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AN ANALYTICAL INVESTIGATION OF THREE GENERAL METHODS
OF CALCULATING CHEMICAL-EQUILIBRIUM COMPOSITIONS

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SUMMARY

The Brinkley, Huff, and White methods for chemical-equilibrium calculations were modified and extended in order to permit an analytical comparison. The extended forms of these methods permit condensed species as reaction products, include temperature as a variable in the iteration, and permit arbitrary estimates for the variables.

It is analytically shown that the three extended methods can be placed in a form that is independent of components. In this form the Brinkley iteration is identical computationally to the White method, while the modified Huff method differs only slightly from these two. The convergence rates of the modified Brinkley and White methods are identical; and, further, all three methods are guaranteed to converge and will ultimately converge quadratically.

It is concluded that no one of the three methods offers any significant computational advantages over the other two.

INTRODUCTION

The determination of equilibrium compositions for systems of many constituents is generally difficult because the equations to be solved are not simultaneously linear. Since a direct solution is usually not feasible, some iterative technique must be used to obtain the solution. In the past few years there have appeared in the literature many articles dealing with chemical-equilibrium calculations of complex systems and describing various systematic iterative techniques (see list of references in ref. 1). These articles present methods of solution applicable to specific chemical systems as well as general methods applicable to most chemical systems. Of the general methods available, those of Brinkley (ref. 2), Huff et al. (ref. 3), and White et al. (ref. 4) are perhaps the most widely used. Because of their wide use, these three methods were investigated to determine whether any one of the three offers significant computational advantages.

The number of iterations and the amount of computation per iteration may be taken as the criteria of computational advantage. Since the amount of computation per iteration is essentially the same for the three methods, the only remaining criterion is the number of iterations. However, for any of the three methods investigated, the number of iterations is strongly dependent upon the initial estimates. Very poor estimates will generally require considerably more iterations than a good set of estimates.

In order to make an analytical comparison, it is essential that all three methods begin with the same initial estimates. The Brinkley and White methods cannot start with the same estimates. The reason for this is that the Brinkley method requires the estimates to satisfy equilibrium conditions, whereas the White method requires them to satisfy mass balance. If a unique, real, and positive solution exists, these requirements are mutually exclusive except at the solution point. To permit identical estimates, these methods were modified to remove unnecessary restrictions on the estimates.

In addition to these necessary modifications, some other modifications were made. These include simplifying the iteration equations of the Huff and Brinkley methods and treating condensed products in a manner different from that originally proposed for the Brinkley method (ref. 2) and White method (ref. 5). The Brinkley and White methods were also extended to permit using temperature as a variable.

It will be shown that the three modified and extended methods are essentially equivalent computationally.

SYMBOLS

A	total mass of reactant
A_0	converged value of A
a_{ij}	formula numbers giving gram-atoms of i^{th} element in j^{th} specie
b_i	gram-atoms of i^{th} element per unit mass of mixture (eq. (3))
b_i^0	assigned value for gram-atoms of i^{th} element per unit mass of reactant
C_j^0	heat capacity per mole at constant pressure divided by R for j^{th} specie = $\frac{1}{R} \left[\frac{\partial (H_T^0)}{\partial T} \right]_P = \frac{T}{R} \left[\frac{\partial (S_T^0)}{\partial T} \right]_P$

c_{ij}	formula numbers of components giving gram-atoms of i^{th} element in j^{th} component
F	total free energy of mixture divided by RT (eq. (7))
$(F_T^O)_j$	standard-state free energy per mole of j^{th} specie = $(H_T^O)_j - T(S_T^O)_j$
f_j	free energy per mole divided by RT for j^{th} specie (eq. (8))
\bar{f}_j	defined by eq. (68)
f_j^*	defined by eq. (25)
G	defined by eq. (48)
$(H_T^O)_j$	enthalpy per mole of j^{th} specie
h	h/RT
h_O	h_O/RT
h_j^O	$(H_T^O)_j/RT$
\bar{h}_j^O	defined by eq. (68)
h	enthalpy per unit mass of reactant (eq. (15))
h_O	assigned enthalpy per unit mass of reactant
l	number of different chemical elements
m	number of gaseous reaction products
n	total number of reaction products
P	static pressure, atm
P_O	assigned static pressure, atm
p_j	partial pressure of j^{th} specie, atm
q_i	defined by eq. (44)
R	universal gas constant
r	number of reduced iteration equations

$(S_T^O)_j$	entropy per mole of j^{th} specie in standard state
s	entropy per unit mass of mixture divided by R (eq. (16))
s_j	entropy per mole of the j^{th} specie divided by R (eq. (17))
s_O	assigned entropy per unit mass of mixture divided by R
s_j^*	defined by eq. (27)
T	absolute temperature
T_O	assigned absolute temperature
u_k	k^{th} component of solution vector of modified Huff iteration equation
\bar{u}_k	k^{th} component of solution vector of modified Brinkley iteration equations
W^i	i^{th} component
\bar{x}	total moles of gaseous products (eq. (41))
x_j	moles of j^{th} specie in a mixture
x_j^t	moles of j^{th} specie in a unit mass of mixture
Y^j	j^{th} specie
y_j	moles of j^{th} specie in a mixture at equilibrium
Z^i	i^{th} element
α_j	activity of j^{th} specie
δ_{ij}	Kronecker delta
ζ_j	defined by eq. (54)
$\bar{\zeta}_j$	defined by eq. (68)
λ_j	defined by eq. (81a)
ν_{jk}	moles of j^{th} component in k^{th} specie [see eq. (36)]
π_i	i^{th} Lagrangian multiplier
σ_j	defined by eq. (34)

GENERAL DESCRIPTION OF ORIGINAL METHODS

The three general methods all use an iterative technique to obtain equilibrium compositions. Initial estimates are made for the variables, and corrections to these estimates are obtained. The process is continued until some arbitrarily selected criterion for convergence has been reached.

Brinkley (ref. 2) was the first to treat the problem of the numerical solution of the nonlinear chemical-equilibrium equations for a general chemical system. In his calculation method the thermodynamic state of the system is specified by assigning the temperature and static pressure of the reaction products. The chemical-equilibrium relations are written in terms of components. Components are defined to be those independent constituents of the mixture that can be used to express the overall composition. The number of components usually equals the number of different chemical elements in the mixture but under some rare circumstances can be less (e.g., if some elements appear in constant ratio in all the reaction products). The choice of components is not unique. The nonlinear set of equations defining the problem is approximated by a linear set of correction equations obtained by a Taylor series expansion of the nonlinear equations neglecting terms higher than first order. In Brinkley's method any condensed reaction products that appear are treated as components.

The method of Huff, Gordon, and Morrell was described in reference 3 and subsequently presented in slightly modified form in reference 1. This method differs from Brinkley's in the following respects:

- (1) The gaseous atoms are arbitrarily selected as components.
- (2) Condensed reaction products are not considered to be components.
- (3) The thermodynamic state of the system may be specified by assigning the pressure and either the temperature, the enthalpy, or the entropy.
- (4) The linear set of equations is obtained from a Taylor series expansion involving both logarithmic and linear variables.
- (5) Corrections are applied to all constituents.

The most recent of the three methods is that due to White, Johnson, and Dantzig (ref. 4). It is based on the criterion for equilibrium $(dF)_{T,p} = 0$. The thermodynamic state of the system is specified by assigning the temperature and pressure. As originally presented, the method could only treat problems involving gaseous reaction products.

It was later extended to include condensed reaction products (ref. 5) by redefinition of one of the variables in the iterations equations.

EQUATIONS FOR DETERMINING EQUILIBRIUM COMPOSITIONS

The formation of any one of n chemical species from l elements may be written in the form

$$\sum_{i=1}^l a_{ij} Z^i = Y^j \quad (1 \leq j \leq n) \quad (1)$$

where Z^i is the symbol for the i^{th} chemical element, and Y^j is the symbol for the j^{th} chemical species. Thus, a_{ij} represents the number of gram-atoms of element Z^i in one formula weight of the chemical compound designated Y^j ; that is, the first subscript on a_{ij} indicates the chemical element and the second subscript gives the chemical compound. The range of any index such as k will usually be associated with specific chemical species:

$1 \leq k \leq l$ gaseous elements

$l + 1 \leq k \leq m$ gaseous compounds

$m + 1 \leq k \leq n$ condensed species (compounds and elements)

where, for any particular problem, l , m , and n are to be considered as fixed integers giving the number of elements, the number of gaseous products, and the total number of all products, respectively. For the chemical elements ($1 \leq j \leq l$),

$$a_{ij} = \delta_{ij} \quad (2)$$

where δ_{ij} is the Kronecker delta.

The overall composition of a mixture of n chemical species may be expressed in terms of b_i , the number of gram-atoms of the i^{th} element per unit mass of mixture:

$$b_i = \sum_{j=1}^n a_{ij} x_j^1 \quad (1 \leq i \leq l) \quad (3)$$

where x_j^1 gives the number of moles of the j^{th} product in a unit mass of the mixture. In some cases it is advantageous to alter the magnitudes

of the $x_j^!$; and therefore, if equation (3) is multiplied by the total mass A , one obtains

$$Ab_i = \sum_{j=1}^n a_{ij}x_j \quad (1 \leq i \leq l) \quad (4)$$

where x_j is the total number of moles of the j^{th} product in the mixture, and is given by

$$x_j = Ax_j^!$$

In the calculation of the equilibrium composition of a mixture, the number of gram-atoms of the i^{th} chemical element per unit mass of mixture is specified to be some assigned value b_i^0 . The condition for conservation of mass then takes the form

$$b_i^0 - b_i = \Delta b_i = 0 \quad (1 \leq i \leq l) \quad (5)$$

If y_j are the values of x_j that satisfy equation (5), then

$$Ab_i^0 = \sum_{j=1}^n a_{ij}y_j = 0 \quad (1 \leq i \leq l) \quad (6)$$

The condition for chemical equilibrium in a system at a temperature T and a pressure P may be stated in two equivalent forms. The first says that the total free energy of the system divided by RT

$$F(x_j, T) = \sum_{j=1}^n f_j x_j \quad (7)$$

is a minimum at a constant temperature and pressure, where

$$f_j = \frac{(F_T^0)_j}{RT} + \ln \alpha_j \quad (1 \leq j \leq n) \quad (8)$$

The values of x_j that minimize equation (7) at T, P are then the equilibrium values. In equation (7) and in all the following equations it is assumed that the standard state for gases is taken to be the ideal gas at 1 atmosphere, while for solids and liquids it is the pure solid or liquid at 1 atmosphere. It is assumed that the gas mixture

behaves as an ideal solution and that, if condensed species occur, they will occur as the pure solids or liquids whose activities are independent of pressure; therefore,

$$\alpha_j = \begin{cases} p_j & (1 \leq j \leq m) \\ 1 & (m < j \leq n) \end{cases} \quad (9)$$

An alternative but equivalent way of stating the condition of chemical equilibrium is that the free-energy change across a reaction is zero:

$$\Delta f_j = 0 \quad (1 \leq j \leq n) \quad (10)$$

The free-energy change across the reactions (1) is

$$\Delta f_j = f_j - \sum_{i=1}^l a_{ij} f_i \quad (1 \leq j \leq n) \quad (11)$$

Nonequilibrium values of the composition variables will not minimize F and will not make all Δf_j equal zero.

The thermodynamic state of the system is specified by assigning the temperature and pressure. The static pressure of a mixture of gases is, by Dalton's law,

$$P = \sum_{i=1}^m p_i \quad (12)$$

The condition that at equilibrium the static pressure of the system is P_0 is

$$P = P_0 \quad (13)$$

The specification of the thermodynamic state may be completed by requiring that, at equilibrium,

$$T = T_0 \quad (14)$$

Equilibrium compositions are usually obtained for a specified pressure and temperature. For a number of problems, it is desired to obtain temperature and other system properties corresponding to an assigned pressure and some other assigned thermodynamic property such as enthalpy or entropy (e.g., determining flame temperatures or conditions following an isentropic expansion). This is generally accomplished by calculating

data at several assigned temperatures followed by interpolation. However, temperature can be determined directly during the iterative process for assigned values of enthalpy or entropy. This is accomplished by permitting temperature to be a variable and including an additional equation involving enthalpy or entropy. The choice of which technique is used - that is, fixed temperature for several points and then interpolation, or temperature as a variable during iteration - is largely a matter of personal preference.

The enthalpy of a mixture is

$$A \left(\frac{h}{R} \right) = \sum_{j=1}^n \left(\frac{H_T^O}{R} \right)_j x_j \quad (15)$$

where it is assumed that the enthalpy of the constituents is independent of the pressure and that reference values consistent with heats of formation have been assigned to all n species. In like fashion the entropy of a mixture is

$$As = \sum_{j=1}^n s_j x_j \quad (16)$$

where

$$s_j = \frac{(S_T^O)_j}{R} - \ln \alpha_j \quad (1 \leq j \leq n) \quad (17)$$

The temperature of the equilibrium mixture may now be specified either by equation (14) or by (18) or (19):

$$h = h_O \quad (18)$$

$$s = s_O \quad (19)$$

where h_O is an assigned enthalpy per unit mass, and s_O is an assigned entropy per unit mass divided by the gas constant.

The problem of chemical equilibrium is completely determined by either the set of conditions (5), (10), (13), and one of the three (14), (18), (19), or by the set of conditions (5), (13), one of the three (14), (18), (19), and the minimization of (7). Except for the simplest of cases, the set of equations selected cannot be solved in closed form and must be solved by iteration. Further, the equations are not all in the same composition variable; some are written in terms of the mole numbers x_j , others in terms of partial pressures p_j , and still others in terms of both x_j and p_j . The selection of the appropriate set of

equations, the choice of the iteration method to be used in their solution, and the relation between x_j and p_j that is used constitute the important differences in the three methods to be discussed.

MODIFIED METHOD OF HUFF ET AL.

The iteration scheme of the Huff method is based on replacing the nonlinear set of equations by a set of linear correction equations obtained by a Taylor series expansion neglecting terms higher than first order. The equations selected are (5) for mass balance, (10) for equilibrium, (13) for assigning the pressure, and either (18) or (19) for assigning the enthalpy or entropy. Although $l + n + 2$ equations appear in this set, only $n + 2$ of these are independent, because with the use of (2) it is easily shown that the first l equations of (10) are merely identities.

If A is considered to be a constant, there are $n + 2$ equations in the $m + n + 1$ unknowns p_j , x_j , and T . However, if A is treated as a variable, there are then $m + n + 2$ unknowns, and it is possible to adjoin to the previous set of equations m additional equations relating p_j to x_j . In particular, the set selected is

$$p_j = x_j \quad (1 \leq j \leq n) \quad (20)$$

These m equations may now be used to eliminate p_j from the previous set of equations, resulting in $n + 2$ independent nonlinear algebraic equations in the $n + 2$ variables x_j , A , and T . If these are expanded in a Taylor series about an estimate for the solution using $\ln x_j (j \leq m)$, $x_j (m < j \leq n)$, $\ln A$, and $\ln T$ as the variables, one obtains the following equations linear in the correction variables $\Delta \ln x_j$, Δx_j , $\Delta \ln A$, $\Delta \ln T$ from the set of nonlinear equations (5), (10), (13), and (18):

$$\begin{aligned} A(b_i^0 - b_i) &= A \Delta b_i \\ &= \sum_{j=1}^m a_{ij} x_j \Delta \ln x_j + \sum_{j=m+1}^n a_{ij} \Delta x_j - \sum_{j=1}^n a_{ij} x_j \Delta \ln A \\ &\quad (1 \leq i \leq l) \end{aligned} \quad (21)$$

$$\begin{aligned} -\Delta f_j^* &= \Delta \ln x_j - \sum_{k=1}^l a_{kj} \Delta \ln x_k - \left(h_j^0 - \sum_{k=1}^l a_{kj} h_k^0 \right) \Delta \ln T \\ &\quad (1 \leq j \leq m) \end{aligned} \quad (22a)$$

$$-\Delta f_j^* = - \sum_{k=1}^l a_{kj} \Delta \ln x_k - \left(h_j^o - \sum_{k=1}^l a_{kj} h_k^o \right) \Delta \ln T \quad (m < j \leq n) \quad (22b)$$

$$P_o - P = \Delta P = \sum_{j=1}^m x_j \Delta \ln x_j \quad (23)$$

$$A(h_o - h) = A \Delta h$$

$$\begin{aligned} &= \sum_{j=1}^m h_j^o x_j \Delta \ln x_j + \sum_{j=m+1}^n h_j^o \Delta x_j - \sum_{j=1}^n h_j^o x_j \Delta \ln A \\ &\quad + \sum_{j=1}^n C_j^o x_j \Delta \ln T \end{aligned} \quad (24)$$

where

$$\left. \begin{aligned} f_j^* &= \begin{cases} \frac{(F_T^o)_j}{RT} + \ln x_j & (1 \leq j \leq m) \\ \frac{(F_T^o)_j}{RT} & (m < j \leq n) \end{cases} \\ \Delta f_j^* &= f_j^* - \sum_{i=1}^l a_{ij} f_i^* & (1 \leq j \leq n) \\ h_j^o &= \frac{(H_T^o)_j}{RT} & (1 \leq j \leq n) \end{aligned} \right\} \quad (25)$$

If y_j , A_o , and T_o are the equilibrium values of x_j , A , and T , then

$$\Delta \ln x_j = \ln y_j - \ln x_j \quad (1 \leq j \leq m)$$

$$\Delta x_j = y_j - x_j \quad (m < j \leq n)$$

$$\Delta \ln A = \ln A_o - \ln A$$

$$\Delta \ln T = \ln T_o - \ln T$$

For x_j , A , and T sufficiently close to the equilibrium values, these linear equations will give the equilibrium values. In general, however, the values obtained will only be better estimates for the equilibrium values than x_j , A , and T .

If the same procedure is followed for (19) and if equation (23) is then added to the result, the following equation is obtained:

$$A(s_0 - s) + \Delta P = A \Delta s + \Delta P$$

$$= \sum_{j=1}^m s_j^* x_j \Delta \ln x_j + \sum_{j=m+1}^n s_j^* \Delta x_j - \sum_{j=1}^n s_j^* x_j \Delta \ln A$$

$$+ \sum_{j=1}^n C_j^0 x_j \Delta \ln T \quad (26)$$

where

$$s_j^* = \begin{cases} \frac{(S_T^0)_j}{R} - \ln x_j & (1 \leq j \leq m) \\ \frac{(S_T^0)_j}{R} & (m < j \leq n) \end{cases} \quad (27)$$

Equations (21), (22), (23), and either (24) or (26) can readily be reduced to the following $l + (n - m) + 2$ linear equations by using (22a) to eliminate $\Delta \ln x_j$, and (25) to eliminate Δf_j^* :

$$\sum_{k=1}^l r_{ik} \sigma_k + \sum_{k=m+1}^n a_{ik} \Delta x_k + \sum_{k=1}^n a_{ik} x_k (-\Delta \ln x_k)$$

$$+ \left(\sum_{k=1}^m a_{ik} h_k^0 x_k - \sum_{k=1}^l r_{ik} h_k^0 \right) \Delta \ln T = A \Delta b_i + \sum_{k=1}^m a_{ik} x_k f_k^*$$

$$- \sum_{k=1}^l r_{ik} f_k^* \quad (1 \leq i \leq l) \quad (28)$$

$$\sum_{k=1}^l a_{kj} \sigma_k + \left(h_j^0 - \sum_{k=1}^l a_{kj} h_k^0 \right) \Delta \ln T = f_j^* - \sum_{k=1}^l a_{kj} f_k^* \quad (m < j \leq n)$$

$$(29)$$

$$\sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} x_j \right) \sigma_k + \left[\sum_{j=1}^m h_j^0 x_j - \sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} x_j \right) h_k^0 \right] \Delta \ln T$$

$$= \Delta P + \sum_{j=1}^m f_j^* x_j - \sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} x_j \right) f_k^* \quad (30)$$

$$\sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} h_j^0 x_j \right) \sigma_k + \sum_{k=m+1}^n h_k^0 \Delta x_k + \sum_{j=1}^n h_j^0 x_j (-\Delta \ln A)$$

$$+ \left[\sum_{j=1}^n C_j^0 x_j + \sum_{j=1}^m h_j^0 h_j^0 x_j - \sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} h_j^0 x_j \right) h_k^0 \right] \Delta \ln T$$

$$= A \Delta h + \sum_{j=1}^m h_j^0 f_j^* x_j - \sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} h_j^0 x_j \right) f_k^* \quad (31)$$

$$\sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} s_j^* x_j \right) \sigma_k + \sum_{j=m+1}^n s_j^* \Delta x_j + \sum_{j=1}^n s_j^* x_j (-\Delta \ln A)$$

$$+ \left[\sum_{j=1}^n C_j^0 x_j + \sum_{j=1}^m s_j^* h_j^0 x_j - \sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} s_j^* x_j \right) h_k^0 \right] \Delta \ln T$$

$$= A \Delta s + \Delta P + \sum_{j=1}^m s_j^* f_j^* x_j - \sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} s_j^* x_j \right) f_k^* \quad (32)$$

where

$$r_{ik} = r_{ki} = \sum_{j=1}^m a_{ij} a_{kj} x_j \quad (1 \leq i \leq l, 1 \leq k \leq l) \quad (33)$$

$$\sigma_k = \Delta \ln x_k \quad (1 \leq k \leq m) \quad (34)$$

The set of $l + (n - m) + 2$ linear equations (28) to (30) and either (31) or (32), which can be solved to give directly the corrections to the estimates for y_j ($1 \leq j \leq l$, $m < j \leq n$), A_0 , and T_0 , is presented in figure 1. These corrections can also be used to obtain the

corrections for the other gaseous species from equation (22a) rewritten using (34) and (25):

$$\sigma_j = -f_j^* + \sum_{k=1}^l a_{kj}(f_k^* + \sigma_k) + \left(h_j^0 - \sum_{k=1}^l a_{kj}h_k^0\right)\Delta \ln T \quad (1 \leq j \leq m) \quad (35)$$

The equations for $(1 \leq j \leq l)$ in (35) are identities for the gaseous atoms but are included for the purpose of later comparisons.

When the temperature is assigned directly by (14), temperature is no longer a variable, and the appropriate set of iteration equations is (28) to (30) with the $\Delta \ln T$ terms deleted. The $\Delta \ln T$ term is also deleted from (35).

MODIFIED METHOD OF BRINKLEY

In the previous section the equations for conservation of mass and for chemical equilibrium were written in terms of the gaseous atoms. The corresponding relations in the Brinkley method are written in terms of components. A set of iteration equations in terms of components is presented first. These equations are then converted to an equivalent set of equations in terms of gaseous atoms.

Iteration Equations in Terms of Components

If the j^{th} component is designated as w^j , then all of the chemical species in an l -element system can usually be written as a linear combination of l components as follows:

$$\sum_{j=1}^l v_{jk} w^j = y^k \quad (1 \leq k \leq n) \quad (36)$$

where v_{jk} gives the number of moles of the j^{th} component in the k^{th} species; w^j may be expressed in terms of the elements as

$$w^j = \sum_{i=1}^l c_{ij} z^i \quad (1 \leq j \leq l) \quad (37)$$

where c_{ij} gives the number of gram-atoms of the i^{th} element in the j^{th} component. Substituting (37) into (36) and comparing coefficients

of Z^i with those in (1),

$$\sum_{j=1}^l c_{ij} v_{jk} = a_{ik} \quad (1 \leq i \leq l, 1 \leq k \leq n) \quad (38)$$

To simplify the discussion, the last l chemical species ($n - l + 1 \leq k \leq n$) will be selected as components; that is, the j^{th} component is the $(j + n - l)^{\text{th}}$ species, or

$$w_j = y_{j+n-l} \quad (1 \leq j \leq l) \quad (39)$$

This selection includes the condensed species as components as required by the Brinkley method. This particular choice of components will in no way restrict the discussion, since it will subsequently be shown that the choice of components does not affect the corrections obtained during the iteration procedure. Because of the particular choice of components (39),

$$c_{ij} = a_{i, j+n-l} \quad (1 \leq i \leq l, 1 \leq j \leq l) \quad (40)$$

The v_{jk} can be obtained from (38) if the matrix c_{ij} is nonsingular and possesses an inverse c_{ki}^{-1} . The requirement that c_{ij} be nonsingular restricts the possible choices of components. In the previous section, because the atoms were used as components, $c_{ij} = \delta_{ij}$ and thus was always nonsingular.

In the previous section, it was found convenient to treat A as variable in order to introduce a simple relation between the moles and partial pressures (20). In this section, A is regarded as an arbitrary constant A' , and a new variable \bar{x} is introduced. The variable \bar{x} is equal to the total moles of gaseous products:

$$\bar{x} = \sum_{j=1}^m x_j \quad (41)$$

The partial pressures are then related to the moles by

$$p_j = \frac{P_0}{\bar{x}} x_j \quad (1 \leq j \leq m) \quad (42)$$

The equations for conservation of species are readily obtained. Substituting (38) into (4), multiplying the resulting equation by c_{ki}^{-1} , and summing on i from 1 to l give

$$A' q_k = \sum_{j=1}^n v_{kj} x_j \quad (1 \leq k \leq l) \quad (43)$$

where

$$q_k = \sum_{i=1}^l c_{ki}^{-1} b_i \quad (44)$$

The conservation equations corresponding to (5) are

$$q_k^0 - q_k = \Delta q_k = 0 \quad (1 \leq k \leq l) \quad (45)$$

The condition for equilibrium is again taken to be (10); however, the free-energy change across the reactions (33) with the choice of components (39) is

$$\Delta f_k = f_k - \sum_{j=1}^l v_{jk} f_{j+n-l} \quad (1 \leq k \leq n) \quad (46)$$

Since the last l species were selected as components,

$$v_{jk} = \delta_{j+n-l, k} \quad (1 \leq j \leq l, n-l < k \leq n) \quad (47)$$

and thus the last l equations of (46) are identically zero.

In his original presentation, Brinkley eliminated the variable \bar{x} from his equations by imposing the condition

$$A' \sum_{k=1}^l q_k^0 = 1$$

For comparison with the other methods, the variable \bar{x} is retained. The use of equation (42) ensures that (13) is satisfied for any choice of x_j . Equation (13) is replaced by the relation

$$G = \sum_{j=1}^m \left(\frac{x_j}{\bar{x}} \right) - 1 \quad (48)$$

If equation (41) is satisfied (i.e., if during the iteration the estimate for \bar{x} is obtained from the sum of x_j ($1 \leq j \leq m$)), then

$$G = 0 \quad (49)$$

If, however, an independent estimate is made for \bar{x} , then G will be zero only when the iteration converges.

The equations that must be satisfied by the system in equilibrium are (45), (10), (49), and either (14), (18), or (19). Using (42) in (10), expanding the resulting equations together with (45), (49), and (18) in a Taylor series as in the previous section, and treating $(x_j/\bar{x})(1 \leq j \leq m)$, $x_j(m < j \leq n)$, \bar{x} , and T as variables give

$$A'(q_i^0 - q_i) = A' \Delta q_i$$

$$= \sum_{k=1}^m \nu_{ik} x_k \xi_k + \sum_{k=m+1}^n \nu_{ik} \Delta x_k + \sum_{k=1}^m \nu_{ik} x_k \frac{\Delta \bar{x}}{\bar{x}} \quad (1 \leq i \leq l) \quad (50)$$

$$-\Delta f_k = \xi_k - \sum_{j=1}^{l+m-n} \nu_{jk} \xi_{j+n-l} - \left(h_k^0 - \sum_{j=1}^l \nu_{jk} h_{j+n-l}^0 \right) \frac{\Delta T}{T} \quad (1 \leq k \leq m) \quad (51a)$$

$$-\Delta f_k = - \sum_{j=1}^{l+m-n} \nu_{jk} \xi_{j+n-l} - \left(h_k^0 - \sum_{j=1}^l \nu_{jk} h_{j+n-l}^0 \right) \frac{\Delta T}{T} \quad (m < k \leq n) \quad (51b)$$

$$\bar{x} - \sum_{j=1}^m x_j = \sum_{k=1}^m x_k \xi_k \quad (52)$$

$$A'(h_0 - h) = A' \Delta h$$

$$= \sum_{k=1}^m h_k^0 x_k \xi_k + \sum_{k=m+1}^n h_k^0 \Delta x_k + \sum_{k=1}^m h_k^0 x_k \frac{\Delta \bar{x}}{\bar{x}} + \sum_{k=1}^n C_k^0 x_k \frac{\Delta T}{T} \quad (53)$$

where

$$\left. \begin{aligned} \xi_k &= \frac{(y_k/\bar{y}) - (x_k/\bar{x})}{x_k/\bar{x}} & (1 \leq k \leq m) \\ \Delta x_k &= y_k - x_k & (m < k \leq n) \\ \Delta \bar{x} &= \bar{y} - \bar{x} \\ \Delta T &= T_0 - T \end{aligned} \right\} \quad (54)$$

Treating (19) in similar fashion and adding $\left(1 + \ln \frac{P_0}{\bar{x}}\right)$ times (52) to the result give

$$\begin{aligned} A'\Delta s + \left(1 + \ln \frac{P_0}{\bar{x}}\right)\left(\bar{x} - \sum_{j=1}^m x_j\right) &= \sum_{k=1}^m s_k^* x_k \zeta_k + \sum_{k=m+1}^n s_k^* \Delta x_k \\ &+ \left(\sum_{k=1}^m s_k^* x_k - \bar{x} \ln \frac{P_0}{\bar{x}}\right) \frac{\Delta \bar{x}}{\bar{x}} + \sum_{k=1}^n c_k^0 x_k \frac{\Delta T}{T} \quad (55) \end{aligned}$$

Assuming that equation (41) is used to obtain an estimate for \bar{x} , the left side of (52) and the corresponding term on the left side of (55) are zero. These terms will therefore be dropped from further consideration. However, it is possible to treat \bar{x} in a manner identical to the other variables and to alter the estimate for \bar{x} as called for by the iteration equations, so that (41) need not be satisfied until equilibrium is reached. Equations (50), (51), (52), and either (53) or (55) can be reduced to $l + 2$ independent equations by using (51a) to eliminate ζ_k from the other equations and (46) to eliminate Δf_k as follows:

$$\begin{aligned} \sum_{j=1}^{l+m-n} \left(\sum_{k=1}^m v_{ik} v_{jk} x_k \right) \zeta_{j+n-l} + \sum_{k=m+1}^n v_{ik} \Delta x_k + \sum_{k=1}^m v_{ik} x_k \frac{\Delta \bar{x}}{\bar{x}} \\ + \left[\sum_{k=1}^m v_{ik} h_k^0 x_k - \sum_{j=1}^l \left(\sum_{k=1}^m v_{ik} v_{jk} x_k \right) h_{j+n-l}^0 \right] \frac{\Delta T}{T} \\ = A' \Delta q_i + \sum_{k=1}^m v_{ik} f_k x_k - \sum_{j=1}^l \left(\sum_{k=1}^m v_{ik} v_{jk} x_k \right) f_{j+n-l} \\ (1 \leq i \leq l) \quad (56) \end{aligned}$$

$$\begin{aligned} \sum_{j=1}^{l+m-n} v_{jk} \zeta_{j+n-l} + \left(h_k^0 - \sum_{j=1}^l v_{jk} h_{j+n-l}^0 \right) \frac{\Delta T}{T} = f_k - \sum_{j=1}^l v_{jk} f_{j+n-l} \\ (m < k \leq n) \quad (57) \end{aligned}$$

$$\begin{aligned} \sum_{j=1}^{l+m-n} \left(\sum_{k=1}^m v_{jk} x_k \right) \zeta_{j+n-l} + \left[\sum_{k=1}^m h_k^0 x_k - \sum_{j=1}^l \left(\sum_{k=1}^m v_{jk} x_k \right) h_{j+n-l}^0 \right] \frac{\Delta T}{T} \\ = \sum_{k=1}^m f_k x_k - \sum_{j=1}^l \left(\sum_{k=1}^m v_{jk} x_k \right) f_{j+n-l} \quad (58) \end{aligned}$$

$$\begin{aligned}
& \sum_{j=1}^{l+m-n} \left(\sum_{k=1}^m h_k^o \nu_{jk} x_k \right) \zeta_{j+n-l} + \sum_{k=m+1}^n h_k^o \Delta x_k + \sum_{k=1}^m h_k^o x_k \frac{\Delta x}{x} \\
& + \left[\sum_{k=1}^n C_k^o x_k + \sum_{k=1}^m h_k^o h_k^o x_k - \sum_{j=1}^l \left(\sum_{k=1}^m h_k^o \nu_{jk} x_k \right) h_{j+n-l}^o \right] \frac{\Delta T}{T} \\
& = A' \Delta h + \sum_{k=1}^m h_k^o f_k x_k - \sum_{j=1}^l \left(\sum_{k=1}^m h_k^o \nu_{jk} x_k \right) f_{j+n-l} \quad (59)
\end{aligned}$$

$$\begin{aligned}
& \sum_{j=1}^{l+m-n} \left(\sum_{k=1}^m s_k^* \nu_{jk} x_k \right) \zeta_{j+n-l} + \sum_{k=m+1}^n s_k^* \Delta x_k + \sum_{k=1}^m \left(s_k^* x_k - \bar{x} \ln \frac{P_o}{x} \right) \frac{\Delta x}{x} \\
& + \left[\sum_{k=1}^n C_k^o x_k + \sum_{k=1}^m s_k^* h_k^o x_k - \sum_{j=1}^l \left(\sum_{k=1}^m s_k^* \nu_{jk} x_k \right) h_{j+n-l}^o \right] \frac{\Delta T}{T} \\
& = A' \Delta s + \sum_{k=1}^m s_k^* f_k x_k - \sum_{j=1}^l \left(\sum_{k=1}^m s_k^* \nu_{jk} x_k \right) f_{j+n-l} \quad (60)
\end{aligned}$$

Equations (57) are identically satisfied and are included only for later use. The $l + 2$ linear equations (56), (58), and either (59) or (60) can be solved to give directly the corrections to $y_k (n - l < k \leq n)$ and T . The corrections to the estimates for $y_k (1 \leq k \leq n - l)$ are obtained from (51a). Equation (51a) can be written in a form similar to (35) as follows:

$$\begin{aligned}
\zeta_k + \ln \frac{P_o}{x} = -f_k^* + \sum_{j=1}^{l+m-n} \nu_{jk} \zeta_{j+n-l} + \sum_{j=1}^l \nu_{jk} f_{j+n-l} \\
+ \left(h_k^o - \sum_{j=1}^l \nu_{jk} h_{j+n-l}^o \right) \frac{\Delta T}{T} \quad (1 \leq k \leq m) \quad (61)
\end{aligned}$$

The equations for the gaseous components $(n - l < k \leq m)$ in (61) are identities.

When the temperature is assigned directly by (14), temperature is no longer a variable, and the appropriate set of iteration equations is (56) to (58) with the $\Delta T/T$ terms deleted. The $\Delta T/T$ term is also deleted from (61).

Iteration Equations in Terms of Atoms

The set of $l + 2$ independent equations (56), (58), (59), plus the $n - m$ identities (57), or the same set of equations with (59) replaced by (60), can be converted to $l + (n - m) + 2$ independent linear equations very similar in form to equations (28) to (32) used in the Huff method as follows:

First, the v_{jk} may be obtained from (38) as

$$v_{jk} = \sum_{i=1}^l c_{ji}^{-1} a_{ik} \quad (62)$$

Next, equations (62) and (44) are used in (56) to (60) and the equations resulting from (56) are also multiplied by c_{ji} and summed on i . The resulting system of equations is:

$$\begin{aligned} \sum_{k=1}^l r_{ik} \bar{\zeta}_k + \sum_{k=m+1}^n a_{ik} \Delta x_k + \sum_{k=1}^m a_{ik} x_k \frac{\Delta \bar{x}}{\bar{x}} + \left(\sum_{k=1}^m a_{ik} h_k^o x_k - \sum_{k=1}^l r_{ik} \bar{h}_k^o \right) \frac{\Delta T}{T} \\ = A' \Delta b_i + \sum_{k=1}^m a_{ik} x_k \left(f_k^* + \ln \frac{P_o}{\bar{x}} \right) - \sum_{k=1}^l r_{ik} \bar{f}_k \quad (1 \leq i \leq l) \end{aligned} \quad (63)$$

$$\sum_{k=1}^l a_{kj} \bar{\zeta}_k + \left(h_j^o - \sum_{k=1}^l a_{kj} \bar{h}_k^o \right) \frac{\Delta T}{T} = f_j^* - \sum_{k=1}^l a_{kj} \bar{f}_k \quad (m < j \leq n) \quad (64)$$

$$\begin{aligned} \sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} x_j \right) \bar{\zeta}_k + \left[\sum_{j=1}^m h_j^o x_j - \sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} x_j \right) \bar{h}_k^o \right] \frac{\Delta T}{T} \\ = \sum_{j=1}^m f_j^* x_j + \bar{x} \ln \frac{P_o}{\bar{x}} - \sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} x_j \right) \bar{f}_k \end{aligned} \quad (65)$$

$$\begin{aligned}
& \sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} h_{jx_j}^o \right) \bar{\xi}_k + \sum_{k=m+1}^n h_k^o \Delta x_k + \sum_{j=1}^m h_{jx_j}^o \frac{\Delta \bar{x}}{x} \\
& + \left[\sum_{j=1}^n c_{jx_j}^o + \sum_{j=1}^m h_j^o h_{jx_j}^o - \sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} h_{jx_j}^o \right) \bar{h}_k^o \right] \frac{\Delta T}{T} \\
& = A' \Delta h + \sum_{j=1}^m h_{jx_j}^o \left(f_j^* + \ln \frac{P_o}{x} \right) - \sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} h_{jx_j}^o \right) \bar{f}_k \quad (66)
\end{aligned}$$

$$\begin{aligned}
& \sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} s_{jx_j}^* \right) \bar{\xi}_k + \sum_{k=m+1}^n s_k^* \Delta x_k + \left(\sum_{k=1}^m s_k^* x_k - \bar{x} \ln \frac{P_o}{x} \right) \frac{\Delta \bar{x}}{x} \\
& + \left[\sum_{j=1}^n c_{jx_j}^o + \sum_{j=1}^m s_j^* h_{jx_j}^o - \sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} s_{jx_j}^* \right) \bar{h}_k^o \right] \frac{\Delta T}{T} \\
& = A' \Delta s + \sum_{j=1}^m s_{jx_j}^* \left(f_j^* + \ln \frac{P_o}{x} \right) - \sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} s_{jx_j}^* \right) \bar{f}_k \quad (67)
\end{aligned}$$

where

$$\left. \begin{aligned}
\bar{\xi}_k &= \sum_{j=1}^{l+m-n} c_{jk}^{-1} \xi_{j+n-l} \\
\bar{h}_k^o &= \sum_{j=1}^l c_{jk}^{-1} h_{j+n-l}^o \\
\bar{f}_k &= \sum_{j=1}^l c_{jk}^{-1} f_{j+n-l} = \sum_{j=1}^l c_{jk}^{-1} f_j^* + \ln \frac{P_o}{x} \sum_{j=1}^{l+m-n} c_{jk}^{-1}
\end{aligned} \right\} (1 \leq k \leq l) \quad (68)$$

In similar fashion, equation (61) becomes

$$\xi_j + \ln \frac{P_o}{x} = -f_j^* + \sum_{k=1}^l a_{kj} (\bar{f}_k + \bar{\xi}_k) + \left(h_j^o - \sum_{k=1}^l a_{kj} \bar{h}_k^o \right) \frac{\Delta T}{T} \quad (1 \leq j \leq m) \quad (69)$$

The set of equations (63), (64), (65), and (66) or (67) represents a more useful form of the iteration equations for automatic computation than the set (56), (58), and (59) or (60). Although the latter contain $n - m$ fewer equations if condensed products are present, it is necessary to obtain a new set of v_{jk} for each new choice of components, and the calculation can be rather lengthy when many species are under consideration. However, using the former set it is only necessary to calculate an inverse matrix for each new choice of components and from it the \bar{f}_k and \bar{h}_k^0 . In a subsequent section it will be shown that it is possible to obtain a set of iteration equations that do not contain \bar{f}_k and \bar{h}_k^0 , and hence it is unnecessary to obtain the matrix c_{ij}^{-1} .

MODIFIED METHOD OF WHITE ET AL.

The methods of Huff and Brinkley are Newton-Raphson iterations where the conditions for chemical equilibrium are given in terms of free-energy changes across reactions (equilibrium constants). The White method uses the alternative but equivalent method of specifying equilibrium conditions as the minimum of the total free energy of the mixture.

With (42), equation (7) becomes

$$F(x_i, T) = \sum_{i=1}^n f_i^* x_i + \bar{x} \ln \frac{P_0}{\bar{x}} \quad (70)$$

If (y_i, T_0) represents a neighboring point to (x_i, T) with y_i satisfying equation (6) with $A = A'$, then the Taylor series approximation for the free energy at (y_i, T_0) , expanded about (x_i, T) and neglecting terms higher than second order, is

$$\begin{aligned} Q(y_i, T_0) = F(x_i, T) &+ \sum_{i=1}^m \left(f_i^* + \ln \frac{P_0}{\bar{x}} \right) \Delta x_i + \sum_{i=1}^1 f_i^* \Delta x_i \\ &- \sum_{i=1}^n h_i^0 x_i \frac{\Delta T}{T} + \frac{1}{2} \sum_{i=1}^m \sum_{k=1}^m \left(\frac{\partial_{ik}}{x_i} - \frac{1}{\bar{x}} \right) \Delta x_i \Delta x_k \\ &- \sum_{k=1}^n h_k^0 \Delta x_k \frac{\Delta T}{T} + \frac{1}{2} \sum_{k=1}^n (Z_{ik}^0 - C_k^0) x_k \left(\frac{\Delta T}{T} \right)^2 \end{aligned} \quad (71)$$

because

$$\frac{\partial F}{\partial x_i} = \begin{cases} f_i^* + \ln \frac{P_o}{x} & (1 \leq i \leq m) \\ f_i^* & (m < i \leq n) \end{cases}$$

$$\frac{\partial F}{\partial T} = - \sum_{i=1}^n \frac{h_i^o x_i}{T}$$

and

$$\frac{\partial^2 F}{\partial x_i \partial x_k} = \begin{cases} \frac{\delta_{ik}}{x_i} - \frac{1}{x} & (1 \leq i \leq m, 1 \leq k \leq m) \\ 0 & (m < i \leq n, m < k \leq n) \end{cases}$$

$$\frac{\partial^2 F}{\partial x_i \partial T} = - \frac{h_i^o}{T} \quad (1 \leq i \leq n)$$

$$\frac{\partial^2 F}{\partial T^2} = \sum_{i=1}^n \frac{(2h_i^o - C_i^o)x_i}{T^2}$$

The function Q is to be minimized as a function of y_i subject to the restriction

$$A' \Delta b_i - \sum_{j=1}^n a_{ij}(y_j - x_j) = 0 \quad (1 \leq i \leq l) \quad (72)$$

obtained by the subtraction of equations (6) and (4) with $A = A'$. Thus, it is necessary to minimize the function

$$U = Q + \sum_{i=1}^l \pi_i \left[A' \Delta b_i - \sum_{j=1}^n a_{ij}(y_j - x_j) \right] \quad (73)$$

where the π_i are Lagrangian multipliers. This requires that the following conditions be satisfied:

$$\frac{\partial U}{\partial y_k} = \frac{\partial Q}{\partial y_k} - \sum_{i=1}^l \pi_i a_{ik} = 0 \quad (1 \leq k \leq n) \quad (74)$$

From equation (71),

$$\frac{\partial Q}{\partial y_k} = \begin{cases} f_k^* + \ln \frac{P_O}{\bar{x}} + \left(\frac{y_k}{x_k} - \frac{\bar{y}}{\bar{x}} \right) - h_k^O \frac{\Delta T}{T} & (1 \leq k \leq m) \\ f_k^* - h_k^O \frac{\Delta T}{T} & (m < k \leq n) \end{cases}$$

Thus, equation (74) becomes

$$f_k^* + \ln \frac{P_O}{\bar{x}} + \left(\frac{y_k}{x_k} - \frac{\bar{y}}{\bar{x}} \right) - h_k^O \frac{\Delta T}{T} - \sum_{i=1}^l \pi_i a_{ik} = 0 \quad (1 \leq k \leq m) \quad (75a)$$

$$f_k^* - h_k^O \frac{\Delta T}{T} - \sum_{i=1}^l \pi_i a_{ik} = 0 \quad (m < k \leq n) \quad (75b)$$

Equations similar in form to the correction equations in the Huff method [(28), (29), (30), and (31) or (32)] and the Brinkley method [(63), (64), (65), and (66) or (67)] may now be obtained as follows. Rewriting equation (72) in the form

$$\sum_{k=1}^m a_{jk}(y_k - x_k) + \sum_{k=m+1}^n a_{jk} \Delta x_k = A' \Delta b_j$$

and eliminating y_k ($1 \leq k \leq m$) with equation (75a) give

$$\begin{aligned} \sum_{k=1}^l \pi_{ik} + \sum_{k=m+1}^n a_{ik} \Delta x_k + \sum_{k=1}^m a_{ik} x_k \frac{\Delta x}{\bar{x}} + \sum_{k=1}^m a_{ik} h_k^O x_k \frac{\Delta T}{T} \\ = A' \Delta b_i + \sum_{k=1}^m a_{ik} x_k \left(f_k^* + \ln \frac{P_O}{\bar{x}} \right) \quad (1 \leq i \leq l) \end{aligned} \quad (76)$$

Solving equation (75a) for y_k and summing over k ($1 \leq k \leq m$),

$$\sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} x_j \right) \pi_k + \sum_{k=1}^m h_k^O x_k \frac{\Delta T}{T} = \sum_{k=1}^m f_k^* x_k + \bar{x} \ln \frac{P_O}{\bar{x}} \quad (77)$$

The remaining iteration equation can be obtained from either (18) or (19). Expanding (18) in a Taylor series about (x_j, T) gives

$$A' \Delta h = \sum_{k=1}^n h_k^0 \Delta x_k + \sum_{k=1}^n C_k^0 x_k \frac{\Delta T}{T} \quad (78)$$

Eliminating y_k ($1 \leq k \leq m$) from (78) using (75a) gives

$$\begin{aligned} \sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} h_j^0 x_j \right) \pi_k + \sum_{k=m+1}^n h_k^0 \Delta x_k + \sum_{k=1}^m h_k^0 x_k \frac{\Delta \bar{x}}{\bar{x}} \\ + \left(\sum_{k=1}^m h_k^0 h_k^0 x_k + \sum_{k=1}^n C_k^0 x_k \right) \frac{\Delta T}{T} = A' \Delta h + \sum_{k=1}^m h_k^0 x_k \left(f_k^* + \ln \frac{P_0}{\bar{x}} \right) \end{aligned} \quad (79)$$

Proceeding in an identical fashion with (19) and adding $\ln \frac{P_0}{\bar{x}}$ times (77) to the result give

$$\begin{aligned} \sum_{k=1}^l \left(\sum_{j=1}^m a_{kj} s_j^* x_j \right) \pi_k + \sum_{k=m+1}^n s_k^* \Delta x_k + \left(\sum_{k=1}^m s_k^* x_k - \bar{x} \ln \frac{P_0}{\bar{x}} \right) \frac{\Delta \bar{x}}{\bar{x}} \\ + \left(\sum_{k=1}^m s_k^* h_k^0 x_k + \sum_{k=1}^n C_k^0 x_k \right) \frac{\Delta T}{T} = A' \Delta s + \sum_{k=1}^m s_k^* x_k \left(f_k^* + \ln \frac{P_0}{\bar{x}} \right) \end{aligned} \quad (80)$$

Equations (76), (75b), (77), and either (79) or (80) are the iteration equations of the extended White method in the variables π_k ($1 \leq k \leq l$), Δx_k ($m < k \leq n$), $\Delta \bar{x}/\bar{x}$, and $\Delta T/T$. The new values for the x_j ($1 \leq j \leq m$) are obtained from (75a) with the use of the solution to the preceding set of equations. Equation (75a) can be written in a form similar to (35) and (61) as follows:

$$\lambda_j + \ln \frac{P_0}{\bar{x}} = -f_j^* + \sum_{k=1}^l a_{kj} \pi_k + h_j^0 \frac{\Delta T}{T} \quad (1 \leq j \leq m) \quad (81)$$

where

$$\lambda_j = \frac{\Delta x_j}{x_j} - \frac{\Delta \bar{x}}{\bar{x}} \quad (81a)$$

COMPARISON OF MODIFIED METHODS

Differences in Presentation from Original Reports

Before making a comparison of the three extended methods, it is appropriate to point out how the methods presented here differ from the original presentation. The Huff et al. method as presented here is substantially the same as that in reference 1, differing primarily in notation, a modified entropy equation, and the use of alternative expressions for the elements of the last two columns of the augmented matrix.

Brinkley expressed his correction equations in terms of ζ_k . In this paper the correction equations are in terms of $\bar{\zeta}_k$. Both sets of equations lead to the identical corrections. The use of $\bar{\zeta}_k$ permits a direct comparison with the other methods as well as offering some computational advantages, as was pointed out in a previous section.

Brinkley's original method was an iteration for assigned temperature and pressure where composition estimates were made only for the components, the remaining composition variables being determined from the equilibrium constants. As presented here, the method may be used for variable-temperature iteration, and the estimates for all the composition variables may be made independently. If, by choice, independent estimates are made only for components, then the free-energy terms on the right side of the iteration equations vanish identically, and only the mass-balance and enthalpy or entropy errors remain. However, this latter procedure may lead to unnecessary difficulties, as for example when some of the components are not major species. In this case small errors in the trace components are magnified to such proportions that convergence may be slow if not impossible.

The extended White method permits variable-temperature iteration, inclusion of condensed reaction products, and the use of estimates that need not satisfy mass-balance restriction. When the temperature of the system is assigned directly (14), only gaseous products are considered, and the estimates satisfy the mass-balance equations, then these equations reduce to those of reference 4. For the case of variable temperature, the minimization procedure has been combined with a Newton-Raphson iteration for temperature.

Comparison of Modified Iteration Equations

The equations for the three modified methods are presented in figure 1. In this comparison the set of equations for the $\bar{\zeta}_k$ variables

will be used for the Brinkley iteration, since these equations characterize the Brinkley iteration as adequately as the equations for the ξ_k variables. A comparison of the corresponding Huff and Brinkley equations discloses a great similarity; the coefficient matrices are identical, except for the last two columns. The second-last columns differ only in that in the Huff equations the summation extends from 1 to n , while in the Brinkley equations the summation is only to m . This is directly attributable to the different roles played by the variables A and \bar{X} . The former is associated with all the species, while the latter refers specifically to the gaseous reaction products. The last columns of the coefficient matrices are both formed in part from linear combinations of the first l columns, differing only in the fact that constants of combination differ. The constants of combination are h_k^0 in one case and \bar{h}_k^0 in the other. The right sides also differ by the use of different constants of combination in forming linear combinations of columns of the coefficient matrix.

FINAL MODIFICATIONS

Derivation of Component-Independent Forms of Huff and Brinkley Equations

The elimination of the linear combination terms from the Huff and Brinkley equations in figure 1 would make these equations independent of components. To eliminate these terms, it is necessary to establish a relation between the solution vector of a set of equations with linear combination terms and the solution vector of a new set of linear equations with these linear combination terms removed.

To accomplish this objective, consider two sets of r linear equations:

$$\left. \begin{aligned} \sum_{j=1}^r N_{ij} u_j &= d_i \end{aligned} \right\} \quad (82a)$$

$$\left. \begin{aligned} \sum_{j=1}^r M_{ij} v_j &= e_i \end{aligned} \right\} \quad (1 \leq i \leq r) \quad (82b)$$

where the relations between the matrices M_{ij} and N_{ij} and between the vectors d_i and e_i are

$$M_{ij} = N_{ij} - \delta_{jr} \sum_{p=1}^r N_{ip} \beta_p \quad (83a)$$

$$e_i = d_i - \sum_{p=1}^r N_{ip} \gamma_p \quad (83b)$$

The constants β_p and γ_p are defined to be zero for p greater than l and nonzero for $(1 \leq p \leq l)$. The equations (82b) are analogous to the Huff or Brinkley equations of figure 1, while (82a) represents these equations with the linear combination terms deleted from the last column of the coefficient matrix and the right side.

To obtain the relation between u_k and v_k , both (82a) and (82b) are multiplied by the inverse matrix N_{ki}^{-1} and summed on i . Using the identities (83a) and (83b), one obtains

$$u_k = \sum_{i=1}^r N_{ki}^{-1} d_i$$

$$v_k - v_r \beta_k = \sum_{i=1}^r N_{ki}^{-1} d_i - \gamma_k$$

and therefore

$$v_k = u_k + v_r \beta_k - \gamma_k \quad (1 \leq k \leq r) \quad (84)$$

From (84) and the definition of the constants of combination there follows

$$v_k = \begin{cases} u_k + v_r \beta_k - \gamma_k & (1 \leq k \leq l) \\ u_k & (l < k \leq r) \end{cases} \quad (85)$$

Equations (85) is the desired relation. It shows that the linear combination terms affect only the first l components of the solution vector, leaving unaltered the remaining components of the solution vector. The following table indicates the correspondence between the variables in (85) and the variables of the modified Huff and Brinkley equations of figure 1:

	Modified Huff	Modified Brinkley
$v_k \ (1 \leq k \leq l)$	σ_k	$\bar{\xi}_k$
v_r	$\Delta \ln T$	$\frac{\Delta T}{T}$
$\beta_k \ (1 \leq k \leq l)$	h_k^o	\bar{h}_k^o
$r_k \ (1 \leq k \leq l)$	f_k^*	\bar{f}_k

With the correspondence of the table and the use of $u_k = \bar{u}_k$ with the Brinkley variables, (85) for $(1 \leq k \leq l)$ gives the two transformation equations

$$\sigma_k + f_k^* = u_k + h_k^o \Delta \ln T \quad (1 \leq k \leq l) \quad (86)$$

$$\bar{\xi}_k + \bar{f}_k = \bar{u}_k + \bar{h}_k^o \frac{\Delta T}{T} \quad (1 \leq k \leq l) \quad (87)$$

Eliminating σ_k from the modified Huff equations (28), (29), (30), (31), and (32) with the transformation (86) and eliminating $\bar{\xi}_k$ from the modified Brinkley equations (63), (64), (65), (66), and (67) with the transformation (87) give a new set of iteration equations for these two iteration methods. These are presented in figure 2, together with the modified White iteration equations from figure 1.

All three sets of iteration equations in figure 2 now give directly the corrections to the condensed species, temperature and either \bar{x} or A ; however, none of the iteration equations give the corrections to the gaseous species directly. The corrections to the gaseous species in the modified White iteration are obtained from (81). Corrections to the gaseous species for the Huff and Brinkley equations of figure 1 are obtained from (35) and (69), respectively. These two equations can be transformed to correspond to the variables of the Huff and Brinkley equations of figure 2 by substituting (86) into (35) and (87) into (69):

$$\sigma_j = -f_j^* + \sum_{k=1}^l a_{kj} u_k + h_j^o \Delta \ln T \quad (1 \leq j \leq m) \quad (88)$$

$$\bar{\xi}_j + \ln \frac{P_o}{x} = -f_j^* + \sum_{k=1}^l a_{kj} \bar{u}_k + \bar{h}_j^o \frac{\Delta T}{T} \quad (1 \leq j \leq m) \quad (89)$$

Comparison of Final Equations

An examination of figure 2 discloses that in this form all three sets of iteration equations are independent of components. Further, in this form the Brinkley and White equations are computationally identical, while the Huff equations differ only slightly from these two. The Huff equations have additional terms in the second-last column of the coefficient matrix, while the other two have additional terms on the right side. When only gaseous products are considered, the three coefficient matrices are identical except for one term in the entropy row.

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OBTAINING AND APPLYING CORRECTIONS

A distinction should be made between the solution of the equations to obtain corrections and the application of these corrections to obtain new estimates.

Obtaining Corrections

As was pointed out previously, all three modified methods give the corrections to the condensed species, temperature and either \bar{X} or A directly. The corrections to the gaseous species are obtained from the auxiliary relations (81), (88), or (89). For the Huff iteration, (88) gives the correction variable σ_j , which may be regarded as either $\Delta \ln x_j$ or $\frac{\Delta x_j}{x_j}$ and applied accordingly. However, (81) and (89) give the variables λ_j and ξ_j , respectively.

The corrections $\Delta \ln x_j$ or $\frac{\Delta x_j}{x_j}$ may be related directly to λ_j or ξ_j if use is made of the approximate relation $\Delta \ln z = \frac{\Delta z}{z}$:

$$\Delta \ln x_j = \frac{\Delta x_j}{x_j} = \begin{cases} \lambda_j + \frac{\Delta \bar{x}}{\bar{x}} & \text{(modified White)} \\ \xi_j + \frac{\Delta \bar{x}}{\bar{x}} & \text{(modified Brinkley)} \end{cases} \quad (90)$$

Since the Brinkley and White iteration equations in figure 2 and also the corresponding auxiliary relations (89) and (81) are identical, it follows that the modified Brinkley and White equations provide identical corrections. These corrections will in general differ from those given by the Huff iteration.

Applying Corrections

Once the corrections have been obtained from one of the three iteration procedures, there still remains the question of how to use these corrections. Some of the possible variations are

- (1) Using the corrections for the gaseous species and temperature linearly or logarithmically, for example, $\frac{\Delta x_k}{x_k}$ or $\Delta \ln x_k$
- (2) Using the entire correction or some fraction of the correction
- (3) Using some or all of the composition corrections:
 - (a) Applying only l of the composition corrections and determining the remaining $n - l$ composition variables from the equilibrium constants
 - (b) Applying $n - l$ of the composition corrections, determining the remaining l composition variables from the mass-balance relations
 - (c) Applying all n composition corrections
- (4) Using some combination of the above three.

In the original papers Huff et al. advocate the use of logarithmic corrections while Brinkley and White use linear corrections. Further, Brinkley makes use of variation (3a), and White (3b), while Huff uses (3c). In addition, White suggests the use of fractional corrections and reference 1 indicates that fractional corrections may also be used with the Huff method.

CONVERGENCE OF THE THREE MODIFIED ITERATION METHODS

Because of the experience factors involved in the use of corrections, no completely analytical discussion can be given to the problem of convergence rate. It is possible, however, to draw some conclusions concerning the relative convergence rates of the three modified methods if it is assumed that all three methods use the corrections in an equivalent manner. The modified Brinkley and Huff methods are Newton-Raphson iterations, which are known ultimately to converge quadratically (ref. 6). Since the modified Brinkley and White methods are identical, all three methods must ultimately converge quadratically. Further, Gleyzal (ref. 7) has demonstrated that the Newton-Raphson iterations are guaranteed to converge if an appropriate use of the corrections is made; thus, all three methods are mathematically guaranteed to converge.

The remaining small differences between the modified Huff and the other two modified methods is due to the use of the variable A in one case and the variable \bar{x} in the other. It would therefore seem reasonable to expect that the rate of convergence would be about the same for all three. This is somewhat substantiated by the fact that, for the particular problem used as an example in reference 4, both the Huff and White methods required six iterations to converge to the same degree of accuracy. This was so even though logarithmic corrections were used in the Huff iteration and fractional linear corrections were used in the White iteration. While one example cannot be considered conclusive, it is indicative of the fact that none of the methods can be expected to offer a marked advantage.

Experience has shown that by the proper use of the corrections it is possible to accelerate the convergence. Thus, if one is in a situation where the errors are primarily in equilibrium, the use of logarithmic corrections will reduce the error most rapidly. This is true because the equilibrium equations are linear in the logarithmic variables. However, where the error is primarily in the mass balance, the linear corrections are best because the mass-balance equations are linear in the variables. Linear corrections permit negative values of x_j , whereas logarithmic corrections do not. While negative x_j for condensed reaction products are significant since they indicate that the particular condensed product is absent, for gaseous products the x_j should be greater than or equal to zero.

Several years of experience (ref. 1) have shown that the use of logarithmic corrections for the gaseous products and linear corrections for condensed products permits rapid convergence for a wide variety of problems even with poor first estimates.

SUMMARY OF RESULTS

Three widely used methods of equilibrium calculations were analytically compared. To permit the comparison, the methods were modified and extended. The Brinkley method was extended to allow variable temperatures and to permit estimates that do not satisfy the equilibrium constants. The White method was extended to accommodate condensed species and variable temperatures and also to permit estimates that do not satisfy mass-balance requirements. The comparison of the methods showed the following results:

1. The modified methods are computationally equivalent.
2. The modified Brinkley and White iterations give identical corrections.

3. Alternative sets of iteration equations for the Brinkley and Huff iterations were obtained that offer computational advantages over the original set.

4. Neither the concept of components nor the particular set of components selected plays a role in obtaining corrections to the estimates.

5. All three methods are guaranteed to converge and will ultimately converge quadratically.

6. No one of the methods offers any significant advantage over the other two.

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National Aeronautics and Space Administration
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REFERENCES

1. Gordon, Sanford, Zeleznik, Frank J., and Huff, Vearl N.: A General Method for Automatic Computation of Equilibrium Compositions and Theoretical Rocket Performance of Propellants. NASA TN D-132, 1959.
2. Brinkley, Stuart R., Jr.: Calculation of the Equilibrium Composition of Systems of Many Constituents. Jour. Chem. Phys., vol. 15, no. 2, Feb. 1947, pp. 107-110.
3. Huff, Vearl N., Gordon, Sanford, and Morrell, Virginia E.: General Method and Thermodynamic Tables for Computation of Equilibrium Composition and Temperature of Chemical Reactions. NACA Rep. 1037, 1951. (Supersedes NACA TN's 2113 and 2161.)
4. White, W. B., Johnson, S. M., and Dantzig, G. B.: Chemical Equilibrium in Complex Mixtures. Jour. Chem. Phys., vol. 28, no. 5, May 1958, pp. 751-755.
5. Kubert, B., and Stephanou, S. E.: Extension to Multiphase Systems of the Rand Method for Determining Equilibrium Compositions. Paper 59-18, presented at Fall Meeting of Western States Section, The Combustion Inst., Los Angeles (Calif.), Nov. 2-5, 1959. (To be publ. by Butterworths Sci. Pub.)
6. Hildebrand, F. B.: Introduction to Numerical Analysis. McGraw-Hill Book Co., Inc., 1956, pp. 447-451.
7. Gleyzal, Andre N.: Solution of Non-Linear Equations. Quarterly Appl. Math., vol. 17, no. 1, Apr. 1959, pp. 95-96.

	Δx_k	Δx_k	Δx_k	Δx_k	Constant	Equation
W	r_{1k}	Δx_k	Δx_k	$\Delta \ln T$	Constant	
B	r_{1k}	Δx_k	Δx_k	$\Delta \ln T$	Constant	
H	r_{1k}	Δx_k	Δx_k	$\Delta \ln T$	Constant	
W	r_{1k}	Δx_k	Δx_k	$\Delta \ln T$	Constant	(76)
B	r_{1k}	Δx_k	Δx_k	$\Delta \ln T$	Constant	(65)
H	r_{1k}	Δx_k	Δx_k	$\Delta \ln T$	Constant	(78)
W	r_{1k}	Δx_k	Δx_k	$\Delta \ln T$	Constant	(77b)
B	r_{1k}	Δx_k	Δx_k	$\Delta \ln T$	Constant	(64)
H	r_{1k}	Δx_k	Δx_k	$\Delta \ln T$	Constant	(29)
W	r_{1k}	Δx_k	Δx_k	$\Delta \ln T$	Constant	(77)
B	r_{1k}	Δx_k	Δx_k	$\Delta \ln T$	Constant	(65)
H	r_{1k}	Δx_k	Δx_k	$\Delta \ln T$	Constant	(30)
W	r_{1k}	Δx_k	Δx_k	$\Delta \ln T$	Constant	(79)
B	r_{1k}	Δx_k	Δx_k	$\Delta \ln T$	Constant	(66)
H	r_{1k}	Δx_k	Δx_k	$\Delta \ln T$	Constant	(71)
W	r_{1k}	Δx_k	Δx_k	$\Delta \ln T$	Constant	(80)
B	r_{1k}	Δx_k	Δx_k	$\Delta \ln T$	Constant	(67)
H	r_{1k}	Δx_k	Δx_k	$\Delta \ln T$	Constant	(32)

† $i, j, k \leq 1$; †† $i, j, k \leq n$.

Figure 1. - Comparison of modified iteration equations (W, White; B, Brinkley; H, Barr).

W	x_k^*	Δx_k^*	$\frac{\Delta x}{x}$	$\frac{\Delta T}{T}$	Constant	Equation
B	u_k	Δx_k	$\frac{\Delta x}{x}$	$\frac{\Delta T}{T}$	Constant	
H	u_k	Δx_k	$-\Delta \ln A$	$\Delta \ln T$	Constant	
W	r_{1k}	a_{1k}	$\sum_{k=1}^m a_{1k} x_k$	$\sum_{k=1}^m a_{1k} h_{k,k}^0 x_k$	$A' \Delta b_1 + \sum_{k=1}^m a_{1k} x_k \left(f_k^* + \ln \frac{P_0}{x} \right)$	(76)
B	"	"	"	"	"	(63) ^a
H	"	"	$\sum_{k=1}^n a_{1k} x_k$	"	$A \Delta b_1 + \sum_{k=1}^m a_{1k} x_k f_k^*$	(28) ^a
W	s_{k1}	0	0	h_{11}^0	f_1^*	(75b)
B	"	"	"	"	"	(64) ^a
H	"	"	"	"	"	(29) ^a
W	$\sum_{j=1}^m a_{kj} x_j$	0	0	$\sum_{j=1}^m h_{j,j}^0 x_j$	$\sum_{k=1}^m f_k^* x_k + \bar{x} \ln \frac{P_0}{x}$	(77)
B	"	"	"	"	"	(65) ^a
H	"	"	"	"	$\sum_{k=1}^m f_k^* x_k + \Delta P$	(30) ^a
W	$\sum_{j=1}^m a_{kj} h_{j,j}^0 x_j$	$h_{k,k}^0$	$\sum_{k=1}^m h_{k,k}^0 x_k$	$\sum_{j=1}^n c_{j,j}^0 x_j + \sum_{j=1}^m h_{j,j}^0 x_j$	$A' \Delta h + \sum_{k=1}^m h_{k,k}^0 x_k \left(f_k^* + \ln \frac{P_0}{x} \right)$	(79)
B	"	"	"	"	"	(66) ^a
H	"	"	$\sum_{k=1}^n h_{k,k}^0 x_k$	"	$A \Delta h + \sum_{k=1}^m h_{k,k}^0 x_k f_k^*$	(31) ^a
W	$\sum_{j=1}^m a_{kj} s_{j,j}^* x_j$	s_k^*	$\sum_{k=1}^m s_k^* x_k - \bar{x} \ln \frac{P_0}{x}$	$\sum_{j=1}^n c_{j,j}^0 x_j + \sum_{j=1}^m s_{j,j}^* h_{j,j}^0 x_j$	$A' \Delta s + \sum_{k=1}^m s_k^* x_k \left(f_k^* + \ln \frac{P_0}{x} \right)$	(80)
B	"	"	"	"	"	(67) ^a
H	"	"	$\sum_{k=1}^n s_k^* x_k$	"	$A \Delta s + \Delta P + \sum_{k=1}^m s_k^* x_k f_k^*$	(32) ^a

[†](1 ≤ k ≤ l), ^{*}(m < k ≤ n).

^aEquation used to derive this equation.

Figure 2. - Comparison of modified iteration equations with linear combination terms deleted (W, White; B, Brinkley; H, Huff).