On the Computation of Complex Equilibria

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A method is described for solving the problem: given fixed pressure, temperature, the amounts of the chemical elements, and the chemical potentials of possible chemical species at the *pressure and temperature specified, determine the equilibrium composition.* The method requires a minimum of judgment on the part of the user.

A modification of Naphtali's method for direct minimization of Gibbs' function provides an estimate of the composition of sufficient accuracy to insure convergence of solution, by the Newton-Raphson method, of the nonlinear equations describing the equilibrium.

Problems in treating multiple phases of unknown stability and chemical species present in small amounts are handled by ignoring unstable phases and small quantities in the direct minimization until the amounts of the major constituents have been at least approximately determined. To accomplish this, species temporarily ignored are assigned a fictitious mol fraction so that their re-entry into the calculation can be established. Truncation errors in the direct minimization can be tolerated because of the two-step method.

Examples of some of the problems solved are given.

The techniques for computation of chemical equilibrium in a system of many species, several elements, and several possible phases have been discussed in the available literature (*1* to *3*, *6*). However, in every case one finds two major sources of difficulty. The first lies in the numerical problem of dealing with species which become small in mol fraction during the course of the computation. The second difficulty is in treatment of multiple phases, particularly those containing more than one species which may be unstable under the conditions specified, for example, vaporization of gasoline.

This paper describes a computational technique which, for cases tested so far, solves the multiple phase problem, minimizes difficulties in dealing with small amounts of some species, and requires a minimum of judgment on the part of the user. Basically, a preliminary estimate of the compositions and the amounts of the various phases is obtained by direct minimization of Gibbs' function [using a modified Naphtali (*4*) method], and this estimate is used to obtain an exact solution by application of the Newton-Raphson method (*3*, *5*) to the nonlinear set of equations describing the equilibrium condition. The latter is necessary because all of the direct minimization methods produce a truncation error which is intolerable.

If the elements are included as possible species, as is usually the case for combustion systems, no estimate of composition is required as input. If formation of the elements is suppressed, as would be the case for certain catalytic systems, an input composition consistent with the element balance is required.

The problem solved is given a fixed pressure p, fixed temperature T, the amounts of the chemical elements E_i, and the chemical potentials of the possible species at a reference pressure μ_j^0, determine the equilibrium composition. For purposes of simplicity it is assumed that gases obey the ideal gas law, that the effect of pressure on the chemical potentials of condensed phases (liquids and solids) is negligible, and that the ideal solution law is obeyed. Thus

$$\mu_j/(RT) = \mu_j^0/(RT) + \log_e(p/p^0) + \log_e \chi_j = \mu_j^*/(RT) + \log_e \chi_j \quad (1)$$

for gases, and

$$\mu_j/(RT) = \mu_j^0/(RT) + \log_e \chi_j = \mu_j^* + \log_e \chi_j \quad (2)$$

for liquids and solids.

For reasons that will be obvious later, the same chemical species in different phases will be treated as different species. The input data for each species consist of the species name, its reference potential μ_j^0, an index ϕ_j indicating the phase of which it is a constituent, the set of numbers $a_{j,i}$ $(i = 1 \rightarrow I)$ giving the number of atomic weights of each element i *in the species molecule* j.

THE MODIFIED NAPHTALI METHOD FOR DIRECT MINIMIZATION OF GIBBS' FUNCTION, SUBROUTINE MINI

The essence of Naphtali's method (*4*) is the shifting of each of the R independent stoichiometric relations among the J species of the system by an amount negatively proportional to the extent to which the relation does not satisfy the condition of equilibrium. To formulate the R $(= J - I)$ independent stoichiometric relations among the species, one may proceed as follows:

1. Select a set of key species $k(i)$ corresponding to the elements (or fixed groups of elements) in the system $i = 1 \rightarrow I$. The set must be selected such that

$$m_k \neq 0 \quad (3)$$

and the determinant

$$[a_{k,i}] \neq 0 \quad (4)$$

2. The stoichiometric coefficients $\nu_{j,r}$ in the r^{th} stoichiometric relation with any of the $J - I$ nonkey species, say s, are given by

$$\sum_k a_{k,i}\nu_{k,r} = a_{s,i} \quad s \neq k \quad (I \text{ equations}) \quad (5)$$

$$\nu_{s,r} = 1 \quad (6)$$

$$\nu_{j,r} = 0 \quad j \neq k, \quad j \neq s \quad (7)$$

The computation is repeated for each nonkey species (R times) and can be programmed easily.

At equilibrium

$$\sum_{j=1}^{J} \nu_{j,r}\mu_j = 0 \qquad (8)^*$$

From an initial set m_j' which satisfies the material balances

$$E_i = \sum_{j=1}^{J} a_{j,i}m_j' \qquad i = 1 \rightarrow I \qquad (9)$$

and from the input data, a corresponding set μ_j' can be computed. From the μ_j' one can compute

$$\Delta G_r' \equiv \sum_{j=1}^{J} \nu_{j,r}\mu_j' \qquad r = 1 \rightarrow R \qquad (10^*)$$

and

$$G' = \sum_{j=1}^{J} \mu_j'm_j' \qquad (10)^*$$

Thus, the values of $\Delta G_r'$ are appropriate measures of the extent to which the conditions of equilibrium are not satisfied by m_j'. A reaction shift parameter $d\xi_r$ is related to the iteration parameter dK by the expression

$$d\xi_r = -(\Delta G_r')dK \qquad r = 1 \rightarrow R \qquad (11)$$

and the increments in the composition are given by

$$dm_j' = -\sum_{r=1}^{R} \nu_{j,r}\Delta G_r' dK \qquad j = 1 \rightarrow J \qquad (12)$$

Since

$$dG' = \sum_{j=1}^{J} \mu_j'dm_j' = -\sum_{j=1}^{J} \mu_j' \sum_{r=1}^{R} \nu_{j,r}\Delta G_r' dK \qquad (13)$$

by using Equation (10) one finds

$$dG'/dK = -\sum_{r=1}^{R} (\Delta G_r')^2 \qquad (14)$$

Equation (14) shows that the slope of a G versus K curve is always negative and reaches zero when all the $\Delta G_r'$ are zero. By judicious choice of the iteration parameter dK a new estimate of the composition may be obtained

$$m_j'' = m_j' - \sum_{r=1}^{R} \nu_{j,r}(\Delta G_r')dK \qquad (m_j'' > 0) \qquad (15)$$

and

$$G'' = \sum_{j=1}^{J} \mu_j''m_j'' \qquad (G'' < G') \qquad (15a)$$

The computation is terminated when dG/dK is smaller than warranted by the precision of the data. In the program tested the convergence criterion used was $dG/dK > -0.0005$. Naphtali (*4*) has given a method for selection of dK which works quite well. It is, of course, necessary to prevent overshooting to avoid negative m_j'' or $G'' > G'$, and this is done by adjusting dK. A little consideration will show that Naphtali's method is really a form of minimization by the method of steepest descent (*6*) with K serving the role of the search parameter.

There are several difficulties with the method. The most obvious of these is excessive truncation error consequent to many iterations. This problem is effectively eliminated by the two-step method because the result of the direct minimization is to be used as an initial estimate for exact solution of the equilibrium relations (see below).

Species which are small in amount and phases which are unstable are another source of difficulty. These can be handled if a method can be devised to ignore species which are small in the early part of the calculation and to have them re-enter the computation scheme as they either become significant or the precision of the computation is increased. The device found successful is simply to ignore species whose mol fraction becomes smaller than a specified tolerance and to ignore phases whose total amount is less than the tolerance. Species thus eliminated are assigned a mol fraction equal to the tolerance or equal to unity if a member of a phase which has been temporarily ignored. This permits computation of a ficticious chemical potential for each of the ignored species, and inclusion of those species in subsequent iterations if the amounts would be increased above the tolerance value (that is, if $dm_j'/dK = +$). After convergence has been obtained with a given tolerance, the tolerance can be reduced, ignored species returned to the calculation at the new tolerance, and the computation continued until a final and acceptable tolerance level has been reached. (In the program tested the final tolerance is 10^{-6}.)

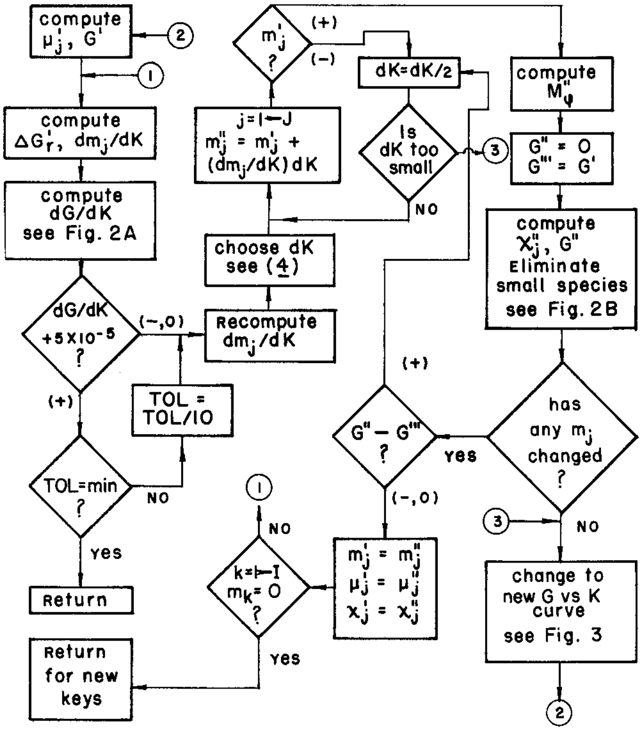

Fig. 1. Subroutine MINI: Flow Chart.

Figures 2a and 2b are flow charts of the methods for rejecting a species and accounting for rejection in computation of dG/dK. The positions of these routines in the overall scheme are shown in Figure 1.

It is clear that this method of treating small amounts and unstable phases introduces a material balance error. Such an error is permissible to some degree because of the two-step method, but it can cause problems with convergence in the direct minimization if the initial tolerance is too large.

An estimate of an allowable tolerance may be made based on an allowable material balance error, provided one can also estimate the total mols of a phase. A species is dropped based on $\chi_j' <$ TOL, and the amount of element i dropped is $a_{j,i}\chi_j'M$. If one allows for the dropping of each species containing element i once, the total amount that could be dropped is

$$\sum_{\phi} \sum_{j} a_{j,i}M_\phi\,(\mathrm{TOL})\,\delta_{\phi,\phi j}$$

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[*] In actual programming it is more convenient to normalize all energy terms by the product RT, that is, replace μ_j by $\mu_j/(RT)$ and $\Delta G_r'$ by $\Delta G_r'/(RT)$. This avoids problems with units.

If u_i is the allowable fractional error in the material balance

$$\text{TOL} = u_i \Bigg/ \left[\sum_j \sum_\phi a_{j,i}(M_\phi/E_i)\delta_{\phi,\phi j} \right]$$

Experience indicates that u_i can be as large as 0.05.

In dealing with trace elements, it is simpler to make the calculation without the trace elements and use the result as an estimated starting composition for the calculation with the trace elements added and an appropriately small initial tolerance.

Finally, convergence is intolerably slow if one stoichiometric relation has a very much larger $ABS(\Delta G_r')$ than the others or when the steepest descent requires that the search parameter K change direction but not magnitude, (that is, contours of constant $G(\chi_j, \ldots)$ are perpendicular to the arc of a circle centered at the origin). In either case dK becomes very small. The situation is signified by negligible change in composition for a given iteration or by testing the quantity $(dG/dK)(dK)/G$ to see that a significant change in G can be effected. It has been found that 0.01% change in species amounts and 0.0002% change in G work reasonably well as criteria.

This circumstance requires a break in the direct minimization routine. In effect the procedure is to adjust the composition so as to reduce the particular $ABS(\Delta G_r')$ which is largest and then return control to the direct minimization routine with the calculation effectively on a new G versus K curve. The method of adjusting the composition is based on the following analysis.

Suppose the existing condition for the particular stoichiometric relation q in question is

$$\Delta G_q' = \sum_{j=1}^{J} \nu_{j,q}\mu_j' \qquad (16)$$

The desired condition is

$$\Delta G_q'' = 0 = \sum_{j=1}^{J} \nu_{j,q}\mu_j'' \qquad (17)$$

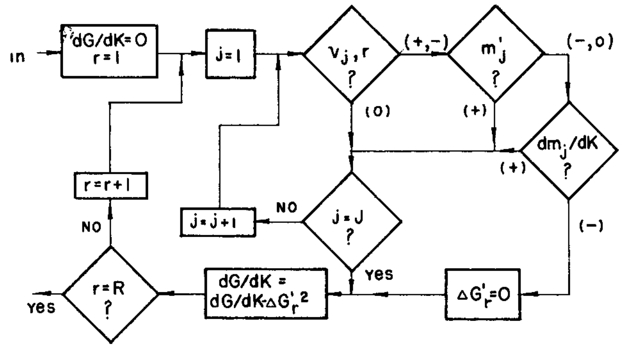

Fig. 2*a*. Subroutine MINI: Computation of *dG/dK*.

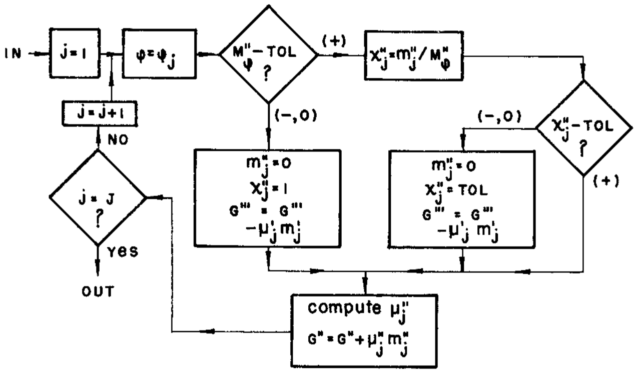

Fig. 2*b*. Subroutine MINI: Computation of *Xj″, G″*.

By subtracting the corresponding sides of Equation (16) from Equation (17), one obtains

$$-\Delta G_q' = \sum_{j=1}^{J} \nu_{j,q}\,(\mu_j'' - \mu_j') \qquad (18)$$

If j is the only constituent of a phase $(\chi_j' = 1)$, $\mu_j'' = \mu_j'$. The index n is defined as those j for which

$$\chi_j = 1 \qquad (19)$$

The ideal solution law may be incorporated into Equation (18), namely

$$-\frac{\Delta G_q'}{RT} = \sum_{j \neq n} \nu_{j,q} \log_e (\chi_j''/\chi_j')$$

$$\equiv \sum_{j \neq n} \nu_{j,q} \log_e ((\chi_j' + d\chi_j)/\chi_j') \qquad (20)$$

where the identity of (20) defines $d\chi_j$. If $d\chi_j$ is sufficiently small, Equation (20) will be approximately

$$-\frac{\Delta G_q'}{RT} = \sum_{j \neq n} \nu_{j,q}\,(d\chi_j/\chi_j') = \sum_{j \neq n} \nu_{j,q}\,(dm_j'/m_j') \qquad (21)$$

where the second equality of Equation (21) is based on the assumption that the change in total amount of any of the phases involved is small.

The change in the extent of reaction parameter $d\xi_q$ is given by

$$dm_j' = \nu_{j,q} d\xi_q \qquad (22)$$

which may be combined with Equation (21) to give

$$d\xi_q = -\Delta G_q' \Bigg/ \left[\sum_{j \neq n} \nu^2_{j,q}/m_j' \right] \Bigg/ (RT) \qquad (23)$$

The composition can then be shifted according to the relation

$$m_j'' = m_j' + \nu_{j,q} d\xi_r \qquad (24)$$

In the event this results in negative m_j'', $d\xi_q$ is adjusted so that the smallest m_j'' is zero.

In case all j for which $\nu_{j,q} \neq 0$ are members of the set $\chi_j = 1$, a phase must be eliminated. The change in the extent of reaction parameter is computed as

$$d\xi_q = -m_s/\nu_{s,q} \qquad (25)$$

with the index s being determined by the relations

$$m_s'/(\lambda\nu_{s,q}) \leqq m_j'/(\lambda\nu_{j,q}) \qquad (j = 1 \rightarrow J)$$

$$\lambda\nu_{j,q} = + \qquad (26)$$

$$\lambda = \Delta G_q'/ABS(\Delta G_q')$$

The new composition is then computed by Equation (24).

In bringing a previously ignored species back into the computation via Equation (24) a certain amount of overcorrection is employed, namely

$$m_j'' = M_\phi \chi_j' (= \text{TOL}) + \nu_{j,q} d\xi_q$$

This insures that the species will have a mol fraction at least as large as the current tolerance. Clearly, where $\nu_{j,q} d\xi_q$ is sufficiently large, an over-correction results. This is apparently necessary because of possible changes in M_ϕ. If the minimum correction were made such that $\chi_j'' =$ TOL, and if M_ϕ is increased by the same amount, species j would be rejected before the next iteration as being

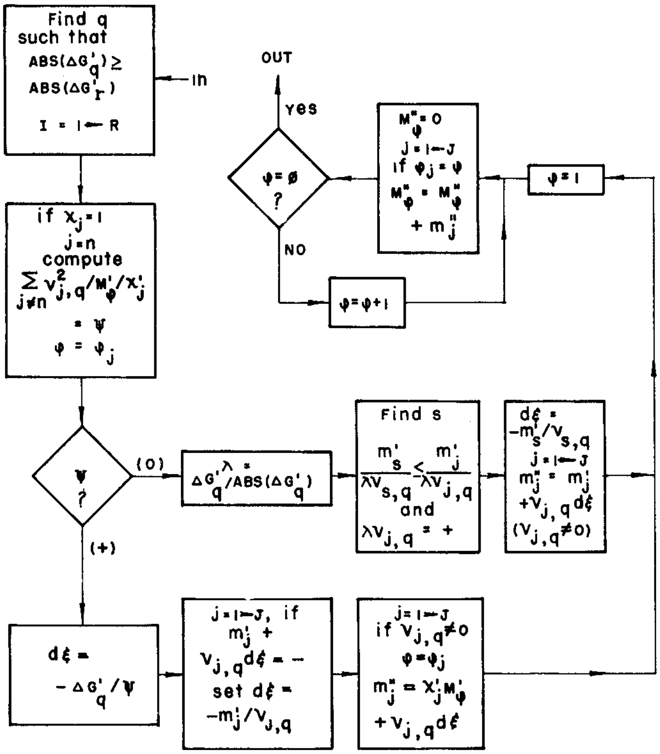

Fig. 3. Subroutine MINI: Change to New G. versus K Curve

too small. The over-correction also tends to correct the material balance error.

The calculations described in this section are implemented in a subroutine, MINI.

SELECTION OF KEY SPECIES, SUBROUTINE TEST

The above procedures for elimination of unstable phases and small species give rise to another problem. To formulate the stoichiometric relations, one chooses a set of key species equal in number to the number of elements (or fixed groups of elements) in the system. If in the course of the computation any of these key species becomes small or is a component of an unstable phase the computation cannot proceed, and a new set of keys and corresponding stoichiometric relations must be formulated. Initially the program uses the elements in their most stable form as keys or, if an initial composition is given, uses the first I species in the initial composition. [This means that the first I species in the initial composition should be legitimate key species as specified by Equations (3) and (4).] When an initial composition is not given, the program automatically assigns the amounts of the elements to the keys, assumes all other species are absent, and assigns a mol fraction of unity or TOL as appropriate to all nonkey species.

The selection of key species $k(i)$ must be made according to the two fundamental criteria represented by Equations (3) and (4). In order to minimize the number of times keys must be selected, the additional constraint, $a_{k,i}m_k \geqq a_{j,i}m_j$ $(j = 1 \rightarrow J)$ is applied.

A matrix $B_{j,i}$ is used to keep track of eligible species as follows:

$B_{j,i} = 0$ if $a_{j,i}m_j = 0$
$B_{j,i} = 1$ if $a_{j,i}m_j > 0$ and "j" has not been selected or evaluated as a key
$B_{j,i} = 2$ if species "j" has already been chosen as a key
$B_{j,i} = 3$ if species "j" gives a singular matrix of the $a_{k,i}$ with the previously chosen keys
$B_{j,i} = 4$ if the species "j" is an eligible key but is temporarily rejected because selection of subsequent keys cannot be made

The selection of key species through subroutine TEST is implemented in four principal steps as follows:

1. Set up the matrix $B_{j,i}$ $(j = 1 \rightarrow J,\ i = 1 \rightarrow I)$ such that

$B_{j,i} = 1$ if $a_{j,i}m_j \neq 0$
$B_{j,i} = 0$ if $a_{j,i}m_j = 0$

The key species are then selected for each element in sequence.

2. For the t^{th} element, search the column $B_{j,t}$ $(j = 1 \rightarrow J)$ and from the set $B_{j,t} = 1$ select a species $k(t)$ such that $a_{k,t}m_k$ is a maximum. If no suitable $k(t)$ is found, control passes to step 3. If a $k(t)$ is found, control passes to step 4.

3. Since no $k(t)$ has been found, the matrix $B_{j,i}$ is returned to its condition after selecting $k(t-1)$. For the previous element, $s = t - 1$, $B_{k,s}$ is set equal to 4, and step 2 is repeated, reselecting $k(s)$ the key for the previous element.

4. Since a $k(t)$ has been found, the determinant $[a_{k(i),i}]$ $(i = 1 \rightarrow t)$ is evaluated. If the determinant is zero, the program sets $B_{k(t),i} = 3$ $(i = t \rightarrow I)$ and step 2 is repeated. If the determinant is finite, the program sets $B_{k(t),i} = 2$ $(i = t \rightarrow I)$. The element index t is then increased and the program returns to step 2.

If a complete set of key species cannot be found, the computation is terminated and the current composition and an appropriate error message are printed. This is especially important for the case where the number of species in significant quantity at equilibrium is less than the number of elements (that is, stoichiometric hydrocarbon-air mixture at low temperature). In such cases tested so far it has been found that the composition so obtained, apart from obvious material balance errors, is correct.

Figure 4 is a simplified flow chart for subroutine TEST.

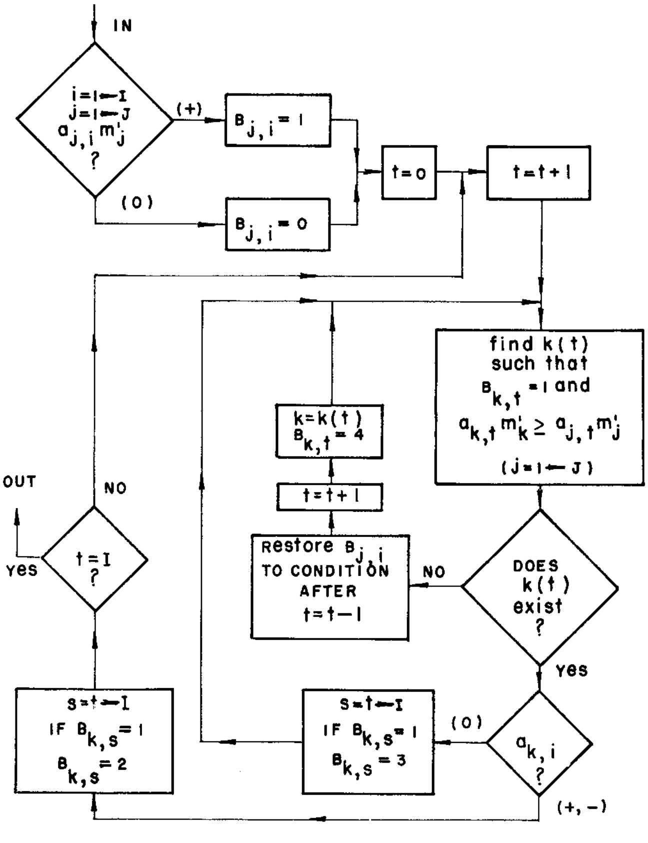

Fig. 4. Subroutine TEST: Flow Chart.

SOLUTION OF THE EXACT EQUATIONS, THE NEWTON-RAPHSON METHOD, SUBROUTINE NEWSON

Once the direct minimization routine has converged and an approximate solution has been obtained, an accurate solution can be obtained by solution of the equilibrium equations by the Newton-Raphson method (3, 5).

The exact equations are

Material balances

$$\sum_{j=1}^{J} a_{j,i} m_j = E_i. \quad (I \text{ equations}) \qquad (27)$$

Phase equations

$$\sum_{j=1}^{J} \chi_j \delta_{\phi,\phi_j} = 1 \quad (\Phi \text{ equations}) \qquad (28)$$

where

$$\delta_{\phi,\phi_j} = 1 \text{ if } \phi_j = \phi$$

$$\delta_{\phi,\phi_j} = 0 \text{ if } \phi_j \neq \phi$$

Equilibrium relations corresponding to the independent stoichiometric equations

$$\sum_{j=1}^{J} \nu_{j,r}(\mu_j^*/(RT) + \log_e \chi_j) = 0 \qquad (R \text{ equations}) \qquad (29)$$

From a trial composition χ_j' and an estimate of the amounts of the various phases M_ϕ' new estimates are obtained by solution of Equations (27), (28), and (29) in error form, namely

$$\sum_{\phi=1}^{\Phi} \sum_{j=1}^{J} a_{j,i} \chi_j' \delta_{\phi,\phi_j} dM_\phi + \sum_{j=1}^{J} a_{j,i} m_j' d(\log_e \chi_j) = E_i - \sum_{j=1}^{J} a_{j,i} m_j' \quad (i = 1 \rightarrow I) \qquad (30)$$

$$\sum_{j=1}^{J} \chi_j' \delta_{\phi,\phi_j} d(\log_e \chi_j) = 1 - \sum_{j=1}^{J} \chi_j' \delta_{\phi,\phi_j} \quad (\phi = 1 \rightarrow \Phi) \qquad (31)$$

$$\sum_{j=1}^{J} \nu_{j,r} d(\log_e \chi_j) = -\sum_{j=1}^{J} \nu_{j,r}(\mu_j^*/(RT) + \log_e \chi_j') \quad (r = 1 \rightarrow R) \qquad (32)$$

and the expressions

$$\log_e \chi_j'' = \log_e \chi_j' + d(\log_e \chi_j) \qquad (33)$$

$$M_\phi'' = M_\phi' + dM_\phi \qquad (34)$$

It has been shown that the method will converge to the correct solution provided the initial estimate of the answer is sufficiently accurate. In all cases tested so far, it has been found that the modified Naphtali method provides such an initial estimate. Experience has shown that usually fewer than 10 iterations are required to reach an answer accurate to one part in ten thousand.

Examination of these equations will show that absent species and phases must be eliminated before the solution can be made. For this reason the problem is condensed to eliminate species and phases found insignificant in the direct minimization of Gibbs' function by subroutine MINI.

The calculations in this section are implemented in a subroutine, NEWSON. Programming is relatively straightforward. However, because of the possibility that some species may become small or a phase unstable, provision must be made to return to the direct minimization routine. Provision must also be made to terminate the calculation if the number of iterations becomes excessive. This latter provision is a safety measure and has never been used when the direct minimization routine converged properly.

Examples of Problems Solved

To illustrate the kinds of problems treated by the methods outlined above, three examples are given below. In each case the problem was run on an RCA Spectra 70/46 computer.

Case I. This case represents the roasting of an ore. It illustrates the situation wherein the number of species at equilibrium is equal to or less than the number of elements.

Temperature: 800°K.
Pressure: 1 atm.
No. of species considered: 20
No. of elements: 5
No. of phases in input species: 14 (1 gas, 1 liquid, 12 solid)
Elemental composition: Cu(1.0), Fe(1.0), N(18.0), O(4.5), S(4.0)
MINI: initial tolerance = 10^{-3}, 56 iterations, key reselected 8 times
NEWSON: not executed, return from MINI showed only keys
Final Composition (output from MINI):

Species	m_j	χ_j	"corrected" m_j
$N_2(g)$	9.000	0.7795	9.0
$SO_2(g)$	1.238	0.1072	1.25
$S_2(g)$	1.308	0.1133	1.375
(Total gas phase = 11.55)			
Cu(s)	$.639 \times 10^{-2}$	1.0	0.
$CuFeO_2(s)$	.9889	1.0	1.0

Species considered but rejected ($< 10^{-6}$): Fe(s), $O_2(g)$, S(liq.), $Cu_2O(s)$, $CuSO_4(s)$, CuO(s), $Cu_2SO_5(s)$, $SO_3(g)$, $FeSO_4(s)$, $Fe_2(SO_4)_3(s)$, $Fe_3O_4(s)$, $Fe_2O_3(s)$, $Cu_2Fe_2O_4(s)$, N(g), O(g).

Note: An examination of the element balances shows that all are slightly deficient Cu(−0.005), Fe(−0.011), O(−0.046), S(−0.146). It is obvious that at equilibrium the only stable solid is copper ferrite, that the remainder of the oxygen is in SO_2, and that the remaining sulfur is $S_2(g)$. That is, the absent solid phases are unstable, and that the appearance of Cu(s) in the output is a consequence of the material balance error in Fe. This problem can then be solved by means of the linear material balance equations alone.

Case II. This problem involves the treatment of an iron silicate slag with hydrochloric acid. It illustrates the handling of a multiple phase problem.

Temperature: 1,200°K.
Pressure: 1 atm.
No. of species considered: 30
No. of elements: 7
No. of phases in input species: 17 (1 gas, 1 liquid, 15 solid)
Elemental composition: Cl(2.0), Fe(1.0), Mg(0.1), N(16.), O(3.1), Si(1.0)
MINI: initial tolerance = 10^{-4}, 133 iterations, keys reselected 15 times
NEWSON: precision = 10^{-5}, 28 iterations.
Final Composition:

Species	m_j	χ_j
ClH(g)	1.266	0.1266
Cl_2Fe(g)	0.3604	0.0361
Cl_3Fe(g)	0.442×10^{-2}	0.4430×10^{-3}
H_2(g)	0.2214×10^{-2}	0.2215×10^{-3}
H_2O(g)	0.3649	0.0365
N_2(g)	8.000	0.8002
(Total gas phase = 9.998)		
FeO(s)	0.6351	1.0
MgO_3Si(s)	0.1	1.0
O_2Si(s)	0.9	1.0

Species considered but rejected ($< 10^{-6}$): Cl(g), Cl_2(g), Cl_2Fe(liq.), Cl_2Fe(s), Cl_2Mg(liq.), Cl_2Mg(s), Cl_3Fe(liq.), Cl_3Fe(s), Cl_6Fe_2(s), $Fe_{0.94}O$(s), MgO(s), Mg(s), Mg_2O_4Si(s), O(g), Fe_2O_4Si(s).

Case III. This is the typical problem of an hydrocarbon-oxygen mixture at very high temperature. An ideal gas approximation is still valid.

Temperature: 4000°K.
Pressure: 20 atm.
No. of species considered: 26
No. of elements: 3
No. of phases in input species: 2 (1 gas, 1 solid)
Elemental composition: C(1.2), H(2.14), O(2.89)
MINI: initial tolerance = 10^{-3}, 30 iterations, keys reselected 2 times
NEWSON: precision = 10^{-4}, 2 iterations

Final Composition:

Species	m_j	χ_j
CHO(g)	0.336×10^{-3}	0.11×10^{-3}
CO(g)	0.9791	0.3217
CO_2(g)	0.2209	0.0726
H(g)	0.3103	0.1020
HO(g)	0.3574	0.1174
HO_2(g)	0.326×10^{-3}	0.107×10^{-3}
H_2(g)	0.2522	0.0829
H_2O(g)	0.4837	0.1589
O(g)	0.2512	0.0825
O_2(g)	0.1882	0.0618
(Total gas phase = 3.043)		

Species considered but rejected ($< 10^{-6}$): C(s), CH_2(g), CH_2O(g), CH_3(g), CH_4(g), C_3O_2(g), C_2(g), C_2H(g), C_2H_2(g), C_2H_4(g), C_2O(g), C_3(g), C_4(g), C_5(g), C(g), CH(g).

The program has been used for literally hundreds of cases in addition to those cited. Most of these involved equilibrium in combustion systems where computation times were less than 60 sec. The program has also been used for equilibrium in catalytic systems where formation of the elements is suppressed, for computation of equilibrium in associating liquids, and for polymerization equilibrium in the gas phase.

ACKNOWLEDGMENT

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NOTATION

$a_{j,i}$ = number of atomic weights of element i in a molecular weight of species j
$ABS(\ )$ = absolute value of ( )
$B_{j,i}$ = matrix for selection of key species (see text, TEST)
E_i = total atomic weights of element i in the system
G = Gibbs' function
ΔG_r = defined by Equation (10)
I = total number of elements of fixed groups of elements in the system
i = element index
J = total number of species in system (the same species in different phases are regarded as different species)
j = species index
dK = search parameter [see Equation (11)]
k = species index of key species, $k = k(i)$
M_ϕ = total amount of phase having index ϕ
m_j = amount of species j
n = the set of indices of species for which $\chi_j = 1$
p = pressure
p^0 = reference pressure
q = index of a particular reaction
R = gas constant
R(index) = total number of independent, stoichiometric relations ($= J - I$)
r = reaction index
s = dummy index
T = absolute temperature
t = element index (see subroutine TEST)

Greek Letters

δ_{ϕ,ϕ_j} = Kronecker's delta, = 1 if $\phi = \phi_j$, = 0 if $\phi \neq \phi_j$
λ = defined by Equation (26).
μ_j = chemical potential of species j in the mixture
μ_j^0 = chemical potential of pure j at the mixture temperature and the reference pressure
μ_j^* = chemical potential of pure j at pressure and temperature of the mixture
$\nu_{j,r}$ = stoichiometric coefficient of j^{th} species in the r^{th} independent stoichiometric relation
Φ = total number of phases in the system considered
ϕ = index of phase
ϕ_j = phase index of species j
χ_j = mole fraction of species j in phase ϕ_j
$'$ = current estimate of value
$''$ = improved estimate of value
0 = reference value

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