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Application of Quasilinearization to Methane Pyrolysis

The rate constants appearing in differential equations derived from proposed mechanisms for methane pyrolysis were estimated from published integral conversion data. Quasilinearization, capable of fitting the differential equation solutions directly to the integral data and therefore not requiring differentiation or transformations, was used. Since differential equations representing free radical reactions have coefficients varying over many orders of magnitude, implicit numerical integration was used to obtain the numerous particular and homogeneous solutions required in the execution of the algorithm. Convergence was achieved by replacing the concentrations after each iteration with values near the solution at that point and by repeatedly estimating a small number of parameters in a cyclic manner in order to improve starting estimates of all parameters simultaneously. The mechanisms attempted were considered plausible when they led to adequate data fits and reasonable rate constant estimates. The major contribution of the work is that the algorithm is capable of testing a mechanistic model over a relatively wide range of conditions with minimal experimental data.

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SCOPE

The modeling of complex reactions as a sequence of free radical reactions is an important objective of chemical kinetics. With such models, yields and conversions for commercially important reactions such as hydrocarbon pyrolysis and oxidation can be predicted.

Most of the previous work in this area consisted of the simultaneous solution of numerous differential equations by numerical methods using a digital computer. This task is made difficult by (1) the large number of differential equations to be solved and (2) the necessity to simultaneously estimate the necessary rate constants for the

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free radical reactions. As the coefficients in the differential equations vary over many orders of magnitude, the step size in integration of such equations must be very small when using conventional numerical methods. The iterative nature of each of these tasks leads to an excessive amount of computation time required for a solution. Thus, the major objective of this study was to decrease the computation time required for solution of the equations by using implicit numerical methods and applying a systematic parameter estimation technique, quasilinearization. Successful completion of this objective would provide a powerful tool for evaluating proposed models as well as for predicting product distributions, yields, and conversions for important reactions.

CONCLUSIONS AND SIGNIFICANCE

The suggested algorithm consisting of integration by methods designed for equations in which the coefficients vary by many orders of magnitude, stiff equations, and of quasilinearization for estimation of parameters is attractive because it can efficiently fit the solutions of differential equations directly to raw data regardless of the type of equation system. The method is particularly suited for the study of free radical mechanisms with widely different kinetic rate constants.

When the algorithm was developed and tested using the methane pyrolysis data and the suggested mechanistic model [Equations (1)] of Eisenberg and Bliss (1967), the integral data were fit well within the experimental error, but the discrepancies between the resulting estimates and the corresponding values expected from the literature for some of the rate constants indicated that the model was invalid. When a revised model [Equations (5)] was formulated and the algorithm was applied, a satisfactory set of Arrhenius parameters providing adequate fits of the data were found (See Table 3). This revised model was capable of extrapolating with respect to temperature and variation of methane and ethane feed proportions but not with respect to inhibition by hydrogen.

This work demonstrated the ability of the proposed algorithm to provide an effective test for a proposed mechanistic model. A model which adequately fits available data by means of reasonable parameter values can be said to have fulfilled a necessary although insufficient condition. This condition becomes more stringent as the data increase in quantity and quality or as the independent evaluations for the rate parameters become more reliable. The fact that the two seemingly reasonable models discussed were found to be not completely satisfactory, in spite of the paucity of data, suggests that the proposed method is a powerful tool for evaluating models with minimum available data.

A proposed mechanism is usually tested by determining whether the model differential equations derived from the mechanism can predict experimentally observed concentration profiles. The test is more effective if the elementary reaction rate constants which must be used to fit the data lie within the bounds suggested by independent measurements (Benson and O'Neal, 1970; Kondratiev, 1972; Ratajzak and Trotman-Dickenson, 1967; Trotman-Dickenson and Milne, 1967) or theoretical approximations of the rate constants. In addition, it is possible to roughly estimate Arrhenius parameters for certain reactions by theoretical means such as transition state theory (for example, Benson, 1968). Although the range of values obtained from either or both of these sources may be very large, these order of magnitude estimates may nevertheless be very helpful in evaluating a proposed mechanism.

A model can be tested by a trial and error search (Eisenberg and Bliss, 1967; Hecht and Seinfeld, 1972; Snow et al., 1959) in which the model equations are solved repeatedly with different sets of reasonable parameter values in an effort to generate solutions which agree with the available concentration profiles. The more systematic approach in which the model is fitted to the concentration profiles by means of a parameter estimation technique was investigated in this work (Denis, 1973).

The various parameter estimation techniques normally used in the analysis of reaction systems have been summarized by Himmelblau et al. (1967). The two basic types that emerge are: (1) methods in which the rate expressions are fitted to differential data or differentiated integral data and, (2) methods in which the integral solutions of model equations are fitted directly to the raw data.

In the case of free radical reactions, the first type does not appear useful because concentration profiles are usually not obtainable for the reactive free radical species. Because of this lack of information, the confidence limits for parameter estimations based only on the stable species can be expected to be much higher than those for estimations based on concentration profiles for all of the species (for example, Seinfeld and Gavalas, 1970). One can therefore ill-afford to increase the error level in the available data by the procedure of data differentiation.

The disadvantage of the second type of methods is that an iterative procedure involving time consuming integrations is normally required. The problem is more serious in the case of free radical reactions because the differential equations representing these reactions are stiff and cannot be integrated efficiently by the usual explicit integration procedures because of step size limitations. An algorithm developed by Snow (1966) obviates this difficulty by implementing the quasi steady state approximation to evaluate the free radical concentrations. In applying this approximation, the differential equations responsible for the stiffness are replaced by algebraic equations which are solved at each step of the integration. In the present study, the reaction systems considered include branching reactions. The quasi steady state approximation is not valid for the free radicals produced by branching reactions. Therefore, the stiffness in the differential equations cannot be completely eliminated by the approximation without affecting the reliability of the solution.

A simplified version of the integration method of Gear (1968, 1971) eliminating automatic step size and order variation coupled with quasilinearization for estimation of rate constants formed the basis of the regression algorithm in this work. As both quasilinearization and stiff integration are based on Newton-Raphson iteration, they can be used together efficiently.

ANALYSIS OF PREVIOUS WORK

Eisenberg and Bliss (1967) employed a flow reactor system to pyrolyze methane at constant temperature. Concentration versus time curves with methane and inert nitrogen gas in the feed stream were obtained at temperatures of 1371°K, 1409°K, and 1458°K. For each case, the methane conversion rate increased initially as shown by the data at 1409°K shown in Figure 1. It was shown experimentally that the presence of hydrogen in the feed stream inhibited methane conversion rate while the presence of ethane in the feed stream catalysed the conversion rate. A simple experiment in which a change in the volume to surface ratio produced no change in conversion indicated that surface effects were negligible. The following reaction scheme was proposed to explain these experimental facts:

Reaction 1:

$$CH_4 \xrightarrow{k_1} CH_3 + H \tag{1a}$$

Reaction 2:

$$CH_3 + CH_4 \xrightarrow{k_2} C_2H_6 + H \tag{1b}$$

Reaction 3:

$$C_2H_6 \xrightarrow{k_3} 2CH_3 \tag{1c}$$

Reaction 4:

$$C_2H_6 \xrightarrow{k_4} H_2 + C_2H_4 \rightarrow H_2 + C_2H_2 \rightarrow H_2 + C \tag{1d}$$

Reaction 5:

$$CH_3 + H_2 \xrightarrow{k_5} CH_4 + H \tag{1e}$$

Assuming plug flow and ideal conditions, they derived model equations for the change in concentration with time for methane, ethane, and methyl radical. Using a trial and error search the model was tested with data at 1409°K. Using a Runge-Kutta integration procedure, they repeatedly solved the equations with different sets of parameter values selecting the set and the associated responses which were found to fit the methane data best as shown in Figure 1.

Since the agreement between the methane response and the data points is acceptable, the validity of the fit should be assessed further by examining whether their parameter estimates are in agreement with approximate values obtained from reported measurements or from theoretical considerations. Using the data of Benson and O'Neal (1970), Trotman-Dickenson and Milne (1967), and Towell and Martin (1961) and applying transition state theory as discussed by Benson (1968), values of the five rate constants were estimated as shown in Table 1. The estimates of Eisenberg and Bliss for k_2, k_3, and k_4 (See Figure 1) are within the bounds suggested by Table 1 while their estimates for k_1 and k_5 are outside the range. The model cannot be rejected on the basis of these discrepancies, however, because the model is overparameterized as only one response curve is being fitted using a total of five parameters. As a result, the confidence limits for the parameters can be expected to be large enough to encompass reasonable values of the parameters. Conversely, there may exist sets of parameter values which fit the data and are also in agreement with the values in Table 1.

Because of the nonuniqueness of their estimates, and because of the excessive computation time required for trial and error curve fitting by an explicit integration procedure, Eisenberg and Bliss made no attempt to fit their data at 1371° and 1458°K. The algorithm of this paper was designed to speed up the integration procedure as well as to curve fit automatically. The problem of overparameterization was alleviated by keeping some of the parameters fixed at reasonable values.

STIFF INTEGRATION

A set of differential equations can be written in vector notation as follows:

$$\frac{dy}{dt} = \mathrm{f}(\mathrm{y}, \mathrm{k}, t) = \mathrm{f} \tag{2a}$$

$$\mathrm{y}(0) = \mathrm{y}_0 \tag{2b}$$

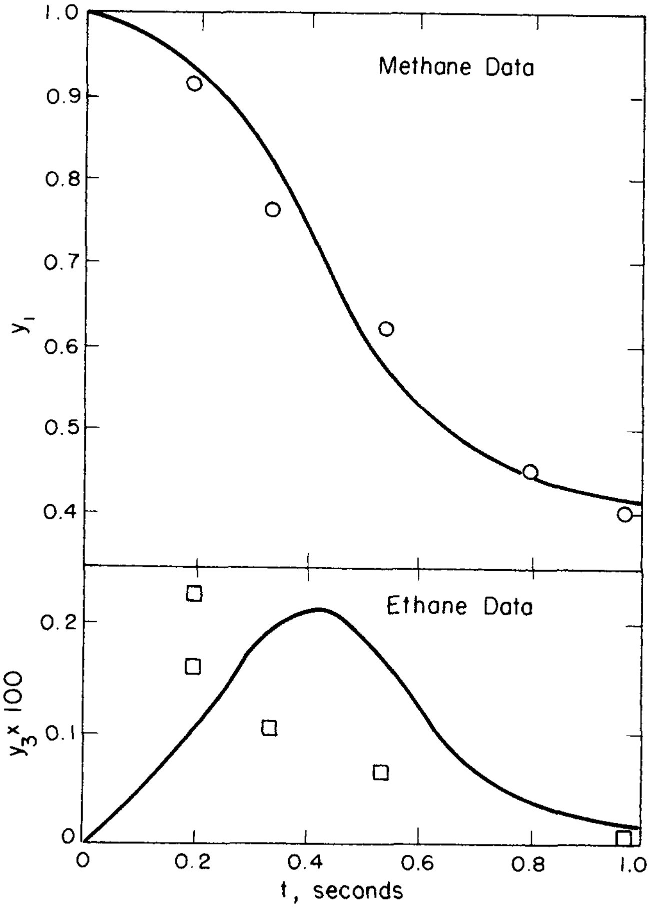

Fig. 1. Data of Eisenberg and Bliss vs. model solution [equations (1)] for pyrolysis of methane at 1409°K
$[CH_4]_0 = 0.0013$ kg-mole/m^3
$k_1 = 0.0045$ s^{-1}, $k_2 = 3.60 \times 10^6$ m^3/kg-mole-s,
$k_3 = 305.0$ s^{-1}, $k_4 = 301.0$ s^{-1}, $k_5 = 4.00 \times 10^6$ m^3/kg-mole-s.

Table 1. Parameter Values Obtained from Literature or Theory

T (°K)	Minimum $k_1 \times$ 100, s^{-1}	Maximum $k_2 \times 10^{-6}$ m^3/kg-mole-s	Range of k_3 s^{-1}	Approximate k_4 s^{-1}	Range of $k_5 \times 10^{-6}$ m^3/kg-mole-s
1371	0.21	4.3	38-680	300	7.8-210
1409	0.59	4.9	90-1580	500	8.7-240
1458	2.04	5.8	260-4800	800	9.8-280

TABLE 2. COEFFICIENTS OF STIFF INTEGRATION FORMULAS

Order p	β	α_1	α_2	α_3	α_4	α_5	α_6
1 (Backward Euler)	1	1	—	—	—	—	—
2	2/3	4/3	−1/3	—	—	—	—
3	6/11	18/11	−9/11	2/11	—	—	—
4	12/25	48/25	−36/25	16/25	−3/25	—	—
5	60/137	300/137	−300/137	200/137	−75/137	12/137	—
6	60/147	360/147	−450/147	400/147	−225/147	72/147	−10/147

where $\mathbf{y}$ is a J-dimensional vector of concentration, $\mathbf{k}$ is a I-dimensional vector of rate parameters, and $\mathbf{f}$ is a J-dimensional vector of the overall rates of change in concentration of the species.

The problem of numerical instability in solving stiff equations of this form has recently been discussed by Gear (1968 and 1971), Lapidus and Seinfeld (1971), Seinfeld et al. (1970), and Sena and Kershenbaum (1972). Although a backward Euler method is classified as unconditionally stable, A-stable linear multistep methods of order higher than two cannot exist. Higher order formulas for the solution of stiff equations, however, have been proposed by Curtiss and Hirschfelder (1952). Although these formulas are not A-stable, they have been shown by Gear to be stable for wide ranges of $h\lambda_j$ and are referred to as being stiffly stable. They are of the same family as the backward Euler method and have the feature that the number of steps in the formula is equal to the order p. The family of formulas is

$$\mathbf{y}_n = h\beta\mathbf{f}_n + \sum_{m=1}^{p} \alpha_m\, \mathbf{y}_{n-m} \tag{3}$$

where $\mathbf{y}_n$, $\mathbf{y}_{n-1}$, etc. is the numerically computed solution to Equations (2) at points $t_n = t_0 + nh$, $t_{n-1} = t_0 + (n-1)h$, etc. The coefficients α_m and β are given in Table 2. The unstable region associated with a given order increases rapidly with the order, and the formulas for $p > 6$ are not stable.

Curtiss and Hirschfelder (1952) illustrated that the formulas can provide stable solutions for positive as well as negative $Re\,(\lambda_j)$. This becomes relevant when integrating differential equations for complex reactions with branching since some of the eigenvalues may become positive during periods when the overall reaction rate is autoaccelerating as reported by Sena and Kershenbaum (1972).

Description of Procedure

Since $\mathbf{f}_n$ is a function of $\mathbf{y}_n$, the integrations were performed by solving Equation (3) implicitly for y_n at each step. This was accomplished by the Newton-Raphson method by which the nonlinear function $\mathbf{f}_n$ is approximated by means of a Taylor Series truncated after the first derivative. This resulting algebraic equation system was solved iteratively for $\mathbf{y}_n$ at each step of the integration until y_n converged. The superscript $(^0)$ denotes variables calculated from $\mathbf{y}_n^0$, the solution of the previous iteration. Convergence was assumed when $(|y_j^0 - y_j|/y_j) < 0.0001$ for all j. For the first iteration at step n, y_n^0 was set equal to $\mathbf{y}_{n-1}$, the dependent variables determined from the previous iteration. For step 1, the initial condition vector $\mathbf{y}_0$, used as an initial guess, did not always lead to convergence if the vector contained many zero elements. In such cases, order of magnitude estimates for $\mathbf{y}_1$ were required to initiate the integration.

The matrix $[\mathbf{I}_j/h\beta - \mathbf{A}_n^0]$ was evaluated and the equation system was solved by pivotal condensation (Conte, 1965) for each iteration at each integration step. Constant order and step size were used throughout the integration except during the initialization period. Since $\mathbf{y}_0$ is the only point known initially, the integrations were started with the first-order backward Euler method. The initial step size was reduced to $h/2^{(p-1)}$ where h and p were the desired final step size and order. During the initialization period, the step size was repeatedly doubled and the order was increased by increments of one until desired final values of h and p were reached.

Fourth-order integration was used throughout most of this work. Step sizes were selected on the basis of test runs. A step size was considered satisfactory if the fourth digit of the solution following the first datum (that is, after $t = 0.2$ s for the case in Figure 1) did not change with a further decrease in the step size. For the example in Figure 1, a step size of 0.025 s was considered adequate. The computer time required for a solution up to $t = 1$ s was approximately one second on an IBM 360/67 computer. The solution agreed to four digits with that obtained from an explicit Adams-Bashforth-Moulton predictor-corrector method with step size control which required more computation time.[*]

PARAMETER ESTIMATION BY QUASILINEARIZATION

Quasilinearization was developed by Bellman and Kalaba (1965) as an approach to solving nonlinear boundary value problems. Bellman et al. (1967) also suggested use of this algorithm for estimating rate parameters from concentration profiles. Several additional examples of this application have been provided by Donnelly and Quon (1970), Lee (1968a, 1968b), and Seinfeld and Gavalas (1970).

Quasilinearization is essentially the extension of the Newton-Raphson method of solving nonlinear algebraic equations to functional equations. This implies that the iterative scheme consists of a sequence of solutions to differential equations rather than a sequence of solutions to algebraic equations.

In parameter estimation, the boundary value problem of interest is formulated by treating the parameters to be estimated, k, as dependent variables. Since these parameters are constant under isothermal conditions, their vector differential equation is

$$\mathbf{k}' = 0 \tag{4}$$

Equations (2a) and (4) are to be solved simultaneously as a boundary value problem using the standard quasilinearization procedure. The parameter estimation examples of this work were ill-posed, that is, relatively large changes in the parameter values often produced only slight changes in $\mathbf{y}$. This behavior results in (1) small convergence regions, that is, convergence occurs only if the initially guessed parameter vector is close to the final vector, and

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[*] Supplementary material on the procedure for stiff integration coupled with quasilinearization has been deposited as Document No. 02392 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 305 E. 46 St., N. Y., N. Y. 10017 and may be obtained for \$1.50 for microfiche or \$5.00 for photocopies.

(2) large confidence intervals for the parameter estimates. Convergence difficulties were partially alleviated by the technique of data perturbation as discussed by Donnelly and Quon (1970). The resulting values of **k** can then be used as $\mathbf{k}^0$ and a new set of iterations initiated with a new set of perturbed data which is closer to the actual data. Convergence on derived sets of data can be repeated until the actual data can be fitted. Automatic data perturbation was incorporated into the algorithm. Starting values were improved by means of a cycled parameter estimation procedure in which only some of the parameters were estimated while the others were held fixed. Reducing the number of parameters being estimated improved convergence properties. After converging on the actual data, the resulting parameter values were used in another estimation in which a larger number of parameters or different parameters were estimated. The objective of such an approach was to obtain a set of starting parameter values which enabled the algorithm to converge on the actual data when estimating all parameters simultaneously.

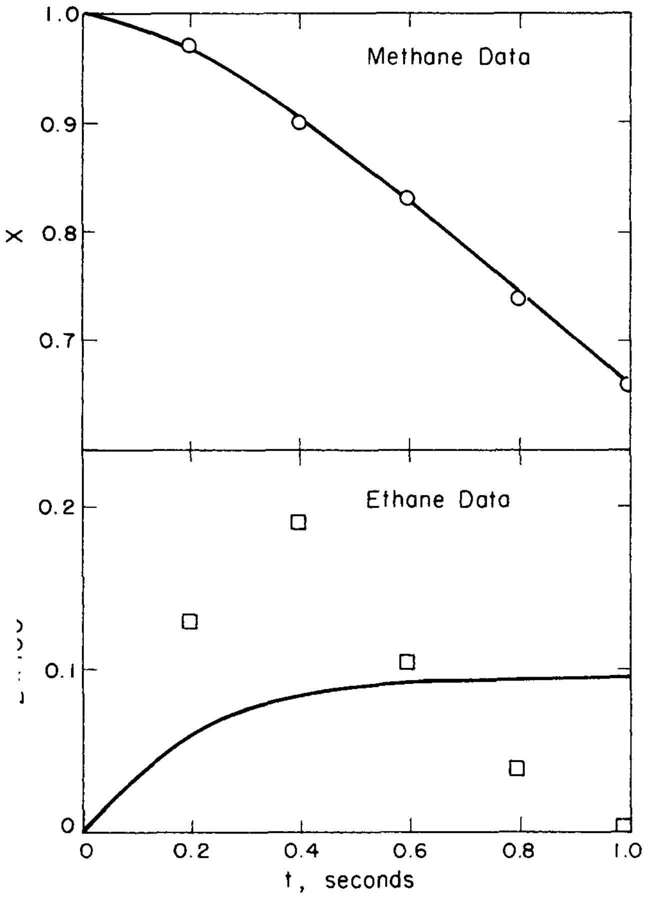
APPLICATION TO THE MODELS

The parameter estimations were based on the data points illustrated in Figures 2, 3, and 4. The points shown were read as precisely as possible from the smooth curves which Eisenberg and Bliss drew through their actual data points. The programming was greatly facilitated by choosing points at regular intervals of t instead of using the actual data which occurred at irregular intervals of t.

Ethane as well as methane data were used for the estimations even though the ethane data were not reliable. Since weighting factors of one were used for each data point, the contributions of the low ethane concentrations were small. Thus, including the ethane data had little effect on the final parameter estimates.

Using the original model of Eisenberg and Bliss [Equations (1)], parameter estimates were made varying all five rate constants at each temperature, holding k_5 constant, and holding k_1 and k_5 constant. In each case one or more of the resulting parameters were either negative or outside the bounds given in Table 1. Since the data are not fitted using reasonable values for the rate constants, the model cannot be extrapolated.

A major objection which one can make to the mechanism given by Equations (1) is that the reverse of Reaction 5 was neglected. Since the hydrogen atoms produced by this reaction as well as by Reactions 1 and 2 are very reactive, and since the concentration of methane is relatively high, the reverse of Reaction 5 is expected to be as important as the forward reaction. Significantly, this fact is supported by various negative estimates of k_5. Certain trials yielded negative responses for y_2 as well as negative estimates for k_2. Since both k_2 and y_2 were negative, the rate of reaction 2 remained positive. In summary therefore, the rate of Reaction 5 was found to be negative at 1371° and 1458°K where data was not taken beyond the region of maximum conversion rate. This is consistent with the fact that the reverse of Reaction 5 is expected to be more important at low contact times when methane concentration is at its



g. 2. Responses of model of Eisenberg and Bliss with five parameter values estimated from the data at 1371°K ($I = 5$)
$[CH_4]_0 = 0.00133$ kg-moles/m^3
$k_1 = 0.009087\ s^{-1}$, $k_2 = 2.902 \times 10^5$ m^3/kg-mole-s,
$k_3 = 212.6\ s^{-1}$, $k_4 = 220.7\ s^{-1}$, $k_5 = -1921$ m^3/kg-mole-s.

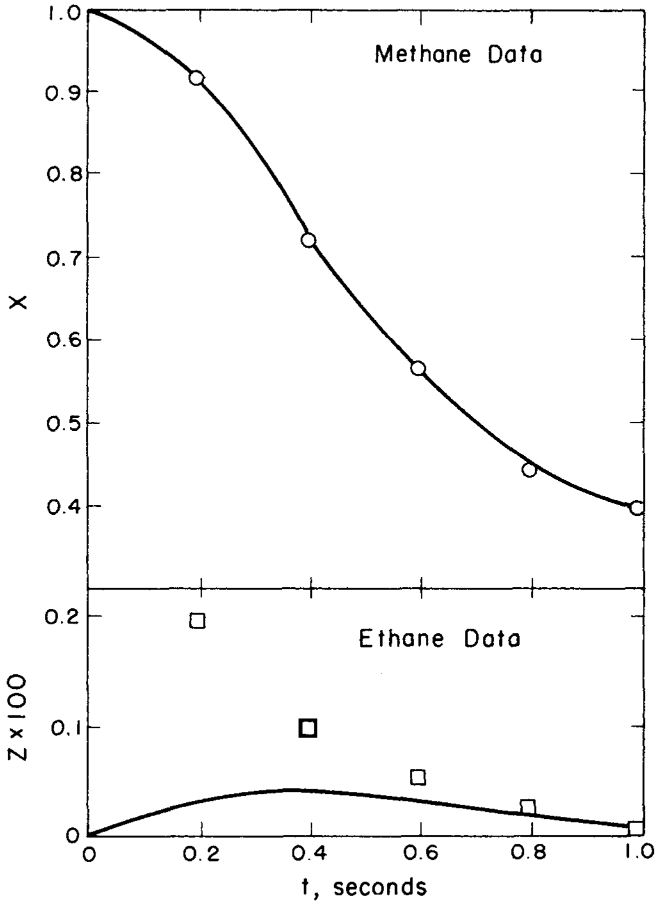


Fig. 3. Responses of model of Eisenberg and Bliss with five parameter values estimated from the data at 1409°K ($I = 5$)
$[CH_4]_0 = 0.0013$ kg-moles/m^3
$K_1 = 0.01438\ s^{-1}$, $k_2 = 2.750 \times 10^5$ m^3/kg-mole-s.
$k_3 = 1238.5\ s^{-1}$, $k_4 = 1237.6\ s^{-1}$, $k_5 = 3350$ m^3/kg-mole-s.

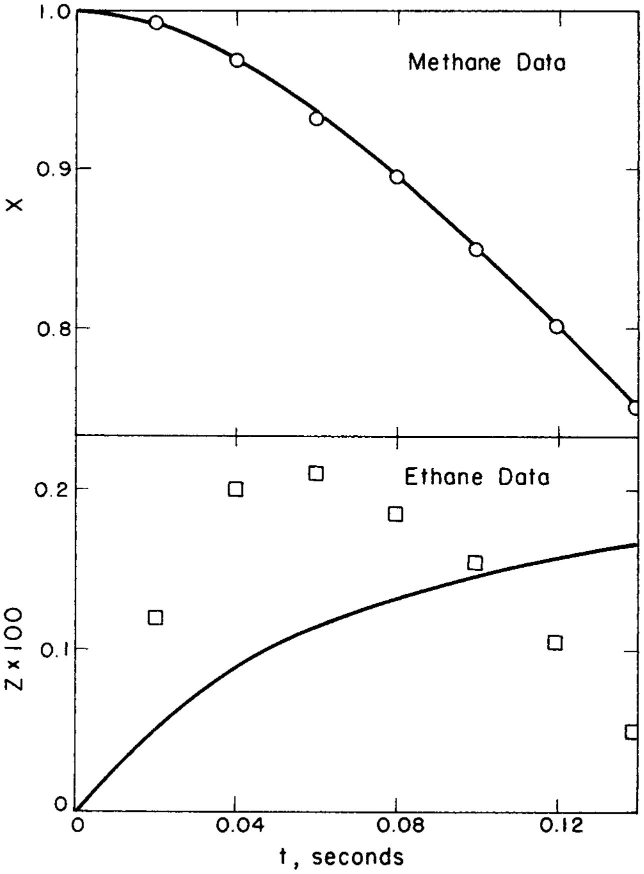


Fig. 4. Responses of model of Eisenberg and Bliss with five parameter values estimated from the data at 1458°K.

$[CH_4]_0 = 0.00127$ kg-moles/m^3
$k_1 = 0.04213$ s^{-1}, $k_2 = 3.188 \times 10^6$ m^3/kg-mole-s,
$k_3 = 765.4$ s^{-1}, $k_4 = 787.9$ s^{-1},
$k_5 = -3.022 \times 10^4$ m^3/kg-mole-s.

highest. Unless the reverse of Reaction 5 is included, the model cannot be expected to extrapolate reliably to high contact times. In addition, it is unlikely that suitable Arrhenius parameters could be found for extrapolation or interpolation to other temperatures.

If the reverse of Reaction 5 is included, the forward reaction will no longer function as a termination step as intended by Eisenberg and Bliss. More conventional termination steps are the reverse of Reactions 1 and 3. Another modification which can be made to the mechanism relates to Reaction 4 which implies that ethane pyrolysis occurs by a nonfree radical route. Benson and Haugen (1967) suggest that ethane reacts according to steps 6 and 7 which are written below in a revised mechanism which includes all of the changes mentioned above:

$$\text{Reaction 1:}\quad CH_4 \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} CH_3 + H \qquad (5a)$$

$$\text{Reaction 2:}\quad CH_3 + CH_4 \xrightarrow{k_2} C_2H_6 + H \qquad (5b)$$

$$\text{Reaction 3:}\quad C_2H_6 \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} 2\,CH_3 \qquad (5c)$$

$$\text{Reaction 5:}\quad CH_3 + H_2 \underset{k_5'}{\overset{k_5}{\rightleftharpoons}} CH_4 + H \qquad (5d)$$

$$\text{Reaction 6:}\quad C_2H_6 + H \xrightarrow{k_6} C_2H_4 + H + H_2 \qquad (5e)$$

$$\text{Reaction 7:}\quad C_2H_6 + CH_3 \xrightarrow{k_7} C_2H_4 + H + CH_4 \qquad (5f)$$

Reactions 6 and 7 implicitly assume the instantaneous decomposition of the ethyl radial into ethylene and the hydrogen atom. This assumption should be valid at the high temperatures considered here. A final modification to the model of Eisenberg and Bliss is the removal of the assumption that $y_4 = 2(1 - y_1)$.

The differential equations consisting of five dependent variables can easily be derived from the revised mechanism. Estimations were initially attempted using fourth-order integration with the rate parameters of each reversible reaction related numerically by means of equilibrium constants evaluated from thermodynamics. Accordingly, only six parameters had to be estimated from the data. Convergence properties were found to be very unfavorable because the solutions were relatively insensitive to large changes in k_1, k_3, and k_5. Changes in these parameters produced corresponding changes in the reverse reaction rate resulting in only slight changes in the responses. Consequently, each rate constant was estimated independently, thereby leaving a total of nine parameters to be estimated from the integral data.

No attempt was made to converge on the data while estimating all nine parameters simultaneously. The approach adopted was somewhat different from that used in dealing with the previous model. From one to five parameters were estimated simultaneously while keeping the remaining parameters fixed. The algorithm was modified slightly by including a third interruption. At the end of each perturbation, the estimates were checked to verify whether they were within specified bounds such as the ones shown in Table 1. If the bounds were exceeded, thereby indicating unsatisfactory estimates, the run was interrupted. A subsequent estimation of a different set of parameters was then conducted with the parameters whose bounds were exceeded held fixed at suitable values calculated from Arrhenius parameters reported in the literature. This procedure was repeated until the variance was reduced to a level indicating an adequate fit and until all of the parameters were reasonable values. This could only be accomplished by basing the estimations on the methane data only rather than on both methane and ethane data as was previously done.

The data at 1409°K were treated first. Only k_2 and k_3' were estimated in the last estimation which lead to $Q_M = 0.00036$ indicating an adequate fit. The estimate for k_2 was 1.48×10^6 m^3/kg-mole-s which is well below the maximum suggested in Table 1, while the estimate for k_3' was 5.45×10^{10} m^3/kg-mole-s which is in agreement with the value of 7×10^{10} used by Snow et al. (1959). All seven remaining parameters were held fixed at the values calculated from the Arrhenius parameters in Table 3.

Only k_2 was estimated from the data at 1371° and 1458°K. Since the activation energy for a free radical recombination is usually assumed to be zero, k_3' was held fixed at 5.45×10^{10} while all other parameters were held fixed at values calculated from the Arrhenius parameters. The algorithm converged readily for both cases leading to the satisfactory values of $Q_M = 0.00015$ and $k_2 = 1.09 \times 10^6$ m^3/kg-mole-s at 1371°K and $Q_M = 0.00005$ and $k_2 = 2.30 \times 10^6$ m^3/kg-mole-s at 1458°K. The estimate of k_2 at 1371°, 1409°, and 1458°K when plotted follow the Arrhenius law and lead to $\log A = 11.6$ and $E = 1.48 \times 10^8$ joules/kg-mole. The methane response of each temperature using the parameters of Table 3 fit the data well and is illustrated for 1458°K in Figure 5.

The revised reaction mechanism is preferred over that of Eisenberg and Bliss because it is capable of fitting the data adequately by means of reasonable rate parameters which obey the Arrhenius law. The model is adequate for predicting methane conversion at higher contact times or for interpolating the temperature range 1371°K to 1458°K.

Although the rate constants appear reasonable, the A-factor for Reaction 2 is probably too high. A small steric factor of the same order of magnitude as that for Reactions 5 and 7 is expected for this reaction. The value $\log A = 11.6$ is probably about three orders of magnitude too high. If a satisfactory set of Arrhenius parameters exist, one can probably be found by repeating the estimation procedure with k_2 fixed at appropriate values. Alternatively, a different explanation for the autoaccelerating effect may be required.

The validity of the model was also tested by examining its ability to extrapolate. The model satisfactorily explains the effect of increased methane concentration in the feed and the accelerating effect of ethane in the feed. However, the model does not satisfactorily predict the inhibiting effect of hydrogen in the feed. The predicted decomposition rate of methane is inhibited by the presence of hydrogen which increases the rate of Reaction 5. As shown in Figure 7, however, the extent of inhibition is far from that suggested by the data of Eisenberg and Bliss. Since the overall methane decomposition rate has been found to be rather insensitive to changes in k_5 or k_5', it is not likely that the response can be improved by manipulating these parameters. Instead, the addition of methylene as an active center in the mechanism is suggested. The production of methylene by the reaction, $CH_4 \rightarrow CH_2 + H_2$, has often been suggested as an initiation step (for example, Kahn and Crynes, 1970). The inhibiting effect of hydrogen would be explained by the reverse of this reaction.

TABLE 3. ARRHENIUS PARAMETERS WHICH FIT THE REVISED MECHANISM [EQUATIONS (5)] TO THE DATA OF EISENBERG AND BLISS

Reaction	log A, A in m³/ kg-mole-s	$E \times 10^{-8}$ joules/ kg-mole	Source
1	13.9	4.35	Minimum from transition state theory
1′	10.4	0	Benson and O'Neal (1970)
2	11.6	1.47	Derived in this work
3	15.45	3.64	Benson and O'Neal (1970)
3′	10.735	0	Estimated from data at 1409°K
5	8.52	0.43	Trotman-Dickenson and Milne (1967)
5′	11.19	0.46	Trotman-Dickenson and Milne (1967)
6	11.1	0.41	Trotman-Dickenson and Milne (1967)
7	8.3	0.44	Trotman-Dickenson and Milne (1967)

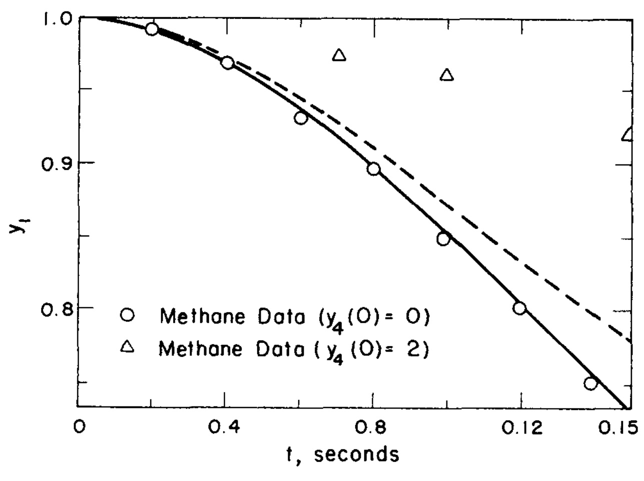


Fig. 5. Methane responses of revised model at 1458°K. Rate parameters from Table 3. $[CH_4]_0 = 0.00127$ kg-mole/m³
Solid Line Initial Conditions
$y_1(0) = 1, y_2(0) = y_3(0) = y_4(0) = y_5(0) = 0$
$Q_M = 0.92 \times 10^{-4}$
Dashed Line Initial Conditions
$y_1(0) = 1, y_4(0) = 2, y_2(0) = y_3(0) = y_5(0) = 0$

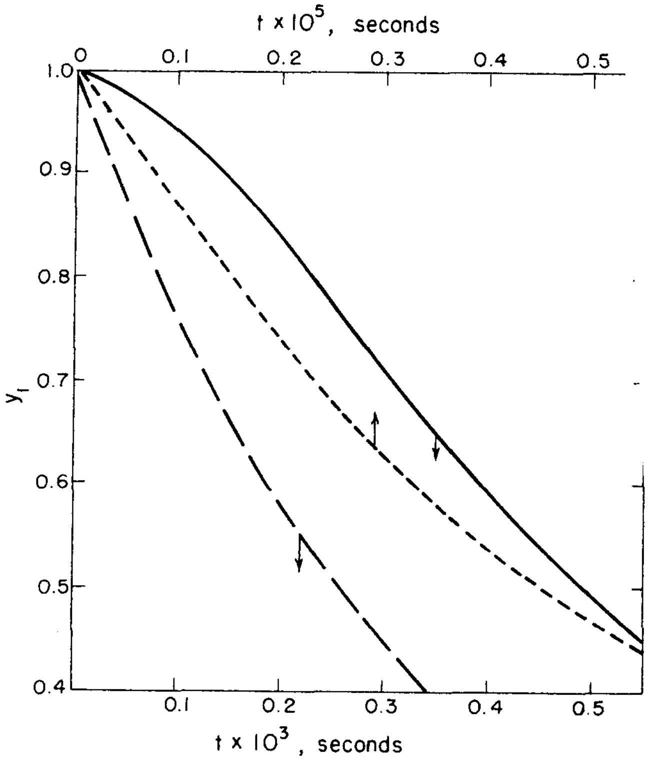


Fig. 6. Methane responses of revised model at 1900°K and 2500°K. Rate parameters from Table 3. Solid line—response at 1900°K, $[CH_4]_0 = 0.000973$; Short dashed line—response at 2500°K, $[CH_4]_0 = 0.000736$; Long dashed line—data of Kevorkian et al. (1960) at 1900°K.

The model was also used to predict conversions at high temperatures. Data in the 1600° to 1900°K range have been taken by several investigators using single pulse shock tubes. In general, these conversion data were found to follow first-order kinetics. The revised model has the potential for explaining this first-order behavior because the rate of Reaction 1 increases more rapidly with temperature than the rate of the other reactions. At sufficiently high temperatures, it is conceivable that all methane decomposition would occur by Reaction 1 and hence be first order with respect to methane. However, as shown in Figure 6, the response at 1900°K still exhibits autoacceleration although the response is no longer sigmoid shaped at 2500°K. In addition, as shown in the same figure, the predicted conversions are lower than those predicted by experimenters such as Kevorkian et al. (1960). These facts suggest that the values for k_1 are too low and/or the values for k_2 are too high.

IMPROVEMENT OF THE ALGORITHM

Several measures can be taken to improve the computations. The integration procedure can be improved by incorporating the entire method of Gear (1968, 1971) which minimizes computation time by using the optimum order and step size in order to achieve a desired error level. This procedure would ensure accuracy as well as increase the computation rate. The regression method may be improved according to various proposals suggested in recent literature. Some of these include: (1) the methods of Ramaker et al. (1970) for increasing convergence regions, (2) Tanner's (1972) fast algorithm for generating starting parameter values for quasilinearization, and (3) an algorithm of Hwang and Seinfeld (1972) requiring fewer integrations per iteration to replace quasilinearization.

The algorithm cannot be of great value unless a suitable user oriented program is made available. Ideally, the user should be required to provide a minimum of input such as the proposed mechanism, the data and associated error estimates, initial parameter estimates, and the bounds within which the parameters should be restricted. A fully automated program should then perform a systematic exploration of the least squares surface, implementing cycled parameter estimation and data perturbation as necessary. Output from a successful fit would consist of a reasonable set of parameter estimates with confidence intervals.

NOTATION

A = frequency factor, m^3/kg-mole-s
$\mathbf{A}$ = $J \times J$ Jacobian matrix of $\mathbf{f}$ with respect to $\mathbf{y}$
$[CH_4]_0$ = concentration of methane in the feed, kg-mole/m^3
E = activation energy, joules/kg-mole
$\mathbf{f}$ = J-dimensional vector of rate of change of concentration
h = integration step size
I = total number of parameters to be estimated
$\mathbf{I}_J$ = $J \times J$ identity matrix
j = index referring to dependent variables: 1-methane, 2-methyl radical, 3-ethane, 4-hydrogen, 5-hydrogen atom
J = total number of dependent variables
k = kinetic rate constant
$\mathbf{k}$ = I-vector of parameters to be estimated
$\mathbf{k}^0$ = I-vector of parameters estimated from previous iteration
n = integration step index
p = order of integration formula
Q_M = sum of the squares of the deviations between methane data and methane model response
t = contact time
X = moles of methane per mole of methane feed
$\mathbf{y}$ = J-dimensional vector of dependent variables
$\mathbf{y}^0$ = J-dimensional vector of dependent variables determined from previous iteration
$\mathbf{y}_0$ = J-dimensional vector of initial conditions
Z = moles of ethane per mole of methane feed
α_m = coefficients in integration formula
β = coefficients in integration formula
λ_j = eigenvalues of $\mathbf{A}$

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