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LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA ○ LOS ALAMOS NEW MEXICO

HUG, A FORTRAN - FAP CODE FOR COMPUTING NORMAL SHOCK AND DETONATION WAVE PARAMETERS IN GASES

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HUG, A FORTRAN - FAP CODE FOR COMPUTING NORMAL SHOCK AND DETONATION WAVE PARAMETERS IN GASES

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ABSTRACT

The computer code described herein permits the solution of the Rankine-Hugoniot equations for normal shock waves in ideal gas mixtures for a large number of optional sets of conditions. The code has been written partly in FORTRAN II and partly in FAP, and is intended for use on the IBM 7090 or 7094 computers operating under the MONITOR system.

ACKNOWLEDGMENTS

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The compilation of coefficients presented in Appendix B has been prepared by Charles W. Hamilton.

CONTENTS

INTRODUCTION

For many practical purposes, a shock wave in a gas can be considered as a discontinuous jump between initial and final conditions, and use can be made of the relationships between these two sets of conditions. These relationships are given for normal shock waves by the so-called Rankine-Hugoniot equations, coupled with the thermal and caloric equations of state. These are a set of algebraic equations which in general require numerical solution because of the complex dependence of the equations of state upon internal molecular excitation and chemical reaction.

The computer code which this report describes permits the solution of the Rankine-Hugoniot equations for a large range of cases. The central problem is that of a shock wave of arbitrary strength in a gas at rest. In addition, the code permits the consideration of the reflection of such a shock wave off a rigid wall or the one-dimensional detonation of the initial gas according to the Chapman-Jouguet model. The composition of the initial gas may be specified arbitrarily, and chemical changes occurring between the initial and final states may be either prohibited, specified arbitrarily, or determined by conditions of chemical equilibrium in the final state. Provision is also made for the consideration of chemical equilibrium problems independent of the occurrence of shock waves.

The code is intended for use on the IBM-7090 or 7094 computers under the MONITOR system. It is written partly in FORTRAN II and partly in FAP.

Chapter 1

SHOCK WAVES IN REACTIVE GASES

1.1 NORMAL SHOCK WAVES

The three Rankine-Hugoniot equations express the conservation of energy, mass, and momentum in the flow through a normal shock wave. The ordinary forms of these equations describe steady, one-dimensional, adiabatic flow with no external forces. In a coordinate system fixed in the shock, they may be conveniently written to state that the specific stagnation enthalpy and the mass flux are the same in the initial and final states, and that the force causing the difference in momentum flux between initial and final states is the difference in pressures. The basis of these equations, and their limitations, are considered in standard textbooks.[1,2]

It is convenient to work with these equations in forms which express (1) the change in specific enthalpy, $(h - h_o)$; (2) the shock velocity, u_s, into stationary initial gas; and (3) the particle velocity, u_p, imparted by passage of the wave, explicitly in terms of the initial (subscript zero) and final (unsubscripted) pressures, P, and specific volumes, v. Thus we have:

$$(h - h_o) = 1/2(P - P_o)(v_o + v) \tag{1}$$

$$u_s = \left[\frac{v_o^2(P - P_o)}{(v_o - v)}\right]^{1/2} \tag{2}$$

$$u_p = [(P - P_o)(v_o - v)]^{1/2} \tag{3}$$

In addition to these basic equations, we use the thermal and caloric equations of state which relate volume and enthalpy to temperature, T, and pressure.

$$t(v,P,T) = 0 \tag{4}$$

$$c(h,P,T) = 0 \tag{5}$$

For ideal gases of given composition, the enthalpy depends only on the temperature. For this reason, temperature is used as the independent parameter in seeking the solution of equation (1). Shock wave conditions for a particular value of some parameter such as shock velocity or particle velocity are obtained by imposing the desired value as an auxiliary condition and varying the temperature for which equations (1)-(5) are solved until the condition is satisfied.

1.2 REFLECTED SHOCK WAVES

Reflected shock waves are treated by equating the final data from the original shock, P, v, and h, to the initial conditions for the reflected shock, P'_o, v'_o, and h'_o, and proceeding to solve equations (1)-(5) for the reflected shock parameters, P', v', h', u'_s, and u'_p for an assumed T'. The coordinate system for reckoning velocities in the reflected shock wave becomes transformed to one which is reversed in direction from that of the incident shock and which is stationary, not in the laboratory, but in the final gas behind the incident shock. The auxiliary condition which matches the reflected shock to the incident one, and thereby fixes T', is that u^*_p, the particle velocity behind the reflected shock in the laboratory system, must be zero. Hence this condition is:

$$u^*_p = u'_p - u_p = 0 \tag{6}$$

The reflected shock wave velocity in the laboratory system then becomes:

$$u^*_s = u'_s - u_p \tag{7}$$

1.3 CHEMICAL REACTIONS

In considering shock waves, we wish to restrict our attention to solutions of equations (1)-(5) which represent compression waves $[(P - P_o) > 0, (v_o - v) > 0]$ with velocities greater than the sound velocity. Normally we are also interested in final temperatures which are greater than the initial temperature. In the absence of chemical reactions or other internal sources or sinks of energy, these conditions are equivalent. However, chemical reactions have profound effects on the equations of state and further affect the regimes of temperature and shock velocity in which solutions of equation (1) represent shock waves.

The occurrence of endothermic reaction generally raises the shock velocity and the final density required to achieve a particular temperature, so that no complication is encountered when T is kept greater than T_o. It can happen, though, that there is a minimum shock velocity, greater than the sound velocity, compatible with a given extent of endothermic reaction. This minimum represents termination of solutions of equation (1) at a large pressure and zero volume.

When exothermic reactions occur, there is an additional complication. There is a temperature, T_1, greater than T_o, which represents reaction at constant volume, $v = v_o$, and below which the solution of equation (1) requires $v > v_o$. At temperatures above T_1, the solutions are such that there is a minimum value of u_s, greater than the sound velocity, above which there are normally two P-v-T conditions for a given u_s and below which there are none.

Of all the stoichiometrically possible states attainable by chemical reactions, one that is of particular interest is that which satisfies the condition of chemical equilibrium. The solutions of equation (1) for conditions in which h and the P-v-T relationship are governed by chemical equilibrium have a particular locus in the P - v plane, the so-called equilibrium Hugoniot curve. Shock waves into media initially at equilibrium are simple in that this locus includes the initial point, and weak shocks approach no-reaction behavior. Shocks into metastable initial media, with the final state determined by chemical equilibrium, are complicated by the effects described above arising from exothermic or endothermic reaction.

1.4 CHAPMAN-JOUGUET DETONATIONS

The Chapman-Jouguet theory treats detonations as steady, one-dimensional shock waves in which the final state is reached by exothermic reaction. The detonation properties are given by the solution of equations (1)-(5) having the minimum shock velocity compatible with equilibrium in the chemically reacting system.[3] This solution is called the Chapman-Jouguet solution, and is determined by the tangency condition:

$$(dP/dv)_{eq\ Hug} + (P - P_o)/(v_o - v) = 0 \qquad (8)$$

where $(dP/dv)_{eq\ Hug}$ is the slope of the locus of equilibrium solutions of equation (1), and $- (P - P_o)/(v_o - v)$ is the slope of the line connecting the Hugoniot point P,v with the initial point, P_o,v_o, and determines u_s by equation (2).

1.5 CHEMICAL SYSTEMS

The extensive properties of the medium considered in equations (1)-(8) are on a specific (per gram) basis. The properties of individual chemical species, however, are most conveniently formulated on a molar basis. The properties of the system may then be formulated from the description of the mixture of chemical species.

The first item in this description is an ordered list of the chemical species included. The subscript $\underline{t}$ is used to denote the position of each species in this list, with the integer $\underline{s}$ denoting the length of the list. The identity of the $\underline{t}^{th}$ species is indicated by its chemical formula. The composition of the system is specified by a set of mole fractions, x_t, which is likewise an ordered list (vector) of length $\underline{s}$.

Two additional sets of data, likewise ordered, suffice to specify the conditions of an ideal gas mixture at a given temperature and pressure. These are the molecular weights, M_t and the molar enthalpies, H_t. Thus the conditions of the initial gas before a shock wave are given in terms of the initial (subscript zero) values of these parameters by

$$v_o = \frac{RT_o}{P_o M_o} = \frac{RT_o}{P_o \sum_{\underline{t}=1}^{\underline{s}} x_{t_o} M_t} \qquad (9)$$

$$h_o = \frac{\sum_{\underline{t}=1}^{\underline{s}} x_{t_o} H_{t_o}}{M_o} = \frac{\sum_{\underline{t}=1}^{\underline{s}} x_{t_o} H_{t_o}}{\sum_{\underline{t}=1}^{\underline{s}} x_{t_o} M_t} \tag{10}$$

The condition of the system after chemical reaction is described as follows. Let n_t represent the numbers of moles of each species formed from one mole of the original gas. Now we allow the possibility that the $\underline{s}^{th}$ species may be a pure condensed (solid) phase. The control integer $\underline{p}$ has the value *zero* if the $\underline{s}^{th}$ species is gaseous, *one* if it is solid. (If $\underline{p} = 1$, $x_{s_o} = 0$.) We then formulate the mole number sums

$$n_{gas} = \sum_{\underline{t}=1}^{\underline{s}-\underline{p}} n_t \tag{11}$$

$$n_{solid} = \underline{p} n_s \tag{12}$$

and the mole fractions, relative to the gaseous phase,

$$x_t = \frac{n_t}{n_{gas}} \tag{13}$$

In these terms, the equations of state become:

$$v = \frac{n_{gas} RT}{PM_o} + \frac{\underline{p} n_s V_s}{M_o} \tag{14}$$

$$h = \frac{n_{gas}}{M_o} \sum_{t=1}^{s} x_t H_t \quad , \tag{15}$$

where V_s is the molar volume of the solid $\underline{s}^{th}$ species.

1.6 CHEMICAL EQUILIBRIUM

Chemical equilibria are treated by the Brinkley[4] method as extended to two-phase systems by Fickett.[5] No outstanding advantage of the Brinkley method over other available methods is claimed; the choice of this method has been based on local familiarity with it. The parameters by which the user communicates with the formalism are discussed here. Additional details of the method and specific examples of its use are provided in Appendix A.

The formulas of the chemical species are represented by a matrix whose elements, α_{tk}, are the formula coefficients specifying the number of atoms of each element in each species. This matrix has a row (index $\underline{t}$) for each of the $\underline{s}$ species and a column (index $\underline{k}$) for each of the $\underline{c}'$ chemical elements.

The elemental composition of the system is specified by an ordered set, Q_k, of length $\underline{c}'$, whose elements are the numbers of gram atoms of each element in the system. From the previous section, the system to be considered in a shock wave calculation is one mole of initial gas, whose composition is specified by x_{t_o}. Thus:

$$Q_k = \sum_{\underline{t}=1}^{s} x_{t_o} \alpha_{tk} \tag{16}$$

In the Brinkley method, chemical equilibrium and stoichiometry are actually formulated in terms of a matrix, ν_{ij}, and a composition vector, q_j, derived from α_{tk} and Q_k. This derivation requires specification of a set of $\underline{c}$ stoichiometrically independent *component* species (species whose formula vectors, α_{jk}, form a $\underline{c}$ by $\underline{c}$ matrix whose determinant is not zero). This number, $\underline{c}$, is normally equal to $\underline{c}'$, the number of chemical elements. It may be smaller than $\underline{c}'$ when two or more elements appear only in fixed combinations.

This specification is accomplished by an auxiliary vector which assigns a unique re-ordering integer, $\underline{a}_t = 1, \ldots \underline{s}$, to each species. The selected set of independent species are assigned elements $\underline{a}_t = 1, \ldots \underline{c}$; the remaining species, for which $a_t = (\underline{c} + 1), \ldots \underline{s}$, are then dependent. Except in cases where the $\underline{s}^{th}$ species represents a second phase, there is no significance to the ordering within these two subsets.

Free energy data for the computation of equilibrium constants are communicated as a set, $F_t^{\dagger}$, whose elements are the dimensionless standardized chemical potentials for each species. The reference temperature in the nondimensionalizing factor, RT, is the temperature at which the equilibrium calculation is to be made. The basis of the standardization is the pressure of the system, P, and a suitable set of standard states for reckoning enthalpies of formation.

1.7 THERMODYNAMIC DATA

The basis for reckoning enthalpies and free energies for all species is the elements in their standard states at 0°K. Thus, the molar enthalpy of each species is given as

$$H_t = (H - H_o)_t + (\Delta H_{f_o})_t \tag{17}$$

where $(H - H_o)_t$ is the molar enthalpy of the $\underline{t}^{th}$ species relative to itself at 0°K, and $(\Delta H_{f_o})_t$ is the molar enthalpy of formation of the $\underline{t}^{th}$ species from the elements at 0°K.

Because the range of initial temperatures normally considered for shock waves is much smaller than the ranges of final temperatures, and because free energy data are needed only for the final temperature ranges, different functional forms are used to express $(H - H_o)_t$ for the different ranges. For ideal gases over the range of initial temperatures, T_o, the following polynomial is used:

$$(H - H_o)_{t_o} = a_t + b_t T_o + c_t T_o^2 + d_t T_o^3 \tag{18}$$

For final temperature ranges, the formulation used for ideal gases is

$$\frac{(H - H_o)_t}{RT} = A_t + B_t T + C_t T^2 + D_t T^3 + E_t T^4 \tag{19}$$

The corresponding expression for the standard Gibbs free energy function is then:

$$\frac{(F^{o} - H_{o})_t}{RT} = A_t(1 - \ln T) - B_t T - 1/2C_t T^2 - 1/3D_t T^3 - 1/4E_t T^4 - k \qquad (20)$$

For ideal gases, the function $F_t^{\dagger}$ referred to in the preceding section takes the form:

$$F_t^{\dagger} = \frac{(F^{o} - H_{o})_t}{RT} + \frac{(\Delta H_{f_o})_t}{RT} + \ln P \qquad (21)$$

where P is the pressure of the system, in units of the standard pressure (1 atmosphere) for reckoning F^{o}.

When a solid is included among the constituents of the final state, it is considered to have a constant molar volume, V_s, over the limited temperature and pressure range involved. In addition, the small effects of pressure on its enthalpy and chemical potential are neglected. Thus, for the $\underline{s}^{th}$ species, equations (19) and (20) are used, and $F_s^{\dagger}$ is given by:

$$F_s^{\dagger} = \frac{(F^{o} - H_{o})_s}{RT} + \frac{(\Delta H_{f_o})_s}{RT} + (1 - \underline{p})\ln P \qquad (22)$$

where $\underline{p}$ is the phase control integer introduced previously.

Chapter 2

THE HUG CODE

The HUG code was written to process data according to the equations of Chapter 1 using the IBM 7090 or 7094 computer under the MONITOR system. Two of its major sub-codes are written in FAP. One of these is the code for solving chemical equilibria by the method of Brinkley as extended to two-phase systems and coded by Fickett.

The other major FAP routine is the linear feedback equation solver, FROOT, also due to Fickett.[6] This routine is used in all the shock wave computations to determine the pressure which satisfies equation (1) for the given temperature. In addition, it is used to control outer iterations to determine the temperature for which the auxiliary conditions, equations (6), (8), or an arbitrarily specified velocity, u_s or u_p, are satisfied. Each use of the FROOT routine requires the specification of a value, ε, such that a value of the variable satisfying the equation with a residual, δ, is accepted as a solution when $\delta<\varepsilon$.

The remainder of the HUG code is written in FORTRAN II. A great deal of the code is logical control which governs the many options available to the user. A run, or job, of computing may consist of one or many separate problems, each of which may contain one or several individual calculations, or points. Most of the options are selected by means of a set of control integers, which are specified anew for each problem within the run. Data on the chemical system may be respecified (block by block) between problems, but if no change is to be made from the previous problem, most of the data are retained and re-used as called for in subsequent problems. Likewise, data specifying the conditions for the sequence of points in the problem may be changed between problems.

Provision is also made for the optional loading of certain problem data which would otherwise be computed internally. These data, if loaded, are used in preference to the results of the internal computations. They are destroyed at the end of the problem for which they were loaded, and hence must be loaded anew for each problem in which they are to be used.

2.1 INPUT SPECIFICATIONS

Input data are entered by the instruction: READ INPUT TAPE IN, etc. The value of IN is assigned in the main program. At LASL, the value 10 is used.

The various types of input data used by the code, and the formats for the cards from which they are transcribed onto the input tape, are specified below. All data prescribed below are decimal numbers. Table I, at the end of this section, summarizes the loading formats.

I. LABEL CARD

This card carries labels for certain columns in the printout and values of ε, the acceptable limit of proximity to zero, for the four FROOT iterations. It is the first data card loaded in a run, and it is loaded only once.

Columns 1-30, Labels (Formats A3)

Hollerith characters are entered in ten fields of width three. Those in the first six fields label the columns (chemical elements) in the α-matrix. (See α-MATRIX CARDS, columns 61-72). The label convention: C, H, O, N, M (noble gas), X (halogen) is used at LASL. The contents of the last four fields label the $\underline{a}$-vectors.

Columns 31-70, Definitions of Zero (Formats E10.2)

Positive floating point numbers containing the decimal point with one digit to the left and two digits to the right of it, (+X.XX±EE), are entered in four fields of width ten.

Columns 33-40, ε_P

In the iteration on pressure to solve equation (1) for a specified temperature, a value satisfying

$$\left| 1.0 - \frac{(P - P_o)(v_o + v)}{82.5856(h - h_o)} \right| = \left|\delta_P\right| < \varepsilon_P,$$

is acceptable as a solution. P is pressure (atmospheres), v is specific volume (cc/gram), and h is specific enthalpy (calories/gram). A value of ε_P of $+1.0 \times 10^{-6}$ usually gives sufficient accuracy.

Columns 43-50, ε_T

In the iteration on temperature to achieve a specified shock wave or particle velocity, the solution is accepted when

$$\left| 1.0 - \frac{u}{\mathrm{DSTORE}} \right| = \left|\delta_T\right| < \varepsilon_T,$$

where u is the velocity, u_s or u_p, being tested and DSTORE is the prespecified value. A value of ε_T of $+1.0 \times 10^{-6}$ provides near machine accuracy.

Columns 53-60, ε_R

The solution for an assumed temperature for a shock wave propagating into the medium behind a given incident shock wave is accepted as the reflected shock solution when

$$\left| 1.0 - \frac{u_p'}{u_p} \right| = \left|\delta_R\right| < \varepsilon_R,$$

where u_p is the particle velocity behind the incident shock (ambient gas stationary) and u_p' is the particle velocity (coordinate system fixed in the gas behind the incident shock) being tested. A value of ε_R of $+1.0 \times 10^{-6}$ provides near machine accuracy.

Columns 63-70, ε_D

The shock wave solution for an assumed temperature, T, is accepted as a Chapman-Jouguet detonation solution when

$$\left| \frac{(v_o - v)}{(P - P_o)} (\Delta P/\Delta v) + 1.0 \right| = \left|\delta_D\right| < \varepsilon_D,$$

where P and v are pressure and specific volume at the temperature T, and $(\Delta P/\Delta v)$ is the approximate slope of the reactive Hugoniot curve (equilibrium, or, if desired, fixed exothermic composition) obtained by evaluating ΔP and Δv as the differences between P and v at two Hugoniot points displaced from T by $+ \delta T$ and $- \delta T$. The size of δT is chosen internally as a minimum needed to make $\Delta P/P \geq 0.001$ and $\Delta v/v \geq 0.001$, thereby assuring numerically meaningful values. A value of ε_D of $+1.0 \times 10^{-4}$ usually provides near machine accuracy.

Lack of precision may prevent acceptable convergence of these iterations under unfavorable circumstances. When ε_P cannot be satisfied, owing to near indeterminacy when $(h - h_o) \approx 0$ or other reasons, the working value of T is increased. Precision in this solution must be maintained to avoid compounded difficulties in the outer iterations. Provision is made for temporary increases in ε_T, ε_R, and ε_D when convergence cannot be obtained with the original values.

Fivefold increases are made, and notes are printed out when this is done. If convergence still fails after two increases, the velocity or reflected shock point, or the entire detonation problem, is rejected. The original ε's are restored when this occurs. They are also restored before all new problems.

II. MPROB CARD (Formats I3)

This card carries the problem control integers which govern the principal options in loading, execution, and printing in each problem. It must be loaded following the LABEL card in the first problem of a run, and as the first data card in subsequent problems. All entries on this card are unsigned, fixed-point integers, right shifted in fields of width three. Eight such fields, beginning with column 1, and five additional fields, beginning with column 37, are used. The following list gives the numbers to be supplied, their possible values, and the significance of each value.

Column 3

MPRO	Specifies the type of calculation to be made.
1	Shock wave(s) in the initial medium.
2	Detonation wave(s) in the initial medium.
3	Equilibrium calculation(s) only, no shock waves.

Column 6

MINC	Specifies the chemical change on the incident shock wave.
1	No chemical reaction.

2 Final composition specified by data loaded on type 03 general data card(s).

3 Equilibrium final composition.

Column 9

MREF when MPRO = 1 or 2 specifies the occurrence of, and chemical change on, reflected shock waves following each incident shock calculation.

0 No reflected shock calculations.

1 Reflected shock wave with composition the same as that behind the incident shock.

2 Reflected shock with composition specified by data loaded on type 03 general data card(s).

3 Reflected shock with equilibrium final composition.

4 Reflected shock with equilibrium final composition; independent components for equilibrium calculation specified differently for incident and reflected shocks. (Usable only if MINC = 3, Ø = 0)

MREF when MPRO = 3 specifies a set of pressures for equilibrium calculations. A set, even if it be of length one, must be specified.

1 Arithmetic progression of pressures, specified by a type 08 general data card.

2 Sequence of pressures, P, individually specified by type 09 general data card(s).

Column 12

MAVECT Specifies the number of <u>a</u>-vectors available in storage, 0, 1, 2, 3, or 4. This number is used whenever equilibrium calculations are called for.

Column 15

MITER when MPRO = 1, specifies whether shock wave calculations are to be made for a sequence of final temperatures, shock velocities, or particle velocities. A sequence, even if of length one, must be specified.

Care must be used in specifying such series for exothermically reactive mixtures. Temperatures for which $v>v_o$ are automatically increased five percent, as many as fifty times if need be, until a solution is obtained for u_s. Shock velocities for which a solution cannot be found are rejected, and the next value in the sequence is tried. When two solutions exist for a given u_s, either one may be obtained, although the higher temperature one is favored by the code's trial values.

1	Arithmetic progression of final temperatures, T, specified by a type 06 general data card.
2	Sequence of final temperatures, T, individually specified by type 07 general data card(s).
3	Arithmetic progression of shock velocities, u_s, specified by a type 08 general data card.
4	Sequence of shock velocities, u_s, individually specified by type 09 general data card(s).
5	Arithmetic progression of particle velocities, u_p, specified by a type 08 general data card.
6	Sequence of particle velocities, u_p, individually specified by type 09 general data card(s).

MITER when MPRO = 2, specifies the choice of a set of initial conditions, temperatures or pressures, for a sequence of detonation calculations. A sequence, even if of length one, must be specified.

1 Arithmetic progression of initial temperatures, T_o, specified by a type 06 general data card.

2 Sequence of initial temperatures, T_o, individually specified by type 07 general data card(s).

3 Arithmetic progression of initial pressures, P_o, specified by a type 08 general data card.

4 Sequence of initial pressures, P_o, individually specified by type 09 general data card(s).

MITER when MPRO = 3, specifies the choice of a set of temperatures, T, for a sequence of equilibrium calculations. A sequence, even if of length one, must be specified.

1 Arithmetic progression of temperatures, T, specified by a type 06 general data card.

2 Sequence of temperatures, T, individually specified by type 07 general data card(s).

<u>Column 18</u>

MCONC controls optional printing of molar concentrations, $\underline{C}_t$.

$\underline{C}_t = x_t \frac{n_{gas}}{M_o v}$ for shock and detonation problems.

(MPRO = 1 or 2.) Solid, if present, is treated as dispersed in the gas.

$\underline{C}_t = x_t$ P/RT for equilibrium problems (MPRO = 3).

	In this case, concentrations are based on the gas volume, and if $\underline{p} = 1$, $\underline{C}_s$ should be ignored.
0	Concentrations not printed.
1	Concentrations printed.

Column 21

MALPHA	Controls loading of α-matrix cards.
0	No α-matrix cards to be loaded.
1	$\underline{s}$ α-matrix cards to be loaded.

Column 24

MA	Specifies the number of $\underline{a}$-vectors, 0, 1, 2, 3, or 4, to be loaded on $\underline{a}$-vector card(s).

Column 39

$\underline{c}$	The number of independent components for equilibrium computations, which must also equal the number of nonzero columns in the α-matrix. (See Appendix A, Example 3.) $\underline{c} \leq 6$.

Columns 40-42

$\underline{s}$	The number of species in the system for shock wave and/or equilibrium computations. $\underline{s} \leq 100$

Column 45

$\underline{p}$	Phase control integer discussed in Section 1.5. The value of $\underline{p}$ loaded here is used when $\phi = 0$.
0	One phase present, a mixture of ideal gases.

1	Two phases present, second phase a pure species. A negative value of x_s may be obtained, indicating an artificial solution.

Column 48

p'	Trial value for p, used for first calculation when $\phi = 1$. Subsequent calculations use the value of p from the previous calculation as the trial value.
0	One-phase system tried first.
1	Two-phase system tried first.

Column 51

ϕ	Controls use of the evaporation-saturation test to determine p.
0	p used as loaded.
1	p determined by code. When this option is used, the code must have at least one equilibrium equation to consider in addition to the question of saturation; thus s must be at least three. If $p = 0$ is determined, the printed values of x_s and C_s are artificial and should be negligibly small.

III. α-MATRIX CARDS

These cards carry the chemical symbol, the molecular weight, enthalpy data for a range of initial temperatures, and the chemical formula of each species. A system of s species requires s such cards. These must follow the MPROB card and be loaded when MALPHA = 1. The order of species used for loading and printing data throughout the problem is determined by the order of the α-matrix cards. Data loaded by these cards are retained and are available for use in subsequent problems. The entries on the $\underline{t}^{th}$ card are given below:

Columns 1-6, Species Symbol (Format A6)

Hollerith characters loaded here are printed as the $\underline{t}^{th}$ entry in the ordered list of species in the system, and serve to label the rows of other data for that species.

Columns 7-12, Molecular Weight (Format F6.3)

The molecular weight of the $\underline{t}^{th}$ species is entered as a fixed-point number with the decimal point assumed to be between the third and fourth positions in the field. Zeros to the right of the decimal point should be entered. The molecular weight is used in shock and detonation wave problems to compute M_o, as defined in equation (9). It is used only for those species with nonzero x_{t_o}, and need not be entered for other species, if the user so chooses.

Columns 13-60, Initial Enthalpy Coefficients (Formats E12.7)

The polynomial coefficients for the molar enthalpy of the $\underline{t}^{th}$ species in the range of initial temperatures for shock and detonation wave problems are entered in four fields of width twelve. These coefficients are defined in equation (18), and are entered in the order d_t, c_t, b_t, a_t, as signed, eight-digit, floating-point numbers with the decimal point assumed to be to the right of the first digit. The unit of enthalpy in equation (18) is calories per gram mole; the unit of temperature is °K. For species which will not be included in the initial gas mixture, these fields may be left blank.

Columns 61-72, The α-matrix (Formats I2)

Six fields of width two are provided for entering the coefficients of up to $\underline{c} = 6$ independent elements in the chemical formula for the $\underline{t}^{th}$ species, i.e., the $\underline{t}^{th}$ row of the α-matrix. These data are needed for all equilibrium computations. The element represented by each field is fixed by the user, and should correspond to the labelling in columns 1-18 of the LABEL card. When fewer than six elements are involved in the system, any $\underline{c}$ fields, not necessarily consecutive, may be selected for use. The remaining $(6 - \underline{c})$ fields may be zero or blank for all species; such superfluous columns are automatically omitted from the printed output. The numbers in the α-matrix are entered as fixed-point integers, right shifted in their fields. Zeros should be punched to avoid -0's appearing in the printout. Positive signs need not be punched. Negative signs may be used; they are useful in ionization and restricted equilibrium problems, as discussed in Appendix A.

IV. $\underline{a}$-VECTOR CARDS (Formats I3)

These cards carry the elements, $\underline{a}_t$, of the renumbering vectors by which are designated the independent component species for equilibrium computations. (See Section 1.6.) Each $\underline{a}$-vector consists of $\underline{s}$ ordered positive integers, which are loaded as unsigned fixed-point numbers, right shifted in up to twenty-four consecutive fields of width three per card. Each a-vector begins with the first field of a card and when $s \leq 24$, is completely contained on that card. Unused fields at the right of a card are left blank. Loading is controlled by the values of s and MA, and the block of a-vectors must be loaded following any α-MATRIX cards whenever MA > 0. Data so loaded are retained for subsequent problems if not replaced.

For a given set of s chemical species composed of c independent elements, any of several selections of component species which will satisfy the requirement of independence are normally possible. As a practical requirement of the code, however, these must be selected so that their mole fractions in the equilibrium solution will exceed a minimum value, presently set at 1.0×10^{-6}. This requirement often restricts the usefulness of a-vectors to particular ranges of temperature, pressure, or composition conditions, and occasionally precludes equilibrium calculations in precisely stoichiometric mixtures at low temperatures.

For this reason, provision is made for the user to supply alternate a-vectors, to be used should the original selection prove inadequate during the course of the problem. Space is provided for as many as four a-vectors. For most problems (MREF < 4, Ø = 0) only one is needed, and only two are available. For MREF = 4 or for Ø = 1, two a-vectors are needed, and alternates for each are available. The selection of a-vectors under the various options is summarized in tabular form on the following page.

a-VECTOR SELECTION

Ø	MPRO	MINC	MREF	MAVECT			
				1	2	3	4
0	3 1 or 2	ignored 3 and/or	1 or 2 3	a1	a1 (or a2)	a1 (or a2) a3 not used	a1 (or a2) a3 and a4 not used
0	1 or 2	3	4	should not be used	a1 used on incident shock a2 used on reflected shock	a1 (or a3) used on incident shock a2 used on reflected shock	a1 (or a3) used on incident shock a2 (or a4) used on reflected shock
1	3 1 or 2	ignored 3 and/or	1 or 2 3	not permitted	a1 used for two-phase system a2 used for gaseous system	should not be used	a1 used for two-phase system a2 used for gaseous system (or a3 used for two-phase system a4 used for gaseous system)

For two-phase systems, there are the following additional requirements on the $\underline{a}$-vectors. When $\phi = 0$, $\underline{p} = 1$, it is required that all $\underline{a}_s = \underline{c}$. When $\phi = 1$, it is required that $\underline{a1}_s = \underline{c}$, $\underline{a2}_s = \underline{s}$, and, if the alternate set be used, $\underline{a3}_s = \underline{c}$, $\underline{a4}_s = s$.

V. GENERAL DATA CARDS (Formats 7E10.5, I2)

All data not prescribed in the foregoing special formats are loaded in a general floating-point format. These general data cards are loaded following the special format cards, and a variable number of such cards may be included with each problem. Data are loaded in the general data format as signed, six-digit, floating-point numbers with the decimal point assumed to be to the right of the first digit, viz., ±XXXXXX±EE. Fields for seven such numbers occupy columns 1-70, and the type of data being loaded is prescribed by a load control integer, an unsigned fixed-point number having a value between one and ten, punched in columns 71-72. Data are loaded field by field. When a blank field is encountered, no further data are read from that card; when a card with the first field blank is encountered, no further data are read for that problem.

The data associated with each load control integer are enumerated below:

TYPE 01, THERMO

These cards, which contain the digits 01 in columns 71-72, carry the constants from which the molar thermodynamic functions for each species are computed by equations (17), (19), and (20) in the temperature range of the equilibrium and final shock solutions. The unit of enthalpy in equation (17) is calories per gram mole. The left hand sides of equations (19) and (20) are dimensionless; the unit of temperature on the right hand sides is °K. A system of s species uses data from s type 01 cards; the order of cards must match that of the α-MATRIX cards. The t^{th} such card contains, in order, the quantities E_t, D_t, C_t, B_t, A_t, k_t, and $(\Delta H_{f_o})_t$, for the t^{th} species. These data are retained for use in subsequent problems if not replaced. Since only one set of these quantities is available in a problem, its range of validity must include the temperatures of both incident and reflected shock waves, when reflected shocks are being considered.

TYPE 02, XCOMPO

On these cards, which contain the digits 02 in columns 71-72, are loaded the ordered list of initial mole fractions, x_{t_o}, for use in shock and detonation wave problems. For equilibrium problems, (MPRO = 3), the formal composition of the system may be loaded in this way, or use may be made of the type 10 card. The sum of the s values of x_{t_o} must be unity, to within one part in 10^5, or problems with $MPRO < 3$ will be rejected. This block of data is retained for subsequent problems if not replaced. Clearly, zeros must be loaded when they occur between nonzero values in the list; zeros at the end of the list need not be loaded, unless they should be needed to overwrite values retained from a previous problem. Thus when s is large, it is well to order the species so that those having nonzero x_{t_o} appear early.

TYPE 03, XMOLE

These cards, which contain the digits 03 in columns 71-72, are used to load the final composition in shock and detonation problems having MINC and/or MREF equal to 2. The quantities loaded are the ordered list of mole numbers, n_t, defined in Section 1.5. These data are retained for use in subsequent problems, and the same precautions apply as in the case of XCOMPO data.

The numbers n_t are readily generated for arbitrary extents of specific chemical reactions by equating the original mole fractions, x_{t_o}, to original mole numbers, n_{t_o}, and adding or subtracting from these numbers by the ordinary rules of stoichiometry. The resulting values of n_t will not, in general, sum to unity, but they will represent the proper mass of material, namely M_o grams. Equation (16) remains satisfied when a proper set of n_t values are substituted for x_{t_o}.

TYPE 04, XCOMP

These cards, which contain the digits 04 in columns 71-72, are used to load estimates of the mole fractions, x_t, to be used in the initial cycle of the iteration in chemical equilibrium computations. Such data are not retained; rather, the results of the preceding computation are used to begin the iteration in each succeeding computation. On entry to each new problem, all x_t estimates are set to 0.1, which value may be replaced, in sequence, by values loaded by type 04 general data cards. In fact, only the estimated mole fractions for the independent component species are used, the remaining values, whether 0.1 or some value specified by the user, are superfluous. In practice, most problems are solved successfully, though perhaps less efficiently, with the initial estimates of the x's of 0.1, and use of the type 04 card is seldom necessary.

TYPE 05, CONDO

This card, with the digits 05 in columns 71-72, is used to load a collection of data specifying initial conditions, the molar volume of a solid $\underline{s}^{th}$ species, and a trial value of temperature to be used in detonation and certain shock wave calculations.

In the first field is loaded the initial temperature, T_o, in °K, for all shock problems (MPRO = 1) and those detonation problems (MPRO = 2) with MITER > 2. The value loaded is retained for subsequent problems if not replaced.

In the second field is loaded the initial pressure, P_o, in atmospheres, for all shock problems (MPRO = 1) and those detonation problems (MPRO = 2) having MITER < 3. The value loaded is retained for subsequent problems if not replaced.

In the third field may be loaded the value of the specific volume, v_o, in cc/gram, of the initial medium for a shock wave or detonation problem. The value of v_o is normally computed internally by equation (9), and this is done unless a value other than zero is loaded by the user. For special problems involving initial media other than mixtures of ideal gases, v_o may be obtained externally and loaded. A value so loaded is used only in the problem for which it is loaded, and zeroed before a new problem is entered.

In the fourth field may be loaded the value of the specific enthalpy, h_o, in calories per gram, of the initial medium for a shock or detonation wave problem. The value of h_o is normally computed internally by equations (10),(17), and (18), and this is done unless a value other than zero is loaded by the user. This loading option is useful for nonideal gas mixtures and for shocks into media outside the normal range of ambient temperatures where the coefficients in equation (18) are valid, e.g., the gas behind another shock wave. A loaded value of h_o is used only in the problem for which it is loaded, and is zeroed before a new problem is entered.

In the fifth field is loaded the molar volume of a solid $\underline{s}^{th}$ species, V_s, in cc/gram mole. This value is used only for two-phase problems; it is retained for use if called for in subsequent problems.

In the sixth field may be loaded an estimated value of the final temperature, T, in °K, for detonation problems (MPRO = 2) or shock problems (MPRO = 1) in which a particular velocity condition is specified (MITER > 2). If no estimate is loaded, a value of $T = 10T_o$ is used for the first trial. The first value is altered by

100°K, in the appropriate direction, for the second trial before the linear feedback routine is entered. For some problems, such as detonations in highly diluted mixtures, these values may be inappropriate, and the user may need to supply a more appropriate trial value. A loaded value is not retained, but is zeroed before a new problem is entered.

TYPE 06, TEMPR

This card, containing the digits 06 in columns 71-72, is used to load data specifying an arithmetic progression of temperatures, $T_i = T_1 + (i - 1) \Delta T$, $i = 1, \ldots N_6$. The first field contains N_6, an integer loaded as a floating-point number. The second field contains T_1, in °K; the third field contains ΔT, likewise in °K, which may be positive or negative. Values loaded by this card are retained for subsequent problems if not replaced.

It is often well, in cases where shock wave solutions may not exist at low temperatures, or where the equilibrium computation may encounter difficulties at the lowest temperatures, to run the sequence in order of decreasing temperature.

TYPE 07, TEMPS

These cards, which contain the digits 07 in columns 71-72, are used to specify an arbitrary sequence of as many as twenty temperatures, T_i, $i = 1, \ldots N_7$. The first field contains the value of N_7, an integer loaded as a floating-point number. Succeeding fields contain the temperatures, in °K. Values loaded on these cards are retained for subsequent problems.

TYPE 08, VELR

This card, which contains the digits 08 in columns 71-72, is used to load data specifying an arithmetic progression of velocities or pressures,

$u_i = u_1 + (i - 1)\Delta u$, or $P_i = P_1 + (i - 1)\Delta P$, $i = 1, \ldots N_8$.

The first field contains the number N_8, an integer loaded as a floating-point number. The second field contains u_1, in cm/sec, or P_1, in atmospheres. The third field contains the value of Δu or ΔP in the above units, and may be positive or negative. Data loaded by this card are retained for subsequent problems.

TYPE 09, VELS

These cards, which contain the digits 09 in columns 71-72, are used to specify an arbitrary sequence of as many as twenty velocities or pressures, u_i or P_i, $i = 1, \ldots N_9$. The first field contains the number N_9, an integer loaded as a floating-point number. The succeeding fields contain the individual values of u, in cm/sec, or P, in atmospheres. Data loaded by these cards are retained for subsequent problems if not replaced.

TYPE 10, QATOM

This card, which contains the digits 10 in columns 71-72, may be used to load the elemental composition of the system, Q_i, $i = 1, \ldots \underline{c}$, for use in equilibrium computations. This is done by loading in $\underline{c} \leq 6$ consecutive fields the values of Q for the chemical elements having nonzero columns of the α-matrix. Values so loaded are used for all equilibrium calculations within the problem for which they are loaded, and are discarded before subsequent problems are entered.

Normally the Q_i are computed internally from the initial mole fractions, x_{t_o}, and the α-matrix by equation (16), in order that the initial and final volumes and enthalpies computed for shock problems be for the same mass of material. However, for pure equilibrium problems, (MPRO = 3), the initial conditions are not relevant, and for these problems and for certain restricted equilibrium problems discussed in Appendix A, the user may wish to load the Q_i.

TABLE I

INPUT DATA SUMMARY

IVY FORM II

PROGRAMMER PROBLEM CODE HUG DATE PAGE 1 of 3

1–6	7–12	13–18	19–24	25–30	31–36	37–42	43–48	49–54	55–60	61–66	67–72	73–80
ELEMENT LABELS			A-VECTOR LABELS		CP(1)		CT(1)	CR(1)		CD(1)		LABEL
HOL HOL	HOL HOL	HOL HOL	HOL HOL	HOL HOL	+ X · XX − EE		+ X · XX − EE	+ X · XX − EE		+ X · XX − EE		
MPRO MINO	MREF MAVECT	MITER MCONC	MALPHA MA			c s	p p'	ø				MPROB
X X	X X	X $\genfrac{}{}{0pt}{}{1}{0}$	$\genfrac{}{}{0pt}{}{1}{0}$ X			X XXX	$\genfrac{}{}{0pt}{}{1}{0}$ $\genfrac{}{}{0pt}{}{1}{0}$	$\genfrac{}{}{0pt}{}{1}{0}$				
SPECIES	MOL WT	d_t		c_t		b_t		a_t		α_{t1} α_{t2} α_{t3}	α_{t4} α_{t5} α_{t6}	α-MATRIX
HOL	XXX.XXX	± X.XXXX	XXX ± EE	± X.XXXX	XXX ± EE	± X.XXXX	XXX ± EE	± X.XXXX	XXX ± EE	XX XX XX	XX XX XX	
Al_1 Al_2	··· ···	Al_t ···	··· Al_s									A-VECTORS
XXX XXX	··· ···	XXX ···	··· XXX									
$A2_1$ $A2_2$	··· ···	$A2_t$ ···	··· $A2_s$									
XXX XXX	··· ···	XXX ···	··· XXX									

TABLE I (continued)

80 COLUMN ENTRY

PROGRAMMER
PROBLEM HUG
DATE
PAGE 2 OF 3

1 – 10	11 – 20	21 – 30	31 – 40	41 – 50	51 – 60	61 – 70	71	73 – 80
E_t	D_t	C_t	B_t	A_t	k_t	H^o_{0t}	01	THERMO
±X.XXXXX±EE	±X.XXXXX±EE	±X.XXXXX±EE	±X.XXXXX±EE	±X.XXXXX±EE	±X.XXXXX±EE	±X.XXXXX±EE	01	
x_{1o}	x_{2o}	. . .	x_{to}	. . .	x_{so}		02	XCOMPO
+X.XXXXX-EE	+X.XXXXX-EE	. . .	+X.XXXXX-EE	. . .	+X.XXXXX-EE		02	
n_1	n_2	. . .	n_t	. . .	n_s		03	XMOLE
+X.XXXXX±EE	+X.XXXXX±EE	. . .	+X.XXXXX±EE	. . .	+X.XXXXX±EE		03	
x_1 guess	x_2 guess	. . .	x_t guess	. . .	x_s guess		04	XCOMP
+X.XXXXX-EE	+X.XXXXX-EE	. . .	+X.XXXXX-EE	. . .	+X.XXXXX-EE		04	
T_o	P_o	v_o (optional)	h_o (optional)	V_s	T_{guess} (optional)		05	CONDO
+X.XXXXX+EE	+X.XXXXX±EE	+X.XXXXX±EE	±X.XXXXX±EE	+X.XXXXX±EE	+X.XXXXX+EE		05	
N_6	T_1	ΔT					06	TEMPR
+X.XXXXX+EE	+X.XXXXX+EE	±X.XXXXX±EE					06	
$N_7 \leq 20$	T_1	T_2	. . .	. . .	. . .	T_6	07	TEMPS
+X.XXXXX+0$^{1}_{0}$	+X.XXXXX+EE	+X.XXXXX+EE	. . .	. . .	. . .	+X.XXXXX+EE	07	
T_7	. . .	. . .	T_{N_7}				07	TEMPS
+X.XXXXX+EE	. . .	. . .	+X.XXXXX+EE				07	

TABLE I (continued)

80 COLUMN ENTRY

PROGRAMMER PROBLEM HUG DATE PAGE 3 OF 3

1 5 6 10	11 15 16 20	21 25 26 30	31 35 36 40	41 45 46 50	51 55 56 60	61 65 66 70	71	73 80
N_8	P_1 or u_1	ΔP or Δu					08	VELR
+X.XXXXX+EE	+X.XXXXX±EE	±X.XXXXX±EE					08	
$N_9 \leq 20$	P_1 or u_1	P_2 or u_2	. . .	. . .	. . .	P_6 or u_6	09	VELS
+X.XXXXX+0$\overset{1}{0}$	+X.XXXXX±EE	+X.XXXXX±EE	. . .	. . .	. . .	+X.XXXXX±EE	09	
P_7 or u_7	. . .	. . .	P_{N_9} or u_{N_9}				09	VELS
+X.XXXXX±EE	. . .	. . .	+X.XXXXX±EE				09	
Q_1	Q_2	. . .	Q_c				10	QATOM
±X.XXXXX±EE	±X.XXXXX±EE	. . .	±X.XXXXX±EE				10	

2.2 OUTPUT SPECIFICATIONS

Data to be printed as output are processed by the instructions WRITE OUTPUT TAPE IO, etc. The value of IO is assigned in the main program. The value 9 is used at LASL.

The initial page of output for each problem contains the input and control data, appropriately labelled, and the results of certain preliminary computations. The numbers of gram atoms of the elements, Q_i, are printed in the order of the nonzero columns of the α-matrix. QBAR is a vector expressing the composition of the system as formal mole fractions of the independent component species. NUMAT is a matrix similar to the α-matrix which expresses by formula coefficients the chemical formulas of the dependent components in terms of those of the independent ones. QBAR and NUMAT are computed internally from the composition, the α-matrix, and the $\underline{a}$-vectors.

The results of shock or detonation wave problems, reflected shock problems, and equilibrium problems are printed as unlabelled blocks of data for each point in the problem. The formats of these blocks are given on the following pages.

SHOCK AND DETONATION CALCULATIONS

The following block of data is listed for each point.

$T(^\circ K)$	$P(atm)$	$T_o(^\circ K)$	$P_o(atm)$	n_{gas}	n_{solid}	
$u_s(cm/sec)$	$u_p(cm/sec)$	δ_P	δ_T	0	δ_D	
T/T_o	P/P_o	$v_o/v = \rho/\rho_o$	n_{gas}	$v(cc/gm)$	$h(cal/gm)$	
x_{1_o}	x_{2_o}		...	...		x_{7_o}
x_{8_o}	...	x_{s_o}				
x_1	x_2		...	...		x_7
x_8	...	x_s				
$\underline{C}_1$ $(\frac{\text{gm mole}}{\text{liter}})$	$\underline{C}_2$		...	...		$\underline{C}_7$
$\underline{C}_8$	...	$\underline{C}_s$				

REFLECTED SHOCK CALCULATIONS

The following block of data is listed following the incident wave data for each point.

u^*_s(cm/sec)	T'/T_o	P'/P_o	$v_o/v'=\rho'/\rho_o$	n'_{gas}		
T'(°K)	P'(atm)	T(°K)	P(atm)	n'_{gas}	n'_{solid}	
u'_s(cm/sec)	u'_p(cm/sec)	δ'_P	0	δ'_R	0	
T'/T	P'/P	$v/v'=\rho'/\rho$	n'_{gas}/n_{gas}	v'(cc/gm)	h'(cal/gm)	
x_1	x_2		...	...		x_7
x_8	...	x_s				
x'_1	x'_2		...	...		x'_7
x'_8	...	x'_s				
$\underline{C}'_1$ $\left(\frac{\text{gm mole}}{\text{liter}}\right)$	$\underline{C}'_2$		...	...		$\underline{C}'_7$
$\underline{C}'_8$	...	$\underline{C}'_s$				

EQUILIBRIUM CALCULATIONS

The following block of data is printed for each point.

T(°K)		P(atm)	n_{gas}		n_{solid}	
x_1	x_2	...	...	...	...	x_7
x_8	...	x_s				
$\underline{C}_1$ $(\frac{\text{gm mole}}{\text{liter}})$	$\underline{C}_2$	...	...	...	...	$\underline{C}_7$
$\underline{C}_8$	...	$\underline{C}_s$				

2.3 OPERATION

Assuming proper specification of input, there should be no machine stops. For many errors in input and for some other difficulties, the code will write a note briefly describing the difficulty and then proceed to the next problem. A machine stop will occur if a supposedly independent set of components are not, in fact, independent.

The make-up of a deck for a MONITOR run is as follows:

*DATE card (if desired)

*ID card

*XEQ card

Other MONITOR control and comment cards as desired

Binary deck

*DATA card

LABEL card

MPROB card

α-MATRIX cards (essential for first problem - require MALPHA = 1)

$\underline{a}$-VECTOR cards (as necessary when MA > 0)

THERMO cards

Other general DATA cards as needed. Order of type of card is not important; order within type may be.

Blank card

Subsequent problems starting with MPROB card and ending with a blank card

End of file card (7 and 8 punch in column 1)

---

*Indicates MONITOR control cards.

APPENDIX A

EXAMPLES OF APPLICATIONS OF THE EQUILIBRIUM CODE

EXAMPLE 1. A System of Gaseous Molecules

Consider the gaseous system composed of atomic and molecular oxygen and the oxides of carbon, with a known initial composition. Let the second column in the table below contain the list of species. The column headings of the third and fourth columns are the chemical elements, and the entries in these columns are the α-matrix.

x_o	species \ elements	C	O	$\underline{a}1$	$\underline{a}2$
0	O	0	1	3	1*
0.50	O_2	0	2	1*	3
0.50	CO	1	1	4	2*
0	CO_2	1	2	2*	4
	Q	0.5	1.5		

---

*denotes species chosen as independent

In this system, $\underline{c} = \underline{c}' = 2$, and $\underline{s} = 4$. The initial composition of the system is indicated by the first column, labelled x_o, and the elemental composition is indicated by the final row labelled Q.

The selection of independent species, from which the set of independent stoichiometric reactions follows, can be made in any of several (in this case, five) ways. The obvious restrictions are that at least one species containing each element must be included, and that both 0 and 0_2 may not be included, since these two species have rows in the α-matrix which are multiples of one another. (In this example, these conditions are redundant; in general they need not be.) The selection made by the $\underline{a}$-vector in column five, labelled $\underline{a1}$, specifies 0_2 and CO_2 as independent. The derived ν-matrix and normalized q-vector for this $\underline{a}$-vector are shown below.

independent species dependent species	0_2	CO_2
0	0.5	0
CO	-0.5	1
$\bar{q}$	0.333	0.667

This formulation of the equilibria might be appropriate for temperatures near 2000°K, at atmospheric pressure, where most of the carbon in the system would be CO_2 and very little 0 atom would be present at equilibrium. The second $\underline{a}$-vector, $\underline{a2}$, might be more appropriate at much higher temperatures.

EXAMPLE 2. A System Containing One Solid Species

Consider the carbon-oxygen system of Example 1 with an elemental composition in which carbon is in excess. In addition to the four oxygen-containing species, let us also include gaseous monatomic carbon, C(gas), and solid carbon, C(s), and consider the possibility that C(s) may or may not all evaporate at equilibrium. Let the α-matrix, a-vectors, and composition be given in a table like that used in Example 1.

elements species	C	O	a1	a2
O	0	1	4	3
O_2	0	2	5	4
CO	1	1	1*	1*
CO_2	1	2	6	5
C(gas)	1	0	3	2*
C(s)	1	0	2*†	6†
Q	1.00	0.98		

---

*denotes species chosen as independent
†choice dictated by code

In order that its free energy function be handled properly (by equation 22), the solid species, C(s), must be listed last in the α-matrix. No initial mole fractions have been shown, since the Q-vector is sufficient for equilibrium computations, and since it is difficult to imagine a system of this atomic composition being gaseous at ambient temperatures.

For the code to determine whether the system consists of one or two phases at equilibrium, it must be supplied specifications for both possibilities. The control constants to be supplied are $\emptyset$, which must be 1, and $\underline{p}'$, which may be zero or one. Two specifications of the independent components are needed. The specification for the two-phase solution is required by the code to have the solid species as the $\underline{c}^{th}$ independent component; the $\underline{a}$-vector labelled $\underline{a}1$ is used for this case, and hence has $\underline{a}1_6 = \underline{c} = 2$. The specification for the one-phase solution must have the solid species as the last dependent species; the $\underline{a}$-vector $\underline{a}2$ is used for this case, and hence has $\underline{a}2_6 = \underline{s} = 6$. There are no other required relationships between the pair of $\underline{a}$-vectors; the choices of CO as an independent component in both cases, and of C(gas) as the second component in $\underline{a}2$, are based on the desire to use species which will be present in appreciable mole fraction at equilibrium in this oxygen deficient system.

The two-phase trial solution is obtained without regard to the value of n_{solid}, and it is accepted or rejected depending on whether n_{solid} is found to be positive or negative. The one-phase trial solution is obtained by treating the solid as a gas having an artificially high value of $F_s^\dagger$, thereby limiting the system to the first $(\underline{s} - 1)$ species. It is accepted or rejected depending on whether or not the mole fractions obtained are compatible with the two-phase equilibria. If the trial solution is accepted, the calculation is finished; if not, the other case is solved and accepted automatically. Numerical difficulty can be encountered in cases where n_{solid} is large and negative or in cases which include gaseous species having very small mole fractions.

EXAMPLE 3. A System with $c < c'$

Let the system consist of the s = 5 gaseous species H_2, H, HCN, CN, and C_2N_2. c' = 3 elements are involved, and the α-matrix is then:

$$\begin{array}{l|ccc}
 & C & H & N \\
\hline
H_2 & 0 & 2 & 0 \\
H & 0 & 1 & 0 \\
HCN & 1 & 1 & 1 \\
CN & 1 & 0 & 1 \\
C_2N_2 & 2 & 0 & 2
\end{array}$$

However, neither C nor N appear in other than one to one combination, and the first and third columns are redundant. Thus c = 2 must be specified in order for the code to handle this case,and the superfluous column in the α-matrix must be omitted.

EXAMPLE 4. Ionization

Let the system consist of the s = 3 gaseous species He, He^+, and e^-. Although there is but one chemical element, in the ordinary sense, the desired equilibrium, $He \rightleftarrows He^+ + e^-$, can be treated by considering e^- to be an element whose coefficient in the formula of the positive ion, He^+, is negative. The α-matrix is then written:

x_o		He	e^-
1.0	He	1	0
0	He^+	1	-1
0	e^-	0	1
	Q	1.0	0

Let the initial gas be pure He, as indicated by the column of initial mole fractions, x_o. Since the system is electrically neutral, the resulting value of Q for the column representing e^- is zero. This is permissible since the Q's being zero does not restrict any independent component to a zero mole fraction.

The thermodynamic functions for He^+ and e^- are readily handled by assigning e^- a zero value of (ΔH_{f_o}) and a value of (ΔH_{f_o}) for He^+ equal to the ionization potential of He. Multiple ionization, negative ions, etc., are handled by simple extension of these principles.

EXAMPLE 5. Restricted Equilibria

The existing general methods[4,7,8] for treating chemical equilibria, including the Brinkley method as incorporated in the HUG code, are based on the specification of the elemental composition of each species. Hence the system is constrained only by the conservation of the chemical elements, and the initial composition is irrelevant. All stoichiometrically possible reactions are covered by the complete set of independent equilibria represented by Brinkley's ν-matrix.

It is sometimes desired to consider the conditions reached by a system when a particular group of reactions has reached equilibrium and other reactions either have not occurred or have occurred to some arbitrary extent. Provided, of course, that the independent reactions in the equilibrium group are fewer than a complete set, the non-equilibrium group is meaningful, and there are additional constraints on the system which depend on the initial conditions and/or the user's whim. To consider such a problem by the general equilibrium codes, it is necessary to introduce the additional constraints by altering the α-matrix and Q-vector.

In many cases this can be done by inspection. Thus it is trivial to simply omit from consideration a species which is not present initially and not formed by any reaction. It is nearly as simple to retain a species in the system but render it inert by adding to the α-matrix a column which contains zero in all rows except that for the particular species. This might be useful, for example, in considering equilibria among oxides of nitrogen in the presence of N_2 diluent which is to be treated as inert.

It is perfectly possible to consider systems in which each species is involved in at least one equilibrium reaction, but all possible equilibria are not allowed. A simple example is that of allowing the equilibrium $O_3 \rightleftarrows O_2 + O$ while excluding the reaction $O_2 \rightleftarrows 2O$. The required α-matrix must have $\underline{c} = 2$. The matrices given below illustrate two of the many possible ways of accomplishing this.

$$\begin{array}{c|cc} & O & "X" \\ \hline O & 1 & 0 \\ O_2 & 2 & 1 \\ O_3 & 3 & 1 \end{array} \qquad \begin{array}{c|cc} & "O" & "X" \\ \hline O & 1 & 0 \\ O_2 & 0 & 2 \\ O_3 & 1 & 2 \end{array}$$

The first of these retains the proper α-matrix and simply augments it; the second does not, but uses instead a matrix borrowed from the analogous case of $N_2O \rightleftarrows N_2 + O$.

One case of restricted equilibrium which is frequently considered in combustion and detonation problems is that in which the pressure-dependent equilibria are established, but dissociation-recombination equilibria are not. This, too, is a case where one additional constraint is needed, and it can be introduced in any system by augmenting the proper α-matrix by a column containing all ones. (Any constant would do, as would any of the sets of coefficients generated by the methods indicated by Kaskan and Schott.[9]) When the column of ones is used, it has a Q value equal to n_{gas}.

It is possible to construct augmented α-matrices for considering restricted equilibria achieved by an arbitrary mechanism of stoichiometrically bona fide reactions in an arbitrary system of species. A recipe for doing this is presented here, not so much to encourage its use in preference to construction by inspection, but to demonstrate its existence in the general case.

Let there be given the list of s species, together with the elemental composition (row of the proper α-matrix) of each, and the list of R chemical reactions to be considered, together with the stoichiometric coefficients, β_{kt}, specifying the involvement of the t^{th} species in the k^{th} reaction. Reactants and products are distinguished by sign.

Let us use the symbol $[\;]$ to denote matrices, and $[\;]\binom{n}{m}$ to indicate their dimensions, n rows and m columns. The proper α-matrix we may denote by $[\alpha_{c'}]\binom{s}{c'}$, whose rank is presumed to be equal to c'. Let the coefficients β_{kt} form the matrix $[\beta^R]\binom{R}{s}$, and let its rank be $r \leq R$. Extract r independent rows from $[\beta^R]$, and let these be denoted by $[\beta]\binom{r}{s}$. r must be less than $r' = (s - c')$ so that restrictions actually exist; the number of independent restrictions is $(r' - r)$, and this is the number of extra columns to be constructed.

Now fix the order of species in the following way. Select for the first c' species ($t = 1, \ldots c'$) a set whose rows of $[\alpha_{c'}]$ form a square matrix, $[\alpha^{j'}]$, whose determinant is not zero. Let the corresponding columns of $[\beta]$ be denoted by $[\beta_{j'}]$, and the remaining r' columns be $[\beta_{i'}]$. Select from $[\beta_{i'}]$ a group of r species whose columns form a square matrix $[\beta_i]$ whose determinant is not zero, and list these species last ($t = (s-r+1), \ldots s$). The remainder of $[\beta]$ is denoted by $[\beta_j]$.

That this can always be done is seen by observing that a reaction coefficient matrix for a complete set of r' independent stoichiometric reactions is obtained by augmenting Brinkley's matrix $[\nu](\overset{r'}{c'})$ by the negative unit matrix of dimension $\underline{r}'$ to obtain $[\nu'](\overset{r'}{s})$, and that $-[\beta_{i'}]$ is the matrix by which one multiplies $[\nu']$ on the left to obtain $[\beta]$. Since the rank of a product cannot exceed that of either factor, the rank of $[\beta_{i'}]$ is not less than $\underline{r}$.

Now the job is to construct $(\underline{r}' - \underline{r})$ additional columns to augment $[\alpha_{c'}]$ to form the final matrix, $[\alpha]$, having $\underline{c} = (\underline{s} - \underline{r})$ independent columns. Subject only to the requirement of independence, the first $\underline{c}$ rows of $[\alpha]$ can be assigned arbitrarily. Thus it is convenient to make the first $\underline{c}'$ rows of the new columns zero, and the next $(\underline{c} - \underline{c}')$ rows a diagonal (conveniently unit) matrix. The remaining $\underline{r}$ rows $(\underline{t} = (\underline{c}+1), \ldots \underline{s})$ are then determined by the relationship

$$[\alpha^i] = -[\beta_i]^{-1}[\beta_j]\,[\alpha^j],$$

where $[\beta_i]^{-1}$ is the inverse matrix of $[\beta_i]$, $[\alpha^j]$ is the first $\underline{c}$ rows of $[\alpha]$, and $[\alpha^i]$ is the last $\underline{r}$ rows of $[\alpha]$. This relationship follows from the requirement that each element be conserved by each reaction, viz. $[\beta]\,[\alpha] = 0$, and although it applies to all columns of $[\alpha]$, it need be applied only to the newly added ones. The operation involving $[\beta_i]^{-1}$ is of course simplified by operating by rows on the original $[\beta]$ until $[\beta_i]$ is the unit matrix of dimension $\underline{r}$. In order to accommodate the loading format for the α-matrix, the added columns must be cleared of fractions.

If the computation is to be restricted to states attainable from the initial composition by the equilibrium reactions only, the proper values of Q are generated by equation (16), whether the columns of $[\alpha]$ represent true chemical elements or pseudo-elements. An arbitrary nonzero extent of any nonequilibrium reactions may also be considered by using an improper set of Q's derived via equation (16) from a set of n_t's (see XMOLE CARDS) which represent the formal composition obtained by adjusting the initial composition for the arbitrary reactions. Such a set of Q's, which may be inconsistent with that based on XCOMPO data, may be used by loading it via a QATOM card. (The inconsistency arises from the restriction(s) on the allowed equilibria and does not represent a violation of the elemental mass conservation requirements.)

APPENDIX B

A LIBRARY OF THERMODYNAMIC COEFFICIENTS DERIVED FROM THE JANAF TABLES

Prepared by Charles W. Hamilton

Tables B.1-B.3 list a library of coefficients used for calculating thermodynamic functions of a number of species by equations (17)-(20). The unit of enthalpy in equations (17) and (18) is calories per gram mole; the left hand sides of equations (19) and (20) are dimensionless. The unit of temperature is °K throughout.

The JANAF tables[10] were sole reference for the enthalpies, free energies, heats of formation, and specific heats used in generating these coefficients.

Table B.1 contains the values of a, b, c, and d in equation (18) for the temperature range 200-400°K found by simultaneous solution of the four equations:

$$a + bT + cT^2 + dT^3 = H'(T), \quad T = 200, 300, 400°K$$

$$b + 2cT + 3dT^2 = C_p(T), \quad T = 300°K$$

where $H'(T) = H(T) - H(0°K)$, and C_p is the tabulated specific heat.

Tables B.2 and B.3 contain values of the coefficients in equations (19) and (20) for the two overalpping ranges of elevated temperatures, 600-3000°K and 1600-6000°K, respectively. The values of A, B, C, D, and E were found by least squares fits of equation (19) at 100° intervals. Equation (20) was then solved for k at each temperature, and the arithmetic mean value of the k's thus generated was tabulated.

Heats of formation at 0°K taken directly from the JANAF tables are also listed in tables B.2 and B.3.

TABLE B.1

SPECIES	TEMPERATURE RANGE	d	c	b	a
BF3	200-400	-6.600-06	+1.538-02	+4.673+00	+2.008+02
B2H6	200-400	+7.000-06	+1.225-02	+4.135+00	+3.240+02
HBR	200-400	+0.000+00	+5.000-05	+6.935+00	-4.900+00
BR2	200-400	-2.900-06	+3.900-03	+7.090+00	-5.690+01
HCN	200-400	-3.500-06	+7.890-03	+4.849+00	+1.574+02
CH4	200-400	+1.050-05	-5.140-03	+8.790+00	-4.490+01
CO	200-400	+1.500-06	-1.340-03	+7.370+00	-4.390+01
CO2	200-400	-7.000-06	+1.234-02	+3.409+00	+3.124+02
C2H2	200-400	-1.050-05	+1.839-02	+2.399+00	+3.244+02
C2H4	200-400	+7.400-06	+4.840-03	+5.554+00	+2.434+02
C2H4O	200-400	+1.050-05	+6.500-03	+4.775+00	+3.160+02
C2N2	200-400	-1.190-05	+1.830-02	+5.850+00	-3.490+01
C3O2	200-400	-1.640-05	+2.715-02	+3.910+00	+1.080+02
C4N2	200-400	-2.100-05	+3.224-02	+6.929+00	-1.335+02
HCL	200-400	+1.000-07	-3.000-05	+6.961+00	-9.300+00
CL2	200-400	-3.300-06	+5.210-03	+5.911+00	+5.860+01
HF	200-400	-3.000-07	+3.600-04	+6.856+00	-1.030+01
F2	200-400	-2.000-07	+2.320-03	+6.187+00	+6.720+01
SF6	200-400	-3.950-05	+6.404-02	-4.365+00	+7.144+02
HI	200-400	+1.000-07	+1.000-05	+6.936+00	-2.300+00
H2	200-400	-4.800-06	+5.360-03	+5.001+00	+1.866+02
H2O	200-400	+1.800-06	-1.060-03	+8.183+00	-2.510+01
H2O2	200-400	-3.640-05	+4.290-02	-5.554+00	+1.404+03
H2S	200-400	+2.400-06	-7.500-04	+7.984+00	+4.400+00
NH3	200-400	+4.100-06	-1.230-03	+8.021+00	+4.600+00
I2	200-400	-1.600-06	+2.230-03	+7.938+00	-1.021+02
NO	200-400	+2.800-06	-2.710-03	+8.008+00	-2.310+01
NO2	200-400	+1.800-06	+2.130-03	+7.123+00	+7.580+01
N2	200-400	+9.000-07	-8.000-04	+7.204+00	-2.750+01
N2O	200-400	-4.600-06	+9.630-03	+4.738+00	+1.458+02
N2O3	200-400	-9.100-06	+1.783-02	+8.493+00	-5.910+01
N2O4	200-400	-1.320-05	+2.712-02	+5.767+00	+1.252+02
N2O5	200-400	-1.520-05	+3.372-02	+4.677+00	+1.792+02
O2	200-400	+7.000-07	+1.700-04	+6.732+00	+3.420+01
SO2	200-400	-1.000-07	+4.530-03	+6.883+00	+7.280+01
O3	200-400	+5.000-07	+5.000-03	+6.265+00	+1.480+02
SO3	200-400	-1.790-05	+2.760-02	+5.400-01	+6.540+02

TABLE B.2

SPECIE	TEMPERATURE RANGE(K)	E	D	C	B	A	K	HEAT OF FORMATION
8F3	600-3000	-9.23984-14	+8.92944-10	-3.41175-06	+6.61146-03	+3.04282+00	+9.71172+00	-2.69327+05
B2H6	600-3000	-5.41448-14	+7.77873-10	-4.41877-06	+1.29454-02	+7.95448-01	+1.57935+01	+1.13550+04
BR	600-3000	+7.54665-15	-6.90353-11	+2.11525-07	-1.87560-04	+2.55078+00	+6.59806+00	+2.81880+04
HBR	600-3000	+2.05135-14	-1.68556-10	+4.57872-07	-2.31105-04	+3.51419+00	+3.92850+00	-6.78500+03
BR2	600-3000	-1.95390-14	+1.73497-10	-5.85796-07	+9.64361-04	+3.77809+00	+7.55097+00	+1.09220+04
C GRAP	600-3000	-4.03541-14	+3.99703-10	-1.57344-06	+3.16724-03	-4.06673-01	+1.29167+00	+0.00000+00
C	600-3000	+4.43083-15	-3.75045-11	+1.28828-07	-2.08432-04	+2.65494+00	+3.95871+00	+1.69576+05
CH	600-3000	+2.14526-14	-1.79117-10	+5.02995-07	-3.09306-04	+3.56313+00	+1.81906+00	+1.41183+05
HCN	600-3000	-1.34325-14	+1.57548-10	-8.08378-07	+2.45161-03	+3.09488+00	+5.28632+00	+3.12910+04
CH2	600-3000	+8.92650-15	-3.58601-11	-2.04674-07	+1.66520-03	+2.97910+00	+3.77530+00	+9.51800+04
CH3	600-3000	+3.06120-14	-1.76763-10	-3.63250-08	+2.36648-03	+3.21452+00	+3.37726+00	+3.28050+04
CH4	600-3000	+5.89119-14	-3.82831-10	+3.40585-07	+3.01387-03	+2.77086+00	+4.52299+00	-1.59910+04
CN	600-3000	+9.17191-15	-5.86202-11	+1.03955-07	+2.69444-04	+3.34560+00	+5.08149+00	+1.08215+05
CO	600-3000	+1.71370-14	-1.28552-10	+2.83921-07	+7.37372-05	+3.40623+00	+4.24236+00	-2.72000+04
CO2	600-3000	-3.28328-14	+3.46968-10	-1.49996-06	+3.48209-03	+2.84696+00	+7.57533+00	-9.39650+04
C2	600-3000	+1.47654-14	-1.43577-10	+5.34842-07	-7.76826-04	+4.76586+00	-2.54623+00	+1.97000+05
C2H2	600-3000	-4.73313-14	+4.66323-10	-1.93665-06	+4.74366-03	+2.93383+00	+4.95133+00	+5.43250+04
C2H4	600-3000	-1.99601-14	+3.37531-10	-2.19624-06	+7.36813-03	+1.94352+00	+1.09729+01	+1.45200+04
C2H4O	600-3000	-6.17172-14	+7.60392-10	-3.90180-06	+1.08773-02	+1.02897+00	+1.70286+01	-9.19900+03
C2N2	600-3000	-6.44233-14	+6.31962-10	-2.50562-06	+5.26621-03	+3.98156+00	+3.70827+00	+7.34280+04
C3	600-3000	-3.74102-14	+3.83795-10	-1.59968-06	+3.52516-03	+3.01929+00	+6.41669+00	+1.88104+05
C3O2	600-3000	-1.08433-13	+1.05809-09	-4.13975-06	+8.45451-03	+3.58521+00	+6.05829+00	-8.72200+03
C4	600-3000	-7.44946-14	+7.33341-10	-2.90030-06	+5.99577-03	+3.39360+00	+6.80112+00	+2.40500+05
C4N2	600-3000	-1.26619-13	+1.22541-09	-4.75425-06	+9.65455-03	+5.13670+00	+7.84399-01	+1.26341+05
C5	600-3000	-1.11693-13	+1.08338-09	-4.20121-06	+8.46555-03	+3.76858+00	+4.22870+00	+2.40298+05
CLATOM	600-3000	-1.59968-14	+1.36179-10	-4.19799-07	+5.22303-04	+2.43303+00	+5.74656+00	+2.85200+04
HCL	600-3000	+1.97418-14	-1.67206-10	+4.77840-07	-3.05374-04	+3.54634+00	+2.39200+00	-2.19260+04

TABLE B.2 (continued)

SPECIE	TEMPERATURE RANGE(K)	E	D	C	B	A	K	HEAT OF FORMATION
CL2	600-3000	-2.36331-14	+2.16536-10	-7.56085-07	+1.29644-03	+3.44690+00	+6.54358+00	+0.00000+00
F ATOM	600-3000	-1.77241-15	+1.01278-11	-3.76671-09	-8.10732-05	+2.70335+00	+3.76286+00	+1.83570+04
HF	600-3000	+7.38136-15	-7.96036-11	+2.96026-07	-2.65164-04	+3.55824+00	+7.60438-01	-6.44880+04
F2	600-3000	-1.99020-14	+1.89362-10	-7.06522-07	+1.37062-03	+3.19683+00	+5.42119+00	+0.00000+00
SF6	600-3000	-3.32181-13	+3.03508-09	-1.06984-05	+1.83727-02	+2.99034+00	+8.90829+00	-2.85173+05
H ATOM	600-3000	+3.62336-17	-2.34719-13	+4.71637-10	-2.33148-07	+2.49982+00	-4.58866-01	+5.16320+04
HI	600-3000	+1.83249-14	-1.40763-10	+3.30412-07	+1.57415-05	+3.42130+00	+5.26696+00	+6.82000+03
OH	600-3000	+1.42218-14	-1.35440-10	+4.55607-07	-4.46839-04	+3.68894+00	+1.31919+00	+9.27300+03
H2	600-3000	+8.68355-16	-2.75719-11	+1.53176-07	-9.36507-05	+3.47263+00	-4.01752+00	+0.00000+00
H2O	600-3000	+2.64412-14	-2.30231-10	+6.43343-07	-6.41383-05	+3.94115+00	+1.87784-01	-5.71030+04
H2O2	600-1500	-2.38884-13	+1.45302-09	-3.69035-06	+5.53996-03	+2.93402+00	+8.36393+00	-3.10250+04
H2S	600-3000	+3.10673-14	-2.28434-10	+4.39690-07	+6.03117-04	+3.71973+00	+3.07175+00	-4.11900+03
NH3	600-3000	+3.70942-14	-2.80057-10	+5.11530-07	+1.21661-03	+3.51525+00	+2.23008+00	-9.36200+03
I ATOM	600-3000	-2.41748-15	+1.74847-11	-3.25909-08	+2.32499-05	+2.49412+00	+7.50894+00	+2.56330+04
I2	600-3000	-1.46377-14	+1.29369-10	-4.33550-07	+7.19088-04	+3.98666+00	+8.31200+00	+1.56600+04
N ATOM	600-3000	+4.12954-16	-2.26639-12	+4.39172-09	-3.41150-06	+2.50072+00	+4.17824+00	+1.12520+05
NO	600-3000	+1.90247-14	-1.42734-10	+3.26067-07	-1.05055-05	+3.58832+00	+4.79145+00	+2.15280+04
NO2	600-3000	-2.52188-14	+2.79915-10	-1.25626-06	+2.92903-03	+3.21308+00	+8.85341+00	+8.73400+03
N2	600-3000	+1.89199-14	-1.47941-10	+3.62019-07	-6.03801-05	+3.45230+00	+3.33369+00	+0.00000+00
N2O	600-3000	-3.75519-14	+3.86735-10	-1.61787-06	+3.57639-03	+2.94380+00	+7.74846+00	+2.03200+04
N2O3	600-3000	-9.99246-14	+9.75034-10	-3.78708-06	+7.55217-03	+4.64171+00	+6.83598+00	+2.15560+04
N2O4	600-3000	-1.54887-13	+1.50076-09	-5.76511-06	+1.12949-02	+3.85060+00	+8.69588+00	+4.59300+03
N2O5	600-3000	-2.08295-13	+2.00606-09	-7.63812-06	+1.47644-02	+3.44607+00	+1.07096+01	+6.15300+03
O ATOM	600-3000	+6.21177-15	-5.58499-11	+1.94773-07	-3.30694-04	+2.78223+00	+3.66962+00	+5.89890+04
O2	600-3000	-6.03317-16	+2.73207-11	-2.03042-07	+7.34250-04	+3.21760+00	+5.85704+00	+0.00000+00
SO2	600-3000	-4.00657-14	+4.00531-10	-1.59710-06	+3.30088-03	+3.34425+00	+8.96833+00	-7.03410+04
O3	600-3000	-5.26852-14	+5.09013-10	-1.93984-06	+3.76115-03	+3.15341+00	+8.70233+00	+3.47390+04
SO3	600-3000	-9.70086-14	+9.31015-10	-3.52419-06	+7.22561-03	+2.83785+00	+1.08113+01	-9.30760+04

TABLE B.3

SPECIE	TEMPERATURE RANGE(K)	E	D	C	B	A	K	HEAT OF FORMATION
BF3	1600-6000	-5.04825-15	+9.63934-11	-7.15269-07	+2.59641-03	+5.26019+00	-5.13226-01	-2.69327+05
B2H6	1600-6000	-1.54261-14	+3.03154-10	-2.34734-06	+9.11196-03	+3.33896+00	+3.63961+00	+1.13550+04
BR	1600-6000	-2.17885-16	+5.61566-12	-5.42161-08	+2.26637-04	+2.31285+00	+7.70376+00	+2.81880+04
HBR	1600-6000	-5.39381-16	+1.20036-11	-1.08772-07	+5.39179-04	+3.13148+00	+5.65029+00	-6.78500+03
BR2	1600-6000	-4.45062-16	+8.33189-12	-6.00690-08	+2.34126-04	+4.15221+00	+5.85440+00	+1.09220+04
C GRAP	1600-6000	-2.66813-15	+5.08496-11	-3.72295-07	+1.34548-03	+6.18844-01	-3.45695+00	+0.00000+00
C	1600-6000	+1.87066-16	-4.61230-12	+3.94596-08	-1.10584-04	+2.62088+00	+4.09580+00	+1.69576+05
CH	1600-6000	-4.42944-16	+1.03191-11	-9.79987-08	+5.18720-04	+3.14494+00	+3.70793+00	+1.41183+05
HCN	1600-6000	-2.60066-15	+5.27223-11	-4.27984-07	+1.84028-03	+3.46013+00	+3.57343+00	+3.12910+04
CH2	1600-6000	-2.54439-15	+5.28430-11	-4.41683-07	+1.91214-03	+2.90518+00	+4.05280+00	+9.51800+04
CH3	1600-6000	-4.54836-15	+9.23628-11	-7.48562-07	+3.10302-03	+2.99401+00	+4.20748+00	+3.28050+04
CH4	1600-6000	-6.49447-15	+1.33426-10	-1.09861-06	+4.65586-03	+2.15113+00	+7.09358+00	-1.59910+04
CN	1600-6000	+6.86524-16	-1.38897-11	+7.51522-08	+1.17599-04	+3.53882+00	+4.08211+00	+1.08215+05
CO	1600-6000	-8.49307-16	+1.73245-11	-1.40657-07	+5.94282-04	+3.18229+00	+5.21173+00	-2.72000+04
CO2	1600-6000	-3.28004-15	+6.41720-11	-4.91130-07	+1.89576-03	+3.77159+00	+3.26291+00	-9.39650+04
C2	1600-6000	+1.20948-15	-2.10855-11	+1.23422-07	-1.68125-04	+4.43142+00	-1.00556+00	+1.97000+05
C2H2	1600-6000	-4.08637-15	+8.31383-11	-6.77247-07	+2.92166-03	+3.91409+00	+4.54796-01	+5.43250+04
C2H4	1600-6000	-9.00125-15	+1.80824-10	-1.44549-06	+5.88965-03	+2.96821+00	+6.03881+00	+1.45200+04
C2H4O	1600-6000	-1.19714-14	+2.37532-10	-1.86622-06	+7.41624-03	+3.18583+00	+6.83783+00	-9.19900+03
C2N2	1600-6000	-4.48256-15	+8.71890-11	-6.65330-07	+2.52738-03	+5.49621+00	-3.27969+00	+7.34280+04
C3	1600-6000	-3.24099-15	+6.27911-11	-4.76314-07	+1.79212-03	+4.01141+00	+1.80655+00	+1.88104+05
C3O2	1600-6000	-6.95349-15	+1.34406-10	-1.01615-06	+3.80366-03	+6.15652+00	-5.80291+00	-8.72200+03
C4	1600-6000	-5.03697-15	+9.73294-11	-7.35449-07	+2.75042-03	+5.20000+00	-1.54359+00	+2.40500+05
C4N2	1600-6000	-7.83576-15	+1.51788-10	-1.15132-06	+4.33261-03	+8.05603+00	-1.26600+01	+1.26341+05
C5	1600-6000	-6.83954-15	+1.31964-10	-9.95089-07	+3.70981-03	+6.38778+00	-7.84357+00	+2.40298+05
CLATOM	1600-6000	-3.94218-17	+2.22829-13	+4.30636-09	-5.14158-05	+2.71723+00	+4.46850+00	+2.85200+04
HCL	1600-6000	-3.75731-16	+9.13387-12	-9.05864-08	+4.92947-04	+3.13393+00	+4.26477+00	-2.19260+04

TABLE B.3 (continued)

SPECIE	TEMPERATURE RANGE(K)	E	D	C	B	A	K	HEAT OF FORMATION
CL2	1600-6000	-8.82790-16	+1.39577-11	-8.62331-08	+3.20573-04	+3.97579+00	+4.11361+00	+0.00000+00
F ATOM	1600-6000	+1.83895-16	-3.57691-12	+2.72626-08	-1.03158-04	+2.70220+00	+3.78127+00	+1.83570+04
HF	1600-6000	+3.79216-16	-4.54785-12	+7.19500-10	+2.38670-04	+3.24478+00	+2.24029+00	-6.44880+04
F2	1600-6000	-9.38819-16	+1.78342-11	-1.31332-07	+5.23151-04	+3.65966+00	+3.29216+00	+0.00000+00
SF6	1600-6000	-1.08195-14	+2.04179-10	-1.48861-06	+5.25111-03	+9.90623+00	-2.26562+01	-2.85173+05
H ATOM	1600-6000	+4.28915-18	-6.55051-14	+3.55631-10	-7.93671-07	+2.50055+00	-4.62602-01	+5.16320+04
HI	1600-6000	-7.96325-16	+1.64326-11	-1.35889-07	+6.03395-04	+3.15779+00	+6.42107+00	+6.82000+03
OH	1600-6000	+2.25867-16	-1.69987-12	-1.85539-08	+2.90797-04	+3.26521+00	+3.28864+00	+9.27300+03
H2	1600-6000	+3.11469-16	-3.83133-12	+2.62835-09	+2.41868-04	+3.22505+00	-2.81433+00	+0.00000+00
H2O	1600-6000	-5.01252-16	+1.54602-11	-1.85599-07	+1.16144-03	+3.27155+00	+3.26708+00	-5.71030+04
H2S	1600-6000	-2.09203-15	+4.34855-11	-3.63272-07	+1.60723-03	+3.27526+00	+5.01099+00	-4.11900+03
NH3	1600-6000	-2.78471-15	+6.16806-11	-5.58105-07	+2.66321-03	+2.80243+00	+5.42979+00	-9.36200+03
I ATOM	1600-6000	+4.82238-16	-8.85388-12	+5.50443-08	-1.03004-04	+2.56044+00	+7.20703+00	+2.56330+04
I2	1600-6000	-3.18693-16	+5.93793-12	-4.25024-08	+1.79327-04	+4.26091+00	+7.07097+00	+1.56600+04
N ATOM	1600-6000	-3.49970-16	+6.56694-12	-3.29578-08	+6.46177-05	+2.45587+00	+4.39243+00	+1.12520+05
NO	1600-6000	-7.99242-16	+1.60889-11	-1.28693-07	+5.34354-04	+3.36193+00	+5.76149+00	+2.15280+04
NO2	1600-6000	-2.92171-15	+5.62756-11	-4.23035-07	+1.56772-03	+4.03230+00	+5.00931+00	+8.73400+03
N2	1600-6000	-7.46882-16	+1.56618-11	-1.31173-07	+5.75350-04	+3.15780+00	+4.63502+00	+0.00000+00
N2O	1600-6000	-3.28369-15	+6.36610-11	-4.83313-07	+1.82030-03	+3.95209+00	+3.06036+00	+2.03200+04
N2O3	1600-6000	-6.06203-15	+1.16232-10	-8.68075-07	+3.18549-03	+7.06555+00	-4.35365+00	+2.15560+04
N2O4	1600-6000	-8.79253-15	+1.68232-10	-1.25239-06	+4.57139-03	+7.56681+00	-8.44405+00	+4.59300+03
N2O5	1600-6000	-1.12358-14	+2.14636-10	-1.59400-06	+5.79574-03	+8.38235+00	-1.20365+01	+6.15300+03
O ATOM	1600-6000	+2.08115-17	-1.02418-12	+1.54998-08	-7.40637-05	+2.64639+00	+4.29018+00	+5.89890+04
O2	1600-6000	-5.06723-16	+9.39526-12	-7.90161-08	+4.50077-04	+3.42972+00	+4.82464+00	+0.00000+00
SO2	1600-6000	-2.73303-15	+5.22797-11	-3.89013-07	+1.45598-03	+4.38876+00	+4.12658+00	-7.03410+04
O3	1600-6000	-2.82616-15	+5.37754-11	-3.97042-07	+1.46189-03	+4.42394+00	+2.84303+00	+3.47390+04
SO3	1600-6000	-6.29097-15	+1.11768-10	-7.83088-07	+3.19847-03	+5.02965+00	+7.37159-01	-9.30760+04

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