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NUMERICAL INTEGRATION OF SYSTEMS OF DIFFERENTIAL EQUATIONS OF CHEMICAL KINETICS

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NUMERICAL INTEGRATION OF SYSTEMS OF DIFFERENTIAL EQUATIONS OF CHEMICAL KINETICS.

I. Methods of integration of equations of chemical kinetics using a computer.

As is well known, the mathemematical description of chemical reactions uses the derivatives of concentration (the rate of the reaction) and their relationship to the numerical values for the concentrations themselves. The choice of differential and not integral equations for the description of chemical processes is based on the consideration that the quantities $\dot{c}_j(t)$ have a completely clear physical meaning, while the parameters of the integral equation establish only the fact that the concentrations themselves are some sort of functions of time: $c_j = c_j(t)$, where $j = 1, 2, \ldots, n$, n being the number of components taking part in the reaction.

Coefficients called constants of speeds of chemical reactions are a part of sets of differential equations which fix the dependence in time of c_j on other concentrations. Without the use of a computer the solution of such sets of differential equations for complex chemical reactions is, as a rule, impossible. The differential equations are replaced with sets of algebraic equations using the method, employed in chemical kinetics, of stationary concentrations. In this method all the $\dot{c}_j$'s are assumed equal to zero. In doing this the unfolding of the process in time is lost, as well as the possibility for investigating the influence of various conditions (in particular, the concentration of various components in the initial moment, temperatures, and so forth).

The development of effective methods of numerical integration of sets of differential equations describing complex chemical reactions, proceeding with the final rates, can permit the solution of these problems. The discovery of a solution for the set of differential equations of the kinetics of complex chemical reactions gives the possibility of obtaining the following information:

1. When the values of the constants of reaction rates for various stages of a complex reaction are known, it is possible in a reasonable amount of computer time to examine the various alternative mechanisms hypothesized for the reaction.

2. For each of the mechanisms examined, it is possible to obtain the values for the concentrations of all components as a function of time for the entire duration of the reaction (for a given sum total of constants of reaction rates). Therefore, the comparison of calculated and experimentally-derived values for concentrations is possible for any one of them for any interval of time, provided that their measurement is experimentally possible.

3. In the mathematical model corresponding to each known mechanism of a complex chemical reaction, it is possible to learn the degree of sensitivity of that mechanism to changes in the constants of reaction rates in separate stages of the reaction and in their different groups, and also to learn the mechanism's degree of sensitivity to varied conditions affecting the way the reaction proceeds (temperature, pressure, initial distribution of concentrations, etc.). Actually, such research may be conducted without any supplementary experimental data at all. Moreover, using special mathematical methods (the gradient method and others), if the experimental data is reworked, it is possible to find approximate values for the constants of rates of reaction as well as the minimum number of experiments needed to obtain the constants to a given degree of accuracy.

However, as will be shown in detail below, when using a computer to integrate sets of differential equations of the kinetics of complex homogeneous isothermal reactions, considerable mathematical difficulties arise in the case -- important in chemistry -- when chemically active particles such as atoms and radicals take part in the reaction. This is so because the constants of rates of reaction for such particles are several orders of magnitude larger than the other constants of rates or reaction going into the equations. In this case the use of the usual methods of numerical integration on a computer turn out to be extremely difficult to put into practice.

It is possible to formulate the equations of chemical kinetics for an isothermal homogeneous reaction (in closed systems) in the following form*:

$$\dot{c}_j = \sum_{m=1}^{n} \sum_{p<m} \alpha_{jmp} c_m c_p + \sum_{p=1}^{n} \beta_{jp} c_p \qquad (1)$$

$$(t > t_0,\ j = 1, 2, \ldots, n).$$

where c_j are the dimensionless concentrations connected with the dimensional multipliers $C_0 = T_0/V_0T$, where $T_0 = 273°$ K, $V_0 = 22.4$ liters/mole, and T is the temperature [°C]; the coefficients α_{jmp} and β_{jp}, which are not equal to zero, are the corresponding constants of rates of second and first order reactions, brought to the dimensionality $\sec^{-1}$; and t_0 is the time of the start of the reaction.

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* For simplicity, the rare zero-order and third-order reactions are here omitted. Their inclusion in equation set (1) does not introduce material changes in the discussion to follow. It must be noted that the form given above is the universal and sole form of notation of equations of chemical kinetics. We also note that generalization of the method offered below to the case of open systems (taking into account hydrodynamic phenomena and non-isothermality) does not entail material difficulties.

The quantities going into the set of equations (1) satisfy the following conditions: 1) $0 \leq c_j \leq 1 (j = 1,2,\ldots,n)$; 2) α_{jmp} and β_{jp} are symmetric with respect to permutations of the indices m and p; 3) if even one of the indices m and p is equal to j, then the corresponding coefficients, if they are different from zero, are negative. Algebraic equations of balance enable us to lower the order of the set of equations (1).

Grouping together in each equation of set (1) the terms containing c_j, we shall rewrite the set in the following form:

$$\dot{c}_j(t) = -b_j(t) c_j + a_j(t) \quad (j = 1, 2, \ldots, n), \qquad (2)$$

where

$$a_j(t) = \sum_{m=1}^{n} \sum_{p<m} \alpha_{jmp} c_m c_p + \sum_{p=1}^{n} \beta_{jp} c_p \, (m \neq j,\ p \neq j),$$

$$b_j(t) = \sum_{p=1}^{n} |\alpha_{jjp}| c_p + |\beta_{jj}|.$$

It is evident that $b_j(t)$, as opposed to $a_j(t)$, may depend linearly on $c_j(t)$. Since $a_j(t)$, $b_j(t)$ are the sums of the non-negative terms, then $a_j(t) \geqslant A_j \geqslant 0$, and $b_j(t) \geqslant B_j \geqslant 0$, where A_j and B_j are constants which are the lower boundaries of the functions $a_j(t)$, $b_j(t)$ when $t > t_0$.

For example, for reactions of the first order, $b_j(t) \equiv B_j = \beta_{jj}$

1. The content of the problem.

The use of computers to solve problems of chemical kinetics has grown sharply recently (see, for instance, sources [1-5]). However, as has already been mentioned, the use of standard methods of numerical integration for sets of equations describing complex chemical reactions meets with various difficulties. This is connected with the fact that source 1 when reagents with substantially different reaction capability take part in the reaction (constants of rates of reaction which when converted to the same dimensionality, differ by ten orders of magnitude or more), certain of the equations (e.g. those describing the kinetics of free radicals) may in the course of numerical integration become unstable with the passage of time.*

This peculiarity is specific to these equations of chemical kinetics inasmuch as, from the point of view of the theory of sets of ordinary differential equations when $B_j \neq 0$, they are absolutely stable.

Actually, we shall examine the conduct of a line of integration of one of the equations of the form (2) $\dot{y}(t) = a(t) - b(t,y)y$. We shall define $(t) = y_1(t) - y_2(t)$, where $y_i(t)$ $(i = 1,2)$ is the basic component of the solution of this equation, corresponding to the various given initial conditions. Adding and calculating $b(t,y_2)y_2$, we get:

$$\dot{\phi}(t) = -b(t, y_1)\ \varphi - y_2[b(t, y_1) - b(t, y_2)].$$

Inasmuch as, in agreement with the above, $db(t,y)/dy \geqslant 0$, then when $y_1 > y_2$, that is $\dot{\phi} > 0$, we have $\dot{\phi} < 0$ and vice versa. Thus, the integration series converges when integration is carried out from left to right, and as the magnitude of $b(t,y)$ increases, stability around the initial conditions increases [source 2].

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*This question will be examined in detail in section I-3 below.

However, as will be shown below, when large enough values of b(t,y) are reached, oscillations of the solution of the equation under examination occur during the process of numerical integration by usual methods. The amplitude of the oscillations depends on the path of integration. As a result of this occurrence, the integration of a set of such differential equations of chemical kinetics by means of standard methods of numerical analysis is in practice impossible.

Until now works have been published on various problems in chemical kinetics in which the difficulties of numerical integration of differential equation set (1) in the case of complex chemical reactions are noted sources [2-4]. Hence, source [2] conducted a qualitative investigation of the carrying out of integral curves for an equation of the form:

$$\dot{y} = \frac{y - G(t)}{Q(t, y)}, \tag{4}$$

where Q(t,y) and G(t) are the given functions, and $Q(t,y) \leqslant \xi$, with ξ quite small (for the purposes of chemical kinetics $|Q| \leqslant \tau_0$, where τ_0 is the time of the reaction).

It is evident that this equation is a particular case of a class of problems in chemical kinetics, since it is essential here that $Q = Q(t) < 0$ and moreover, it excludes, for instance, reactions of recombination. In source 2 it is noted that when $Q < 0$ the integration series during integration from left to right approaches $y = G(t)$, and the speed of approach sharply increases with the growth of $|Q|^{-1}$. As a result of the investigation in source 2 a different method of solution of such equations (called "stiff" equations by the authors of source [2]) is suggested. This method is interesting for the theory of electric circuits and for rocket guidance problems, when $Q \gg 0$ and the integral curves, when $y \neq G(t)$, increase sharply in the vicinity of the modulus. But as applied to the problems of chemical kinetics, this method has not been developed.

The difficulties which we have described in numerical integration of problems of the kinetics of complex chemical reactions led us to attempts at approximate solutions on a computer by means of linearizing the equation set (1) (source [3]); such linearization is usually undertaken with the aim of analytical investigation of the solution. Obviously, without obtaining an estimate of the accuracy of the solution when the set is linearized, this method can not be used for numerical integration by computer.

Attention is paid in source [4]* to the peculiarities of behavior of set (2); in source [4] a method of computation** is suggested, without any mathematical substantiation, which is in many ways analogous to the method developed in article [1] and similar to the one outlined in the following section of this paper.

Thus, in source [4] , it is asserted a priori that in the equations for certain concentrations which are assumed to be small in the course of the whole reaction, the derivatives, starting from a certain moment in time, will also be quite small. Consequently, during the process of calculation on the computer program, this moment in time is determined and the right-hand parts of the corresponding equations are assumed to be approximately zero.

Thus, in source [4] , the reasons for the peculiarities of behavior of the numerical solution of equations of kinetics for complex chemical reactions remained undiscovered, which led to the fact that the authors of that source erroneously opened up the prospect of solving beforehand (without the results of a numerical integration) those equations which can make the set unstable during the process of integration. Therefore in source [4] it was impossible to determine the region of useability of the calculation method, or to give an evaluation of its accuracy. Because of all this, the use of the method is made more difficult and in certain situations, (for example, for second-order reactions, see below) can lead to significant mistakes.

2. Details of the solutions of equation set (1) when there are particles of different reaction capability taking part in the complex chemical reaction.

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*Source [4] became known to us after the method presented by us had already been worked out and confirmed on several examples.

**In this method an idea is used which had already been formulated by Bodenstein [5] ,known as the method of quasi-stationary (or partially stationary) concentrations (source [6]).
Bodenstein's idea, more simplified, was used in Blackmore's work D.R. Blackmore. Trans. Faraday Soc., 62, 518, 415 (1966) . In this work the differential equations of chemical kinetics for components with a high reaction capacity were immediately replaced by algebraic equations. Such a replacement is not always correct. It was shown by us under what conditions such a replacement may be done correctly.

We shall explain the nature of the influence of chemically active components on the solution of equation set (1); for simplicity's sake, we shall first examine the case where one component--the k-th--has a high reaction capacity (definition of sufficient conditions for this to apply are given after inequalities (4) and (5) below).

Let us assume that all concentrations $c_j(t)(j = 1,2,\ldots n)$ for all times $t > 0$ were somehow previously determined for us. Then the k-th equation in set (1), in agreement with equation set (2), may be written in the form

$$\dot{c}_k(t) = -b_k(t)\ c_k + a_k(t), \tag{3}$$

Here $b_k(t)$ and $a_k(t)$, determined by the k-th equation of set (1) and by the known values of the concentrations, are assumed to be known functions of time. Now with the aid of equation (3), which we set up only for the purpose of qualitative investigation, we shall obtain an evaluation for the analysis of $c_k(t)$.

It is evident that for a particular choice of $c_k(t)$ for the equation being examined, two cases are possible:

Case 1) The following conditions hold for the entire duration of the reaction, whose total time is τ_0:

$$b_k(t) \gg b_j(t) \quad (j = 1,2,\ldots, k-1, k+1,\ldots, n), \tag{4}$$

$$B_k > \frac{|\ln \varepsilon|}{\tau_0}, \quad b_k(t) \gg a_j(t). \tag{5}$$

(the latter of the inequalities in (5) derives from the former; ε is the desired degree of accuracy*)

From an examination of set (2) together with conditions (4) and (5) it follows that components participating in a first-order reaction, and having relatively high constants of reaction rate $|\beta_{kk}|$, are intentionally included in this case.

Case 2) It is not possible to confirm ahead of time that conditions (4) and (5) are fulfilled over the whole duration of the reaction, but they at least hold for certain parts of the reaction. In this case high reaction capabilities of components may occur, for instance, in reactions of the second

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*Because the values of the various concentrations change widely (over a range from 0 to unity), the magnitude of must be chosen quite small compared with unity.

order. Then whether or not conditions (4) and (5) hold depends on the magnitude of the value of the concentrations having large constants of rates of reaction as co-factors in the expression for function $b_k(t)$.

In the simplest case, (which has been examined in source [6], for example), where $b_k(t) \equiv B_k \gg a_k(t) \equiv A_k \gg 0$, the solution of the equation obtained from equation (3) has the form:

$$c_k(t) = c_k(0)\exp(-B_k t) + \frac{A_k}{B_k}[1 - \exp(-B_k t)].$$

Since $0 \leqslant c_k(0) \leqslant 1$, then when conditions (4) and (5) are fulfilled, the first item, which expresses the influence of the initial conditions, may be excluded from consideration when $t \geqslant t_0 = |\ln \varepsilon|/B_k$; that is, when $\exp(-B_k t) \leqslant \varepsilon$. Hence when $t > t_0$ we have within the limits of accuracy:

$$c_k(t) \approx \check{c}_k = \frac{A_k}{B_k}, \quad \frac{d\check{c}_k}{dt} \equiv 0,$$

where $\check{c}_k(t)$ and consequently, $c_k(t)$ will be small compared to unity. The concentration $\check{c}_k$, which we have obtained in this particular case we have been examining, is known as the quasi-stationary concentration, and is widely used in chemical kinetics.

An analysis of the behavior of $c_k(t)$ in the general case, where $a_k = a_k(t)$ and $b_k = b_k(t)$ are determined by solving the whole set of equations of chemical kinetics, presents considerable difficulties. However, for components whose equations satisfy conditions (4) and (5), and in the case of equation set (1), quasi-stationary concentrations also occur. It is evident that the latter concentrations will be substantially different from those examined earlier in the particular case. In fact, from equation (3), inasmuch as $a_k(t)$ and $b_k(t)$ are assumed to be known functions of time,

$$c_k(t) = c_k(0)\exp\left[-\int_0^t b_k(s)\,ds\right] + \int_0^t a_k(s)\exp\left[-\int_s^t b_k(r)\,dr\right]ds. \quad (6)$$

Hence, similar to the particular case examined above, the first item, which directly reflects the influence of the initial conditions, becomes small enough to ignore when $t \geqslant t_0 = |\ln \varepsilon| / B_k$. From the boundedness of $a_k(t)$, $b_k(t)$ it follows that it is always possible to also choose d_i = const. and g_i = const. ($i = 1,2$) so that $d_1 \leqslant a_k(t) < d_2$, and $g_1 \leqslant b_k(t) < g_2$, where $d_i \gg 0$, $g_i > 0$ and, in accordance with inequality (5), $g_1 \gg B_k$.

Then:

$$\alpha_1[1-\exp(-g_1 t)] < \int_0^t a_k(s)\exp\left[-\int_s^t b_k(r)\,dr\right]ds <$$
$$< \alpha_2[1-\exp(-g_2 t)],$$

where:

$$\alpha_1 = \frac{d_1}{g_1}, \quad \alpha_2 = \frac{d_2}{g_2}.$$

From equation (6), for $t > t_0$, in accordance with the foregoing, and within the accuracy limits, we have

$$\alpha_1 < c_k(t) < \alpha_2.$$

Inasmuch as $\alpha_i \ll 1 (i = 1,2)$ in accordance with inequality (5), we obtain the result that the concentrations of the highly reactive elements that we have been examining become small in relation to unity and consequently, the change in $a_k(t)$ and $b_k(t)$ for $t > t_0$ is basically determined by the concentration of the substances having a relatively small capacity of reaction compared to $c_k(t)$. Then, using the continuous nature of the solution of equation (3), a $\delta > 0$ is deliberately chosen such that, when $t \in (t, t + \delta)$ we have occurring:*

$$|\alpha_i - \check{c}_k(t)| < \varepsilon \, (i = 1, 2),$$

where

$$\check{c}_k(t) = \frac{a_k(t)}{b_k(t)}.$$

Thus, if in equation set (1) there is one equation satisfying conditions (4) and (5) over the duration of the entire reaction, then for all $t \gg |\ln\varepsilon|/g_1$ the error made in substituting the corresponding concentration $c_k(t)$ for $\check{c}_k(t)$ becomes less than the given maximum allowable error; and in accordance with equation (3) $\dot{c}_k(t)$ becomes as close to zero as desired. Characteristically, in this event the individual terms in the right-hand part of equation (3) are large compared with the magnitude of $\dot{c}_k(t)$.

From now on we shall call the function $\check{c}_k(t)$ the quasi-stationary solution of equation (3). It is evident that the quasi-stationary situation for individual substances that are participating in the reaction is typical for reactions where there are stages with constants of reaction rates sufficiently large and varied in magnitude. Also, the quasi-stationary

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*If $b_k = b_k(t, c_k)$, then $\check{c}_k$ is found in a similar fashion.

values change over time as a function of the behavior of the separate, less reactive components of reaction.

In the case where there are several components with reactive capacity whose constants of reaction rate exceed that of the rest of the components by a considerable margin, the line of reasoning is analogous. The quasi-stationary values in this case are determined from the solution of a set of algebraic equations obtained by setting the right-hand parts of the corresponding equations in set (1) to zero. The times when these components appear in the quasi-stationary condition is inversely proportional to the corresponding values of B_k. Since the constants of reaction rate incorporated in $b_k(t)$ materially depend on temperature, the time of appearance of $c_k(t)$ in the quasi-stationary condition under various conditions of the course of the reaction may change considerably, decreasing with an increase in temperature. From the determination of $\check{c}_k(t)$ it can be seen that the magnitude of $a_k(t)$ influences the magnitude of corresponding quasi-stationary value $c_k(t)$.

3. The algorithm of numerical integration of the set of equations of chemical kinetics under conditions of equations (4) and (5).

As was shown earlier, if in the right-hand side of the equation for any concentration there are one or several members containing the indicated concentration with coefficients sufficiently large in the vicinity of the modulus, then for a short time interval (compared with the duration of the reaction) the concentration in question for all practical purposes reaches its quasi-stationary value for that time. It follows from equation (3) that when the conditions of equations (4) and (5) are fulfilled, the concentrations $c_k(t)$, having reached (to the degree of accuracy required) their quase-stationary values when $t_k = |\ln \varepsilon| / B_k$, will remain in their quasi-stationary state when $t > t_k$ also.

However, the numerical integration of this set of nonlinear equations which is under examination, including in itself one or several equations satisfying the conditions of equations (4) and (5), leads to an oscillation of the solution around its quasi-stationary value for practically any path of integration different from zero, when $t > t_k$. This phenomenon is connected with the discreteness of counting in numerical integration, since the calculation of the right-hand parts in equation set (1) is conducted at fixed points of the integration path. For explanation we shall introduce the designation $z_k(t) = c_k(t) - \check{c}_k(t)$. Then, subtracting from equation set (3) the equation which it has been determined satisfies the concentration $\check{c}_k(t)$

$$0 = -b_k(t, \check{c}_k)\check{c}_k + a_k(t),$$

we get, using the Lagrange theorem,

$$\dot{z}_k(t) = -M_k(t)\, z_k(t), \tag{7}$$

where

$$M_k(t) = b_k(t, c_k) + \check{c}_k \left.\frac{db_k}{dc_k}\right|_{\xi} > b_k(t, c_k);$$

$$\xi \in (c_k(t),\ \check{c}_k(t)), \quad \text{if} \quad c_k(t) < \check{c}_k(t);$$

$$\xi \in (\check{c}_k(t),\ c_k(t)), \quad \text{if} \quad \check{c}_k(t) < c_k(t).$$

When the conditions of equations (4) and (5) are fulfilled, we have from equation (7) that a small increase in $|z(t)|$ leads to a large change in $c_k(t)$, as a result of which $|z(t)|$ decreases. Hence with the passage of time $z(t)$ tends toward zero. However, in numerical integration with an interval $\Delta t \geqslant 1/B_k$ (which is sufficiently small to meet the conditions of equations (4) and (5), $z_k(t)$, and hence, $\check{c}_k(t)$ change sign within the limits of one interval. As a result the numerical integration of equations (2), which satisfies the conditions of equations (4) and (5), leads to an oscillation in the solution of $c_k(t)$ relative to $\check{c}_k(t)$. Decreasing the interval of the integration process naturally reduces the amplitude of the oscillation. However, when $c_k(t)$ appears in the quasi-stationary state, that is, when $z(t)$ is located within the limits of accuracy for the calculations, the integration--even with the smallest possible interval--leads to oscillation whose amplitude increases with time. Therefore, the numerical integration of this set of equations, one or several of whose equations satisfies the conditions of equations (4) and (5), leads to an extremely small integration interval (intentionally not increasing over time) and, hence, to a long computation time and the accumulation of error. If the integration is conducted with a constant integration interval, the accuracy of the computation quickly falls, and the oscillation in the solution occurs with sharply increasing amplitude leading to computer overload.

As is known, under certain circumstances a chemical process may have an oscillatory character [source 8]. However, if it were possible to lower the amplitude of the oscillation of the numerical solution caused by the discreteness of the computation on the computer, the amplitude of the "real" oscillation [source 8] caused by the oscillatory nature of chemical process, would remain constant. Moreover, the amplitude of the oscillation of the solution, caused by the discreteness of the computation, could also grow without limit, which could lead to violation of the law of conservation of matter and even cause the appearance of negative values for the concentrations. Such phenomena do not occur if the oscillations of the solution of equation set (1) are "real." Thus, the different behavior of the two types of oscillations of the solution of equation set (1) in principle allows us to tell these oscillations one from the other.

On the basis of the foregoing, the following algorithm is proposed for solving problems in chemical kinetics when chemically active particles are participating in the reaction. The integration of equation set (1) in this case must be carried out in two stages.

In the first, transitional stage, where the concentration magnitude materially depends on the selected initial conditions, the set is integrated like the problem of Koshi by one of the methods of numerical analysis. The duration of the first stage, as was pointed out earlier, is determined by the magnitude of the corresponding values of $b_k(t)$. [In practice, the duration is of the order of $10/\min B_k$, if there are several components capable of reaction whose equations satisfy the conditions of equations (4) and (5).] Here the integration absolutely must be carried out using an automatic selection of integration interval, but the initial value for the interval must be taken less than $1/\max B_k$.

When it is taken into account that the magnitudes of the concentrations differ from each other by many orders of magnitude, but that scaling them is difficult because of their rapid change over time, it can be seen that the integration must be conducted to a given relative degree of accuracy; that is, to a certain number of significant figures regardless of the magnitudes themselves.

The final goal of the process of integrating the problem in the first stage is the arrival of the components capable of reaction into the quasi-stationary state. After each integration interval a comparison is made between $c_k(t)$ and $\gamma_k(t)$. If the difference between the solution to the equation having the characteristic examined above and its quasi-stationary value for any moment of time--if this difference is within the accuracy limits, then we can go into the second stage of the integration. Here the order of the set is lowered, and the differential equation that has been described is replaced by an algebraic equation (by setting its right-hand side equal to zero). In the general case, when there are a number of elements capable of reaction, a set of non-linear algebraic equations results from the replacement. As will be shown later, when the conditions of equations (4) and (5) are met, such a replacement does not introduce divergence and does not yield an accumulation of error, but instead the effectiveness of the computation is sharply increased, enabling us to eliminate the difficulties described above.

In the general case it is necessary to solve the set of non-linear algebraic equations obtained in the second stage by integration methods at each referral to the computer program for the right-hand sides of the equations in the set of differential equations. In so doing, the computation time may significantly increase. Hence it is expedient to solve such problems on high-speed computers.

4. Evaluation of the accuracy of the algorithm.

The proposed algorithm, with the successive replacement of the differential equations with algebraic equations for the several components with high reaction capability which satisfy the conditions of equations (4) and (5) when $t_k = |\ln \varepsilon| / B_k$, insures that the solution of equation set (1) is obtained to the desired degree of accuracy.

For proof of this we shall examine the change in deviation of $z_k(t)$ of the solution of equation (3) from its quasi-stationary state when $t > t_k$. Taking into account the determination of $\check{c}_k(t)$, the equation for $z_k(t)$ from equation (3) may be written in the form

$$\dot{z}_k + M_k(t)\, z_k = \frac{d\check{c}_k}{dt} = \frac{\dot{a}_k}{b_k} - \check{c}_k\, \frac{\dot{b}_k}{b_k},$$

where, in accordance with our earlier examination, $M_k \geqslant b_k(t, c_k)$. It follows from equation sets (1) and (2) that when expression (4) is achieved, $|\dot{a}_k(t)|$ has the order $a_k b_k$, and $|\dot{b}_k|$ the order b_k^2. Therefore

$$|\dot{z}_k + M_k z_k| \leqslant N_k, \qquad (8)$$

where N_k is some value which is the upper boundary of the expression that is in the left-hand side of equation (8). If the condition of equation (5) holds, $N_k \ll B_k$.

We shall examine the integral curves (equation 8) and the straight lines $z_k = \pm R_k$, where $R_k = N_k/B_k$. It can be seen that if for some $t^* > 0$ we have $z_k(t^*) > R_k$, then $\dot{z}_k(t^*) > 0$, and the integral line of equation (8) may only decrease as far as its intersection with the straight line $z_k = R_k$. If $z_k(t^*) > R_k$, then $\dot{z}_k(t^*) > 0$, and the integral curve of equation (8) increases until it intersects $z_k = -R_k$. But if $|z_k(t^*)| \leqslant R_k$, then the integral curves of equation (8), for $t \geqslant t^*$, can not intersect the corresponding straight lines $z_k = \pm R_k$. Hence:

$$\min\{z_k(t^*);\ -R_k\} < z_k(t) < \max\{z_k(t^*);\ R_k\}$$

for t   t* and for t* t_k. When the components with high reaction capability reach (to the desired accuracy) the quasi-stationary values, the following evaluation occurs:

$$\min\{\varepsilon;\ R_k\} < z_k(t) < \max\{\varepsilon;\ R_k\}.$$

Because under the conditions of equation (5) R_k is quite small, the difference between the quasi-stationary solution and the real solution will be within the limits of the accuracy of the computation, when $t > t_k$. Thus the proposed algorithm of the solution of a set of differential equations describing the kinetics of complex chemical reactions when components of high reactive capability are present that satisfy the conditions of equations (4) and (5)--this algorithm insures the obtaining of a solution with sufficient accuracy for practical purposes.

The above evaluation of the magnitude of the quasi-stationary concentrations, as well as the qualitative evaluation of the accuracy of the algorithm, both of which depend on the ratios of the constants of reaction rates of the elementary stages of the reaction (that is, the degree to which the conditions of equations (4) and (5) are fulfilled)--these evaluations may be obtained in a similar way in every concrete case. It is evident that these evaluations are excessive conservative . Therefore when the equations of balance are done (and these are the practical standards for judging the results of the integration of equation set (1)) it will actually be done with greater accuracy than the evaluations obtained above would indicate.

We note in conclusion, that in the case of reactions of the second order and higher, after arrival into the quasi-stationary state, it is essential from time to time in the course of the solution to check that the conditions of equations (4) and (5) are being met. If during the reaction process b_k decreases so that $b_k < |\ln \varepsilon| / \Delta t$, where Δt is the interval of integration, then in order to get the required accuracy it is essential to replace the corresponding algebraic equation with the initial differential equation, etc.

This method that has been developed by us above will be used in the following sections of this chapter. It will be applied to various problems of the kinetics of complex chemical reactions.

II. A calculation of the kinetics of chlorination of ethylene and an analysis of the accuracy of the algorithm of the solution.

The complex, multi-stage reaction of the chlorination of ethylene offers considerable difficulties for investigation. In this section we obtain the functions $c_j = c_j(t)$ for concentrations of intermediate and final products of this reaction by the mechanism of combination in the temperature interval 600 - 1200°K and for differing initial ratios of $Cl_2 : C_2H_4$. An appropriate analysis of the accuracy is conducted for the results of a numerical integration of a set of differential equations of the kinetics of the chlorination of ethylene. This analysis also has a more general significance for the nature of the method of numerical integration of kinetic equations of complex chemical reactions that was developed in section I-3 of this paper.

On the basis of the data now available it is considered that substitutional chlorination may proceed in two directions [sources 8,9] :

$$\begin{aligned} &C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2, \\ &C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl, && (9) \\ &C_2H_4 + Cl_2 \rightarrow C_2H_3Cl + HCl. && (10) \end{aligned}$$

In the first case vinylchloride is formed from the products of combination ($C_2H_4Cl_2$), and in the second case there is a direct replacement process [source 10] . On the basis of present computations the first of these mechanisms, which is considered the basic mechanism by many authors, is assumed. A reaction process was constructed for mechanism (9) that was considered to be one of the possible models for the chlorination of ethylene.

1. Formulation of the problem.

We have examined the following reaction process, in which elementary stages known in the literature are used [sources 11-14]:

$$\left.\begin{array}{rl}
1) & Cl + C_2H_4 \rightarrow C_2H_4Cl \\
2) & C_2H_4Cl \rightarrow Cl + C_2H_4 \\
3) & C_2H_4Cl + Cl \rightarrow C_2H_4Cl_2 \\
4) & C_2H_4Cl + HCl \rightarrow C_2H_5Cl + Cl \\
5) & C_2H_5Cl + Cl \rightarrow C_2H_4Cl + HCl \\
6) & C_2H_4Cl + Cl_2 \rightarrow C_2H_4Cl_2 + Cl \\
7) & C_2H_4Cl_2 + Cl \rightarrow C_2H_4Cl + Cl_2 \\
8) & C_2H_4Cl_2 + Cl \rightarrow C_2H_3Cl_2 + HCl \\
9) & C_2H_3Cl_2 + HCl \rightarrow C_2H_4Cl_2 + Cl \\
10) & C_2H_3Cl_2 + Cl_2 \rightarrow C_2H_3Cl_3 + Cl \\
11) & C_2H_3Cl_3 + Cl \rightarrow C_2H_3Cl_2 + Cl_2 \\
12) & C_2H_3Cl_2 + Cl \rightarrow C_2H_3Cl_3 \\
13) & C_2H_3Cl_2 \rightarrow C_2H_3Cl + Cl \\
14) & C_2H_3Cl + Cl \rightarrow C_2H_3Cl_2 \\
15) & Cl_2 + M \rightarrow Cl + Cl + M \\
16) & Cl + Cl + M \rightarrow Cl_2 + M \\
17) & C_2H_4Cl + C_2H_4Cl \rightarrow \text{продукты} \\
18) & C_2H_3Cl_3 + Cl \rightarrow C_2H_2Cl_3 + HCl
\end{array}\right\} \qquad (11)$$

Since further chlorination does not interest us, we limited ourselves to the reactions listed above.

Corresponding to the reaction process (11) was constructed a set of 12 non-linear, ordinary differential equations (12) which were numerically integrated on the "Strela" ['Arrow'] computer of the computer center of Moscow State University. The integration was carried out using the algorithm of integration of a set of equations of kinetics of complex chemical reactions which was examined earlier in this paper in section I-3.

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*The authors thank V. Ya. Stern and A. F. Revzin for help given in the construction of this reaction process.

$$\left.\begin{aligned}
\frac{dc_1}{dt} &= -k_6c_4c_1 + k_7c_5c_2 - k_{10}c_8c_1 + k_{11}c_9c_2 - k_{16}c_1c_0 + k_{16}c_2^2c_0\\
\frac{dc_2}{dt} &= -k_1c_2c_3 + k_2c_4 - k_3c_4c_2 + k_4c_4c_6 - k_5c_7c_2 + k_6c_4c_1 -\\
&\quad - k_7c_5c_2 - k_8c_5c_2 + k_9c_8c_6 + k_{10}c_8c_1 - k_{11}c_9c_2 - k_{12}c_8c_2 +\\
&\quad + k_{13}c_8 - k_{14}c_{10}c_2 + 2k_{16}c_1c_0 - 2k_{16}c_2^2c_0 - k_{18}c_2c_9\\
\frac{dc_3}{dt} &= -k_1c_2c_3 + k_2c_4\\
\frac{dc_4}{dt} &= k_1c_2c_3 - k_2c_4 - k_3c_4c_2 - k_4c_4c_6 + k_5c_7c_2 - k_6c_4c_1 +\\
&\quad + k_7c_5c_2 - 2k_{17}c_4^2\\
\frac{dc_5}{dt} &= k_3c_4c_2 + k_6c_4c_1 - k_7c_5c_2 - k_8c_5c_2 + k_9c_8c_6\\
\frac{dc_6}{dt} &= -k_4c_4c_6 + k_5c_7c_2 + k_8c_5c_2 - k_9c_8c_6 + k_{18}c_2c_9\\
\frac{dc_7}{dt} &= k_4c_4c_6 - k_5c_7c_2\\
\frac{dc_8}{dt} &= k_8c_5c_2 - k_9c_8c_6 - k_{10}c_8c_1 + k_{11}c_9c_2 - k_{12}c_8c_2 - k_{13}c_8 +\\
&\quad + k_{14}c_{10}c_2\\
\frac{dc_9}{dt} &= k_{10}c_8c_1 - k_{11}c_9c_2 + k_{12}c_8c_2 - k_{18}c_2c_9\\
\frac{dc_{10}}{dt} &= k_{13}c_8 - k_{14}c_{10}c_2\\
\frac{dc_{11}}{dt} &= k_{17}c_4^2\\
\frac{dc_{12}}{dt} &= k_{18}c_2c_9
\end{aligned}\right\}\quad(12)$$

In set (12) the following designations are hereby adopted for convenience:

(1) Вещество	(2) Концентрация	(3) Вещество	(4) Концентрация;
Cl_2	c_1	C_6H_6Cl	c_7
Cl	c_2	$C_6H_5Cl_2$	c_8
C_6H_6	c_3	$C_6H_5Cl_3$	c_9
C_6H_6Cl	c_4	C_6H_5Cl	c_{10}
$C_6H_6Cl_2$	c_5	(5) Продукты семнадцатой реакции	c_{11}
HCl	c_6	$C_6H_5Cl_3$	c_{12}

Key:
1. Substance
2. Concentration
3. Substance
4. Concentration
5. Products of the 17th reaction.

In the case where this process occurs in a current, equations of hydrodynamics should be added to the set of differential equations of kinetics (12) and the set thus obtained should be solved concurrently, as was done for instance in source for the process of the conversion of methane to acetylene.

For the initial conditions of the equation set (12) we use the initial concentrations of ethylene, molecular chlorine, and elemental chlorine, where the initial value for the concentration of elemental chlorine is found by means of a balanced degree of dissociation of molecular chlorine at the moment $t = 0$.

The values of the constants of reaction rate, which are necessary for numerical integration, were computed (with the exception of the constant for the dissociation and reassociation of chlorine) by means of the well-known formula:

$$k_i = k_{0i} \exp(-E_i / RT), \qquad (13)$$

where the factor before the exponential, k_{0i}, and the energy of activation, E_i were taken from sources [12, 16, 17] which have the data which is most complete and mutually substantiating. These data are listed in Table 1. Because data are lacking for the higher temperatures, the values indicated for the constant of reaction rates for the 1200°K region were extrapolated by us.

Table 1.
Values of the energy of activation and pre-exponential factors for the elementary stages of the reaction of

i	k_{0i}, ① 1/сек	E_i, ② ккал/моль	i	k_{0i}, ③ 1/сек	E_i, ④ ккал/моль
1	$1,6\cdot10^{10}c_0$	0	10	$6,3\cdot10^{8}c_0$	1
2	$7,9\cdot10^{13}$	23,6	11	$2\cdot10^{11}c_0$	20,6
3	$2\cdot10^{11}c_0$	0	12	$2\cdot10^{11}c_0$	0
4	$10^{9}c_0$	9,1	13	$6,3\cdot10^{13}$	23,8
5	$3,2\cdot10^{10}c_0$	1,5	14	$1,6\cdot10^{10}c_0$	0
6	$2,5\cdot10^{9}c_0$	1	17	$1,3\cdot10^{10}c_0$	0
7	$2\cdot10^{11}c_0$	21,3	18	$3,2\cdot10^{10}c_0$	3,5
8	$2,5\cdot10^{10}c_0$	3			
9	$7,9\cdot10^{8}c_0$	10,2			

Key:

1.	1/sec.	3.	1/sec.
2.	kilocal./mole	4.	kilocal./mole

The reaction process (11) also embodies reactions of dissociation and recombination of chlorine.

A number of authors have shown in experiments using impact tubes [sources 18, 19] in the temperature interval from 1500 to 2500°K that the experimental data on the constants for the dissassociation of chlorine, for corresponding choices of a, n, k_0, and E, are equally well described by either of the two following formulas:

$$k_{diss} = a\sqrt{T}(D_0/RT)^n \exp(-D_0/RT), \tag{14}$$

$$k_{diss} = k_0 \exp(-E/RT), \tag{15}$$

where n is the numbered parameter. Usually, n is taken to be $n \approx 2$ [sources 18, 19] .

As far as the numerical value of the energy of activation is concerned, different authors give values for this temperature interval that do not agree with each other--from 40 to 48 kilocal./mole. [sources 17 - 19].

For the integration of equation set (12) in this study, the constants of disassociation and recombination were computed according to the following formulas [source 18] :

$$k_{15} = 1{,}1\cdot10^{9}\, T^{1/2}\, (D_0/RT)^2 \exp[-(D_0/RT)], \tag{16}$$

$$k_{16} = 3{,}6\cdot10^{8}\, (D_0/RT)^2/[1 - \exp\ (-813/T)]. \tag{17}$$

2. The algorithm of the solution of equation set (12).

From what has been written above it follows that the constants of rates of reaction change within wide limits over different stages of the reaction under investigation (for example, at temperature 600°K from 10^{-8} to 10^{9}). As was pointed out earlier (middle of section I-2), this wide range of values creates considerable difficulties for the numerical integration to a desired degree of accuracy.

In the case of equation set (12) the components whose equations satisfy the conditions of equations (4) and (5), are C_2H_4Cl, $C_2H_3Cl_2$, and also under certain conditions Cl (our designations c_4, c_8, and c_2 correspondingly).

In the temperature range from 600 to 1200°K the concentrations $c_4(t)$ and $c_8(t)$ reach their quasi-stationary states with values $c_k(t) = a_k(t)/b_k(t)$ $(k = 4,8)$ correspondingly, not later than from 10^{-4} to 10^{-8} sec. after the start of the reaction, and in agreement to what was written above, (section I-2), the concentrations shall intentionally be allowed to stay in the quasi-stationary state.* It is here evident from equation set (12) that $\dot{c}_1(0) = 0$, $\dot{c}_2(0) < 0$, $\dot{c}_3(0) < 0$, $\dot{c}_4(0) > 0$.

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*As was shown, under certain conditions this is also justified for Cl.

The integration of equation set (12), as was shown earlier (section I-3), must be carried out in two stages. The initial interval of integration must be intentionally not more than

$$\frac{1}{\min b_k(0)} \quad (k = 2, 4, 8),$$

that is:

$$\min\left\{\frac{1}{k_3 c_2(0)}, \frac{1}{k_2}, \frac{1}{k_{13}}\right\}.$$

In this case $c_4(t)$ and $c_8(t)$ enter the quasi-stationary state almost simultaneously, because $b_k(t)$, when $k = 4, 8$, (the lower evaluations of which are correspondingly equal to k_2 and k_{13}) are closed to each other. Since $\dot{c}_8(t)$ and $\dot{c}_4(t)$, in accordance with equation (12), do not clearly depend on $c_4(t)$ and $c_8(t)$ respectively, in this case $\check{c}_4(t)$ and $\check{c}_8(t)$ may be found independently of each other from the equations:

$$\dot{c}_8(t) = 0$$

$$\text{and} \quad \dot{c}_4(t) = 0$$

Besides this, the condition $\dot{c}_4(t) = \dot{c}_8(t) = 0$ allows the equation for $\dot{c}_2(t)$ to be brought into a more convenient form for numerical integration:

$$\dot{c}_2(t) = 2(k_{15}c_1c_0 - k_3\check{c}_4c_2 - k_{17}\check{c}_4^2 - k_{12}\check{c}_8c_2 - k_{16}c_0c_2^2) - k_{18}c_2c_9,$$

where the magnitude of the coefficient for c_2 decreases significantly compared to equation set (12).

A check showed that when equation (4) was solved using the proposed algorithm, the equation of balance is fulfilled to the desired accuracy, which is determined by the relative degree of error inherent in the method of numerical integration over the whole integration process. The computation time machine time required for one variant of the Runge-Kutt method, using an automatic choice of interval of integration and a relative error of 10^{-4} and 10^{-5}, is about one hour on a "Strela-4" [Arrow-4] computer with a computer speed of about 2000 operations per second.

3. An evaluation of the accuracy of the results of the numerical integration of equation set (12)

We shall show that in the temperature range being examined (600 - 1200°K) the algorithm of the solution of equation set (12) insures an absolute accuracy not lower than plus or minus 10^{-6}.

Beforehand we shall obtain the upper evaluation of the magnitude of the concentration of atomic chlorine as a function of time in the given temperature range. For this purpose we shall examine the equation for Cl in the form

$$\dot{c}_2(t) = f(c_1; c_2, \dots, c_{12}) = -c_2[k_2c_4 + k_8c_7 + (k_7 + k_8)c_5 + k_{13}c_8 + k_{14}c_{10} + 2k_{16}c_0c_2 + k_1c_3 + (k_{18} + k_{11})c_9] + c_4(k_3 + k_6c_6 + k_8c_1) + c_3(k_{12} + k_7c_6 + k_{10}c_1) + 2k_{15}c_1c_0. \qquad (18)$$

We shall find a c_2^0 such that for $c_2(t) \gg c_2^0$ and for any other possible values of the other concentrations, the following holds:

$$f(c_1, c_2, \dots, c_{12}) < 0.$$

This means that the reaction being examined may proceed with an increase in the concentration of atomic chlorine only if $c_2 < c_2^0$.

As follows from equation (18), the positive terms do not clearly depend on c_5, c_7, c_9, and c_{10}. We shall hold the values of the other concentrations constant and write the equation of balance for Cl in the form:

$$2c_5 + c_7 + 3c_9 + c_{10} = a - 2c_1 - c_2 - c_4 - c_6 - 2c_8 - 2c_{11} - 3c_{12}, \qquad (19)$$

where

$$a = 2c_1(0) + c_2(0).$$

It is evident that the function <u>f</u> will reach a maximum if, for arbitrarily fixed values of the indicated concentrations, the negative terms in equation (18) are at their minima. This condition is fulfilled if the expression obtained from equation (18) and presented, taking equation (19) into account, in the form

$$R_1 = k_8c_7 + \frac{1}{2}(k_7 + k_8)2c_5 + k_{14}c_{10} + \frac{1}{3}(k_{18} + k_{11})3c_9.$$

is at its minimum. In view of the fact that, in accordance with Table 1, the following inequality holds:

$$\frac{1}{3}(k_{10}+k_{11}) < \min\left\{k_5,\ \frac{1}{2}(k_7+k_8),\ k_{14}\right\},$$

R_1 reaches its minimum, (as a consequence of equation (19), if

$$c_5 = c_7 = c_{10} = 0. \qquad (20)$$

Thus the condition of equation (20) is essential if function f is to reach its maximum value. Then expression (18) takes the form

$$f = -c_2\left[k_3c_4 + k_{12}c_8 + 2k_{16}c_0c_2 + (k_{10}+k_{11})c_9 + k_1c_3\right] + \\ + c_4(k_2 + k_4c_6 + k_6c_1) + c_8(k_{13} + k_9c_6 + k_{10}c_1) + 2k_{15}c_0c_1. \qquad (21)$$

Further search for the majorant of $\dot{c}_2(t)$ will be accomplished by means of varying c_1, c_4, c_8, c_{11}, and c_{12}, which heretofore were held constant.

Let us look at the contents making up c_1 and c_6 in formula (21), taking into account expression (20), and for the values of c_9, c_4, c_8, c_{11}, c_{12}, and c_2 being held arbitrarily constant. Then from the balance in equation (19) we have

$$2c_1 + c_6 = a - 3c_9 - c_4 - 2c_8 - 2c_{11} - 3c_{12} - c_2. \qquad (22)$$

Consequently the expression entering the right-hand side of equation (21) and written taking equation (22) into account, in the form

$$R_2 = c_6(k_4c_4 + k_9c_8) + c_1(k_6c_4 + k_{10}c_8 + 2k_{15}c_0),$$

reaches its maximum when $c_6 = 0$, since $k_6 \gg 2k_4$, $k_{10} \gg 2k_9$, and also, in accordance with equation (18), $k_{15} > 0$. Consequently

$$\frac{1}{2}(k_6c_4 + k_{10}c_8 + 2k_{15}c_0) > k_4c_4 + k_9c_8.$$

From the above it follows that when expression (20) is satisfied, (regardless of the values of the other concentrations), the condition

$$c_6 = 0 \qquad (23)$$

leads to the maximum value of $\dot{c}_2(t)$ for the given state of the system. As a result of formula (21) we get

$$\dot{c}_2(t) \leqslant c_4(k_2 + k_6c_1 - k_3c_2) + c_8(k_{13} + k_{10}c_1 - k_{12}c_2) + \\ + 2k_{15}c_0c_1 - 2k_{16}c_0c_2^2 - (k_{10}+k_{11})c_9c_2 - k_1c_2c_3. \qquad (24)$$

It is evident that when $c_2(t) \gg c_2(0)$, the following holds:

$$k_{15}c_1(t) - k_{16}c_2^2(t) \leqslant 0, \quad t > 0. \tag{25}$$

Thus, when $c_2 = c_2^0$, the only terms in the right-hand side of formula (24) which may be positive are $R_3 = k_2 + k_6c_1 - k_3c_2^0$ and $R_4 = \frac{1}{2}(k_{13} + k_{10}c_1 - k_{12}c_2^0)$. In accordance with Table 1, $k_2 > k_{13}$, $k_6 > k_{10}$, and $k_3 \geq k_{12}$ independent of the temperature. Hence, if $R_3 \leqslant 0$, then $R_4 < 0$ and $f(c_1, c_2^0, c_3, \ldots, c_{12}) < 0$. Consequently a maximum of *f* is possible when $R_3 > 0$. Then $R_3 > R_4$ and $c_4R_3 + 2c_8R_4$ will not be large, if for the arbitrary values of the other concentrations (taking into account equations 19,20, and 23), we take

$$c_8 = 0. \tag{26}$$

Thus from expression (24), taking into account equation (26), we get

$$f(c_1, c_2^0, c_3, \ldots, c_{12}) \leqslant c_4(k_2 + k_6c_1 - k_3c_2^0) + \\ + 2(k_{15}c_1 - k_{16}c_2^{0 2})c_8 - (k_{14} + k_{11})c_8c_2 - k_1c_2c_3. \tag{27}$$

Throwing out the last terms of equation (27) (here the right-hand side of equation (27), in agreement with equation (25), is not allowed to decrease) we finally have:

$$f(c_1, c_2^0, c_3, \ldots, c_{12}) \leqslant 0$$

with

$$c_2^0 = \max\{c_2(0), \bar{c}_2\},$$

where

$$\bar{c}_2 = \frac{k_2 + k_6c_1}{k_3}.$$

When there is a surplus of ethylene, $\alpha = 1$, and since $c_1(t) < c_1(0) < \alpha/2$, $\bar{c}_2 < 5 \cdot 10^{-3}$ for the temperature interval from 600 to 1000°K. Inasmuch as the degree of disassociation in this interval changes from 10^{-8} to $2.5 \cdot 10^{-3}$, $\bar{c}_2 > c_2(0)$, and the evaluation we are seeking has the form

$$c_2(0) \leqslant c_2(t) < 5 \cdot 10^{-3}. \tag{28}$$

The evaluation obtained in equation (28) is sufficiently effective for the high temperatures within the limits of the temperature interval under examination. But for a lowered temperature the evaluation of equation (28) becomes substantially increased; therefore for the temperature range from 600 to 800° K, (degree of dissassociation of which is 10^{-8}--10^{-5}) it is expedient to use the following evaluation. From formula (12) we have

$$\dot{c}_2(t) + \dot{c}_4(t) + \dot{c}_8(t) = \\ = -2\left(k_3c_4c_2 + k_{17}c_4^2 + k_{12}c_8c_2 + k_{18}c_8c_4^2 + \frac{1}{2}k_{18}c_2c_8\right) + 2k_{15}c_0c_1. \quad (29)$$

We shall designate $c_2(t) + c_4(t)$ $c_8(t) = \Phi(t)$, whereby, since $c_4(0) = c_8(0) \equiv 0$, we have $\Phi(0) = c_2(0)$. Then from equation (29) it follows that $\Phi(t) < 2k_{15}{}^2c_1c_0$ for any $t > 0$. Hence we have

$$\varphi(t) < 2k_{15}c_1c_0t + c_2(0).$$

Since for temperatures up to 600°K the rate of disassociation $k_{15} < 10^{-7}$, and the balanced values of $c_2(0) \leqslant 10^{-8}$, for a time of reaction of the order of one second we have, finally, (for $c_1 \leqslant 1$, $c_0 < 0.05$);

$$c_2(t) + c_4(t) + c_8(t) < 2k_{15}c_0 + c_2(0) \approx 10^{-8}.$$

Taking into account that the values for the concentrations can not be negative, it follows that

$$c_k(t) < 10^{-8} \quad (k = 2,4,8). \qquad (30)$$

At 800°K $c_k(t) < 10^{-6}$. It is evident that for high temperatures this evaluation becomes rougher than that of equation (28).

The rather rough upper evaluation of the magnitude of $c_2(t)$, carried out above, permits the evaluation of the magnitude $\bar{c}_k(t)$ $(k = 4,8)$ in the reaction process. From formula (4) it follows that $a_k(t)$ $(k = 4,8)$ is proportional to c_2. In accordance with Table 1, in the temperature range from 600° to 1200°K, the constants of reaction rates going into $a_k(t)$ do not exceed 10^9 in the dimensionless form. Consequently, for temperatures from 600 to 1200°K, $a_k(t)$ does not exceed 10 and $5 \cdot 10^6$ [sic.] respectively. In this range and for these conditions, $B_k(t)$ $(k = 4,8)$ is not lower than $2.5 \cdot 10^5$ and $4 \cdot 10^7$, respectively.

As a result in the temperature range being examined the upper evaluation for the magnitude of the quasi-stationary values of the chemically active elements in the reaction process has the following form:

$$\bar{c}_k(t) < 10^{-8}, \quad t > 0, \quad k = 4,8. \qquad (31)$$

It is evident that for temperatures of less than 1200°K the evaluation of equation (31) becomes quite increased.

With the help of the results that have been obtained we shall find a qualitative evaluation of the accuracy of the proposed algorithm of the solution of equation set (12), this solution being connected with the replacement of the differential equations by algebraic equations for the components capable of reaction (Cl, C_2H_4Cl and $C_2H_3Cl_2$) for all $t > t_o = 10^{-5}|\ln \varepsilon|$. Here the same designations will be used that were used in section II,1, where a proof was offered for the accuracy evaluation in its general form.

We shall evaluate the magnitude $N_k(t)$ (see formula 8, section I). From equation set (12) it can be seen that the only term of the first order not containing $c_k(t)$ ($k = 2,4,8$) is $k_{15}c_1c_o$. This term, which characterizes the disassociation of chlorine, does not exceed $2.5 \cdot 10^{-3}$ in the temperature range from 600 to 1200°K and is quite small compared with $B_k \gg 10^5$. Only concentrations of the reactive components c_4 and c_8 go into the other first-order terms. In addition, in the second-order terms, at least one of the concentrations coincides with c_2c_4 or c_8. Thus, in agreement with the evaluations of equation (28) and equation (31), $c(t)$, $j = 1,2,..,12$, are at least three orders of magnitude less than the maximum for the constants of reaction rates in the positive terms in the right-hand sides of the corresponding equations. Here the derivatives of the concentrations of the reactive components after entry into the quasi-stationary state are quite small. This circumstance enables us to obtain an evaluation for the magnitude of $\dot{a}_k(t)$, $\dot{b}_k(t)$ ($k = 4,8$) and also for $\dot{a}_2(t)$, $\dot{b}_2(t)$ when there is a surplus of ethylene present and $t > t_o$. Actually, $\dot{a}_k(t)$ (where $k = 2,4,8$) is composed of the final sum of terms having the form $k_i \dot{c}_j$ and $k_i(\dot{c}_m c_n + \dot{c}_n c_m)$, which are obtained by differentiating the respective first and second order terms. It is evident that the first of the indicated terms are small, since the corresponding components are capable of reaction.

Let us assume that c_n has little capability of reaction (then c_m is quite reactive). Hence in the worst case from the standpoint of evaluation (when T = 1200°K) we shall obtain $k_i(\dot{c}_m c_n + \dot{c}_n c_m) < 10^{-6}k_i k_r$, where k_r is the greatest of the constants of rates of reaction in the right-hand side of $\dot{c}_n(t)$. If c_n and c_m are capable of reaction, then the corresponding term will be quite small. As a result we have

$$\dot{a}_k(t) < 10^{12}.$$

In an analogous manner, since $\dot{b}_k(t)$ is composed of terms of the form $k_i c_p(t)$, where c_p may have a small capability of reaction, we have

$$\dot{b}_k(t) \approx 10^{-3} k_i k_r < 10^{11}.$$

Hence in the worst case we obtain

$$|N_k(t)| = \left| \frac{\dot{a}_k(t)}{b_k(t)} - \xi_k \frac{\dot{b}_k(t)}{b_k(t)} \right| < 10^{3},$$

since for a temperature of 1200°

$$b_k(t) > 10^{8}.$$

For $t > t_0$ the error in replacing the concentrations of the indicated components with their quasi-stationary values satisfies the condition

$$z_k(t) < \max\{\varepsilon, R_k\}, \qquad (32)$$

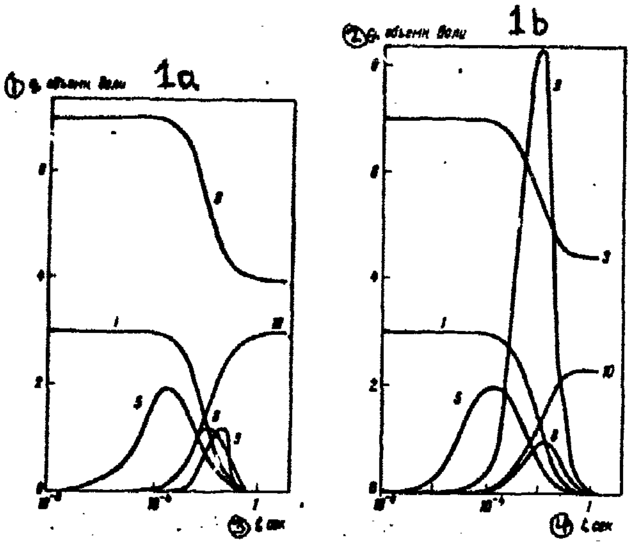
where $R_k < 10^{-6}$ at 1200°K. As follows from equation (30), for lower temperatures R_k is still smaller.

Thus, the proposed algorithm describes the kinetics of chlorination of ethylene and insures the obtaining of a solution with an accuracy sufficient for practical purposes.

4. A discussion of the results of the numerical integration of equation set (12).

Numerical integration of equation set (12) was carried out for various initial conditions of the ratio of the concentration of chlorine to the concentration of ethylene in the temperature range from 600 to 1200°K. The corresponding mathematical experiments were carried out on a computer for evaluating the influence on the solution of equation set (12) of the following: changes in the constants of reaction rates k_{13} and k_{15}; changes in the reaction processes (equation set (11)) by means of excluding individual stages (particularly, reactions 17 and 18 of equation set (11)).

Figures 1a and 1b show in semi-logarithmic scale the results of the numerical integration of equation set (12) without taking into account reactions 17 and 18 in reaction process (11), and with the full set of 12 differential equations [equation set (12)], respectively. The calculations carried out showed that the exclusion of reactions 17 and 18 from the reaction process (11) had insignificant influence on the time dependence of the concentrations of the majority of the components taking part in the reaction. What influence there was exerted to a greater degree on the concentrations of the components which are directly connected with reactions 17 and 18.

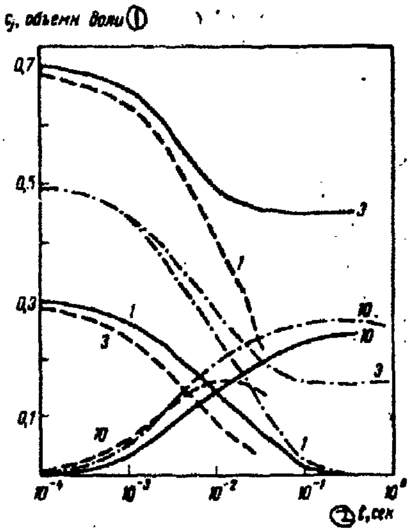


Key:
1. c_i in volumetric shares
2. c_i in volumetric shares
3. t in sec.
4. t in sec.

Figures 1a, 1b. The dependence on time of the concentrations c_i of various components of the reaction a) excluding, and b) including reactions number 17 and 18 of equation set (11) in the reaction process.

Initial ratio to Cl_2 to C_2H_4 = 0.3 : 0.7;^{4} $T = 1200^oK$; 1) 10 $[Cl_2]$; 3) 10 $[C2H_4]$; ^{2}5) 10 $[C_2H_4Cl_2]$; 8) 10^4 $[C_2H_3Cl_2]$; 9) $[C_2H_3Cl_3]$; 10) 10 $[C_2H_3Cl]$. In Figures 1a, 1b the numbers 1--3 and 5--9 on the curves correspond to the numbers of the components in the table immediately following equation set (12).

In order to study the influence of the [initial] conditions of the proportions of the concentrations on the kinetics of the chlorination of ethylene a numerical integration of equation set (12) was carried out for various ratios of chlorine to ethylene. (See Figure 2)



Key:
1. c_i in volumetric shares
2. t in sec.

Figure 2. The dependence on time of concentrations of chlorine, ethylene, and vinylchloride for a temperature of 1200°K and various initial proportions of the concentrations.

Cl : C_2H_4 = 0.3 : 0.7 (solid lines)
Cl : C_2H_4 = 0.5 : 0.5 (mixed dotted and dashed lines)
Cl : C_2H_4 = 0.7 : 0.3 (dotted lines)
1) Cl_2; 3) C_2H_4; 10) C_2H_3Cl

We examined the case where there was a surplus of chlorine* present, the case of a surplus of ethylene, and also the intermediate case between these two cases. In practice, the chlorination of ethylene is usually carried out with an initial surplus of ethylene in order to maintain isothermal conditions and to avoid having to purge the reaction products of free chlorine.

As can be seen in Figure 2, in the case where $Cl_2 : C_2H_4 = 0.3 : 0.7$, for a time span of about one second, the chlorine is practically expended; thereupon the concentrations of vinylchloride and ethylene do not change further. It is evident that the graph lines for concentrations of ethylene,

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*Of course, such concentrations of Cl_2 are examined only for the purposes of explaining the basic tendencies of the process; in practice a phenomenon having an explosive nature occurs for such concentrations.

vinylchloride, and a number of other components become asymptotic because the chlorine has been expended. In order to exclude this factor, a variant where $Cl_2 : C_2H_4 = 0.7 : 0.3$ was calculated. As can be seen from Figure 2, the kinetics of the process in this case differ markedly from that of the former case: the concentration of vinylchloride reaches a maximum value, after which its intensive decomposition occurs. At the moment when the concentration of vinylchloride reaches its maximum value, the concentration of ethylene is about 0.06 and that of chlorine is about 0.40 (concentrations of the substances are given in volumetric shares).

Thus in the case where $Cl_2 : C_2H_4 = o.7 : 0.3$, as could have been expected, the process tends toward a more intensive chlorination than in the case $Cl_2 : C_2H_4 = 0.3 : 0.7$; the appearance of vinylchloride is decreased, and the concentration of HCl continues to increase even after the concentration of vinylchloride has reached its maximum. Also calculated was the intermediate case where $Cl_2 : C_2H_4 = 0.5 : 0.5$. As can be seen in Figure 2 the concentration of vinylchloride reaches a maximum value of about 0.25 and thereafter practically does not decompose at all.

Also investigated was the question of the influence of the constant of reaction rate of reaction number 13 in the reaction process described by equation set (11) , which is the only reaction in the reaction process we have chosen that leads to the formation of vinylchloride. To this purpose equation set (12) was numerically integrated for a temperature $T = 600^{\circ}K$, an initial ratio of $Cl_2 : C_2H_4 = 1 : 10$, and for values of $\tilde{K}_{13}$ 10 and 100 times larger than the values of k_{13} corresponding to $600^{\circ}K$.

Figure 3 shows the appearance of vinylchloride at time $t = 0.3$ sec. as a function of the value of $\tilde{K}_{13}/k_{13}$. It is easy to see from this figure that the further increase in value of this constant does not lead to a substantial increase in the appearance of vinylchloride.

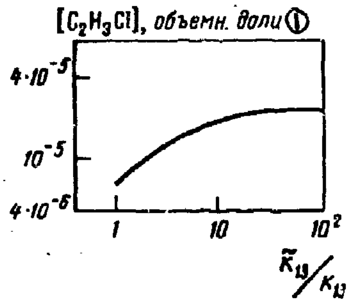

Figure 3. The dependence of the appearance of vinylchloride on the value of K_{13}/K_{13}.

$T = 600^{\circ}K$; $Cl : CH = 1 : 10$

Key: 1) $[C_2H_3CL]$ in volumetric shares.

In connection with the great sensitivity of the process to changes in the constant of reaction rate of disassociation, the question of the influence of changes in magnitude of this constant was studied. There are no exact measurements of this constant; moreover, the possibility of the walls having a significant influence on its magnitude must be taken into account. Therefore calculations were carried out for various values of the energy of activation of disassociation and various values of the constant of reaction rate of disassociation.

Figure 4 shows curves of expenditure of chlorine for conditions of temperature 600°K and initial concentration ratio $Cl_2 : C_2H_4 = 1 : 50$, where constant k_{16} is computed by the formula of Arrenius and not by formula (16). The values 38 and 41 kilocal. per mole [source 20] were taken for the energy of activation of disassociation. For an energy of activation of 38 kilocal. per mole, 81% of the original chlorine was left after 10^{-1}sec.; for an energy of activation of 41 kilocal. per mole, 92.5% of the chlorine was left after 10^{-1}sec.

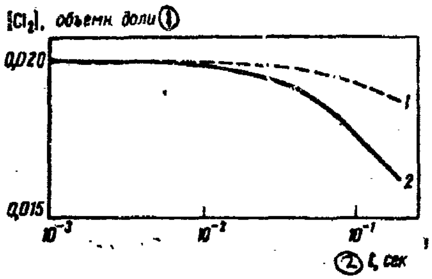

Figure 4. Curves of expenditure of chlorine for E = 41(1) and E = 38 (2) kilocal./mole.
Key:
1. $[Cl_2]$ in volumetric shares
2. t in seconds.

According to data from source [21], for a temperature of 593°K and a speed of supply of the initial mixture of 0.323 moles/liter·sec., the reaction time is $8 \cdot 10^{-2}$sec. and 84.5% of the original amount of chlorine was left. This is in satisfactory agreement with our calculation. At the same time the appearance of vinylchloride, which was obtained as a result of the calculation, for the same conditions already listed was considerably less than that experimentally obtained by the authors of source [21]. Evidently this is connected with the fact that the reaction process used by us has only one route for the formation of vinylchloride--reaction number 13 in equation set (11)--which is insufficient to describe the given process. Actually, as was already shown, even increasing the magnitude of the constant of this reaction (k_{13}) can not insure an appearance of vinylchloride comparable to that obtained experimentally.

This important result, obtained by means of a numerical computation, supports the well-known supposition that the formation of vinylchloride proceeds concurrently by two routes (equations 9 and 10). In other words the formation of a certain part of the vinylchloride is connected with the reaction of direct replacement (equation 10); a calculation for this reaction is as yet impossible because of the lack of data for the constants. Thus the question of the relationship between the reaction of combination and the reaction of replacement in the process of the chlorination of ethylene for various temperature ranges needs further investigation.

There are also a number of experimental results of a qualitative nature from source [21] which agree with the results of our calculations:

1) Under the conditions of experiments described in source [21] HCl and C_2H_3Cl are formed in equi-molecular amounts. The very same conclusion follows from our calculations. (For example, see Figure 1a.)

2) The replacement process has a certain period of induction that decreases with an increase in temperature. A similar dependence on temperature of the period of induction was obtained as a result of the calculations. (See Figure 1a, 1b).

3) With an increase in time the presence of products of combination reaches a maximum and then falls during the continued development of processes of replacement. Such behavior of concentrations of products of combination and replacement was found by means of the calculation. (See Figure 1a, 1b.)

4) In the studied interval from 600 to 660°K, the appearance of products of replacement continuously increases; the appearance of products of combination continuously decreases. Our calculation results also showed that the appearance of products of replacement increases with an increase of temperature, while those of combination decrease. (See Figure 1a, 1b.)

5) In contradiction to the conclusions of source [2], an increased chlorine content in the initial mixture does not facilitate a furtherance of the replacement process but rather only the formation of HCl and products of intensive chlorination. Our calculations also lead to a similar conclusion. (See Figure 2.)

Figure 5 shows curves obtained for temperatures of 600° and 800°K, given a ratio of $Cl_2 : C_2H_4 = 1 : 10$ for the constant of disassociation of chlorine; this constant is 1000 times larger than the one computed by formula (16) and corresponds to an energy of activation of 39.7 kilocal./mole at

600°K and 37 kilocal./mole at 800°K.

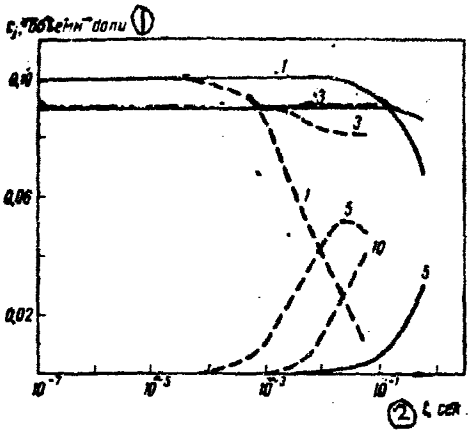

Figure 5. The dependence on time of concentrations of chlorine, ethylene, and di-chlor-ethane, under conditions where k = 1000 k_{15}.

T = 600°K (continuous lines)
T = 800°K (dashed lines)
1) Cl_2, 3) 10^{-1} $[C_2H_4]$,
5) $[C_2H_4Cl_2]$ 10) $[C_2H_3Cl]$
Key:
1) C_j in volumetric shares
2) t; in seconds

Calculations were carried out in which only k_{15} was changed; all other k_i were held constant. Or, all k_i were permitted to change and k_{15} was held constant.

These computations were carried out for the very same initial ratio $Cl_2 : C_2H_4 = 1 : 10$ for the following cases: 1) all constants (including k_{15} calculated for 600°K; 2) k_{15} calculated for 600°K, all other constants calculated for 800°K; 3) all constants of reaction rates calculated for 800°K. Here it turned out that the time required for expenditure of chlorine sharply decreases with an increase in the constant of reaction rate of the disassociation of chlorine. Thus, for instance, for 15% expenditure of chlorine the time required in the first case was about 10^{-1} sec., while in the third case, about 10^{-3} sec.

Thus, in the process of the chlorination of ethylene according to reaction process (11), the value of the constant of reaction rate for the disassociation of chlorine has the greatest influence on the process. Therefore even a relatively small variation in the values of the energy of activation or in the factor before the exponential of the constant of reaction rate of the disassociation of chlorine may substantially distort the results of kinetics calculations, while at the same time, such a variation in the values of the other constants of reaction rates evidently does not have such an influence. Because of this as accurate an experimental determination of the constant k_{15} as possible is desirable, as well as a study of the conditions of the experiment on its value (the ratio of surface to volume, the nature of the walls of the reaction chamber, etc.*)

III. A calculation of the kinetics of the oxidation of methane and a comparison of the results with experimental data.

The reaction of the oxidation of methane may be considered as a model of a large class of complex linked processes of the oxidation of hydrocarbons. (Source [22]).

The most valuable products of the oxidation of methane are formaldehyde, if the oxidation is conducted at pressures not exceeding atmospheric pressure, and methanol, if the reaction occurs at high pressures (about 100 atmospheres). Formaldehyde and methanol are intermediate products of the oxidation reaction; the final products of this reaction are, of course, carbonic acid and water.

In many works devoted to the study of the process of the oxidation of methane, relatively small production of formaldehyde has been achieved for a single passage of the raw material through the reactor. (Sources [23-28]). It is well known that when this reaction is carried out at relatively low temperatures, and for a short period of contact, the methane oxidizes practically totally into formaldehyde. However under these conditions the quantity of oxidized methane is small and consequently, the absolute production of formaldehyde is small. (Source [24]). Raising the temperature or increasing the contact time leads to an increase in the quantity of oxidezed methane, but not to the increase in the production of formaldehyde, which itself under these conditions oxidizes easily.

At the present time the best results in obtaining formaldehyde by the direct oxidation of methane (natural gas) by oxygen in the air are achieved by the method advance in source [25]. The basis of this method is the catalytic action of potassium tetraborate on the oxidation of methane, and the braking action on the oxidation of formaldehyde caused by a nozzle introduced into the reaction chamber. Also nitrous gases are added to the reacting mixture; these catalyze the oxidation of methane. The reacting mixture is composed of about 33% methane and about 67% air. The process is carried out at a temperature of about 1000°K. The time the mixture remains in the reaction chamber, T_{cont}, is about 0.14-0.16 sec. The concentration of nitric oxides is about 10.6% by volume.

The production of formaldehyde for one pass through the

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*The authors thank V. Ya. Shtern, A. F. Revsin, G. V. Gulyaev, A. I. Subbotin, and Yu. A. Treger for their useful comments.

reaction chamber is about 2.4-2.6% of the methane by volume; for circulation six times the production is about 10.6% by volume.

Attempts to analyze the kinetics of this interesting reaction have been made in source [3] for a solution of the problem of a one-dimensional combustion of methane. The basis of these attempts is the method, proposed in source [3], of the linearization of a set of equations which describes the oxidation of methane. It is evident that without obtaining an evaluation of the accuracy of the solution when linearization of the equation set is performed, this method can not be used. (See Section I.) Using the method developed in Section I we have solved on a computer a set of differential equations describing the process of the oxidation of methane.

1. Setting up the problem and the methodology of the computation.

A numerical solution is sought for the set of differential equations describing the kinetics of the gaseous, isothermal oxidation of methane by a mechanism that shall be examined below. In Section I can be found the detailed exposition of the algorithm of numerical integration, to a desired degree of accuracy, developed for complex chemical reactions for any proportions of constants of reaction rates in the equation set of the kinetics, the algorithm which we are using here.

The chemical model used in this article for the process of the oxidation of methane is based on the radical-chain model of the process proposed by N. N. Semenovyy. (See Table 2.*)

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*The authors discussed the mechanism used here in detail with A. B. Nalvandyan, V. Azatyan, V. I. Vedeneyev, and S. S. Polyak, and express their deep appreciation to them.

① № п.п	② Реакция	③ Константа скорости *
1	$CH_4 + O_2 \xrightarrow{k_1} CH_3 + HO_2$	$10^{11} \exp(-55000/RT)$
2	$CH_3 + O_2 \xrightarrow{k_2} CH_3OO$	10^{9}
3	$CH_3OO \xrightarrow{k_3} CH_2O + OH$	$10^{13} \exp(-20000/RT)$
4	$CH_4 + OH \xrightarrow{k_4} CH_3 + H_2O$	$10^{11} \exp(-8500/RT)$
5	$CH_2O + OH \xrightarrow{k_5} H_2O + HCO$	$10^{13} \exp(-6300/RT)$
6	$CH_2O + O_2 \xrightarrow{k_6} HCO + HO_2$	$10^{11} \exp(-32000/RT)$
7	$HCO + O_2 \xrightarrow{k_7} CO + HO_2$	10^{9}
8	$CH_4 + HO_2 \xrightarrow{k_8} H_2O_2 + CH_3$	$10^{11} \exp(-19750/RT)$
9	$CH_2O + HO_2 \xrightarrow{k_9} H_2O_2 + HCO$	$10^{11} \exp(-8500/RT)$
10	$CO + OH \xrightarrow{k_{10}} CO_2 + H$	$10^{11} \exp(-7000/RT)$
11	$CH_4 + H \xrightarrow{k_{11}} CH_3 + H_2$	$1{,}5 \cdot 10^{10} \exp(-11200/RT)$
12	$CH_2O + H \xrightarrow{k_{12}} HCO + H_2$	$4 \cdot 10^{9} \exp(-2000/RT)$
13	$CH_3 + CH_3 \xrightarrow{k_{13}} C_2H_6$	10^{10}
14	$HO_2 + HO_2 \xrightarrow{k_{14}} H_2O_2 + O_2$	10^{10}
15	$OH + HO_2 \xrightarrow{k_{15}} H_2O + O_2$	10^{10}
16	$H + HO_2 \xrightarrow{k_{16}} H_2 + O_2$	10^{10}
17	$CH_3 + HO_2 \xrightarrow{k_{17}} CH_4 + O_2$	10^{10}

④ * Все константы, за исключением k_3, имеют размерности л/моль·сек; k_3 — имеет размерность сек$^{-1}$.

Table 2. The mechanism of the oxidation of methane.
Key:
1. Number
2. Reaction
3. Constant of rate of reaction rate.
4. All constants with the exception of k_3 have the dimensions liter/mole·sec. The constant k_3 has the dimension sec.$^{-1}$.

As can be seen, reaction #1 is a reaction representing the start of the chain; reactions #2-5 and 7-12 are a continuation of the chain; reaction #6 represents the branching of the chain; reactions #13-17 represent the mass breakage of chains (in which reactions #13 and 14 represent a quadratic breakage). In the same Table 2 are shown the constants of reaction rates corresponding to the various reactions. Most of the values for the constants listed were determined in a temperature range not exceeding about 1000°K. The usual values were used for all recombinational chain breakages.

Using the method of quasi-stationary concentrations, from the set of reaction processes and generally coinciding with it, it is possible to extract expressions for the change over time of the reaction (source [22]). This permits us to establish that the maximum concentration of formaldehyde depends only on the temperature and is determined by the following relationship:

$$[HCHO]_{max} = \exp(-8500/RT)\,[CH_4], \qquad (33)$$

This is close to the result obtained experimentally in source [29]:

$$[HCHO]_{max} \simeq \exp(-10000/RT)\,[CH_4]. \qquad (34)$$

It is essential to note that this relationship is obtained for the case where the intermediate product is formed and disforms itself by means of a chain reaction. It should also be pointed out that the experimental results supporting the validity of relationship (34) were obtained for temperatures not higher than 900°K (source [30]).

For the computations we examined 15 components, for whose concentrations we have adopted the following designations:

Соединение ①	CH_4	O_2	CH_3	HO_2	CH_3OO	CH_2O	OH	
Концентрация ②	c_1	c_2	c_3	c_4	c_5	c_6	c_7	
Соединение ③	H_2O	HCO	CO	H_2O_2	H_2	CO_2	H	C_2H_6
Концентрация ④	c_8	c_9	c_{10}	c_{11}	c_{12}	c_{13}	c_{14}	c_{15}

Key:

1. radical	3. radical
2. concentration	4. concentration

Corresponding to the chemical model chosen, a set of 15 non-linear, ordinary differential equations (35) was set up:

$$
\left.\begin{aligned}
\frac{dc_1}{dt} &= -k_1c_1c_2 - k_4c_1c_7 - k_8c_1c_4 - k_{11}c_1c_{14} + k_{17}c_3c_4 \\
\frac{dc_2}{dt} &= -k_1c_1c_2 - k_2c_2c_3 - k_6c_2c_6 - k_7c_2c_9 + k_{14}c_4^2 + \\
&\quad + k_{15}c_4c_7 + k_{16}c_4c_{14} + k_{17}c_3c_4 \\
\frac{dc_3}{dt} &= -k_2c_2c_3 - 2k_{13}c_3^2 - k_{17}c_3c_4 + k_1c_1c_2 + k_4c_1c_7 + \\
&\quad + k_8c_1c_4 + k_{11}c_1c_{14} \\
\frac{dc_4}{dt} &= -k_8c_1c_4 - k_9c_4c_6 - 2k_{14}c_4^2 - k_{15}c_4c_7 - k_{16}c_4c_{14} - \\
&\quad - k_{17}c_3c_4 + k_1c_1c_2 + k_6c_2c_6 + k_7c_2c_9 \\
\frac{dc_5}{dt} &= -k_3c_5 + k_2c_2c_3 \\
\frac{dc_6}{dt} &= -k_5c_6c_7 - k_6c_2c_6 - k_9c_4c_6 - k_{12}c_6c_{14} + k_3c_5 \\
\frac{dc_7}{dt} &= -k_4c_1c_7 - k_5c_6c_7 - k_{10}c_7c_{10} - k_{15}c_4c_7 + k_3c_5 \\
\frac{dc_8}{dt} &= k_4c_1c_7 + k_5c_6c_7 + k_{15}c_4c_7 \\
\frac{dc_9}{dt} &= -k_7c_2c_9 + k_5c_6c_7 + k_6c_2c_6 + k_9c_4c_6 + k_{12}c_6c_{14} \\
\frac{dc_{10}}{dt} &= -k_{10}c_7c_{10} + k_7c_2c_9 \\
\frac{dc_{11}}{dt} &= k_8c_1c_4 + k_9c_4c_6 + k_{14}c_4^2 \\
\frac{dc_{12}}{dt} &= k_{11}c_1c_{14} + k_{12}c_6c_{14} + k_{16}c_4c_{14} \\
\frac{dc_{13}}{dt} &= k_{10}c_7c_{10} \\
\frac{dc_{14}}{dt} &= -k_{11}c_1c_{14} - k_{12}c_6c_{14} - k_{16}c_4c_{14} + k_{10}c_7c_{10} \\
\frac{dc_{15}}{dt} &= +k_{13}c_3^2
\end{aligned}\right\} \qquad (35)
$$

In the case where the reaction proceeds in a current flow, the proper equations of hydrodynamics should be added to a differential equation set (35) and the aggregate set should be solved together, as was done, for instance, in source [15]. If each of the equations of the set is presented in the form

$$\frac{dy}{dt} = -a^2(t, y)\,y + b^2(t),$$

then, as was shown in Section I,3, when the following condition holds:

$$a^2 \gg \frac{|\ln \varepsilon|}{\tau_0},$$

where τ_0 is the reaction time and ε the required accuracy, several components will enter the so-called quasi-stationary state within a time short by comparison with the reaction time. For this reaction which we are examining--the oxidation of methane--such components are c_5 (since, for instance, when the temperature is 1000°K $a_5^2 = 0.454 \cdot 10^9$) and also under certain circumstances c_7 and c_9 (in particular, when c_1 and c_2 are sufficiently large at the start of the reaction). Here c_5 enters the quasi-stationary state at a time of the order of 10^{-6}, while c_7 and c_9--if the conditions concerning $c_1(0)$ and $c_2(0)$ are fulfilled--enter the quasi-stationary state at a time one or two orders of magnitude later. As was shown earlier in Section I,3, a solution of this set of equations using usual methods is practically impossible, since the indicated equations, for entry of the corresponding concentrations into the quasi-stationary state, yield oscillating, unstable solutions in the numerical integration process. The algorithm used by us enables us to remove this difficulty entirely.

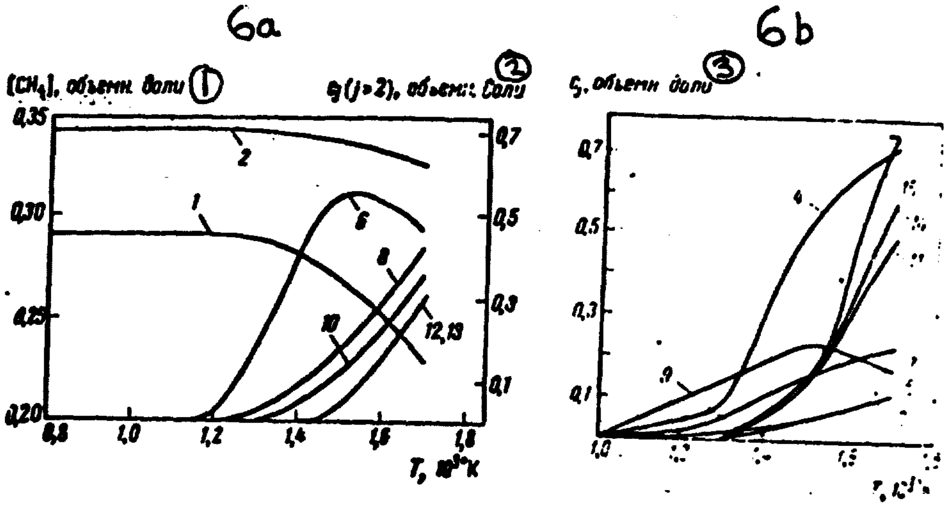
It is important that in this case the equations for the determination of c_5, c_7, and c_9 are independent of each other; this considerably simplifies the computation. The difference between the value of concentration c_5 from its quasi-stationary value becomes negligibly small when $t > |\ln \varepsilon| / k_3$. Moreover, inasmuch as c_7 and c_9 take part in second-order reactions (and consequently, a_7^2 may decrease as a function of the rates of disassociation c_1, c_6, c_{10}, c_4; likewise a_9^2 as a function of the rate of disassociation of c_2), they may with the passage of time leave the quasi-stationary state. Hence, in order to insure the desired degree of accuracy in the computation process, it is essential to check for the satisfying of the conditions for the quasi-stationary condition for c_7 and c_9.

The numerical integration of this set of equations was done by the method of Runge--Kutt with automatic selection of the interval of integration and a relative error of from 10^{-4} to 10^{-5}. Initial concentrations of methane and oxygen ($c_1^0 : c_2^0 = 0.29 : 0.71$) are taken to be the initial conditions of the set of differential equations (35) that is under examination.

2. Discussion of the results of the numerical integration of set (35) and a comparison of them with experimental data.

2a) The functions $c_j = c_j(T)$, $c_j = c_j(t)$, $dc_j/dt = f(t)$.

The numerical integration of equation set (35) was carried out for the temperature range 800-1700°K. As a result, the dependence on time of the concentrations of all substances taking part in the reaction was obtained for various temperatures in this range, as well as curves of their expenditure and formation. The dependence on temperature of all concentrations that was thus found for the instant 10^{-4} sec. is shown in Figures 6a and 6b. Moreover, in order to clarify the influence of chain breakages (see equations #13-17 in Table 2) on the process, calculations were carried out under the same conditions for the reaction process 1-12.



а) 1 — $[CH_4]$; 2 — $[O_2]$; 6 — 10^3 $[CH_2O]$; 8—10 $[H_2O]$; 10—10 $[CO]$; 12—10^3 $[H_2]$; 13—10^3 $[CO_2]$.
б) 3—10^3 $[CH_3]$; 4—10^3 $[HO_2]$; 5—10^7 $[CH_3OO]$; 7—10^4 $[OH]$; 9—10^3 $[HCO]$; 11—10 $[H_2O_2]$; 14—10^4 $[H]$; 15—10^3 $[C_2H_6]$

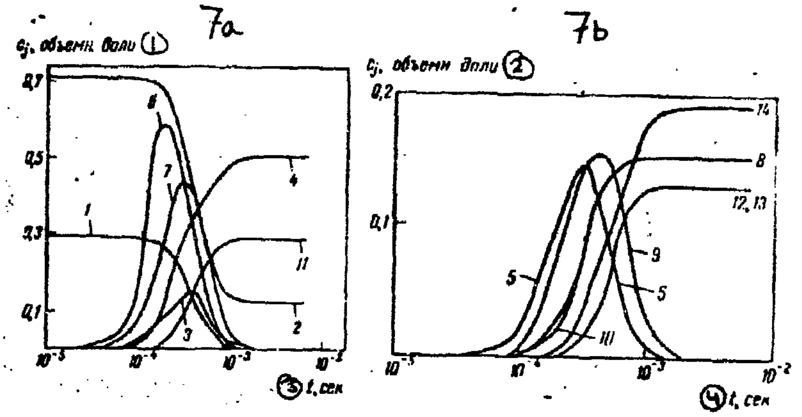
Figures 6a, 6b
The dependence on temperature of concentrations of substances taking part in the oxidation of methane.

Key:

1. $[CH_4]$ in volumetric shares.
2. $c_j (j = 2)$ in volumetric shares.
3. c_j in volumetric shares.

Figures 7a, 7b and 8a and 8b show in semi-logarithmic scale the computation results at 1300°K for the abbreviated (not taking into account chain breakages) and full reaction process, and Figures 9a and 9b show the same curves at 800°K for the full reaction process.

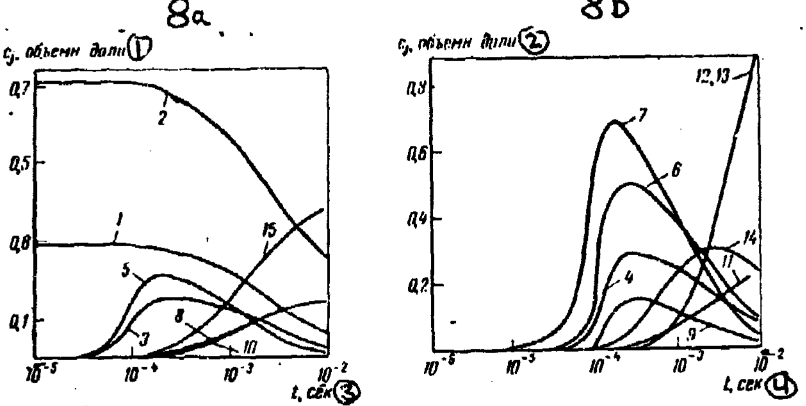
It follows from an examination of Figures 7a and 7b that the curves for concentrations of O_2, HO_2, H, H_2O_2, H_2O, H_2 and CO_2 reach saturation at a time of the order of 10^{-3} sec.



а) 1 — [CH_4]; 2 — [O_2]; 3—10^8[CH_3]; 4—10^3 [HO_2]; 6—10^2 [CH_2O]; 7—10^4[OH]; 11—[H_2O_2].
б) 5—10^8 [CH_3OO]; 8 — [H_2O]; 9—10^2 [HCO]; 10 — [CO]; 12 — [H_2]; 13 — [CO_2]; 14—10^3 [H]

Figures 7a, 7b. The dependence on time of the concentrations for the reaction set #1-12 from Table 1 (without reactions of chain breakage)

Key:
1. c_j in volumetric shares.
2. c_j in volumetric shares.
3. t in seconds.
4. t in seconds.



а) 1 — [CH_4]; 2 — [O_2]; 3—10^8 [CH_3]; 5—10^7 [CH_3OO]; 8 — [H_2O]; 10 — [CO]; 15—10^8 [C_2H_6].
б) 4— 10^3 [HO_2]; 6—10^2 [CH_2O]; 7—10^5 [OH]; 9—10^3 [HCO]; 11 — [H_2O_2]; 12—10 [H_2]; 13 —1 [CO_2]; 14—10^4 [H]

Figures 8a, 8b. The dependence on time of the concentrations for the complete set of reactions #1-17 from Table 2 (including reactions of chain breakage).

Key:

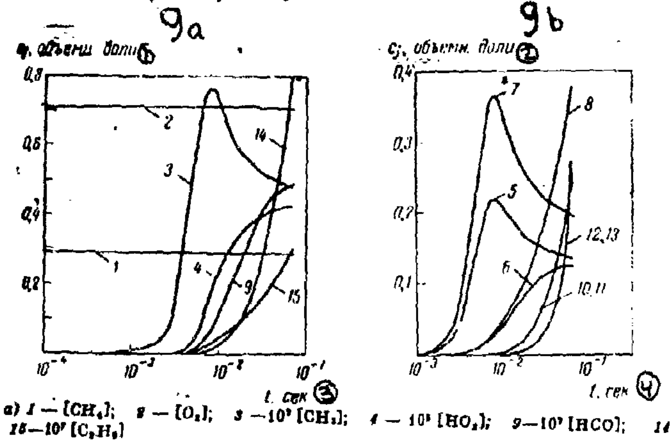
1. c_j in volumetric shares.
2. c_j in volumetric shares.
3. t in seconds.
4. t in seconds.

In the case where the complete set of reactions is examined (see Figures 8a, 8b), as could have been expected, the curves for the concentrations of the radicals (such as HO_2 and H) pass through a maximum, while the concentrations of H_2O, H_2O_2, H_2 and others (which are the products of the reactions of chain breakage continue to increase. For the same temperatures and for the set of reactions #1-12 (see Table 2), calculations were carried out for a decrease in constant k_3 by a factor of 1000, which corresponds to an increase in the energy of activation of, for example, 14 kilocal. at 1000°K and almost 18 kilocal. at 1300°K. Here it would seem that such a decrease in the value of k_3 has practically no effect at all on the process. This situation agrees with N.N. Semenov's proposition that the process of the formation of formaldehyde is determined by the reaction

$$CH_3 + O_2 \rightarrow CH_2O + OH,$$

since reaction #3 follows quite quickly after reaction #2 (See Table 2) (Source [31]).

As could have been expected, with an increase in temperature the curves, while maintaining their likenesses, are displaced ("compressed," and "stretched out") along the time axis. (See Figures 8a, 8b, 9a, 9b.)



a) 1 — $[CH_4]$; 2 — $[O_2]$; 3 — $10^3 [CH_3]$; 4 — $10^3 [HO_2]$; 9 — $10^7 [HCO]$; 14 — $10 [H]$; 15 — $10^7 [C_2H_6]$

) 5 — $10^8 [CH_3OO]$; 6 — $10^2 [CH_2O]$; 7 — $10^7 [OH]$; 8 — $10^2 [H_2O]$; 10 — $10^2 [CO]$; 11 — $10^2 [H_2O_2]$; 12 — $10^4 [CO_2]$; 13 — $10^4 [H_2]$

Figures 9a, 9b. The dependence on time of the concentrations for the full set of reactions.

Key:

1. c_i in volumetric shares.
2. c_j in volumetric shares.
3. t in seconds.
4. t in seconds.

Figures 10 and 11 show the dependence on time of the expenditure of CH_4 and O_2 for temperatures of 1000°K and 1500°K. For purposes of comparison the curves of dependence on time of the concentration of formaldehyde corresponding to these temperatures has been added to these figures. From an examination of Figures 10 and 11 it can be seen that with an increase in temperature the maxima of the expenditure curves of CH_4 and O_2 get closer (in time) to the maximum of the curve for the concentration of CH_2O.

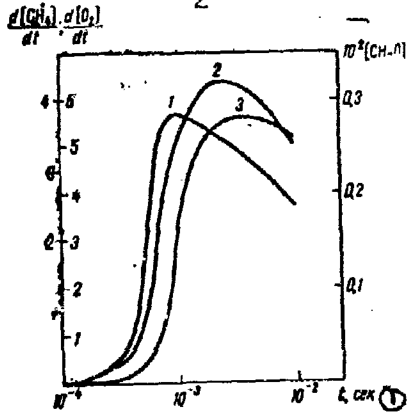


Figure 10. The dependence on time of the rate of expenditure of 1) methane, 2) oxygen, and 3) the concentration of formaldehyde for a complete set of reactions at 1000°K.

Key:
1. t in seconds.

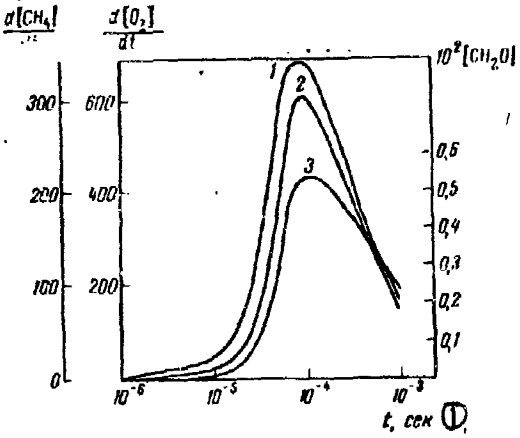


Figure 11. The dependence on time of the rate of expenditure of 1) methane, 2) oxygen, and 3) the concentration of formaldehyde for a complete set of reactions at 1500°K.

Key:
1. t in seconds.

Figure 12 shows the dependence on time of the rate of formation of CH_2O for different temperatures. With an increase in temperature the curves are displaced leftward along the time axis in the direction of smaller times; the maximum values of the curves increase; but their forms do not change.

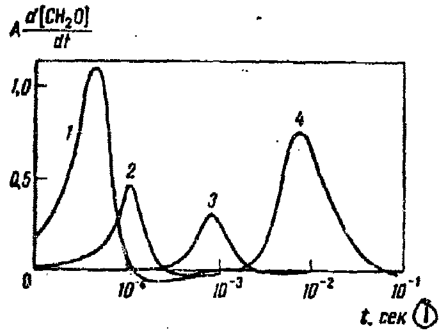


Figure 12. Dependence on time of the rate of formation of formaldehyde for different temperatures.

Key:
1. t in seconds.

1 — T = 1500°K; $A = 10^{-3}$; 2 — T = 1300°K; $A = 10^{-2}$; 3 — T = 1000°K, $A = 10^{-1}$; 4 — T = 800°K, A = 10

In order to study the change in the mechanism of the oxidation of methane in the temperature range under consideration, the length of the chains was calculated. The numerical values for the calculation were taken at points where the concentration of formaldehyde was 90% of its maximum.

The results of the computation were as follows:

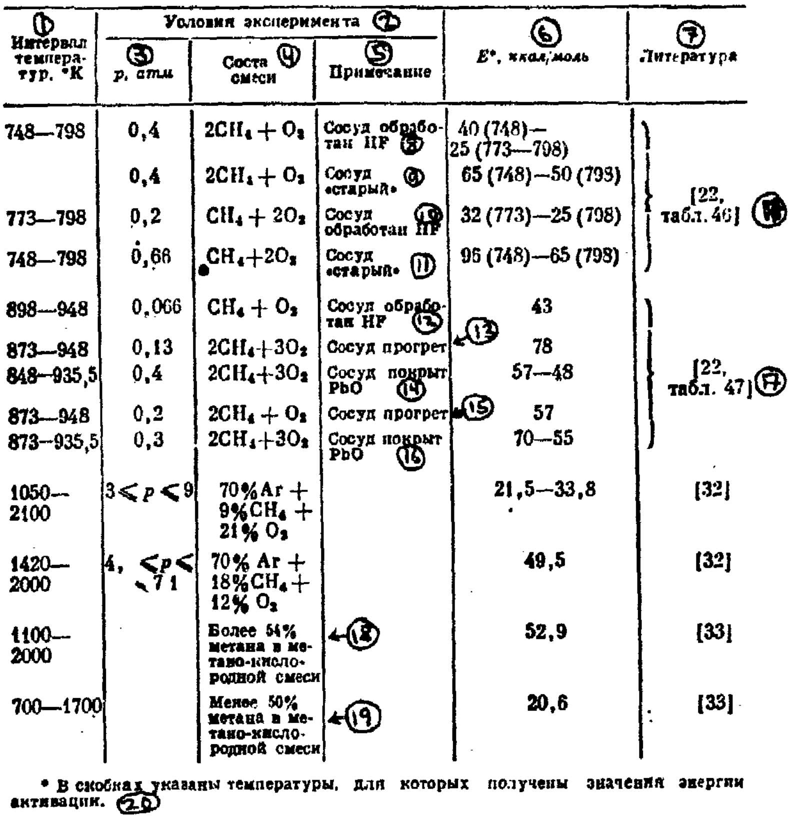
T, °K	1000	1300	1500	1700
① ν (длина цепи) . . .	120	77	17	0,41

Key:
1. ν (the length of the chain)

It is evident from these data that the chain mechanism for the oxidation of methane occurs only up to temperatures of about 1600-1700°K, in which range equation (33), obtained on the basis of a chain process of reactions, is already no longer in effect. We have no data of any kind at our disposal concerning the type of mechanism for the oxidation of methane at higher temperatures. It may be supposed with some degree of certainty that it will be of the free-radical type.

2b) The energy of activation of the oxidation of methane.

As is well known, the energy of activation of the oxidation of methane decreases with an increase in temperature. The corresponding data are presented in Table 3, in which the conditions of the experiment are also indicated, since the numerical values obtained also depend on the condition of the surface of the reaction chamber and the nature of the mixture.



① Интервал темпера-тур. °K	Условия эксперимента ②			⑥ E^*, ккал/моль	⑦ Литература
	③ p, атм	Соста ④ смеси	⑤ Примечание		
748—798	0,4	$2CH_4 + O_2$	Сосуд обработан HF ⑧	40 (748)— 25 (773—798)	[22, табл. 46] ⑰
	0,4	$2CH_4 + O_2$	Сосуд «старый» ⑨	65 (748)—50 (798)	
773—798	0,2	$CH_4 + 2O_2$	Сосуд обработан HF ⑩	32 (773)—25 (798)	
748—798	0,66	CH_4+2O_2	Сосуд «старый» ⑪	96 (748)—65 (798)	
898—948	0,066	$CH_4 + O_2$	Сосуд обработан HF ⑫	43	[22, табл. 47] ⑰
873—948	0,13	$2CH_4+3O_2$	Сосуд прогрет ⑬	78	
848—935,5	0,4	$2CH_4+3O_2$	Сосуд покрыт PbO ⑭	57—48	
873—948	0,2	$2CH_4 + O_2$	Сосуд прогрет ⑮	57	
873—935,5	0,3	$2CH_4+3O_2$	Сосуд покрыт PbO ⑯	70—55	
1050—2100	$3 \leqslant p \leqslant 9$	70% Ar + 9% CH_4 + 21% O_2		21,5—33,8	[32]
1420—2000	4, $<p<$ 7 1	70% Ar + 18% CH_4 + 12% O_2		49,5	[32]
1100—2000		Более 54% метана в метано-кислородной смеси ⑱		52,9	[33]
700—1700		Менее 50% метана в метано-кислородной смеси ⑲		20,6	[33]

* В скобках указаны температуры, для которых получены значения энергии активации. ⑳

Table 3. The dependence of the energy of activation upon the conditions of the experiment.

Key:
1. temperature range, °K.
2. conditions of the experiment.
3. p in atmospheres.
4. nature of the mixture.
5. notes.
6. E in kilocal./mole.
7. Source of data.
8. Reaction chamber treated with hydrofluoric acid.
9. Reaction chamber "old."
10. Reaction chamber treated with hydrofluoric acid.

11. Reaction chamber "old."
12. Reaction chamber treated with hydrofluoric acid.
13. Reaction chamber heated up.
14. Reaction chamber covered with lead oxide.
15. Reaction chamber heated up.
16. Reaction chamber covered with lead oxide.
17. table 46, table 47, etc.
18. More than 54% methane in a methane-oxygen mixture.
19. Less than 50% methane in a methane-oxygen mixture.
20. * The numbers in parentheses are the temperatures for which the values of the energy of activation were obtained.

For all of the picture's complexity, it can be seen that the energy of activation decreases with an increase in temperature (and also, evidently, with an increase in pressure).

Source [22] offers several reflections on this subject. At any rate, the indicated tendency is distinctly noticeable in all of the experiments.

In this connection let us examine the energies of activation of the oxidation of methane shown in Table 4, which were derived from the relationships:

$$\ln\left|\frac{d[CH_4]}{dt}\right|_{\max} = f\left(\frac{1}{T}\right) \quad (1),$$

$$\ln\left|\frac{d[O_2]}{dt}\right|_{\max} = f\left(\frac{1}{T}\right) \quad (2),$$

$$\ln\left|\frac{d[CO]}{dt}\right|_{\max} = f\left(\frac{1}{T}\right) \quad (3),$$

$$\ln\left|\frac{d[H_2O]}{dt}\right|_{\max} = f\left(\frac{1}{T}\right) \quad (4).$$

① Интервал температур, °К	E, ккал/моль ②			
	1	2	3	4
1200—1300	25,0	24,2	30,0	32,8
1300—1400	25,0	23,62	26,6	28,0
1500—1600	18,6	18,6	18,2	17,0

Key:
1. Temperature range, °K.
2. E in kilocal./mole.

Table 4. Various values for the energy of activation of the oxidation of methane.

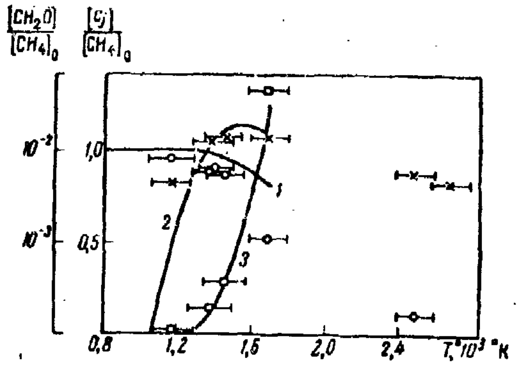
It can be seen from Table 4 that the tendency (noted in the experiments listed in Table 3) for the energy of activation of the oxidation of methane to decrease for an increase in temperature--that this tendency derives from the mechanism shown in Table 2, because the data of Table 4 are the mathematical consequence of a computation of that mechanism.

The values for the energy of activation calculated by different methods agree well with each other, with the exception of the values determined in the 1200-1300°K range using the expenditure of CH_4 and O_2, on the one hand, and using the formation of CO and H_2O, on the other hand. The reason for this discrepancy is not clear, although the problem was noted in several sources (source [32]).

2c) Comparison of computation results with experimental data.

An experimental investigation of the oxidation of methane was conducted in a plasma stream of argon (sources [34], [35]). We shall compare these experimental data with the results of the computation. First of all it must be noted that the results of experiemnts in a stationary plasma stream at atmospheric pressure for various chemical reactions agree well with data obtained under static conditions (source [36]). The error of temperature measurement in sources [34], [35] was ± 10 - 12%, which does not exceed the usual errors in that temperature range; the error in measuring the concentrations of most of the gases was ± 5%, and that in the determination of CH_2O was ± 20%.

The following can be seen from an examination of Figure 13:



$1 - \frac{[CH_4]}{[CH_4]_0}$ (○—экспериментальные точки) ①; $2 - \frac{[CH_2O]}{[CH_4]_0}$ (□ — экспериментальные точки) ③;
$3 - \frac{[CO]}{[CH_4]_0} \cdot 10^1$ (×—экспериментальные точки) ②

Figure 13
A comparison of calculated curves with experimental data.
Key:
1. experimental points.
2. experimental points.
3. experimental points.

1) the experimental points for the temperature interval of calculation from 800 to 1700°K satisfactorily agree with the calculated curves.

2) Both the calculated curve and the experimental data for the formation of formaldehyde show a maximum approximately in the 1500-1600°K range. Thus, this important result of the calculation is fully confirmed by experiment. It is essential to note that this maximum determines a formerly unknown frontier in the usefulness of equation (33). It remains an open question whether this frontier is connected with a change in the mechanism of reaction or occurs for some other reason.

3) Calling attention to itself is the fact that production of CH_2O (curve 2 in Figure 13) grows considerably faster up to the maximum point than it decreases after the maximum. This is easily seen from an examination of the experimental data and is noticeable on the calculated curve (although the part of the calculated curve after the maximum is not large).

Let us now compare the calculated data shown in Table 4 with the result of a calculation of the energy of activation found in source [35] for pressure p = 1 atmosphere (See Table 5).

① Интервал температур, °K	E, ккал/моль ②					
	1		2		3	
	вычисл. ③	эксперим. ④	вычисл. ⑤	эксперим. ⑥	вычисл. ⑦	эксперим. ⑧
1200—1300	$25 \cdot 10^3$	$(29{,}6 \pm 6) \cdot 10^3$	$24{,}2 \cdot 10^3$	$(18{,}3 \pm 3{,}9) \cdot 10^3$	$30{,}0 \cdot 10^3$	$(28{,}5 \pm 4{,}8) \cdot 10^3$
1500—1600	$18{,}6 \cdot 10^3$	$(10{,}0 \pm 3{,}3) \cdot 10^3$	$19{,}6 \cdot 10^3$	$(10{,}6 \pm 2{,}1) \cdot 10^3$	$18{,}2 \cdot 10^3$	$(18{,}0 \pm 3{,}1$

Table 5. Values of the energy of activation determined by 1) the expenditure of CH_4, 2) the expenditure of O_2 and 3) the formation of CO.

Key:

1.	temperature range, °K	5.	calculated
2.	E in kilocal./mole	6.	experimental
3.	calculated	7.	calculated
4.	experimental	8.	experimental

If the inaccuracies of the experiment and of the initial data for the calculation are taken into account, then the agreement between calculated and experimental values of the energy of activation must be conceded to be a good one. Thus, the experimental data and the calculation according to the mechanism of Table 2 agree and both indicate what has already been mentioned by many authors--that the energy of activation of the oxidation of methane decreases with an increase in temperature.

In conclusion we shall make one comment in the spirit of the proposition developed later in this book [in a chapter much later than the chapter here being translated..Trans.] about using the computer to search for the most probable mechanism of this or that chemical reaction. For the calculation of the mechanism of reaction of the oxidation of methane, listed in Table 2, we have: a good approximation by experimental points; the absence of the influence of K_2 on the oxidation process; the fulfilling within discrete limits of equation (34); the agreement of the calculated values for the energy of activation with experimental observations, and the fulfillment of the experimentally-found tendency for the energy of activation to decrease with an increase in temperature. Although we did not examine other possible mechanisms for the oxidation of methane (this was not the purpose of the present article), a review of the results, which were not earlier inserted into the computer program, shows that the mechanism of Table 2 is, at the least, one of those which correctly reflect both the totality and the sequence of stages of the reactions of the real process of oxidation of methane.

IV. The influence of initial conditions on the solution of a set of equations of chemical kinetics and hydrodynamics (for example the pyrolysis of methane in a current stream).

An investigation of chemical processes (especially the non-isothermal ones in a current, which are one of the more widely encountered types in chemical technology), demands a clarification of the effect of a change in the initial conditions (temperature, the ratios of concentrations, etc.) on the solution of the differential equation set that is the model of the process. In this section, using the pyrolysis of methane in a plasma stream as an example, such an investigation is carried out by means of a numerical solution on an electronic digital computer.* In source [15], on the mathematical model of a plasma-chemical process of the conversion of methane to acetylene, the following items were taken: the initial temperature T(0), the initial speed v(0) of the plasma stream, the

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*In an appendix [to the book in which this article is found, on p. 232] the question of using electronic analog computers for problems of this type is discussed.

initial concentration $\tilde{c}_1(0)$ of methane; and the influence of these items on the maximum concentration of acetylene $\tilde{c}_3(z_m)$, the length of the reaction chamber $\underline{L}$, and other magnitudes was studied. As a result it was noted that the dependence of $\tilde{c}_3(z_m)$, $\underline{L}$, and other variables on the initial conditions enables us to take a look at the possibility of optimally controlling the plasma-chemical process by means of corresponding changes in these [initial] conditions.

We regard the plasma-chemical reaction chamber as a device of automatic control. It is well known that in order to describe a device of automatic control, it is necessary to specify the relationships between its outputs and inputs. These relationships may be found for a plasma-chemical reaction chamber by using the mathematical model of source [15] of the process of the conversion of methane to acetylene. In this source was examined the following set of ordinary, non-linear differential first-order equations, which to certain degrees of approximation simulate the plasma-chemical reaction of the conversion of methane to acetylene in a hydrogen plasma stream:

$$\left.\begin{aligned}
\frac{d\tilde{c}_1(z)}{dz} &= -\frac{1}{v(z)} k_1(T)\tilde{c}_1(z)\\
\frac{d\tilde{c}_2(z)}{dz} &= \frac{1}{v(z)}\left[\frac{1}{2}\frac{\mu_2}{\mu_1} k_1(T)\tilde{c}_1(z) - k_2(T)\tilde{c}_2(z)\right]\\
\frac{d\tilde{c}_3(z)}{dz} &= \frac{1}{v(z)}\left[\frac{\mu_3}{\mu_2} k_2(T)\tilde{c}_2(z) - k_3(T)\tilde{c}_3(z)\right]\\
\frac{d\tilde{c}_4(z)}{dz} &= \frac{1}{v(z)}\, 2\frac{\mu_4}{\mu_3} k_3(T)\tilde{c}_3(z)\\
\frac{d\tilde{c}_5(z)}{dz} &= \frac{1}{v(z)}\left[\frac{\mu_5}{\mu_1} k_1(T)\tilde{c}_1(z) + \frac{\mu_5}{\mu_2} k_2(T)\tilde{c}_2(z) + \right.\\
&\qquad \left. + \frac{\mu_5}{\mu_3} k_3(T)\tilde{c}_3(z)\right]\\
\frac{dT(z)}{dz} &= -\frac{\left[\frac{N}{M} - 2v(z)\right]\sum_{j=1}^{6}\frac{d\tilde{c}_j(z)}{dz}h_j + v(z)RT(z)\sum_{j=1}^{6}\frac{d\tilde{c}_j(z)}{dz\mu_j}}{\left[\frac{N}{M} - 2v(z)\right]\sum_{j=1}^{6}\tilde{c}_j(z)\frac{du_j}{dT} + v(z)R\sum_{j=1}^{6}\tilde{c}_j(z)/\mu_j}\\
\frac{dt}{dz} &= \frac{1}{v(z)}
\end{aligned}\right\}, \quad (36)$$

where

$$v(z) = \frac{N}{2M} - \sqrt{\left(\frac{N}{2M}\right)^2 - RT(z)\sum_{j=1}^{6}\frac{\tilde{c}_j(z)}{\mu_j}}$$

($\underline{N}$ and $\underline{M}$ are constants determined by the initial conditions.)

The numerical integration on a computer of the equation set (36), for a given aggregate of constants of reaction rates $k_1(T)$, $k_2(T)$, and $k_3(T)$, enables us, by changing the initial conditions $T(0)$, $v(0)$, and c (0), to establish a dependence on $T(o)$, $v(0)$, $\tilde{c}_1(0)$ of the solutions of this equation set for any $\underline{z}$. In connection with this it is natural to take the magnitudes $T(0)$, $v(0)$, and $\tilde{c}_1(0)$ as inputs to the plasma-chemical reaction chamber.*

The choice of magnitudes [variables] to be taken as outputs depends on the end-purpose of the process and is, to a certain extent, given. As quantities to be taken as outputs of the plasma-chemical reaction in this article the following will be examined, all determined at the point where the concentration of acetylene reaches a maximum (z_m):

a) the length of the segment measured from the end of the reaction chamber $z = 0$ to $z = z$. This segment, in which the reaction of the conversion of methane to acetylene takes place for the most part, is designated L and is called the effective length of the plasma-chemical reactor, in accordance with the term used in source [37];

b) the maximum of the concentration of acetylene, $\tilde{c}_3(z_m)$;

c) the degree of decomposition of methane.

$$s = \frac{\tilde{c}_1(0) - \tilde{c}_1(z_m)}{\tilde{c}_1(0)}. \qquad (37)$$

Each of the outputs is a function of all of the inputs, and also parametrically depends on the constants of reaction rates k_1, k_2, and k_3, which are coefficients in equations set (36). That is:

$$\left.\begin{aligned} L &= g_1[T(0), \tilde{c}_1(0), v(0); k_1, k_2, k_3] \\ \tilde{c}_3(z_m) &= g_2[T(0), \tilde{c}_1(0), v(0); k_1, k_2, k_3] \\ s &= g_3[T(0), \tilde{c}_1(0), v(0); k_1, k_2, k_3] \end{aligned}\right\}. \qquad (38)$$

---

*We shall not further be interested in the dependences of the outputs on input $v(0)$, since it is shown in source [15] that a change in $v(0)$ does not influence the kinetics of the chemical reactions, but only changes the special extent of the process.

Because equation set (36) can not be solved analytically, it is impossible to determine directly the functional dependences (38) of the outputs using the inputs and constants k_1, k_2, and k_3. However, numerical integration by computer of our equation set enables us to solve the following problems:

1) The construction of the approximate dependence of the outputs on the inputs for a given choice of the constants k_1, k_2 and k_3. These dependences will be called the static characteristics of the plasma-chemical reactor in the discussion to follow.

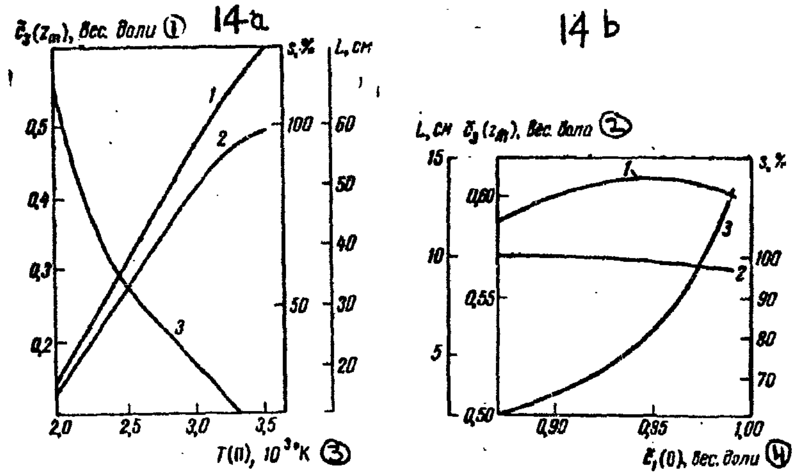
2) The clarification of the degree to which the static characteristics of the plasma-chemical reactor change for a change in the aggregate of constants k_1, k_2, and k_3, and as a result of this, the examination of the influence of an inaccurate determination of the constants of reaction rates on the outputs of the reactor. Differences in the values of the outputs for fixed inputs, caused by changes in one or another of the constants of reaction rates, may serve as a measure of the sensitivity of the mathematical model of the plasma-chemical reactor to such changes in these constants of reaction rates.

In view of the fact that under real conditions the inputs undergo random perturbations, the problem arises of studying the effect of these perturbations on the outputs of the reactor. We consider this problem as a problem of the passage of a random perturbation through a transformer, the latter in this case being the plasma-chemical reactor. The mathematical expectations concerning the outputs will depend on the statistical characteristics of the perturbations. It is evident that these dependences need not be taken into account when the variation in the value of the outputs caused by an inexact determination of the constants of the reaction rates is considerably larger than the changes in outputs caused by random perturbations.

1. Setting up the static characteristics of the plasma-chemical reactor.

By numerically integrating the equation set (36) for five variants of each of the inputs c (0) or T(0) with the other input held constant, it is possible to construct the graphical dependences of all of the outputs L, c_3, z_m and s on each of the inputs $c_1(0)$ and T(0).

Figure 14a shows the dependence of $\tilde{c}_3(z_m)$, s and L on T(0) for fixed values of inputs $\tilde{c}_1(0) = 0.95$ by weight and $v(0) = 3 \cdot 10^4$ cm/sec. Figure 14b shows the dependence of c (z), s and L on c (0) for fixed values of inputs $T(0) = 3.5 \cdot 10^3$ °K and $v(0) = 3 \cdot 10^4$ cm/sec.



Figures 14a, 14b. The dependence of 1) the maximum concentration of acetylene, $\tilde{c}_3(z_m)$, 2) the degree of decomposition of methane, s, and 3) the length of the reactor, L, on different inputs into the plasma-chemical reactor.

Key:

1. $\tilde{c}_3(z_m)$, by weight.
2. $\tilde{c}_3(z_m)$, by weight.
3. T(0), 10^3 °K
4. $\tilde{c}_1(0)$, by weight

Using the curves it is possible to write the approximate analytical dependences between the given inputs and outputs, by means of approximating these curves with linear and quadratic functions.

The dependences of outputs $\tilde{c}_3(z_m)$, L and s on the outputs T(0) and c (0) are shown by the corresponding formulas (39-41) and (42-44).

$$\tilde{c}_3(z_m) = 0{,}125 + 3{,}5\cdot 10^{-4}\{T(0) - 2000\}, \qquad (39)$$
$$[2000 \leqslant T(0) \leqslant 3000^\circ\,\text{K}].^*$$

$$\tilde{c}_3(z_m) = 0{,}476 + 3{,}44\cdot 10^{-4}\{T(0) - 3000\} - 1{,}6\cdot 10^{-7}\{T(0) - 3000\}^2, \qquad (39a)$$
$$[3000 \leqslant T(0) \leqslant 3500\,^\circ\text{K}].$$

$$L = 67 - 9\cdot 10^{-2}\{T(0) - 2000\} + 0{,}44\cdot 10^{-4}\{T(0) - 2000\}^2, \qquad (40)$$
$$[2000 \leqslant T(0) \leqslant 3000^\circ\,\text{K}].$$

$$L = 21 - 2{,}6\cdot 10^{-2}\{T(0) - 3000\} - 0{,}8\cdot 10^{-5}\{T(0) - 3000\}^2, \qquad (40a)$$
$$[3000 \leqslant T(0) \leqslant 3500\,^\circ\text{K}].$$

$$s = 24{,}7 + 5{,}83\cdot 10^{-2}\{T(0) - 2000\}, \qquad (41)$$
$$[2000 \leqslant T(0) \leqslant 3000\,^\circ\text{K}].$$

$$s = 83 + 0{,}558\cdot 10^{-1}\{T(0) - 3000\} - 0{,}464\cdot 10^{-4}\{T(0) - 3000\}^2, \qquad (41a)$$
$$[3000 \leqslant T(0) \leqslant 3500\,^\circ\text{K}].$$

$$\tilde{c}_3(z_m) = 0{,}5887 + 0{,}33\{\tilde{c}_1(0) - 0{,}87\}, \qquad (42)$$
$$[0{,}87 \leqslant \tilde{c}_1(0) \leqslant 0{,}93 \text{ вес. доли}].$$

$$\tilde{c}_3(z_m) = 0{,}6085 + 0{,}1758\{\tilde{c}_1(0) - 0{,}93\} - 4{,}29\{\tilde{c}_1(0) - 0{,}93\}^2 \qquad (42a)$$
$$[0{,}93 \leqslant \tilde{c}_1(0) \leqslant 0{,}99 \text{ вес. доли}].$$

$$L = 2{,}0 + 21{,}7\{\tilde{c}_1(0) - 0{,}87\} + 3{,}88\cdot 10^2\{\tilde{c}_1(0) - 0{,}87\}^2, \qquad (43)$$
$$[0{,}87 \leqslant \tilde{c}_1(0) \leqslant 0{,}93 \text{ вес. доли}].$$

$$L = 4{,}7 + 24{,}17\{\tilde{c}_1(0) - 0{,}93\} + 2{,}04\cdot 10^3\{\tilde{c}_1(0) - 0{,}93\}^2, \qquad (43)$$
$$[0{,}93 \leqslant \tilde{c}_1(0) \leqslant 0{,}99 \text{ вес. доли}].$$

$$s = 100; \; [0{,}87 \leqslant \tilde{c}_1(0) \leqslant 0{,}93 \text{ вес. доли}]. \qquad (44)$$

$$s = 100 - 0{,}391\cdot 10^2\{\tilde{c}_1(0) - 0{,}93\} - 0{,}417\{\tilde{c}_1(0) - 0{,}93\}^2, \qquad (44a)$$
$$[0{,}93 \leqslant \tilde{c}_1(0) \leqslant 0{,}99 \text{ вес. доли}].$$

The above formulas for all outputs as functions of the inputs $\tilde{c}_1(0)$ and T(0) show that the plasma-chemical reactor is a non-linear transformer for these inputs, and the curves we have constructed, together with the corresponding approximate analytical expressions, are its non-linear characteristics.

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*Note to formula (39): Within the brackets are indicated the ranges of change of inputs for which these dependences hold.

2. The influence of fluctuating initial conditions on the solution to equation set (36): setting up the problem.

In carrying out the calculations above, the initial conditions $\tilde{c}_1(0)$ and T(0) were assumed to be independent of time. In connection with this the characteristics obtained for the reactor, when the reactor is regarded as a non-linear transformer, are the reactor's static characteristics. Under real conditions the initial concentration of methane and the initial temperature of the gas mixture undergo random fluctuations over time. We shall describe in terms of stationary random functions (source [38],[39]) these mathematically random time fluctuations of the initial concentration $\tilde{c}_1(0)$ and of the initial temperature T(0), assuming $\tilde{c}_1(0)$ and T(0) to be absolutely continuous, normal, random functions of ..* Since the random functions under examination vary over a finite interval $[x_0, x^0]$ (where x is either of the two functions $\tilde{c}_1(0)$ and T(0) it is necessary to use truncated normal distributions (source [40]).

The one-dimensional truncated normal law of distribution has the following form:

$$f_1(x_1) = \begin{cases} 0 & \text{for } x_1 \leqslant x_0, \\ D\dfrac{1}{\sqrt{2\pi\sigma_x^2}}\exp\left[-\dfrac{(x_1 - \langle x\rangle)^2}{2\sigma_x^2}\right] & \text{for } x_0 < x_1 \leqslant x^0, \\ 0 & \text{for } x_1 > x^0, \end{cases} \quad (45)$$

where $x_1 = x(t_1)$ and σ_x is the mean square deviation of the random function. The magnitude D is chosen such that $f_1(x_1)$ is normal to unity in the interval of definition for the random function.

If the inputs of a non-linear transformer are stationary random functions of time, then the transformer's outputs L, $\tilde{c}_1(z_m)$, and s will also be stationary random functions of time (assuming that the non-linear transformer has stationary characteristics). For the determination of the statistical

---

*In order to compare the results obtained for such an approach, with experimental data, it is evident that it must also be assumed that these random functions are ergodic. For this it is sufficient that their self-correlative functions do not approach zero too slowly (source [39]).

characteristics of these random functions we use formulas (39)-(44). Here it is assumed that the non-linear transformer is non-inertial (sources [39], [41], [42]); that is, any output y(t) at a given moment of time $\underline{t}$ is expressed as a function of any input x(t) at the same moment of time:

$$y(t) = \varphi[x(t)]. \tag{46}$$

3. The determination of the mathematical expectations and of the correlation functions of L, $c_3(z_m)$, and s.

The basic practical consideration in the study and construction of non-linear systems at the present time is knowledge of the correlation function and the mathematical expectation of the random output function. The mathematical expectation $\langle y\rangle$ of a stationary random process y(t) for an output of a non-linear transformer is determined in the following way (source [43]):

$$\langle y\rangle = \langle y_1\rangle + \langle y_2\rangle, \tag{47}$$

where

$$\langle y_1\rangle = D\sum_{k=0}^{s} A_{k_1}\left\{\sum_{l=0}^{k} \frac{k!}{l!\,(k-l)!}\,\sigma_x^l(\langle x\rangle - x_*)^{k-l}\,[Q_l(\xi_0) - Q_l(\xi_*)]\right\}, \tag{48}$$

$$\langle y_2\rangle = D\sum_{k=0}^{s} A_{k_2}\left\{\sum_{l=0}^{k} \frac{k!}{l!\,(k-l)!}\,\sigma_x^l(\langle x\rangle - x_0)^{k-l}\,[Q_l(\xi^0) - Q_l(\xi_0)]\right\}, \tag{49}$$

and

$$Q_l(\xi) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\xi} \xi^l \exp\left(-\frac{1}{2}\xi^2\right)d\xi \tag{50}$$

and

$$\xi = \frac{x - \langle x\rangle}{\sigma_x}. \tag{51}$$

Here A_{k1}, A_{k2} are the constant coefficients in formulas (39)-(44), x_0 is the value of $\underline{x}$ dividing the region of variation $[x_*, x^*]$ into two equal parts.

The computational formula for the correlation function of the output $R_y(\theta)$ is written in the following form (source [43]):

$$R_y(\theta) = \sum_{n=1}^{\infty} B_n^2(\langle x\rangle, \sigma_x)\,\frac{r_x^n(\theta)}{n!}, \tag{52}$$

where

$$B_n(\langle x\rangle, \sigma_x) = D\sum_{k=0}^{2}\sum_{l=0}^{k} A_{k_1}\,\frac{k!}{l!\,(k-l)!}\,\sigma_x^l(\langle x\rangle - x_0)^{k-l}[M_{ln}(\xi_0) -$$

$$- M_{ln}(\xi_0)] + D\sum_{k=0}^{2}\sum_{l=0}^{k} A_{k_2}\,\frac{k!}{l!\,(k-l)!}\times$$

$$\times\,\sigma_x^l(\langle x\rangle - x_0)^{k-l}\,[M_{ln}(\xi^0) - M_{ln}(\xi_0)],$$

$$\theta = t_2 - t_1, \tag{53}$$

where $r_x(\theta)$ is the normal self-correlation function of input $\underline{x}$,

$$M_{ln}(\xi) = \int_{-\infty}^{\xi} \xi^{l} \frac{d^{n}\psi(\xi)}{d\xi^{n}}\, d\xi, \qquad (54)$$

$$\psi(\xi) = \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{1}{2}\xi^{2}\right). \qquad (55)$$

In practice in computations using formula (52) it is necessary to be limited by the finite number of terms of order $\underline{m}$. The evaluation of accuracy of the approximated determination of the correlation function $R_y(\theta)$ is given by the following formula (source [43]):

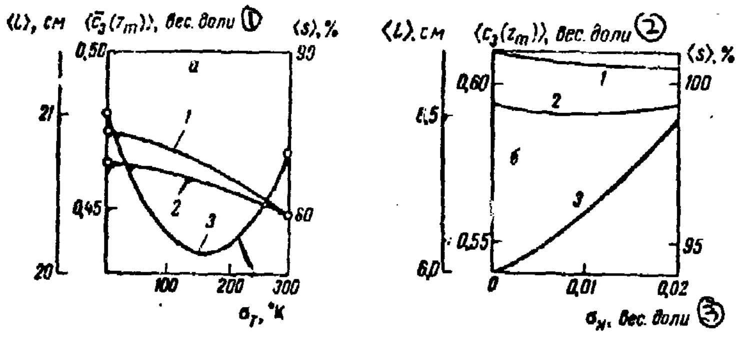
$$|R_y(\theta) - R'_y(\theta)| \leqslant \sigma_y^{2} - \sigma_y'^{2}, \qquad (56)$$

where

$$R'_y(\theta) = \sum_{n=1}^{m} B_n^{2}(\langle x\rangle, \sigma_x) \frac{r_x^{n}(\theta)}{n!}, \qquad (57)$$

$$\sigma_y'^{2} = R'_y(0) = \sum_{n=1}^{m} \frac{B_n^{2}(\langle x\rangle, \sigma_x)}{n!}. \qquad (58)$$

The results of computing the dependences of the mathematical expectations $\langle c_3(z_m)\rangle$, $\langle \underline{s}\rangle$ and $\underline{L}$ on the mean-square deviation of initial temperature (for a given mathematical expectation of the initial temperature $\langle T(0)\rangle = 3000^{\circ}K$ and a constant value of the initial concentration of methane $c_1(0) = 0.95$ by weight) are shown in Figure 15a, curves 1-3 respectively. Figure 15b, curves 1-3 show the dependencies of $\langle c_3(z_m)\rangle$, $\langle s\rangle$, and $\langle L\rangle$ on the mean-square deviation of the initial concentration of methane σ_M (where the mathematical expectation of the initial concentration of methane $\langle c_1(0)\rangle = 0.95$ by weight and the constant of the initial temperature $T(0) = 3500^{\circ}K$ [sic.]).



Figures 15a, 15b.

For Figures 15a, 15b: The dependence of the mathematical expectation of (1) the maximum concentration of acetylene $\langle \tilde{c}_3(z_m)\rangle$, (2) the degree of decomposition of methane $\langle s\rangle$, and (3) the length of the reaction chamber $\langle L\rangle$ on the mean-square deviation of different inputs to a plasma-chemical reactor $v(0) = 3\cdot 10^4$ m/sec.

Key:
1. $\tilde{c}_3(z_m)$, by weight
2. $\tilde{c}_3(z_m)$, by weight
3. $\tilde{c}_3(z_m)$, by weight.

On the basis of these curves the following approximate analytical functions were set up:

$$
\begin{aligned}
&\langle \tilde{c}_3(z_m)\rangle = 0{,}475 - 3{,}166\cdot 10^{-5}\sigma_T - 1{,}833\cdot 10^{-7}\sigma_T^2,\\
&\langle L\rangle = 21 - 1{,}135\cdot 10^{-2}\sigma_T + 0{,}355\cdot 10^{-4}\sigma_T^2,\\
&\langle s\rangle = 83 - 0{,}217\cdot 10^{-3}\sigma_T - 0{,}283\cdot 10^{-4}\sigma_T^2\\
&(\text{for } 0 \leqslant \sigma_T \leqslant 300\,^{\circ}\mathrm{K}).
\end{aligned}
\qquad (59)
$$

$$
\begin{aligned}
&\langle \tilde{c}_3(z_m)\rangle = 0{,}6103 - 0{,}425\,\sigma_M + 9{,}5\,\sigma_M^2,\\
&\langle L\rangle = 6{,}0 + 15\sigma_M + 5\cdot 10^2\sigma_M^2,\\
&\langle s\rangle = 99{,}2 - 40\,\sigma_M + 2\cdot 10^3\sigma_M^2\\
&(\text{for } 0 \leqslant \sigma_M \leqslant 0{,}02\ \%\ \text{by weight}
\end{aligned}
\qquad (60)
$$

A calculation of formulas (52), (53), and (54) gave the following formula for the correlation function of the output $\tilde{c}_3(z_m)$ $R_A(\theta)$. (In the calculation, $m = 3$, $T(0) = 3000\,^{\circ}\mathrm{K}$, $c_1(0) = 0.95$, and $\sigma_T = 100\,^{\circ}\mathrm{K}$):

$$R'_A(\theta) = 1{,}122\cdot 10^{-3} r_T(\theta) + 1{,}62\cdot 10^{-6} r_T^2(\theta) + 6{,}61\cdot 10^{-8} r_T^3(\theta). \quad (61)$$

The relative error in the determination of the correlation function of the output $\tilde{c}_3(z_m)$ is about 10%.

4. The influence of the values of the constants of reaction rates on the inputs of a plasma-chemical reactor, for the high-temperature decomposition of methane and ethylene.

It is well known that the values found by various authors for the energy of activation and the pre-exponential coefficients of the constants of reaction rates, for one or another chemical reactions, often fluctuate over wide ranges; hence, selection of their most probable values is a matter of considerable difficulty. Such a situation is true for the process of conversion of methane into acetylene (sources [44-46]).

Table 6 shows the reaction process and values for the energy of activation and for the pre-exponential coefficients of the consta   of reaction rates which have been obtained by various authors for this process in different experiments using various methods.

Реакция ①	k^0, сек$^{-1}$ ②	E, ккал/моль ③	Литература ④
$2CH_4 \xrightarrow{k_1} C_2H_4 + 2H_2$	$4{,}5 \cdot 10^{13}$ 10^{14}	91 103	[44] [45]
$C_2H_4 \xrightarrow{k_2} C_2H_2 + H_2$	$2{,}57 \cdot 10^{8}$ $2{,}2 \cdot 10^{11}$	40 60	[44] [46]
$C_2H_2 \xrightarrow{k_3} 2C + H_2$	$1{,}7 \cdot 10^{6}$	30	[44]

Table 6. The values of the constants of reaction rates of the process of the pyrolysis of methane, according to various sources.

Key:

1. reaction
2. k^0 in sec.$^{-1}$
3. E in kilocal./mole
4. source.

In order to clarify the question of the sensitivity of the mathematical model of the plasma-chemical reactor to a change in the constants of reaction rates k_1 and k_2, for different initial temperatures $T(0)$, we have constructed the static characteristics reflecting the output $\mathcal{C}_3(z_m)$ as a function of input $T(0)$ for various selections of the indicated constants and for fixed inputs $v(0) = 3 \cdot 10^4$ cm./sec. and $\mathcal{C}_1(0) = 0.9$ by weight. For this purpose an integration by computer was carried out on equation set (36) for the following combinations of constants taken from Table 6;

$$(k_1^A, k_2^A), \ (k_1^B, k_2^A), \ (k_1^A, k_2^C), \ (k_1^B, k_2^C)^*$$

and for the following three inputs of $T(0)$: $2.5 \ 10^3$; $3.0 \cdot 10^3$ and $3.5 \cdot 10^3$, for fixed inputs $v(0) = 3 \cdot 10^4$ cm./sec. and $c(0) = 0.9$ by weight.

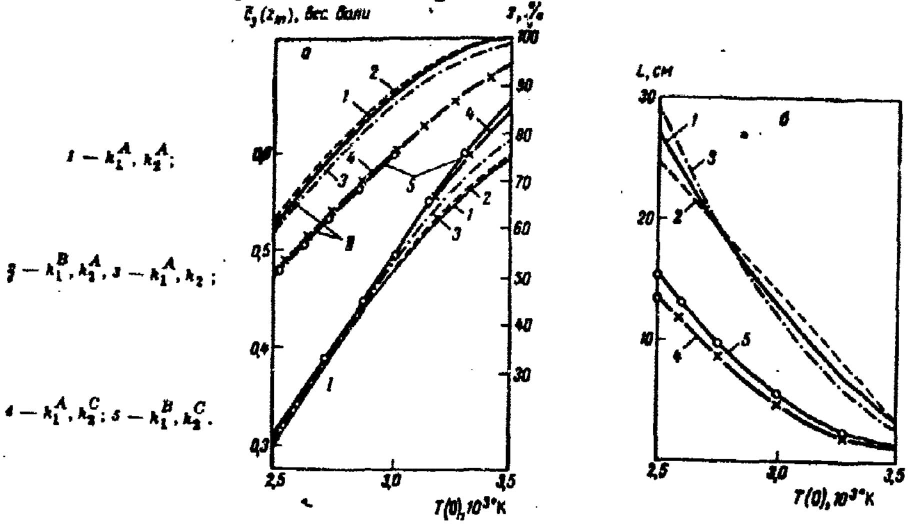
The computations were carried out at the computer center of the Academy of Sciences of the USSR on a "Strela" Arrow computer using the Adams-Stermer method with automatic selection interval of integration and a relative accuracy of 10^{-4}. The computation time for one variant was about 10 minutes. The statistical characteristics obtained as a result of these com-

---

*The indices A, B, and C for the constants of reaction rates of the chemical reactions indicate that they were taken from sources [44], [45], and [46] respectively. The constant k_3 was in all cases the same (see Table 6).

putations are shown in Figures 16a, 16b. An examination of the curves shown in these figures permits the following qualitative conclusions to be made:

1. As could have been expected, the influence of a change in the constants of reaction rates was different for different temperature ranges.



Figures 16a, 16b. The dependence of various outputs of a plasma-chemical reactor on the initial temperature T(0) for different selections of constants of reaction rates k_1 and k_2. 16a: the maximum concentration of acetylene, $\tilde{c}_3(z_m)$ (curves I) and the degrees of decomposition of methane, S (curves II). 16b: the length of the reaction chamber.

Key:
1. $\tilde{c}_3(z_m)$, shares by weight.

2. Replacing the constant of the reaction rate of the decomposition of methane k_1^A with k_1^B has practically no effect on the values and intervals of the curves, but replacing the constants of reaction rates of the decomposition of ethylene (k^A for k_2^C) has a substantial effect on the curves. This is naturally explained by the fact that in the given temperature range, the relative change k_1 is small compared to the relative change of k_2.

3. In accordance with the physical sense of the constant of reaction rate of a chemical reaction, a change in k_2 most of all affects the effective length of the reaction chamber (that is, in practical terms, it affects the time of the reac-

tion up to the point when the formation of C_2H_2 reaches a maximum). It affects less the absolute magnitude of this maximum. Hence it follows that the experimental value of k_2 must be determined with far greater accuracy, and the possible sources of errors and discrepancies in the values of K_2 obtained in sources [44] and [46] should be analyzed.

In order to clarify the effect on the numerical solution of equal relative changes of k_1 and k_2, we examined the intermediate value of the latter constant $k_2' = 5.8 \cdot 10^9 \exp(-51/RT)$, for which

$$\frac{k_2}{k_2^A} = \frac{k_1^B}{k_1^A},$$

that is, its relative change is equal to the relative change of k_1.

Figures 16a and 16b show the results of the computation, given equal relative changes in k_1 and k_2. As could have been expected, the effect of replacing k_2^A with k_2 is somewhat larger than that of replacing k_1^A with k_1^B (the relative change of the constants in both cases being equal). The influence on the time of the reaction is not large and decreases with an increase in temperature. The influence on $\tilde{c}_3(z_m)$ is somewhat greater for higher temperatures than for lower ones, and greater than the influence of an equal relative change of k_1^A for k_1^B.

It is possible that the results found above have a somewhat more general significance for the high-temperature processes that are a successive link in the chain of conversions. In each concrete case the decisive role will of course be played by the ratios of the magnitudes of the constants and the "remoteness" of the reaction to which they relate from the end product whose output is being monitored. At the present time there is no criterion to indicate to what degree this or that constant of reaction rate affects the output of the plasma-chemical reactor. The results obtained point to a possibility of using the following sensitivity criterion of the outputs of the plasma-chemical reactor to a change in a constant of reaction rate:

$$\eta = \frac{[\tilde{c}_3(z_m)]_{k_I} - [\tilde{c}_3(z_m)]_{k_{II}}}{[\tilde{c}_3(z_m)]_{k_I}} \left[\frac{k_I - k_{II}}{k_I}\right]^{-1},$$

where $[\tilde{c}_3(z_m)]_{k_I}$, $[c_3(z_m)]_{k_{II}}$ are the values of output $\tilde{c}_3(z_m)$ corresponding to two different values of the same constant of reaction rate, k_I and k_{II} respectively.

It is possible to construct analogous criteria of sensitivity for the outputs L and S.

In conclusion we note that the question touched on above is a part of a more general problem concerning the sensitivity of solutions of an equation set of chemical kinetics to the change of the constants of reaction rates that are embodied in the equation set (see Section V, beginning).

The investigation that has been carried out allowed us, to construct the static characteristics of the process and to show that the reactor may be regarded as a non-linear transformer. In the latter sense approximate analytical dependences may be established between the inputs (for instance, the initial concentration of methane $\tilde{c}_1(0)$, the initial temperature T(0) of the gas mixture) and the outputs, that is to say, the magnitudes characterizing the process of conversion of methane to acetylene (for instance, the maximum concentration of the end product $\tilde{c}_3(z_m)$, the effective length of the reaction chamber $\underline{L}$, and the degree of decomposition of methane, $\underline{s}$). These dependences may be established for several selections of constants.

The relationships found for reactor outputs as functions of reactor inputs enable the clarification of the degree of sensitivity of various outputs to one particular input, and also the effect of one particular input on various outputs, both for the case of fixed inputs as well as the case of continuous random fluctuations of the inputs. The results obtained for this enable a comparison of the effect on the outputs of fluctuating inputs with the effect on outputs of inaccuracy in the given constants of reaction rates used in the equations. In particular, for the process of the pyrolysis of methane examined above, it can be seen from a comparison of curves 1 in Figures 14a and 14b that in the given region of change for the magnitudes of inputs T(0) and $\tilde{c}_1(0)$, the maximum of the concentration of acetylene $\tilde{c}_3(z_m)$ is more sensitive to a change in input T(0); it is evident that this must be taken into account in the regulation of output $\tilde{c}_3(z_m)$. In the case where the inputs [in our case, T(0) and $\tilde{c}_1(0)$] continuously and stationarily fluctuate, they may be mathematically modeled with the aid of stationary random functions of time. The approximate static characteristics of the process enable us to find the mathematical expectations of the outputs (in this example, $\tilde{c}_3(z_m)$, $\underline{L}$ and $\underline{s}$) as functions of the mean-square deviations of the inputs--in this example, T(0) and $\tilde{c}_1(0)$--and also compute the self-correlation functions of the outputs--for example, $\tilde{c}_3(z_m)$. In particular, the graphs of mathematical expectation $\langle \tilde{c}_3(z_m) \rangle$ in Figures 15a and 15b show that for random oscillations of inputs $\tilde{c}_1(0)$ and T(0), the average value of the output of the end product, acetylene, $\tilde{c}_3(z_m)$ may be as much as about 5.5% lower than the value of this magnitude for constant initial conditions.

The static characteristics of the plasma-chemical reactor that have been obtained in this article may be used for the solution of a number of problems:

a) for investigating the question of controlling the end-condition of the process [e.g. achieving a maximum of the concentration of acetylene by means of changes in the inputs $\tilde{c}_1(0)$ and $T(o)$];

b) for solving the more general problem of choosing the optimal (for a given criterion of optimality) value of the inputs--e.g., $T(o)$ and $c_1(o)$ and others.

The correlation functions of outputs and inputs may be used for solving problems of predicting the behavior of outputs of the reactor given fluctuating inputs (by using the theory of prediction of stationary random functions).

It can be seen in Figure 16a that the scatter of values for the output $\tilde{c}_3(z_m)$ caused by inaccuracy in the determination of constants of reaction rates k_1 and k_2, for different values of input $T(0)$, lies in the 2-10% range. Since the decrease in output $\tilde{c}_3(z_m)$ due to random fluctuations of inputs is of about the same order of magnitude, these fluctuations must be taken into account in any calculation for the plasma-chemical reactor.

The approach developed in this article may be applied without difficulty to problems with a great number of inputs, outputs, and constants of reaction rates.

It should be noted that we have examined, strictly speaking, one section of the characteristic surface in that multidimensional space called "input-output;" to construct approximately that surface in its entirety could be done only with the expenditure of a large amount of computer time.

In conclusion we note that certain of the problems examined above are problems of information theory as well, and warrant the corresponding written exposition in that field as well .

V. The influence of the values of the constants of reaction rates of chemical reactions on the solution of a set of equations of chemical kinetics (for example, the oxidation of methane).

In looking at one or another variant of a reaction mechanism, chemists evaluate the possible influence of a change in value of certain constants of reaction rates on the course and results of the reaction, if the reactions are relatively non-complex. It is evident that such evaluations of the sensitivity of a reaction mechanism to a change in values of constants of reaction rates, if such evaluations are even possible, become more difficult in the case where quite complex reactions are under study. It is in this regard that the problem arises of working out objective, quantitative criteria of "sensitivity" of mechanisms of complex chemical reactions and standard methods for computing these criteria.

As will be shown, the method developed earlier (see Section I) allows us to obtain by computer useful and objective information about the sensitivity of mechanisms under study to changes in different constants of reaction rates in various stages of the reaction, for various conditions under which the reaction is proceeding.

This section is devoted to the working out of a mathematical method which will permit:

1) giving a quantitative expression of sensitivity of this or that reaction mechanism (for a given aggregate of constants) to a change in values of the constants of reaction rates of individual stages, using the quantitative criteria of sensitivity to be introduced below:

2) constructing an algorithm of computation of the criteria we have introduced;

3) finding the dependence on time of these criteria for various conditions under which the reaction is proceeding and for various selections of constants.

This method will aid in increasing the information derived from experimental kinetics data, and will help give the chemist objective criteria for evaluating and comparing the influence of various constants in various stages of this or that reaction.

The methodology proposed is illustrated below for the example of the oxidation of methane.

1. Formulation of the problem.

As is well known the problems of chemical kinetics, from a mathematical point of view, come down to the problem of solving and analyzing sets of non-linear, ordinary differential equations of the first order with coefficients representing constants of reaction rates $k_q (q = 1,2,\ldots,m)$. For the sake of simplicity the exposition that follows examines the case of isothermal reactions (for which all k_q = const.) under static conditions; expanding the results obtained below to non-isothermal reactions in a current stream does not offer difficulties in principle.

The set of equations of chemical kinetics may be written in the following form:

$$\frac{dc_j}{dt} = f_j(c, k)\,(j = 1, 2, \ldots, n) \qquad (62)$$

for initial conditions $c_j(0) = c_j^0$, where the function $f_j(c,k)$ is the sum of terms of the form

$$k_q[c_j]^p[c_k]^s,$$

where c_j are the present concentrations; n is the number of components taking part in the reaction; p,s is the order of the reactions.

The solutions to equation set (62) are functions of time and depend on k_q as well as on the parameters, namely $c_j = c_j(t,k)$. From the linearity of the right-hand sides of equation set (62) relative to k_q, it follows (source [47]) that the derivatives $\partial c_j(t,k)/\partial k_q$ exist and are continuous. Hence the mixed second-order derivative of the functions $c_j(t,k)$ with respect to t and k_q exist and are continuous. Differentiating the equation set (62) with respect to k_q (for a given aggregate of k_q) and designating

$$u_{jq}(t, k) = \frac{\partial c_j}{\partial k_q},$$

we obtain the following set of equations for the functions u_{jq}:

$$\frac{du_{jq}}{dt} = F_{jq}[c(t), u(t), k], \qquad (63)$$

where

$$F_{jq}[c(t), u(t), k] = \frac{\partial f_j[c(t), k]}{\partial k_q} + \sum_{l=1}^{n} a_{jl}[c(t), k]\, u_{lq}[c(t), k],$$

$$a_{jl}[c(t), k] = \frac{\partial f_j[c(t), k]}{\partial c_l}.$$

In view of the fact that the functions F_{jq} depend not only on u_{jq} but also directly on c_j, the equation sets (62) and (63) should be solved concurrently for the following initial conditions:

$$c_j(0) = c_j^0;\; u_{jq}(0) = 0. \qquad (64)$$

The second of the two equalities in conditions (64) reflects the fact that c_j^0 does not depend on the constants of reaction rates k_q.

Solving concurrently the equation sets (62) and (63), we obtain all the concentrations c_j and also functions u_{jq} for all moments of time. At present, it is not possible to solve such equation sets (62) and (63), even for not very complex chemical reactions, except on electronic computers. The method proposed in section I of this article enables us to obtain a numerical solution to the equation sets on a computer, to the required degree of accuracy.

The basic difference between equation set (63) and equation set (62) is that the functions u_{jq} may take both positive and negative values (in distinction from c_j), and also that there are no limits whatsoever on the magnitudes of u_{jq}. These peculiarities of equation set (63) are not crucial if the numerical integration is carried out with the use of the algorithm worked out earlier in this article.

However, it should be taken into account that for the functions u_{jq} as well as for the concentrations c_j, the equation of balance must be satisfied. Actually at any moment of time t $\sum u_{jq}(t) = 0$, and inasmuch as $\sum u_{jq}(0) = 0$ from conditions (64), $u_{jq}(t) = 0$. Thus solving the set of equations (62) and (63), in addition to the information derived from the solution of the equation set (62) of chemical kinetics, also yields quantitative evaluations of the sensitivity of the solutions of equation set (62) to a change in the constants of reaction rates embodied in the equation set.

2. Criteria of the sensitivity of equations of chemical kinetics of isothermal reactions to a change in the constants of reaction rates embodied in the equation set.

Using the numerical solution of equation set (62) and (63) it is possible to determine the following criteria of sensitivity of the set of equations of chemical kinetics (62) to a change in the constants of reaction rates embodied in it.

Most evident, probably, but not the most suitable criterion is the very function itself:

$$u_{jq} = \frac{\partial c_j}{\partial k_q}. \qquad (65)$$

The difficulty in using this criterion is connected with the known fact that k_q may take on various dimensionalities because of the various orders of the reactions that are a part of the mechanism under study. Also the values of k_q may differ from each other by many orders of magnitude. Moreover, the various concentrations c_j may differ greatly from each other, as well as change considerably during the course of the reaction. Because of all of the foregoing it is expedient to introduce the following criteria of sensitivity:*

$$\frac{k_q\,\partial c_j(t,k)}{\partial k_q}=\frac{\partial c_j(t,k)}{\partial \ln k_q}=k_q u_{lq}(t,k), \tag{66}$$

$$\frac{\partial c_j(t,k)}{c_j(t,k)\,\partial k_q}=\frac{\partial \ln c_j(t,k)}{\partial k_q}=\frac{u_{jq}(t,k)}{c_j(t,k)}, \tag{67}$$

$$\frac{k_q\,\partial c_j(t,k)}{c_j(t,k)\,\partial k_q}=\frac{\partial \ln c_j(t,k)}{\partial \ln k_q}=\frac{u_{jq}(t,k)\,k_q}{c_j(t,k)}, \tag{68}$$

$$\frac{k_q}{\tilde{c}_j(k)}\,\frac{\partial c_j(t,k)}{\partial k_q}=\frac{\partial c_j(t,k)}{\tilde{c}_j(k)\,\partial \ln k_q}=\frac{k_q u_{jq}(t,k)}{\tilde{c}_j(k)}, \tag{69}$$

where $\tilde{c}_j(k)$ is some characteristic (depending on the constants of reaction rates k_q as well as on the parameters) value of the concentration of the j-th component. The maximum value of c_j may be taken as $\tilde{c}_j(k)$.

The criteria (65)-(69) give answers to several different questions. For example, criterion (65) shows (for all values of t) to what extent the concentrations c_j change as a result of a change of Δk_q in a constant of reaction rate k_q, where $\Delta k_q \to 0$. At the same time criterion (68) determines for each moment of time the relative change $\Delta c_j/c_j$ in the concentration c_j caused by the corresponding change $\Delta k_q/k_q \to 0$ of the constant k_q, etc. The constants of sensitivity (65)-(69) may be particularly useful in evaluating the influence of a change in each of the constants k_q on any of the concentrations c_j for any moment of time t, and also for evaluating the influence of any of the constants on all or some of the concentrations for any moment of time. It is evident that in the course of this procedure it becomes clear which of the constants, and for what stages of the reactions, (and at what moment in time) are crucial or conversely, have little influence on the reaction (for a given aggregate of k_q). Such research may be carried out for any initial ratios of the concentrations and any initial thermodynamic conditions.

We shall make one more remark. All of the results which have been described concerning the criteria of sensitivity are good for infinitesimally small changes in the constants k_q (for a given aggregate of k_q). In practice, as it is usually done, the final increments of k_q are examined. Inasmuch as the solutions of equation set (62) and (63), yielding $c_j = c_j(t,k)$ and $u_{jq} = u_{jq}(t,k)$ are for most moments of time smooth functions of the parameters k_q, such an assumption does not lead to significant errors if the necessary watchfulness is maintained. It is evident that a sufficient

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*We note that criteria (67) and (68) may be used only when values of $c_j \neq 0$.

mathematical condition for this is the smallness of higher-than-first-order terms in the expansion of the functions $c_j(t,k)$ by degrees Δk_q in size. Since equation set (63) is linear with respect to u_{jq}, the sensitivity of the concentrations to a simultaneous change of several constants k_q may be shown as the sum of the respective sensitivities of the concentrations c_j to a change of the individual constants [taken separately].

3. The reaction of the oxidation of methane.

As an example of the use of the method outlined above we shall examine the isothermal reaction of the gaseous oxidation of methane. The reaction process of this reaction, not including the reactions of chain breakage, is described in sources [48] and [49] and is shown in Table 7. In Table 7 the values of the constants k_q for T = 10^3 °K are converted to the dimension sec.$^{-1}$ using the following relationships:

$$\bar{k}_q = k_q c_0;\quad c_0 = \frac{T}{T_0 V_0} = 0{,}122\cdot 10^{-4} \quad \text{moLe/cm}^3$$

where

$$T_0 = 273^\circ\text{K},\ V_0 = 2{,}24\cdot 10^4 \quad \text{cm}^3/\text{mole}$$

Реакция ①	k_{0q}, см³/моль·сек ②	E_q, ккал/моль ③	Значения* k_q, сек⁻¹ (T=1000 °K) ④
$CH_4 + O_2 \rightarrow CH_3 + HO_2$	10^{14}	55	$0{,}116\cdot 10^{-2}$
$CH_3 + O_2 \rightarrow CH_3OO$	10^{11}	0	$0{,}122\cdot 10^{7}$
$CH_3OO \rightarrow CH_2O + CH$	10^{13} **	20	$0{,}425\cdot 10^{9}$
$CH_4 + OH \rightarrow CH_3 + H_2O$	10^{14}	8,5	$0{,}169\cdot 10^{8}$
$CH_2O + OH \rightarrow H_2O + HCO$	10^{15}	6,3	$0{,}512\cdot 10^{8}$
$CH_2O + O_2 \rightarrow HCO + HO_2$	10^{14}	32	$0{,}123\cdot 10^{3}$
$HCO + O_2 \rightarrow CO + HO_2$	10^{11}	0	$0{,}122\cdot 10^{7}$
$CH_4 + HO_2 \rightarrow H_2O_2 + CH_3$	10^{14}	19,75	$0{,}588\cdot 10^{5}$
$CH_2O + HO_2 \rightarrow H_2O_2 + HCO$	10^{14}	8,5	$0{,}169\cdot 10^{8}$
$CO + OH \rightarrow CO_2 + H$	10^{16}	7	$0{,}359\cdot 10^{10}$
$CH_4 + H \rightarrow CH_3 + H_2$	$1{,}5\cdot 10^{13}$	11,2	$0{,}643\cdot 10^{11}$
$CH_2O + H \rightarrow HCO + H_2$	$4\cdot 10^{11}\sqrt{T}$	2	$0{,}563\cdot 10^{8}$

* $k_q = k_{0q}\exp(-E/RT)$. ** $[k_{03}]$ = сек⁻¹. ⑤

Table 7. The mechanism of the oxidation of methane.

Key:
1. reaction
2. cm³/mole-sec.
3. kilocal./mole.
4. the values of k_q in sec.$^{-1}$
5. ** $[k_{03}]$ = sec.$^{-2}$

The equation set (62) for this reaction and the part of equation set (63) corresponding to a change in only one constant of reaction rate, k_1, has the following form:

$$\left.\begin{aligned}
\frac{dc_1}{dt} &= -c_1(k_1c_2 + k_4c_7 + k_8c_4 + k_{11}c_{14})\\
\frac{dc_2}{dt} &= -c_2(k_1c_1 + k_2c_3 + k_6c_6 + k_7c_9)\\
\frac{dc_3}{dt} &= -k_2c_2c_3 + c_1(k_1c_2 + k_4c_7 + k_{11}c_{14} + k_8c_4)\\
\frac{dc_4}{dt} &= -c_4(k_8c_1 + k_9c_6) + c_2(k_1c_1 + k_6c_6 + k_7c_9)\\
\frac{dc_5}{dt} &= -k_3c_5 + k_2c_2c_3\\
\frac{dc_6}{dt} &= -c_6(k_5c_7 + k_6c_2 + k_9c_4 + k_{12}c_{14}) + k_3c_5\\
\frac{dc_7}{dt} &= -c_7(k_4c_1 + k_5c_6 + k_{10}c_{10}) + k_3c_5\\
\frac{dc_8}{dt} &= c_7(k_4c_1 + k_5c_6)\\
\frac{dc_9}{dt} &= -k_7c_2c_9 + c_6(k_5c_7 + k_6c_2 + k_9c_4 + k_{12}c_{14})\\
\frac{dc_{10}}{dt} &= -k_{10}c_7c_{10} + k_7c_2c_9\\
\frac{dc_{11}}{dt} &= c_4(k_8c_1 + k_9c_6)\\
\frac{dc_{12}}{dt} &= c_{14}(k_{11}c_1 + k_{12}c_6)\\
\frac{dc_{13}}{dt} &= k_{10}c_7c_{10}\\
\frac{dc_{14}}{dt} &= -k_{11}c_1c_{14} - k_{12}c_6c_{14} + k_{10}c_7c_{10}
\end{aligned}\right\} \quad (70)$$

$$\left.\begin{aligned}
\frac{d}{dt}\left(\frac{\partial c_1}{\partial k_1}\right) &= -\frac{\partial c_1}{\partial k_1}\left(k_1c_2 + k_4c_7 + k_8c_4 + k_{11}c_{14}\right) - \\
&\quad - c_1\left(k_1\frac{\partial c_2}{\partial k_1} + k_4\frac{\partial c_7}{\partial k_1} + k_8\frac{\partial c_4}{\partial k_1} + k_{11}\frac{\partial c_{14}}{\partial k_1}\right) - c_1c_2 \\
\frac{d}{dt}\left(\frac{\partial c_2}{\partial k_1}\right) &= -\frac{\partial c_2}{\partial k_1}\left(k_1c_1 + k_2c_3 + k_6c_6 + k_7c_9\right) - \\
&\quad - c_2\left(k_1\frac{\partial c_1}{\partial k_1} + k_2\frac{\partial c_3}{\partial k_1} + k_6\frac{\partial c_6}{\partial k_1} + k_7\frac{\partial c_9}{\partial k_1}\right) - c_1c_2 \\
\frac{d}{dt}\left(\frac{\partial c_3}{\partial k_1}\right) &= \frac{\partial c_1}{\partial k_1}\left(k_1c_2 + k_4c_7 + k_{11}c_{14} + k_8c_4\right) +
\end{aligned}\right\} \quad (71)$$

$$\left.\begin{aligned}
&\quad + c_1\left(k_1\frac{\partial c_2}{\partial k_1} + k_4\frac{\partial c_7}{\partial k_1} + k_{11}\frac{\partial c_{14}}{\partial k_1} + k_8\frac{\partial c_4}{\partial k_1}\right) - \\
&\quad - k_2c_3\frac{\partial c_2}{\partial k_1} - k_2c_2\frac{\partial c_3}{\partial k_1} + c_1c_2 \\
\frac{d}{dt}\left(\frac{\partial c_4}{\partial k_1}\right) &= -\frac{\partial c_4}{\partial k_1}\left(k_8c_1 + k_9c_6\right) - c_4\left(k_8\frac{\partial c_1}{\partial k_1} + k_9\frac{\partial c_6}{\partial k_1}\right) + \\
&\quad + \frac{\partial c_2}{\partial k_1}\left(k_1c_1 + k_6c_6 + k_7c_9\right) + \\
&\quad + c_2\left(k_1\frac{\partial c_1}{\partial k_1} + k_6\frac{\partial c_6}{\partial k_1} + k_7\frac{\partial c_9}{\partial k_1}\right) + c_1c_2 \\
\frac{d}{dt}\left(\frac{\partial c_5}{\partial k_1}\right) &= -k_3\frac{\partial c_5}{\partial k_1} + k_2c_2\frac{\partial c_3}{\partial k_1} + k_2c_3\frac{\partial c_2}{\partial k_1} \\
\frac{d}{dt}\left(\frac{\partial c_6}{\partial k_1}\right) &= -\frac{\partial c_6}{\partial k_1}\left(k_5c_7 + k_6c_2 + k_9c_4 + k_{12}c_{14}\right) - \\
&\quad - c_6\left(k_5\frac{\partial c_7}{\partial k_1} + k_6\frac{\partial c_2}{\partial k_1} + k_9\frac{\partial c_4}{\partial k_1} + k_{12}\frac{\partial c_{14}}{\partial k_1}\right) + k_3\frac{\partial c_5}{\partial k_1} \\
\frac{d}{dt}\left(\frac{\partial c_7}{\partial k_1}\right) &= -\frac{\partial c_7}{\partial k_1}\left(k_4c_1 + k_5c_6 + k_{10}c_{10}\right) - \\
&\quad - c_7\left(k_4\frac{\partial c_1}{\partial k_1} + k_5\frac{\partial c_6}{\partial k_1} + k_{10}\frac{\partial c_{10}}{\partial k_1}\right) + k_3\frac{\partial c_5}{\partial k_1} \\
\frac{d}{dt}\left(\frac{\partial c_8}{\partial k_1}\right) &= \frac{\partial c_7}{\partial k_1}\left(k_4c_1 + k_5c_6\right) + c_7\left(k_4\frac{\partial c_1}{\partial k_1} + k_5\frac{dc_6}{\partial k_1}\right) \\
\frac{d}{dt}\left(\frac{\partial c_9}{\partial k_1}\right) &= -k_7c_2\frac{\partial c_9}{\partial k_1} - k_7c_9\frac{\partial c_2}{\partial k_1} + \\
&\quad + \frac{\partial c_6}{\partial k_1}\left(k_5c_7 + k_6c_2 + k_9 \quad + k_{12}c_{14}\right) + \\
&\quad + c_6\left(k_5\frac{\partial c_7}{\partial k_1} + k_6\frac{\partial c_2}{\partial k_1} + k_9\frac{\partial c_4}{\partial k_1} + k_{12}\frac{\partial c_{14}}{\partial k_1}\right) \\
\frac{d}{dt}\left(\frac{\partial c_{10}}{\partial k_1}\right) &= -k_{10}c_7\frac{\partial c_{10}}{\partial k_1} - k_{10}c_{10}\frac{\partial c_7}{\partial k_1} + k_7c_2\frac{\partial c_9}{\partial k_1} + k_7c_9\frac{\partial c_2}{\partial k_1} \\
\frac{d}{dt}\left(\frac{\partial c_{11}}{\partial k_1}\right) &= \frac{\partial c_4}{\partial k_1}\left(k_8c_1 + k_9c_6\right) + c_4\left(k_8\frac{\partial c_1}{\partial k_1} + k_9\frac{\partial c_6}{\partial k_1}\right) \\
\frac{d}{dt}\left(\frac{\partial c_{12}}{\partial k_1}\right) &= \frac{\partial c_{14}}{\partial k_1}\left(k_{11}c_1 + k_{12}c_6\right) + c_{14}\left(k_{11}\frac{\partial c_1}{\partial k_1} + k_{12}\frac{\partial c_6}{\partial k_1}\right) \\
\frac{d}{dt}\left(\frac{\partial c_{13}}{\partial k_1}\right) &= k_{10}c_7\frac{\partial c_{10}}{\partial k_1} + k_{10}c_{10}\frac{\partial c_7}{\partial k_1} \\
\frac{d}{dt}\left(\frac{\partial c_{14}}{\partial k_1}\right) &= -\frac{\partial c_{14}}{\partial k_1}\left(k_{11}c_1 + k_{12}c_6\right) - \\
&\quad - c_{14}\left(k_{11}\frac{\partial c_1}{\partial k_1} + k_{12}\frac{\partial c_6}{\partial k_1}\right) + k_{10}c_7\frac{\partial c_{10}}{\partial k_1} + k_{10}c_{10}\frac{\partial c_7}{\partial k_1}
\end{aligned}\right\} \quad (71)$$

Used here for the concentrations (in volumetric shares) of the fourteen components taking part in the reaction are the designations introduced in Section III-1. In order to determine the influence of the magnitude of constant k_1 on the solution of equation set (70), the equation set (70) and (71) must be solved concurrently. In the case where it is necessary to find the influence of a change in other constants, equations analogous to those of equation set (71) must be written and then solved concurrently with equation set (70). Thus it is possible to find the sensitivity of all concentrations with respect to all constants k_q. In order to obtain data about the sensitivity of all concentrations c_j to a change in one constant, it is sufficient to write an equation set of the type (71) and then integrate it concurrently with equation set (70). However, in order to determine the sensitivity of one concentration to a change in all the constants k_q it is necessary to obtain a solution to all $n(m + 1)$ equations for functions c_j and u_{jq}. In order to obtain such a solution it is possible (if the capacity of the computer permits it) to construct and integrate concurrently all $n(m + 1)$ equations. If it impossible to do it all at once, however, then the functions $u_{jq} = \partial c_j / \partial k_q$ should be integrated first for one group of constants, then for another, and so on until all the constants k_q have been included.

The equation set (70) and (71) for various k_q was integrated on the computer 'BESM' at the computing center of the Academy of Sciences of the USSR by the method proposed in Section I-3 of this article with a relative accuracy of from 10^{-4} to 10^{-5}, using automatic selection of the interval of integration. The computation time for one variant, corresponding to changing one of the constants of reaction rates, is about 30 minutes.

In the integration process on the computer, significant time is wasted on the computation of those concentrations [having $c_j(0) = 0$] whose values become greater than zero very slowly. For example, for an integration up to $t = 10^{-2}$ sec. about 50% of the machine time is spent on the integration of equation set (70) and (71) during its induction period (up to $t \approx 10^{-4}$ sec.). During this period the state of the system has practically not changed at all from that of the initial conditions. The computation time may be considerably decreased by means of removing the accuracy check with respect to these concentrations while they are still small within the limits of accuracy. In the computation process, balance with respect to c_j as well as to u_{jq} is satisfied to an accuracy of five or six significant figures.

4. A discussion of the results of the integration of equation set (70), (71) for the reaction of the oxidation of

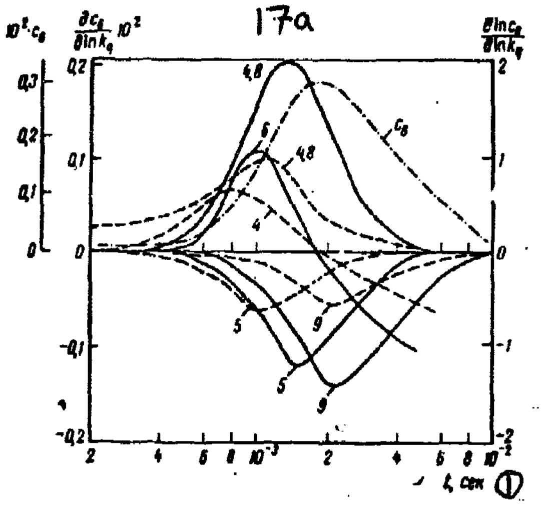
methane.*

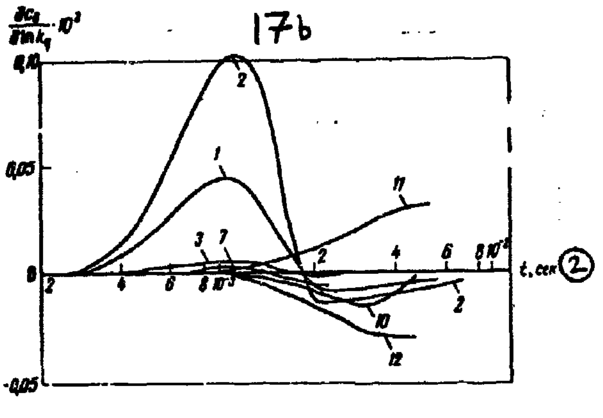
The curves shown in Figures 17-22 illustrate the computations for criteria of sensitivity (65)-(69) for the oxidation of methane. These curves were obtained as a result of the integration of the set of differential equations (70), (71) for the model isothermal reaction of the gaseous oxidation of methane under the following conditions:

$$T_0 = 10^3\ {}^\circ\mathrm{K};\ c_1(0) = 0{,}29;\ c_2(0) = 0{,}71;\ c_p(0) = 0$$

$$(p = 3,4,\ldots,14);\ \left(\frac{\partial c_j}{\partial k_q}\right)_{t=0} = 0\ \ (j = 1,2,\ldots,14;\ q = 1,2,\ldots,12),\ (72)$$

and also under the condition of a fixed aggregate of values of constants of reaction rates for the reaction (see Table 7).





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*The authors thank I.V. Igonina, who carried out the numerical integration of equation set (70)-(71) and checked the preliminary graphing of the results of the computation.

Figure 17. The dependence on time of the sensitivity of the concentration of formaldehyde (c_6) to a change in constants k_q ($q = 1,2,\ldots,12$).

Solid lines: $\partial c_6 / \partial \ln k_q$; Dotted lines: $\partial \ln c_4 / \partial \ln k_q$.

The numbers on the curves correspond to the numbers of the constants k_q that are being allowed to vary.

The line of mixed dots and dashes: the concentration of formaldehyde.

Key: 1. t in sec.
2. t in sec.

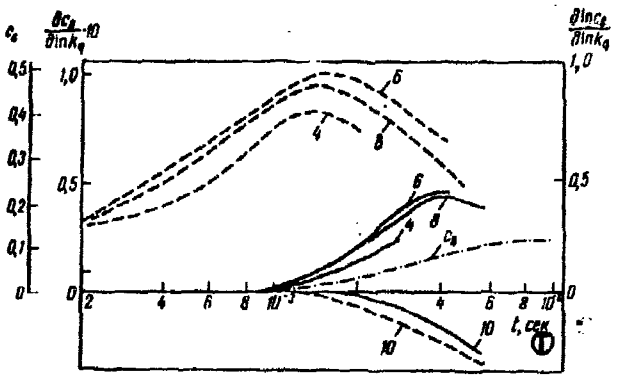

Figure 18. The dependence on time of the sensitivity of the concentration of water (c_8) to changes in the constants k_4, k_6, k_8, k_{10}.

Solid lines: $\partial c_8 / \partial \ln k_q$; Dotted lines: $\partial \ln c_8 / \partial \ln k_q$.

The numbers on the curves correspond to the numbers of the constants k_q that are being allowed to vary.

The line of mixed dots and dashes: the concentration of water.

Key: t in sec.

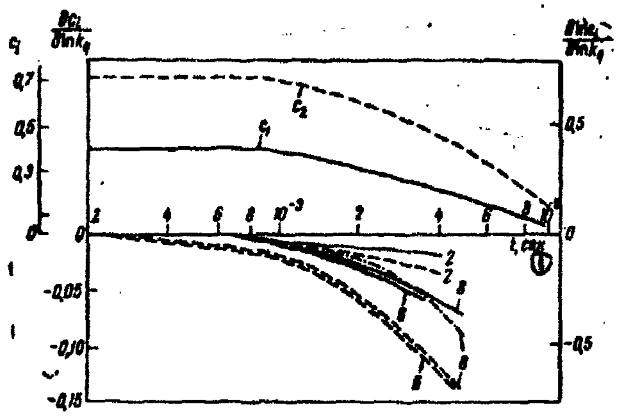

Figure 19. The dependence on time of concentrations of methane (c_1) and oxygen (c_2) and their sensitivity to a change in the constants k_2, k_6, k_8.

Solid lines: $\partial c_1 / \partial \ln k_q$; Dotted lines: $\partial c_2 / \partial \ln k_q$.

The numbers on the curves correspond to the numbers of the constants k_q that are being allowed to vary.

The line of mixed dots and dashes: $\partial \ln c_1 / \partial \ln k_q$.

Key: 1. t in sec.

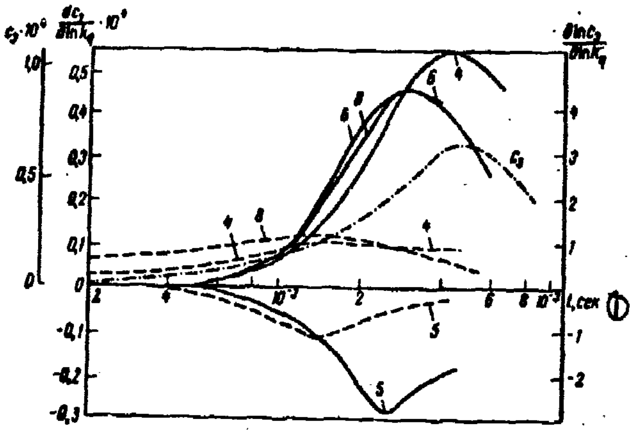

Figure 20. The dependence on time of the concentration CH_3 (c_3) and its sensitivity to a change in constants k_4, k_5, k_6, k_8.

Solid lines: $\partial c_3 / \partial \ln k_q$; Dotted lines: $\partial \ln c_3 / \partial \ln k_q$.

The numbers on the curves correspond to the numbers of the constants k_q that are being allowed to vary.

The line of mixed dots and dashes: the concentration of CH_3 (c_3).

Key: 1. t in sec.

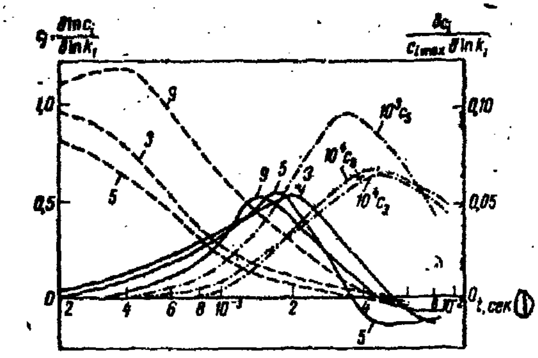

Figure 21. The dependence on time of the concentrations CH_3 (c_3), CH_3OO (c_5), and HCO (c_9) and their sensitivity to a change in the constant k_1.

Solid lines: $\partial c_i/c_{i\,max}\ \partial \ln k_1$; Dotted lines: $\partial c_i/c_i \cdot \partial \ln k_1$.

The lines of mixed dots and dashes: the concentrations of $CH_3(c_3)$, CH_3OO (c_5), and HCO (c_9).

Key: 1. t in sec.

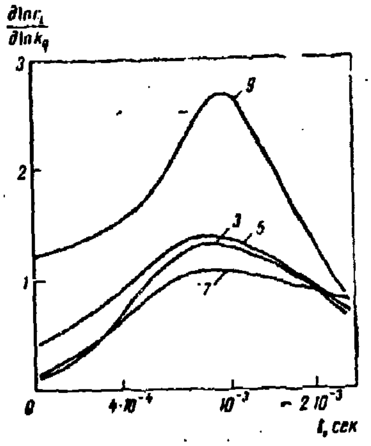

Figure 22. The dependence on time of the sensitivity of the concentrations CH_3 (c_3), CH_3OO (c_5), OH (c_7), HCC (c_9) to a change in constant k_6.

The numbers on the curves correspond to the numbers of the concentrations c_i under study.

Key: 1. t in sec.

In Figures 17-22 are shown the dependences on time of the criteria of sensitivity of five concentrations $[CH_4]$, $[O_2]$, $[CH_3]$, $[CH_2O]$ and $[H_2O]$ to a change in various constants of reaction rates (see Figures 17-20); as well as the criteria of sensitivity of various concentrations to a change in two constants of reaction rates (k_1 and k_6) (see Figures 21,22). For several of these figures, for purposes of comparison, are shown curves of the dependence on time of various criteria of sensitivity for the same concentrations (c_j) or constants (k_q), and also--for convenience--the curves of the dependence on time of the concentrations themselves.

As can be seen from the figures, the values of the criteria of sensitivity may be positive, negative, or approach zero. The positive (negative) value of a criterion of sensitivity at the moment t means that for the given values of the constants, an increase in the given constant of reaction rate leads to an increase (decrease) of the value of concentration c_j for that given moment of time. It is evident that when the value of the criterion is zero at time t, this means that at that point in time a small change in k_q does not lead to any change in c_j.

An examination of Figures 17-22 shows also the following details.

For concentrations having a maximum (for example, for CH_2O in Figures 17a, 17b), the curves for the sensitivity with respect to a change in various constants of reaction rates fall into two categories: a) curves that remain in the positive region (or the negative region) of values of the criterion of sensitivity for all values of t (that is, for the whole duration of the reaction); b) curves that may go from a region of one sign for the values of the criterion to a region of the other sign.

For concentrations whose values simply rise continuously or fall continuously over time (for example, H_2O in Figure 18), only curves of the first category occur.

Thus, the magnitude and sign of the value of a criterion of sensitivity of any concentration c_j with respect to the same constant k_q may in the course of the reaction change considerably. Hence it follows that for a comparison of the values of criteria of sensitivity for various c_j or k_q, it is necessary to stipulate the time or at least the stage of the reaction at which the comparison is being made.

As could have been expected, for one moment of time and under the same conditions of the reaction, different criteria of sensitivity have different numerical values but of the same sign (in particular, they simultaneously cross the x-axis) (see Figures 17a, 18-21).

If the curves corresponding to some criterion have a positive maximum (or negative minimum), then the curves for the other criteria may have the same characteristic at a location shifted some vertical and horizontal distance away. (See Figures 17a, 10 and 11.) The criteria of each of the concentrations of CH_2O, H_2O, CH_4, O_2 and CH_3 with respect to a change in various constants of reaction rate k_9 at various stages of the reaction are shown in Figures 17a, 17b, 18-20.

Let us look at the behavior, for example, of the criteria of sensitivity of the above-mentioned concentrations at a time close to $t_m = 2 \cdot 10^{-3}$ sec., where the concentration of CH_2O reaches a maximum (see Figure 17a). We note that the concentration of formaldehyde at this stage of the reaction is most sensitive to a change in the constants of reaction rates k_4 and k_8 (which determine the rate of reaction of CH_4 with the radicals OH and HO_2) and in the constants k_5 and k_9. The sign of the criteria of sensitivity of the concentration of CH_2O to a change in k_4 and k_8 is positive, while the sign of the criteria with respect to a change in k_5 and k_9 is negative.*

At the same time the sensitivity of the concentration of CH_2O to a change in the constant k_6 (determining the reaction rate of CH_2O with O_2) is small near $t_m = 2 \cdot 10^{-3}$ sec. It can be seen in Figure 17b that near $t_m = 2 \cdot 10^{-3}$ sec. the sensitivity of the concentration of formaldehyde to a change in constants k_1, k_2, k_3, k_7, k_{11} (see Table 7) is relatively small. (Near this point of time several of the values of these constants change sign.) Near $t_m = 2 \cdot 10^{-3}$ sec. the concentration of H_2O has the greatest sensitivity to a change in k_6 (see Figure 18). The concentration of CH_3 has the maximum sensitivity, with a positive sign for the criterion, to a change in constant k_6; and a somewhat smaller absolute magnitude (but with a negative sign for the criterion) of sensitivity to a change in k_5 (see Figure 20). It is possible to compare the sensitivities

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*It can be seen in Figure 17a that an increase in k_4 (or k_8) of about 10% at time $t_m = 2 \cdot 10^{-3}$ sec. leads to an increase in the concentration of CH_2O of about 30%; at the same time an increase in k_9 of 10% causes a decrease in the concentration of CH_2O of about 70%.

of the concentrations of O_2 and CH_4 to a change in the constants k_2, k_6 and k_8 (see Figure 19).

It is also possible to see from these figures the extent to which the relationship of the values of the criteria of sensitivity of one concentration with respect to various constants changes over the course of the reaction. In this instance there are several cases:

a) The qualitative relationship (less-more) is maintained over the whole course of the reaction, but the quantitative relationship of the values of the criteria differs in various stages of the reaction (for example, it can be seen in Figure 17a that the sensitivity of the concentration of CH_2O to a change in k_4 and k_8 is greater than the sensitivity of this concentration to a change in k_6, for the whole duration of the reaction).

b) The qualitative relationship changes in the course of the reaction. For example, in Figures 17a, 17b it can be seen that this is the case for the sensitivity of CH_2O with respect to a change in the constants k_5 and k_9; k_2 and k_{11}, etc.

Figures 17a, 19 and 20 show for purposes of comparison the curves illustrating the change with respect to time of criteria (66) and (68); while Figure 21 shows the same for criteria (68) and (69). It can be seen from these figures that, as could have been expected, with the passage of time these curves behave differently. This behavior is easily explained. For example, the difference in the behavior of criteria (68) and (69) in Figure 21 is explained by the fact that criterion (68) determines the change of the concentration relative to its current value, while criterion (69) determines the change of the concentration relative to its maximum value.

We also note that the computations that have been carried out enable us to separate out those constants whose changes have the least effect on one or another concentration over the whole course of the reaction. Thus it can be seen from Figure 17b that the curves of dependence on time of the criteria for k_3 and k_7, for the entire reaction, are closer than other curves to the axis of time. This means that changes in constants k_3 and k_7 have the least influence on the concentration of CH_2O.

Computations showed that a change in constant k_3 had little influence on other concentrations as well (with the exception of the concentration of CH_3OO, whose magnitude is, however, small itself). This circumstance indicates that in the reaction process, the stage that is determined by the constant k_3 occurs with great speed. Such a conclusion agrees with the results obtained by Semenov (source [31]). From the point of view of the mathematical structure of equation set (70), the small influence of constant k_3 is explained by the fact that this constant enters the equations only in the form of the derivative of k_3 with respect to c_5, and the latter is small over the whole course of the reaction.

In conclusion we shall make several observations.

1. The criteria of sensitivity that have been constructed must permit us objectively to evaluate the role of one or another constants of reaction rates of individual stages of complex chemical reactions. At the same time we find which reactions are determining [crucial] for the process in its various stages. However, we do not yet consider the interpretation of the curves obtained above to be clear enough.

It is necessary to keep in mind that both in the mechanism of the complex reaction, as well as in the set of differential equations corresponding to this mechanism, a change in one of the constants k_q causes in the system as a whole other changes which affect, strictly speaking, all of the concentrations to one extent or another over the course of the whole reaction. In determining with the help of criteria (65)-(69) the sensitivity of various concentrations to a change in the constants k_q, we are really determining the sensitivity of the whole chemical process to that stage of its mechanism that is characterized by the given constant k_q. At the same time it can not be forgotten that because of the very character of the set of differential equations of the process, in any such criterion there is reflected to some degree or other the changes in all of the concentrations; that is to say, there is reflected the indirect influence of the values of the other constants k_q. From the standpoint of cybernetics the reaction mechanism is a system whose elements are mutually interdetermined, both at any instant of time t and also in the system's evolution over time.

A knowledge of the magnitude $\partial c_j / \partial k_q$ is essential for the proper organization of the experiment for determining the constants of reaction rates k_q and for evaluating the quality of the results obtained.*

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*In carrying out isothermal reactions, for example, the temperature is determined with a certain amount of error ΔT. Then the consequent error in the determination of the constants $\Delta k_q = (dk_q/dT)\,\Delta T$. Using the Arrenius equation with the energy of activation $E \gg RT$, we find

$$\frac{\Delta c_j}{c_j} = \sum_q \frac{\partial \ln c_j}{\partial \ln k_q} \frac{E}{RT} \varepsilon, \text{ where } \varepsilon = \frac{\Delta T}{T} .$$

Hence it follows that $\Delta c_j/c_j$ may be quite large even when $\varepsilon \ll 1$.

The criteria of sensitivity may be used not only in the case of homogeneous gaseous reactions, but also in any other types of chemical processes (heterophasic processes, processes occurring in condensed phases, solid state processes, etc.). This approach, analogous to that developed above, may be used for the study of the influence of various parameters (for example, the degree to which the surface of a catalyst is occupied, the length of a molecular chain, etc.) on the course of a chemical reaction.

2. In non-isothermal reactions it is possible to forcibly alter the temperature of this or that stage of the reaction (it can be done, for instance, in the case of reactions occurring in a stationary current). Then a knowledge of the magnitude of $\partial c_j/\partial k_q$ will help in the evaluation of the consequences of such an extraneous thermal action on the course of the complex chemical reaction. A similar situation arises when it is necessary to take into account the influence of the walls of a reaction chamber , additional radiation from outside the system , or additional quantities of one or another reagents introduced into the area of reaction.

The approach that we have developed may be extended to the case of non-isothermal reactions. For this purpose it is only necessary to look at the magnitudes of $\partial c_j/\partial k_{0q}$ and $\partial c_j/\partial E_q$ instead of the magnitude of $\partial c_j/\partial k_q$, where k_{0q} is the pre-exponential coefficient and E_q is the energy of activation. The number of equations of type (71) then increases, but the methods for solving the equations remain the same.

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