RATE-CONTROLLED CONSTRAINED EQUILIBRIUM CALCULATION OF 
IGNITION DELAY TIMES IN HYDROGEN-OXYGEN MIXTURES

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The Rate-Controlled Constrained-Equilibrium (RCCE) method has been used to describe 
the evolution of the hydrogen-oxygen system. Stoichiometric mixtures of hydrogen and ox-
ygen having initial temperatures in the range 900 K to 1500 K and pressures in the range 
0.1 atm to 10 atm were studied. The state of the system was determined by imposing con-
straints on the total moles of gas, the moles of free valence and the moles of active valence. 
The rate equations for these constraints were integrated for various one and two constraint 
combinations to obtain temperature—time profiles at constant volume and energy. Reason-
able agreement with results obtained by integrating a full set of nine rate equations was 
obtained over a range of ignition delay times spanning five orders of magnitude using just 
two constraints corresponding to total moles and moles of active valence.

Introduction

The development of theoretical models for de-
scribing the time evolution of complex reacting sys-
tems is a fundamental objective of non-equilibrium 
thermodynamics. It is also of great importance for 
a variety of practical problems related to combus-
tion, hypersonic aerodynamics, chemical process-
ring, biology, and economics.

For systems involving a large number of degrees 
of freedom, it is a formidable task to integrate the 
large sets of equations required to describe their 
evolution. To treat such complex reacting systems, 
Keck and Gillespie\(^1\) proposed the rate-controlled 
partial-equilibrium method later renamed rate-con-
trolled constrained-equilibrium (RCCE) by Galant 
and Appleton\(^2\) to distinguish it from the partial-
equilibrium assumption originally proposed by 
Bulewicz, James and Sugden\(^3\) and subsequently used 
by a number of other workers\(^4-8\) to treat the re-
combination region of the H\(_2\)/N\(_2\)/O\(_2\) flames.

The RCCE method combines the use of rate 
equations for both internal and external constraints 
with the techniques of thermodynamics for deter-
mining the constrained-equilibrium state. It is based 
on the assumption that slow reactions impose pas-
sive constraints which retard the relaxation of a 
complex system to complete equilibrium while fast 
reactions equilibrate the system subject to the con-
straints imposed by the slow reactions. As a con-
sequence the system relaxes to complete equilib-
rium through a sequence of constrained-equilibrium 
states at a rate controlled by the slowly changing 
constraints. A detailed discussion of the method and 
a review of prior applications to reactions in com-
bustion products has been given by Keck.\(^9\) Appli-
cations to combustion reactions have been reported 
by Takeda, Koshi and Matsui.\(^10\)

There has been a wide spread tendency to iden-
tify the RCCE method with the well known quasi-
steady-state approximation also used to reduce the 
number of differential equations required to de-
scribe the evolution of complex systems. However, 
the two methods are quite different both from a 
fundamental and an applied point of view. The 
steady state approximation is based on the assump-
tion that at some times 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 cor-
responding rate equations to be replaced by alge-
braic equations obtained by equating the produc-
tion and removal rates. The total number of 
differential plus algebraic equations remains the same
and the solution 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 Second Law of thermodynamics and it is assumed that the system evolves through a sequence of constrained-equilibrium states obtained by maximizing the 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 plus algebraic equations required to describe the evolution of the system is reduced to the total number of constraints used and the solution depends only on the rate constants for those reactions which change the value of a constraint. It can also be shown that the entropy production for a system evolving through a sequence of constrained-equilibrium states is non negative. No corresponding proof for a system to which the quasi-steady state approximation has been applied is known to the authors and in fact it appears that for such systems the entropy production may become negative during the approach to equilibrium in violation of the Second Law.

The purpose of this investigation was to explore the application of the method to combustion processes. The oxidation of hydrogen at constant volume was chosen for initial studies because its kinetics are simple and well documented. Calculations of temperature, pressure and species concentrations were first made using a full set of eight rate equations for the eight species H, HO, HO2, H2, H2O, H2O2, O, and O2. Identical calculations were then made using the RCCE method. Both the low and high pressure regions were included in the investigation. Comparison of the results showed that reasonable agreement for ignition delay times could be achieved over a range of several orders of magnitude using only two rate equations for constraints on (1) total moles of gas and (2) active valence. Considering the relatively small number of species involved, this is a significant reduction in the number of rate equations needed to describe the system. In addition the results give considerable insight into the important mechanisms controlling hydrogen oxidation and the optimum method of choosing the constraints.

Rate-Controlled Constrained Equilibrium Method

The constraints imposed on the closed reacting system as a result of slow reactions are assumed to be of the form:

\[ C_i = \sum_j a_{ij} X_j, \quad i = 1, 2, \ldots n + r \]  

where the coefficients \( a_{ij} \) are determined by the nature of the constraint, \( X_j \) is the number of moles of species \( j \) in the system, \( m \) is the number of different species, \( n \) is the number of elements in the system, and \( r \) is the number of constraints in addition to those associated with the elements. For given values of the constraints \( C_i \), the constrained equilibrium composition of system may be obtained either by the method of equilibrium constants or by minimizing the Gibbs free energy of the system.

The rate equation which determines the changes in the constraints may be obtained by differentiating Eq. (1). This gives

\[ \dot{C}_i = \sum_j a_{ij} \dot{X}_j, \quad i = 1, 2, \ldots n + r \]  

from which \( \dot{X}_j \) may be eliminated using the rate equations for the species

\[ \dot{X}_j = V \sum_k \left( v_{jk} - v_{jk}^* \right) \left( \omega_k^* - \omega_k \right), \quad j = 1, 2, \ldots m \]  

where \( V \) is the volume of the system, \( v_{jk} \) and \( v_{jk}^* \) are the corresponding stoichiometric coefficients for the species, and \( \omega_k^* \) and \( \omega_k \) are the forward and reverse rate of reaction \( \omega_k \). This gives

\[ \dot{C}_i = \sum_k b_{ik} \left( \omega_k^* - \omega_k \right), \quad i = 1, 2, \ldots n + r \]  

where

\[ b_{ik} = \sum_j a_{ij} \left( \omega_{jk} - \omega_{jk}^* \right), \quad i = 1, 2, \ldots n + r \]  

is the change of constraint \( i \) in reaction \( k \).

For a closed system with no nuclear or ionization reactions, the elements are conserved in all reactions and Eq. (5) gives

\[ b_{ik} = 0, \quad i = 1, 2, \ldots n \]  

Using Eq. (6), the first \( n \) equation of the set Eq. (4) can be integrated to give

\[ C_i(t) = C_i(0), \quad i = 1, 2, \ldots n \]  

The remaining equations can be integrated numerically in stepwise fashion using a standard integration routine such as LSODE \(^{12}\) and any available algorithm such as CNSEQL \(^{12}\) or STANJAN \(^{13}\) for determining the constrained equilibrium composition. This is the method used in the present and prior work. An alternative procedure which is currently being implemented is to use a differential-algebraic equation solver such as DASSL \(^{14}\) to integrate the combined set of differential rate-equations for the constraints and algebraic equations for
the constrained-equilibrium composition. It is anticipated that this latter procedure will be very much more efficient than the former, particularly for systems of modest size.

An important question which arises in connection with the use of the RCCE method is how to choose the constraints. This question cannot be fully answered at the present time but some choices are fairly obvious. In general these are associated with known classes of slow reactions. A few examples are: 1) total moles of gas, 2) moles of free electrons, 3) moles of fixed nitrogen, 4) moles of CO, and 5) moles of free or active valence. Clearly, experience and a knowledge of the kinetics of the system are valuable but trial and error can also be used. If the addition of a new constraint to an existing set produces no significant effect on the evolution of the system it may be discarded at least temporarily. On the other hand if it does produce an effect it would seem logical to retain it.

**Application to the H-O System**

A major objective of the present work was to explore the above question and gain experience in the application of the RCCE method to combustion systems. For this purpose we have chosen the H-O system because its kinetics are well known and the corresponding set of rate equations can be easily integrated to obtain exact results with which the approximate results obtained from the RCCE method can be compared. It was not expected that the RCCE method applied to such a simple system would provide any advantages over the technique of integrating a full set of rate equations, but it was hoped that the investigation would provide information useful for extending the method to the very much more complex C-H-O system.

The comparisons were carried out for a system of constant volume and energy made up of the eight species H, HO, HO2, H2, H2O, H2O2, O and O2. The full set of 17 reactions included in the detailed model are listed in Table I along with their standard reaction enthalpies ΔH°300 and the parameters A, n and Ea for calculating their exothermic rate constants in the form

\[ k^+ = A T^n \exp(-E_a/RT) \]  

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

\[ k^+ / k^- = K_c \]

where the equilibrium constant K_c based on concentration was computed from data in the JANAF tables. This insured that the system relaxed to the correct stable equilibrium state.

**TABLE I**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH°300</th>
<th>Log A</th>
<th>n</th>
<th>E_a</th>
<th>M</th>
<th>FV</th>
<th>AV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. H + O2 + M = HO2 + M</td>
<td>-47.10</td>
<td>15.22</td>
<td>0</td>
<td>1.00</td>
<td>-1</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>2. OH + OH + M = H2O2 + M</td>
<td>-51.39</td>
<td>14.96</td>
<td>0</td>
<td>-5.07</td>
<td>-1</td>
<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>3. H + O + M = OH + M</td>
<td>-102.23</td>
<td>16.00</td>
<td>0</td>
<td>0.00</td>
<td>-1</td>
<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>4. H + H + M = H2 + M</td>
<td>-104.20</td>
<td>15.48</td>
<td>0</td>
<td>0.00</td>
<td>-1</td>
<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>5. O + O + M = O2 + M</td>
<td>-119.12</td>
<td>15.67</td>
<td>-0.28</td>
<td>0.00</td>
<td>-1</td>
<td>-4</td>
<td>-4</td>
</tr>
<tr>
<td>6. H + OH + M = H2O + M</td>
<td>-119.33</td>
<td>23.15</td>
<td>-2</td>
<td>0.00</td>
<td>-1</td>
<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>7. O + OH = H + O2</td>
<td>-16.89</td>
<td>13.12</td>
<td>0</td>
<td>0.68</td>
<td>0</td>
<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>8. HO2 + HO2 = H2O2 + O2</td>
<td>-42.53</td>
<td>13.00</td>
<td>0</td>
<td>1.00</td>
<td>0</td>
<td>-2</td>
<td>0</td>
</tr>
<tr>
<td>9. HO2 + O = OH + O2</td>
<td>-55.13</td>
<td>13.70</td>
<td>0</td>
<td>1.00</td>
<td>0</td>
<td>-2</td>
<td>-1</td>
</tr>
<tr>
<td>10. HO2 + H = H2 + O2</td>
<td>-57.10</td>
<td>13.40</td>
<td>0</td>
<td>0.70</td>
<td>0</td>
<td>-2</td>
<td>-1</td>
</tr>
<tr>
<td>11. HO2 + OH = H2O + O2</td>
<td>-72.23</td>
<td>13.70</td>
<td>0</td>
<td>1.00</td>
<td>0</td>
<td>-2</td>
<td>-1</td>
</tr>
<tr>
<td>12. H + OH = O + H2</td>
<td>-1.97</td>
<td>9.92</td>
<td>1</td>
<td>6.95</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>13. H2O2 + H = HO2 + H2</td>
<td>-14.57</td>
<td>12.23</td>
<td>0</td>
<td>3.75</td>
<td>0</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>14. H2 + OH = H + H2O</td>
<td>-15.13</td>
<td>13.34</td>
<td>0</td>
<td>5.15</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15. OH + OH = O + H2O</td>
<td>-17.10</td>
<td>12.50</td>
<td>0</td>
<td>1.10</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>16. H2O2 + OH = HO2 + H2O</td>
<td>-29.70</td>
<td>13.00</td>
<td>0</td>
<td>1.80</td>
<td>0</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>17. HO2 + H = OH + OH</td>
<td>-38.24</td>
<td>14.40</td>
<td>0</td>
<td>1.90</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>
**Detailed Kinetic Model:**

The detailed calculations were carried out for stoichiometric mixtures of 2 moles H₂ and 1 mole of O₂ at initial temperatures Tᵢ = 900, 1100 and 1500 K and initial pressure pᵢ in the range 0.01 to 1000 atm. The eight rate-equations for the listed species were integrated in conjunction with the equation for the temperature using the LSODE routine. 

Typical results for low and high pressure regimes are presented in Figs. 1 and 2 which show the temperature and species mole fractions as a function of time. It can be seen that there is an initial delay interval τ during which the product mole fractions rise from zero to values of order 10⁻² but the temperature rise is negligible. This is followed by a relatively short interval during which the temperature and species concentrations adjust to their final equilibrium values. It can also be seen that in the low pressure case, the dominant radical in the ignition delay interval is H while in the high pressure case it is HO₂. All the above results are in good agreement with prior work. 

**RCCE Calculations:**

RCCE calculations were carried out for Tᵢ = 900, 1100 and 1500 K and pᵢ = 0.1, 1.0 and 10 atm. The constraints used were the total moles:

\[ M = H + HO + HO₂ + H₂ + H₂O + H₂O₂ + O + O₂ \]  

the free valence:

\[ FV = H + HO + HO₂ + 20 \]  

and the active valence

\[ AV = H + HO + 20 \]

The coefficients bₖₗ appearing in the rate Eqs. 4 for these constraints are given in the last three columns of Table I. One and two constraint cases were investigated. The rate equations were integrated using LSODE and the same rate constants employed for the detailed calculations. No energy
equation is required for these calculations because the temperature is calculated by the CNSEQL 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 present algorithm 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. 3 which shows the temperature-time curves for both low and high pressure regimes. The curve labeled M refers to the total moles constraint. The free valence FV and active valence AV curves are identical to the accuracy with which they can be plotted. The curve labeled 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 states are incorrect.

**Fig. 3.** Temperature-time curves for one constraint calculations for the same condition as Figs. 1 and 2. M = total moles, FV = moles free valence, AV = moles active valence, and FS = full set of rate equations.

**Fig. 4.** Temperature-time curves for the two constraint combinations M + FV and M + AV and the same conditions as Fig. 4.

**Fig. 5.** Comparison of temperature vs binary-scaled time curves for M + AV and FS calculations at $T_i = 1500$ K and $p_i = 0.01, 0.1, 1.0$ and 10 atm.
The requirement that the initial state be correctly reproduced is an important condition which may be used in the selection of the constraint. This requirement is satisfied by the two constraint calculations examples of which are shown in Fig. 4. 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 $M + FV$ combination 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 I 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 Figs. 5–9. Fig. 5 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. 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 I.

Figs. 6–8 show temperature time plots for initial temperatures of 1500, 1100 and 900 K and initial pressures of 0.1, 1.0 and 10 atm. Again the overall agreement between the M + AV results and the FS results is reasonably good. The major discrepancy in all cases is a slight shift in the ignition delay time. A premature temperature rise is also evident in the low temperature high pressure M + AV curves. Both these discrepancies confirm the observation made in connection with Fig. 5 that one or more additional constraints are needed in the ignition delay interval.

A summary of the results is shown in Fig. 9 where the product of the ignition delay times \( \tau \) and the
Discussion and Conclusions

Considering the range of condition spanned and the simplicity of the H-O kinetics, the overall agreement between the temperature profiles and ignition delay times obtained from the two constraint RCCE calculations and the detailed nine equation calculations is remarkably good. Although the results clearly indicate that two constraints are insufficient to give a very precise representation of the temperature time histories it may be noted that the discrepancies are comparable to those associated with present uncertainties in the rate constants for this system. Thus from a practical point of view a two constraint calculation might well be adequate for many purposes if it were more efficient. As previously pointed out the algorithm used in the present investigation is not efficient but it is anticipated that this situation can be improved through the use of improved equilibriums routines such as STANJAN and differential algebraic-equation solvers such as DASSL. It may be noted in this regard that if the evolution equations for a constrained-equilibrium system are written in terms of the generalized potentials (Lagrange multipliers) conjugate to the constraints the total number of algebraic plus differential equations required is just equal to the total number of fixed plus time independent constraints employed.

With respect to potential applications to the more complex systems such as the C-H-O system for which the RCCE method was developed, the results are very encouraging. For such systems the ratio of the number of possible species to the number of constraints necessary to provide an acceptable description of their evolution is expected to increase very rapidly with the size of the system. Moreover the number of parallel reactions tending to drive the system toward a constrained-equilibrium state is also expected to increase rapidly with the size of the system. This should improve the accuracy of the constrained-equilibrium assumption and it is not unreasonable to anticipate that systems involving upwards of hundreds of species could be adequately described with less than ten appropriately chosen constraints.

Further investigation are clearly needed to determine the best methods for the apriori selection of constraint but the results of the present investigation are very encouraging in this regard also.

Acknowledgment

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REFERENCE

C. Morley, Shell Research Ltd., England. Could you say how this method relates to that described earlier at this Symposium by Law and Goussis? Is there any rational basis for choosing the constraints or is it necessary to rely on chemical intuition?

Author's Reply. The "reactant groups" in the CSP algorithm of Law and Goussis are equivalent to a full set of linearly independent constraints in the RCCE theory. However, the methods used to reduce the order of the corresponding system of rate equations represent opposite extremes. In CSP attention is focused on the groups (constraints) having the shortest characteristic times at each time step and only the equations for these groups are integrated. The characteristic times for the remaining groups are assumed to be infinite. In RCCE attention is focussed on the constraints (groups) having the longest characteristic times and only the equations for these constraints are integrated. The composition of the system is determined at each time step by assuming its entropy to be a maximum subject to the current values of the constraints. It may be noted that since the reduction of the system in CSP involves a mathematical approximation, it can not be proved in general that the entropy production will be non-negative at all times.

The advantage of CSP is that the procedure for selecting the appropriate groups (constraints) is an objective one. The disadvantage is that the complete set of reaction rates must be known and monitored at all times. For complex systems this requires a large number of rate constants, the vast majority of which are uncertain or unknown.

The advantage of RCCE is that only the reactions which changed an assumed constraint (group) are required and these are just the reactions for which the rate constants are most likely to be known and reasonably reliable. The disadvantage of RCCE is, of course, that the appropriate constraints (groups) must be identified by the user.

Which of the two methods will prove to be most efficient and provide the greatest insight remains to be determined. It is possible that they could be combined to advantage.

In response to your second question, "Chemical intuition" as well as experience are both very valuable in the selection of constraints. However, there are also a number of objective criteria which may be applied: 1) The constraints must be linearly independent; 2) They should correspond to classes of slow reactions, e.g., nuclear, ionization and dissociation reactions; 3) A change in the value of a constraint should be a necessary condition for the progress of the overall reaction, e.g., for the reaction $2H_2 + O_2 \rightarrow \text{Products}$, the number of molecules must change, active radicals must be produced and H-H bonds must be broken. 4) The initial composition of the constrained equilibrium state should approximate the actual initial composition. For the reaction just cited this can be achieved exactly by using the total number of molecules and the free valence as constraints. 5) If the addition of a constraint to an existing set produces no significant effect it may be discarded. Note that the solution becomes exact when the number of linearly independent constraints equals the number of species included in the system. Thus, convergence is assured.

These are the criteria we have used to date. It is anticipated, however, that other objective criteria will be found as experience is gained in using the method.