

# Constrained-equilibrium calculations for chemical systems subject to generalized linear constraints using the NASA and STANJAN equilibrium programs

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**Abstract.** Fast efficient numerical programs for determining the equilibrium composition of large chemical systems subject to generalized linear constraints are needed for chemical kinetic calculations involving both the conventional local thermodynamic equilibrium (LTE) and the more general rate-controlled constrained-equilibrium RCCE assumptions. For this purpose two callable subroutines based on the well known NASA and STANJAN equilibrium codes have been developed by a simple modification of their input files. To evaluate the performance of these subroutines, test calculations have been made for the hydrogen–oxygen (H–O) and carbon–hydrogen–oxygen–nitrogen (C–H–O–N) systems with various combinations of constraints on the elements, the total moles and the free valence (number of unpaired electrons) in the system. The allowed domain of the constraints was determined and both interior and boundary points were investigated for several temperature and pressure conditions. The results showed that STANJAN was superior to NASA both in convergence and speed under all conditions investigated.

## 1. Introduction

Fast efficient numerical programs are needed both for static calculations of the equilibrium composition of large chemical systems and for dynamic calculations involving the assumption of local thermodynamic equilibrium (LTE) [1, 2]. At the present time, the most readily available and widely used programs of this type are the NASA [3] and STANJAN [4] equilibrium programs. Both these programs use the method of Lagrange multipliers to determine the chemical equilibrium state of a system by minimizing the appropriate free energy, subject to the constraints on the elements imposed by the infinitesimal rate of nuclear reactions at ordinary temperatures. They have the important advantage over the method of equilibrium constants that they do not require a reaction model and they can easily be modified to accept additional linear constraints imposed by relatively slow chemical reactions. Two examples of constraints imposed by chemical reactions in gas-phase systems are the total moles of mixture which is controlled by slow three-body association and dissociation reactions and the free valence (number of unpaired electrons) which is controlled by slow branching and termination reactions. Such additional constraints are required for dynamic calculations using the partial-equilibrium (PE) [5–8] or the more general rate-controlled constrained-equilibrium (RCCE) [9, 10] methods.

In initial attempts to use the generalized NASA and STANJAN codes in RCCE calculations many 'singular matrix' and 'divide by zero' error messages were received and it became clear that these two codes differed considerably in their ability to converge, especially when constraints in addition to the elements were imposed. They also differed considerably in their computational speed. To investigate these problems in more detail, test equilibrium calculations using both programs have been made and compared for various combinations of the elemental constraints: carbon, hydrogen and oxygen and the added constraints: total moles and free valence. These two additional constraints were chosen because they are basic and are expected to be important in virtually all chemical kinetic calculations.

Although we recognize that the NASA and STANJAN programs were not originally designed for use with constraints other than the elements, this is a completely unnecessary restriction on the very general and powerful methods they employ. It is our hope that the discussion and results presented in this paper will provide motivation and guidance for the development of faster, more robust codes of this type for use not only in RCCE calculations but for conventional equilibrium calculations as well.

## 2. Generalized equilibrium programs

### 2.1. Method of Lagrange multipliers

As noted previously, both the NASA and STANJAN programs use the method of Lagrange multipliers to determine the equilibrium composition of a chemical system by minimizing its Gibbs energy function subject to elemental constraints of the form

$$C_i = \sum_{j=1}^{n_s} a_{ij} N_j(t) \quad i = 1, \dots, n_e$$

where  $N_j(t)$  is the number of moles of the  $j$ th element in the system,  $a_{ij}$  is the number of atoms of the  $i$ th element in the  $j$ th species,  $n_s$  is the number of different species and  $n_e$  is the number of different elements in the system. To generalize these programs, it is simply necessary to modify their input routines to accept additional user-specified rate-controlled constraints of the same form as (1)

$$C_i = \sum_{j=1}^{n_s} a_{ij} N_j(t) \quad i = 1, \dots, n_e, n_e + 1, \dots, n_c \quad (1)$$

where  $n_c$  is the total number of constraints imposed, elemental plus rate-controlled. For convenience, the generalized versions of the NASA and STANJAN codes will be referred to as GNASA and GSTANJAN in the remainder of this paper.

In the following brief summary of the equations used in these calculations, we shall limit our considerations to gas-phase systems which obey the ideal gas equation of state

$$pV = MRT \quad (2)$$

where  $p$  is the pressure,  $V$  is the volume,  $T$  is the temperature,  $M$  is the mole number and  $R$  is the universal gas constant. For such a system, the dimensionless Gibbs energy function,  $\tilde{\mu} = \mu/RT$ , is given by

$$\tilde{\mu} = \sum_{j=1}^{n_s} \tilde{\mu}_j N_j \quad (3)$$

where

$$\tilde{\mu}_j(T, p_j) = \tilde{\mu}_j^0(T) + \ln p_j \quad j = 1, \dots, n_s \quad (4)$$

is the dimensionless Gibbs energy function for the species  $j$ ,  $\tilde{\mu}_j^0$  is the dimensionless standard Gibbs energy function for the species  $j$  and  $p_j$  is the partial pressure of  $j$ th species in atmospheres. Minimizing the Gibbs energy function (3) subject to constraints (1) using the method of Lagrange multipliers leads to the result

$$N_j = \frac{M}{P} \exp\left(-\tilde{\mu}_j^0 + \sum_{i=1}^{n_c} a_{ij} \lambda_i\right) \quad j = 1, \dots, n_s \quad (5)$$

where  $\lambda_i$  is the dimensionless ‘constraint potential’ (Lagrange multiplier) conjugate to the constraint  $C_i$ . Equation (5) can, in turn, be substituted back into the constraint equations (1) to obtain a set of  $n_c$  transcendental equations which can be solved in conjunction with the equation of state (2) for the  $n_c$  constraint potentials and the mole number  $M$ . For systems which include a large number of species,  $n_c$  is much smaller than  $n_s$  and solving for the  $n_c$  constraint potentials is much easier than solving for the  $n_s$  species concentrations using the method of equilibrium constants. The primary differences between GNASA and GSTANJAN is in the techniques used to solve these equations and the manner in which the calculations are initialized.

## 2.2. Generalized constraints

The generalized constraints on a chemical system can be divided into three classes: (i) modelling constraints imposed to define the system and simplify the calculations; (ii) structural constraints imposed by the nature of the bonds between atoms and (iii) rate-controlled constraints imposed by the relative speed of the reactions occurring in the system.

The model used in the present work was an ideal-gas phase mixture of atoms and molecules containing the elements C, H, O and N. This choice has the advantage that the elements are related uniquely to their valences. We further specified that there were no ions or electrons in the system and placed an upper bound,  $a_m$ , on the number of atoms present in any molecule. The structural constraints considered were those imposed by the requirement that all bonds between atoms be valence bonds. Finally, the rate-controlled constraints used were the total mole number,  $M$ , and the free valence of the radicals,  $FV$ . As discussed in the introduction, constraints on  $M$  and  $FV$  are expected to be important in most chemically reacting systems.

Under the above conditions, the number of atoms in the system and the total valence are given by

$$A = EH + EO + EN + EC \quad (6)$$

and

$$TV = EH + 2EO + 3EN + 4EC \quad (7)$$

where  $EH$ ,  $EO$ ,  $EN$  and  $EC$  denote the number of atoms of the elements H, O, N and C in the system. The number of bonds and valence bonds are defined by

$$B = B_1 + B_2 + B_3 + B_4 \quad (8)$$

and

$$VB = B_1 + 2B_2 + 3B_3 + 4B_4 \quad (9)$$

where  $B_k$  is the number of bonds of order  $k$  in the system. The free valence of the radicals is defined by

$$FV = TV - 2VB \quad (10)$$

and equals the number of unpaired electrons in the system available for bond formation. The number of bonds is given by

$$B = A - M + B_c \quad (11)$$

where  $M$  is the mole number (free atoms plus molecules) and  $B_c$  is the number of cyclic bonds in the system.

Absolute bounds for  $FV$  and  $M$  are given by

$$0 \leq FV \leq TV \quad (12)$$

and

$$A/a_m \leq M \leq A \quad (13)$$

where  $a_m$  is the upper bound imposed on the number of atoms in a molecule. For fixed  $M$ , a conditional upper bound on  $FV$  is imposed by the inequality

$$0 \leq VB - B. \quad (14)$$

Substituting (8)–(11) into (14) we find

$$2(B_c + B_2 + 2B_3 + 3B_4) \leq TV - FV - 2(A - M) \quad (15)$$

and setting the left-hand side of (15) equal to zero and using (6) and (7) gives

$$FV \leq 2M + 2EC + EN - EH. \quad (16)$$

Also for fixed  $M$ , conditional lower bounds on  $FV$  obtained from equations (6)–(10) are

$$FV \geq 2M - A \quad (17)$$

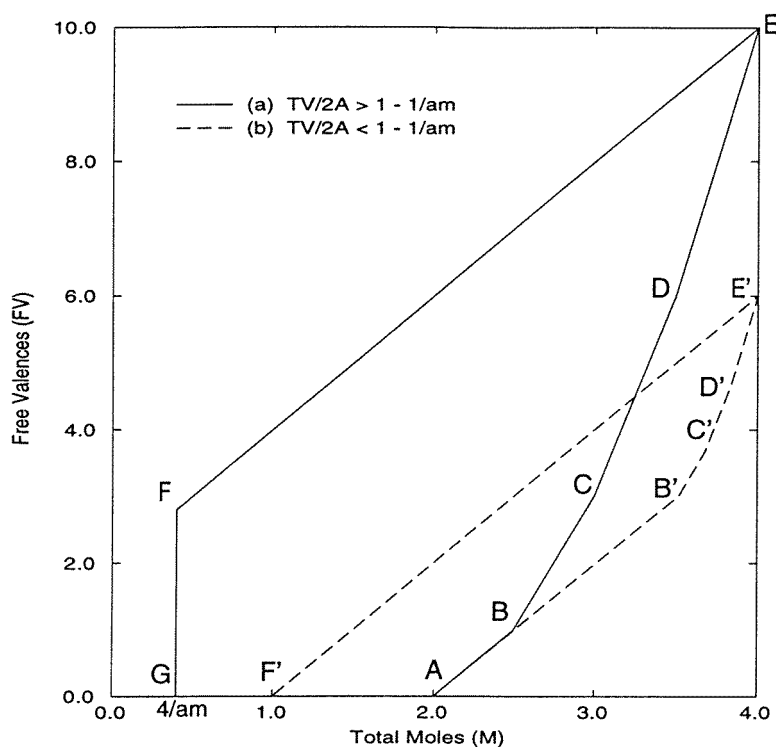
$$FV \geq 4M - 2A - EH \quad (18)$$

$$FV \geq 6M - 3A - EO - 2EH \quad (19)$$

$$FV \geq 8M - 4A - EN - 2EO - 3EH. \quad (20)$$

For fixed elemental composition, the inequalities above define a convex polyhedron in the  $M$ – $FV$  plane. All allowed states of the system fall on or inside its boundaries. The ‘chemical equilibrium’ states are the interior points at which for fixed energy and volume, the entropy is maximum and for fixed temperature and volume or temperature and pressure, the Helmholtz or Gibbs energy functions are minimum. The topology of this polygon is shown in figure 1 for the two cases: (a)  $TV/2A > 1 - 1/a_m$  and  $TV/2A < 1 - 1/a_m$ . In (a), the polygon has six sides and in (b), it has seven sides. Along the boundaries  $ABCDE$  and  $AB'C'D'E'$  the composition of the system is fully determined by the constraints (19)–(22) and is given by

$$\begin{aligned} 0 \leq H = 2M - A \leq EH & \quad H_2 = (EH - H)/2 \\ O = 0 & \quad O_2 = EO/2 \\ N = 0 & \quad N_2 = EN/2 \\ C = 0 & \quad C_2 = EC/2 \end{aligned} \quad (21)$$



**Figure 1.** Allowed domain of the variable constraints  $M$  and  $FV$  for the C-H-N-O system for  $A = 4$  and  $a_m = 10$  showing the two cases (a)  $TV/2A > 1 - 1/a_m$  and (b)  $TV/2A < 1 - 1/a_m$ .

$$\begin{array}{ll}
 H = EH & H_2 = 0 \\
 0 \leq O = 2M - A - EH \leq EO & O_2 = (EO - O)/2 \\
 N = 0 & N_2 = EN/2 \\
 C = 0 & C_2 = EC/2
 \end{array} \quad (22)$$

$$\begin{array}{ll}
 H = EH & H_2 = 0 \\
 O = EO & O_2 = 0 \\
 0 \leq N = 2M - A - EH - EO \leq EN & N_2 = (EN - N)/2 \\
 C = 0 & C_2 = EC/2
 \end{array} \quad (23)$$

$$\begin{array}{ll}
 H = EH & H_2 = 0 \\
 O = EO & O_2 = 0 \\
 N = EN & N_2 = 0 \\
 0 \leq C = 2M - A - EH - EO - EN \leq EC & C_2 = (EC - C)/2
 \end{array} \quad (24)$$

with all other species absent. On the boundaries  $EF$  and  $E'F'$ , there are no molecules containing cyclic or multiple bonds and all other species are in constrained equilibrium. Along the boundary  $FG$ , which is present in the case  $TV/2A > 1 - 1/a_m$ , only the largest species are present in constrained equilibrium and all smaller species are absent. Finally, along the boundaries  $GA$  and  $F'A$ , there are no radicals and the stable molecules are in

constrained equilibrium. Metastable mixtures of reactants leading to chemical reactions exist primarily along this boundary.

On the boundaries of the polygon defining the domain of allowed states in  $M$ - $FV$  space, there is always at least one dependent constraint and one species the concentration of which is identically zero and the chemical potential of which is therefore infinite. Any equilibrium code which does not recognize this explicitly may encounter singularities and have difficulties in converging. As will be seen in the next section, the initialization procedure employed by GSTANJAN is superior in this regard than that employed by GNASA.

### 3. Results of test calculations

To test the performances of NASA and STANJAN, a series of constrained-equilibrium calculations were made at several temperatures and pressures for C-H-O systems using various combinations of the constraints  $EC$ ,  $EH$ ,  $EO$ ,  $M$  and  $FV$  ( $EN$  was omitted for simplicity).

#### 3.1. Stoichiometric H-O System

For the H-O system, a limit of  $a_m = 4$  was placed on the maximum number of atoms in any molecules and ozone was omitted since it contains ionic bonds. Under these conditions, only eight species are allowed. The constraints considered are defined by

$$\text{elemental hydrogen: } EH = 2H_2 + 2H_2O + 2H_2O_2 + H + HO + HO_2 \quad (25)$$

$$\text{elemental oxygen: } EO = 2O_2 + H_2O + 2H_2O_2 + O + HO + 2HO_2 \quad (26)$$

$$\text{total moles: } M = H_2 + O_2 + H_2O + H_2O_2 + H + O + HO + HO_2 \quad (27)$$

$$\text{free valence: } FV = H + 2O + HO + HO_2 \quad (28)$$

and the transpose of the corresponding  $a_{ij}$  matrix is shown in table 1.

As discussed previously, the input routines for the NASA and STANJAN codes only allow the elemental constraints given in the first two columns of the transposed  $a_{ij}$  matrix, whereas GNASA and GSTANJAN allow all the columns. The elemental constraints are assumed to be fixed, but the additional constraints  $M$  and  $FV$  can vary over a domain which, as discussed above, is uniquely determined by the elemental constraints.

**Table 1.** Transpose of the coefficient matrix  $a_{ij}$  for the constraints considered.

Species	Constraints			
	$EH$	$EO$	$M$	$FV$
$O_2$	0	2	1	0
$H_2$	2	0	1	0
$H_2O$	2	1	1	0
$H_2O_2$	2	2	1	0
$O$	0	1	1	2
$H$	1	0	1	1
$OH$	1	1	1	1
$HO_2$	1	2	1	1

3.1.1. *Two (elemental) constraints: EH–EO (chemical equilibrium).* One of the aims of this work was to find the effectiveness of GNASA and GSTANJAN in an equilibrium calculation, where the number of numerically significant species is less than the number of constraints. This can occur in the water vapour system under conditions close to the saturation line where  $\text{H}_2\text{O}$  is the only major species. The calculations were carried out for  $EH = 2EO = 4$  mole. The pressure and temperature conditions investigated are plotted in figure 2 and the results are summarized in tables 2 and 3. Table 2 gives the calculated values of the mole number,  $M$ , the two constraint potentials,  $EH$  and  $EO$ , and the CPU time for the calculations. Table 3 gives mole fractions of the eight species calculated from the constraint potentials given in table 2. A dash indicates a failure of the program to converge.

As expected for the given state conditions,  $\text{H}_2\text{O}$  was the only major species in all the cases investigated. GSTANJAN converged at all points but GNASA failed to converge at the boiling point  $BP$  and at temperatures below 540 K where the mole fraction of the most abundant minor species at 1.0 atm was less than  $1\text{E}-14$ . In all cases where both programs converged, the results were in good agreement. However, the CPU times for GNASA were four times as long as those for GSTANJAN.

3.1.2. *Three constraints: EH–EO–M.* Three-constraint calculations were carried out for  $EH = 2EO = 2$  mole at a temperature of 1500 K and a pressure of 1.0 atm. The allowed range of  $M$  given by (13) and (16) is  $2 \leq M \leq 6$ . The results are given in tables 4 and 5.

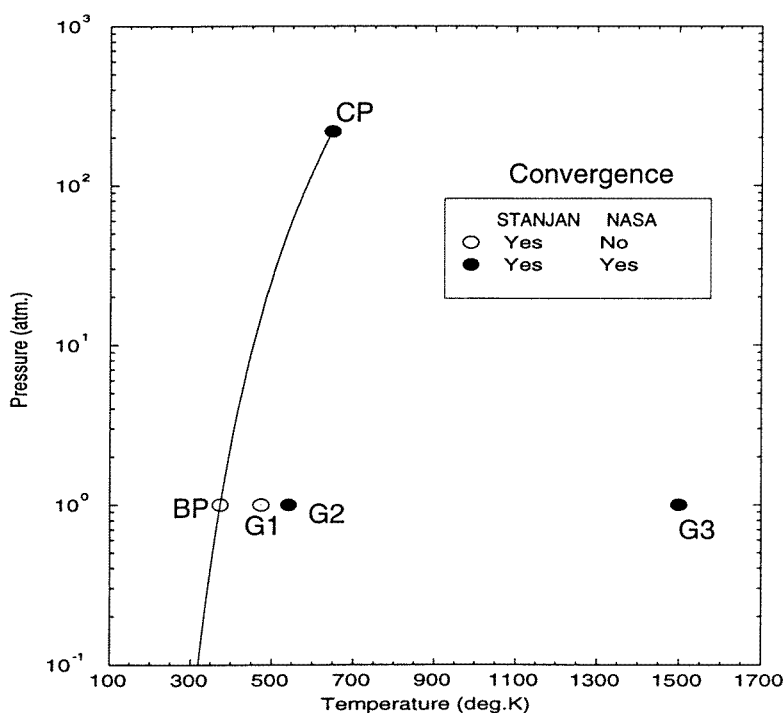
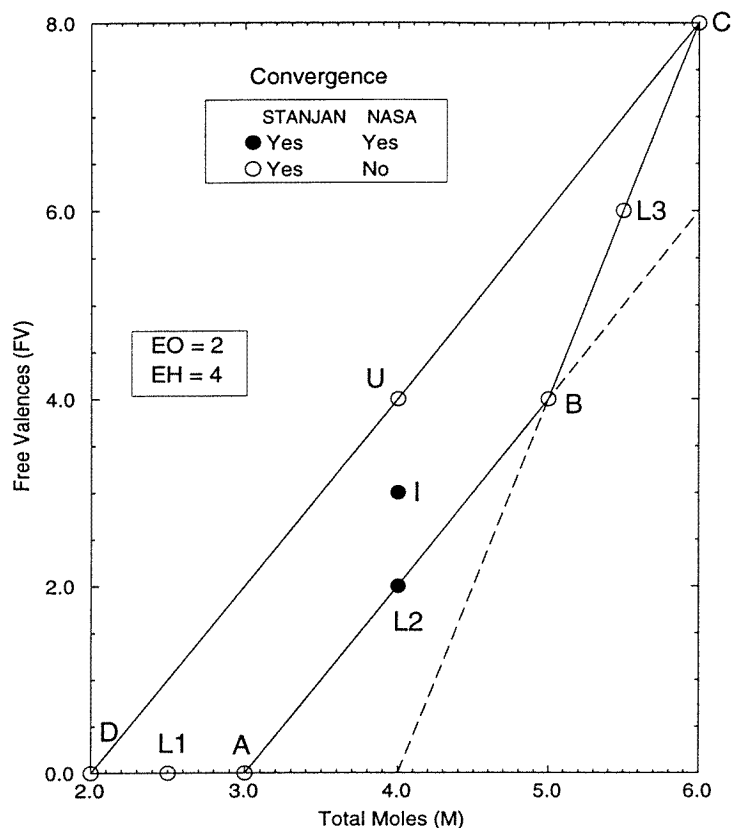


Figure 2. Test points for the H–O system in the pressure–temperature plane for two-constraint equilibrium (element potential) calculations using NASA and STANJAN programs with  $EH = 4$  and  $EO = 2$ .



**Figure 3.** Allowed domain of the variable constraints  $M$  and  $FV$  for the H-O system with four constraints  $EH-EO-M-FV$  for  $EH/EO = 2$ .

**Table 2.** Chemical equilibrium composition of the H-O system for  $EH = 4, EO = 2$ . Constraint potentials and CPU times.

Code	Figure 2	Temperature, pressure	$M$ (mole)	Potential		CPU time (s)
				$EH$	$EO$	
STANJAN	BP	$T = 373.15$ K	2.000 0000	-31.9700	-36.7900	0.3
NASA		$P = 1$ atm	—	—	—	—
STANJAN	G1	$T = 473.15$ K	2.000 0000	-26.5700	-31.4000	0.2
NASA		$P = 1$ atm	—	—	—	—
STANJAN	G2	$T = 541.15$ K	2.000 0000	-24.0700	-28.9000	0.3
NASA		$P = 1$ atm	2.000 0000	-24.0450	-28.9570	1.1
STANJAN	G3	$T = 1500.00$ K	2.000 2164	-13.5590	-18.5450	0.2
NASA		$P = 1$ atm	2.000 2164	-13.5580	-18.5430	1.1
STANJAN	CP	$T = 647.25$ K	2.000 0000	-19.4600	-24.3000	0.3
NASA		$P = 218$ atm	2.000 0000	-19.4600	-24.3000	1.1

GSTANJAN converged for all the cases investigated. However, GNASA only converged at the interior point  $M = 4$  where it was in good agreement with GSTANJAN. At the upper limit  $M = 6$  where the composition of the system is fully determined by the constraints,



**Table 3.** Chemical equilibrium composition of the H-O system for  $EH = 4$ ,  $EO = 2$ . Mole fractions.

Code	Figure 2	Temperature, pressure	O <sub>2</sub>	H <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>	O	H	OH	HO <sub>2</sub>
STANJA	BP	$T = 373.15$ K	6.11E-22	1.22E-21	1.00000	3.43E-29	0	0	2.02E-26	0
NASA		$P = 1$ atm	—	—	—	—	—	—	—	—
STANJAN	G1	$T = 473.15$ K	3.78E-17	7.56E-17	1.00000	1.13E-23	2.30E-33	3.02E-30	1.78E-20	1.46E-28
NASA		$P = 1$ atm	—	—	—	—	—	—	—	—
STANJAN	G2	$T = 541.15$ K	6.80E-15	1.36E-14	1.00000	4.39E-21	9.23E-29	4.47E-26	1.11E-17	4.69E-25
NASA		$P = 1$ atm	6.13E-15	1.44E-14	1.00000	5.15E-21	8.83E-29	4.59E-26	1.01E-17	2.73E-25
STANJAN	G3	$T = 1500.00$ K	8.98E-05	1.98E-04	0.99968	1.92E-09	3.80E-08	2.46E-07	3.65E-05	2.18E-09
NASA		$P = 1$ atm	9.00E-05	1.98E-04	0.99968	2.07E-09	3.82E-08	2.46E-07	3.55E-05	1.84E-09
STANJAN	CP	$T = 647.25$ K	4.28E-13	8.58E-13	1.00000	2.40E-17	4.61E-25	7.17E-23	2.90E-15	4.71E-21
NASA		$P = 218$ atm	4.28E-13	8.63E-13	1.00000	2.90E-17	4.64E-25	7.18E-23	2.72E-15	3.20E-21

**Table 4.** Constrained equilibrium composition of H–O system as a function of  $M$  for  $EH = 4, EO = 2, T = 1500$  K and  $P = 1$  atm. Constraint potentials and CPU times.

Code	$M$ (mole)	Potential			CPU time (s)
		$EH$	$EO$	$M$	
GSTANJAN	2	Dependent	–12.77	–32.88	0.3
GNASA		—	—	—	—
GSTANJAN	4	–22.04	–26.55	23.03	0.3
GNASA		–22.04	–26.55	23.03	1.1
GSTANJAN	6	3.81	Dependent	–2.56	0.3
GNASA		—	—	—	—

**Table 5.** Constrained equilibrium composition of H–O system as a function of  $M$  for  $EH = 4, EO = 2, T = 1500$  K and  $P = 1$  atm. Dimensionless Gibbs free energies and mole fractions.

Code	$M$ (mole)	O <sub>2</sub>	H <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>	O	H	OH	HO <sub>2</sub>
		–27.77	–18.59	–45.66	–44.16	–1.46	1.66	–21.9	–30.35
Constrained	0	0	6.17E–07	1	6.17E–0	0	0	0	0
GSTANJAN	2	4.81 E–14	6.17E–07	1	6.17E–0	6.35E–20	9.92E–16	4.71E–11	9.04E–13
GNASA		—	—	—	—	—	—	—	—
GSTANJAN	4	0.1101	0.0855	0.1440	9.22E–14	0.1285	0.5155	0.0254	5.1E–10
GNASA		0.1101	0.0857	0.1443	9.96E–14	0.1288	0.5154	0.0247	4.3E–10
Determined	6	0	0	0	0	1/3	2/3	0	0
GSTANJAN	0	0	0	0	0	0.3333	0.6667	0	0
GNASA		—	—	—	—	—	—	—	—

GSTANJAN identified  $EO$  as a dependent constraint and found the correct values of the potentials for  $EH$  and  $M$  subject to the condition  $O_2 + H_2 + H_2O + H_2O_2 + HO + HO_2 = 0$  imposed by the constraint  $M = A$ . At the lower bound  $M = 2$ , GSTANJAN identified  $EH$  as a dependent constraint, but failed to recognize the condition  $O_2 + O + H + HO + HO_2 = 0$  imposed by the constraints  $FV = 0$  and  $B_2 = 0$ . As a result, very nearly correct values were obtained for the mole fractions of the major species  $H_2O$  and the two balanced minor species  $H_2$  and  $H_2O_2$ , but small finite values were obtained for species which should have been absent. CPU times were the same as for the two-constraint case.

**3.1.3. Four constraints:  $EH$ – $EO$ – $M$ – $FV$ .** The four-constraint calculations were carried out at the same conditions as those for three constraints. The allowed domain for  $M$  and  $FV$  obtained from the equations in the previous section is shown in figure 3 which also shows the test points investigated coded to indicate which programs converged. The complete results are give in tables 6 and 7.

GSTANJAN converged at all points while GNASA only converged at the interior point  $I$  and the boundary point  $L2$ . At the interior point GNASA and GSTANJAN agreed well. At the point  $L2$  on the lower bound where the composition is fully determined, GSTANJAN recognized the constraint  $FV = 2M - A$  obtained from (17) and found the exact mole fractions and constraint potentials. Although GNASA failed to do this, it found approximately correct mole fractions by appropriate adjustment of the constraints potentials. It should be noted in this connection that as a result of the fact that the

**Table 6.** Constrained equilibrium composition of H–O system as a function of  $M$  and  $FV$  for  $EH = 4$ ,  $EO = 2$ ,  $T = 1500$  K and  $P = 1$  atm. Constraint potentials and CPU times.

Code	Figure 3	$M$	$FV$	Potential				CPU time (s)
				$EH$	$EO$	$M$	$FV$	
GSTANJAN	$D$	2	0	Dependent	-12.77	-32.88	Dependent	0.3
GNASA				—	—	—	—	—
GSTANJAN	$L1$	2.5	0	-22.13	-27.07	24.76	Dependent	0.3
GNASA				—	—	—	—	—
GSTANJAN	$A$	3	0	Dependent	-4.93	-18.99	Dependent	0.3
GNASA				—	—	—	—	—
GSTANJAN	$L2$	4	2	-9.98	-14.58	Dependent	10.95	0.3
GNASA				-53.69	-58.28	87.41	-32.75	0.9
GSTANJAN	$I$	4	3	-22.36	-26.76	23.67	-0.34	0.3
GNASA				-22.31	-26.76	23.67	-0.34	1
GSTANJAN	$U$	4	4	-10.69	-25.88	Dependent	11.53	0.3
GNASA				—	—	—	—	—
GSTANJAN	$B$	5	4	Dependent	-14.69	Dependent	1.43	0.3
GNASA				—	—	—	—	—
GSTANJAN	$L3$	5.5	6	Dependent	-12.00	-6.16	7.50	0.3
GNASA				—	—	—	—	1.1
GSTANJAN	$C$	6	8	Dependent	Dependent	5.06	-3.81	0.3
GNASA				—	—	—	—	—

constraints are not independent at the point  $L2$ , there exists a linear relations between the constraint potentials found by GSTANJAN and those found by GNASA given by  $\lambda_i \text{ GSTANJAN} = (\lambda_I + \lambda_M/2)_{\text{GNASA}}$ . Since the results for the allowed mole fractions do not depend on the value of  $\lambda_M$ , it may be chosen arbitrarily to make the remaining mole fractions as small as desired. GNASA met its convergence requirements for  $\lambda_M = 87.41$ . The exact mole fractions are obtained in the limit  $\lambda_M = \infty$ .

In general, GSTANJAN performed well on the boundary of the allowed domain and recognized all applicable constraints. The only exception was point  $D$  where it failed to recognize  $B_2 = 0$  and assigned a small value to the mole fraction of  $\text{O}_2$ . CPU times were nearly the same as for the two- and three-constraint cases showing that there was little time penalty for the added constraints.

### 3.2. C–H–O System

A few test calculations were also carried out for a C–H–O mixture with  $EH = 2EO = 2EC = 2$  mole at a temperature of 1000 K and a pressure of 1.0 atm. The variable constraints used were the same as those for the H–O studies: total moles  $M$  and free valence  $FV$ .

**3.2.1. Three (elemental) constraints: EC–EH–EO (chemical equilibrium).** Four-constraint chemical equilibrium calculations were carried out for the 400 C–H–O species common to the NASA and CHEMKIN data bases. As expected both codes converged and the results were in good agreement. The CPU time was 1.5 for GNASA and 0.4 for GSTANJAN.

**3.2.2. Four constraints: EC–EH–EO–M.** For simplicity, the four-constraint calculations were carried out using only the 39 most abundant species found in the four-constraint

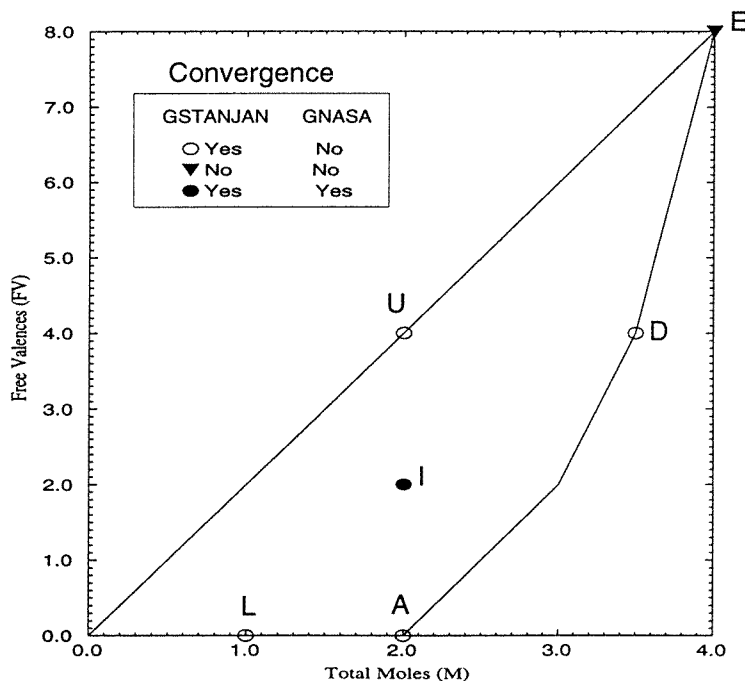


calculations discussed above. This was sufficient to give an excellent estimate of the Gibbs energy function for the system. The results are given in tables 8 and 9 for  $M = 1, 2$  and 4 mole. Table 8 gives the constraint potentials and CPU times and table 9 gives the mole fractions for the three atoms, the six possible diatoms and the 10 molecules with the lowest standard Gibbs energy function at 1000 K.

GSTANJAN converged in all cases and correctly identified one dependent constraint at the upper limit  $M = 4$  where it obtained exact values for the mole fractions. GNASA converged at the interior points where it agreed well with GSTANJAN but failed to converge at  $M = 4$ . CPU times were roughly twice those for the H–O calculations and again GSTANJAN was 3–4 times as fast as GNASA when both converged. It is interesting to note that GSTANJAN took longer to find the fully determined mole fractions at  $M = 4$  than to obtain the constrained equilibrium mole fractions at  $M = 1$  and 2.

**Table 8.** C–H–O System with  $M$  constraint:  $EC = 1, EH = 2, EO = 1, T = 1000$  K and  $P = 1$  atm. Constraint potentials and CPU times.

Code	$M$	Potential			$M$	CPU time (s)
		$EC$	$EH$	$EO$		
GSTANJAN	1	1.91	-6.55	-33.83	-10.70	0.4
GNASA		1.91	-6.55	-33.83	-10.67	1.6
GSTANJAN	2	-0.40	-15.45	-51.90	12.72	0.4
GNASA		-0.39	-15.45	-51.90	12.72	1.5
GSTANJAN	4	56.62	2.55	Dependent	7.92	0.7
GNASA		—	—	—	—	—



**Figure 4.** Allowed range of the variable constraints  $M$  and  $FV$  for the C–H–O system with five constraints  $EC-EH-EO-M-FV$  where  $EC = 1/EH = 2/EO = 1$ .

**Table 9.** C-H-O System with  $M$  constraint:  $EC = 1, EH = 2, EO = 1, T = 1000$  K and  $P = 1$  atm. Dimensionless Gibbs free energies and mole fractions.

Method	$M$	C	H	O	C <sub>2</sub>	H <sub>2</sub>	O <sub>2</sub>	CO	OH	CH	HCOOH
GSTANJAN	1	3.55E-33	4.59E-13	4.16E-24	0	1.83E-03	3.18E-23	0.0240	1.45E-14	4.41E-28	7.32E-05
GNASA		3.66E-33	4.69E-13	4.28E-24	1.03E-35	1.86E-03	3.23E-23	0.0243	1.41E-14	3.06E-28	3.12E-05
GSTANJAN	2	5.24E-24	9.23E-07	8.74E-22	7.16E-28	0.5000	9.44E-28	0.5000	4.12E-16	8.81E-23	3.96E-19
GNASA		5.30E-24	9.22E-07	8.78E-22	1.49E-27	0.5000	9.44E-29	0.5000	3.95E-16	6.04E-23	1.70E-19
Determined		1/4	1/2	1/4	0	0	0	0	0	0	0
GSTANJAN	4	0.2500	0.5000	0.2500	0	0	0	0	0	0	0
GN4SA		—	—	—	—	—	—	—	—	—	—
Code	$M$	CO <sub>2</sub>	C <sub>2</sub> H <sub>6</sub> O	CH <sub>3</sub> OH	H <sub>2</sub> O	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	CH <sub>2</sub> O	CH <sub>4</sub>	SUM( $X_j$ ) - 1
GSTANJAN	1	0.4753	2.63E-10	4.80E-06	0.0252	3.08E-03	7.26E-11	7.91E-20	2.66E-06	0.4508	-0.0196
GNASA		0.4751	1.64E-09	4.71E-06	0.0254	3.31E-03	8.04E-11	9.04E-24	1.10E-06	0.4504	-0.0196
GSTANJAN	2	1.40E-07	3.41E-32	3.38E-20	9.72E-08	5.09E-27	2.11E-19	4.31E-33	1.02E-12	2.24E-07	0
GNASA		1.39E-07	2.18E-32	3.35E-20	9.69E-08	5.75E-27	2.37E-19	4.90E-33	4.22E-13	2.25E-07	0
Determined		0	0	0	0	0	0	0	0	0	0
GSTANJAN	4	0	0	0	0	0	0	0	0	0	0
GNASA		—	—	—	—	—	—	—	—	—	—

**Table 10.** C–H–O system with  $M$  and  $FV$  constraints:  $EC = EH = 2$ ,  $EO = 1$ ,  $T = 1000$  K and  $P = 1$  atm. Constraint potentials and CPU times.

Code	Figure 4	$M$	$FV$	Potential					CPU time (s)
				$EC$	$EH$	$EO$	$M$	$FV$	
GSTANJAN	$L$	1	0	1.91	-6.54	-33.80	-10.70	Dependent	0.4
GNASA				—	—	—	—	—	—
GSTANJAN	$A$	2	0	14.50	Dependent	-35.90	-18.10	Dependent	0.5
GNASA				—	—	—	—	—	—
GSTANJAN	$I$	2	2	-3.18	-9.12	-37.20	-0.38	17.00	0.5
GNASA				-3.14	-9.10	-37.22	-0.42	17.02	1.5
GSTANJAN	$U$	2	4	-14.50	-1.60	-27.20	-24.10	25.90	0.4
GNASA				—	—	—	—	—	—
GSTANJAN	$D$	3.5	4	29.60	Dependent	Dependent	13.10	-2.54	0.9
GNASA				—	—	—	—	—	—
GSTANJAN	$E$	4	8	—	—	—	—	—	—
GNASA				—	—	—	—	—	—

3.2.3. *Five constraints: EC–EH–EO–M–FV.* The five-constraint calculations were carried out for the same condition as the four-constraint case. The allowed domain for the variable constraints  $M$  and  $FV$  obtained from the inequalities (13) and (16)–(20) is plotted in figure 4 which also shows the points where test calculations were made, coded to show convergence. The detailed results are given in tables 10 and 11 in the same format as tables 8 and 9. GSTANJAN converged in all cases except for the upper limit  $E$ . It correctly identified the dependent constraints at the boundary points  $L$ ,  $A$  and  $D$ . However, as in the previous calculations for the H–O system, it failed to recognize the dependent constraint at the point  $U$  on the upper bound. GNASA converged only at the interior point  $M = FV = 2$  where it agreed well with GSTANJAN but was much slower. CPU times were comparable with the five-constraint case, again indicating little time penalty for added constraints.

#### 4. Summary and conclusions

Fast reliable subroutines for calculating the constrained-equilibrium state of gas-phase mixtures are needed for chemical kinetic calculations using either the well known shifting-equilibrium method or the more recently proposed rate-controlled constrained-equilibrium method. The best currently available programs for this purpose are the NASA and STANJAN equilibrium codes. Although these programs were designed primarily for use in calculating the chemical equilibrium state of a system subject to conservation of the elements, they can also be used for calculating the constrained-equilibrium states of systems subject to any constraints which are linear in the species concentrations. This requires only a simple modification of their input routines which enables them to accept more general constraints and two callable subroutines, GNASA and GSTANJAN, which incorporate this modification have been developed. The convergence and speed of these subroutines were compared by making a series of test equilibrium calculations for H–O and C–H–O gas-phase systems using various combinations of constraints on the elements, total moles and free valence. Inequalities for determining the allowed ranges of the constraints for the general C–H–N–O system were derived and calculations were carried out both in the interior and on the boundaries of the allowed domain.

**Table 11.** C–H–O system with  $M$  and  $FV$  constraints:  $EC = EH = 2$ ,  $EO = 1$ ,  $T = 1000$  K and  $P = 1$  atm. Dimensionless Gibbs free energies and mole fractions.

Code	Figure 4	$M$	$FV$	C	H	O	$C_2$	$H_2$	$O_2$	CO	OH	CH	HCOOH
Constrained													
GSTANJAN	$L$	1	0	0	0	0	0	1.83E-03	3.18E-23	0.0240	0	0	7.32E-05
GNASA				—	—	—	—	1.83E-03	3.18E-23	0.0240	0	0	7.32E-05
Constrained													
GSTANJAN	$A$	2	0	0	0	0	2.60E-28	0.5000	2.60E-28	0.5000	0	0	0
GNASA				—	—	—	—	0.5000	2.60E-28	0.5000	0	0	0
GSTANJAN	$I$	2	2	0.2420	0.0262	2.58E-06	0	0.3240	1.10E-21	0.1498	2.78E-05	9.29E-05	8.94E-08
GNASA				0.2424	0.0256	2.48E-06	1.20E-35	0.3243	1.06E-21	0.1501	2.61E-05	6.47E-05	4.02E-08
Constrained													
GSTANJAN	$U$	2	4	0.4997	1.81E-05	1.59E-04	0	5.21E-05	2.22E-23	1.62E-12	3.98E-04	4.47E-05	6.81E-08
GNASA				0.4997	1.81E-05	1.59E-04	0	5.21E-05	2.22E-23	1.62E-12	3.98E-04	4.47E-05	6.81E-08
Determined													
GSTANJAN	$D$	3.5	4	0	4/7	2/7	1/7	0	0	0	0	0	0
GNASA				—	0.5714	0.2857	0.1429	0	0	0	0	0	0
Determined													
GSTANJAN	$E$	4	10	1/4	1/2	1/4	0	0	0	0	0	0	0
GNASA				—	—	—	—	—	—	—	—	—	—





Both subroutines converged well at interior points of the allowed domain, but GSTANJAN was 3–4 times as fast as GNASA. At boundary points, where the constraints were not all independent, and at points near the saturation line of water vapour, where H<sub>2</sub>O was the only numerically significant species, GSTANJAN converged in all but one case whereas GNASA failed to converge in almost all cases. The results indicate that GSTANJAN is superior to GNASA for both conventional equilibrium and constrained-equilibrium calculations. They also suggest that both programs could be improved by more sophisticated algorithms for handling limiting cases in which the constraints become dependent and it is hoped that this study will provide both motivation and guidance for further work on this problem.

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