

CHEMICAL PROCESSES IN LOW-TEMPERATURE PLASMAS

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INTRODUCTION

Chemical processes in low-temperature plasmas ($T \sim 10^3\text{--}5 \times 10^4$ °K) and in plasma jets are attracting ever increasing attention. In this temperature range, deviations from the classical description of chemical processes due to the non-equilibrium and relaxation characteristics of systems, collective effects and specific features of elementary events are important.

On the other hand, one of the main trends in the development of present-day chemical processing is an ever growing use of more intense operating conditions: higher temperatures, velocities, reduced residence times of reagents in the reaction zone, etc. This trend finds its response in plasma chemical processing.

The thermodynamic aspects of plasma chemical processing, as well as that of the whole of high temperature chemistry, have been elaborated in considerable detail¹⁻⁴; a great number of constants have been determined and methods for calculating thermodynamic values and equilibrium constants have been developed.

It is well known in thermodynamics that:

$$\left. \begin{aligned} \Delta Q &= \Delta H - T \Delta S \\ \Delta Q &= -RT \ln K \end{aligned} \right\} \quad (1)$$

It can easily be seen that the role of the entropy factor increases with temperature. As changes in ΔH and ΔS with temperature are small for many gaseous reactions as compared with a change in T , $T\Delta S$ and ΔQ can be regarded roughly as linear functions of T and $\ln K$ as a linear function of $1/T$. Therefore, at high temperatures and constant pressures, the most important factor is the intensification of processes of dissociation, deaggregation and decomposition, which is associated with an increased role of the entropy factor.

However, the actual situation is more complicated⁵. Earlier notions of simplification of chemical relations at high temperatures proved to be one-sided. In addition to the dissociation of complex substances, and a sharp increase in reactivity and in reaction rates, compounds appear which do not exist at usual temperatures, as well as new kinds of particles (such as CaCl , SiO , Al_2O , SO , AlO or C_3 , C_9 , Na_2 , Ba_2O_3 , etc.).

Nevertheless, thermodynamic calculations provide exceedingly valuable

information on plasma chemical processes. The situation regarding the kinetic aspect of plasma chemical reactions and the determination of reaction rates at high temperatures is much less satisfactory.

Rate constants of high-temperature reactions at $T > 2000^\circ\text{K}$ are currently determined mainly in shock tubes or by an adiabatic compression method.

Attempts can be made to obtain these constants from the analysis of spectral data and by other methods of plasma diagnostics. However, rather a small number of rate constants of sufficient accuracy obtained for this temperature range indicate the difficulties encountered in this field.

It is no exaggeration to say that lack of information on rate constant values for high temperature chemical reactions, inhibits the development of plasma chemistry in both its theoretical and applied aspects. For these processes, reaction times lie in the range of 10^{-3} to 10^{-6} sec and this creates many difficulties in conducting experiments. In any case the main and primary task of plasma chemistry is to determine rate constants of chemical reactions.

It should be said that at present there are no well-founded mechanisms to explain most of the chemical reactions occurring in low-temperature plasma.

NON-EQUILIBRIUM STATE OF LOW-TEMPERATURE PLASMA REACTIONS

From the standpoint of the kinetics of high temperature chemical reactions, the first problem arising is that the equilibrium-activated complex method. The Arrhenius equation, and some other relationships based on the concepts (although also approximate) of equilibrium statistical mechanics and thermodynamics cannot be applied to plasma chemistry.

One of the main assumptions in the application of a classical statistical method is that there exists an equilibrium (Maxwell-Boltzmann) distribution of reacting particles (in particular, particles in the initial and activated states) and that the chemical reaction does not disturb this equilibrium. This is the "heel of Achilles" of the activated complex theory.

A chemical reaction is a non-equilibrium process. Therefore this assumption is not justified thermodynamically. However, disagreement between the calculations based on the activated complex theory and experimental data is not great for not very high temperatures.

The activated complex theory is known to lead to the Arrhenius equation. Therefore the application of the activated complex method is in the region of the applicability of the Arrhenius equation and of Dalton's law. The Arrhenius equation is not true for the area where deviations from a Maxwell-Boltzmann distribution exist. These deviations increase as kT tends to E_{act} and reaction rates increase. Therefore the (even approximate) applicability of the Arrhenius equation at high pressures has not only to be proved, but it appears to be inapplicable at $E_{\text{act}} \sim kT$ and the reaction rate can no longer be defined by this equation.

Disturbance of the initial equilibrium distribution due to a chemical reaction is apparently essential for the reactions in which $E_{\text{act}} \sim kT$, i.e.

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$E_{\text{act}}/kT \leq 5$. This fact which is not important at temperatures up to 1000°K, should not be neglected in high temperature processes.

In the fast reaction in a high temperature mixture, high energy molecules can be converted into final products too quickly to be replenished by means of inelastic collisions¹. What is the situation with theoretical investigations of the non-equilibrium in the system set up by fast chemical reactions? As there is no appropriate theory, several approximate models have been suggested for defining disturbances caused by a chemical reaction in the equilibrium system⁶⁻⁹.

Strictly speaking, all problems associated with the approach of a system to equilibrium are particular cases of a "many-bodies" problem. This type of problem deals with systems with a great number of degrees of freedom and the approach of systems to equilibrium is defined by relations which exist between these degrees of freedom. Analysis of these extremely difficult problems becomes more feasible in connection with the development of diagram techniques adopted from quantum field theory. One of such techniques for studying the evolution of n -body systems which are solved mainly by a perturbation theory method is described by Prigogine¹⁰ as an example of "a sui generis feedback between classical and quantum mechanics". It is worth noting the possible use of "a reaction function" and a T-matrix of statistical quantum mechanics¹¹ and the methods developed by N. N. Bogolyubov.

MAXWELLIZATION AND TEMPERATURES OF LOW-TEMPERATURE PLASMAS IN CHEMICAL REACTIONS

A non-equilibrium system cannot be described by means of temperature which is characteristic of equilibrium systems and which can be used for their definition. Each component of a plasma consisting of electrons, atoms of various fragments of molecules excited differently (electronically, vibrationally, or rotationally) can be characterized by its own "temperature".

For a non-equilibrium reactive system, one may speak of a "rotational temperature", a "vibrational temperature", etc., which are different and coincide only if the system is in the equilibrium state. Therefore, for systems in which chemical reactions are occurring, it is necessary to study separately energy distribution at rotational, vibrational and electronic energy states. As the energy supplied from outside is used mainly for the excitation to higher levels of molecules and radicals, the "temperature" of a non-equilibrium system will in general be higher than that of the initial equilibrium distribution. A Boltzmann (or pseudo-Boltzmann) distribution is set up most rapidly for translational and rotational degrees of freedom as the corresponding energy quanta are relatively small. The energy distribution by vibrational degrees of freedom will deviate most of all from the Boltzmann distribution, but as a matter of fact, one cannot speak of any "vibrational temperature".

The problem of setting up the equilibrium distribution or the Maxwellization of a system is of special importance if a chemical process is realized by means of turbulent mixing of a high temperature plasma jet with cold gas. In this case, of fundamental importance is the solution of the

problem whether or not chemical reactions proceed up to the complete Maxwellization of a system*.

It is probable that some progress in this direction can be made using a theory of stochastic processes, for example the theory of stochastic transitions over a barrier with chemical reactions¹².

As is generally known, investigation of the transition of the non-equilibrium system to equilibrium belongs to physical kinetics which deals with time and space evolution of non-equilibrium macroscopic systems. A non-equilibrium system not subjected to any effects relaxes into an equilibrium (most probable) state through a number of intermediate states, whose probabilities monotonically approach a maximum. Such a system may be described by a certain distribution function. For example, a mixture of two gases (one of which is partially ionized and dissociated) of different initial temperatures (a scheme which is typical of many plasma chemical processes) approaches the complete equilibrium through a few steps with different relaxation times†.

One of the methods of calculating the Maxwellization of a system consisting of mixed gases with different temperatures (both in the absence and in the presence of chemical reactions) is a method of statistical tests or Monte Carlo calculation. Application of this method by Polak and co-workers¹³ allowed an estimation of the Maxwellization time for a mixture of argon ($T \cong 10^4$ °K) and methane ($T \cong 3 \times 10^2$ °K). *Figure 1* shows

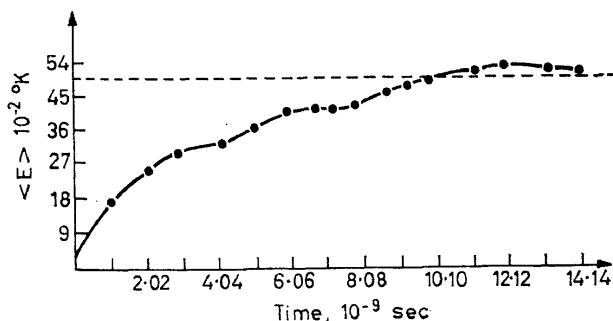


Figure 1. Time dependence of an average energy of methane molecules (Dotted line is the value of the equilibrium energy).

time dependence of an average energy of methane molecules and *Figure 2* represents time dependence of the ratios of average velocities of methane and argon molecules to average Maxwell velocities. The Maxwellization time as calculated using the Monte Carlo method is $\sim 10^{-8}$ sec.

* In the case of partial ionization of plasma and sufficiently high pressures there is usually a Maxwellization of its separate components observed (therefore use of spectral methods is justified in this case). A plasma in which a distribution is Maxwellian either only for particles of a given type or for velocities in a given direction is called a thermal plasma. In other words, the thermal plasma is a plasma which may be described to a certain extent in terms of temperature.

† If the evolution of such a system is a Markov process, i.e. a process "without memory", it is described by the Fokker-Planck equation. Another microscopic method of describing the behaviour of such a system is equivalent to the use of the Boltzmann non-linear integral differential kinetic equation.

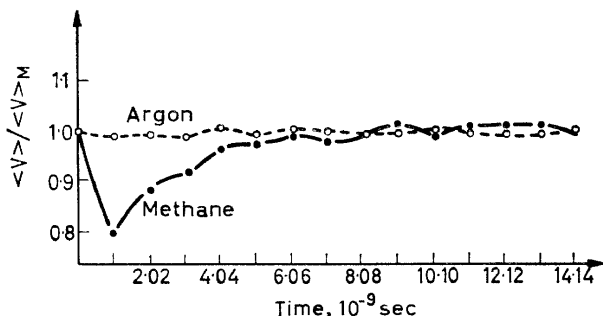


Figure 2. Time dependence of the ratios of average velocities to average Maxwell velocities in the case of methane and argon.

COLLISIONS, IONIZATION, PARTICLE EXCITATION IN LOW-TEMPERATURE PLASMAS

In order to give an accurate description of phenomena in a plasma it is necessary to make an exhaustive study of collisions. The kinetic theory of the plasma is different from the kinetic theory of gases in that in the former one cannot neglect the interaction between plasma particles while in the latter it is assumed that particles move freely interacting only in collisions (binary collisions only being considered). As there is no satisfactory description of the interaction between plasma particles, single-particle distribution functions are used to describe phenomena in a plasma and the terms derived by Fokker and Planck are added to the terms of the Boltzmann equation for binary collisions to yield a Boltzmann non-linear integro-differential equation. In practice one cannot solve the Boltzmann non-linear equation with binary collisions or with additional terms for small-angle scattering which are determined by a statistical method. It gives, however, useful information on transfer coefficients, which is now its main value*.

In a plasma consisting of neutral and charged particles, in addition to separate gas-kinetic collisions at small distances there are distant collisions due to electromagnetic interaction (associated, first of all, with Coulomb potentials) the determination of which creates additional difficulties.

PRESENT STATUS OF PLASMA CHEMISTRY AND ITS PRACTICAL APPLICATIONS

Investigations into theoretical and applied problems of plasma chemistry have been reviewed by the author¹³ in detail. Further research is aimed, first of all, at developing separate processes such as nitrogen fixation, production of acetylene from methane and of mixtures of unsaturated hydrocarbons (ethylene, propylene, acetylene) from gaseous and liquid hydrocarbons, oxidation of methane to formaldehyde, production of

* Thermodynamics of irreversible processes does not allow absolute values of transfer coefficients to be obtained, but it gives a sufficiently complete idea of the phenomena in a system to be studied. Transfer coefficients have to be calculated independently of the kinetic theory of gases.

dicyanogen, hydrazine, hydroxylamine, finely dispersed powders of vanadium, nickel, iron, molybdenum, etc., reduction of metal and non-metal oxides, production of chlorosilanes from SiCl_4 , production of hydrogen peroxide, oxidation of propylene and ammonia to acrylonitrile, direct oxidation of benzene to phenol, spraying of metals, mono- and polycrystal growing, etc.

Production of acetylene from natural gas (by Hüls in the Federal Republic of Germany and by Du Pont in the U.S.A.), processes of metal reduction and crystal growing, etc. have been carried out on a commercial scale. A number of pilot plants have been built.

A possible combination of plasma chemical processes with magneto-hydrodynamic generation of electrical energy is being discussed in detail.

DISTINGUISHING FEATURES OF PLASMA CHEMICAL PROCESSES

The present-day development of plasma chemistry is based on the great improvements in methods for investigation of high temperatures, on the development of the hydrodynamics of heat and mass transfer with chemical reactions proceeding in a plasma, on investigations of parameters and properties of electric arcs and a gas-discharge plasma, on the use of statistical mechanics and thermodynamics, on the development of spectral methods (giving general information on processes in a plasma) and some other methods of plasma diagnostics, etc.

Use of plasma jet chemical reactions offers new possibilities for an approach to the optimum control of chemical reactions, as well as for the production of super-equilibrium concentrations of some reaction products and fixing of the equilibrium concentrations of reaction products by means of their "quenching" by some method of plasma jet cooling (quenching velocities being $dT/dt \sim 10^4\text{--}10^8$ degree/sec). For the correct choice of the way to exercise optimum control of chemical reactions and for the selection of the most reasonable space-time scales of quenching, it is necessary to have sufficient information on the dependence of the kinetics of chemical reactions proceeding in a plasma jet, on its characteristics (temperature, composition, velocity, etc.), as well as information on the space-time distribution of some substances which participate in the reaction, on the effect of hydrodynamic conditions, on the kinetics of chemical reactions, and on the effect of chemical reactions in jet dynamics, etc.

Use of low-temperature plasmas and plasma jets (of direct current, low-frequency alternating current, B 4 and CB 4) at Mach numbers of 0.2 to 0.8, at input power of 10–5000 kW and with various gas carriers (Ar , H_2 , N_2 , $\text{N}_2 + \text{O}_2$, CH_4 , etc.) permits the realization of a number of chemical and physico-chemical processes which are highly effective as to their technical and economic parameters¹³.

The advantages of plasma chemical processes are as follows:

1. High temperatures and enthalpies obtained and high velocities of the processes (short contact times, $\sim 10^{-3}\text{--}10^{-5}$ sec).
2. Possibility of controlling and optimizing processes in very simple feedback flowsheets.

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3. Possibility of calculating processes as hydrodynamic problems of a jet movement with ionization and chemical reactions.

4. An extremely simple flowsheet, high reliability, interchangeability and safety.

5. Possibility of obtaining the yields (impossible at lower temperatures) of desirable reaction products, pure and ultrapure substances, films, single crystals, etc.

6. Economic efficiency associated with high yields, low losses, processing simplicity.

7. Possibility of using feedstocks which are difficult to process (natural gas, air, water, infusible metal-containing minerals).

A low-temperature plasma may be used not only as a powerful enthalpy source, but also as an electron and ion source and as a very intensive ultra-violet source.

In effect, plasma jets from arc plasmatrons are streams of gases with a temperature of about $10\text{--}20 \times 10^3$ °K along the jet axis, and gradients of about 400 degree/mm along the jet axis and about 3000 degree/mm in the external parts of the jet.

Plasma chemical processes are characterized by the possibility of the optimum turbulent mixing of a plasma jet with other gases which are reagents. This process may be realized in various space-time intervals of the jet depending on the aim and conditions of chemical processing. It should also be noted that in plasma processes a chemical reactor is separated from the gas discharge gap of a plasmatron, which provides a stable performance of the plasmatron and a possibility of separate chemical reactor design.

QUENCHING IN PLASMA CHEMICAL REACTIONS

There are two types of reactions in a plasma jet for which the product distribution is dependent on quenching conditions. Reactions of the first type involve the formation of a number of intermediate products some of which are to be fixed. An example of these reactions is the conversion of methane into acetylene. It is natural that these reactions should be affected by initial points of a temperature decrease, as well as by quenching velocities. It is important not to be late with quenching. Reactions of the second type are characterized by the fact that the substance obtained is a final product of the reaction which proceeds only at high temperatures, and is sufficiently stable at room temperature. In this case the purpose of quenching is to cool the reaction product so fast that it cannot decompose in the intermediate temperature range. Thermal formation of nitrogen oxides in the air is a typical reaction of this type. In this case it is important to provide a desired quenching velocity and not to start it too early before equilibrium is set up.

Quenching conditions greatly affect the product yield in plasma chemical reactions. For example, in the conversion of methane to acetylene the 2×10^{-3} sec retardation in quenching results in a decrease in the acetylene yield from 15.5 to 10 per cent. A decrease in the velocity of the nitrons gas quenching in the synthesis of nitrogen oxides from 10^8 to 10^7 degree/sec leads to a decrease in the nitrogen oxide concentration from 9.6 to 6.4 per cent. Moreover, it is necessary not only just to provide an average quenching

velocity in a certain temperature range but to observe a definite law $dT/dt = f(T)$. Figure 3 illustrates the limiting law $dT/dt = f(T)$ for the quenching of nitrogen oxides. The violation of this law in any temperature range cannot be offset by an increase in the quenching velocity in another range.

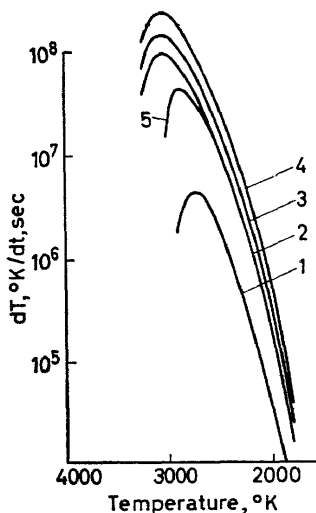


Figure 3. Limiting dependences (dT/dt) for different conditions

- curve 1: $T_i = 3000^\circ\text{K}$; $T_f = 1800^\circ\text{K}$; $p = 1$ atm
- curve 2: $T_i = 3300^\circ\text{K}$; $T_f = 1800^\circ\text{K}$; $p = 10$ atm
- curve 3: $T_i = 3300^\circ\text{K}$; $T_f = 1800^\circ\text{K}$; $p = 20$ atm
- curve 4: $T_i = 3300^\circ\text{K}$; $T_f = 1800^\circ\text{K}$; $p = 50$ atm
- curve 5: $T_i = 3100^\circ\text{K}$; $T_f = 1800^\circ\text{K}$; $p = 20$ atm

It is often, however, insufficient to provide a necessary quenching velocity and a high yield of the product. In some cases it is important not only to remove heat rapidly from a system but also to utilize as much of it as possible.

Let us now consider the known methods of quenching:

1. *Quenching in a heat exchanger.* The method is well studied and can be easily commercialized. It provides a quenching velocity of up to 10^6 degree/sec at a gas temperature of 3500°K . Heat withdrawn from a system is not practically utilized.

2. *Quenching in recuperators.* Recuperators are being designed for a gas temperature of up to 2000°K . The quenching velocity will be 10^5 degree/sec. It is possible to utilize the heat for preheating reagents.

3. *Quenching in Laval nozzle.* This may be used for a sharp decrease in the temperature of a gas stream at a certain process step. It should be remembered that when passing from the supersonic stream velocities in the nozzle to the subsonic velocities the temperature of the stream increases again up to the initial value. The quenching velocity in the Laval small-sized nozzle amounts to 10^8 degree/sec, but the character of the dependence $dT/dt = f(T)$ is very unfavourable; the quenching velocity increases with decreasing

temperature while the inverse dependence is necessary for most of the processes.

4. *Quenching by mixing hot and cold gases.* A very effective quenching can be achieved when a hot stream is mixed with jets of cold liquid or cold gas. This method provides quenching velocities up to 10^8 degree/sec provided proper mixing of hot and cold gases is attained, but the coolant dilutes the product and introduces undesirable contaminants. This may be avoided using the cooled product itself for quenching. In some cases the quenching by mixing permits sufficiently full utilization of heat as, for instance, in the nitrogen fixation process.

A specific type of such quenching is feasible in a plasma jet. The reaction and the quenching occur simultaneously if reagents are mixed at essentially different temperatures. For example, considerable amounts of nitrogen oxides have been found to form when a nitrogen plasma jet is mixed with water.

High velocities of quenching (up to 10^8 degree/sec) can be achieved in a fluidized bed reactor.

AN EXAMPLE OF PLASMA CHEMICAL PROCESSES: PRODUCTION OF ACETYLENE FROM METHANE

Let us consider, in brief, an example of plasma chemical processes involving some of the results of theoretical and experimental investigations of the most fully studied reaction; the production of acetylene from methane.

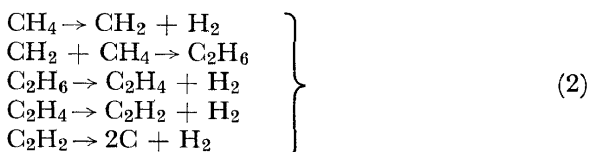
General Characteristics

The conversion of methane injected into hydrogen plasma jet to acetylene is an example of a process in which the practical aim is to obtain and fix an intermediate product (acetylene) formed and decomposed in successive chemical reactions. Hydrogen plasma jet is injected into a reactor from the arc chamber of a plasmatron through a nozzle in its anode; the jet has an average temperature of about 4500°K . Hydrogen dissociated by 70 to 80 per cent has a very large energy content at this temperature, which provides a sufficient degree of methane conversion at a slight additional dilution by a plasma-forming hydrogen.

The yields of acetylene obtained in practice are not different from the theoretical ones according to thermodynamic calculations. The yield of acetylene homologues is also very close to the thermodynamic yield.

The production of acetylene from methane in hydrogen plasma jet is also characterized by a sound energy balance in which about 45 per cent of the total energy is consumed for a direct reaction, which exceeds the parameters of the other processes¹⁴.

Investigations of the kinetics of this process in time, the distribution of concentrations of separate reaction components, jet temperature and velocities inside the reactor have been made using a simplified scheme of the reactions suggested by Kassel¹⁶:



This scheme is a rough representation of the reaction sequence and cannot be considered as an elucidation of the actual mechanism of the process under consideration, but it is sufficient for calculations and the macrosequence of reactions is confirmed by the experimental data of Guliaev and Polak¹³.

Rate Constants

The conversion of methane to acetylene is a good illustration of the above comments concerning difficulties in obtaining substantiated and sufficiently accurate values for rate constants of high temperature reactions although this process is probably one of the most fully studied of all chemical reactions.

For a simultaneous solution of hydrodynamic and chemical kinetic equations, which permits, in principle, a full description of a plasma jet with chemical reactions we have used rate constants for the thermal decomposition of methane, ethane, ethylene and acetylene obtained experimentally in shock tubes. These data are in good agreement with the data of other authors¹⁸⁻²³ (Figure 4), but unlike the latter data, they were obtained in the higher temperature range.

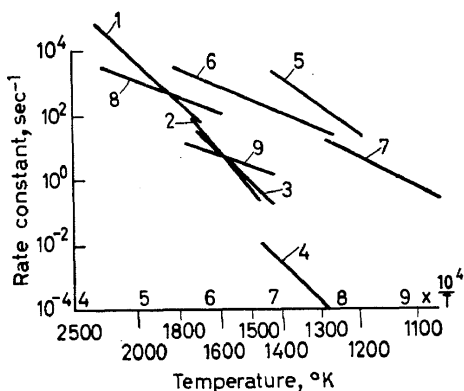


Figure 4. Temperature dependence of rate constants
 curves 1, 2, 3, 4 for methane decomposition
 curve 5 for ethane decomposition
 curves 6, 7 for ethylene decomposition
 curves 8, 9 for acetylene decomposition

It should be noted that the curves in Figure 5 are based on a great number of experimental points reported by various authors. More than 60 experimental points from six literature sources^{15, 18, 22}, as well as their own experimental data, were used by the authors¹⁷. The average experimental point scatter is ± 17 per cent. These data are in agreement within the same accuracy range with our results obtained with an adiabatic compression device in a temperature range of 1900 to 2600°K (see also references 24-29).

Curves 5, 6 and 8 in Figure 3 are plotted on the basis of rate constants for the decomposition of ethane, ethylene and acetylene obtained by comparing experimental data from other authors' results¹⁷.

In calculations we have used the following values¹⁷ for the rate constants:

$$\left. \begin{aligned}
 k_1 &= -\frac{d(\text{CH}_4)}{(\text{CH}_4) dt} = 4.5 \times 10^{13} \exp(-91,000/RT), \text{ sec}^{-1} \\
 k_2 &= -\frac{d(\text{C}_2\text{H}_6)}{(\text{C}_2\text{H}_6) dt} = 9 \times 10^{13} \exp(-69,000/RT), \text{ sec}^{-1} \\
 k_3 &= -\frac{d(\text{C}_2\text{H}_4)}{(\text{C}_2\text{H}_4) dt} = 2.57 \times 10^8 \exp(-40,000/RT), \text{ sec}^{-1} \\
 k_4 &= -\frac{d(\text{C}_2\text{H}_2)}{(\text{C}_2\text{H}_2) dt} = 1.7 \times 10^6 \exp(-30,000/RT), \text{ sec}^{-1}
 \end{aligned} \right\} (3)$$

APPROXIMATE EQUATIONS AND THEIR NUMERICAL SOLUTION

The flow of a high temperature plasma jet is considered to be stationary, unidimensional along the semiconfined straight line ($0 \leq Z \leq \infty$). In this case one can write down the equations known from reference 30 which are reported in reference 31 for the process under consideration and which, after eliminating the dissipative terms on the basis of special estimates of their values^{32, 33}, assume a simple form:

$$\left. \begin{aligned}
 \frac{d}{dz} (\rho v) &= 0 \\
 \frac{d}{dz} (n_i V) &= W_i \\
 \rho v \frac{dv}{dz} + \frac{dp}{dz} &= 0 \\
 \rho v \frac{dU}{dz} + \frac{d(Pv)}{dz} + \rho v^2 \frac{dv}{dz} &= 0 \\
 P &= nkT
 \end{aligned} \right\} (4)$$

where N_i is the number of i -kind molecules ($\text{CH}_4, \text{C}_2\text{H}_4, \text{C}_2\text{H}_2, \text{C}_2, \text{H}_2$); ρ is the gas density in g/m^3 ; U is the intrinsic energy in ergs/g ; v is the velocity of a gas stream in cm/sec ; and W_i is the velocity of chemical reactions determined by the generation and destruction of every kind of molecule.

The resulting set of non-linear first order equations may be solved with a proper choice of initial conditions as the Cauchy problem using an electronic digital computer. The solution is presented in *Figure 6* on a semi-logarithmic scale. The experimental points given in *Figure 6* and obtained in the time area where sampling is feasible are in good agreement with theoretical curves.

As can be seen from the plot in *Figure 5*, the plasma jet temperature $T(z)$ varies in rather a complicated way. First, within the time range of the order of 10^{-3} sec, the temperature decreases. Then, on passing through a minimum it begins to increase rapidly. The temperature in the first stages of the reaction under consideration decreases rapidly (*ca.* at the rate of

10^9 to 10^{10} degree/sec), then the velocity of the plasma jet decreases by several orders amounting to 10^6 degree/sec or below and finally the cooling of the plasma jet ceases and then changes into heating which occurs at rates somewhat lower than those of the cooling, but also very fast owing to the exothermic decomposition of acetylene.

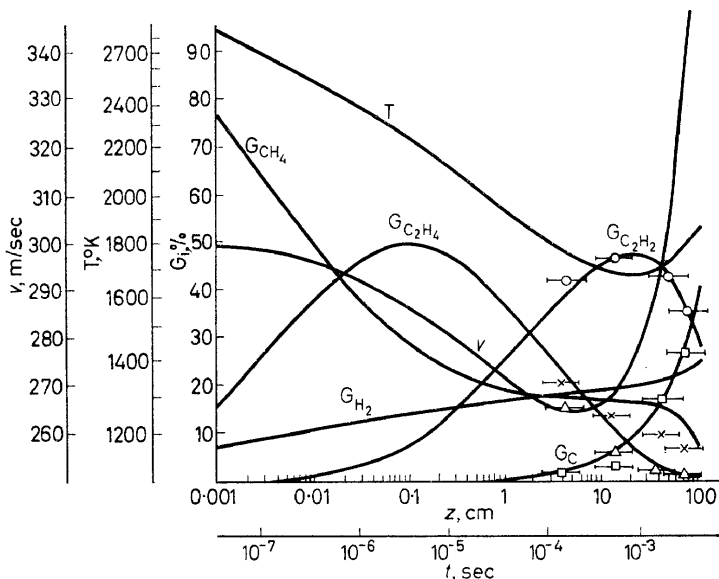


Figure 5. Kinetics of methane decomposition in a plasma jet (theoretical curves and experimental points)

In the initial stages of the reaction where the plasma jet temperature is still rather high (close to 3×10^3 °K) the velocity of methane decomposition is high and therefore the absorption of heat required for this reaction to proceed occurs very quickly. However, the rate of methane decomposition decreases as the plasma jet is cooled, which results in decreasing velocity of the jet cooling. As the decomposition of methane and ethylene formed continues the heat absorption continues, the temperature decreases but already at a lower rate, for reaction velocities decrease with decreasing temperature.

Thus, the first part of the process is characterized by a rapid cooling of a plasma jet in the course of the reaction, which leads to a quenching (or at any rate to a partial quenching) of the reaction products. Such a quenching occurring in the course of the reaction may be called an autoquenching in contrast to a forced quenching due to special external effects.

The plot shows that the maxima of ethylene and acetylene concentrations are spatially separated: the acetylene maximum is much further from the origin of the coordinates than the ethylene maximum. Thus, if the gas stream is stationary, one can distinguish, in the laboratory coordinate system for this stream, spatially separated zones some of which are enriched by ethylene and others by acetylene.

FORCED QUENCHING

The space separation mentioned above creates the problem of quenching of one or other product easier, for it permits one to interrupt in the reaction at one of its stages¹³.

When choosing the point and the velocity of the forced quenching one should take into account both the distribution of concentration and that of the velocities of formation and decomposition of reagents (as formation and decomposition velocities are different functions of temperature and concentration).

The intensity (the heat absorbed per unit time from a unit volume) of negative heat sources should be so chosen that they provide an additional constant negative heat gradient A . Based on general considerations, it may be concluded that negative heat sources should be introduced and forced quenching should be started at a certain point $Z = Z_0$ which is somewhat to the left of the point Z_m .

This assumption has been confirmed by calculations.

Figure 6 shows the curves obtained by solving with an electronic digital computer a modified set of equations (4) involving the constant temperature gradient A resulting from negative heat sources $Q(Z)$.

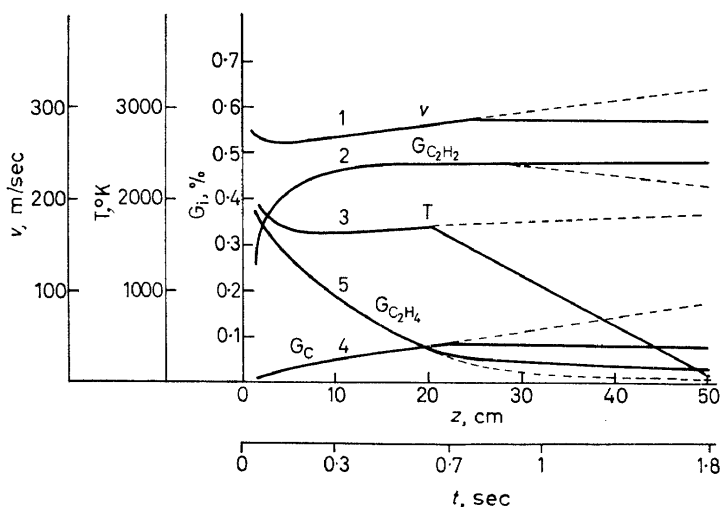


Figure 6. Curves for various concentrations (G), temperature and velocity of the mixture flow (v) with a forced quenching
 curve 1: velocity of the mixture flow, m/sec
 curve 2: acetylene concentration, % by weight
 curve 3: temperature of the mixture, °K
 curve 4: concentration, % by weight
 curve 5: ethylene concentration, % by weight

As can be seen from Figure 6, the forced quenching leads to decreased temperature according to a nearly linear relationship with a slope somewhat greater than A . As a result, the reaction is "frozen", acetylene decomposition is retarded sharply and the measurable yield of acetylene is increased.

As can be seen from *Figure 6* ($T_{in} = 3 \times 10^3$ °K) when introducing a negative heat source corresponding to a value A of 50 degree/m² at the point $Z_0 = 19.89$ m² (which corresponds to the moment $t_0 = 0.74 \times 10^{-3}$ sec), the high concentration of acetylene is not decreased up to the value $Z_t \geq 25$ m² ($t_f = 0.92 \times 10^{-3}$ sec) where the temperature of a plasma jet decreases to such a low level ($T < 1400$ °K) that the danger of acetylene decomposition practically vanishes. (*Figure 6* represents the results of integration in the range $2 < Z < 49$ m².) The maximum concentration of acetylene remains at about 100 per cent.

PROCESS CONTROL BY VARYING TEMPERATURE CONDITIONS

The process of the production of acetylene from methane in a plasma jet can be controlled by varying the initial temperature of the process (as well as the other initial conditions). It is natural that the kinetics of plasma chemical processes under consideration may be more effectively controlled by a forced change of temperature conditions not at one point $Z = 0$, but in different zones of the plasma jet¹³. In this case the temperature gradient and the corresponding heat sources may be positive (for the simplest case $A = \text{constant}$). *Figure 7* shows the results of the electronic

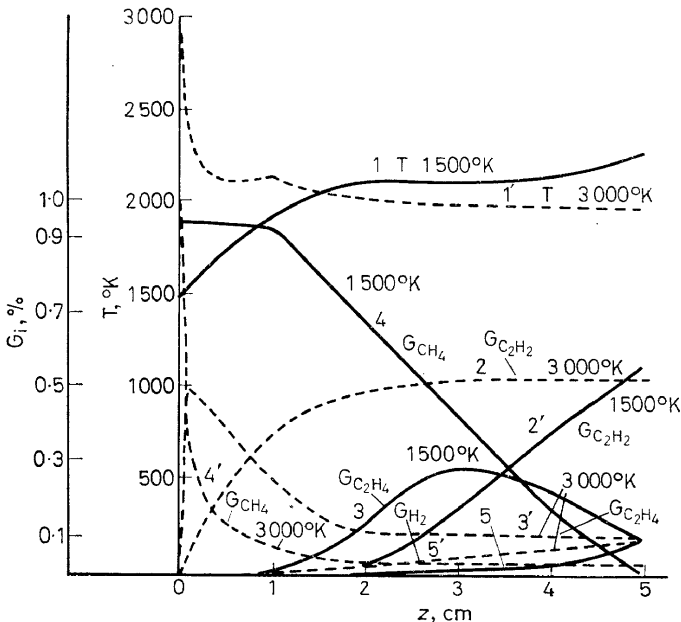


Figure 7. Changes in concentrations and temperatures at additional heat supply
 curve 1: $T(z)$, for temperature changes
 curve 2: $G_{C_2H_2}(z)$, for acetylene concentration
 curve 3: $G_{C_2H_4}(z)$, for ethylene concentration
 curve 4: $G_{CH_4}(z)$, for methane concentration
 curve 5: $G_{H_2}(z)$, for hydrogen concentration
 - - - - $T_0 = 3000$ °K; $A = 500$ degree/m² at $Z < 1$
 ——— $T_0 = 1500$ °K; $A = 500$ degree/m² at $Z > 0$

digital computer integration of the modified set of equations (4) taking such control into account.

Equations (4) were integrated at $T_{(0)} = 3000 \text{ }^\circ\text{K}$

$$A = \begin{cases} 500 \text{ degree/m}^2 & \text{at } 0 \leq Z \leq 1 \\ 0 \text{ degree/m}^2 & \text{at } Z > 1 \end{cases}$$

as well as at $T_{(0)} = 1500 \text{ }^\circ\text{K}$, $A = 500 \text{ degree/m}^2$ at all $Z > 0$. It appears from *Figure 7* that the preheating at a high initial temperature in a short initial zone (as compared with the analogous case without control) results in increasing decomposition of methane (up to 3 per cent), an increase in the maximum concentration of acetylene (up to 58 per cent), and a marked shift of the point Z_m to the left. As a whole, this case is similar, as regards the curves obtained, to the case with a high initial temperature $T_{(0)} = 350 \text{ }^\circ\text{K}$, $A = 0$, but it seems to be more advantageous from an energetic point of view due to a substantial difference in plasma jet heat capacities at $T > 3 \times 10^3 \text{ }^\circ\text{K}$ and $T < 3 \times 10^3 \text{ }^\circ\text{K}$. In the case where $T_{(0)} = 1500 \text{ }^\circ\text{K}$, $A = 500 \text{ degree/m}^2$ the reaction does not proceed at low time values. The process is strongly prolonged. The ethylene concentration maximum becomes broad and is markedly shifted to the right, which results in somewhat deteriorating conditions for the spatial separation of ethylene and acetylene. Methane decomposes completely followed by a sharp increase in the plasma jet temperature.

The investigation under consideration permits the judgment of the effects of controlling factors introduced into various parts of the reactor on the kinetics of a plasma jet chemical process.

The information obtained may be used for the development of a theory for the optimum control of plasma jet chemical reactions on the basis of the present-day mathematical control theory.

It should be noted that by a proper choice of a sign for the A value, its numerical value and the coordinates of introducing and varying the corresponding controlling factors one can approximate, with a certain degree of accuracy, different functions $T(z)$ obtained in the development of the optimum control of plasma chemical processes.

Plasma chemical processes may, however, be optimized by a number of parameters by choosing the proper initial conditions, values and signs of controlling factors even before a strict consistent theory is worked out for controlling plasma chemical processes.

CONCLUSION

Investigations (both theoretical and experimental) of plasma physical and chemical problems are only in the initial stages. It is hoped that this symposium which is more representative than the previous national conferences on a low-temperature plasma^{33, 34} will play an important role in the development of this new field of science and technology.

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