RATE-CONTROLLED CONSTRAINED-EQUILIBRIUM THEORY OF CHEMICAL REACTIONS IN COMPLEX SYSTEMS*

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1. INTRODUCTION

The development of theoretical models for describing the time evolution of complex reacting systems is a fundamental objective of nonequilibrium thermodynamics. It is also of great importance for a variety of practical problems related to combustion, hypersonic aerodynamics, chemical processing and biology.

Although in principle the equations of motion governing the microscopic behavior of such systems can be obtained from the laws of quantum mechanics. in practice the integration of these equations for macroscopic systems containing extremely large numbers of degrees of freedom is impossible. To circumvent this difficulty, Keck and Gillespie¹ proposed an alternative approach based on the Second Law of Thermodynamics which they originally called the rate-controlled partial-equilibrium method. This was later renamed rate-controlled constrained equilibrium (RCCE) by Galant and Appleton² to distinguish it from the partial-equilibrium method proposed by Bulewicz, James and Sugden³ and used by a number of investigators⁴⁻⁸ to treat the recombination region of the $H_2/N_2/O_2$ flames.

In the RCCE method it is assumed that for many practical applications, the evolution of a complex system can be described with acceptable accuracy by a relatively small number of rate-controlling reactions which impose slowly changing constraints on the allowed states of the system. It is also assumed, as in thermodynamics, that fast reactions exist which relax the system to the associated constrained-equilibrium state on a time scale short compared to that on which the constraints are changing. Under these conditions, a nonequilibrium system will relax to its final equilibrium state through a sequence of rate-controlled constrained-equilibrium states which can be determined by maximizing the entropy subject to the instantaneous values of the constraints. Thus only the rate equations for the constraints must be integrated. The set of all dissociation-recombination reactions is an example of a class of rate-controlling reactions important in chemical kinetics. These impose a constraint on the total number of particles in a gas which cannot change unless at least one such reaction occurs. The results can be systematically improved by adding constraints imposed by increasingly faster reactions until the required accuracy is achieved. When the number of independent constraints included equals the number of degrees of freedom of the system the method becomes exact.

The RCCE method has been used with considerable success by Keck and coworkers to investigate the formation of air pollutants in combustion products⁹⁻¹¹ and to calculate ignition delay times for hydrogen oxidation.¹² It has also been applied by Takeda, Hoshi and Matsui¹³ to the homogeneous oxidation of hydrogen and methane under constant volume adiabatic conditions. A discussion of the method and reviews of some prior applications have been given by Keck¹⁴ and Beretta and Keck.¹⁵ Similar methods have been used by: Alberty¹⁶ and Oppenheim¹⁷ to investigate the constrained equilibrium of isomer groups, Kestin and coworkers in studies of irreversible thermodynamics¹⁸ and continuum mechanics,¹⁹ Keck²⁰ and Levine²¹ to estimate chemical reaction rates, Pope²² to calculate pdfs for turbulent flows, Kerner²³ to study speciation in ecological systems, and Dornbush²⁴ to investigate exchange rate overshooting in monetary systems.

There has been a widespread tendency to identify the RCCE method with the well known pseudo-steady-state approximation (PSSA) also used to reduce the number of differential equations required to describe the evolution of complex systems. As will be seen, however, the two methods are quite distinct both from a fundamental and an applied point of view. In particular the pseudo-steady-state approximation (PSSA) requires a complete kinetic model for the system whereas the rate-controlled constrainedequilibrium (RCCE) method only requires a knowledge of the rate-controlling reactions.

The statistical mechanical methods used to determine the equilibrium thermodynamic state of systems subject to fixed external constraints are reviewed in the next section of this paper. In Section 3 these methods are generalized to include additional constraints (passive resistances) imposed by the internal dynamics of the system. The thermodynamics of constrained equilibrium is reviewed in Section 4 and the evolution of rate-controlled constrainedequilibrium gas mixtures is discussed in Section 5. The RCCE method is compared with conventional methods for treating such mixtures in Section 6. An illustrative example of the application of the method to the pure oxygen system is given in Section 7 and practical applications are discussed in Section 8. The advantages and disadvantages of the RCCE method are summarized in the final section.

2. STATISTICAL THERMODYNAMICS

2.1. Micro- and Macrostates

The microstate of a system may be defined as the most complete description of its condition that can possibly be given. For a mechanical system, the possible microstates are the energy eigenfunctions of the Hamiltonian describing its evolution.

The macrostate of a system corresponds to the most probable mixture of microstates consistent with those properties of the system which can be independently measured or controlled by an observer. Examples of such properties for mechanical systems are the energy, volume, pressure and elemental composition of the system.

2.2. Maximum Entropy Principle

Let p_j be the probability that a system whose condition is not precisely known is in one of its possible microstates *j*. According to the general principles of statistical mechanics,²⁵ thermodynamics²⁶ and information theory,²⁷ the macrostate of such a system can be determined by maximizing the dimensionless function.

$$\tilde{S} = -\sum_{j} p_{j} \ln p_{j} \qquad (2.1)$$

subject to the normalization condition

$$\sum_{j} p_{j} = 1 \qquad (2.2)$$

and all other constraints which restrict the probabilities p_i .

The informational entropy $S_1(\underline{p})$ is identical to (2.1), the statistical mechanical entropy is $S_B(\underline{p}) = k_B \tilde{S}(\underline{p})$, where k_B is the Boltzmann constant, and the thermodynamic entropy $S(E, V, \underline{N})$ is the maximum value of the statistical entropy for given values of the energy, volume and composition.

2.3. Method of Lagrange Multipliers

The maximum of (2.1) subject to the constraint (2.2) can easily be found using the elegant method of undetermined Lagrange multipliers. Since we shall be using this method repeatedly for increasingly complex sets of constraints, a brief description of it will be given here.

The general problem is to find the extrema of a function S(x) subject to a set of r constraints

$$F_i(x) = C_i \ (i = 1...r)$$
 (2.3)

where the C_i are constants. The solution proposed by Lagrange involves, first, finding the unconstrained extrema of the function

$$G(\underline{x}, \underline{\lambda}) = S(\underline{x}) - \sum_{i} \lambda_{i} F_{i}(\underline{x}) \qquad (2.4)$$

where the λ_i are arbitrary constant multipliers. This requires solving the set of equations

$$\partial G(x,\lambda)/\partial x_i = 0$$
 (2.5)

to obtain $\underline{x}(\underline{\lambda})$. The undetermined multipliers can then be found by substituting $\underline{x}(\underline{\lambda})$ back into (2.3) to obtain the set of equations

$$F_i(x(\lambda)) = C_i \quad (i = 1 \dots r) \quad (2.6)$$

which can be solved for $\lambda(\underline{C})$. Note that to obtain a solution of the problem the constraints $F_i(\underline{x})$ must be linearly independent. In the present application, one must also verify that the extrema found are maxima. For a convex function such as the entropy (2.1) this will always be the case.

2.4. Normalization Constraint

Applying the above method to (2.1) and (2.2) we find

$$\partial/\partial p_j \left(-\sum_k p_k \ln p_k - \alpha \sum_k p_k \right) \qquad (2.7)$$
$$= -\ln p_j - 1 - \alpha = 0$$

which gives

$$\ln p_i = -1 - \alpha \qquad (2.8)$$

where α is the undetermined Lagrange multiplier conjugate to the constraint (2.2). It can be seen from (2.8) that, in this case, the macrostate corresponds to a uniform distribution over microstates.

To determine the value of α , (2.8) may be substituted back into (2.2) to obtain

$$\exp\left(\alpha + 1\right) = W \tag{2.9}$$

where W is the number of microstates of the system. Combining (2.8) and (2.9) gives

$$p_i = W^{-1} (2.10)$$

which when substituted into (2.1) gives the familiar result

$$\tilde{S} = \ln W. \tag{2.11}$$

2.5. Energy Constraint

If we now consider an isolated system for which the energies of the microstates are given by ε_j then the energy

$$E = \sum_{j} \varepsilon_{j} p_{j} \qquad (2.12)$$

is a constant. Again using the method of Lagrange multipliers to maximize the entropy (2.1) subject to the two constraints (2.2) and (2.12) we obtain

$$\ln p_i = -1 - \alpha - \beta \varepsilon_i. \qquad (2.13)$$

Substituting (2.13) back into (2.2) gives

$$\exp (\alpha + 1) = \sum_{j} \exp (-\beta \varepsilon_{j}) = Q(\beta)$$
(2.14)

where $Q(\beta)$ is the partition function for the system. Combining (2.13) and (2.14) we obtain the canonical distribution function

$$p_i = Q^{-1} \exp(-\beta \varepsilon_i). \qquad (2.15)$$

The corresponding energy and entropy obtained by substituting (2.15) into (2.12) and (2.1) are

$$E(\beta) = Q^{-1} \sum_{j} \varepsilon_{j} \exp(-\beta \varepsilon_{j}) = -\partial \ln Q / \partial \beta$$

and

(2.16)

$$\widetilde{S}(E) = \ln Q + \beta E. \qquad (2.17)$$

It can be seen from Eqs (2.15)-(2.17) that a knowledge of the partition function Q is sufficient to

completely determine the thermodynamic state of a system. To calculate Q, the energies of the microstates must be known and for complex systems these can only be determined experimentally or estimated using various approximations.

2.6. Independent Particle Model

For a system composed of N independent distinguishable particles in a volume V, the probability of finding the system in a specified microstate may be separated as a product in the form

$$p(k_1, k_2 \dots k_N) = cx(k_1)x(k_2)\dots x(k_N)$$
 (2.18)

where $x(k_j)$ is the probability of finding a particle in its 'private' microstate k_j , and c is a constant determined by the normalization conditions. The normalization condition (2.2) for the system is

$$1 = \sum \sum \dots \sum p(k_1, k_2 \dots k_N) / N! \quad (2.19)$$

where the summations over k_j are carried out as though the particles were distinguishable and the result is divided by N! to correct for the fact that permutations of indistinguishable particles do not lead to new microstates. Substituting (2.18) into (2.19) and using the normalization condition for the particles

$$1 = \sum_{k} x(k)$$
 (2.20)

we find c = N! so that (2.18) becomes

$$p(k_1, k_2 \dots k_N) = N! x(k_1) x(k_2) \dots x(k_N).$$
(2.2)

The energy of the system is simply the sum of the energies of the particles

$$E = N \sum_{k} \varepsilon(k) x(k) \qquad (2.22)$$

The corresponding entropy obtained by substituting (2.21) into (2.1) is

$$\tilde{S} = -N \sum_{k} x(k) \ln x(k) - \ln N!.$$
 (2.23)

It should be noted that the expression (2.23) is valid for any number of particles and in particular for n = 1 it reduces to (2.1). For large N one can make the approximation $\ln N! \sim N(\ln N - 1)$ and (2.23) becomes

$$\tilde{S} = -N\left(\sum_{k} x(k) \ln x(k) + \ln N - 1\right).$$

(2.24)

In the more general case of a system composed of *ns* distinguishable groups of particles each containing N_j identical members, the energy and entropy may be obtained by simply summing (2.22) and (2.24) over all groups. Thus

$$E = \sum_{j} N_{j} \sum_{k} \varepsilon_{j}(k) x_{j}(k) \qquad (2.25)$$

and

$$\tilde{S}_{j} = -\sum_{j} N_{j} \left(\sum_{k} x_{j} \left(k \right) \ln x_{j} \left(k \right) + \ln N_{j} - 1 \right)$$

$$(2.26)$$

where $\varepsilon_j(k)$ is the energy of a particle of type j in the microstate k and $x_j(k)$ is the probability of finding a particle of type j in the microstate k.

Maximizing the entropy (2.26) subject to the constraint (2.25) and the normalization conditions

$$\sum_{k} x_j(k) = 1$$
 $(j = 1...ns)$ (2.27)

we obtain for the equilibrium state

$$\ln x_j(k) = -1 - \alpha_j/N_j - \beta \varepsilon_j(k) \quad (2.28)$$

where, α_j and β are the Lagrange multipliers conjugate to the constraints (2.27) and (2.25).

Substituting (2.28) back into the normalization conditions (2.27), gives

$$\exp (\alpha_j/N_j + 1) = \sum_k \exp (-\beta \varepsilon_j(k))$$
$$= Q_j(V, \beta), \quad (j = 1 \dots ns)$$
(2.29)

where Q_j is the partition function for the species *j*. If we assume that the energies of the particles are independent of their position in the volume V,

$$Q_i(V, \beta) = [Q_i]V$$
 (2.30)

where the partition function per unit volume $[Q_j]$ is only a function of β . Combining (2.29) and (2.28) we find

$$x_j(k) = Q_j^{-1} \exp(-\beta \varepsilon_j(k)), \qquad (2.31)$$

and substituting (2.31) into (2.25) gives

$$E = \sum_{j} N_{j} E_{j}(\beta) \qquad (2.32)$$

where

)

$$E_{j}(\beta) = \sum_{k} \varepsilon_{j}(k)Q_{j}^{-1} \exp(-\beta\varepsilon_{j}(k)) \quad (2.33)$$
$$= -\partial \ln Q_{j}/\partial\beta$$

is the average energy per particle of species j. The entropy obtained from (2.26), (2.31), (2.32) and (2.33) is

$$\widetilde{S}(E, V, \underline{N}) = \beta E - \sum_{j} N_{j} (\ln (N_{j}/Q_{j}) - 1).$$
(2.34)

When working with (2.34), it is important to keep in mind that, by virtue of (2.32), $\beta = \beta(E, N)$ is an implicit function of both energy and composition, and

that, by virtue of (2.29), $Q_j = Q_j(V, \beta)$ is also an implicit function of these variables as well as the volume.

3. CONSTRAINED EQUILIBRIUM

In the previous section we have tacitly assumed that the particles of our system maintain their identity but are capable of exchanging energy. The only constraints considered were those imposed by the normalization conditions for the probability functions and the universal law for conservation of the energy. The equilibrium state determined by maximizing the entropy subject to these constraints is that to which the system relaxes at times large compared to the time scale τ_E on which energy is exchanged between particles.

If we now suppose that our particles are composed of a smaller set of (more) fundamental particles and are capable of undergoing interactions in which their identity may change but the number of fundamental particles remains constant, then we must consider the possibility of additional constraints of the form

$$C_i = \sum_j a_{ij} N_j$$
 (*i* = 1...*ne*) (3.1)

where *ne* is the number of different types of fundamental particles, C_i is the number of fundamental particles of type *i* in the system and a_{ij} is the number of fundamental particles of type *i* in a complex particle of type *j*.

In any real system, the apparent nature of the fundamental particles will depend both on the energy of the system and the time scale on which it is observed. If the observation time is large compared to the time scale τ_c on which chemical reactions occur, but small compared to the time scale τ_1 on which ionization reactions occur, the fundamental particles will be the neutral atoms; if the observation time is large compared to τ_i but short compared to the time scale $\tau_{\rm N}$ on which low energy nuclear reactions occur, the fundamental particles will be the electron and the atomic nuclei; if the observation time is large compared to τ_N but small compared to the time scale τ_{β} for β -decay, the fundamental particles will be the electron, proton and neutron; if the observation time is large compared to τ_{θ} but small compared to ... and so on to infinity.

It follows that the concept of an equilibrium state has meaning only when the constraints on the system are carefully specified and that all equilibrium states are in fact constrained-equilibrium states.

3.1. Chemical Equilibrium

If we assume that the rates of nuclear and ionization reactions are infinitesimal, then the fundamental particles are the neutral elements. In this case, the equilibrium chemical composition of an ideal gas

mixture containing ns different species composed of ne different elements can be obtained by maximizing the entropy (2.34) subject to the ne constraints (3.1). Once again using the method of Lagrange multipliers we obtain

$$N_j = Q_j \exp\left(-\sum_i \gamma_i a_{ij}\right)$$
 (3.2)

where Q_j is given by (2.29). Note that in using the expression (2.34) for the entropy, it has been tacitly assumed that energy exchange processes are sufficient to equilibrate the internal energy state of the system.

Substituting (3.2) into the constraints (3.1) and the expression (2.32) for the energy we obtain the ne + 1 equations

$$C_{i} = \sum_{j} a_{ij} Q_{j}(V, \beta) \exp\left(-\sum_{k} \gamma_{k} a_{kj}\right)$$
(3.3)
(*i* = 1...*ne*)

and

$$E = \sum_{j} E_{j}(\beta) Q_{j}(V, \beta) \exp\left(-\sum_{k} \gamma_{k} a_{kj}\right) (3.4)$$

which can be solved for the ne + 1 unknown Lagrange multipliers

 $\gamma_i = \gamma_i(V, E, C_1 \dots C_{ne}) \quad (i = 1 \dots ne) (3.5)$

and

$$\beta = \beta(V, E, C_1 \dots C_{ne}). \qquad (3.6)$$

Substituting (3.5) and (3.6) into (3.2) we obtain the composition

$$N_j = N_j(V, E, C_1 \dots C_{ne})$$
 $(j = 1 \dots ns)$
(3.7)

as a function of V, E and $C_1 ldots C_{ne}$. This completely determines the equilibrium state of the system.

This method of determining the equilibrium composition of a chemical system was apparently first proposed by Powell and Sarner²⁸ and named the method of 'element potentials'. An important advantage of the method over the well known alternative method of equilibrium constants²⁹ is that it depends only on a knowledge of the thermodynamic properties of the species in the system and does not require any information about the reactions which allow it to relax to equilibrium as long as such reactions exist. It is therefore evident that the equilibrium composition of a reacting gas mixture is completely independent of any reaction mechanism even though it might appear otherwise from the method of equilibrium constants which requires specification of as many linearly independent reactions as there are species in the system. In addition to its fundamental importance this feature of the method of element potentials can be of considerable practical value since for systems involving a very large number of possible species, the specification of the very large number of linearly independent reactions required by the method of equilibrium constants can be a nontrivial task.

3.2. Constrained Chemical Equilibrium

As mentioned in the introduction, there are many situations of practical interest in which it is possible to identify classes of slow chemical reactions which if completely inhibited would prevent the relaxation of the system to chemical equilibrium. Some of the constraints which have been investigated to date in connection with a variety of combustion problems are listed in Table 1.

Except for the inclusion of additional constraints

$$C_i = \sum_j a_{ij} N_j$$
 (*i* = *ne* + 1...*nc*) (3.8)

of the same form as (3.1), the calculation of the constrained-equilibrium composition can be carried out in exactly the same manner as in the previous section. In this case one obtains the nc + 1 unknown Lagrange multipliers

$$\gamma_i = \gamma_i(V, E, C_1, \dots C_{nc}) \quad (i = 1 \dots nc)$$
(3.9)

and

$$\beta = \beta(V, E, C_1, \dots C_{nc}) \qquad (3.10)$$

from which the composition can be obtained in the form

$$N_j = N_j(V, E, C_1, \dots, C_{nc})$$
 $(j = 1 \dots ns).$
(3.11)

3.3. Multiple Temperature Gas Mixtures

It is often possible to approximate the energy of a system as the sum of the energies in a set of independent 'normal modes'. In an ideal gas mixture such a set is represented by the translational, rotational, vibrational and electronic degrees of freedom of the molecules. Under some conditions the time scales for energy exchange between different degrees of freedom can be long compared to those for energy exchange

TABLE 1. Examples of generalized constraints

Number of molecules	M
Fixed nitrogen	FN
Free oxygen	FO
Carbon monoxide	CO
Free valence	FV
Active valence	AV
Bonded atom pairs	PB
Valence bonds	VB
Valence bonds of order k	B_k
n Atom molecules	A_n

within the individual degrees of freedom. For example, behind shock waves in diatomic gases the characteristic time τ_{TV} for energy exchange between translation and vibration can be five or more orders of magnitude slower than the characteristic times τ_{TT} and τ_{VV} for translational or vibrational relaxation. Thus on an intermediate time scale the translational and vibrational energies E_T and E_V constitute additional constraints on the allowed state of the gas.

In such cases the constrained-equilibrium state of a Gibbs-Dalton mixture of molecules each having *nm* normal modes can be obtained by maximizing the entropy

$$\widetilde{S} = -\sum_{j} N_{j} \left(\sum_{k} \sum_{i} x_{kj}(i) \ln x_{kj}(i) + \ln N_{j} - 1 \right)$$
(3.12)

subject to the constraints

$$1 = \sum_{i} x_{ki}(i)$$
 $(j = 1...ns, k = 1...nm)$

$$\varepsilon_k = \sum_j \sum_i \varepsilon_{kj}(i) \ x_{kj}(i) \ N_j \qquad (k = 1 \dots nm)$$
(3.13)
(3.13)
(3.14)

where $x_{kj}(i)$ is the probability of finding a molecule of type j in the microstate i of normal mode k and $\varepsilon_{kj}(i)$ is the corresponding energy of the microstate.

Again using the method of Lagrange multipliers we find

$$x_{kj}(i) = Q_{kj}^{-1} \exp(-\beta_k \varepsilon_{kj}(i))$$
 (3.15)

where

$$Q_{kj} = \sum_{i} \exp(-\beta_k \varepsilon_{kj}(i)). \qquad (3.16)$$

Substituting (3.15) back into the constraint (3.14) gives

$$\varepsilon_k = \sum_j \varepsilon_{kj}(\beta_k) N_j$$
 (3.17)

where

$$\varepsilon_{kj}(\beta_k) = -\partial \ln Q_{kj}/\partial \beta_k.$$
 (3.18)

Note that for the translational modes (k = 1)

$$Q_{1j} = Q_{1j}(V, \beta_1) = [Q_{1j}]V$$
 (3.19)

is a function of both volume and β_1 whereas for the internal modes

$$Q_{kj} = Q_{kj}(\beta_k)$$
 (k = 2...nm). (3.20)

The entropy of a gas in a multiple temperature constrained-equilibrium state, obtained by substituting (3.15) into (3.12) and using (3.17) is

$$\widetilde{S}(V, \underline{\varepsilon}, \underline{N}) = \sum_{k} \beta_{k} \varepsilon_{k} - \sum_{j} N_{j} (\ln (N_{j}/Q_{j}) - 1)$$
(3.21)

where

$$Q_{j}(V, \underline{\beta}) = V \prod_{k} [Q_{kj}] \qquad (3.22)$$

Maximizing (3.21) subject to a constraint on the total energy

$$E = \sum_{k} \varepsilon_{k} \qquad (3.23)$$

gives $\beta_k = \beta$ and (3.21) reduces to (2.34).

Maximizing (3.21) with respect to the constraints (3.1) and (3.17), the constrained-equilibrium composition of a multiple β gas mixture is once again found to be

$$N_j = Q_j \exp\left(-\sum_i \gamma_i a_{ij}\right)$$
 (3.24)

in which Q_i is given by (3.22).

3.4. Linear Independence of Constraints

To obtain solutions of the equations derived in the preceding sections, it is necessary that the constraints be linearly independent. For arbitrarily specified constraints, such as those listed in Table 1 above, it is not always clear when this is the case and some interesting and useful general relations exist.

Among the obvious relations are:

$$E = \sum_{k} \varepsilon_{k} \qquad (3.25)$$

$$M = \sum_{j} N_{j} = \sum_{n} A_{n} \quad (3.26)$$

$$C = \sum_{i} C_{i} = \sum_{n} nA_{n} \quad (3.27)$$

where C is the total number of elemental atoms and A_n is the number of *n*-atom molecules. Also by definition:

$$PB = \sum_{k} B_{k} \qquad (3.28)$$

$$VB = \sum_{k} kB_{k} \qquad (3.29)$$

where PB is the number of bonded pairs of atoms, VB is the number of valence bonds and B_k is the number of bonds of order k.

If we now consider systems containing only linear or branched molecules, then the number of bonded pairs in any species j is

where

 $p_i = a_i - 1$ (3.30)

$$a_j = \sum_i a_{ij} \qquad (3.31)$$

is the number of atoms in species j. The number of bonded pairs in the system obtained by summing (3.30) over all species is

$$PB = \sum_{j} p_{j}N_{j} = \sum_{i} C_{i} - M = C - M.$$

(3.32)

Thus for a given system PB and M are related.

The free valence of a species *j* may be defined as

$$f_j = \sum_i v_i a_{ij} - 2b_j$$
 (3.33)

where v_i is the valence of element *i*, and b_j is the number of valence-bonds in the species *j*. Summing (3.33) over all species we obtain the free valence of the system

$$FV = \sum_{j} f_{j} N_{j} = TV - 2VB \qquad (3.34)$$

where

$$TV = \sum_{i} v_i C_i \tag{3.35}$$

is the total valence of the system and

$$VB = \sum_{j} b_{j} N_{j} . \qquad (3.36)$$

Thus FV and VB are related.

Given the elemental composition of the system $C_1 ldots C_{ne}$, the number of molecules M, and the free valence FV, we find from (3.26) and (3.27)

$$A_1 = -C + 2M + A_3 + 2A_4 + 3A_5 \dots \quad (3.37)$$

$$A_2 = C - M - 2A_3 - 3A_4 - 4A_5 \dots \qquad (3.38)$$

and from (3.28), (3.29), (3.32) and (3.34)

$$B_{1} = -\frac{1}{2} (TV - FV) + 2(C - M) + B_{3}$$

+ 2B₄ + 3B₅... (3.39)
$$B_{2} = \frac{1}{2} (TV - FV) - (C - M) - 2B_{3}$$

$$B_2 = \frac{1}{2} (TV - FV) - (C - M) - 2B_3 - 3B_4 - 4B_5 \dots$$
(3.40)

It can be seen from (3.37) and (3.38) that for gas mixtures containing only molecules with no more than 3 atoms, the number of monatomic and diatomic molecules is determined by the total number of molecules and the number of triatomic molecules. It can also be seen from (3.39) and (3.40) that for gas mixtures containing only single and double bonds, the number of such bonds is determined by the total number of molecules and the free valence. Failure to recognize the existence of these relationships led to many 'singular matrix' warnings in early calculations. In complex systems containing large numbers of possible constraints, many other such relationships will exist and it is the opinion of the author that the methods of group theory may be useful in this connection.

4. THERMODYNAMICS OF CONSTRAINED EQUILIBRIUM

In the preceding analysis we have considered only the final state in which an isolated system subject to fixed constraints will be found after an infinitely long period of time. We now wish to extend the analysis to include situations in which as a result of interaction with the environment the constraints may be functions of time. The science of *thermodynamics* enables us to do this by introducing the assumption that, if the changes in the constraints are sufficiently slow, a system such as the gas mixture under consideration will evolve through a sequence of quasistatic states which at all times remain close to the static equilibrium states determined by the instantaneous values of the constraints. In a gas, this condition is supposed to be maintained by molecular collision processes whose relaxation time τ_r is short compared to the characteristic time for a change in the constraints, e.g. $\tau_r \ll \tau_v = (dln V/dt)^{-1}$.

4.1. Thermodynamic Variables

In conventional thermodynamics the constraints considered are the energy E, the volume V, and the numbers N_j of the various species in the system. In this case, the differential change in the entropy produced by small changes in the constraints is given by the Gibbs equation

$$TdS = dE + pdV - \sum_{j} \mu_j dN_j \qquad (4.1)$$

where by definition

$$T = (\partial S / \partial E)^{-1} \tag{4.2}$$

is the temperature

$$p = T(\partial S/\partial V) \tag{4.3}$$

is the pressure and

$$\mu_i = - T(\partial S / \partial N_i) \tag{4.4}$$

is the Gibbs free energy per particle.

The relationship between the thermodynamic variables T and μ_j and the statistical variables β and Q_j can now be established. Recalling that $S = k_B \tilde{S}$ and using (2.34) and (2.32) to evaluate the partial derivatives in (4.2)-(4.4), we find

$$T = (k_{\rm B}\beta)^{-1} \tag{4.5}$$

$$\mu_i = k_{\rm B} T \ln (N_i / Q_i) \tag{4.6}$$

and

$$pV = k_{\rm B}T\sum_{j}N_j \tag{4.7}$$

which is the Equation of State for an ideal gas mixture.

Substituting (3.24) into (4.6) we find for a system in constrained equilibrium

$$\mu_j = -k_{\rm B}T\sum_i \gamma_i a_{ij} = \sum_i \lambda_i a_{ij} \qquad (4.8)$$

where we have introduced the 'constraint potential'

$$\lambda_i = -k_{\rm B}T\gamma_i . \qquad (4.9)$$

If the constraint conjugate to γ_i is an element then λ_i is also the 'element potential'.

Multiplying (4.8) by N_j and summing over species we obtain the Gibbs free energy

$$F = \sum_{j} \mu_{j} N_{j} = \sum_{i} \lambda_{i} C_{i} \qquad (4.10)$$

in which

$$C_i = \sum_j a_{ij} N_j$$
 (*i* = 1...*nc*). (4.11)

Substituting (4.8) into (4.1) we obtain the Gibbs equation in the form

$$TdS = dE + pdV - \sum_{i} \lambda_i dC_i$$
 (4.12)

from which we also find

$$\lambda_i = -k_{\rm B}T\gamma_i = -T(\partial S/\partial C_i)_{E,V}. \quad (4.13)$$

The last term in (4.12) represents the entropy production due to chemical reactions which change constraints. Note that for the elements

$$dC_i = 0$$
 $(i = 1...ne)$. (4.14)

4.2. Free Energy Functions

For systems interacting with the environment in such a way that either T and V or T and p rather than E and V are specified, the constrained-equilibrium composition can be determined by minimizing either the dimensionless Helmholtz free energy

$$A(T, V, \underline{N}) = E - TS = k_{\rm B}T \sum_{j} N_j \left(\ln \left(N_j / Q_j \right) - 1 \right)$$

$$(4.15)$$

or the Gibbs free energy

$$F(T, p, \underline{N}) = A + pV = k_{\rm B}T\sum_{j}N_{j}\ln(N_{j}/Q_{j})$$
(4.16)

subject to the constraints (4.11). In either case one obtains

$$N_j = Q_j \exp\left(-\sum_i \gamma_i a_{ij}\right)$$
 (4.17)

which is identical to the result (3.2) obtained by maximizing the entropy for sytems at fixed E and V. The difference occurs in the constraint equations which must be solved to obtain the unknown multipliers.

For the case where T and V are the independent variables, substitution of (4.17) into (4.11) gives the *nc* equations

$$C_{i} = \sum_{j} a_{ij} Q_{j}(V, T) \exp\left(-\sum_{k} \gamma_{k} a_{kj}\right) \qquad (4.18)$$
$$(i = 1 \dots nc)$$

which can be solved for the nc unknowns

$$\gamma_k = \gamma_k(V, T, C_1, \dots, C_{nc}) \quad (k = 1 \dots nc). \quad (4.19)$$

For the case of fixed p and T, substitution of (4.17) into (4.11) and (4.7) gives the nc + 1, equations

$$C_{i} = \sum_{j} a_{ij} Q_{j}(V, T) \exp\left(-\sum_{k} \gamma_{k} a_{kj}\right)$$

(*i* = 1...*nc*) (4.20)

and

$$p = (k_{\rm B} T/V) \sum_{j} a_{ij} Q_{j}(V, T) \exp\left(-\sum_{k} \gamma_{k} a_{kj}\right)$$
(4.21)

which can be solved for the nc + 1 unknowns

$$\gamma_k = \gamma_k(p, T, C_1, \dots C_{nc}) \qquad (k = 1 \dots nc)$$
(4.22)

and

$$V = V(p, T, C_1, \dots C_{nc}).$$
 (4.23)

For a few very simple systems, the constraint equations above can be solved explicitly and an illustrative example is given in Section 7. In general, however, they must be solved numerically and algorithms for doing this have been developed by Warga,³⁰ Zeleznik and Gordon,³¹ Gordon and McBride³² and Reynolds.³³ Once the γ values have been found, the constrained-equilibrium composition can be obtained from (4.17).

In concluding this section we observe that differential changes in A and F are given by

$$dA = -pdV - SdT + \sum_{j} \mu_{j} dN_{j} \qquad (4.24a)$$

$$= -pdV - SdT + \sum_{i} \lambda_{i}dC_{i} \qquad (4.24b)$$

and

$$dF = Vdp - SdT + \sum_{j} \mu_{j} dN_{j} \qquad (4.25a)$$

$$= V dp - S dT + \sum_{i} \lambda_i dC_i \qquad (4.25b)$$

from which we find

$$\lambda_i = -k_{\rm B}T\gamma_i = (\partial A/\partial C_i)_{T,V} = (\partial F/\partial C_i)_{T,P}$$
(4.26)

which is the analog of (4.13).

It can be seen from (4.24) and (4.25) that the 'constraint potentials' λ_i play exactly the same role with respect to the constraints C_i as the chemical potentials μ_j play with respect to the species numbers N_j . The important distinctions are that the λ 's are independent whereas the μ 's are not, and that in constrained equilibrium, a small number of λ 's can determine a very large number of μ 's.

5. RATE-CONTROLLED CONSTRAINED EQUILIBRIUM (RCCE)

In conventional thermodynamics it is assumed that

a system subject to slowly changing externally controlled constraints, such as the energy and volume, will evolve through a sequence of 'quasi-static' states which are very close to the equilibrium state determined by the instantaneous values of the external constraints. Under these conditions the time-dependent composition can be obtained in the form

$$N_j(t) = N_j(E(t), V(t), C_1, \dots, C_{ne})$$
 (5.1)

analogous to (3.7).

Shifting equilibrium calculations carried out in this manner are widely used in thermodynamics, aerodynamics and chemistry and are familiar to most scientists and engineers. They clearly describe reversible processes since the energy distribution and composition are functions only of the constraints, in this case energy and volume, so that in any cycle in which the constraints are returned to their initial values, the system will be returned to its initial state.

5.1. Chemical Rate Equations

We now wish to consider a more general situation in which there may be additional contraints on the composition of a gas mixture which are controlled by the internal dynamics of the system and are slowly changing functions of time.

If this is the case, it should be possible to obtain the composition in the form

$$N_j(t) = N_j(E(t), V(t), C_1, \dots C_{nc}, (5.2)$$

 $C_{nc+1}(t) \dots C_{nc}(t))$

analogous to (3.11). Some examples of such constraints are those listed in Table 1.

We shall assume that the gas is contained in a volume V(t) which may be a slowly varying function of time and that energy exchange reactions have equilibrated so that the energy distribution of the molecules can be characterized by a single temperature T(t), which may also be a slowly varying function of time. We further assume that changes in the composition of the gas are the result of chemical reactions of the type

$$\sum_{j} v_{jk}^{+} B_{j} \leftrightarrow \sum_{j} v_{jk}^{-} B_{j}$$
(5.3)

where B_j is the symbol for species *j*, and v_{jk}^+ and v_{jk}^- are the corresponding stoichiometric coefficients for the forward and reverse directions of the elementary reaction *k*. An example of a reaction of the type (5.3) is the dissociation-recombination reaction

$$H_2 + He \leftrightarrow 2H + He$$
.

If this reaction is denoted by the index k = 1, and the species are denoted by the symbols $B_1 = H_2$, $B_2 =$ He, and $B_3 =$ H then the nonzero stoichiometric coefficients would be $v_{11}^+ = 1$, $v_{21}^+ = 1$, $v_{31}^- = 2$, and $v_{21}^- = 1$. Notice that the catalyst He which supplies energy for the forward dissociation reaction and removes energy for the reverse recombination reaction appears on both sides of the reaction equation even though its concentration is not changed. This establishes the order of the reaction which is 2 for the forward direction and 3 for the reverse direction.

The phenomenological rate equation for an individual species j is

$$\dot{N}_j = V \sum_k v_{jk} r_k \tag{5.4}$$

where

$$v_{jk} = v_{jk} - v_{jk}^+$$
 (5.5)

and

$$r_k = r_k^+ - r_k^-$$
 (5.6)

is the net reaction rate per unit volume.

The forward and reverse reaction rates are given by the phenomenological expressions

$$r_k^+ = k_k^+(T) \prod_i [N_j]^{ik}$$
 (5.7a)

and

$$r_k^- = k_k^-(T) \prod_j [N_j]^{v_j^-}$$
 (5.7b)

where $k_k^+(T)$ and $k_k^-(T)$ are rate constants for the forward and reverse reactions and $[N_j] = N_j/V$ is the concentration of species *j*.

At equilibrium the gas composition must be independent of time and thus the left hand side of (5.4)must vanish for all species. A sufficient condition for this is the detailed balancing equation

$$r_{ke}^{+} = r_{ke}^{-} \tag{5.8}$$

where the subscript e denotes equilibrium with respect to the elements. To prove that (5.8) is also a necessary condition, we note that to fix the equilibrium composition of a reacting gas mixture containing *ns* species, (5.8) must be true for *ns* linearly independent reactions involving the species. Since the equilibrium composition cannot depend on the choice of the independent reactions, (5.8) must be true for all possible reactions.

Substituting (5.7) into (5.8) we obtain the rate quotient law

$$k_k^+/k_k^- = \prod_j [N_{je}]^{\nu_{jk}} = K_{ck}(T)$$
 (5.9)

where

$$K_{ck}(T) = \prod_{j} [Q_j]^{v_{jk}}$$
 (5.10)

is the equilibrium constant for reaction k based on concentration.

5.2. Rate Equations for Constraints

Differentiating the equations (4.11) for the constraints with respect to time gives

$$\dot{C}_i = \sum_j a_{ij} \dot{N}_j \qquad (5.11)$$

from which we may eliminate N_j using (5.4) to obtain the rate equations for the constraints

$$\dot{C}_i = V \sum_k b_{ik} r_k \tag{5.12}$$

where

$$b_{ik} = \sum_{j} a_{ij} v_{jk} \qquad (5.13)$$

is the change in constraint C_i due to reaction k.

Since elements are conserved in all reactions, we have

$$b_{ik} = 0$$
 $(i = 1...ne)$ (5.14)

which by virtue of (5.12) gives

$$C_i(t) = C_i$$
 $(i = 1...ne).$ (5.15)

Using the rate-controlled constrained-equilibrium composition given by (4.17) to evaluate the reaction rates (5.7), we obtain a set of *nc-ne* first order differential equations of the form

$$\hat{C}_{i}(t) = \hat{C}_{i}(T(t), V(t), N_{1}(t) \dots N_{ns}(t))$$

 $(i = ne + 1 \dots nc)$ (5.16)

where

$$N_{j}(t) = N_{j}(T(t_{*}), V(t), C_{1} \dots C_{ne},$$

$$C_{ne+1}(t) \dots C_{nc}(t)) \qquad (j = 1 \dots ns). (5.17)$$

is the rate-controlled constrained-equilibrium composition. Given the initial values of T, V and $C_1 ldots C_{ac}$ these equations can be integrated in conjunction with the equation of state and the conservation equations of thermodynamics and fluid mechanics to determine the evolution of the system. In a few simple cases this can be done analytically but, in general, numerical methods must be employed. It should be noted that, except for the addition of the rate equations for the time-dependent constraints, a constrained equilibrium calculation may be carried out in exactly the same manner as a 'shifting equilibrium' calculation.

5.3. Rate Equations for the Lagrange Multipliers

The integration of the Eqs (5.16) for the constraints requires a calculation of the rate-controlled constrained-equilibrium composition (5.17) at each time step. For this reason the calculations for small systems, in which the number of species is not very much larger than the number of constraints, may take more time than that required to integrate the full set of rate equations.

An alternative approach is to integrate the rate equations for the Lagrange multipliers themselves. A problem which can arise in this method is that some of the Lagrange multipliers become infinite if any constraint is zero. Although this never occurs in real systems since no constraint can ever be identically zero, it may occur in idealized calculations if the initial value of any constraint is set equal to zero. The problem may be circumvented by introducing the alternative set of variables

$$\Gamma_i = \exp(-\gamma_i). \quad (5.18)$$

Substitution of (5.18) into (4.17) then gives the constrained composition in the form

$$[N_j] = [Q_j] \prod_i \Gamma_i^{\mathbf{a}_{ij}} . \tag{5.19}$$

To obtain the rate equations for Γ_i we consider first the case in which T and V are the independent variables. Substituting (5.19) into the constraints (4.11) and differentiating the resulting equations with respect to time gives

$$\dot{C}_{i}/V = C_{i\nu}(\dot{V}/V) + C_{iT}(\dot{T}/T) + \sum_{n} C_{in}\dot{\Gamma}_{n},$$

(5.20)

where

$$C_{iV} = \sum_{j} a_{ij}[N_j] \qquad (5.21a)$$

$$C_{iT} = \sum_{i} a_{ij} (E_j(T)/k_{\rm B}T)[N_j]$$
 (5.21b)

$$C_{in} = \sum_{j} a_{ij} d_{nj}[Q_j], \qquad (5.21c)$$

in which

$$d_{ni} = 0$$
 for $a_{ni} = 0$ (5.22a)

and

$$d_{nj} = a_{nj} \sum_{k} \Gamma_{k}^{a_{kj} - \delta_{\mathbf{k}n}}$$
 for $a_{nj} \neq 0$ (5.22b)

where $\delta_{kn} = 1$ for k = n, $\delta_{kn} = 0$ for $k \neq n$ is the Kronecker delta. Substituting (5.12) into (5.20) we find

$$\sum_{n} C_{in} \dot{\Gamma}_{n} + C_{iT} (\dot{T}/T) + C_{iV} (\dot{V}/V) - \sum_{k} b_{ik} r_{k} = 0$$
(5.23)

in which $r_{\ell}(T, [N])$ is given by (5.6) and (5.7).

For the case in which E and V are the independent variables, we obtain from the expression (2.32) for the energy an additional equation for T

$$\sum_{n} C_{En} \dot{\Gamma}_{n} + C_{ET} (\dot{T}/T) + C_{EV} (\dot{V}/V) - \dot{E}/V = 0$$

(5.24)

where

$$C_{EV} = \sum_{j} E_{j}(T)[N_{j}]$$
 (5.25a)

$$C_{ET} = \sum_{j} (C_{vj}(T)T + E_{j}^{2}(T)/k_{\rm B}T)[N_{j}]$$
 (5.25b)

$$C_{En} = \sum_{j} E_j(T) \mathbf{d}_{nj}[Q_j]$$
 (5.25c)

in which

$$C_{\nu j} = \mathrm{d}E_j/\mathrm{d}T \qquad (5.26)$$

is the heat capacity of species j.

Alternatively for the case in which p and T are the independent variables, we obtain from the Equation of State an additional equation for V

$$\sum_{n} C_{pn} \dot{\Gamma}_{j} + C_{pT} (\dot{T}/T) + C_{pV} (\dot{V}/V) - \dot{p} = 0$$
(5.27)

where

$$C_{pV} = -p \tag{5.28a}$$

$$C_{pT} = p + \sum_{j} E_{j}(T)[N_{j}]$$
 (5.28b)

$$C_{pn} = k_{\rm B} T \sum_{j} d_{nj}[Q_j].$$
 (5.28c)

Given the initial values of the constraints the rate equations for the constraints can be integrated numerically using codes such as LSODI³⁴ or DASSL.³⁵ It is anticipated that this approach will be more efficient than stepwise integration of the equations for the constraints although no such calculations have yet been implemented.

5.4. Degree of Disequilibrium

A useful parameter for measuring the departure of a reaction from equilibrium is the degree of disequilibrium

$$\phi_{dk} = \ln r_k^+ / r_k^-. \tag{5.29}$$

Using the phenomenological expressions (5.7) for the reaction rates and the rate quotient law (5.9) we obtain from (5.29)

$$\phi_{dk} = -\sum_{j} v_{jk} \ln (N_j/Q_j).$$
 (5.30)

Substituting (4.6) into (5.30) we find for any system

$$\phi_{dk} = -\sum_{j} (\mu_{j}/k_{\rm B}T)v_{jk}$$
 (5.31)

and using (4.8) and (5.13) we obtain for constrainedequilibrium systems

$$\phi_{dk} = \sum_{i} \gamma_{i} b_{ik} = -\sum_{i} (\lambda_{i} / k_{\rm B} T) b_{ik} .$$
 (5.32)

It follows from (5.32) that any reaction k for which all $b_{ik} = 0$ will be at equilibrium and its net rate will be zero. This provides an alternative method of determining the constrained-equilibrium composition which if the only constraints are those on the elements, reduces to the method of equilibrium constants.

It also follows that all reactions which change only a single constraint will relax to equilibrium at the same rate i.e. $\phi_{dk} = \gamma_i(t)b_{ik}$. Finally, since the constraints are linearly independent, $\gamma_i = 0$ at equilibrium for any constraints changed by chemical reactions, i.e. all constraints except those for the elements.

5.5. Entropy Production in Chemical Reactions

From the Gibbs Equation (4.1) it can be seen that the entropy production due to chemical reactions is

$$\sigma_{\rm R} = -\sum_{j} \mu_j \dot{N}_j / T \qquad (5.33)$$

and from (4.8) we find for constrained equilibrium

$$\sigma_{\rm R} = -\sum_i \lambda_i \dot{C}_i / T. \qquad (5.34)$$

Using the rate equations (5.4) and (5.12) and the expressions for the degree of disequilibrium (5.32), we obtain for either case

$$\sigma_{\rm R} = k_{\rm B} V \sum_{k} r_{k} \phi_{dk} = k_{\rm B} V \sum_{k} (r_{k}^{+} - r_{k}^{-}) \ln (r_{k}^{+}/r_{k}^{-}) \ge 0.$$
(5.35)

Thus for the phenomonical model described, the entropy production is always non-negative as required by the Second Law. If the only constraints on the system are those involving conservation of the elements, all reactions contribute to the sum in (5.35). If the system is evolving through a sequence of ratecontrolled constrained-equilibrium states, only the reactions which change a constraint contribute to the entropy production. It may be noted that the magnitude of the entropy production due to a particular reaction is a useful measure of its relative importance in determining the evolution of a system.

It can also be seen from (4.24) and (4.25) that the rate of decrease of the Helmholtz and Gibbs free energy due to chemical reactions is

$$\dot{A} = \dot{F} = -T\sigma_{\rm R} \tag{5.36}$$

which vanishes at equilibrium.

5.6. Entropy Production in Energy Exchange Reactions

The Gibbs equation for a multiple temperature gas mixture is

$$T_1 dS = dE + p dV - \sum_j \mu_j dN_j$$
$$- \sum_k (1 - T_1/T_k) d\varepsilon_k \qquad (5.37)$$

in which $T_1 = T_T$ is the translational temperature and we have used the equation for the energy

$$E = \sum_{k} \varepsilon_{k} \tag{5.38}$$

and the Equation of State

$$vV = k_{\rm B}T_1 \sum_j [N_j].$$
 (5.39)

From (5.37) it can be seen that the entropy production rate due to energy exchange reactions in a multiple temperture gas is

$$\sigma_{\rm E} = \sum_{k} (T_k^{-1} - T_1^{-1}) \dot{\varepsilon}_k. \qquad (5.40)$$

Assuming that the energy transfer to a degree of freedom k can be represented as the sum of the contributions from all other degrees of freedom i, then

$$\dot{\varepsilon}_k = \sum_i \dot{\varepsilon}_{ki} \qquad (5.41)$$

and (5.40) can be written

$$\sigma_{\rm E} = \sum_{k} \sum_{i} (\dot{\epsilon}_{ki}/T_k + \dot{\epsilon}_{ik}/T_i - (\dot{\epsilon}_{ki} + \dot{\epsilon}_{ik})/T_i). \quad (5.42)$$

A sufficient condition for $\sigma_E \ge 0$ is that ε_{ki} be antisymmetric in T_k and T_i . This is true for the commonly used relaxation equations

$$\dot{\varepsilon}_{ki} = k_{\mathrm{B}}(T_i - T_k)/\tau_{ik}, \qquad (5.43)$$

and substituting (5.43) into (5.42) we obtain

$$\sigma_{\rm E} = k_{\rm B} \sum_{k} \sum_{i} (T_i - T_k)^2 / T_i T_k \tau_{ik} \ge 0 \qquad (5.30)$$

which satisfies the requirements of the Second Law.

6. CONVENTIONAL TREATMENTS OF CHEMICAL REACTIONS

Before discussing the applications of the RCCE method to practical combustion problems, we shall review briefly some of the conventional methods of treating chemical reactions in nonequilibrium systems.

6.1. Shifting Equilibrium

Shifting equilibrium calculations are a special case of RCCE in which fixed constraints on the elements are imposed but the thermodynamic variables such as energy, volume, temperature, and pressure are allowed to change slowly. Such calculations are the basis of classical thermodynamics and are routinely carried out by scientists and engineers. The NASA³² and STANJAN³³ codes were explicitly developed to implement such calculations.

6.2. Linear Rate Equations

Under some conditions, especially in the early and late stages of reaction, the rate equations can be linearized. In such cases, the system is amenable to linear analysis and a complete analytic solution is available.²⁹ This can be of considerable value in starting or terminating a calculation. However, for complex systems involving a large number of species, the algebra involved can be substantial. In particular inversion of an $ns \times ns$ matrix is required where ns is the number of species in the system.

6.3. Integration of a Complete Set of Rate Equations

In principle, the most accurate method of determin-

ing the evolution of a homogeneous chemically reacting system for which the reaction mechanism is completely known is to integrate the full set of rate equations

$$\dot{N}_{j} = V \sum_{k} v_{jk} r_{k}$$
 $(j = 1...ns).$ (6.1)

For systems of interest in combustion involving hundreds of potentially interesting species and tens of thousands of possible reactions, this is a truly formidable task and truncation of both the species and reaction lists is necessary especially if the chemical kinetics are to be combined with a flow calculation. The problem with truncation is that, unless great care is taken, the omission of an important fast reaction can result in serious errors. Furthermore, most of the rate constants needed to integrate even a modest set of rate equations are unknown and must be estimated. Thus, unless the corresponding reactions are at, or close to, equilibrium the results will depend strongly on the estimated rate constants and one is probably better off making the constrained-equilibrium assumption in the first place. In connection with this the following quotation from W.C. Gardiner's book Rates and Mechanisms of Chemical Reactions,³⁶ provides food for thought:

The drawback of using computers to determine the predictions of mechanisms is that too much information must be given to a computer and that too much is returned. Extracting the *significant* information from a computer output is likely to be more difficult than analyzing the differential equations in the first place. When the differential equations can not be understood, however, computed solutions can be quite helpful, or indeed the only path for progress.

6.4. Pseudo-Steady-State Approximation (PSSA)

To reduce the number of differential equations which must be integrated, the pseudo-steady-state approximation is frequently used. This involves the assumption that for certain species, say $j = 1 \dots np$,

$$\sum_{k} v_{jk} r_{k} = 0.$$
 (6.2)

This provides np nonlinear algebraic relations which can be used to reduce the number of differential equations to ns - ne - np. Although this can result in some simplification in the calculations for small systems, for large systems it may be difficult to find a sufficient number of steady state species to produce a significant effect. Moreover the results still depend explicitly on the rate constant for all the reactions in the system and as previously observed many of these may be uncertain or unknown.

Finally a more subtle difficulty which must be faced is that it can no longer be proved, as for the RCCE method or for a full set of rate equations, that the entropy production will always be non-negative when the steady state assumption is employed. To illustrate this problem we start by separating the equation (5.33) for the entropy production into two parts

$$T\sigma_{\rm R} = -\sum_{1}^{np} \mu_j \dot{N}_j - \sum_{np+1}^{ns} \mu_j \dot{N}_j . \qquad (6.3)$$

Substituting the rate equations (6.1) into the second term of this expression we obtain

$$T\sigma_{\mathbf{R}} = -\sum_{1}^{np} \mu_j \dot{N}_j - \sum_{np+1}^{ns} \mu_j \left(\sum_k v_{jk} \mathbf{r}_k\right).$$
(6.4)

By virtue of the steady state relations (6.2) the lower limit np + 1 on the second sum can be replaced by 1. This gives

$$T\sigma_{\mathbf{R}} = -\sum_{1}^{np} \mu_{j} \dot{N}_{j} - \sum_{k} \left(\sum_{j} \mu_{j} v_{jk} \right) r_{k} \quad (6.5)$$

where we have changed the order of the summation. Substituting (5.31) and into (6.5), and using (5.29) and (4.27) we obtain

$$T\sigma_{\rm R} = -\sum_{1}^{np} \mu_j \dot{\rm N}_j + k_B T_V \sum_{k} (r_k^+ - r_k^-) \ln (r_k^+/r_k^-)$$
(6.6)

so that the second term is non-negative. The first term can be either positive or negative and its magnitude depends explicitly on the values of the rate constants involved in the steady state equations (6.2). To see this we note that these equations can in principle be solved to obtain

$$N_j = N_j (\underline{k}^+, \underline{K}_c, N_{np+1} \dots N_{ns}) \qquad (j = 1 \dots np).$$
(6.7)

The only a priori restrictions on the rate constants k^+ is that they are non-negative and bounded above. Whether this is sufficient to determine the sign of the PSSA entropy production (6.6) is not clear to the author and is left as an exercise for the reader.

6.5. PSSA versus RCCE

As mentioned in the introduction there has been a wide spread tendency to identify the rate-controlled constrained-equilibrium method (RCCE) as a special case of the pseudo-steady-state approximation (PSSA). It should be clear from the above discussion, however, that the two are quite distinct. If anything PSSA is a special case of RCCE involving the imposition of nonlinear constraints on the species concentrations. Such constraints are, in fact, admissible provided the necessary information about the rate constants is known. To the author's knowledge they have not yet been considered and no algorithms for dealing with them have been developed. The following additional observations are also relevant.

The steady-state approximation is based on the assumption that at some time during the evolution of a complex reacting system the difference between the production and removal rates of certain species is small compared to their sum. This permits the corres-

ponding differential rate equations to be replaced by algebraic equations. The total number of differential plus algebraic equations remains the same, however, and the solution still depends explicitly on the rate constants for all the reactions included in the model of the system. The RCCE method on the other hand is based directly on the Maximum Entropy Principle of Thermodynamics and it is assumed that the system evolves through a sequence of constrained-equilibrium states obtained by maximizing the statistical entropy subject to a set of constraints imposed on the system by certain classes of slow reactions. No assumption of a quasi-steady state in the usual sense is made or implied. The total number of differential rate equations required to describe the evolution of the system is reduced to the total number of variable constraints used and the solution depends only on the rate constants for those reactions which change the value of a constraint. Finally, as shown above, the entropy production for a system evolving through a sequence of constrained-equilibrium states is nonnegative. No corresponding general proof for the quasi-steady state approximation is known to the author.

7. ILLUSTRATIVE EXAMPLE: THE O-SYSTEM

To illustrate the RCCE method we shall consider its application to the pure oxygen system at constant temperature and volume. For this system which contains only a single element O and the three species O, O_2 and O_3 most of the results can be obtained analytically and the various steps in the method can be easily followed free of the numerical complications associated with more complex systems.

The calculations will be divided into three parts: (1) Chemical equilibrium; (2) constrained equilibrium; and (3) rate-controlled constrained equilibrium.

7.1. Chemical Equilibrium

In numerical calculations it is convenient to replace the concentrations $[N_i]$ with the partial pressures

$$p_j = [N_j] k_{\rm B} T.$$
 (7.1)

Substituting this expression into (3.2) we obtain

$$\ln \tilde{p}_j = - \tilde{\mu}_j^0 - \sum_i \gamma_i a_{ij}, \qquad (7.2)$$

where $\tilde{p}_j = p_j/p_0$ is the pressure of species *j* measured in standard atmospheres and

$$\tilde{\mu}_{j}^{0} = -\ln\left([Q_{j}]k_{\rm B}T/p_{0}\right)$$
(7.3)

is the dimensionless standard Gibbs free energy which can be obtained from thermodynamic tables using the relation

$$\tilde{\mu}_{j}^{0} = F_{j}^{0}/RT = (H_{j}^{0} - TS_{j}^{0})/RT,$$
 (7.4)

where F_j^0 , H_j^0 and S_j^0 are the standard molar Gibbs free

TABLE 2.

Α.	Fundamenta	l constants ³⁸
----	------------	---------------------------

Ice Point	$T_0 = 273.15 \text{ K}$
Standard atmosphere	$p_0 = 101,325 \text{ N/m}$
Molar volume	$V_0 = 22.414 \text{ cc}$
Gas constant	R = 8.3144 J/mol K
R/p_0	$R_0 = 82.06 \text{ atm cc/mol K}$

B. Thermodynamic properties³⁷ of species for pure O-system at T = 4000 K, (RT = 7.9488 kcal/mol)

i	Species	<i>H</i> ° kcal/mol	S° cal/mol K	F kcal/mol	μ̃°
1	0	78.124	51.546	- 128.06	- 16,110
2	0,	33.201	70.766	-249.86	- 31.433
3	O ₃	84.393	90.196	- 276.39	- 34.771

energy, enthalpy and entropy, R is the universal molar gas constant and the notation is that used in the JANAF tables.³⁷

For convenient reference the values of p_0 and R are given in Table 2A along with the values for the gas constant per atmosphere R_0 , the standard molar volume V_0 , and the ice point T_0 . In terms of these constants

$$\tilde{p}_{j} = [\tilde{N}_{j}]R_{0}T = [\tilde{N}_{j}]V_{0}T/T_{0}$$
 (7.5)

where $[\tilde{N}_i] = N_i k_B / RV$ is the particle concentration in moles per unit volume.

For a system containing only the element oxygen, Eq. (7.2) reduces to

$$\ln \tilde{p}_{j} = - \tilde{\mu}_{j}^{0} - \gamma_{1} a_{1j}$$
 (7.6)

where the subscript 1 denotes elemental oxygen for which the constraint equation is

$$[\tilde{E}O] = [\tilde{O}] + 2[\tilde{O}_2] + 3[\tilde{O}_3].$$
 (7.8)

In terms of partial pressures this becomes

$$\tilde{p}_{\rm E} = [\tilde{E}O] RT = \tilde{p}_1 + 2\tilde{p}_2 + 3\tilde{p}_3$$
 (7.9)

where the subscripts 1, 2 and 3 denote O, O₂ and O₃ respectively. Substituting (7.6) into (7.10) and noting that $a_{11} = 1$, $a_{12} = 2$ and $a_{13} = 3$ we obtain the cubic equation

$$\tilde{p}_{\rm E} = b_1 \Gamma_1 + 2b_2 \Gamma_1^2 + 3b_3 \Gamma_1^3 \qquad (7.10)$$

in which

$$b_j = \exp(-\tilde{\mu}_j^0)$$
 (7.11)

and

$$\Gamma_1 = \exp(-\gamma_1). \quad (7.12)$$

The partial pressures in terms of Γ_1 are simply

$$\tilde{p}_j = b_j \Gamma_1^j. \tag{7.13}$$

Although the general solution for cubic equations such as (7.10) is well known,³⁸ it is simpler in this case as well as instructive to regard γ_1 as the independent



FIG. 1 Partial pressures of species and elemental oxygen as a function of the 'element potential' $\gamma(1)$.

variable and find a parametric solution. All thermodynamic properties can then be obtained as functions of this parameter and cross plotted in any manner desired.

The thermodynamic properties necessary to carry out numerical calculations are tabulated in Table 2B for a temperature of 4000 K and plots of the species partial pressures \tilde{p}_j and the elemental pressure \tilde{p}_E are shown in Fig. 1 as a function of γ_1 . It can be seen from this figure as well as (7.6) that plots of ln \tilde{p}_j as a function of γ_1 are simply straight lines with slopes d ln $\tilde{p}_j/d\gamma_1 = -j$ and intercepts at $\gamma_1 = 0$ of $-\tilde{\mu}_j^0$. Other thermodynamic properties can easily be calculated from the partial pressures (7.13). In particular: (1) total pressure

(1) total pressure

$$\tilde{p} = \sum_{j} \tilde{p}_{j} \qquad (7.14)$$



FIG. 2. Mass fractions of species as a function of element concentration times molar volume, $[EO]V_0$.

(2) mass fractions

$$Y_j = jp_j/p_{\rm E} \tag{7.15}$$

(3) dimensionless energy

$$E/EORT = \sum_{j} (p_{j}/p_{\rm E})(\tilde{H}_{j}^{0} - 1)$$
 (7.16)

(4) dimensionless Helmholtz free energy

$$A/EORT = \sum_{j} (p_j/p_E)(\tilde{\mu}_j^0 - 1 + \ln \tilde{p}_j).$$

$$(7.17)$$

Figure 2 shows a cross-plot of species mass fractions as a function of the dimensionless elemental concentration

$$[\tilde{E}O]V_0 = \tilde{p}_{\rm E}T_0/T.$$
 (7.18)

7.2. Constrained Equilibrium

To illustrate the method by which the properties of constrained-equilibrium states can be determined, we consider two possible constraints: one on the concentration of total moles

$$[\tilde{M}] = [\tilde{O}] + [\tilde{O}_2] + [\tilde{O}_3]$$
 (7.19)

and the other on the concentration of 'free oxygen'

$$[\tilde{F}O] = [\tilde{O}] + [\tilde{O}_3].$$
 (7.20)

In terms of partial pressure, (7.19) and (7.20) can be also written

$$\tilde{p} = [\tilde{M}]R_0T = \tilde{p}_1 + \tilde{p}_2 + \tilde{p}_3$$
 (7.21)

and

$$\tilde{p}_{\rm F} = [\tilde{F}O]R_0T = \tilde{p}_1 + \tilde{p}_3.$$
 (7.22)

The a_{ij} coefficients for the three constraints (7.8), (7.19) and (7.20) are shown in matrix form in Fig. 3. The species themselves can also be considered as constraints and their coefficients are also given.

It can easily be verified, by calculating the appropriate determinants and checking that they are not zero, that any two of the variable constraints in conjunction with the fixed elemental constraint form a linearly independent set. Thus the corresponding 3×3 matrix can be inverted and the composition determined in terms of the values of the constraints. Examples of inverse matrices are shown for the constraints (EO, M, FO) and (EO, O, O₃). Fixed values for all the constraints occur only when all possible reactions are zero and correspond to the case of Gibbs-Dalton mixtures.

If only two constraints are fixed then the composition is no longer fixed and a nonequilibrium system will relax to the corresponding constrained-equilibrium state. For the case of a constraint on the total moles, the constrained-equilibrium partial pressures obtained from Eq (7.2) are

$$\tilde{p} = \exp(-\tilde{\mu}_{j}^{0} - \gamma_{1}a_{1j} - \gamma_{2}a_{2j}) = b_{j}\Gamma_{1}^{a_{1j}}\Gamma_{2}^{a_{2j}}.$$
(7.23)

Constraint matrix a(i,j)

Species	0	02	03					
Constraint	i	1	2	3				
EO	1	1	2	3	Fixed			
MO	2	1	1	1	Variable			
FO	3	1	0	1				
0	4	1	0	0				
02	5	0	1	0				
03	6	0	0	1				
Inverse	matri	x (EO	, мо,	FO)	a ⁻¹ (i, j)			
Constrai	int –	EO	MO	FO				
Species	j	1	2	3				
0	1	-1/2	1	1/2				
02	2	0	1	-1				
03	3	1/2	-1	1/2				
Invers	e ma	itrix (E0, 0	, 03)	a ⁻¹ (i, j)			
Constra	Constraint		0	03				
Species	j	1	4	6				
0	1	0	. 1	0				
02	2	1/2	-1/2	-3/2				
03	з	0	0	1				

FIG. 3. Matrix of constraint coefficients for O-system and examples of inverse matrices.

Substituting (7.23) into the constraints (7.9) and (7.21) we obtain

and

where

$$\tilde{p} = b_1 \Gamma_1 \Gamma_2 + b_2 \Gamma_1^2 \Gamma_2 + b_3 \Gamma_1^3 \Gamma_2 \quad (7.25)$$

 $\tilde{p}_{\rm E} = b_1 \Gamma_1 \Gamma_2 + 2b_2 \Gamma_1^2 \Gamma_2 + 3b_3 \Gamma_1^3 \Gamma_2 \quad (7.24)$

in which we have used the a_{ij} coefficients in Fig. 3. From (7.25)

$$\Gamma_2 = \tilde{p}/\Gamma_1(b_1 + b_2\Gamma_1 + b_3\Gamma_1^2) \quad (7.26)$$

and substituting in (7.24) we obtain the quadratic equation

$$a_M \Gamma_1^2 + b_M \Gamma_1 + c_M = 0 \qquad (7.27)$$

$$a_M = (3 - p_E/p)b_1$$
 (7.28a)

$$b_M = (2 - p_{\rm E}/p)b_2$$
 (7.28b)

$$c_M = (1 - p_{\rm E}/p)b_3.$$
 (7.28c)

For $1 \le p_E/p \le 3$, Eq. (7.27) has one non-negative root

$$\Gamma_{1M} = ((b_M^2 - 4a_M c_M)^{1/2} - b_M)/2a_M.$$
(7.29)

Combining (7.29), (7.24), (7.23) and (7.15) we obtain the mass fractions

$$Y_{jM} = jb_j \Gamma_{1M}^{j-1} / (b_1 + 2b_2 \Gamma_{1M} + 3b_3 \Gamma_{1M}^2)$$
(7.30)

which are independent of Γ_2 and therefore also independent of the absolute value of the pressure.

In the numerical evaluation of (7.29) some care is required in the neighborhood of the singularities at $p_{\rm E}/p = 1$ and 3. In particular $\Gamma_{1M} \rightarrow (c_M/a_M)^{1/2} \rightarrow 0$ as $p_{\rm E}/p \rightarrow 1$ and $\Gamma_{1M} \rightarrow b_M/a_M \rightarrow \infty$ as $p_{\rm E}/p \rightarrow 3$. In the latter case the mass fractions are given by

$$Y_{jM} = jb_j \Gamma_{1M}^{j-3} / (b_1 \Gamma_{1M}^{-2} + 2b_2 \Gamma_{1M}^{-1} + 3b_3).$$
(7.31)

For the case in which the 'free oxygen' concentration is fixed, the constrained equilibrium partial pressures are given by

$$\tilde{p}_{j} = \exp((-\tilde{\mu}_{j}^{0} - \gamma_{1}a_{1j} - \gamma_{3}a_{3j})) = b_{j}\Gamma_{1}^{a_{1j}}\Gamma_{3}^{a_{3j}}$$
(7.32)

and substituting in the constraints (7.9) and (7.22) we obtain

$$\tilde{p}_{\rm E} = b_1 \Gamma_1 \Gamma_3 + 2b_2 \Gamma_1^2 + 3b_3 \Gamma_1^3 \Gamma_3 \quad (7.33)$$

and

$$\tilde{p}_{\rm F} = b_1 \Gamma_1 \Gamma_3 + b_3 \Gamma_1^3 \Gamma_3.$$
 (7.34)

From (7.34)

$$\Gamma_3 = \tilde{p}_{\rm F} / \Gamma_1 (b_1 + b_3 \Gamma_1^2) \tag{7.35}$$

and substituting in (7.33) we obtain the quartic equation

$$a_{\rm F}\Gamma_1^4 + b_{\rm F}\Gamma_1^2 + c_{\rm F} = 0 \qquad (7.36)$$

where

с

$$a_{\rm F} = 2b_2 b_3$$
 (7.37a)

$$b_{\rm F} = 2b_1b_2 + (3p_{\rm F}/p_{\rm E} - 1) b_3\tilde{p}_{\rm F}$$
 (7.37b)

$$_{\rm F} = (p_{\rm F}/p_{\rm E} - 1)b_1\tilde{p}_{\rm E}$$
 (7.37c)

For $0 \le p_F/p_E \le 1$ Eq. (7.36) has one non-negative root

$$\Gamma_{\rm IF} = (((b_{\rm F}^2 - 4a_{\rm F}c_{\rm F})^{1/2} + b_{\rm F})/2a_{\rm F})^{1/2}.$$
 (7.38)

This completely determines the constrained-equilibrium state for the case of fixed elemental oxygen and 'free oxygen' concentrations. Once again one must be careful in evaluating (7.38) in the neighborhood of the singularity at $p_{\rm F}/p_{\rm E} = 1$ where $\Gamma_{\rm 1F} \rightarrow (c_{\rm F}/a_{\rm F})^{1/2} \rightarrow 0$ as $p_{\rm F}/p_{\rm E} \rightarrow 1$.

Plots of mass fractions obtained from the above



FIG. 4. Constrained mass fraction, Helmholtz free energy, and 'constraint potentials' for elemental oxygen EO and total moles M as a function of EO/M.

equations are shown for the case of the total moles constraint as a function of $EO/M = p_E/p$ in Fig. 4. Also shown are the dimensionless Helmholtz free energy obtained from (7.17) and the dimensionless potential $\gamma_2 = -\ln\Gamma_2$. It can be seen that the composition is an exceedingly sensitive function of EO/Min the neighborhood of EO/M = 2 where the O_2 mass fraction is a maximum. As previously observed the composition plots in Fig. 4 are independent of the absolute value of the pressure and depends only on the temperature. Chemical equilibrium occurs at the point where the Helmholtz free energy is a minimum. By virtue of (4.26), this is also the point where $\gamma_2 = 0$.

Similar plots are shown in Fig. 5 for the case of the 'free oxygen' constraint. Although the dependence of the mass fractions on $FO/EO = p_F/p_E$ is very different from that in the previous case, the equi-



FIG. 5. Constrained mass fraction, Helmholtz free energy, and 'constraint potentials' for elemental oxygen EO and 'free oxygen' FO as a function of FO/EO.

librium composition and the minimum value of the Helmholtz free energy are exactly the same.

Examples of the trajectories along which an Osystem subject to slowly changing constraints on total moles and 'free oxygen' will move are shown on the $Y_1 - Y_3$ plane in Fig. 6. The dotted diagonal lines with positive slopes correspond to states of fixed total moles and are given by the equation

$$Y_3 = 3(2M/EO - 1 + Y_1).$$
 (7.39)

The lines with negative slope correspond to states of fixed 'free oxygen' and given by the equation

$$Y_3 = 3(FO/EO - Y_1)$$
 (7.40)

The solid curves are contours of constant Helmholtz free energy. The constrained-equilibrium states



FIG. 6. Upper: Contours of constant Helmholtz free energy in the O_3 -O mass fraction plane. The light lines show states of constant total moles M and constant 'free oxygen' FO. Constrained-equilibrium M states lie very close to the O_3 and O axes; constrained-equilibrium FO states lie close to the O axis. Middle: Constrained-equilibrium states on an expanded O_3 scale. M and FO curves cross at the equilibrium state. Lower: Helmholtz free energy A for constrained Mand FO states as a function of M/EO and FO/EO. On the scale of the plot the curves are indistinguishable. A and Bshow states of pure O_2 and O. D and F are the constrainedequilibriumM and FO states corresponding to the nonequilibrium state C. E is the equilibrium state of minimum Helmholtz free energy.

plotted in the two previous figures lie very close to the Y_1 axis and are shown on a greatly expanded scale at the bottom of the plot. Also shown in the lower part of the figure are the corresponding Helmholtz free energy curves. On the scale of the plot they are indistinguishable although, in fact, they differ slightly.

The state A, which corresponds to pure O_2 , lies on the 'free oxygen' curve at the point FO/EO = 0. It can relax to chemical equilibrium along the FO curve from A to E. The state B, which corresponds to pure O, lies on the 'free oxygen' curve at FO/EO = 1 and on the total moles curve at MO/EO = 1. This state can relax to chemical equilibrium along either the FOor MO curves from B to E depending on which constraint is imposed.

On the other hand a nonequilibrium state such as C which does not lie on a constrained curve will jump along a line of constant FO/EO to the constrained FO state at F or along a line of constant M/EO to the constrained M state at D again depending on which constraint is imposed. It will then relax slowly to chemical equilibrium either through constrained FO states from F to E or constrained M states from D to E.

The trajectories described above represent limiting cases approached when the time scale for relaxation along the slow path is very much longer than that for the fast path. In principle, any trajectory from the initial state to the equilibrium state for which the Helmholtz free energy never increases is possible.

In concluding this section we note that if two constraints are specified the composition of the system is uniquely determined and its evolution is governed by the full set of rate equations. Examples of inverse matrices for determining composition from the two linearly independent sets of constraints $\{EO, M, FO\}$ and $\{EO, O, O_3\}$ are given in Fig. 3.

7.3. Rate-Controlled Constrained Equilibrium

The principle reactions occurring in the pure Osystem are listed in Table 3A along with their stoichiometric coefficients v_{jk} . Also shown are the changes produced by the reaction in:

(1) number of particles

$$\Delta v_k = \sum_j v_{jk} \qquad (7.41)$$

(2) molar enthalpy

$$\Delta H_k^0 = \sum v_{jk} H_j^0 \qquad (7.42)$$

(3) dimensionless Gibbs free energy

$$\Delta \tilde{\mu}_k^0 = \sum_j v_{jk} \tilde{\mu}_j^0 \qquad (7.43)$$

and (4) the log of the equilibrium constant based on pressure

$$\log K_{pk} = \sum_{j} v_{jk} \log p_{j} = -\Delta \tilde{\mu}_{k}^{0} / \ln 10.$$
(7.44)

The constraint coefficients b_{ik} and the parameters required to determine the reaction rates are given in Table 3B. These include:

(1) the parameters log A^+ and E^+ necessary to compute the forward exothermic rate constant in the Arrhenius form

$$\log K^+ = \log A^+ - E^+/RT \ln 10;$$
 (7.45)

TABLE 3. Principle reactions for species in the O-system (units: cc, mol, sec, K, kcal)

А . Т	Thermodynamic data ³⁷ (T = 4000 Species:							
k	Reaction	v _{1k}	v _{2k}	v _{3k}	Δv	ΔH°	$\Delta ilde{\mu}^{\circ}$	$\log K_{\rm p}$
1 2	$O + O + M \leftrightarrow O_2 + M$ $O + O_2 + M \leftrightarrow O_3 + M$	-2 -1	1 - 1	0	-1 -1	- 123.05 - 29.93	0.79 12.77	- 0.34 - 5.55
3	$\mathbf{O} + \mathbf{O}_3^2 \leftrightarrow \mathbf{O}_2 + \mathbf{O}_2^2$	- 1	2	- 1	0	- 96.12	-12.05	5.24

B. Rate parameters²⁸ ($R_0 T = 32,824$ atm. cc/mol)

	Constraint:		М	FC)				
k	Reaction	b_{1k}	b_{2k}	<i>b</i> _{3k}	$\log A^+$	E^+	$\log k^+$	$\log K_{\rm c}$	$\log k^{-}$
1	$0 + 0 + M \leftrightarrow 0_2 + M$	0	- 1	- 2	13.8	0.0	13.8	5.2	8.6
2	$O + O_2 + M \leftrightarrow O_3 + M$	0	- 1	0	13.5	-0.9	13.5	0.0	13.5
3	$O + O_3 \leftrightarrow O_2 + O_2$	0	0	- 2	13.5	5.7	13.2	5.2	8.0

(2) the log of the forward rate constant k⁺;
(3) the log of the equilibrium constant based on concentration;

$$\log K_{ck} = \sum v_{jk} \log [\tilde{N}_j] = \log K_{pk} - \Delta v_k \log R_0 T$$
(7.46)

and (4) the log of the reverse endothermic rate constant

 $\log k_k^- = \log k_k^+ - \log K_{ck}.$ (7.47)

The one-way reaction rates can be conveniently obtained from the expressions

$$\log r_k^+ = \log k_k^+ + \sum_j v_{ik}^+ \log [\tilde{N}_j] \quad (7.48)$$

and

$$\log r_{k}^{-} = \log k_{k}^{-} + \sum_{j} v_{ik}^{-} \log [\tilde{N}_{j}] \quad (7.49)$$

and the net forward reaction rate is then

$$r_k = r_k^+ - r_k^-. (7.50)$$

The full set of rate equations can now be written

$$d[\tilde{O}]/dt = -2r_1 - r_2 - r_3 \tag{7.51}$$

$$d[\tilde{O}_2]/dt = r_1 - r_2 + 2r_3$$
(7.52)

$$d[\tilde{O}_{2}]/dt = r_{2} - r_{1} \tag{7.53}$$

and because of their nonlinear character these must be integrated numerically. A useful check on any reaction scheme is to make sure elements are conserved, i.e. $d([O] + 2[O_2] + 3[O_3])/dt = 0$, and this is easily seen to be true in the above case.

To carry out a rate-controlled constrained-equilibrium (RCCE) calculation we must now identify a suitable constraint and an examination of Table 3B shows that by far the smallest rate constants are those for the reverse of reactions 1 and 3. It can also be seen from the b_{ik} coefficients that these are the reactions responsible for changes in the 'free oxygen' constraint FO. If their rates were identically zero FO would be a constant. On the other hand reaction 2 which changes the total moles M can readily relax any nonequilibrium state to a corresponding constrained-equilibrium state having the same value of FO. For our illustration we shall therefore choose FO as our constraint and integrate the rate equation

$$d[F\tilde{O}]/dt = -2r_1 - 2r_2 \qquad (7.54)$$

using the constrained-equilibrium composition obtained from (7.38), (7.35) and (7.32) to evaluate the reaction rates 1 and 2. No information about the rate of reaction 3 is required other than the assumption that it is faster than 1 and 2. Also the total number of equations required is 2 (1 differential and 1 algebraic) rather than the 3 required for either a comprehensive or steady-state treatment.

Since Eq. (7.54) is separable its integration can be reduced to quadratures. However to facilitate comparison of the results it is more convenient to use the same numerical routine to integrate both the full set of Eqs (7.51)–(7.53) and the constraint equation (7.54). The calculations were carried out using the DASSL³⁴ integrator run on a MacPlus.

The three initial states A, B, and C in Fig. 6 were considered and the results are shown in Figs 7–9 plotted as function of log time (sec). The properties calculated were the species mass fractions Y, the degree of disequilibrium ϕ_d and dimensionless entropy production σ_R/EOR for the reaction, the dimensionless Helmholtz free energy A/EORT, the pressure p, and the dimensionless energy E/EORT. The continuous curves show the results of integrating the full set of rate equations (7.51)–(7.53) and the points are the results of integrating the rate equation for the constraint (7.54).

The results for the initial state A are shown in Figs 7a and b. These correspond to the dissociation of pure O_2 . It can be seen that even though all reactions are out of equilibrium in the reverse direction ($\phi_d < 0$) at early times, the mass fractions and entropy production for the major species O and O_2 and the ther-



FIG. 7a. Comparison of exact and FO RCCE calculations of O_2 dissociation at T = 4000 K and $[EO]V_0 = 1.0$. Mass fractions Y for the species and degree-of-disequilibrium ϕ_d and entropy production σ_{R} for the reactions are shown as a function of log time. Curves show exact results; solid points show constrained results using reactions 1 and 3; open points show RCCE results using only reaction 1.

modynamic properties A, p and E are well represented over a span of 6 orders of magnitude in time. During the final approach to equilibrium reaction 2 goes to equilibrium and the constrained values for the minor species O₃ approach the exact values. It should be noted that degree of disequilibrium ϕ_{d2} and the entropy production $\tilde{\sigma}_{R2}$ for reaction 2 are identically zero in the RCCE case and that ϕ_{d1} and ϕ_{d3} are equal. That this should be true can be seen by substituting the values of b_{ik} from Table 3B into the expression

$$\phi_{dk} = b_{1k}\gamma_1 + b_{3k}\gamma_3 \tag{7.55}$$

obtained from (5.32). This gives $\phi_{d2} = 0$ and

 $\phi_{d1} = \phi_{d3} = -2\gamma_3$ and it follows from (5.35) that $\tilde{\sigma}_{R2} = 0$. It may also be noted that the entropy production is a measure of the thermodynamic importance of a reaction and that σ_{R1} is roughly an order of magnitude larger than σ_{R2} and σ_{R3} . On this basis it can be anticipated the reaction 1 is the rate-controlling reaction and the only one which really needs to be included. As can be seen from the open points, this is indeed the case.

The results for the initial state B are shown in Figs 8a and b. These correspond to the recombination of pure O. In this case, reaction 2 is close to equilibrium over a very much wider range and even the mass fraction of the minor species O₃ is well represented. The reason there are no points for the RCCE calculations at very early times is because the initial step size chosen by the DASSL integrator was several orders of magnitude larger for the RCCE calculations than for the exact calculations. The first point shown is the first point calculated.



FIG. 7b. Helmholtz free energy A, pressure p, and energy Ecorresponding to Fig. 7a.



FIG. 8a. Comparison of exact and FO RCCE calculations for O recombination. Conditions and code are the same as in Fig. 7a. the solid and open points are indistinguishable in these calculations.

In the two previous examples the initial states Aand B were already in constrained equilibrium. In our final example the initial state C corresponds to a nonequilibrium state for which the mass fractions of O, O₂ and O₃ are 0.3, 0.4 and 0.3 and the constraint FO/EO = 0.4. In this case one would not expect RCCE to be a very good approximation because the initial state is so far from the corresponding constrained state. Nevertheless as can be seen in Figs 9a and b all of the properties are reasonably well represented over the entire time scale on which two calculations overlap and are very well represented over the decade in which the system approaches final equilibrium. Once again the first point plotted is the first point calculated. It illustrates the discontinuous jump at zero time from the initial nonequilibrium state C to the corresponding initial constrained-equili-

brium state F in Fig. 6. It is coincidental that the first point occurs at approximately the time when reaction 3 goes to quasi-equilibrium. Tighter tolerances on the integration would have produced points at earlier times.

In concluding this discussion we note that in all the cases above the RCCE calculations had a significant time advantage over the exact calculations. For a relative error tolerance of 1E-3 and an absolute error tolerance of 1E-8 the running time on the MacPlus was approximately 20 sec for RCCE and 50 sec for the exact calculations. Decreasing the relative tolerance to 1E-5 produced little change in the running time for the RCCE calculations but increased that for the exact calculations by about a factor of 2. One would expect that this advantage would become even greater for larger systems where the ratio of the number of required constraints to the number of species should be very much smaller. Whether this will prove to be the case depends very much on the efficiency of the



FIG. 8b. Helmholtz free energy A, pressure p, and energy E corresponding to Fig. 8a.



FIG. 9a. Comparison of exact and FO RCCE calculations for an initial state with $Y(O) = Y(O_3) = 0.3$ and $Y(O_2) = 0.4$. Conditions and code are the same as in Fig. 7a.

numerical algorithm available for computing the constrained-equilibrium composition. The present calculations are quite encouraging, however.

8. PRACTICAL APPLICATIONS OF RCCE

8.1. Reactions in Combustion Products

The rate-controlled constrained-equilibrium method has been applied with considerable success to the problem of predicting CO and NO formation in the combustion products from internal combustion engines and burners. These species, which are important air pollutants, are formed in relatively high concentrations at temperatures $T \ge 2000$ K. Their removal is controlled by strongly temperature-depen-



FIG. 9b. Helmholtz free energy A, pressure p, and energy E corresponding to Fig. 9a.

dent reactions many of which involve trace species such as N atoms as collision partners. The problem has also been treated using conventional methods discussed in the preceding sections. In all the cases, truncation of the species and reaction rate list has been used to siplify the calculations. Comparisons between these methods and the constrained equilibrium method will be discussed below.

8.1.1. CO freezing in a steady flow burner

The RCCE method has been used by Morr and Heywood⁹ to interpret their measurements of CO concentrations in a steady flow cylindrical burner. This work illustrates in a dramatic way the effect of using different constraints as well as the effect of combining constraints.

The experimental geometry is shown schematically in the upper part of Fig. 10. The mean temperature



FIG. 10. Temperature and CO profiles in a steady flow cylindrical burner.⁹

profile along the axis of the burner and the experimental and theoretical results are shown in the lower part. It can be seen that upstream of the heat exchanger where the temperature is high, the measured CO mole fractions agree well with the calculated equilibrium values. However, downstream of the heat exchanger where the temperatures are low, the measured CO levels far exceed the equilibrium value giving evidence for the freezing of CO oxidation reactions.

To predict the CO levels in this highly nonequilibrium region, Morr and Heywood carried out a 14 species RCCE calculation involving two constraints. The first was that on the total moles of gas

$$M = N_2 + H_2O + CO_2 + CO + O_2 + ... (8.1)$$

controlled by the dissociation and recombination reactions

$$(\mathbf{r}_{11}) \quad M + \mathbf{H} + \mathbf{H} \leftrightarrow \mathbf{H}_2 + M \tag{8.2}$$

$$(\mathbf{r}_{12}) \quad M + \mathbf{H} + \mathbf{OH} \leftrightarrow \mathbf{H}_2\mathbf{O} + M \tag{8.3}$$

$$(\mathbf{r}_{11}) \quad M + \mathbf{H} + \mathbf{O}_2 \leftrightarrow \mathbf{HO}_2 + M \tag{8.4}$$

$$(\mathbf{r}_{14}) \quad M + \mathrm{OH} + \mathrm{OH} \leftrightarrow \mathrm{H}_2\mathrm{O}_2 + M$$
 (8.5)

and governed by the rate equation

$$\frac{\mathrm{d}M}{\mathrm{d}t} = \sum_{1}^{4} (r_{1k}^{-} - r_{1k}^{+}). \tag{8.6}$$

The results obtained when this constraint was used alone are shown by the curve marked $(CO)_M$ in Fig. 10. Although the $(CO)_M$ levels are substantially higher than the equilibrium levels $(CO)_{eq}$ they are still far below the measured values. The second constraint used was that on the moles of CO which was assumed to be controlled by the CO oxidation reactions

$$(\mathbf{r}_{21}) \quad \mathrm{OH} + \mathrm{CO} \leftrightarrow \mathrm{CO}_2 + \mathrm{H}$$
 (8.7)

 $(\mathbf{r}_{22}) \ \mathbf{O}_2 + \mathbf{CO} \leftrightarrow \mathbf{CO}_2 + \mathbf{O}$ (8.8)

$$(r_{23})$$
 NO₂ + CO \leftrightarrow CO₂ + NO (8.9)

$$(\mathbf{r}_{24}) M + \mathbf{O} + \mathbf{CO} \leftrightarrow \mathbf{CO}_2 + M$$
 (8.10)

$$(\mathbf{r}_{25}) \quad M + \mathbf{H} + \mathbf{CO} \leftrightarrow \mathbf{HCO} + M \tag{8.11}$$

and governed by the rate equation

$$\frac{dCO}{dt} = \sum_{1}^{5} (r_{2k} - r_{2k}^{+}). \quad (8.12)$$

The results obtained when this constraint was used alone are shown by the curve marked $(CO)_{CO}$ in Fig. 10. It gives CO levels which substantially exceed the measured values.

The effect of imposing both constraints simultaneously is shown by the remaining curve marked $(CO)_{M,CO}$. Although this curve is slightly lower than the measured values, the agreement is well within the combined uncertainty of the experimental measurements and the rate constants used. Additional constraints could in principle have been employed to improve the agreement but no further useful information would have been obtained.

The reason for the difference between the $(CO)_{CO}$ curve and the $(CO)_{M,CO}$ curve is due to the effect of the total moles constraint which greatly increases the number of free radicals, especially OH, in the gas. This in turn increases the rate of the most important CO oxidation reaction r_{21} .

8.1.2. NO concentrations in an I.C.E.

A calculation of NO formation and removal in an internal combustion engine (I.C.E.) has been carried out by Keck and Gillespie.¹ One of the objectives of this work was to compare a RCCE calculation with a corresponding steady-state calculation and the results are shown in Fig. 11. In the RCCE calculations 14 species and two constraints were considered. The first constraint, was that on 'fixed nitrogen'.

$$FN = NO + NO_2 + NH + N$$
 (8.13)

controlled by the reactions

$$(\mathbf{r}_{31}) \mathbf{N} + \mathbf{NO} \leftrightarrow \mathbf{N}_2 + \mathbf{O}$$

$$(8.14)$$

$$(\mathbf{r}_{32}) \mathbf{N} + \mathbf{N}\mathbf{H} \leftrightarrow \mathbf{N}_2 + \mathbf{H}$$

$$(8.15)$$

$$(\mathbf{r}_{33}) \quad \mathbf{NO} + \mathbf{NO} \leftrightarrow \mathbf{N}_2\mathbf{O} + \mathbf{O} \tag{8.16}$$

$$(\mathbf{r}_{34}) \mathbf{NH} + \mathbf{NO} \leftrightarrow \mathbf{N}_2\mathbf{O} + \mathbf{H}$$

$$(8.17)$$

$$(\mathbf{r}_{35}) \mathbf{N}_2 + \mathbf{NO} + \mathbf{NO} \leftrightarrow \mathbf{N}_2\mathbf{O} + \mathbf{N}_2\mathbf{O} \qquad (8.18)$$

and governed by the rate equation

$$\frac{\mathrm{d}FN}{\mathrm{d}t} = 2\sum_{1}^{5} (r_{3k}^{-} - r_{3k}^{+}). \qquad (8.19)$$



FIG. 11. Comparison of equilibrium, steady-state and constrained equilibrium NO, N and O mole fractions during the power stroke of an I.C.E.¹

The mole fractions of NO, O and N obtained in a calculation in which this was the only constraint are shown by the solid curves in Fig. 11. The freezing of nitrogen fixing reactions can clearly be seen by comparison of the $(NO)_N$ and $(N)_N$ with the corresponding equilibrium values shown by the short dashed curve. By way of contrast the $(O)_N$ levels remain close to their equilibrium values.

The second constraint considered was that on total moles *M*. It can be seen in Fig. 11, that the addition of this constraint had no effect on the single constraint curves indicating that dissociation and recombination reactions were in equilibrium throughout. This was checked by a single constraint calculation involving only total moles and found to be the case.

The corresponding steady-state calculations were based on the engine thermodynamic model of Lavoie, Heywood and Keck.³⁹ The major combustion reactions were assumed to be in equilibrium and the extended Zeldovich mechanism

$$(\mathbf{r}_{z1}) \mathbf{N} + \mathbf{NO} \leftrightarrow \mathbf{N}_2 + \mathbf{O}$$
 (8.20)

 $(\mathbf{r}_{z2}) \mathbf{N} + \mathbf{O}_2 \leftrightarrow \mathbf{NO} + \mathbf{O}$ (8.21)

$$(r_{z3})$$
 N + OH \leftrightarrow NO + H (8.22)

was used to describe the kinetics of N and NO. The rate equations used for these species were

$$\frac{dN}{dt} = r_{z1}^{-} + r_{z2}^{-} + r_{z3}^{-} - r_{z1}^{+} - r_{z2}^{+} - r_{z3}^{+}$$
(8.23)

and

$$\frac{\mathrm{d}NO}{\mathrm{d}t} = r_{z1}^{-} - r_{z2}^{-} - r_{z3}^{-} - r_{z1}^{+} + r_{z1}^{+} + r_{z2}^{+} + r_{z3}^{+}$$

and the steady-state assumption dN/dt = 0 was made for N. As can be seen from the long-dashed curves in Fig. 11, the steady-state NO concentration (NO)_{ss} was lower than the RCCE concentration $(NO)_{N}$ early in the cycle when it was being removed. It can also be seen that the N atom concentration behaved in just the opposite way. These discrepancies are due to the fact that the reactions r_{z2} and r_{z3} included in the steady-state model were not sufficiently fast to maintain relative equilibrium between the fixed nitrogen species N and NO. Which of the two calculations gives the better approximation is difficult to say without a comprehensive calculation. The list of species and reactions included in the steady-state calculation is of course highly trunacted and parallel reactions would tend to drive the fixed nitrogen system closer to a constrained-equilibrium state. In any case, as can be seen in Fig. 12 which shows the average NO concentration in the exhaust of an I.C.E. as a function of fuel/air ratio, either calculation predicts the experimental results reasonably well. The steady state predictions shown by the dashed curve are based on unpublished work by Keck and Gillespie. The RCCE predictions shown by the solid curve were obtained by Delichatsios and Keck.¹⁰ The experimental points are from Heywood, Mathews and Owen.11



FIG. 12. Comparison of predicted and measured average NO concentration in exhaust of an I.C.E. as a function of fuel/air equivalence ratio.¹⁰

8.1.3. Degree of disequilibrium in I.C.E. combustion products

Considerable insight into the validity of the RCCE method as applied to NO and CO formation and removal in internal combustion engines can be gained from the results of a 13 species 17 reaction 'exact' calculation carried out by Newhall.⁴⁰

Of particular interest is the degree of disequilibrium calculated for 14 reactions during the expansion stroke and shown in Fig. 13. It can be seen that the 5 exchange reactions involving the C/H/O system and the dissociation reaction $M + N_2O \leftrightarrow N_2 + O$ + M involving the most abundant species N_2 are in equilibrium throughout. The 5 remaining dissociation reactions and the 3 exchange reactions involving NO all exhibit highly nonequilibrium behaviour, however. At first sight it is not obvious that the behavior of the nonequilibrium reactions is related in any simple way. In fact, only 2 constraints, one on total moles M and another on NO are necessary to obtain an excellent approximation to the behavior of the system and the combinations of the Lagrange multipliers required to fit the various reactions are given in the figure. If desired, a perfect fit can be obtained with 2 additional constraints on N and H.

These results indicate that the previously discussed RCCE calculations of NO concentrations in I.C.E. by Keck and Gillespie could have been improved by taking the constraint to be NO rather than fixed nitrogen.

8.2. Primary Combustion Reactions

The first application of the RCCE method to primary combustion processes was made by Takeda, Koshi and Matsui¹³ who studied the homogeneous oxidation of hydrogen and methane in constant volume adiabatic vessels. Similar more detailed studies of hydrogen oxidation have also been reported by Law, Metghalchi and Keck.¹² The studies provide considerable insight into the method and are very encouraging with respect to potential applications to more complex reacting systems.



FIG. 13. Degree of disequilibrium, $\ln r_i^-/r_i^+$, for 14 reactions in the combustion products of an I.C.E. as a function of time after top dead center.¹⁴

TABLE 4. Hydrogen-oxygen reaction mechanism and rate data⁴¹

Units: cm ³ , mol, sec, K, kcal Forward rate constant: $k^+ = AT^n \exp(-E_a/RT)$									
Reaction	ΔH°_{300}	Log A	n	E _a	М	FV	AV		
$H + O_2 + M = HO_2 + M$	-47	15.22	0	- 1.00	-1	0	- 1		
$OH + OH + M = H_2O_2 + M$	-15.39	14.96	0	-5.07	- 1	- 2	- 2		
H + O + M = OH + M	-102.23	16.00	0	0.00	- 1	- 2	- 2		
$\mathbf{H} + \mathbf{H} + \mathbf{M} = \mathbf{H}_2 + \mathbf{M}$	-104.20	15.48	0	0.00	- 1	- 2	- 2		
$O + O + M = O_2 + M$	-119.12	15.67	-0.28	0.00	- 1	-4	-4		
$H + OH + M = H_2O + M$	- 119.33	23.15	-2	0.00	- 1	-2	-2		
$O + OH = O_2 + H$	-16.89	13.12	0	0.68	0	-2	-2		
$HO_2 + HO_2 = H_2O_2 + O_2$	- 42.53	13.00	0	1.00	0	-2	0		
$HO_2 + O = OH + O_2$	- 55.13	13.70	0	1.00	0	- 2	- 1		
$HO_{2} + H = H_{2}O + O_{2}$	- 57.10	13.40	0	0.70	0	-2	1		
$HO_{2} + OH = H_{2}O + O_{2}$	- 72.23	13.70	0	1.00	0	- 2	- 1		
$H + OH = O + H_2$	- 1.97	9.92	1	6.95	0	0	0		
$H_2O_2 + H = HO_2 + H_2$	- 14.57	12.23	0	3.75	0	0	- 1		
$H_2 + OH = H + H_2O$	-15.13	13.34	0	5.15	0	0	0		
$OH + OH = O + H_2O$	-17.10	12.50	0	1.10	0	0	0		
$H_2O_2 + OH = HO_2 + H_2O$	-29.70	13.00	0	1.80	0	0	- 1		
$HO_2 + H = OH + OH$	- 38.24	14.40	0	1.90	0	0	1		

8.2.1. H_2/O_2 system

Because they are somewhat more carefully documented, the studies of Law, Metghalchi and Keck will be discussed first. These studies were carried out for stoichiometric mixtures of H₂ and O₂ in a constant volume adiabatic chamber at initial temperatures $T_i = 900, 1100$ and 1500 K and initial pressures $p_i = 0.01, 0.1, 1.0$ and 10 atm. Eight species H, HO, HO₂, H₂, H₂O, H₂O₂, O and O₂ governed by 17 reactions were included in the kinetic model. The reactions used are listed in Table 4 along with their standard reaction enthalpies ΔH^o_{300} and the parameters A, n and E_a for calculating their exothermic rate constants in the form

$$k^+ = AT^n \exp(-E_a/RT)$$
 (8.25)

where T is the temperature and R is the molar gas constant. The values of ΔH°_{300} were obtained form the JANAF tables³⁷ and the values of A, n and E_a were taken from the compilation of Pitz and Westbrook.⁴¹ The reverse endothermic rate constants were calculated using the rate quotient law

$$k_k^+ / k_k^- = K_{ck}$$
 (8.26)

where the equilibrium constant K_{ck} based on concentration was computed from data in the JANAF tables. This ensured that the system relaxed to the correct stable equilibrium state.

Detailed calculations were carried out by integrating the set of eight rate equations for the species in conjunction with the energy equation using the LSODE routine.⁴² RCCE calculations were carried out using constraints on:

the total moles

$$M = H + HO + HO_2 + H_2 + H_2O + H_2O_2 + O + O_2$$
(8.27)

the free valence

$$FV = H + HO + HO_2 + 2O$$
 (8.28)

and the active valence

$$AV = H + HO + 2O.$$
 (8.29)

The coefficients b_{ik} appearing in the rate equations (5.12) for these constraints are given in the last three columns of Table 4. One and two constraint cases were investigated. The rate equations were integrated using the same rate constants employed for the detailed calculations. No energy equation is required for these calculations since the temperature is calculated by the CNSEQL⁴³ code used to determine the constrained-equilibrium composition at each time step. Integration times for the one and two constraint cases were respectively 2 and 4 times those required for the detailed calculations so the algorithm used offers no time advantage for a system as simple as the H/O system. However, as previously mentioned it should be possible to improve this situation.

Typical results for the one-constraint calculations are presented in Fig. 14 which shows the temperaturetime curves for both low and high pressure regimes. The curve labelled M refers to the total moles constraint. The free valence FV and active valence AVcurves are identical to the accuracy with which they can be plotted. The curve labelled FS is the result of integrating the full set of 9 equations in the detailed model. As might be expected no single constraint is sufficient to reproduce the detail calculations with any degree of accuracy although the M constraint shows some qualitative similarity. All the curves relax to the correct equilibrium state but the initial behavior is incorrect.

The requirement that the initial state by correctly reproduced is an important condition which may be used in the selection of the constraints. This require-



FIG. 14. Temperature-time curves for H_2/O_2 mixtures: One constraint calculations M = total moles, FV = moles free valence, AV = moles active valence, and FS = full set of rate equations.¹²

ment is satisfied by the two-constraint calculation examples which are shown in Fig. 15. It can be seen that for the $p_i = 1.0$ atm. case, the combinations M + FV and M + AV give similar results which reproduce the shape of the detailed temperature-time curve FS quite well. The ignition delay times are a bit too short however. In the $p_i = 10$ atm. case the M + AV combination still gives a reasonable estimate of the ignition delay time but the M + FVcombination is a miserable failure. The reason for this has not yet been fully established but a strong possibility suggested by the b_{ik} values in Table 4 is that the FV constraint allows the rate limiting reaction 13 to come to equilibrium whereas the AV constraint does not. It is anticipated that the addition of a third constraint to the M + AV combination would improve the agreement still further but calculations for three constraints have been deferred pending improvements in the integration routines.

Additional results for the M + AV combination are presented in Fig. 16 which shows the temperature as a function of the product of the time and the initial pressure for an initial temperature of 1500 K and initial pressures of 0.01, 0.1, 1.0 and 10 atm. It can be seen that the overall agreement with the detail calculation is reasonably good. The initial temperature rise from 1500 to 1710 K is controlled by the AV constraint and obeys binary scaling. The later temperature rise is controlled by the M constraint and shows the expected additional pressure dependence.



FIG. 15. Temperature-time curves for H_2/O_2 mixtures: two constraint combinations M + FV and M + AV and the same conditions as Fig. 14.¹²

The results indicate that to improve the agreement an additional constraint is needed in the ignition delay interval and it is probable that this involves reaction 12 in Table 4.



FIG. 16. Comparison of temperature vs binary-scaled time curves for H_2/O_2 mixtures. M + AV and FS calculations at $T_i = 1500$ K and $p_i = 0.01, 0.1, 1.0$ and 10 atm.¹²



FIG. 17. Comparison of binary-scaled ignition-delay times in H_2/O_2 mixtures as a function of pressure for $T_i = 900, 1100$ and 1500 K. Points show M + AV results; curves show FS results. Curve labelled $2kg_7^- = k_1^+ [M]$ Divides high and low pressure regimes.¹²

A summary of the results is shown in Fig. 17 where the product of the ignition delay time τ and the density ratio ρ/ρ_0 has been plotted versus the initial pressure on a log-log scale. The points are the results of the two constraint M + AV calculations and the curves are the result of integrating the full set of nine equations for the detailed model. Also shown is the dividing line between low and high pressure regimes given by the condition $2k_7^- = k_1^+$ [M]. It can be seen that in all cases the agreement between the RCCE and detailed calculations is within 40%. The results of the



FIG. 18. Time dependent temperatures in the explosion of a stoichiometric mixture of hydrogen and oxygen. Initial condition: $p_i = 1.0$ atm., $T_i = 1500$ K. Symbols represent RCCE calculations.¹³



FIG. 19. Time dependent hydrogen atom concentrations for the same conditions as Fig. 8^{13}

detailed model are also in excellent agreement with prior work.⁴⁴

Except for the constraints used, the calculations of Takeda, Koshi and Matsui are almost identical to those of Law, Metghalchi and Keck. The constraints included in this study were: the total moles of mixture (XM), the pressure p and the individual species concentrations (O) and (O₂).

Typical time-dependent profiles for the temperature and the hydrogen atom concentration are shown in Figs 18 and 19. It can be seen that no single constraint is sufficient to reproduce both profiles with any degree of accuracy but that dual constraints on either p and (O_2) or (XM) and (O_2) do a remarkably good job. It should be noted in this connection that a constraint on the pressure is not really acceptable since pressure is one of the variables one wishes to predict. It should also be noted that there appears to be some problem with the (O) and (O_2) profiles since these do not go to the correct equilibrium values as required by the RCCE method.

8.2.2. CH_4/O_2 System

RCCE calculations for stoichiometric mixtures of CH₄ and O₂ in constant volume adiabatic chambers have also been carried out by Takeda, Hoshi and Matsui.¹³ Sixteen species and 42 reactions were included in the kinetic model which was based on previous work.45 The constraints considered were: pressure, total moles, and the individual species concentrations (CH₄), (O₂) and (CO). Typical timedependent profiles for the temperature and CO concentration are shown in Figs 20 and 21. It can be seen that in this case three constraints on (CH_4) , (O_2) , and (XM) are sufficient to reproduce the exact solution with acceptable accuracy. This corresponds to a reduction in the number of differential equations required to describe the system from 17 to 3. Unfortunately no information on the computer time required to integrate these two sets of equations was



FIG. 20. Time dependent temperatures in the explosion of a stoichiometric mixture of methane and air. Initial conditions: $p_i = 1.0$ atm., $T_i = 1500$ K.¹³



FIG. 21. Time dependent carbon monoxide concentrations for the same conditions as Fig. 20.¹³

given so it is not clear which of the methods was more efficient. It would appear however that as the size and complexity of the systems considered increase, the RCCE method will eventually become the winner.

9. ADVANTAGES AND DISADVANTAGES OF RCCE

The rate-controlled constrained-equilibrium method offers a number of advantages over other techniques currently in use for treating reactions in complex systems:

- (1) Since in general the number of constraints necessary to determine the state of a complex system to a specified degree of accuracy is very much smaller than the number of degrees of freedom of the system, there are fewer differential equations to integrate.
- (2) Only the rate constants for the fastest ratecontrolling reactions are needed to carry out a calculation and these are the most likely to be known.

- (3) Since they enter explicitly as constraints, the conservation laws are satisfied at all times and are not subject to round-off errors during integration.
- (4) The entropy production for a system relaxing through a sequence of constrained equilibrium states is non-negative at all times and the system always approaches the correct stable equilibrium state.
- (5) The accuracy of the calculations can be systematically improved by the addition of constraints one at a time and they become 'exact' when the number of independent constraints equals the number of degrees of freedom.
- (6) The method can be extended to include constraints imposed by steady state reactions, selection rules, body forces and diffusion.
- (7) The method can be applied to extremely complex systems and is expected to improve as the size of the system increases. The only obvious disadvantages of the method are:
- Efficient algorithms for integrating the differential rate equation for the constraints or conjugate Lagrange multipliers need to be developed.
- (2) The constraints must be identified.

In the opinion of the author, the last disadvantage is really an advantage since it forces one to *think* before embarking on elaborate calculations!

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