

RATE-CONTROLLED CONSTRAINED EQUILIBRIUM METHOD FOR TREATING 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 statistical thermodynamics. It is also of great importance in connection with a variety of practical problems related to combustion, energy conversion, hypersonic aerodynamics, chemical processing, electrical discharges, lasers and biology.

It is generally accepted that the equilibrium state of such systems can be found by "maximizing the entropy subject to the constraints." To do this two types of constraints must be considered. The first are those imposed by the external environment of the system and are under the control of the observer. The volume of the system and its position in a gravitational field are examples of such external constraints. The second are those imposed by the internal structure of the system and the laws of mechanics. Such constraints which are not under the control of the observer and which limit the states accessible to a system on the time scale of interest were termed passive resistance by Gibbs. Semipermeable membranes which segregate species and extremely slow nuclear reactions which imply conservation of the elements are the most familiar examples of passive resistances.

In ordinary thermodynamic calculations involving systems subject to slowly changing external constraints, such passive resistances are set either "on" or "off." The system is assumed to relax through a sequence of shifting equilibrium states determined by the instantaneous values of the external constraints and fixed values of the internal constraints imposed by the passive resistances which are "on," that is by the slow reactions. It is further assumed that all reactions associated with passive resistances which are "off" are sufficiently fast to maintain the shifting equilibrium state. This technique has been used with remarkable success in the design and analysis of a wide variety of practical devices ranging from steam engines and chemical reactors to power plants and refineries.

In cases where the rates of change in external constraints are too high to justify the shifting equilibrium assumption of thermodynamics, as in combustion processes or shock waves, it is necessary to describe the changes in the internal state of a system using a set of rate equations. These must be integrated in conjunction with the equations for the external constraints

using a computer. For systems involving a large number of degrees of freedom, this can be a truly formidable task which is further complicated by the fact that most of the reaction rates involved are usually unknown and must be estimated.

To treat such complex reacting systems, Keck and Gillespie (1) have proposed the "rate-controlled partial equilibrium method." This method combines the use of rate equations for both internal and external constraints with the techniques of thermodynamics for determining the constrained equilibrium state. It is based on the assumption that under many conditions it is possible to identify classes of slow reactions which if completely inhibited would prevent the relaxation of the system to complete equilibrium. It is further assumed that fast reactions will equilibrate the system subject to the constraints imposed by the slow reactions and that the system will relax to complete equilibrium through a sequence of constrained equilibrium states at a rate controlled by the slow reactions. Although Keck and Gillespie originally used the term "partial equilibrium" to describe their method, in later work by Galant and Appleton (2) the more accurate term "constrained equilibrium" was substituted.

Prior to the work of Keck and Gillespie, the concept of a "partial equilibrium" state imposed by slow dissociation and recombination reactions was used by Kaskan (3), Schott (4) and Lezberg and Franciscus (5) to treat the problem of hydrogen-oxygen combustion. It was also used by Bray (6) in his development of the "sudden freezing" approximation for treating rapidly expanding nozzle flows.

As described in companion papers in this volume, variations of the method are also currently being used by Levine (7) to treat reactions in molecular beams, Ross (8) to investigate relative stability in highly nonequilibrium systems and Kerner (9) to investigate speciation in ecological systems.

In the present paper we shall limit our detailed description of the rate-controlled constrained equilibrium method to chemically reacting dilute gas mixtures. The extension of the method to include energy exchange reactions will be obvious. Since the method may truly be regarded as an extension of the familiar techniques of ordinary thermodynamics, we shall begin in section 2 with a review of these techniques as applied to gas mixtures. This will be followed in section 3 by a discussion of the rate-controlled constrained equilibrium method and in section 4 by a brief commentary on conventional methods of treating nonequilibrium gas mixtures. A discussion of some practical applications to combustion will be given in section 5 and the summary and conclusions will be given in the final section.

2. Equilibrium Gas Mixtures

Consider a uniform homogeneous reacting gas mixture of weakly

interacting molecules with fixed total energy E in a fixed volume V . Let X_j be the number of moles of species B_j in the gas and a_{kj} the number of atoms of element A_k in a molecule of species B_j . Then the number of moles of element A_k in the gas will be

$$C_k = \sum_{j=1}^m a_{kj} X_j \quad : \quad k = 1 \dots n \quad (1)$$

where m is the number of different species and $n \leq m$ is the number of different elements.

Our problem is to determine the equilibrium state of such a system and, in accord with the general principles of statistical thermodynamics, we shall assume that this can be done by simply maximizing the Gibbs entropy

$$S = -R \sum_i x_i \ln x_i \quad (2)$$

subject to the constraints

$$1 = \sum_i x_i \quad (3)$$

$$E = \sum_i \epsilon_i(V) x_i \quad (4)$$

where x_i is the probability that the system is in a microstate (wave function) of energy $\epsilon_i(V)$ and the summations are over all microstates.

If we further assume that the gas is sufficiently dilute so that the interaction energy between molecules can be neglected, then the total energy of the gas can be approximated by

$$E = \sum_{j=1}^m e_j X_j \quad (5)$$

where

$$e_j = \sum_i \epsilon_{ji}(V) x_{ji} \quad (6)$$

is the mean energy of a molecule of species B_j and x_{ji} is the probability that such a molecule will be found in a microstate of energy $\epsilon_{ji}(V)$ determined only by its internal structure and the volume V of the container. Furthermore, since the molecules have been assumed independent, the probability x_i for the system to be in a state of energy ϵ_i can be expressed as product of the probabilities x_{ji} for the individual molecules to be in microstates of energy $\epsilon_{ji}(V)$ and the entropy (2) then takes the form

$$S = -R \sum_{j=1}^m X_j \left(\sum_i x_{ji} \ln x_{ji} + \ln X_j - 1 \right) \quad (7)$$

Maximizing this expression subject to the constraints

$$1 = \sum_i x_{ji} \quad : \quad j = 1 \dots m \quad (8)$$

$$C_k = \sum_{j=1}^m a_{kj} X_j \quad : \quad k = 1 \dots n < m \quad (9)$$

$$E = \sum_{j=1}^m \left(\sum_i \epsilon_{ji}(V) x_{ji} \right) X_j \quad (10)$$

we obtain for the equilibrium state

$$\ln x_{ji}^\circ = -\alpha_j - \beta \epsilon_{ji}(V) \quad (11)$$

$$\ln X_j^\circ = \alpha_j - \sum_{k=1}^n \gamma_k a_{kj} \quad (12)$$

where α_j , β , and γ_k are the Lagrange multipliers conjugate to the constraints (8) - (10)

Substituting x_{ji} from (11) back into the normalization condition, (8) we obtain

$$e^{\alpha_j} = \sum_i e^{-\beta \epsilon_{ji}(V)} = Q_j(\beta, V) \quad (13)$$

where $Q_j(\beta, V)$ is the Boltzmann partition function for the species β_j .

Given the partition function all the other thermodynamic properties of the individual molecules can be determined as functions of β and V from the well known formulae of statistical thermodynamics. In particular, the temperature is

$$T = (R\beta)^{-1} \quad (14)$$

and the chemical potential is

$$\mu_j = RT \ln X_j / Q_j(T, V) \quad (15)$$

To determine the equilibrium composition of the gas, we may use (13) to eliminate α_j in (12). This gives

$$\ln X_j^\circ = \ln Q_j(\beta, V) - \sum_{k=1}^n \gamma_k a_{kj} \quad (16)$$

which in turn may be substituted into (9) to obtain a set of n equations

$$C_\ell = \sum_{j=1}^m a_{\ell j} Q(\beta, V) \exp\left(-\sum_{k=1}^n \gamma_k a_{kj}\right) \quad : \quad \ell = 1 \dots n \quad (17)$$

which can be solved numerically using the methods developed by Warga (10), Zeleznik and Gordon (11) and Agmon, Alhassid and Levine (12) to obtain the n unknown Lagrange multipliers

$$\gamma_k = \gamma_k(T, V, C_1 \dots C_n) \quad : \quad k = 1 \dots n \quad (18)$$

Substituting (18) and (13) into (11) and (12) and using (14), we obtain the energy distribution

$$x_{ji} = x_{ji}^\circ(T, V, C_1 \dots C_n) \quad (19)$$

and composition

$$X_j = X_j^\circ(T, V, C_1 \dots C_n) \quad (20)$$

as functions of T, V , and $C_1 \dots C_n$. This completely determines the equilibrium state of the system.

2.1 Thermodynamics of Gas Mixtures In the above analysis, which may be properly termed thermostatistics, we have considered only the final equilibrium state in which a gas mixture subject to fixed external constraints will be found after an infinitely long period of time. We now wish to extend the analysis to include situations in which the external 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 external constraints are sufficiently slow, a system such as the gas mixture under consideration will relax through a sequence of quasistatic states which remain close to equilibrium at all times. In a gas, this condition is supposed to be maintained by molecular collision processes whose relaxation time τ_c is short compared to the characteristic time for a change in the constraints, e.g. $\tau_c \ll \tau_v = (d \ln V / dt)^{-1}$. Under these conditions, the time dependent energy distribution and composition can be obtained from (19) and (20) in the form

$$x_{ji}(t) = x_{ji}^\circ(T(t), V(t), C_1 \dots C_n) \quad (21)$$

and

$$X_j(t) = X_j^{\circ}(T(t), V(t), C_1 \dots C_n) \quad (22)$$

Shifting equilibrium calculations carried out using equations (21) and (22) 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 instantaneous values of the constraints, in this case temperature and volume.

3. Rate-Controlled Constrained Equilibrium

In thermodynamic calculations of the type considered in the previous section, it is usually assumed that the only constraints on the allowed composition of a reacting gas mixture are those imposed by nuclear reactions which are extremely slow at ordinary temperatures and imply conservation of the elements. However, as has already been observed in the Introduction, there are many situations of practical interest in which it is possible to identify classes of slow chemical or energy exchange reactions which if completely inhibited would prevent the relaxation of the system to complete equilibrium. Some examples of such reactions important in high temperature chemistry and combustion are given below.

<u>Passive Resistance</u>	<u>Constrained Property</u>
Nuclear Reactions	Moles of Elements
Ionization Reactions	Moles of Ions
Dissociation Reactions	Moles of Gas
Nitrogen Fixing Reactions	Moles of Fixed Nitrogen
CO Oxidation Reactions	Moles of CO ₂
T-V Transfer Reactions	Vibrational Temperature
V-V Selection Rules	Vibrational Quanta

A common feature of all these reactions is that, under the conditions of interest, their characteristic relaxation times are long compared to the relaxation times for the large majority of binary energy transfer or particle exchange reactions occurring in a reacting gas mixture.

The fundamental hypothesis of the rate-controlled constrained equilibrium method is that the fast reactions will equilibrate the system subject to the constraints implied by the slow reactions and that the approach to complete equilibrium will proceed through a sequence of constrained equilibrium states at a rate controlled by the slow reactions.

3.1 Constrained Equilibrium Gas Mixtures Except for the inclusion of additional constraints

$$C_k = \sum_{j=1}^m a_{kj} X_j \quad : \quad k = n+1 \dots n+r \quad (23)$$

of the same form as (9) imposed by the rate-controlling reactions, the calculation of the constrained equilibrium composition may be carried out in exactly the same manner as in the equilibrium case. Depending on the choice of the thermodynamic variables which are held fixed, one may then either

1) Maximize the Entropy

$$S = -R \sum_{j=1}^m X_j \left(\sum_i x_{ji} \ln x_{ji} + \ln X_j - 1 \right) \quad (24)$$

subject to the constraints

$$1 = \sum_i x_{ji} \quad : \quad j = 1 \dots m \quad (24)$$

$$C_k = \sum_{j=1}^m a_{kj} X_j \quad : \quad k = 1 \dots n+r \quad (25)$$

$$E = \sum_{j=1}^m \sum_i \epsilon_{ji}(V) x_{ji} X_j \quad (27)$$

2) Minimize the Helmholtz Free Energy

$$A(T, V) = \sum_{j=1}^m X_j (e_j(T) - T s_j(T, V, X_j)) \quad (28)$$

subject to the constraints

$$C_k = \sum_{j=1}^m a_{kj} X_j \quad : \quad k = 1 \dots n+r \quad (29)$$

3) Minimize the Gibbs Free Energy

$$F(T, p) = \sum_{j=1}^m X_j (e_j(T) + RT - T s_j(p, T, X_j)) \quad (30)$$

subject to the constraints

$$C_k = \sum_{j=1}^m a_{kj} X_j \quad : \quad k = 1 \dots n+r \quad (31)$$

In all cases, one obtains the result

$$\ln X_j^c = \ln [Q_j(T)] + \ln V - \sum_{k=1}^{n+r} \gamma_k a_{kj} \quad (32)$$

where $[Q_j(T)] = Q_j(V, T)/V$ is the partition function per unit volume for molecules of species B_j .

From a computational point of view the most convenient independent variables are T and V or T and p . For the case where T and V are the independent variables, substitution of (32) back into the constraints (29) then gives the set of $n+r$ equations

$$C_\ell = \sum_{j=1}^m a_{\ell j} \exp\left(-\sum_{k=1}^{n+r} \gamma_k a_{kj} - A_j(V, T) - 1\right) : \ell = 1 \dots n+r \quad (33)$$

where

$$A_j(T, V) = - (\ln[Q_j(T)] - \ln V + 1) \quad (34)$$

which may be solved for the $n+r$ unknowns

$$\gamma_k = \gamma_k(T, V, C_1 \dots C_{n+r}) \quad : \quad k = 1 \dots n+r \quad (35)$$

For the case where T and p are the independent variables, the situation is slightly more complicated since equation (32) can not be solved explicitly for X_j^C in terms of T and p after the equation of state

$$pV = RT \sum_{j=1}^m X_j^C \quad (36)$$

has been introduced to eliminate V . It has therefore been found convenient by Warga (10) to introduce an additional unknown X_o and an additional equation

$$X_o = \sum_{j=1}^m X_j^C \quad (37)$$

to the original set. Substitution of (32) into (37) and the constraints (31) then leads to the set of $n+r+1$ equations

$$C_\ell = X_o \sum_{j=1}^m a_{\ell j} \exp\left(-\sum_{k=1}^{n+r} \gamma_k a_{kj} - F_j(pT)\right) : \ell=1 \dots n+r \quad (38)$$

and

$$1 = \sum_{j=1}^m \exp\left(-\sum_{k=1}^{n+r} \gamma_k a_{kj} - F_j(pT)\right) \quad (39)$$

where

$$F_j(T, p) = - (\ln[Q_j(T)] + \ln(p/RT)) \quad (40)$$

which may be solved for the $n+r+1$ unknowns

$$\gamma_k = \gamma_k(T, p, C_1 \dots C_{n+r}) \quad : \quad k=1 \dots n+r \quad (41)$$

and

$$X_o = X_o(T, p, C_1 \dots C_{n+r}) \quad (42)$$

It should be noted that equation (37) which gives the total moles of gas does not constitute an additional constraint on the system but is merely an algebraic identity introduced for mathematical convenience.

Substituting (35) or (41) back into (32) we obtain the constrained equilibrium composition of the gas for the two cases considered.

$$X_j = X_j^C(T, V, C_1 \dots C_{n+r}) \quad (43)$$

or

$$X_j = X_j^C(T, p, C_1 \dots C_{n+r}) \quad (44)$$

as functions of T and V or T and p and the $n+r$ constraints.

In concluding this discussion it may be observed that the same procedures can be used in conjunction with any other free energy function to treat cases where the energy states of the molecules may be affected by gravitational, electromagnetic, or other body forces.

3.2 Thermostatistics of Constrained-Equilibrium Once the composition of the gas mixture has been determined, all its other thermodynamic properties may easily be calculated. In particular, the chemical potential and Gibbs free energy can be expressed

$$\mu_j \equiv RT \ln X_j / Q_j = \sum_{k=1}^{n+r} \lambda_k a_{kj} \quad (45)$$

and

$$F \equiv \sum_{j=1}^m \mu_j X_j = \sum_{k=1}^{n+r} \lambda_k C_k \quad (46)$$

in which we have introduced the parameter

$$\lambda_k = -R T \gamma_k \quad (47)$$

It follows from (46) that

$$\mu_j = (\partial F / \partial X_j)_{T,p,\underline{X}} \quad (48)$$

and

$$\lambda_k = (\partial F / \partial C_k)_{T,p,\underline{C}} \quad (49)$$

Also from (45), (46) and (31)

$$\sum_{j=1}^m X_j d\mu_j = \sum_{k=1}^{n+r} C_k d\lambda_k \quad (50)$$

and

$$\sum_{j=1}^m \mu_j dX_j = \sum_{k=1}^{n+r} \lambda_k dC_k \quad (51)$$

Substituting (51) into the Gibbs equation

$$T dS = dE + p dV - \sum_{j=1}^m \mu_j dX_j \quad (52)$$

we obtain

$$T dS = dE + p dV - \sum_{k=1}^{n+r} \lambda_k dC_k \quad (53)$$

It can be seen from equations (46), and (48) - (53) that the parameters λ_k play precisely the same role with respect to the constraints C_k as the chemical potentials μ_j play with respect to the mole numbers X_j . We may therefore define λ_k as the *generalized chemical potential* conjugate to the constraint C_k . The important distinction between the λ 's and the μ 's is that, since the number of constraints $n+r$ is in general much smaller than the number of species m , it is far more efficient to determine the composition in terms of the λ 's than the μ 's.

For processes at constant T and p , the Gibbs free energy must be a minimum at equilibrium and since the constraints C_k must be linearly independent, it can be seen from (49) that, unless dC_k vanishes identically in any allowed process, the corresponding λ_k must be zero at equilibrium. Thus, in general, a condition for chemical equilibrium will be

$$\lambda_k^\circ = 0 \quad : \quad dC_k \neq 0 \quad (54)$$

3.3 Dynamics of Constrained Equilibrium Following the lead of

thermodynamics, we now wish to consider the situation in which the constraints C_k on the composition of a gas mixture may be slowly varying functions of time. We assume that energy exchange reactions have equilibrated so that the internal degrees of freedom 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

$$\sum_{j=1}^m v_{ji}^+ B_j \xrightleftharpoons[R_i^-]{R_i^+} \sum_{j=1}^m v_{ji}^- B_j \quad (55)$$

where R_i^+ and R_i^- denote the forward and reverse rates of the reaction R_i and v_{ji}^+ and v_{ji}^- are the corresponding stoichiometric coefficients. Finally we assume that the rate equations for the individual species are of the form

$$\dot{X}_j = \sum_i v_{ji} (R_i^+ - R_i^-), \quad (56)$$

where

$$v_{ji} = (v_{ji}^- - v_{ji}^+), \quad (57)$$

and that the reactions rates are given by the phenomenological equations

$$R_i^\pm(T, V, X) = k_i^\pm(T) V \prod_j [X_j]^{v_{ji}^\pm}, \quad (58)$$

where $k_i^+(T)$ and $k_i^-(T)$ are rate constants for the forward and reverse reactions and $[X_i] \equiv X_i/V$ is the concentration of species B_j .

At equilibrium the gas must be in a stationary state and thus the left hand side of (56) must vanish. A *sufficient* condition for this is the *detailed balancing condition*

$$R_i^+ = R_i^- = R_i^0 \quad (59)$$

If we further assume, consistent with the laws of mechanics and thermodynamics, that the forward and reverse rates of a reaction can only vanish simultaneously at equilibrium and that the equilibrium composition of a reacting gas mixture must be independent of the magnitude of the reaction rates provided there is at least one reaction whose rate is not identically zero, then (59) becomes a *necessary* condition. This proof of necessity, which

to the author's knowledge has not been given before, is of considerable fundamental importance. It is also of practical importance since in actual calculations of rate processes only a small fraction of the possible reactions can be included and, for these, the condition *must* be imposed.

Substituting (58) into (59) we obtain the rate quotient law

$$k_i^+ / k_i^- = \prod_{j=1}^m [Q_j]^{v_{ji}} = K_i(T) \quad (60)$$

where $K_i(T)$ is the equilibrium constant of the reaction R_i . This law *must* hold under constrained-equilibrium as well as equilibrium conditions as long as the internal degrees of freedom of the individual molecules are in equilibrium at the temperature T .

3.3.1 Relaxation Times The characteristic times τ_{Bj} and τ_{Ri} for the relaxation of a species of B_j or reaction R_i to equilibrium may be defined by

$$\tau_{B_j}^{-1} = \left| \partial \ln \dot{X}_j / \partial t \right|_{TV}^{\circ} \quad (61)$$

and

$$\tau_{R_i}^{-1} = \left| \partial \ln (R_i^+ - R_i^-) / \partial t \right|_{TV}^{\circ} \quad (62)$$

Substituting (56) and (58) into (61) and (62) and using (57) and (59) we find

$$\tau_{B_j}^{-1} = (X_j^{\circ})^{-1} \sum_i v_{ji}^2 R_i^{\circ} \quad (63)$$

and

$$\tau_{R_i}^{-1} = R_i^{\circ} \sum_j v_{ji}^2 (X_j^{\circ})^{-1} \quad (64)$$

These equations, which also apply under constrained equilibrium conditions, are useful for determining which species are close to equilibrium and which reactions are rate-controlling.

3.3.2 Rate Equations for Constraints Differentiating the equations for the constraints with respect to time gives

$$\dot{C}_k = \sum_{j=1}^m a_{kj} \dot{X}_j \quad : \quad k = 1 \dots n+r \quad (65)$$

from which we may eliminate \dot{X}_j using (56) to obtain the rate equation for the constraints

$$\dot{C}_k = \sum_i b_{ki} (R_i^+ - R_i^-) \quad : \quad k = 1 \dots n+r \quad (66)$$

where

$$b_{kj} = \sum_{j=1}^m a_{kj} v_{ji} = \sum_{j=1}^m a_{kj} (v_{ji}^- - v_{ji}^+) \quad (67)$$

is the change in constraint C_k due to reaction R_i . Assuming elements are conserved in all reactions, we obtain

$$b_{ki} = 0 \quad : \quad k = 1 \dots n \quad (68)$$

which by virtue of (66) gives

$$\dot{C}_k(t) = C_k \quad : \quad k = 1 \dots n \quad (69)$$

Using the rate-controlled constrained equilibrium composition given by (32) to evaluate the reaction rates $R_i^{\pm}(T, V, X)$ in (66), we obtain a set of r first order differential equations of the form

$$\dot{C}_k(t) = \dot{C}_k(T(t), V(t), C_1 \dots C_n, C_{n+1}(t) \dots C_{n+r}(t)) : k=n+1 \dots n+r \quad (70)$$

for the remaining unknown constraints. Given the initial values of T, V and $C_1 \dots C_{n+r}$ these equations can be integrated in conjunction with the equations of state and the conservation equations of thermodynamics and fluid mechanics to determine the evolution of the system. In simple cases this can be done analytically but, in general, numerical methods must be employed. In this connection 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.

3.3.3 Degree of Disequilibrium A useful parameter for measuring the departure of a reaction from equilibrium is the ratio of the reverse to forward reaction rates

$$R_i^-/R_i^+ = (k_i^-/k_i^+) \prod_{j=1}^m [X_j]^{v_{ji}} \quad (71)$$

Substituting the constrained-equilibrium composition (32) into (71) and using the rate quotient law (60), we find under constrained-equilibrium conditions

$$R_i^-/R_i^+ = (k_i^-/k_i^+) \prod_{j=1}^m [Q_j]^{v_{ji}} \exp\left(-\sum_{k=1}^{n+r} \gamma_k b_{ki}\right) = \exp\left(-\sum_{k=1}^{n+r} \gamma_k b_{ki}\right) \quad (72)$$

The *degree of disequilibrium* may be defined as

$$\ln R_i^-/R_i^+ = -\sum_{k=1}^{n+r} \gamma_k b_{ki} \quad (73)$$

Using the definition (45) and (43), (73) may also be written

$$\ln R_i^-/R_i^+ = (RT)^{-1} \sum_{k=1}^{n+r} \lambda_k b_{ki} = (RT)^{-1} \sum_{j=1}^m \mu_j v_{ji} \quad (74)$$

From (74) it can be seen that a condition for chemical equilibrium is

$$\sum_{k=1}^{n+r} \lambda_k b_{ki} = \sum_{j=1}^m \mu_j v_{ji} = 0 \quad (75)$$

It also follows from (74) that for any set of reactions which change only a single constraint, say C_ℓ , we have

$$b_{\ell i}^{-1} \ln R_i^-/R_i^+ = (RT)^{-1} \lambda_\ell = -\gamma_\ell \quad (76)$$

This relation can be useful for evaluating the validity of the constrained equilibrium assumption under practical conditions.

3.3.4 Entropy Production Using the rate equations (66) for the constraints, the Gibbs equation (53) can be written in the form

$$T\dot{S} = \dot{E} + p\dot{V} + T\sigma_R \quad (77)$$

where

$$\sigma_R = -\frac{1}{T} \sum_{k=1}^{n+r} \lambda_k \dot{C}_k = -\frac{1}{T} \sum_i \left(\sum_{k=1}^{n+r} \lambda_k b_{ki} \right) (R_i^+ - R_i^-) \quad (78)$$

is the entropy production due to chemical reactions. Substituting (74) into (78), we obtain the familiar positive definite form

$$\sigma_R = R \sum_i (R_i^+ - R_i^-) \ln(R_i^+/R_i^-) \geq 0 \quad (79)$$

Thus it can be seen that, for a gas in a fixed volume V passing through a sequence of constrained equilibrium states of fixed energy E , the entropy production is always greater than or equal to zero and is zero if and only if $R_i^+ = R_i^-$ for all reactions. It follows that such a gas will relax unconditionally to a unique stable equilibrium state determined only by the values of E and V and the fixed constraints $C_1 \dots C_n$. It can also be clearly seen from the Gibbs equation written in the alternative forms

$$\dot{A} = -S \dot{T} - p \dot{V} - T \sigma_R \quad (80)$$

or

$$\dot{F} = -S \dot{T} + V \dot{p} - T \sigma_R \quad (81)$$

that, for systems at fixed T and V or T and p , the Helmholtz free energy $A(T,V)$ or Gibbs free energy $F(T,p)$ must always decrease and will be a minimum at equilibrium. These results can be generalized to include systems subject to external constraints in addition to volume and internal rate-controlled constraint due to slow energy exchange reactions or selection rules.

4. Conventional Treatments of Nonequilibrium

Before discussing the applications of the constrained-equilibrium method to a few practical combustion problems, we should like to consider briefly two of the conventional methods for treating chemical reactions in nonequilibrium systems with which we shall wish to compare it.

4.1 Integration of Complete Set of Rate Equations In principle, the most accurate method of determining the evolution of a homogeneous chemically reacting system is to integrate a complete set of rate equations

$$\dot{X}_j = \sum_{i=1}^m v_{ji} (R_i^+ - R_i^-) \quad : \quad j = 1 \dots m-n \quad (82)$$

sufficient in number to determine all the unknown species concentrations given the concentrations of the n elements. For systems such as those encountered in combustion involving 50 or more interesting species and thousands of potentially significant reactions, this is an extremely difficult task and truncation of both the species and reaction lists are necessary,

especially if the chemical kinetics are to be combined with a flow calculation. The problem with truncation is that, unless great care is used, the omission of an important intermediate species or 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 view of this, it seems obvious that the best method of carrying out an "exact" calculation would be to include all interesting species, but limit the number of rate equations to those for which the reaction rates are known and use the constrained equilibrium assumption to determine the remaining unknowns.

4.2 Steady State Approximation To reduce the number of differential equations which must be integrated, the steady state approximation is frequently used. This involves the assumption that for certain species, say B_1 to B_ℓ ,

$$0 \approx \sum_i v_{ji} (R_i^+ - R_i^-) \quad : \quad j = 1 \dots \ell \quad (83)$$

Equation (83) may then be solved in conjunction with the reduced set of $m-n-\ell$ differential equations

$$X_j = \sum_i v_{ji} (R_i^+ - R_i^-) \quad : \quad j = \ell+1 \dots m-n \quad (84)$$

Although this can result in considerable simplification of the calculations, the steady state species must be identified and the other problems discussed above still remain. In addition, a more subtle problem which must be faced is that it can no longer be proved, as for the constrained equilibrium approximation or a full set of rate equations, that the entropy production will be non-negative. This could, in principle, lead to a Second Law violation or failure of the system to reach a unique stable equilibrium point. Whether this is serious in practice will depend on the particular situation involved however.

5. Applications in Combustion

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 at relatively high concentrations at temperatures $T \geq 2000$ °K and their removal is controlled by strongly temperature dependent reactions many of which involve

trace species such as N atoms as collision partners. For these reasons, chemical kinetic models of CO and NO formation can easily involve 30 or more "significant" species. A typical list of such species in the order of their abundance in the equilibrium combustion products of a stoichiometric mixture of isooc-tane and air at a temperature of 2000°K and pressure of 1 atmos-phere is given below.

N ₂	H ₂ O	CO ₂	CO	O ₂	NO	H ₂	OH	H	O
NO ₂	N ₂ O	HO ₂	H ₂ O ₂	HNO ₂	HNO	NH ₃	NH ₂	HCO	HNCO
NH	N	H ₂ CO	O ₃	HCN	NCO	HNO ₃	NO ₃	H ₂ N ₂	N ₂ O ₃
CN	CH ₃	CH ₄	...						

Clearly the integration of a full set of rate equations neces-sary to determine the concentrations of so many species would be a formidable task. In addition, when one also considers the fact that for such a species list it is easily possible to id-entify upwards of 1000 potentially significant reactions and that for the overwhelming majority of these the rate constants are unknown, one might well be discouraged from even attempting it. This is, of course, just the situation in which the con-strained equilibrium method can be of most value.

The problem has also been treated using the conventional methods discussed in the preceding section. In all the cases considered severe truncation of the species and reaction rate list has been used to simplify the calculations. Comparisons between these methods and the constrained equilibrium method will be made in the discussion below.

5.1 CO Freezing in a Steady Flow Burner The constrained equi-librium method has been used by Morr and Heywood (13) to inter-pret their measurements of CO concentrations in a steady flow cylindrical burner. This work illustrates in a dramatic way both the effect of using different constraints and the effect of com-bining constraints.

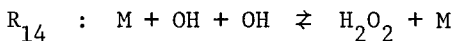
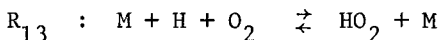
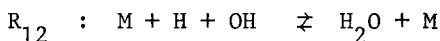
The experimental geometry is shown schematically in the upper part of Figure 1. Below it are shown the mean temperature pro-file along the axis of the burner and the experimental and theo-retical results. It can be seen that, upstream of the heat ex-changer where the temperatures are high, the measured CO mole fractions, shown as points, agree well with the calculated equi-librium values, shown as a dashed line. However, downstream of the heat exchanger where the temperatures are low, the measured CO levels far exceed the equilibrium value, giving clear

evidence for the freezing of CO oxidation reactions.

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



controlled by the dissociation and recombination reactions

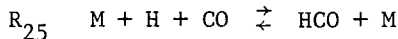
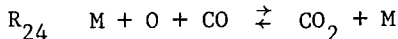
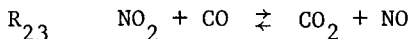
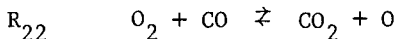


and governed by the rate equation

$$\frac{dM}{dt} = \sum_{i=1}^4 (R_{1i}^- - R_{1i}^+) \quad (87)$$

The results obtained when this constraint was used alone are shown by the curve marked $(CO)_M$ in Figure 1. Although the $(CO)_M$ levels are substantially higher than the $(CO)_{eq}$ levels they are still far below the measured values.

The second constraint which was tried was that on the moles of CO controlled by the CO oxidation reactions



and governed by the equation

$$\frac{d \text{CO}}{dt} = \sum_{i=1}^5 (R_{2i}^- - R_{2i}^+) \quad (89)$$

The results obtained when this constraint was used alone are shown by the curve marked $(\text{CO})_{\text{CO}}$ in Figure 1 which gives CO levels which substantially exceed the measured values.

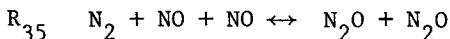
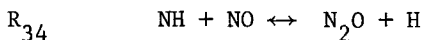
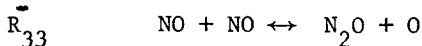
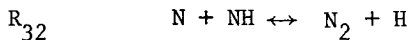
The effect of imposing both constraints simultaneously is shown by the remaining curve marked $(\text{CO})_{\text{M,CO}}$. Although this curve is slightly lower than the measured values the agreement was felt to be well within the combined uncertainty of the experimental measurements and the rate constants 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 $(\text{CO})_{\text{CO}}$ curve and the $(\text{CO})_{\text{M,CO}}$ curve is due to the effect of the total moles constraint which greatly increases the number of free radicals, especially OH, in the gas which in turn increases the rate of the most important CO oxidation reaction R_{21} .

5.2 NO concentrations in an I.C.E. A theoretical investigation 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 the results of a constrained equilibrium calculation with a corresponding steady state calculation and the results are shown in Figure 2. In the constrained equilibrium calculations 14 species and two constraints were again considered. The first constraint was that on "fixed nitrogen."

$$\text{NO}_F = \text{NO} + \text{NO}_2 + \text{NH} + \text{N} \quad (90)$$

controlled by the reactions



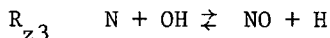
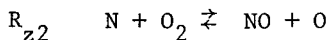
and governed by the rate equation

$$\frac{d \text{NO}_F}{dt} = 2 \sum_{i=1}^5 (R_{3i}^- - R_{3i}^+) \quad (92)$$

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 Figure 2. The freezing of nitrogen fixing reactions can clearly be seen by comparison of the $(\text{NO})_N$ and $(\text{N})_N$ with the corresponding equilibrium values shown by the short dashed curve. By way of contrast the $(\text{O})_N$ levels remain close to their equilibrium values.

The second constraint considered was that on total moles M previously discussed. As indicated by the "Note" in Figure 2 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 model of Lavoie, Heywood and Keck. The major combustion reactions were assumed to be in equilibrium and the extended Zeldovich mechanism



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

$$\frac{dN}{dt} = R_{z1}^- + R_{z2}^- + R_{z3}^- - R_{z1}^+ - R_{z2}^+ - R_{z3}^+ \quad (94)$$

$$\frac{d \text{NO}}{dt} = R_{z1}^- - R_{z2}^- - R_{z3}^- - R_{z1}^+ + R_{z2}^+ + R_{z3}^+ \quad (95)$$

and the steady state assumption $dN/dt = 0$ was made for N. As can be seen from the long dashed curves in Figure 2, the steady state NO concentration $(\text{NO})_{SS}$ was lower than the constrained equilibrium concentration $(\text{NO})_N$ early in the cycle when it was being formed and lower later 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 N species N and NO. Which of the two calculations gives the better approximation is difficult to say without additional information. The list of species and reactions included in the steady state calculation is of course highly truncated and parallel reactions would tend to drive the fixed nitrogen system closer to a constrained equilibrium situation. In any case, as can be seen in Figure 3 which shows average NO concentration in the exhaust of an I.C.E. as a function of fuel/air ratio, either calculation predicts the experimental results within the expected accuracy. The steady state predictions shown by the dashed curve are based on unpublished work by Keck and Gillespie. The constrained equilibrium predictions shown by the solid curve were obtained by Delichatsios and Keck (14). The experimental points are from Heywood, Mathews and Owen (15).

5.3 Degree of Disequilibrium in I.C.E. Combustion Products

Considerable insight into the validity of the constrained equilibrium approximation 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 (16). The species included were the first twelve in the list above plus N, the twenty second.

Of particular interest is the degree of disequilibrium calculated for 14 reactions during the expansion stroke and shown in Figure 4. It can be seen that the 5 exchange reactions involving the C-H-O system and the dissociation reaction $M+N_2O \rightarrow N_2 + O+M$ involving the most abundant species N_2 were in equilibrium throughout. The 5 remaining dissociation reactions and the 3 exchange reactions involving NO all exhibit highly non-equilibrium behavior, however. At first sight it is not obvious that the behavior of most of the non-equilibrium reaction 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 necessary to do this are given in the figure for the various reactions. If desired, a perfect fit can be obtained with 2 additional constraints on N and H.

- These results indicate that the previously discussed constrained equilibrium 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. They also cast considerable doubt on the use of the steady state approximation for N. As seen in Figure 2, this predicts N concentrations less than equilibrium during expansion whereas Figure 4 shows N concentrations greater than equilibrium. However, because of the severe truncation of the species and reaction rate lists in the

"exact" calculations even these conclusions must be regarded as tentative. In a general way one would expect parallel reactions to drive the system closer to a constrained equilibrium thus improving the accuracy of this method relative to both the "exact" and steady state methods.

6 Summary and Conclusions

The rate-controlled constrained equilibrium method of treating reactions in complex systems has been reviewed and its application to the treatment of chemically reacting gas mixtures considered in detail. For systems with a large number of degrees of freedom, the method offers a number of advantages over the conventional techniques of integrating the full set of rate equations necessary to determine its state: 1) Since in general the number of constraints necessary to specify 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. This greatly simplifies numerical calculations. 2) Only the rate constants for the fastest rate-controlling 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 greater than or equal to zero at all times and the system approaches a unique stable equilibrium point. This is not necessarily true for calculations in which the steady state approximations have been used. 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 constraints equals the number of degrees of freedom. 6) The method can easily be generalized to include constraints imposed by slow energy exchange reactions, selection rules, body forces and diffusion. 7) As indicated by the work of Kerner (9) on ecological cycles, the method can be applied to extremely complex systems.

The only obvious disadvantage of the method is that the constraints must be identified. Even this can be an advantage, however, because it forces one to *think* about the problem before embarking on elaborate calculations !

Acknowledgement The author would like to acknowledge his indebtedness to the late Professor Joseph H. Keenan for valuable insight into the structure of classical thermodynamics gained over a period of years from his published works and in conversations with him. He is also indebted to Drs. John P. Appleton,

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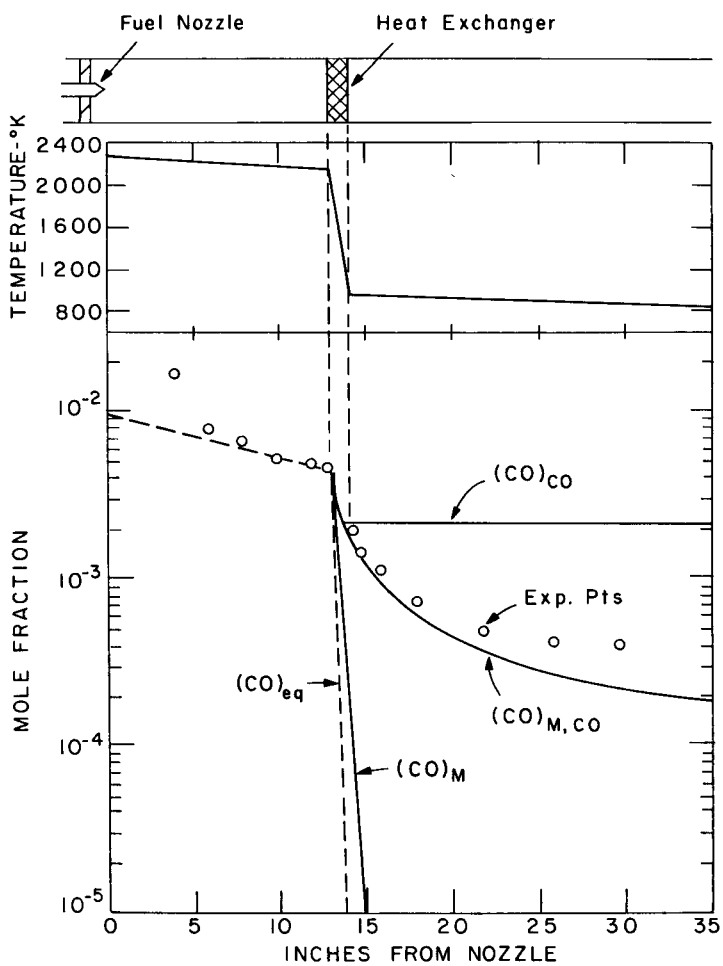


Figure 1. Temperature and CO profiles in a steady flow cylindrical burner.

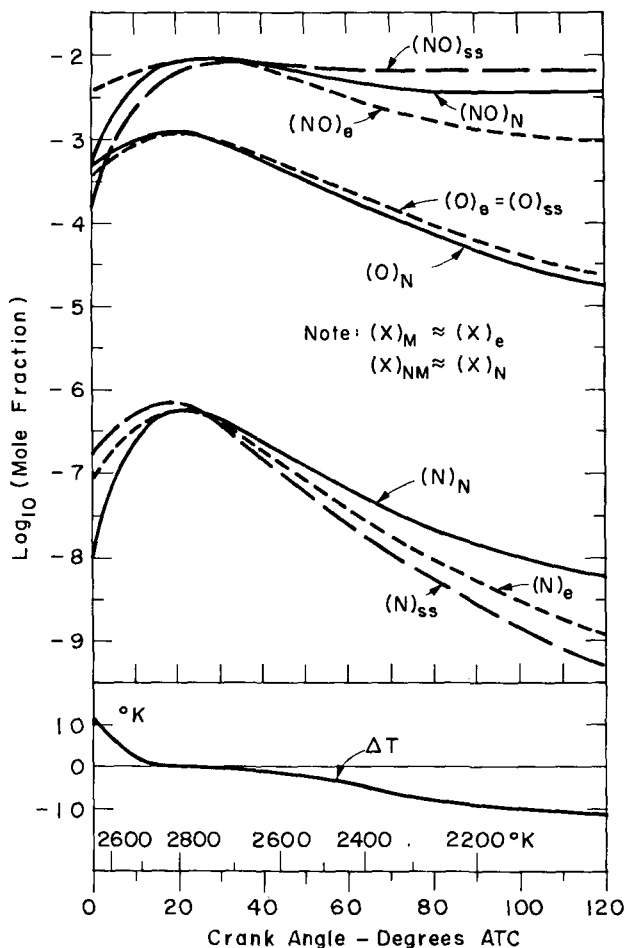


Figure 2. Comparison of equilibrium, steady state and constrained equilibrium NO, N and O mole fractions during the power stroke of an I.C.E.

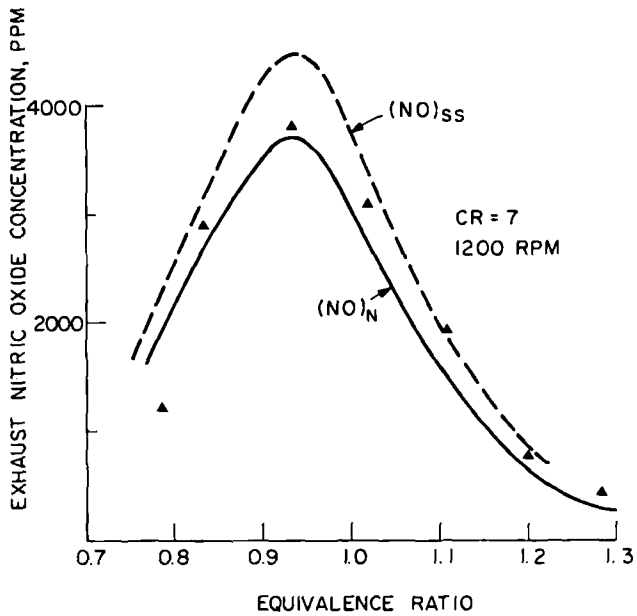
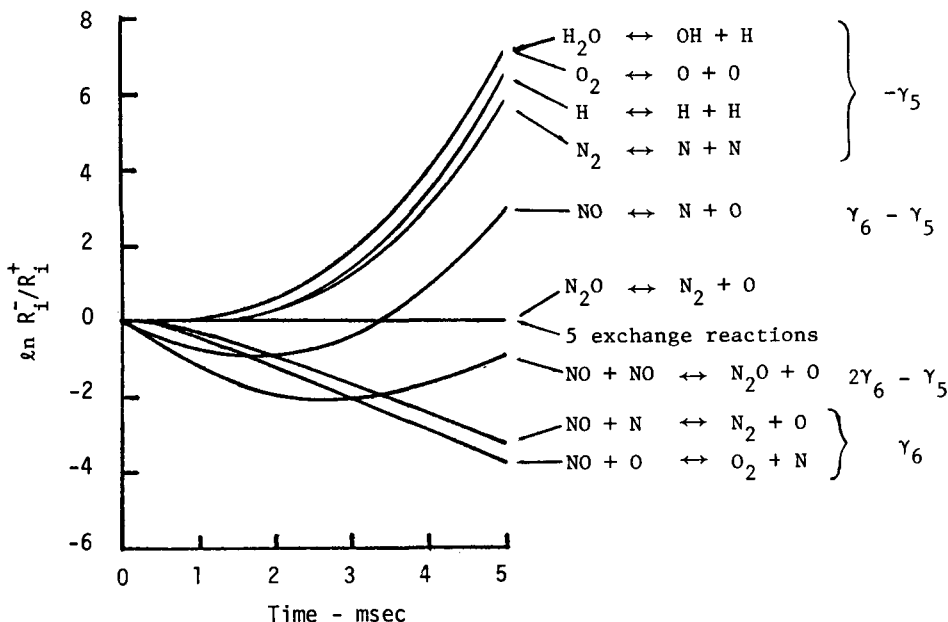
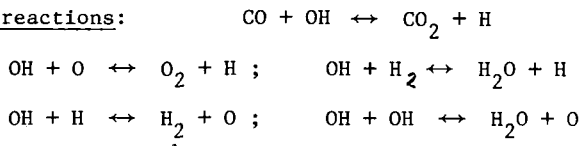


Figure 3. Comparison of predicted and measured average NO concentration in the exhaust of an I.C.E. as a function of fuel/air equivalence ratio.



5 exchange reactions:



Time dependent constraints:

M ; NO

Lagrange multipliers

γ_5 ; γ_6

Figure 4. 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.