SOLUTION OF COMPLEX THERMOCHEMICAL EQUILIBRIA IN SYMBOLIC FORM

Dudley J. Benton, Ph.D.
Tennessee Valley Authority
Engineering Laboratory
Norris, Tennessee

ABSTRACT

A method is presented by which chemical reactions can be conveniently expressed and automatically decomposed into the implied thermochemical equations. A variation of the RAND method with enhancements to the numerical algorithm that improve computational stability and convergence rate is used to solve these equations. A generalized equation of state capable of handling both vapor and liquid systems is used to obtain the partial fugacities and free energies. Results are presented for gaseous and aqueous systems.

NOMENCLATURE

A   =   square matrix containing $\partial g_I / \partial y_J$
B   =   column matrix containing $-g_I$
C   =   matrix containing elemental compositions
C   =   specific heat [J/gram-mole/K]
D   =   column matrix containing elemental abundances
g   =   specific Gibbs free energy [J/gram-mole]
G   =   Gibbs free energy of the system [J]
h   =   specific enthalpy of a component [J/gram-mole]
M   =   the number of components
N   =   the number of elements or irreducible members
s   =   specific entropy of a component [J/gram-mole/K]
y   =   component quantity [gram-moles]
Y   =   column matrix containing y_J

Greek
Φ =   quadratic function with linear constraints
φ =   quadratic function
λ =   Lagrange multipliers
Λ =   column matrix containing λ_I
Ω =   column matrix containing linear constraints

Subscripts
0   =   reference or ground state
I   =   first index or row number
J   =   second index or column number

[1] Abundance of elements, reactants, or products is the quantity (or the number of moles) present in the system. This is different from concentration which might be moles per unit volume and mole fraction which is the abundance of one species divided by the total number of moles.

INTRODUCTION

Chemical reactions are the controlling phenomena in many processes of interest to the utility and process industry. The primary method for analyzing chemical reactions is to consider their ultimate or equilibrium state. The CREST (Chemical Reactions and Equilibrium Thermodynamics) computer code was developed to be a convenient and versatile means of determining chemical equilibria.

The Gibbs Condition or Minimum Free Energy Postulate

The Gibbs condition or Minimum Free Energy Postulate is an extension of the Second Law of Thermodynamics and is equivalent to the condition of maximum entropy subject to the constraint of energy conservation or the First Law of Thermodynamics (van Wylen and Sonntag, 1973). Implicitly assumed in equilibrium analyses is the Ergodic Surmise which can be stated: the ultimate description of an equilibrium system is independent of time (Pierce, 1968). The Gibbs condition can then be summarized: the tendency is for reactions to proceed such that the free energy is reduced, the final condition being that of minimum free energy.

Throughout this development it will be assumed that the thermodynamic systems in question are "open" (viz. maintained at constant pressure). In order to apply the developments to a system that is "closed" (viz. maintained at constant volume) all references to the Gibbs free energy and enthalpy can be replaced by Helmholtz free energy and internal energy, respectively. This is done automatically by the CREST computer program.

Solution of Chemical Equilibria

The equilibrium chemical reaction problem is defined as satisfying the Gibbs condition subject to the element abundance[1] and non-negativity[2] constraints.

[2] The non-negativity constraint is the same as recognizing that one cannot have negative moles of something.

The Gibbs condition is nonlinear; whereas the element abundance constraints are linear. The strategy employed here is a variation of the RAND method (White, et al., 1958), where the unknowns are the molar abundances. The resulting nonlinear system is solved in an iterative manner as a sequence of linearized systems which satisfy the non-negativity constraint at every iteration and the element abundance constraint at most iterations (excepting those which would violate the non-negativity constraint), leaving the free energy extrema to be approached only as the iterations converge.

FORMULATION

The formulation begins with the mathematical expression for the Gibbs condition and the elemental abundance constraints. As with the RAND algorithm, these constraints are imposed through the use of Lagrange multipliers. The resulting set of nonlinear simultaneous equations is solved using a hybrid method which will be described subsequently.

The Gibbs Condition

The Gibbs free energy of a system is the sum of the product of the molar abundances and the specific free energies of the components, or

$$G = \sum y_I g_I \tag{1}$$

The extrema (and in particular the minima) of G are located at the point(s) where the gradient of G is zero (i.e., where the partial derivatives of G with respect to the molar abundances, y_I, are zero). This can be expressed as

$$\frac{\partial G}{\partial y_I} = 0 \tag{2}$$

Substituting the definition of G, or Equation 1, into Equation 2 yields a set of nonlinear simultaneous equations which can be expressed in matrix form by

$$AY - B = 0 \tag{3}$$

where Y is the column matrix containing the molar abundances, y_I, A is the square matrix having the elements

$$A_{IJ} = \frac{\partial g_I}{\partial y_J} \tag{4}$$

and B is the column matrix containing the free energy of the components, or

$$B_I = - g_I \tag{5}$$

Equation 3 is nonlinear because the elements of the matrix (i.e., the component specific free energies and their partial derivatives) depend on several factors, including the molar abundances, y_I.

The Element Abundance and Non-Negativity Constraints

The constraints conserving the abundance of the N elements (or irreducible members--which could be ions) of the system can be expressed as a system of N simultaneous linear equations involving the M molar abundances, or

$$CY - D = \Omega \rightarrow 0 \tag{6}$$

where C is a rectangular matrix having N rows and M columns and D and Ω are column matrices having M elements. The non-negativity constraints can be expressed by

$$y_I > 0 \tag{7}$$

Application of Lagrange Multipliers

The method of Lagrange multipliers is the typical way of solving constrained extrema (Wylie, 1975). In order to implement this method, it is necessary to define a function whose solution is the desired extrema (i.e., the Gibbs condition). The quadratic function whose solution is Equation 3 can be expressed in matrix form by Equation 8 (Ortega and Rheinboldt, 1970).

$$\phi = \%_0 Y^T A Y - Y^T B \tag{8}$$

Defining the Lagrange multipliers,

$$\Lambda = [\ \lambda_I\ ]^T \tag{9}$$

the element abundance constraints can be added to form the constrained function:

$$\Phi = \phi + \Lambda^T \Omega = \%_0 Y^T A Y - Y^T B + \Lambda^T [CY - D] \tag{10}$$

The extrema of the function Φ occur when the partial derivatives with respect to the molar abundances, y_I, and the Lagrange multipliers, λ_I, are all zero. This condition can be expressed by the following partitioned matrix, having N+M rows and columns.

$$\begin{bmatrix} A & C^T \\ C & 0 \end{bmatrix} \begin{bmatrix} Y \\ \Lambda \end{bmatrix} = \begin{bmatrix} B \\ D \end{bmatrix} \tag{11}$$

METHOD OF SOLUTION

Equation 11 is the essence of what Smith and Missen (1982) refer to as the "RAND algorithm." White, Johnson, and Dantzig (who were working for the RAND Corporation at the time) introduced the same basic equations in 1958, although they came to them through a different approach. They began with an expression for the free energy of a mixture of ideal gases, applied in their words the "Method of Steepest Descent", and used the first term in a Taylor's expansion of the mixture free energy to

arrive at essentially the same equations. In the terminology of Smith and Missen, what White, Johnson, and Dantzig developed was a second order, nonstoichiometric, algorithm using the Newton-Raphson method of solution. Formulating these equations is one matter; developing a practical manner in which to solve them is quite another. Smith and Missen (1982) and Cruise (1964) provide some helpful flow charts which illustrate the basic steps involved.

Solving the Simultaneous Equations

In Equation 11 matrices A and B are nonlinear, while C and D are linear. The original RAND method is basically a straight Newton iteration. Newton's method is not always stable or rapid. An adaptive hybrid of the Newton, Steepest Decent, and Conjugate Gradient methods is used to make the solution more robust. This method is described by Benton (1991); however, the necessity and basis for it can well be gleaned from Ortega and Rheinboldt (1970), Powell (1977), More and Sorensen (1984), and Fletcher (1987).

Computation of the Free Energy

How one evaluates the elements of matrix A determines whether the method is restricted to a mixture of ideal gases--as was the case with White, et al.--or whether it can be applied to real systems composed of real substances. The mathematics are the same until actually evaluating Equation 4 (i.e., the partial derivatives of the free energy with respect to the molar abundances). The effort which must be invested in evaluating these partials depends on the accuracy required and the degree of nonideality exhibited by the system. The CREST computer code was developed in such a way that it provides varying levels of complexity. Some substances are treated as ideal gases while others are not. The mixing rule can also be selected.[3]

Equation of State and Mixing Rule

Equations of state and mixing rules abound in the literature. The reasons for selecting one over the others vary almost as much as the equations and rules themselves. The current selection was based on the criteria that there be exactly three roots of any subcritical isotherm, that Maxwell's Criterion[4] hold, that all the critical properties match exactly, that an excessive number of empirical data are not required, and that the equations be reasonably accurate not only for "well-behaved" substances but for a group of substances chosen for their notorious "ill" behavior: water, ammonia, carbon dioxide, and neon.

[3] A mixing rule is a model for the behavior of a mixture--specifically how the properties of the individual species are influenced by the presence of the other species in the mixture.

The cubic equation of state described by Fuller (1976) was found to be the most satisfying in regards to these criteria. Maxwell's Criterion is used to infer the saturation pressure from the equation of state.[5] As stated previously, opinions vary

considerably as to the selection of equations of state. Abbott (1973) provides a very enlightening discussion of the advantages and limitations of cubic equations of state. The correspondence by Chung, Hamam, and Lu (1977) in which they discuss the greater accuracy of the method which Chung and Lu developed-- provided one is not so concerned about polar molecules-- illustrates these varying preferences and perspectives.

Mixing rules also vary considerably. Smith and Missen (1982), Prausnitz (1969), and Stadler (1989) provide detailed discussions of mixing rules. The mixing rule currently used by the CREST code is that of Redlich and Kwong (1949) as it is easily implemented and provides a significant level of improvement over the ideal mixture model. Eventually the method described by Liu, Wimby, and Gren (1989) will be implemented as an option.

Initial Estimates of the Molar Abundances

There is also the necessity of obtaining initial estimates of the molar abundances, y_I, and satisfying the non-negativity constraints. The SIMPLEX method (cf. Wagner, 1975) is used to accomplish this. The molar abundances are bounded below by a small positive number (for practical purposes this needs to be somewhere between the square and cube root of the smallest number greater than zero that the computer can store) and bounded above by the abundance of the most restrictive irreducible constituent (e.g., the upper bound on CO_2 would be the smaller of the total number of moles of C and half that of O). Matrices A and B can be linearized in order to obtain the initial estimates by computing secant partials at the lower and upper bound.

IMPLEMENTATION

A computer code, CREST, was developed in order to implement these algorithms. The substances participating in the reaction and their properties as well as how their state is to be treated and their mixture computed is defined for CREST in a symbolic form which is interpreted based on syntax.

The Use of Syntax to Define Substances and Reactions

Syntax is used not only to identify the species but to distinguish between irreducible, conserved participants (i.e., elements or ions) and reducible participants (i.e., compounds). The elemental

[4] Satisfying Maxwell's Criterion is equivalent to requiring continuous saturation phase fugacity.

[5] Another way of stating Maxwell's Criterion is that the area under a subcritical isotherm (on a pressure-volume diagram) is equal to the saturation pressure times the difference in phase volumes.

(and electron) abundance constraints can be determined automatically from the composition of the compounds which is specified in a user-defined database. Table 1 is an abbreviated excerpt from a CREST database. In the interest of brevity, not all of the information for each substance is listed in the table. This

other information includes such things as the temperature dependence of the constant pressure specific heat at zero pressure, Cp_0, the standard state, and critical properties if known. The thermodynamic and transport properties in the absence of any chemical reactions can be accessed through a separate computer code, FEAST (Benton, 1987).

The reaction to be solved is defined by entering it in symbolic form interactively or in a file as illustrated in Equation 12. The number of moles of the reactants must be specified (or assumed to be 1). Of course, the number of moles of products must not be specified, as these are the solution sought after. Various conditions such as temperature, pressure, and heat transfer and constraints such as adiabatic, isobaric, and isometric can also be prescribed interactively, in a batch file, or progmatically. The equation of state to be used for each species as well as the mixing rule is also specified by the syntax. The equation of state is specified by a special character preceding the name of the substance and the mixing rule is specified by a special character preceding the equals sign in the reaction.

Acetylene+2.7Odia=Water+Cmonox+Cdiox+H+Hdia
$$\text{\textit{+O+Odia+Hydroxl+...}} \qquad (12)$$
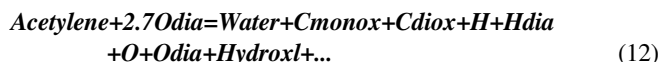
Programmatic Control

The method is implemented in the form of a computer code which can be run interactively, from a batch file, or spawned as a subtask from within another process with complete programmatic control. A source code written in C is supplied with the CREST executable which illustrates how the program can be spawned within a loop or loops in order to model sequential reactions, variation of reactant species, and produce custom graphical output.

Program Performance

Solution of 72 simultaneous reacting species in an aqueous solution requires between 4 and 12 minutes on a PC (20 MHz 80386/7) depending on the mixing model used. Solution of 100 simultaneous reacting species in a gaseous mixture requires between 10 and 30 minutes on such a machine depending on the mixing model used. Simple reactions (e.g., 20 species in an ideal gas mixture) requires only a few seconds. Most of the CREST code was written in FORTRAN, except for the I/O, full-screen editor, reaction interpreter, and matrix solver which were written in assembler.

Program Results

Figure 1 shows the computed variation with temperature of 20 product species resulting from the combustion of coal. Figure 2 shows the computed variation with oxygen of 14 product species resulting from the combustion of a hydrocarbon in the presence of sulfur. Figure 3 shows the computed variation with hypochlorite of 23 product species resulting from the corrosion of cement containing 3 variants of asbestos in an aqueous

solution. Every step from the reaction to the hard copy of these plots was provided by the program CREST. Certainly many more examples could be given. More complex reactions (e.g., sequential steps such as occur in the presence of a catalyst and more species) have been analyzed using the program; but this increased complexity is difficult to present graphically and concisely.

Table 1. Excerpts from a CREST Database

```
*define elements (order is immaterial)
*name h0 s0 Cp0 ... other ...  weight
*
C 0 1.4 6.05 ................  12.011 carbon
H 93800 27.4 4.97 ..........  1.008 monatomic hydrogen
O 107000 38.5 5.24 ..........  15.999 monatomic oxygen
*
*define compounds (order is immaterial)
*name [composition] h0 s0 Cp0 ...other...
*
Hdia [H2] 0 31.2 6.53 ..................
Odia [O2] 0 49.0 6.69 ..................
Acetone [CH3COCH3] -93200 70.5 17.90 ...
Acetylene [C2H2] 97500 48.0 10.50 ......
Mek [CH3COC2H5] -101000 80.8 24.60 .....
Cmonox [CO] -47600 47.3 6.71 ...........
Cdiox [CO2] -169000 51.1 8.01 ..........
Water [H2O] -104000 45.1 6.87 ..........
```

Model Comparison

The CREST computer code is similar in concept to the STANJAN computer code which was developed by Prof. William Reynolds of Stanford University. The basic methodology of finding the minimum free energy subject to the elemental abundance and non-negativity constraints is the same. Both codes are interactive, make use of an expandable database of substances, and run on IBM compatible PCs. CREST, however, has several features not present in STANJAN. These include: optional real gas equations of state, nonideal mixing rules, a built-in full-screen editor, graphical output to 12 different devices, batch or complete programmatic control, and all of the matrix operations are coded in assembler for maximum speed. The addition of non-ideal mixing rules alone represents a considerable increase in complexity.

CLOSING

The rather complicated task of determining thermochemical equilibria has been implemented in the form of a computer code which is relatively simple to use. The code (CREST) has been available on the ASME/CIME computer in one form or another since 1988 and has been satisfactorily used to model a variety of problems including: flue gas desulfurization, ammonia injection into flue gas, calcium oxide production, and calcium leaching from wetted fiber reinforced cement products.

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