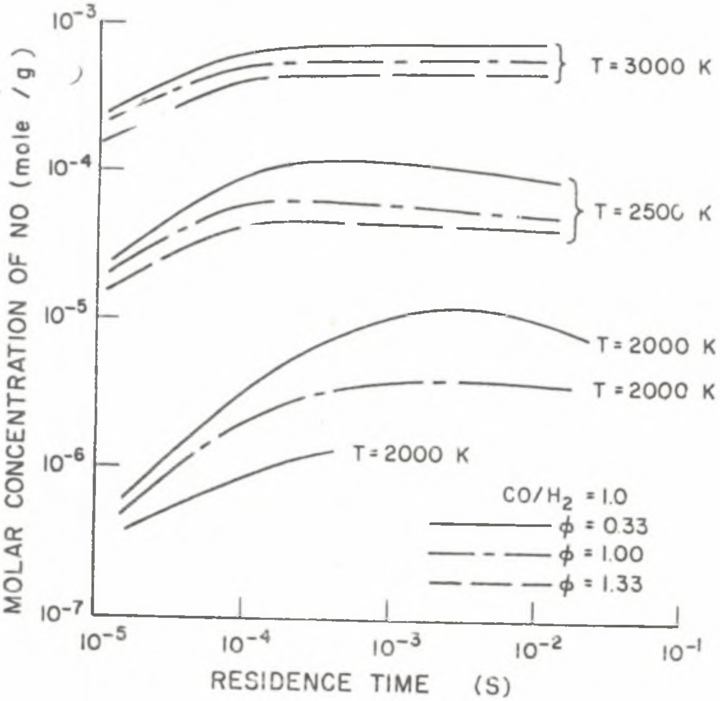

Fig. 5. Predicted molar concentration of NO as a function residence time for three temperatures and three equivalence ratios when a homogeneous mixture of CO and H_2 is burnt at atmospheric pressure in air

A similar analytical approach can be applied to consider the formation of oxides of nitrogen when these constraints are not present and the entire set of reaction steps of Table 2 are considered. This can be made an integral part of any kinetic scheme describing a reacting system. Figure 5 shows typical calculated molar concentrations of NO as a function of residence time [8] for a range of temperature and initial concentrations when assuming the reactions to be deliberately maintained at constant temperature. Moreover, the results indicate that the concentrations of NO are almost exponentially dependent on temperature and as the temperature is increased the shorter will be the time required to achieve the corresponding equilibrium values. Moreover, as shown in Figure 6, the comprehensive kinetic scheme when incorporated in the modelling of a compression ignition engine fuelled with hydrogen indicates clearl that the

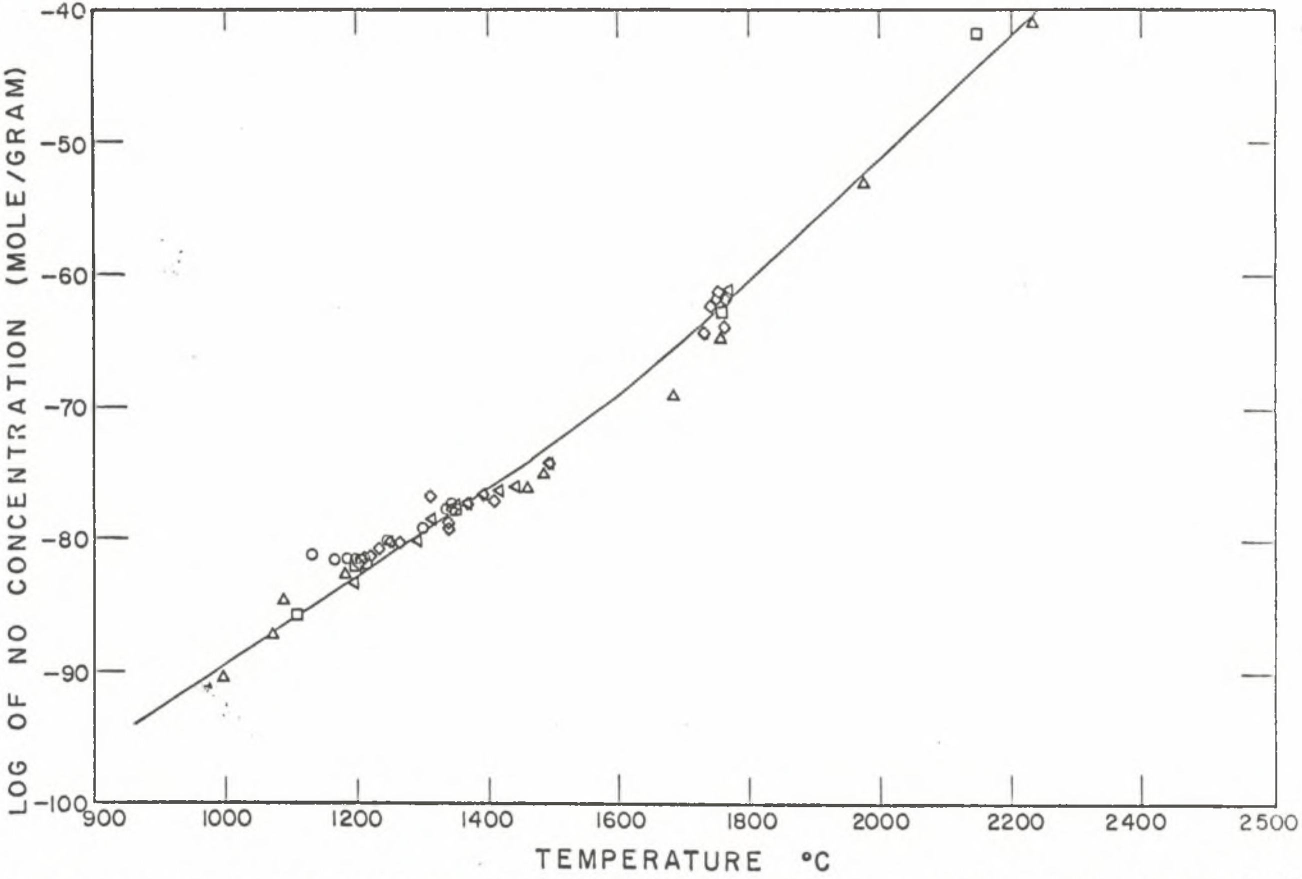

Fig. 6. Calculated exhaust concentration of the oxides of nitrogen in a compression ignition engine fuelled with hydrogen as a function of peak cycle temperature

concentration of NO_x surviving to the exhaust stage can be calculated reliably and that it is almost logarithmically dependent on the peak temperature achieved during the combustion process irrespective of the wide range of operating conditions [9]. Moreover, it can be shown that NO is the main oxide of nitrogen that is normally produced. Recent literature is abundant in numerous similar examples where the productions of oxides of nitrogen has been predicted analytically.

Figure 7 shows a typical comparison between the calculated concentrations of NO when based on the limited Zeldovitch mechanism and the corresponding concentrations when more complete and detailed kinetic scheme is employed.

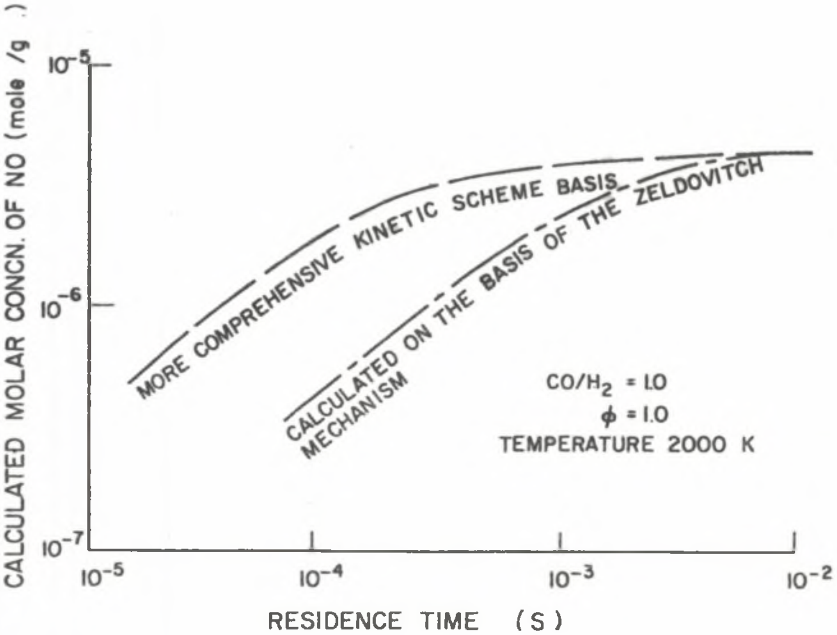

Fig. 7. Calculated concentrations of NO on the basis of the Zeldovitch mechanism and that on the basis of detailed chemical scheme of Table 2

Some further examples involving detailed chemical kinetics

Obviously, numerous examples can be cited to demonstrate some of the applications of detailed chemical kinetic schemes in the modelling of combustion phenomena and engineering devices. However, only a few examples will be mentioned briefly here merely as an illustration of the many applications posible. Of course, the preceding two sections discussed two such applications in relation to the time requirement to achieve near chemical equilibrium conditions in a reacting system and in terms of the prediction of the formation and survival to the exhaust stage of oxides of nitrogen in combustion processes.

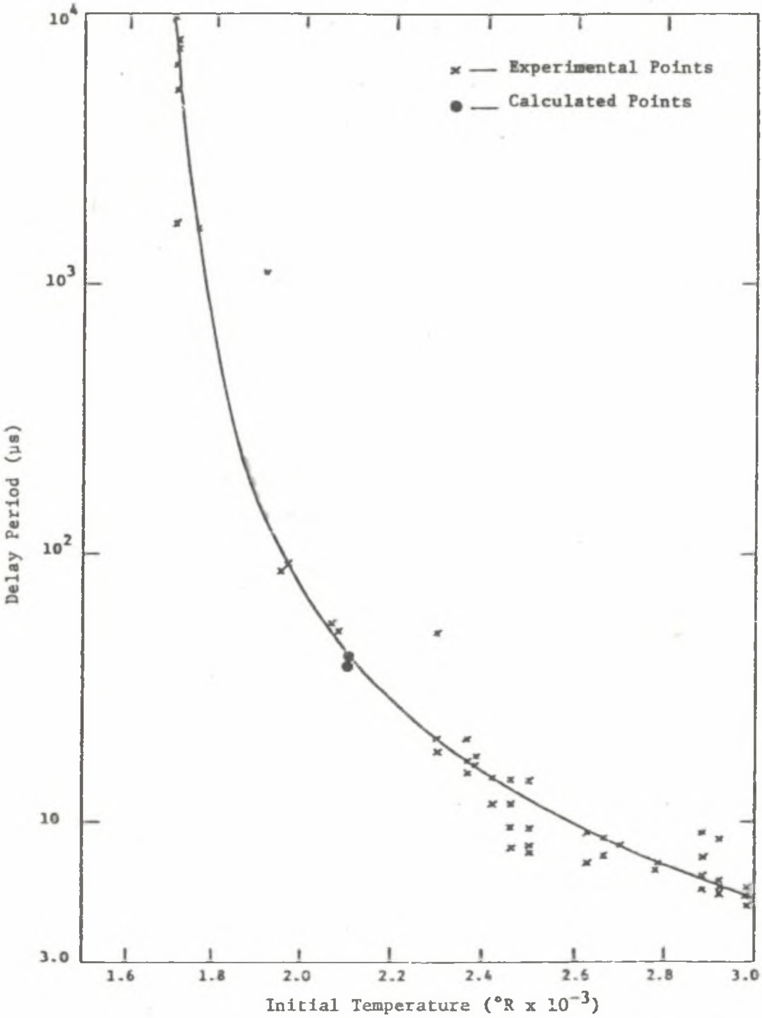

Fig. 8. Comparison of experimental ignition delay of hydrogen-oxygen homogeneous mixture as compiled by Momtchiloff et al [10] with a predicted result using detailed kinetics of Table 1

Figure 8 shows the ignition delay of homogenous stoichiometric and near stoichiometric mixtures of H_2-air at atmospheric pressure as a function of initial temperature. The experimental points shown have been gathered from several sources in the literature by Momtchiloff et al [10]

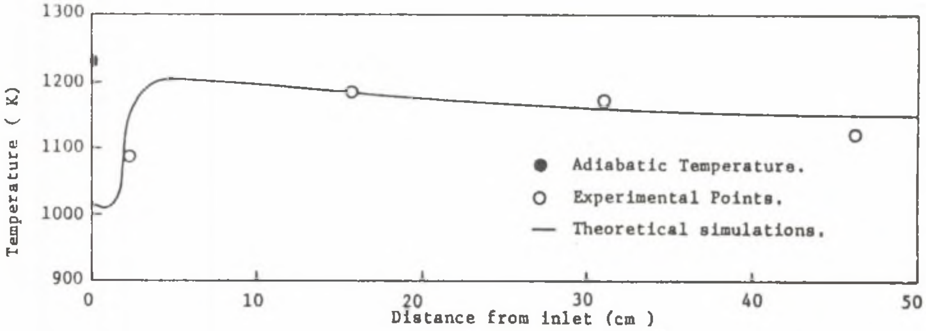

Fig. 9. Theoretical simulation of experimental results for H_2 - air oxidation in a non - adiabatic circular tubular reactor

in an investigation of supersonic combustion for ramjet applications. Also shown is our computed ignition delay based on the reaction scheme of Table 1. Such predicted values appear to agree remarkably well with experimental trends [11]. Similarly, figure 9 shows equally good agreement between measured temperature profiles within a non-adiabatic tubular reactor of our design when operating on hydrogen as a fuel at atmospheric pressure; the corresponding predicted temperature values are also shown. Moreover,we have demonstrated earlier [12] that chemical considerations can be employed to predict the course of reactions in a homogenous mixture of hydrogen and air in a motored piston engine and that good agreement can be obtained between the predicted pressure development record and experiment, as shown in figure 10.

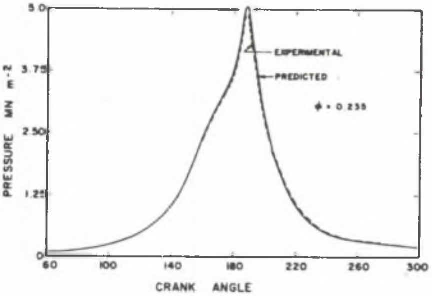

Fig. 10. Predicted and experimental pressure time diagram in a motored compression ignition piston engine fuelled with hydrogen and air at 0,235 of the stoichiometric ratio [12]

In an investigation of the yield of hydrogen from the uncatalyzed thermal reforming of natural gas by steam at high temperature,the reaction scheme of methane listed in Table 1 was used with appropriate corresponding chemical kinetic data [13]. Figure 11 shows typically how the relative yield of hydrogen will vary for a certain feed steam to methane ratio as a function of time and temperature. Throughout, such predictions were demonstrated to be in good agreement with experiment to an extent that may encourage the employment of such a scheme in the modelling of reforming and allied processes involving natural gas.

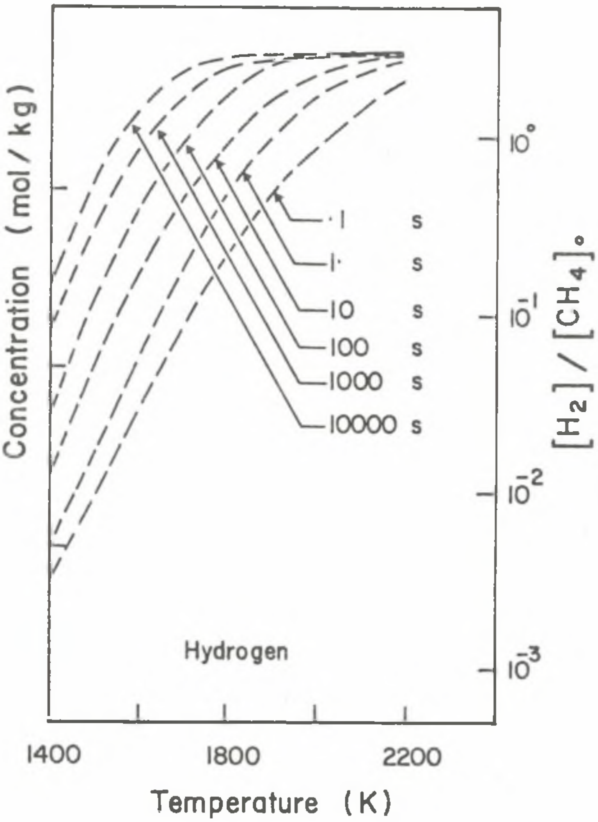

Fig. 11. Predicted variation of the concentration of hydrogen with temperature for the range of residence times shown when a stoichiometric feed of methane and steam are employed at atmospheric pressure

Recently, the chemical kinetic scheme of the combustion of methane was incorporated in a model describing the autoignition of natural gas-air mixtures in a piston engine over a number of consecutive cycles. Thus, perhaps for the first time it was possible to consider changes in all operating parameters including the determination of the instantaneous values of the concentrations of the species involved over a number of cycles even when underaccelerating or decelerating conditions. Moreover, this approach offered the unique opportunity of examining the role played by the residual gas trapped in the clearance volume of the cylinder on the events of the following cycle. It can be seen from the typical results of such calculations of figure 12, that these residuals have a strong kinetic contribution as well as the known thermal effect on the ignition phenomena of the following cycle and the associated rate of pressure rise[14].

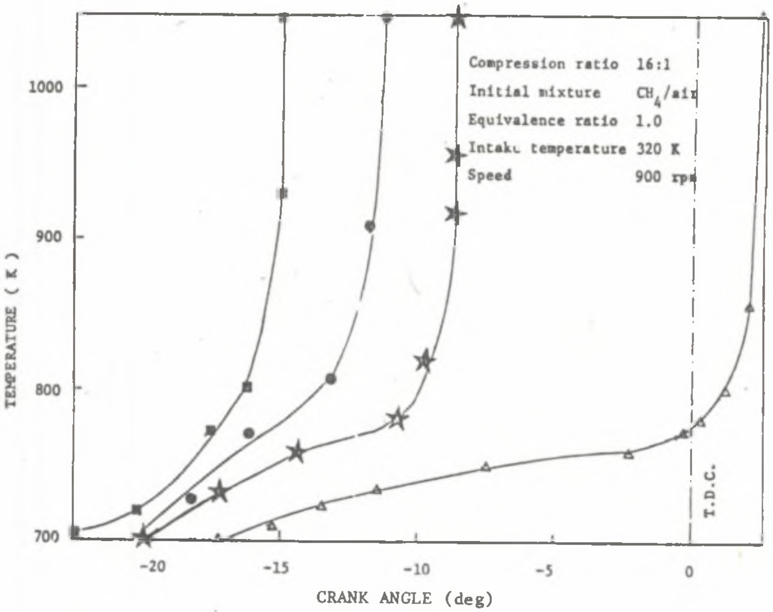

Fig. 12. The effect of residual gases on the combustion kinetics of a homogeneous mixture of methane in air in an autoignition engine. The clearance volume is occupied by: △ fresh charge at T_{intake}; ● residual gas at T_{intake}; ■ residual gas at residual gas temperature; ☆ the concentration of the radicals O , H and OH are reduced arbitrarily by a factor of 10^{-2} in the latter case

The above very few examples describing the results of analytical models incorporating detailed chemical kinetics were listed merely to show that much can be achieved by such considerations. Clearly, much further research is needed in this area, particularly in relation to other fuels.

Acknowledgement

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ZNACZENIE KINETYKI CHEMICZNEJ W OBLICZENIACH SPALANIA

Streszczenie

Podano krótki przegląd problematyki związanej z modelowaniem chemicznych aspektów procesu spalania oraz niektórych sposobów podejścia stąd wynikających, z włączeniem rozważań nad chemiczną kinetyką. Odwołano się do szeregu przykładów, w których te sposoby podejścia zastosowano dla rozpatrzenia niektórych potocznych zagadnień inżynierskich.

ЗНАЧЕНИЕ ХИМИЧЕСКОЙ КИНЕТИКИ В РАСЧЕТАХ ГОРЕНИЯ

Резюме

Дается осмотр проблемм связанных с математическим моделированием химических явлений в процессе горения и некоторых возможных путей подхода, с включением рассуждений связанных с химической кинетикой. Рассматриваются некоторые примеры применения рассмотренных методов к решению практических технических задач.