COMBUSTION AND FLAME, 17, 237–241 (1971)

Rate-Controlled Partial-Equilibrium Method for Treating Reacting Gas Mixtures

James C. Keck
Massachusetts Institute of Technology, Cambridge, Massachusetts, U.S.A.

AND

David Gillespie
Illinois State University, Normal, Illinois, U.S.A.

A rate-controlled partial-equilibrium method for treating reacting gas mixtures has been developed that is very much simpler than the usual technique of integrating the full set of rate equations. The method is based on the observation that a rate-controlling reaction is equivalent to a "passive constraint" on the gas, so that the corresponding partial-equilibrium state can be calculated by minimizing the appropriate free energy function. An example illustrating the application of the method to the "freezing" of threebody reactions in an internal combustion engine is given.

Introduction

In thermodynamics, gas dynamics, and chemistry, it is often necessary to determine the state of nonequilibrium gas mixtures in which a large number of reactions are occurring simultaneously. The usual method of doing this is to integrate the set of rate equations for the reactions on a digital computer. This can be a formidable task requiring sophisticated programming and expensive calculations even when the "steady-state approximation" is used to reduce the number of differential equations that must be integrated. It is further complicated by the fact that many of the reaction rates may be unknown and must be estimated.

To avoid these difficulties we have developed a "rate-controlled partial-equilibrium method" for treating complex reacting gas mixtures. The method is based on the observation that in many cases the changes occurring in a reacting gas are determined by only a few rate-controlling reactions and that existence of such reactions implies certain "passive constraints" on the chemical composition of the gas. A familiar example of such "passive constraints" is provided by nuclear reactions, which are extremely slow at ordinary temperatures and imply conservation of the elements on the time scale of interest for chemical reactions.

The assumption of a "partial-equilibrium" state has frequently been made in the past to simplify the analysis of complex reactions in specific cases. It was used by Bray [1] in his development of the "sudden freezing" approximation for treating nozzle flows. In addition, Kaskan [2], Schott [3], and Lezberg and Franciscus [4] have applied it with considerable success to the problem of hydrogen–oxygen combustion. In all these investigations the rate-controlling reactions were assumed to be the threebody recombination and dissociation reactions, and the term partial equilibrium was introduced by Schott to describe this situation. In the present work we use the term in a more general sense to describe the state approached

Published by American Elsevier Publishing Company, Inc.

by a chemical system subject to slowly changing constraints introduced by any chemical reaction or set of reactions.

The first step in using the present method is to identify the important rate-controlling reactions. This of course requires some physical insight, but trial and error can be used as well. Next, the constraints that would exist if the rate-controlling reactions did not proceed at all are identified and the corresponding partial-equilibrium state of the gas is determined using the familiar thermodynamic technique of minimizing the appropriate free energy subject to all constraints. Finally, the rate equations for the controlling reactions are used to calculate the rate of change of the constraints from the previously determined partial-equilibrium composition.

The method has the advantage over the technique of integrating a full set of rate equations that only the rate-controlling reactions need to be known. This reduces the number of equations to be integrated by a large factor and eliminates the need for estimating the rates of unknown reactions of peripheral importance. It may also be observed in this connection that increasing the number of species considered does not necessarily increase the difficulty of the calculation and may even improve the assumption that a partial-equilibrium state will exist. Mass addition and nuclear reactions can easily be taken into account by simply specifying the rates of change of the corresponding constraints. Finally, the results can be systematically improved by including additional constraints one at a time until the desired accuracy is achieved. If enough constraints are included to completely determine the state, the method becomes equivalent to integrating the full set of rate equations.

The basic equations used in this method are presented in the next section. Some preliminary results are given in the final section.

Basic Equations

Consider a uniform homogeneous gas containing m different species of atoms and molecules. Let X_j be the number of moles of species j and

$$X_0 = \sum_{j=1}^{m} X_j \tag{1}$$

be the number of moles of gas. The equilibrium composition of such a mixture for given values of temperature T and pressure p may be obtained by minimizing the Gibbs free energy

$$F(T,p) = \sum_{j=1}^{m} X_j[F_j + RT\ln(X_j/X_0)] \tag{2}$$

subject to the constraints

$$c_i = \sum_{j=1}^{m} a_{ij}X_j, \qquad i = 1, 2, \ldots, n \tag{3}$$

implied by conservation of atoms for the n elements of which the species in the gas are composed. This leads to the result

$$X_j = X_0 \exp\left(-\sum_{i=1}^{n} \mu_i a_{ij} - F_j/RT\right) \tag{4}$$

where μ_i is a Lagrange multiplier that may be identified as the negative of the chemical potential of the element i divided by RT, a_{ij} is the number of atoms of element i in the species j,

$$F_j(T,p) = \mathrm{H}_j(T) + S_j(T,p_0) + RT\ln(p/p_0) \tag{5}$$

is the Gibbs free energy of species j, $S_j(T,p_0)$ is the entropy of species j at the reference pressure p_0, and R is the gas constant per mole. The constraints (3) apply to systems of constant mass in which nuclear reactions do not occur and c_i is just the number of moles of element i.

Substituting (4) into (1) and (3), we obtain a set of $n + 1$ equations

$$c_i = X_0 \sum_{j=1}^{m} a_{ij} \exp\left(-\sum_{k=1}^{n} \mu_k a_{kj} - F_j/RT\right) \tag{6}$$

and

$$1 = \sum_{j=1}^{m} \exp\left(-\sum_{i=1}^{n} \mu_i a_{ij} - F_j/RT\right) \tag{7}$$

which may be solved for the $n+1$ unknowns, $\mu_1, \mu_2, \ldots, \mu_n$ and X_0 using, for example, the methods developed by Warga [5] or Zeleznik and Gordon [6].

To include nonequilibrium reactions we now impose additional constraints

$$c_i = \sum_{j=1}^{m} a_{ij} X_j, \qquad i-n = 1, 2, \ldots, r \tag{8}$$

of the same form as (3), where the new a_{ij} are determined by the character of the rate-limiting reactions.

If we assume these reactions are of the type

$$\sum_{j=1}^{m} \alpha^{+}_{ikj} X_j \underset{R^{-}_{ik}}{\overset{R^{+}_{ik}}{\rightleftharpoons}} \sum_{j=1}^{m} \alpha^{-}_{ikj} X_j \tag{9}$$

then the rate of change of the number of moles of species j will be given by

$$\frac{1}{V}\frac{dX_j}{dt} = \sum_{k=1}^{s_i} (\alpha^{-}_{ikj} - \alpha^{+}_{ikj})(R^{+}_{ik} - R^{-}_{ik}) \tag{10}$$

where s_i is the number of reactions involved in changing the value of the constraint c_i, R^{+}_{ik} and R^{-}_{ik} are the forward and reverse rates, respectively, of reaction k for constraint i, α^{+}_{ikj} and α^{-}_{ikj} are the corresponding stoichiometric coefficients, and V is the volume occupied by system.

Differentiating (8) and substituting (10) for dX_j/dt, we obtain the following set of differential equations for the additional c_i's.

$$\frac{1}{V}\frac{dc_i}{dt} = \sum_{k=1}^{s_i} b_{ik}(R^{+}_{ik} - R^{-}_{ik}) \tag{11}$$

where

$$b_{ik} = \sum_{j=1}^{m} a_{ij}(\alpha^{-}_{ikj} - \alpha^{+}_{ikj}) \tag{12}$$

In general, the reaction rates will be of the form

$$R^{\pm}_{ik} = k^{\pm}_{ik} \prod_{j=0}^{m} [X_j]^{\alpha^{\pm}_{ikj}} \tag{13}$$

where $[X_j] = X_j/V$ is the concentration of X_j and k^{+}_{ik} and k^{-}_{ik} are forward and reverse rate constants which we assume to obey the detailed balancing condition

$$k^{+}_{ik}/k^{-}_{ik} = \prod_{j=0}^{m} [X_j]_e^{(\alpha^{-}_{ikj} - \alpha^{+}_{ikj})} \tag{14}$$

$$= \prod_{j=0}^{m} \exp\left[(\alpha^{+}_{ikj} - \alpha^{-}_{ikj})\left(\frac{H_j}{RT} - \frac{S_j}{R} + \ln\frac{V_0 T}{T_0}\right)\right]$$

where $V_0 = RT_0/p_0$ is the molar volume at the reference temperature T_0 and pressure p_0. Note that the "species" X_0 may participate in the reactions as a catalyst but does not enter the detailed balancing equation since by definition $\alpha^{+}_{ik0} = \alpha^{-}_{ik0}$.

Given the rate-limiting reactions and the initial condition of the gas, the set of equations (11) may now be integrated numerically in stepwise fashion using the partial-equilibrium concentrations computed at each step to advance to the next. Mass addition and nuclear reactions may also be taken into account at this point by specifying the rates of change for the number of moles of each element in the gas (i.e., the first n c_i).

Application to Internal Combustion Engines

To illustrate the practical application of the method we have used it to investigate the effect of finite threebody recombination and dissociation rates on the "freezing" of CO in internal combustion engines. The constraint introduced by inhibiting such reactions is of the form

$$M = \sum_j X_j \tag{15}$$

where M is the total number of particles in the system. The rate equation for the constraint is

$$dM/dt = \sum_k (R_{dk} - R_{rk}) \tag{16}$$

where R_{dk} and R_{rk} are the dissociation and recombination rates for the kth reaction. Some examples of threebody reactions important in internal combustion engines are given in Table 1, where the rate constants were taken from Schofield [7]. For simplicity we have included

Table 1. Examples of Threebody Recombination and Dissociation Reactions of Potential Importance in Internal Combustion Engines[a]

118.0	$+ H_2O + X \leftrightarrow OH + H + X$	3×10^{-31}
71.9	$+ NO_2 + X \leftrightarrow NO + O + X$	6×10^{-32}
25.8	$+ NO_2 + NO_2 \leftrightarrow NO + NO + O_2$	1×10^{-38}
38.6	$+ {}^1N_2O + X \leftrightarrow {}^1N_2 + {}^3O + X$	
125.8	$+ {}^1CO_2 + X \leftrightarrow {}^1CO + {}^3O + X$	1×10^{-34}
21.4	$+ HCO + X \leftrightarrow CO + H + X$	

[a] Exothermicities and activation energies in kilocalories: rate constants in cm^6/sec.

only the first three in our preliminary analysis. In this connection it should be noted that only one threebody reaction is required to equilibrate the system; however, different reactions may be rate controlling at different times during the expansion.

The calculations were carried out for stoichiometrically correct mixtures of air and C_8H_{18} and included the 14 species: N_2, CO_2, H_2O, CO, O_2, NO, OH, O, H_2, H, NO_2, N_2O, HCO, N. Measured pressure time curves for a typical CFR engine were used and the initial value of M was taken to be the number of particles in the unburned fuel–air mixture. In addition, the expansion was assumed to be adiabatic, leading to the auxiliary condition

$$dH - V\,dp = 0 \tag{17}$$

which may be integrated using the equation of state

$$pV = RT \sum_j X_j \tag{18}$$

and the relation

$$dH = RT \sum_j X_j\,dS_j \tag{19}$$

to obtain

$$\sum_j X_j[S_j - \ln(p/p_0)] = \text{constant} \tag{20}$$

Note that (20) is identical in form to the condition for an isentropic expansion but in this case the X_j are not, in general, equilibrium values.

Some typical results for a cycle having a peak temperature of 2800°K are shown in Fig. 1 as a function of crank angle and temperature.

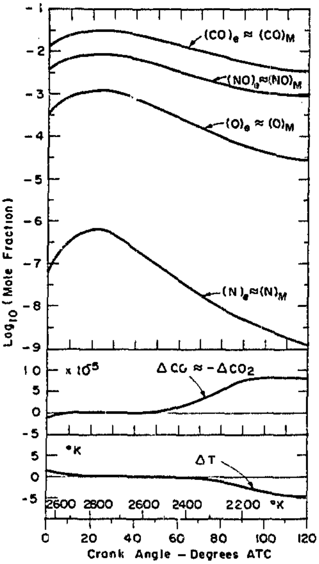

Figure 1. Comparison of rate-controlled (subscript M) and equilibrium (subscript e) concentrations and temperatures in an internal combustion engine as a function of crank angle for a cycle with a peak temperature of 2800°K.

The upper part of the figure shows the mole fractions of CO, NO, N, and O, which are of particular interest in connection with the kinetics of pollutant formation in internal combustion engines. The subscripts e and M denote full-equilibrium and threebody rate-controlled solutions, respectively. On the scale of the figure the two solutions are indistinguishable. The central part of the figure shows the difference between the rate-controlled and equilibrium CO mole fractions, and it can be seen that although some departure from equilibrium begins to appear late in the cycle, it is very small. Finally, the lower part of the figure shows the difference between the rate-controlled and equilibrium temperatures, which is also very small.

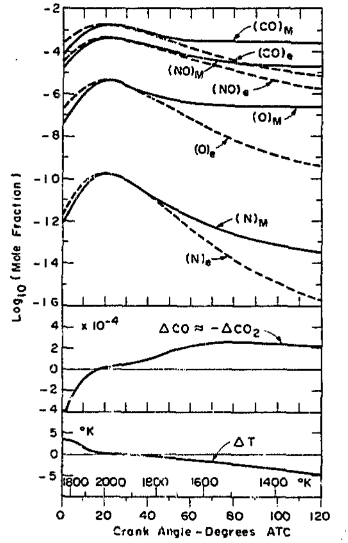

Figure 2. Comparison similar to that of Fig. 1 for a cycle with a peak temperature of 2000°K.

By way of contrast, similar results for a cycle having a peak temperature of only 2000°K are shown in Fig. 2. In this case, the rate-controlled mole fractions lag behind the equilibrium values at early times due to the relatively slow dissociation rate associated with the lower prevailing temperatures. Full equilibrium is reached a little past peak temperature and is maintained during the initial part of the expansion. As the temperature drops below 1800°K, however, "sudden freezing" of the rate-controlled mole fractions occurs, resulting in a highly nonequilibrium condition thereafter. Note that the "frozen" CO level of approximately 0.1 % is typical of that observed in the exhaust of well-adjusted internal combustion engines. Although this does not necessarily mean that binary reactions are not also important in determining exhaust CO concentrations, it does indicate that threebody reactions can play a major role. This situation is the opposite of that for NO where binary reactions are almost certainly rate controlling and produce higher NO levels [8] than those due to "freezing" of threebody reactions. The effect of coupling between binary and threebody reactions on NO production is currently being investigated.

The results of these preliminary calculations support the frequently used assumption that the combustion products in an internal combustion engine are in local equilibrium near peak pressure. They also suggest that the levels of CO found in the exhaust are the result of "frozen" threebody recombination rates rather than a slow rate of removal in exchange reactions.

This investigation was supported in part by Public Health Service Research grant 1-R01-AP-01228-01 from N.A.P.C.A., and in part by a grant from the Ford Motor Co.

References

1. Bray, K. N. C., *J. Fluid Mech.*, 6, 1 (1959).
2. Kaskan, W. E., *Combustion & Flame*, 3, 229, 286 (1958).
3. Schott, G. L., *J. Chem. Phys.*, 32, 710 (1960).
4. Lezberg, E. A., and Franssciscus, L. C., *AIAA J.*, 1, 2077 (1963).
5. Warga, J., *J. Soc. Indust. Appl. Math.*, 11, 594 (1963).
6. Zeleznik, F. J., and Gordon, S., *Ind. Eng. Chem.*, 60, 27 (1968).
7. Schofield, K., *Planet. Space Sci.*, 15, 643 (1967).
8. Lavoie, G. A., *Combustion & Flame*, 15, 97 (1970).

(Received March 1971; revised May 1971)