THERMODYNAMIC CALCULATIONS WITH TK!SOLVER

By

Esmaiel Jabbari

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APPROVED:

G. H. Beyer, Chairman

J. B. Jones

W. L. Conger

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(ABSTRACT)

The objective of this research was to apply the TK!Solver program for thermodynamic calculations. The TK!Solver program is equation-solving software that can solve both linear and non-linear sets of equations. To achieve the above objective, six programs have been developed.

Program ESTATE.TK calculates volumetric properties of compounds using the ideal gas law, Pitzer correlation, van der Waals, Redlich-Kwong, Dieterici, or Berthelot equation of state. The volumetric properties include temperature, pressure, volume, and compressibility factor.

Program RESIDUAL.TK calculates residual and total properties of compounds as a function of temperature and pressure using the Pitzer correlation, van der Waals, or Redlich-Kwong equation of state. The residual and total properties include residual volume, residual internal energy, residual enthalpy, and residual entropy.

Program FRENERGY.TK calculates standard free energy of formation, standard enthalpy of formation, and standard entropy of formation for a compound or a reaction as a

function of temperature. This program also calculates the equilibrium constant for a reaction as a function of temperature.

Program CHON.TK calculates the equilibrium composition for an adiabatic or non-adiabatic reactor as a function of the temperature and pressure of the reactor, hydrogen-to-oxygen ratio, and nitrogen-to-oxygen ratio in the feed. The feed to the reactor consists of the elements carbon, hydrogen, oxygen, and nitrogen. The products of the reactor are methane, water, carbon monoxide, carbon dioxide, hydrogen, and nitrogen.

Program CRITICAL.TK furnishes critical data for more than fifty compounds. The critical data includes critical temperature, critical pressure, critical volume, critical compressibility factor, and the acentric factor. Programs ESTATE.TK and RESIDUAL.TK have access to data file CRITICAL.TK for state property calculations.

Program DATBANK1.TK supplies heat capacity data, heat of formation, and entropy of formation data for more than one hundred compounds. Programs RESIDUAL.TK and FRENERGY.TK have access to data file DATBANK1.TK for enthalpy and entropy calculations.

These six programs may be considered as a basis for an "expert" system for thermodynamic calculations. Data can be easily added to extend the calculations to include additional compounds.

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I. Introduction

The following introduction is divided into two parts. In the first part the focus is on chemical engineering thermodynamics, and introducing each of the six programs in this package. In the second part the focus is on the TK!Solver program and the development of each of the six programs.

1. Chemical Engineering Thermodynamics

Chemical engineering thermodynamics can be subdivided into two types of problems. The first type is centered on the calculation of state properties. the other type is centered on the calculation of phase equilibria. There are six programs in this package. Programs ESTATE.TK and RESIDUAL.TK calculate the state properties of a compound. Programs FRENERGY.TK and CHON.TK involve phase equilibrium calculations. Programs CRITICAL.TK and DATBANK1.TK are data files, and they are used in conjunction with the other programs.

1.1. State Property Calculations

The two programs, ESTATE.TK and RESIDUAL.TK, should be used to calculate the state properties of a compound in the gaseous state. In thermodynamics, there are many equations of state that describe the state properties of compounds in the gaseous state(e.g. ideal gas law, Pitzer correlation, etc.), but there are few equations of state to describe, with reasonable accuracy, the state properties of a compound in the liquid or the solid state. The reason is that it is very difficult to quantify and formulate the intermolecular and intramolecular forces of molecules in the liquid and solid state. Therefore, the programs developed in this package should be used only to describe the state properties of a compound in the gaseous state. The introduction for programs ESTATE.TK and RESIDUAL.TK is given below.

1.1.1. ESTATE.TK Program: Program ESTATE.TK calculates volumetric properties of a compound in the gaseous state. The accomplishments of this program are:

1) The program can identify the specified state variables and solve the equation of state for the unknown state variable.

2) The program can choose among six different equations of state for calculating state properties of different

compounds.

3) The program has the capability to select critical data from the data file CRITICAL.TK.

Many equations of state in this program need critical data in order to solve the equation of state. Therefore, it is essential for this program to be able to select critical data for different compounds from the data file. An equation of state is a rule that defines the relationship among pressure, temperature, and volume for a compound. For a system consisting of only one compound and one phase, the phase rule states that if two variables are specified, the third variable can be calculated using an equation of state. Program ESTATE.TK solves an equation of state for the unknown state variable if two state variables are defined for the system. For example, if temperature and pressure of a gas are specified, program ESTATE.TK calculates the specific volume of the gas using an equation of state. Figure I.1 shows the P-V diagram for a pure material.

The dotted section of the P-V digram shows the applicable range of the program ESTATE.TK for calculating the state properties of compounds.

Program ESTATE.TK can choose among six different equations of state. These equations are the ideal gas law, Pitzer correlation, van der Waals, Redlich Kwong, Dieterici, and Berthelot equations of state. Also, this program has the

ability to obtain data from the data file CRITICAL.TK, which has critical data for more than 50 compounds.
There are two limitations in using the ESTATE.TK program. First, this program should be used to calculate the state properties of compounds in the gaseous state. Also, all of the equations of state included in this program are good for nonpolar compounds. State properties of many compounds have been calculated using this program, and the results show that it can predict the state properties of nonpolar and small molecules generaly with less than two percent error. Also, the results show that, for polar and large molecules, the error in the calculation of state properties can be as high as fifty percent. Therefore, this program should be used with caution for polar molecules.

1.1.2. RESIDUAL.TK Program: Program RESIDUAL.TK calculates the change in properties of a compound from the initial state to the final state in the gas phase. The properties that the program calculates are internal energy, enthalpy, entropy, and volume. The accomplishments of this program are:

1) The program RESIDUAL.TK can choose among three different equations of state.

2) The program has the capability to select data from the CRITICAL.TK data file, as most equations of state need

critical constants.

3) The program has access to heat capacity data from DATBANK1.TK data file.

4) The program has the capability of activating or deactivating different parts of the rule sheet. More will be said about this feature of the program in the section on TK!Solver.

Figure I.2 shows the different steps that are involved in calculating the change in properties of a gas from one state to another.

Step 1) The gas is transferred from the initial state at temperature ti, and pressure pi, to the same temperature and pressure, but as an ideal gas. The first step is the calculation of the residual properties of the gas for the initial state.

Step 2) The gas is heated from the initial temperature ti, to the final temperature tf, at constant initial pressure pi, in the ideal state. Note that this step requires ideal heat capacity data for the compound.

Step 3) The gas is pressurized from the initial pressure pi, to the final pressure pf, at constant final temperature ,tf, in the ideal state. Since pressure has no effect on the enthalpy and internal energy of a compound in the ideal state, the change in enthalpy and internal energy is zero for the third step. Note that pressure does have an effect on the entropy of a gas, even in the ideal

state. Also, note that the second and the third step calculate the change in the properties of a compound from the initial state(e.g., ti, pi) to the final state(e.g., tf, pf), assuming that the gas is ideal.

Step 4) The gas is transferred from the ideal state at the temperature tf, and the pressure pf, to the same temperature and pressure, but as a real gas. Therefore, the fourth step is the calculation of the residual properties of the gas for the final state.

Summation of all the changes in the properties of the gas for steps one, two, three, and four is the overall change in the properties of the compound from the initial state to the final state.

As discussed in the previous section, for a nonreacting system with only one compound and one phase, two state variables can completely define the system. Therefore, specifying pressure and temperature of both the initial and the final states completely defines the change in the properties of the gas from the initial to the final state.

In order to calculate the residual properties of a compound, an equation of state is needed. Program RESIDUAL.TK can choose among three different equations of state. these equations are Pitzer correlation, van der Waals, and Redlich Kwong equations of state. Note that the residual properties for an ideal gas are zero, therefore, it would be redundant to include the ideal gas law as one

of the equations of state.

Program RESIDUAL.TK uses both data files CRITICAL.TK and DATBANK1.TK. Data file CRITICAL.TK provides critical data for the calculation of residual properties of a compound, and, data file DATBANK1.TK provides heat capacity data for calculating property changes due to temperature.

There are two limitations in using the RESIDUAL.TK program. First, this program should only be used to calculate the property changes of a compound from the initial to the final state, only if both states of the compound are gaseous. This program may not be applied to liqiuds or solids. Secondly, all of the equations of state in this program are good for nonpolar molecules, therefore, this program should be only applied to nonpolar compounds. For small and nonpolar molecules, the error in the property changes is generaly less than three percent, but for polar and large molecules, the error may be as high as a hundred percent.

1.2. Phase Equilibria Calculations

The branch of thermodynamics dealing with Phase Equilibria can be subdivided into two classes. One class deals with multicomponent equilibria(e.g. gas phase reactions), and the other class deals primarily with multiphase equilibria, such as distillation and liquid liquid

extraction. Multiphase equilibria are primarily vapor liquid equilibria such as distillation, or, liquid liquid equilibria such as liquid liquid extraction. Therefore, multiphase equilibria involve the calculation of activity coefficients for each compound in the liquid phase. Since it is very difficult to formulate the variation of liquid phase properties with temperature and pressure, no attempt has been made to use the TK!Solver programs for multiphase equilibrium calculations. Instead, attention is focused on multicomponent ideal gas phase equilibria, for which it is easy to formulate the changes in the properties of ideal gases. Also, we should mention that TK!Solver may have the capacity to do multiphase equilibrium calculations, if activity data for compounds in the liquid phase are available.

There are two programs for the calculation of phase equilibria in this package. These programs are FRENERGY.TK and CHON.TK. The introduction for each of these programs is given below.

1.2.1. FRENERGY.TK Program: Program FRENERGY.TK calculates the standard free energy, enthalpy, and entropy of formation for a compound at the pressure of one atmosphere and any temperature. The program can also calculate the standard free energy, enthalpy, and entropy for a reaction at the pressure of one atmosphere and any

temperature. The accomplishments of this program are:

1) This program has the ability to obtain heat capacity and heat of formation data from the data file DATBANK1.TK.

2) The program has the capability to activate or deactivate different parts of the rule sheet, in order to calculate the standard free energy of a compound or a reaction. This feature of the program will be discussed further in the section on TK!Solver programs.

Figure I.3 shows the steps that are involved in the calculation of free energy of formation of a compound at temperature T.

Standard free energy of formation is the change in the free energy when a compound is formed from its elements at the same temperature. These elements considered here are hydrogen(H2), oxygen(O2), nitrogen(N2), carbon(graphite), sulfur(S2), and chlorine(Cl2). This means that the compound should consist of the elements mentioned above.

Step 1) The elements are transferred from temperature t to the temperature of 298.15 Kelvin at constant pressure of 1 atmosphere. Note that heat capacity data are needed for all of the elements to accomplish the first step.

Step 2) The elements react to form the compound at 298.15 Kelvin and one atmosphere. In the second step, enthalpy and entropy data are used to calculate the free energy of formation of the compound at 298.15 Kelvin.

Step 3) The compound is heated to the desired temperature

t at constant pressure of one atmosphere. Note that heat capacity data is needed for the compound in order to calculate the free energy change for the third step. Addition of all of the changes in free energy for each step results in the change in the standard free energy of formation of the compound at temperature t.

Program FRENERGY.TK uses the data file DATBANK1.TK, in order to obtain heat capacity data, enthalpy of formation data at 298.15 Kelvin, and entropy of formation data at 298.15 Kelvin for the compound. Data file DATBANK1.TK has heat capacity and heat of formation data for more than 100 compounds.

There are two limitations involving the use of this program. First of all, there should be heat capacity data and heat of formation data for the compound in the data file, in order to find the standard free energy of formation of the compound at a given temperature. Secondly, the compound should consist of the elements hydrogen, oxygen, nitrogen, carbon, sulfur, and chlorine.

1.2.2. CHON.TK Program: Program CHON.TK calculates the equilibrium composition for a system consisting of the elements carbon, hydrogen, oxygen, and nitrogen. The program also calculates the heat requirments and the heating value of the product stream for this system. The accomplishments of this program are:

1) The program has the ability to solve many nonlinear equations, simultaneously.

2) The program has the capability to activate or deactivate different parts of the rule sheet in order to calculate equilibrium constants, product stream compositions, and the heat requirements of the reactor. This feature of the program will be discussed in more detail in the section on TK!Solver.

The feed to this reactor is carbon as graphite, water, hydrogen, oxygen, and nitrogen gas. There are three reactions that take place in this reactor as shown below:

$$C + H_2O \text{ ------> } CO + H_2$$

$$CO + H_2O \text{ -----> } CO_2 + H_2$$

$$C + 2\ H_2 \text{ -----> } CH_4$$

In the first reaction, carbon reacts with water to form carbon monoxide and hydrogen gas. In the second reaction, carbon monoxide reacts with water to form carbon dioxide and hydrogen gas. In the third reaction, carbon reacts with hydrogen to form methane. Therefore, the products of this reactor are hydrogen, water, methane, carbon monoxide, carbon dioxide, and nitrogen assuming all of the oxygen fed to the reactor is consumed completely. Note that carbon as graphite is in the solid state. Also, note that no allowance has been made for the production of higher

hydrocarbons. Also, it is assumed that nitrogen does not react at all, so there is no ammonia or nitrogen oxides produced.

Figure I.4 shows the control volume for the above system for energy balance calculations.

Figure I.4 shows that all of the reactants enter the control volume at the temperature of 298.15 K and atmospheric pressure. Carbon as graphite is fed as a solid, water enters as a liqiud, and the compounds hydrogen, oxygen, and nitrogen enter the reactor as a gas. The products of the reactor are all in the gaseous state.

The program also has the capability to find the equilibrium composition for an adiabatic reactor. The control volume for the adiabatic case is shown in figure I.5.

For the adiabatic reactor, solid carbon enters at temperature 298.15 K and the reactor pressure, Pr. Water enters as saturated steam at the reactor pressure, Pr. The gaseous reactants hydrogen, oxygen, and nitrogen enter at reactor pressure and at the temperature that the reactants would reach if they were compressed isentropically from 298.15 K and 1 atm. The gaseous products leave at the temperature and the pressure of the adiabatic reactor.

According to the phase rule, a system consisting of only one phase and the elements carbon, hydrogen, oxygen, and nitrogen has four degrees of freedom. This means that two more variables beside temperature and pressure must be

specified in order to define the system completely. Therefore, the atomic ratio of the hydrogen to oxygen in the feed(H/O) and the ratio of the nitrogen to Oxygen(N2/O2) should also be specified to completely define the system. Note that, if there is no nitrogen in the feed, the ratio of the hydrogen to oxygen in the feed along with the temperature and the pressure of the reactor would be sufficient to define the state of the system. Since the heat requirement of the adiabatic reactor is zero, this reduces the number of degrees of freedom for the reactor by one. Therefore, for the adiabatic reactor, the ratio of the nitrogen to oxygen in the feed(N2/O2) along with the temperature and the pressure defines the state of the system completely.

Program CHON.TK has heat capacity and heat of formation data for compounds hydrogen, water, methane, carbon monoxide, carbon dioxide, oxygen, nitrogen, and solid carbon as graphite. Therefore, this program does not use the data files CRITICAL.TK and DATBANK1.TK.

There are three limitations in using program CHON.TK. First of all, the reactants should consist of the elements carbon, hydrogen, oxygen, and nitrogen. Secondly, it is assumed that the gaseous reactants and products are all ideal gases. In other words, no adjustments have been made for nonideality of the gaseous reactants and products. The above assumption may introduce as much as five percent

error in the calculations of the equilibrium composition and the heat requirements of the reactor at high pressure and low temperature. However, the error may be as low as one percent at low pressure and high temperature. Third, no allowance has been made for the production of higher hydrocarbons, ammonia, and nitric oxides in the reactor.

1.3. CRITICAL.TK and DATBANK1.TK Data Files

There are two data files in this package with the names CRITICAL.TK and DATBANK1.TK. Data file CRITICAL.TK contains critical data for more than 50 organic compounds. The data includes critical temperature(tc), critical pressure(pc), critical volume(vc), critical compressibility factor(zc), acentric factor(omega), and the molecular weight(mw) of the compound. Program CRITICAL.TK provides data for programs ESTATE.TK and RESIDUAL.TK.

Data file DATBANK1.TK contains data for more than 100 organic compounds. the data includes ideal heat capacity data in the form shown below:

$$Cp = a + b*T + c*T^2 + d*T^3$$

The program provides the coefficients a, b, c, and d in the above equation. The applicable temperature range for the heat capacity data is also included. The data also include standard enthalpy and entropy of formation at 25 degrees

Celcius for the compound. Molecular formula, number of carbon atoms, hydrogen atoms, Oxygen atoms, nitrogen atoms, sulfur atoms, and chlorine atoms in the compound are also included in this data file. Data file DATBANK1.TK provides data for programs RESIDUAL.TK and FRENERGY.TK.

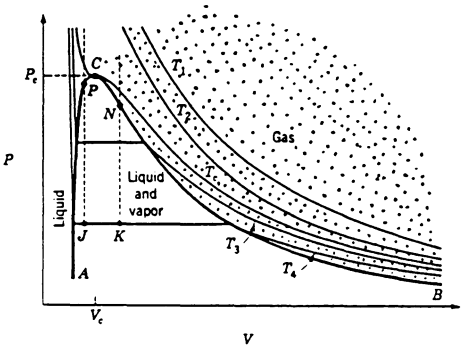


Figure I.1
P-V diagram for a pure material.

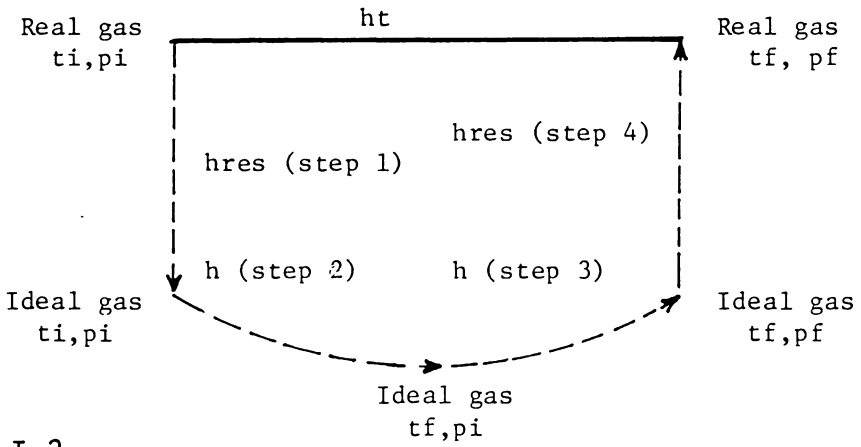


Figure I.2
Steps involved in enthalpy calculations.

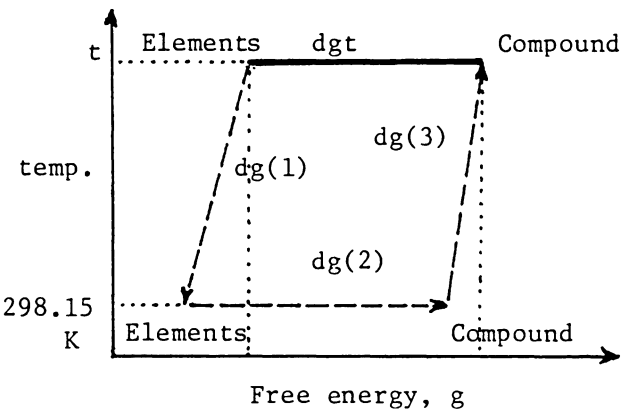


Figure I.3
Steps involved in free energy calculations.

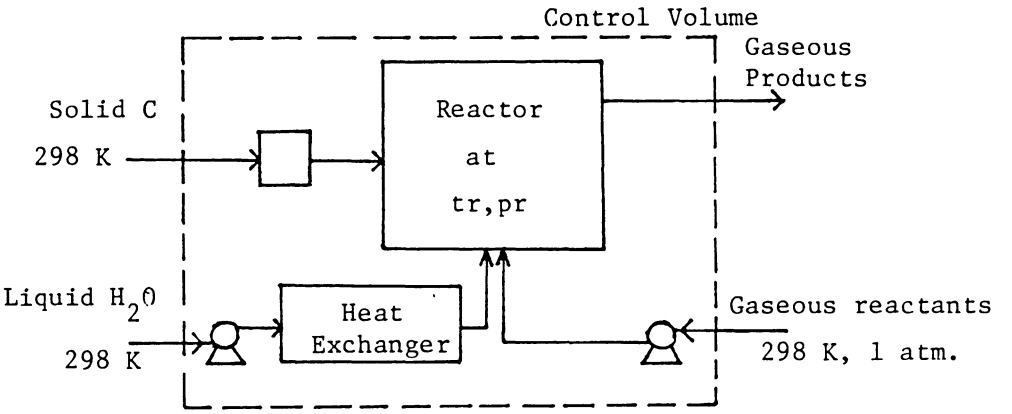


Figure I.4
Control volume for non-adiabatic reactor.

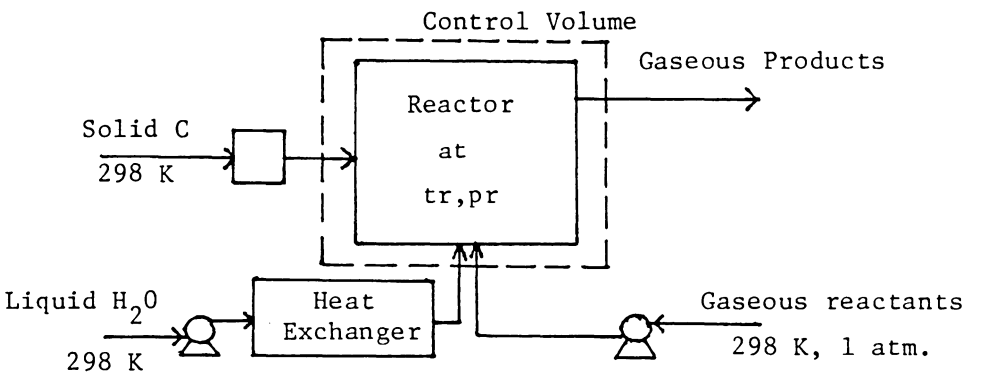


Figure I.5
Control volume for adiabatic reactor.

2. TK!Solver Program

2.1. TK!Solver Sheets

TK!Solver program consists of eight different sheets. The names of these sheets are variable sheet, rule sheet, unit sheet, global sheet, list sheet, function sheet, table sheet, and plot sheet. The variable, rule, global, list, and the function sheets are the most important sheets of the TK!Solver program for the purpose of performing calculations and data processing. The unit, table, and plot sheets of the program are used to show the results of the calculations in different formats or different units. The description for each of the sheets is given below. For a complete description of all of the TK!Solver sheets see references (1) and (2).

2.1.1. Variable Sheet: The variable sheet allows the name and the status of each variable to be defined. The variable sheet is shown in Figure I.6.

Figure I.6 shows that the variable sheet is divided into six columns with heading St, Input, Name, Output, Unit, and Comment. Each row of the variable sheet belongs to only one variable. Column 'St' defines the status of a

variable. The column 'St' can have the characters 'L' and 'G'. The charactor 'L' indicates that there is a list associated with the variable, and the 'G' indicates that the variable has iterative solution. The column 'Input' defines whether the variable is an input or an output variable. If there is no number in the 'Input' column, the variable is treated as an output variable and the program tries to find the solution for this variable. If there is a number in the 'Input' column, the variable is treated as an input variable.

In the column with the heading 'Name', the name of the variable is defined. The solution to a variable is sent to the 'Output' column of the variable. Note that nothing can be inserted in the 'Output' column. In the column 'Unit', the units associated with a variable are entered. In the column with the heading 'Comment', any comments or the description of the variable can be entered. The column 'comment' is not executed by the computer, therefore, anything can be typed in this column.

The variable sheet identifies the input and the output variables. Also, the status column of this sheet determines if a variable requires iterative solution.

2.1.2. Rule Sheet: The rule sheet allows the relationships among the variables to be defined. The rule sheet is shown in Figure I.7.

Figure I.7 shows that the rule sheet is divided into two columns. In each row of the rule sheet a rule or a mathematical function is entered. Column 'St' defines the status of a rule. The character '*' in the status column indicates that the rule is not satisfied, and the character '>' indicates that there is an error in this rule. If there is nothing in the status column, the rule is satisfied.

The most important feature of the rule sheet is that the rule can be entered in the form of '<expression>=<expresssion>', where each expression can be a mathematical function. Note that the equal sign means the two expressions must be equal contrary to the Basic or Fortran language where an equal sign means 'assign to'. Also, note that the computer executes every rule on the rule sheet. In other words, there are no control variables as to how many rules should be executed once the program begins execution.

2.1.3. Global Sheet: The global sheet contains definitions that affect the behavior of TK!Solver on a global scale. The global sheet of TK!Solver is shown in Figure I.8.

The most important definitions on the global sheet are those that affect program execution. These definitions are 'Automatic Iteration On', 'Comparison Tolerance', and

'Maximum Iteration Count'. The 'Automatic Iteration On' begins the iterative solver if the direct solver fails to find a solution. The 'Comparison Tolerance' sets the tolerance for the iterative solver. The default value for tolerance is 0.000001. The 'Maximum Iteration Count' sets the maximum number of iterations as the name implies. the default value for the maximum number of iterations is 10. If a problem needs more than ten iterations, it is possible that the first guesses are not well chosen.

2.1.4. List Sheet: The list sheet contains the name of all the lists for a model. The list sheet of TK!Solver is shown in Figure I.9.

Figure I.9 shows that the list sheet is divided into four columns. Each row of the list sheet belongs to only one variable. The first column with the heading 'Name', shows the name of the list. The second column with the heading 'Elements', shows the number of the elements in the list. The third column with the heading 'Unit', shows the units associated with the variable. In the column with the heading 'Comment', the description of the list can be entered. Every variable on the list sheet has a subsheet associated with it to store the name or the value of each element of that list.

2.1.5. User Function Sheet: The user function sheet is

used to express the functional relationship between two variables. The user function sheet is shown in Figure I.10.

As figure I.10 shows, the user function sheet is divided into five columns. each row of this sheet is used to express the functional relationship between two variables. The relationship between two variables on the function sheet is of the form 'y=f(x)'. For a given value of 'x' which is the domain value, the program finds the value of 'y' which is the range value. Therefore, a functional relationship between two variables has to have a name(e.g. 'f'), a list for the domain(e.g. 'x'), and a list for the range(e.g. 'y').

Figure I.10 shows that the first column with the heading 'Name', defines the name of the function. In the second column with the heading 'Domain', the listname for domain of the function is entered. In the third column with the heading 'Mapping', the type of functional relationship is specified. The type can be linear function, step function, or a table lookup function. In the fourth column with the heading 'range', the listname for range of the function is entered. The fifth column is used for function description. A subsheet is associated with each function that contains the lists for domain and range of the function.

2.2. Solving Simultaneous Nonlinear equations With TK!Solver

TK!Solver program has the capacity to solve nonlinear equations simultaneously. The iterative solver uses the Newton Raphson iterative procedure to solve nonlinear equations. No attempt has been made to explore how the iterative solver of TK!Solver program works; however, many nonlinear equations have been solved with TK!Solver. programs ESTATE.TK, RESIDUAL.TK, FRENERGY.TK, and CHON.TK involve iterative solution.

In particular, program CHON.TK involves the solution of more than ten nonlinear equations for the product composition of an adiabatic reactor. The number of unknown variables is seven for the above program. The findings show that if the initial guesses are reasonable, the iterative solver has the ability to solve the above problem. However, the results also show that the execution time can be as high as five minutes for problems that have many nonlinear equations and many unknown variables.

2.3. Storing Chemical Data With TK!Solver

TK!Solver program can be used to store chemical data using the list sheet and the user function sheet. Variable 'compound' can be declared as a list variable using the list sheet, and the name of all of the compounds(e.g.

methane, ethane, propane, etc.) are stored in the variable 'compound' subsheet. Then, the property of interest, such as critical temperature for each compound, is declared as a list variable on the list sheet, and the corresponding critical temperature for each compound is entered in the variable 'critical temperature' subsheet. Next, the two lists 'compound' and 'critical temperature' can be related using the user function sheet in the form of 'critical temperature=function(compound)'.

Therefore, for a given compound, the TK!Solver program finds the name of the compound in the list 'compound', and then, it finds the corresponding critical temperature from the user function sheet. In this package, programs CRITICAL.TK and DATBANK1.TK are data files for the purpose of storing data. Data file CRITICAL.TK contains critical data for more than fifty compounds, and data file DATBANK1.TK contains heat capacity and heat of formation data for more than one hundred compounds.

2.4. Making Choices With TK!Solver

In order to use TK!Solver to make choices, the bypass command of TK!Solver program is used (Ref. 3). The bypass command and its function for making choices with TK!Solver is discussed below.

Bypass Commands: There are five operations in TK!Solver program that are indeterminate. If the program encounters such operations, the rule containing that operation is ignored or bypassed. These indeterminate operations are '0/0', '0^0', '0=0^x', '1=x^0', and '1=1^x'. Therefore, any rule in the form of '0/x + <expression>=<expression>' is bypassed if 'x' is equal to zero, and the rule is evaluated if 'x' is equal to one.

In order to choose among different equations of state, it is necessary to be able to turn off some parts of the rule sheet while other parts of the rule sheet are being executed. For example, if there are six different equations of state in the rule sheet, and we want to use the ideal gas law, it is necessary to turn off the part of the rule sheet containing the other five equations of state, while the rule for the ideal gas law is being executed.

Suppose there are four rules on the rule sheet, as shown below, and we want only one rule to be turned on each time the program is executed.

<expression 11>=<expression 12>

<expression 21>=<expression 22>

<expression 31>=<expression 32>

<expression 41>=<expression 42>

First of all, each one of the four rules has to be named such as 'rulel', 'rule2', 'rule3', and 'rule4', respectively. Then, the name of each rule is stored in a subsheet of the list sheet, and, a four by four square matrix is constructed as shown in Figure I.11.

In the above matrix the diagonal elements have the value of one, and the non-diagonal elements have the value of zero. In other words, the above matrix is an 'identity' matrix. Each column of the above matrix is stored in a separate subsheet of the list sheet. Then, each column of the above identity matrix is related to the name of the rules using the user function sheet. Therefore, there are four user functions on the user function sheet in the form of 'column#i = function#i(rule names)'. Then, the following additions are made to each of the four rules on the rule sheet, as shown below.

```
0/function#1(rule names) +<expression 11>=<expression 12>
0/function#2(rule names) +<expression 21>=<expression 22>
0/function#3(rule names) +<expression 31>=<expression 32>
0/function#4(rule names) +<expression 41>=<expression 42>
```

Note that the variable 'rule names' can have the names rulel, rule2, rule3, or rule4, however, the variable 'function#i(rule names)', which is a user function variable, can only have the values of zero and one. If the

user function variable has the value of one, the computer encounters the statement '0/1', which has the value of zero, and the rule is executed. If the user function variable has the value of zero, the computer encounters the statement '0/0', which is indeterminate, and the rule is ignored or bypassed. Therefore, to make a choice among four rules, it is necessary to create five lists with four elements in each list and four user functions.

In general, In order to make a choice among 'N' rules, it is necessary to create (N+1) lists with N elements in each list and N user functions. The above procedure is used in every program to turn off or turn on different parts of the rule sheet so that the computer will execute only the desired part of the rule sheet.

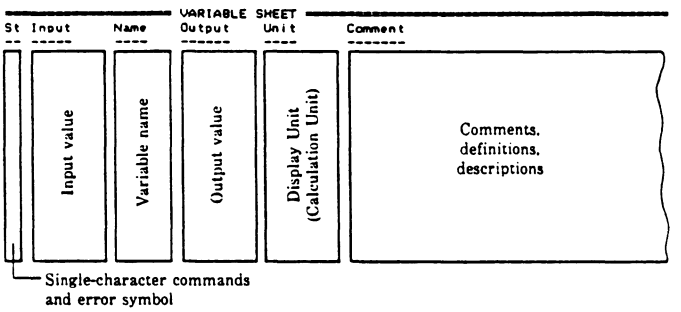


Figure I.6
Variable sheet of TK!Solver.

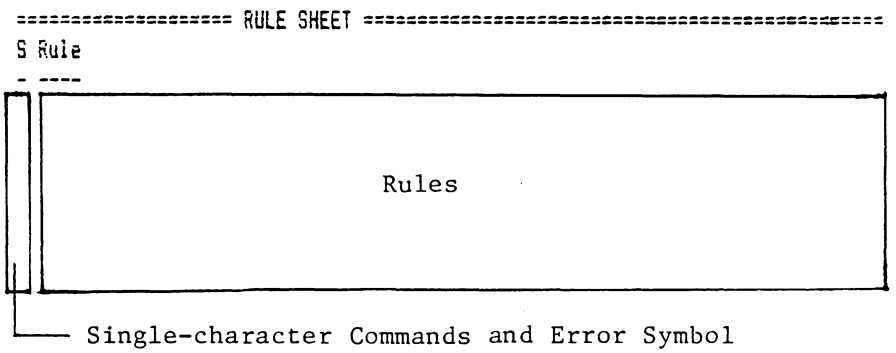


Figure I.7
Rule sheet of TK!Solver.

```
==================== GLOBAL SHEET ==...
Variable Insert ON:          Yes

Intermediate Redisplay ON:   Yes
Automatic Iteration ON:      Yes
Comparison Tolerance:        .000001
Typical Value:               1
Maximum Iteration Count:     10

Page Breaks ON:              Yes
Page Numbers ON:             Yes
Form Length:                 66
Printed Page Length:         60
Printed Page Width:          80
Left Margin:                 0
Printer Device or Filename:  PRN
Printer Setup String:
Line End (CR/LF or CR):      CR/LF
```

Figure I.8
Global sheet of TK!Solver.

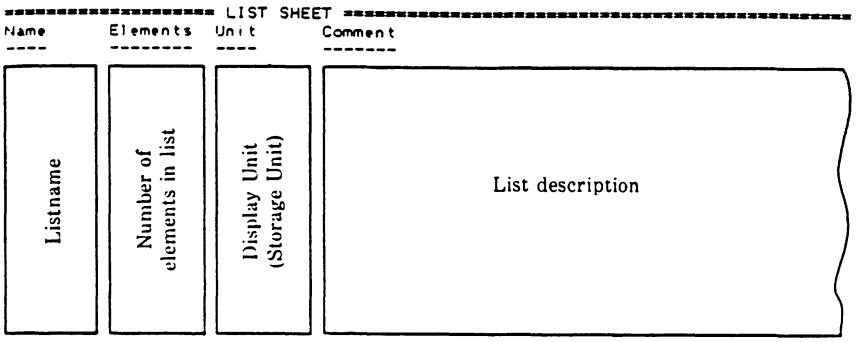


Figure I.9
List sheet of TK!Solver.

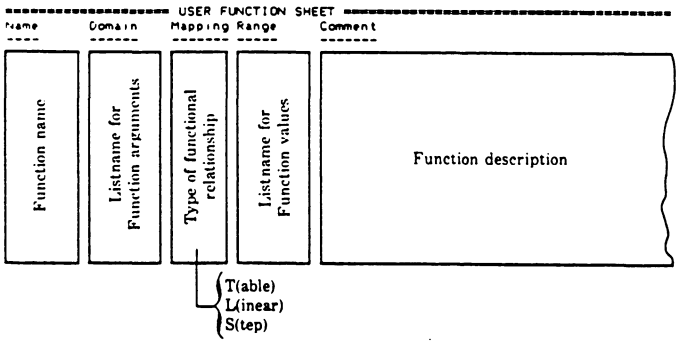


Figure I.10
User function sheet Of TK!Solver.

List 1	List 2	List 3	List 4	List 5
Rule 1	1	0	0	0
Rule 2	0	1	0	0
Rule 3	0	0	1	0
Rule 4	0	0	0	1

Figure I.11
A four by four identity matrix.

II. Program ESTATE.TK: P-V-T Calculations

1. Theory

Program ESTATE.TK calculates volumetric properties of a compound in the gaseous state. The phase rule specifies the number of degrees of freedom for a system, as given in equation(II.1).

$$\text{number of degrees of freedom for a system} = C + P + 2 \qquad \text{Eq.(II.1)}$$

In the above equation, C is the number of compounds, and P is the number of phases. According to the phase rule, a non-reacting system consisting of only one compound and one phase has two degrees of freedom. This means that if two state variables are specified for this system(e.g., temperature and pressure), the state of the system would be completely defined.

An equation of state is a rule that defines the relationship between pressure, temperature, and volume of a compound at a given state. Therefore, for a system consisting of only one compound and one phase, if two variables are specified, the third variable can be

calculated using an equation of state. Program ESTATE.TK solves an equation of state for the unknown state variable, if two state variables are defined for the system. For example, if temperature and pressure of a gas are specified, program ESTATE.TK calculates the specific volume of the gas using an equation of state.

Figure II.1 shows the pressure versus volume(e.g., P-V) diagram for a pure material.

The dotted section of the above figure shows the applicable range for the program ESTATE.TK for calculating the state properties of a compound. Program ESTATE.TK can be used to calculate the state properties of a compound anywhere in the gaseous phase.

Program ESTATE.TK can choose among six different equations of state. These equations are ideal gas law, Pitzer correlation, van der Waals, Redlich Kwong, Dieterici, and Berthelot equation of state. The description for each one of the above equations is given below.

Ideal gas law: It is the simplest form of an equation of state. The ideal gas equation (Ref. 9) is given by equation (II.2).

p * vmole = r * t + 0/ideal(type) Eq.(II.2)

Symbol p is the pressure, vmole is the molar specific volume, r is the gas constant, and t is the temperature. The user function variable ideal is a control variable for activating the ideal gas equation. The variable type is the name of the equation of state. It can be either ideal gas, Pitzer correlation, van der Waals, Redlich Kwong, Dieterici, or Berthelot equation of state. However, the user function variable ideal can only take one and zero. If the variable is 'ideal gas', then, the user function variable ideal has a value of one, otherwise, the variable ideal has a value of zero.
Note that the ideal gas equation does not involve iterative solutions. It can solve for any of the unkown variables p, vmole, or t directly.

Pitzer correlation: The Pitzer correlation (Ref. 9) is given by the following equations:

$$p * vmole/(r*t) = 1 + bb * pr/tr + 0/pitzer(type) \quad \text{Eq.(II.3)}$$

where

$$bb = .083 - .422/tr^{1.6} + omega * (.139 - .172/tr^{4.2}) \quad \text{Eq.(II.4)}$$

$$tr = t/tc \quad \text{Eq.(II.5)}$$

$$pr = p/pc \quad \text{Eq.(II.6)}$$

Symbol pr is the reduced pressure, tr is the reduced temperature, tc is the critical temperature, pc is the critical pressure, bb is the constant for Pitzer

correlation, and omega is the acentric factor of the compound. The user function variable pitzer is a control variable. it has a value of one if the variable type is 'pitzer correlation'; otherwise, the user function variable pitzer has a value of zero.

Note that the pitzer correlation is a linear function of pressure and volume, but it is nonlinear with respect to temperature. Therefore, Pitzer correlation can be solved directly if the unknown state variable is pressure or volume, and it can be solved iteratively if the unknown state variable is temperature.

van der Waals: The van der Waals equation of state (Ref. 9) is given by the following equations:

$$(p + avan/vmole^{\wedge}2)*(vmole-bvan) = r*t + 0/vander(type) \qquad \text{Eq.(II.7)}$$

$$avan = 27 * r^{\wedge}2 *tc^{\wedge}2 / (64 * pc) \qquad \text{Eq.(II.8)}$$

$$bvan = r * tc / (8 * pc) \qquad \text{Eq.(II.9)}$$

Symbols avan and bvan are the constants for the van der Waals equation of state. The user function variable vander is a control variable. It has a value of one , if the variable type is 'van der waals'; otherwise, the user function variable vander has a value of zero.

Note that the van der Waals equation is linear in pressure and nonlinear in volume and temperature. Therefore, van der Waals equation can be solved directly if the unknown

state variable is pressure, and it can be solved iteratively if the unkown state variable is volume or temperature.

Redlich Kwong: The Redlich Kwong equation of state (Ref. 9) is given by the following equations:

$$p = r * t/(vmole-bred) - ared/t^{.5}/vmole/(vmole - bred) + 0/redwg(type) \quad \text{Eq.(II.10)}$$

where

$$ared = .4278 * r^2 * tc^{2.5} / pc \quad \text{Eq.(II.11)}$$

$$bred = .0867 * r * tc / pc \quad \text{Eq.(II.12)}$$

Symbols ared and bred are constants for the Redlich Kwong equation of state. The user function variable redwg can have the values of zero and one. It has the value of one if the variable type is 'redlich kwong'; otherwise, the user function variable redwg has the value of zero.
Note that the Redlich Kwong equation of state is linear in pressure and nonlinear in temperature and volume. Therefore, equation (10) can be solved directly if the unknown state variable is pressure, and it can be solved iteratively if the unknown variables are temperature and pressure.

Dieterici: The Dieterici equation of state (Ref. 10) is given by the following equations:

```
p = r * t * exp ( adie/( t* vmole * exp(2))) / (vmole-bdie)
                                    + 0/dieter(type)    Eq.(II.13)
```

where

```
adie = 4 * r^2 * tc^2 / pc / exp(2)                     Eq.(II.14)

bdie = r * tc /pc / exp(2)                              Eq.(II.15)
```

Symbols adie and bdie are the two constants for the Dieterici equation of state. The user function variable dieter can have the values of one and zero. It has the value of one if the variable type is 'dieterici'; otherwise, the user function variable dieter has the value of zero.

Note that the Dieterici equation of state is linear in pressure and nonlinear in temperature and volume. Therefore, equation (13) can be solved directly if the unknown state variable is pressure, and it can be solved iteratively if the unknown state variable is temperature or pressure.

Berthelot: the Berthelot equation of state (Ref. 10) is given by the following equations:

```
p = r*t/( vmole- bber) - aber/t/vmole^2  +0/berth(type)
                                                        Eq.(II.16)
```

where

```
aber = 27 * r^2 * tc^3/ 64/ pc                          Eq.(II.17)

bber = r * tc / 8/ pc                                   Eq.(II.18)
```

Symbols aber and bber are the two constants for the Berthelot equation of state. The user function variable berth can have the values of zero and one. It has the value of one if the variable type is 'berthelot'; otherwise, the user function variable berth has the value of zero.

Program ESTATE.TK also calculates the specific volume on a mass basis(e.g., vmass) and the compressibility factor for a compound by the following equations:

vmass = vmole / mweight Eq.(II.19)

z = vmole * p / r / t Eq.(II.20)

Symbol vmass is the mass specific volume, mweight is the molecular weight of a compound, and z is the compressibility factor.

Program ESTATE.TK obtains data from the CRITICAL.TK data file. The CRITICAL.TK data file has data for more than fifty compounds. The data includes critical temperature, critical pressure, critical volume, critical compressibility factor, acentric factor, and the molecular weight of a compound.

There are two limitations in using the ESTATE.TK program:

1) This program should be used to calculate the state properties of a compound in the gaseous state.

2) All of the equations of state included in this program

are good for nonpolar compounds. State properties of many compounds have been calculated using this program, and the results show that this program can predict the state properties of nonpolar and small molecules most accurately with less than two percent error. Also, the results show that, for polar and large molecules, the error in the calculation of state properties can be as high as fifty percent. Therefore, this program should be used cautiously for polar compounds.

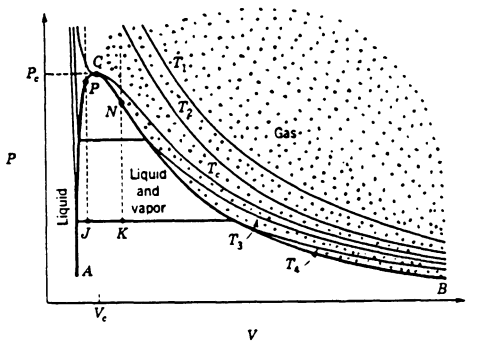


Figure II.1
P-V diagram for a pure material.

2. Instructions

Program ESTATE.TK calculates the volumetric properties of compounds using six different equations of state. These equations are ideal gas law, Pitzer correlation, van der Waals, Redlich Kwong, Dieterici, and Berthelot equation of state. In the following instructions, if a phrase is typed in double emphasized format and it is in quotation marks, it indicates that the phrase should be typed by the user.

In order to use the ESTATE program you need these additional programs :

1) A DOS diskette(version 2.1 0r 2.0)

2) The TK!Solver diskette.

3) The disk containing the ESTATE and CRITICAL programs.

4) A formatted storage diskette to save your solution. The formatted storage diskette and the disk containing the ESTATE and CRITICAL programs may be the same diskette.

In the following instructions it is assumed that your personal computer has a double disk drive. It is also assumed that the disk containing CRITICAL, and ESTATE.TK programs and the storage diskette are the same diskette.

Load the TK!Solver program into the memory of the computer as described in Appendix 1. After loading the TK!Solver program, the screen should be like Figure II.2.

Loading CRITICAL.TK

You need to transfer the CRITICAL program from storage diskette to the memory of the computer. Type '/sl'.
When the computer asks for the filename, type 'b:critical.tk' and push the 'Return' key. The computer responds: loading the b:critical.tk. Wait until the program is loaded into the computer memory.
If you have executed the above steps correctly, the screen should be like Figure II.3.
Before you load the ESTATE program into the computer memory, you need to make a few changes in the variable sheet of the CRITICAL program.
Delete the 1's in the status column of the variables comp, tc, pc, vc, zc, omega, and mweight using the blank command(e.g. type '/b' after placing the curser in the status field). Also, blank the contents of the input field of the variable comp if a value shows there. Also, in the input field of the variable flag, type '1'.
If you have performed the above commands correctly, the variable sheet should be like Figure II.4.

Loading ESTATE.TK

The next step is to transfer the ESTATE program which contains the equations of state into the memory. Note that

you want to link the ESTATE and CRITICAL programs together, therefore you should not attempt to erase CRITICAL program from the memory. Type '/sl'.
when the computer asks for the filename, type 'b:estate.tk' and push the 'Return' key. Then the computer responds: loading the b:estate.tk. Wait until the program is loaded into the memory.
If you have performed the above steps correctly, the variable sheet should be like Figure II.5.
Figure II.5 is the variable sheet of the merged ESTATE and CRITICAL programs. Type '=r' to go to the rule sheet.
The rule sheet should be like Figure II.6.
Figure II.6 is the rule sheet of the merged ESTATE and CRITICAL programs.

Example One

PROBLEM STATEMENT: Calculate the specific molar volume of water vapor at 1000 Kelvin and 100 atmospheres by ideal gas law, Pitzer correlation, van der Waals, Redlich Kwong, Dieterici, and Berthelot equations of state.
In order to solve the problem, perform the following steps:
1) In the input column of the variable comp type ''water'.
2) In the status column of the variable type type '1'

to indicate that you have a list of equations of state . If there is already an 1 in this space skip this step.

3) Press '>' twice while the cursor is on the row of variable type in order to go to the variable type subsheet. Enter the name of each equation of state one at a time as shown below:

'ideal_gas
'pitzer_correlation
'van_der_waals
'redlich_kwong
'dieterici
'berthelot

The variable type subsheet should be like Figure II.7.

If the names of the equations of state are already in the subsheet, skip this step. Press '<' twice to go back to the variable sheet. Type any character in the input column of the variable type to indicate it is an input variable(e.g. type ''input').

4) In the input column for t type the temperature of the gas in Kelvin(e.g. type '1000').

5) In the input column for p type the pressure of the gas in atmospheres(e.g., type '100').

6) In the status column of the variable z type 'lg'. L indicates that there is a list of values for z corresponding to each equation of state, and g indicates that the problem may have an iterative solution.Note that the value of 1 appears in the input column of this variable, which is the ideal gas value of z.

7) press '>' twice to go to the variable z list subsheet and enter the initial guess for each equation of state. The ideal gas value of z (e.g. 1) is the best first guess for a compound at any state. After you enter the initial guesses, the list subsheet of the variable z should be like Figure II.8.

Type '<' twice to return to the variable sheet.

8) If the upper portion of the variable sheet is like Figure II.9a and the lower portion of the variable sheet is like Figure II.9b at the completion of the previous steps then you are ready to execute your program. type '/l!' and wait until the computer stops execution. To solve the problem for all of the equations of state may take a few minutes.

9) When the computer stops executing, press '>' twice while the cursor is on the row of the variable vmole to go into the variable vmole list subsheet in order to see the solution. the screen should be like Figure II.10a .

Each value corresponds to the vmole calculated using the corresponding equation of state. You can get a copy of the solution by pressing Prtsc or you can type '/p'. Type '<' twice to go back to the variable sheet. Repeat step 9 for variables vmass and z. The list subsheet of the variables vmass and z should be like Figures II.10b and II.10c respectively. Vmass is the specific volume on mass basis and z is the compressibility factor of the compound

at the given temperature and pressure.

10) In order to obtain a copy of your solution in tabular format go to the table sheet by typing'=t'. Reset the Table sheet by typing '/r s y'. Enter the title of the table on the row beginning with the word title. Then enter the rest of the information on this sheet as shown in Figure II.11. Figure II.11 is the completed table sheet. Then press '!' to see the table containing each equation of state with its corresponding molar volume, mass volume, and compressibility factor on the screen. The screen should be like Figure II.12.

To get a copy of this on your printer you can press Prtsc or you can change to the printer mode on the first row of the table sheet.

Type '/qy' to quit TK!Solver and return to the DOS system, or turn to the next page to do example two.

```
==================== VARIABLE SHEET ========================================
St Input     Name    Output    Unit      Comment
-- -----     ----    ------    ----      -------

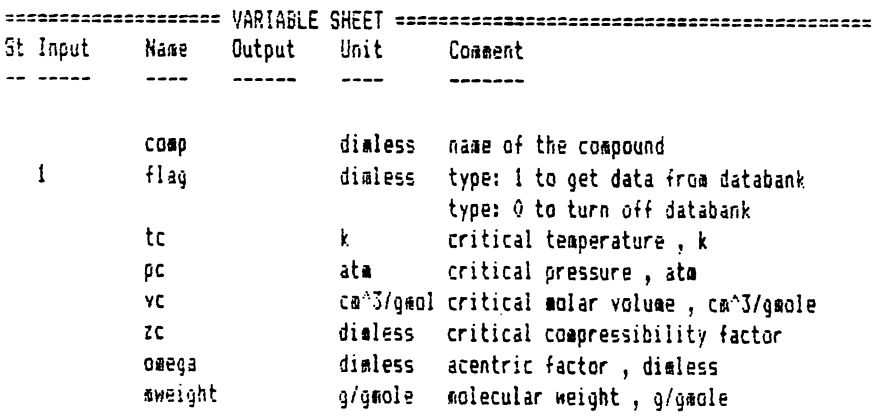

==================== RULE SHEET ============================================
S Rule
- ----
```

Figure II.2
Variable and rule sheets of TK!Solver.

```
==================== VARIABLE SHEET ========================================
St Input     Name    Output    Unit      Comment
-- -----     ----    ------    ----      -------
                                         PROGRAM   CRITICAL.TK   10-3-1984
                                         CRITICAL DATA FOR MORE THAN  50
                                         COMPOUNDS.
                                         1) CRITICAL TEMPERATURE AND PRESSURE;
                                                 Tc  ,  Pc
                                         2) CRITICAL SPECIFIC VOLUME AND
                                            COMPRESSIBILITY FACTOR;  Vc , Zc
                                         3) ACENTRIC FACTOR AND MOLECULAR
                                            WEIGHT;  OMEGA  ,  MWEIGHT

L            comp            dimless     name of the compound
             flag            dimless     type: 1 to get data from databank
                                         type: 0 to turn off databank
L            tc              k           critical temperature , k
L            pc              atm         critical pressure , atm
L            vc              cm^3/gmol   critical molar volume , cm^3/gmole
L            zc              dimless     critical compressibility factor
L            omega           dimless     acentric factor , dimless
L            mweight         g/gmole     molecular weight , g/gmole
```

Figure II.3
Variable sheet of CRITICAL.TK.



```
==================== VARIABLE SHEET ========================================
St Input     Name     Output    Unit       Comment
-- -----     ----     ------    ----       -------

            comp               dimless    name of the compound
  1         flag               dimless    type: 1 to get data from databank
                                          type: 0 to turn off databank
            tc                 k          critical temperature , k
            pc                 atm        critical pressure , atm
            vc                 cm^3/gmol  critical molar volume , cm^3/gmole
            zc                 dimless    critical compressibility factor
            omega              dimless    acentric factor , dimless
            mweight            g/gmole    molecular weight , g/gmole
```

Figure II.4
Variable sheet of CRITICAL.TK.

St	Input	Name	Output	Unit	Comment
					PROGRAM CRITICAL.TK 10-3-1984
					CRITICAL DATA FOR MORE THAN 50
					COMPOUNDS.
					1) CRITICAL TEMPERATURE AND PRESSURE;
					Tc , Pc
					2) CRITICAL SPECIFIC VOLUME AND
					COMPRESSIBILITY FACTOR; Vc , Zc
					3) ACENTRIC FACTOR AND MOLECULAR
					WEIGHT; OMEGA , MWEIGHT
		comp		dimless	name of the compound
	1	flag		dimless	type: 1 to get data from databank
					type: 0 to turn off databank
		tc		k	critical temperature , k
		pc		atm	critical pressure , atm
		vc		cm^3/gmol	critical molar volume , cm^3/gmole
		zc		dimless	critical compressibility factor
		omega		dimless	acentric factor , dimless
		mweight		g/gmole	molecular weight , g/gmole
					PROGRAM ESTATE.TK 10-3-1984
					CALCULATES VOLUMETRIC PROPERTIES OF
					COMPOUNDS BY SIX EQUATIONS OF STATE:
					1) IDEAL GAS LAW
					2) PITZER CORRELATION
					3) VAN DER WAALS
					4) REDLICH KWONG
					5) DIETERICI
					6) BERTHELOT
L		type		dimless	name of equation of state , dimless
		t		k	temperature , k
		p		atm	pressure , atm
L		vmole		cm^3/gmol	molar specific volume , cm^3/gmole
L		vmass		cm^3/g	mass specific volume , cm^3/g
	82.05	r		atm*cm^3/	gas constant , cm^3*atm/gmole/k
L		z		dimless	compressibility factor , dimless

Figure II.5
Variable sheet of the merged CRITICAL and ESTATE.TK.

```
S Rule
- ----
                    "maps a compound to its critical properties.
! 0/flag    + tc = mapc1(comp)
! 0/flag    + pc = mapc2(comp)
! 0/flag    + vc = mapc3(comp)
! 0/flag    + zc = mapc4(comp)
! 0/flag    + omega = mapc5(comp)
! 0/flag    + mweight = mapc6(comp)
! tr = t/tc
! pr = p/pc
                          "Ideal gas law
! p*vmole = r*t
                          "Pitzer correlation
! p*vmole/r/t = 1 + bb*pr/tr
! bb = .083 - .422/tr^1.6 + omega*(.139 - .172/tr^4.2)
                          "van der Waals
! (p + 27*r^2*tc^2/64/pc/vmole^2 ) * (vmole - r*tc/8/pc ) = r*t
                          "Redlich Kwong
! p = r*t/(vmole - bred) - .4278*r^2*tc^2.5/pc/t^.5/vmole/(vmole + bred)
! bred = .0867*r*tc/pc
                          "Dieterici
! p = r*t*exp(-4*r^2*tc^2/r/t/vmole/pc/exp(2)) / (vmole - r*tc/pc/exp(2))
                          "Berthelot
! p = r*t/(vmole - r*tc/8/pc) - 27*r^2*tc^3/64/pc/t/vmole^2
! vmass = vmole/mweight
! z     = vmole*p/t/r
```

Figure II.6
Rule sheet of the merged CRITICAL and ESTATE.TK.

```
==================== LIST: type ================================================
Comment:                  list for type of equation of state
Display Unit:             dimless
Storage Unit:             dimless
Element Value
------- -----
1       'ideal_gas
2       'pitzer_correla
3       'van_der_waals
4       'redlich_kwong
5       'dieterici
6       'berthelot
```

Figure II.7
Subsheet of list type.

```
==================== LIST: z ===================================================
Comment:                  list for variable Z
Display Unit:             dimless
Storage Unit:             dimless
Element Value
------- -----
1       1
2       1
3       1
4       1
5       1
6       1
```

Figure II.8
Subsheet of list z.

St	Input	Name	Output	Unit	Comment
	'water	comp		dimless	name of the compound
	1	flag		dimless	type: 1 to get data from databank
					type: 0 to turn off databank
		tc		k	critical temperature , k
		pc		atm	critical pressure , atm
		vc		cm^3/gmol	critical molar volume , cm^3/gmole
		zc		dimless	critical compressibility factor
		omega		dimless	acentric factor , dimless
		mweight		g/gmole	molecular weight , g/gmole

Figure II.9a
Upper portion of the variable sheet.

St	Input	Name	Output	Unit	Comment
L	'input	type		dimless	name of equation of state , dimless
	1000	t		k	temperature , k
	100	p		atm	pressure , atm
L		vmole		cm^3/gmol	molar specific volume , cm^3/gmole
L		vmass		cm^3/g	mass specific volume , cm^3/g
	82.05	r		atm*cm^3/	gas constant , cm^3*atm/gmole/k
LG	1	z		dimless	compressibility factor , dimless

figure II.9b
Lower portion of the variable sheet.

LIST: vmole

Element	Value
1	820.5
2	798.8909178
3	783.9999043
4	788.0385074
5	766.9962882
6	808.9279126

Figure II.10a
Subsheet of list vmole.

LIST: vmass

Element	Value
1	45.5428508
2	44.3434124
3	43.51686858
4	43.74103616
5	42.57306218
6	44.90052801

Figure II.10b
Subsheet of list vmass.

LIST: z

Element	Value
1	1
2	.9736635195
3	.9555148132
4	.9604369377
5	.9347913324
6	.9858962981

Figure II.10c
Subsheet of list z.

```
==================== TABLE SHEET ==============================================
Screen or Printer:          Screen
Title:                      volume of steam using different equations of state
Vertical or Horizontal:     Vertical
List      Width First Header
----      ----- ----- ------
type      25    1     type
vmole     15    1     v,cm^3/gmole
vmass     15    1     v,cm^3/g
z         10    1     z
```

Figure II.11
Table sheet of ESTATE.TK.

volume of steam using different equations of state

type	v,cm^3/gmole	v,cm^3/g	z
ideal_gas	820.5	45.5428508	1
pitzer_correlation	798.8909178	44.3434124	.973663520
van_der_waals	783.9999043	43.51686858	.955514813
redlich_kwong	788.0385074	43.74103616	.960436938
dieterici	766.9962882	42.57306218	.934791332
berthelot	808.9279126	44.90052801	.985896298

Figure II.12
Molar Volume of water vapor.

Example Two

Let's do one more example in order to use the plot sheet of TK!Solver program. First, go to the variable sheet by typing '=v'. Then clear the contents of the variable sheet by typing '/r v y'. The upper portion of the variable sheet should be like Figure II.13a and the lower portion of the variable sheet should be like Figure II.13.

PROBLEM STATEMENT: Find the variation of molar specific volume of water vapor as a function of temperature using the Redlich Kwong equation of state. The pressure of steam is 100 atmospheres and the temperature range of interest is from 700 to 900 Kelvin with intervals of 50. In order to solve the problem, perform the following steps:

1) In the input column of the variable comp type ''water'.

2) In the input column of the variable flag type '1'. This enables the program to get data from the databank.

3) In the input column of the variable type type ''redlich_kwong'. Also erase the 1 in the status column of the variable type by typing '/b' while the cursor is on the status column of the variable type.

4) In the status column of the variable t type '1' to indicate you have a list of temperatures.

5) In the input column of the variable t type any number to indicate that the variable t is an input variable(e.g.

type '700'). Then press '>' twice to go to the list subsheet of the variable t. Enter the list of the temperatures on this sheet. After you enter the list of temperatures, the subsheet should be like Figure II.14. Press '<' twice to go back to the variable sheet.

6) In the input column of the variable p type the pressure of the gas(e.g. type '100').

7) In the status column of variable z type 'lg' as you did in the previous example. Note that the value of 1 appears in the input column of this variable, which is the ideal gas value for z.

8) Press '>' twice to go to the variable z list subsheet and enter the initial guess for each temperature. It is the same procedure as step 7) of the previous example. after you enter the initial guesses the subsheet should look like Figure II.15.
Press '<' twice to return to the variable sheet.

9) In the input column of the variable r type '82.05', the value of the gas constant in cm©3*atm/(gmole*k). 10)

10) If the upper portion of the variable sheet is like Figure II.16a and the lower portion is like Figure II.16b at the completion of the previous steps, you are ready to execute your program. Type '/l!' and wait until the computer stops execution. To solve the problem for all of the temperatures may take as long as three minutes.

11) When the computer stops executing, press '>' twice

to go to the variable vmole list subsheet in order to see the solution. The screen should be like Figure II.17a.
Each value corresponds to the vmole calculated for the corresponding temperature. You can get a hard copy of the solution by pressing Prtsc or you can type '/p'.
Press '<' twice to go back to the variable sheet.
12) Repeat step 11) for variables vmass and z. The list subsheets of the variables vmass and z should be like Figure II.17b and Figure II.17c respectively .
13) In order to obtain a copy of your solution in graphical format go to the plot sheet by typing '=p'.
Enter the title of the plot on the row beginning with the word title. Then enter the rest of the information on this sheet as shown in Figure II.18. Figure II.18 is the completed plot sheet for the variable vmole .
Then press '!' to see the plot containing molar volume of water vapor as a function of temperature on the screen. The screen should be like Figure II.19.
To get a copy of this on your printer you can press Prtsc or you can change to printer mode on the first row of the plot sheet.
14) You can repeat step 13) for the variables vmass and z. The plot sheet for the variable z is shown in Figure II.20 and the plot of z , compressibility factor , as a function of temperature is shown in Figure II.21.
In order to quit type '/q y', then the computer gives

you the A prompt(e.g., A>). The A prompt indicates that you are out of the TK!Solver program.

St	Input	Name	Output	Unit	Comment
		comp		dimless	name of the compound
		flag		dimless	type: 1 to get data from databank
					type: 0 to turn off databank
		tc		k	critical temperature , k
		pc		atm	critical pressure , atm
		vc		cm^3/gmol	critical molar volume , cm^3/gmole
		zc		dimless	critical compressibility factor
		omega		dimless	acentric factor , dimless
		mweight		g/gmole	molecular weight , g/gmole

Figure II.13a
Upper portion of the variable sheet.

St	Input	Name	Output	Unit	Comment
L		type		dimless	name of equation of state , dimless
		t		k	temperature , k
		p		atm	pressure , atm
L		vmole		cm^3/gmol	molar specific volume , cm^3/gmole
L		vmass		cm^3/g	mass specific volume , cm^3/g
		r		atm*cm^3/	gas constant , cm^3*atm/gmole/k
L		z		dimless	compressibility factor , dimless

Figure II.13b
Lower portion of the variable sheet.

```
==================== LIST: t ================================================
Comment:
Display Unit:              k
Storage Unit:              k
Element Value
------- -----
1       700
2       750
3       800
4       850
5       900
```

Figure II.14
Subsheet of list t.

```
==================== LIST: z ================================================
Comment:                   list for variable Z
Display Unit:              dimless
Storage Unit:              dimless
Element Value
------- -----
1       1
2       1
3       1
4       1
5       1
6       1
```

Figure II.15
Subsheet of list vmole.

St	Input	Name	Output	Unit	Comment
	'water	comp		dimless	name of the compound
	1	flag		dimless	type: 1 to get data from databank
					type: 0 to turn off databank
		tc		k	critical temperature , k
		pc		atm	critical pressure , atm
		vc		cm^3/gmol	critical molar volume , cm^3/gmole
		zc		dimless	critical compressibility factor
		omega		dimless	acentric factor , dimless
		mweight		g/gmole	molecular weight , g/gmole

Figure II.16a
Upper portion of the variable sheet.

St	Input	Name	Output	Unit	Comment
	'redlich_	type		dimless	name of equation of state , dimless
L	700	t		k	temperature , k
	100	p		atm	pressure , atm
L		vmole		cm^3/gmol	molar specific volume , cm^3/gmole
L		vmass		cm^3/g	mass specific volume , cm^3/g
	82.05	r		atm*cm^3/	gas constant , cm^3*atm/gmole/k
LG	1	z		dimless	compressibility factor , dimless

Figure II.16b
Lower portion of the variable sheet.

LIST: vmole

Element	Value
1	497.0524697
2	549.8406567
3	600.1571519
4	648.7489301
5	696.0739789

Figure II.17a
Subsheet of list vmole.

LIST: vmass

Element	Value
1	27.58950209
2	30.51957464
3	33.31245292
4	36.00959869
5	38.63643311

Figure II.17b
Subsheet of list vmass.

LIST: z

Element	Value
1	.8654173756
2	.8935050281
3	.9143161972
4	.9302060151
5	.9426149081
6	1

Figure II.17c
Subsheet of list z.

```
==================== PLOT SHEET ================================================
Screen or Printer:          Screen
Title:                      variation of volume of steam with temperature
Display Scale ON:           Yes
X-Axis:                     t
Y-Axis    Character
------    ---------
vaole     v
```

Figure II.18
Plot sheet of ESTATE.TK.

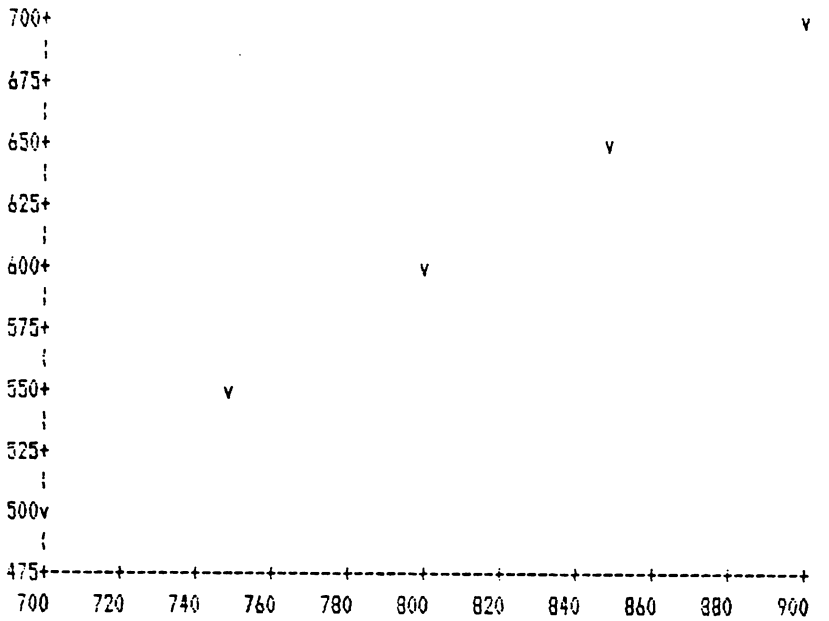


Figure II.19
Variation of volume of water with temperature at 100 atm.

```
==================== PLOT SHEET ================================================
Screen or Printer:          Screen
Title:                      variation of z of steam with temperature
Display Scale ON:           Yes
X-Axis:                     t
Y-Axis    Character
------    ---------
z         z
```

Figure II.20
PLot sheet for z.

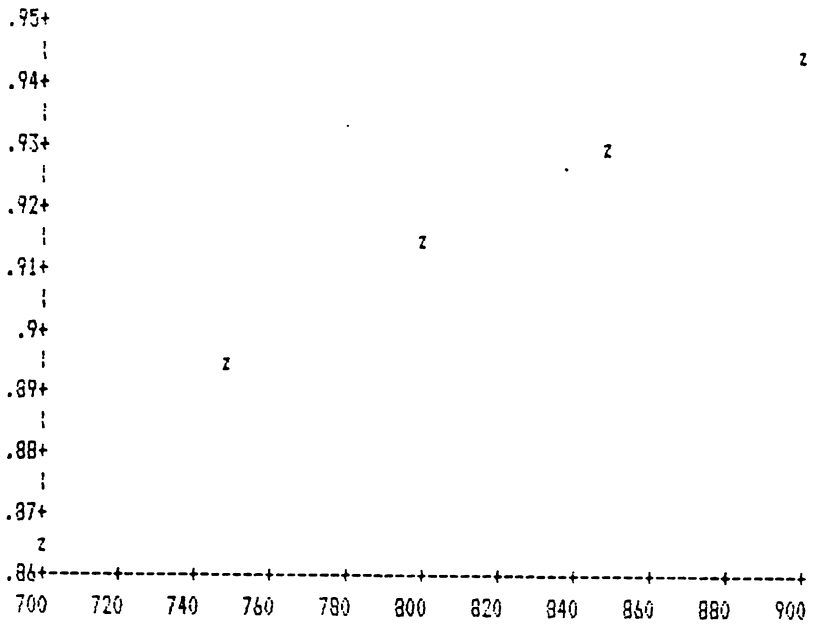


Figure II.21
Variation of z of water vapor with temperature at 100 atm.

III. Program RESIDUAL.TK: Residual Property Calculations

1. Theory

Program RESIDUAL.TK calculates the change in the properties of a compound from the initial state to the final state in the gas phase. The properties that the program calculates are internal energy, enthalpy, entropy, and volume. Figure III.1 shows the different steps that are involved in calculating the changes in properties of a gas from one state to another.

Step 1) The gas is transferred from the initial state at temperature ti and pressure pi to the same temperature and pressure, but as an ideal gas. Note that this step is the calculation of residual properties of the gas for the initial state. Also, note that an equation of state is needed to calculate the residual properties of the gas.

Step 2) The gas is heated from the initial temperature ti to the final temperature tf, at constant initial pressure pi, in the ideal state. Note that this step requires ideal heat capacity data for the compound.

Step 3) The gas is pressurized from the initial pressure pi to the final pressure pf, at constant final

temperature tf, in the ideal state. Since pressure has no effect on the enthalpy and internal energy of a compound in the ideal state, the change in enthalpy and internal energy is zero for this step, however, pressure does have an effect on the entropy of a gas , even in the ideal state. Also, note that the second and the third step calculate the change in the properties of a compound from the initial state(e.g. ti, pi) to the final state(e.g. tf, pf), assuming that the gas is ideal.

Step 4) The gas is transferred from the ideal state at the temperature tf and the pressure pf to the same temperature and pressure, but as a real gas. Note that this step is the calculation of residual properties of the gas for the final state. Also, note that an equation of state is needed to calculate the residual properties of the gas.

Summation of all of the changes in the properties of the gas for steps 1), 2), 3), and 4) is the overall change in the properties of the compound from the initial to the final state.

As it was discussed in the theory section of the program ESTATE.TK, for a nonreacting system with only one compound and one phase, two state variables can completely define the state of the system. Therefore, specifying the pressure and the temperature for both the initial and the final states, completely defines the change in the properties of the gas from the initial to the final

state.

In order to calculate the enthalpy, entropy, internal energy, and volume of a compound, as a function of temperature and pressure, the following equations are used:

$$h(t,p) = \int_{v}^{\infty} [p - t*(dp/dt)v] * dv + p*v - r*t + h(ideal) \qquad \text{Eq.(III.1)}$$

$$s(t,p) = \int_{v}^{\infty} [r/v - (dp/dt)v] * dv + r*\ln(v*p/r/t) + s(ideal) \qquad \text{Eq.(III.2)}$$

$$u(t,p) = h(t,p) - p*v \qquad \text{Eq.(III.3)}$$

$$v(t,p) = f(t,p) \qquad \text{Eq.(III.4)}$$

Lower case variables are molar variables(e.g. They are based on one mole). Variables t, p, and v are the temperature, pressure, and the molar volume of the gas, respectively. Symbols h, s, and u are the molar enthalpy, entropy, and internal energy of the gas, respectively. For a more detailed discussion of the above equations see references (4) and (11).

Equations (III.1) through (III.4) can be rearranged to calculate the residual properties of a compound at a given temperature and pressure. The residual properties can be calculated by the following equations:

$$hres(t,p) = r*t - p*v - \int_{v}^{\infty} [p - t*(dp/dt)v] * dv \qquad \text{Eq.(III.5)}$$

$$sres(t,p) = \int_{v}^{\infty} [(dp/dt)v - r/v] * dv - r*\ln(v*p/r/t) \qquad \text{Eq.(III.6)}$$

$$ures(t,p) = hres(t,p) - p*v \qquad \text{Eq.(III.7)}$$

$$vres(t,p) = f(t,p) - r*t/p \qquad \text{Eq.(III.8)}$$

Symbols hres, sres, ures, and vres are residual molar enthalpy, entropy, internal energy, and specific volume, respectively. Symbol r is the gas constant, and v is the molar specific volume. Symbol (dp/dt)v is the derivative of pressure with respect to temperature at constant molar specific volume. Function f(t,p) is an equation of state that relates pressure and temperature to volume. The upper limit of the integrals is infinity, and the lower limit for the integrals is the molar specific volume of the gas, v. As the above equations indicate, an equation of state is needed in order to evaluate the integrals in Equations (III.5) and (III.6).

Program RESIDUAL.TK can choose among three different equations of state to evaluate the residual properties of a gas. These equations are Pitzer correlation, van der Waals, and Redlich Kwong equation of state. The description for each one of the above equations is given below.

Pitzer correlation: The Pitzer correlation (Ref. 12) is given by the following equations:

```
p = r * t / ( vmole - b)  +0/pitzer(type)          Eq.(III.9)
```

where

```
b = b0 + omega * b1                                Eq.(III.10)
```

and

$$b0 = .1445 - .33/tr - .1385/tr^2 - .0121/tr^3 \qquad \text{Eq.(III.11)}$$

$$b1 = .073 + .46/tr - .5/tr^2 - .097/tr^3 - .0073/tr^8 \qquad \text{Eq.(III.12)}$$

$$tr = t/tc \qquad \text{Eq.(III.13)}$$

$$pr = p/pc \qquad \text{Eq.(III.14)}$$

Symbols b, b0, and b1 are the constants for the Pitzer correlation. Symbol omega is the acentric factor for the compound, and vmole is the molar specific volume. Symbols tr and pr are the reduced temperature and reduced pressure, respectively. Symbols tc and pc are the critical temperature and the critical pressure, respectively. Substitution of Equations (III.9) through (III.12) into Equations (III.5) and (III.6) and performing the integrations, result in the following equations:

$$hres = tr*p* ((db/dtr) - b/tr) + 0/pitzer(type) \qquad \text{Eq.(III.15)}$$

$$sres = p * (db/dtr) / tc + 0/pitzer(type) \qquad \text{Eq.(III.16)}$$

$$vres = vmole - r*t/p \qquad \text{Eq.(III.17)}$$

Symbol (db/dtr) is the derivative of b with respect to reduced temperature. Variable type is the name of the equation of state. It can be either 'pitzer correlation', 'van der waals', or 'redlich kwong'. The user function variable pitzer can have values of zero and one. If the variable type is 'pitzer correlation', the user function variable pitzer has the value of one, otherwise,

it has a value of zero. Note that no iteration is involved, because Pitzer correlation is linear in volume.

van der Waals: van der Waals equation of state(Ref. 9) is given by the following equations:

```
p = r*t/(vmole- bvan) - avan/vmole^2  +0/vander(type)
                                                    Eq.(III.18)
```

where

```
avan = 27 * r^2 * tc^2 /(64 * pc)                   Eq.(III.19)

bvan = r * tc / (8* pc)                             Eq.(III.20)
```

Symbols bvan and avan are constants for van der Waals equation of state. The user function variable vander can have the values of zero and one. If the variable type is 'van der waals', the user function variable vander has the value of one, otherwise, it has a value of zero. Substitution of Equation (III.18) in Equations (III.5) and (III.6) and performing the integrals, result in the following equations:

```
hres = r*t* (1- vmole/(vmole-bvan) +2*avan/r/t/vmole)
                                  +0/vander(type) Eq.(III.21)

sres = r* ln( r*t/p/ (vmole -bvan) )  +0/vander(type)
                                                    Eq.(III.21)
```

Residual internal energy, ures, is calculated by Equation (III.7), and residual volume, vres, is calculated by Equation (III.17). Note that the solution to van der Waals equation of state is iterative, because the equation is

nonlinear in volume.

Redlich Kwong: Redlich Kwong equation of state (Ref. 9) is given by the following equations:

```
p = r*t/ (vmole-bred) -ared/t^.5/vmole/ (vmole+bred)
                                +0/redwg(type)     Eq.(III.23)
```

where

```
ared = .4278 * r^2 * tc^2.5 / pc                   Eq.(III.24)
```

```
bred = .0867 * r * tc / pc                         Eq.(III.25)
```

Symbols ared and bred are the constants for Redlich Kwong equation of state. The user function variable redwg can have the values of zero and one. If the variable type is 'redlich kwong', the user function variable redwg has the value of one, otherwise, it has a value of zero. Substitution of Equation (III.23) into Equations (III.5) and (III.6) and performing the integrals, result in the following equations:

```
hres = r*t -p*vmole + ln( (vmole+bred) /vmole )*
            (3*ared/2/bred/t^.5) +0/redwg(type) Eq.(III.26)
```

```
sres = r*ln (vmole/z/(vmole-bred))+ ln((vmole+bred)/vmole)*
          (ared/2/bred/ t^1.5)  +0/redwg(type) Eq.(III.27)
```

where

```
z = p* vmole/ r/ t                                 Eq.(III.28)
```

Symbol z is the compressibility factor for the gas. The residual internal energy can be calculated by Equation

(III.7), and the residual volume can be calculated by Equation (III.17). Note that the solution to Redlich Kwong equation of state is iterative, because Redlich Kowng equation of state is nonlinear in volume.

The enthalpy and entropy changes for steps 2) and 3) are calculated by the following equations:

$$h(step2) = \int_{ti}^{tf} cp(t) * dt \qquad \text{Eq.(III.29)}$$

$$s(step2) = \int_{ti}^{tf} cp(t)/t * dt \qquad \text{Eq.(III.30)}$$

$$h(step3) = 0 \qquad \text{Eq.(III.31)}$$

$$s(step4) = -r * \ln(pf/pi) \qquad \text{Eq.(III.32)}$$

Symbol cp(t) is the heat capacity as a function of temperature. Symbols pf and pi are the final and initial pressures, respectively.

Therefore, the sum of the enthalpy and entropy changes for steps 1), 2), 3), and 4) gives the change in the properties of a gas from the initial to the final state, as given by the following equations:

$$ht = hres(step1) + h(step2) + h(step3) - hres(step4) \qquad \text{Eq.(III.33)}$$

$$st = sres(step1) + s(step2) + s(step3) - sres(step4) \qquad \text{Eq.(III.34)}$$

$$ut = ht - d (p* vmole) \qquad \text{Eq.(III.35)}$$

$$vt = vmolef - vmolei \qquad \text{Eq.(III.36)}$$

Symbols ht, st, ut, and vt are the total changes in enthalpy, entropy, internal energy, and volume from the

initial state to the final state, respectively. Symbols vmolef and vmolei are the final and initial volume, respectively.

Program RESIDUAL.TK uses both data files CRITICAL.TK and DATBANK1.TK. CRITICAL.TK data file contains critical data for more than fifty compounds. The data includes critical temperature, critical pressure, critical volume, critical compressibility factor, acentric factor, and molecular formula.

DATBANK1.TK data file contains heat capacity data for more than one hundred compounds. The data file provides the first, second, third, and fourth coefficients for the heat capacity equation shown below:

$$cp = a + b*t + c*t^2 + d*t^3 \qquad [t]=K \qquad \text{Eq.(III.37)}$$

There are two limitations in using the RESIDUAL.TK program. First, this program should be used to calculate the property changes of a compound from the initial to the final state only if both states of the compound are gaseous. Secondly, all of the equations of state in this program are valid only for nonpolar molecules, therefore, this program should be applied to nonpolar compounds. For small and nonpolar molecules, the error in the property changes may be less than three percent, but for polar and large molecules, the error may be as high as one hundred percent.

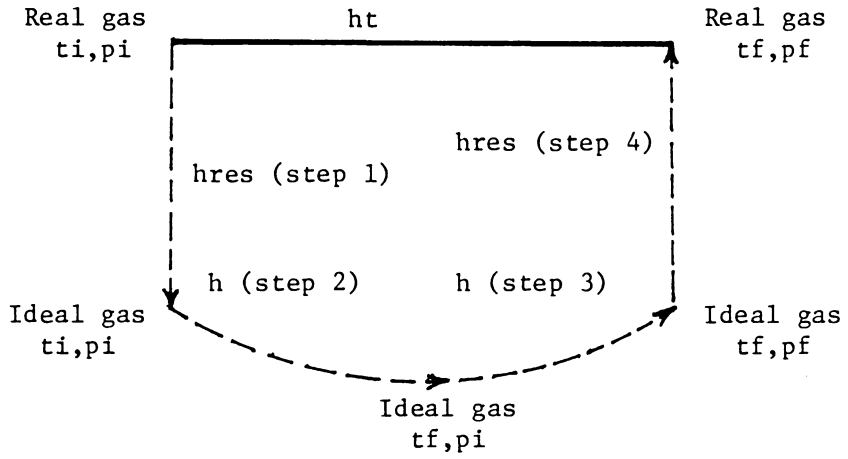


Figure III.1
Steps involved in enthalpy calculations.

2.Instructions

Program RESIDUAL.TK calculates the residual properties of different compounds at a given temperature and pressure. The program calculates residual volume, internal energy, enthalpy, and entropy. The program also calculates the change in volume, internal energy, enthalpy, and entropy of a compound from the initial state(e.g. temperature=ti and pressure=pi) to the final state(e.g. temperature=tf and pressure=pf) in the gaseous state.

In the following instructions, if a phrase is typed in double emphasized format and it is in quotation marks, it indicates that the phrase should be typed by the user.

In order to use the RESIDUAL program you need these additional programs :

1) A DOS diskette(version 2.1).

2) The TK!Solver diskette.

3) The disk containing the RESIDUAL, CRITICAL, and DATBANK1 programs.

4) A formatted storage diskette to save your solution. The formatted storage diskette and the disk containing the RESIDUAL, CRITICAL, and DATBANK1 programs may be the same diskette.

In the following instructions it is assumed that your personal computer has a double disk drive. It is also assumed that the disk containing RESIDUAL, CRITICAL, and

DATBANK1 programs and the storage diskette are the same diskette.

Load the TK!Solver program into the memory of the computer as described in Appendix 1. After loading the TK! Solver program, the screen should be like Figure III.2.

EXAMPLE ONE

PROBLEM STATEMENT: In this example, we would like to calculate the residual properties of methane which is a non-polar compound. Methane is compressed from the initial state of 40 degrees Fahrenheit and 300 psia to the final state of 200 degrees Fahrenheit and 1500 psia. We would like to calculate the residual properties of this gas for both initial and final states, and we would also like to find the total change in the properties of the gas from the initial to the final state.

Loading CRITICAL.TK

To solve the problem, you need to transfer the CRITICAL program which contains critical data of compounds from the storage diskette to the memory of the computer. Type '/sl'.

When the computer asks for the filename, type 'b:critical.tk' and push the 'Return' key. The computer responds: loading the b:critical.tk. Wait till

the program is loaded into the computer memory.

If you have executed the above steps correctly, the screen should be like Figure V.3.

Figure III.3 is the variable sheet of the CRITICAL program. It may take a few minutes for the computer to load the CRITICAL program into the memory.

Loading DATBANK1.TK

Next, transfer the DATBANK1 program which contains the heat capacity data for compounds into the memory of the computer. Note that you want to merge the programs CRITICAL and DATBANK1 together in the computer memory. Therefore, you should not attempt to erase the CRITICAL program from the memory. Type '/sl'.

When the computer asks for the filename, type 'b:datbank1.tk' and push the 'Return' key. The computer responds: loading The b:datbank1.tk. Wait until the program is loaded into the memory.

If you have performed the above commands correctly, the variable sheet should be like Figure III.4a. Figure III.4a is the variable sheet of the merged CRITICAL and DATBANK1 programs. It may take a few minutes for the computer to load DATBANK1 into the memory.

Type '=r' to go to the rule sheet. The rule sheet should be like Figure III.4b. Figure III.4b is the rule sheet of the merged CRITICAL and DATBANK1 programs.

Type '=v' to go back to the variable sheet. On the top right hand corner of the variable sheet there is an index which indicates how much free memory is available. Before loading the CRITICAL and DATBANK1 programs into the memory, the index shows 184 which means 184K bytes of memory are free to use. After loading the CRITICAL program the index shows 166, and after loading DATBANK1 program the index shows 112 which means 112K bytes of memory is free to use. The CRITICAL and DATBANK1 programs take up as much as 72k bytes of memory. If you merge the RESIDUAL program with the CRITICAL and DATBANK1 programs, the computer may not have enough free memory to execute the program and to do internal calculations. Therefore, it is recommended to get data from the CRITICAL and DATBANK1 programs and then delete the above programs from the memory before loading the RESIDUAL program. If your personal computer has a larger memory size, you may be able to merge the above three programs and execute them simultaneously. In the following instructions, the data for the compound is obtained from the CRITICAL and DATBANK1 programs. Then the above programs are deleted before loading the RESIDUAL program.

Let's get critical and heat capacity data for the compound methane. In order to get the data, you should do the following:

1) In the input column of the variable comp type the name

of the compound(e.g., type ''methane').

2) In the input column of the variable flag type '1' to indicate that you want to get data from the databank.

3) If the upper portion of the variable sheet is like Figure III.5 at the completion of the above steps, you are ready to execute the program. Note that there is no change in the lower portion of the variable sheet which is shown in Figure III.4a. Type '!' and wait until the computer stops execution which may take as long as a minute.

After the computer stops executing, the upper portion of the variable sheet is like Figure III.6a, and the lower portion of the variable sheet is like Figure III.6b.

4) As you see on the variable sheet, the data obtained is in the output column of each variable. You need to transfer the data from the output column to the input column of each variable before the data can be used by the RESIDUAL program. To transfer the data from the output to the input column, type 'g' in the status column of each variable. After this step, the upper portion of the variable sheet is like Figure III.7.

You can do the same for the lower portion of the variable sheet to transfer the values from the output to the input column. Then, in order to get rid of g's in the status column of the variables, you can either type g again or you can use the blank command(e.g. /b command) while the

cursor is on the status column of each variable. Using either method, the upper portion of the variable sheet should be like Figure III.8 after performing the above instruction.

5) If the whole variable sheet is like Figure III.9 after the completion of the above steps, save the variable sheet in a file in order to use the data later in this example. Type '/sv'. When the computer asks for the filename, type the name of the file that you want to store the data for methane(e.g., type 'b:methane'). The above command saves the data for compound methane in a storage file named methane.

6) Type '/r a y' to clear the input and output columns of each variable. If you want to do the second example for the residual properties of ammonia, Then, get the data for ammonia as you did in the above steps for methane and save the data for ammonia in a storage file. After performing steps 1) through 5) for ammonia, the variable sheet containing critical and heat capacity data for ammonia is like Figure III.10.

7) after obtaining all the data for as many compounds as you need, delete the merged CRITICAL and DATBANK1 programs using the reset command(e.g., type '/r a y'). After reseting the TK!Solver program, the screen should be like Figure III.2.

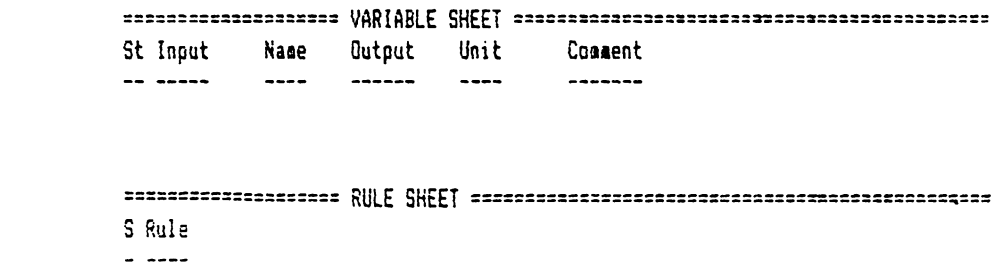


Figure III.2
Variable and rule sheets of TK!Solver.

St	Input	Name	Output	Unit	Comment
L		comp		dimless	name of the compound
		flag		dimless	type: 1 to get data from databank type: 0 to turn off databank
L		tc		k	critical temperature , k
L		pc		atm	critical pressure , atm
L		vc		cm^3/gmol	critical molar volume , cm^3/gmole
L		zc		dimless	critical compressibility factor
L		omega		dimless	acentric factor , dimless
L		mweight		g/gmole	molecular weight , g/gmole

Figure III.3
Variable sheet of CRITICAL.TK.

			1) CRITICAL TEMPERATURE AND PRESSURE; Tc , Pc 2) CRITICAL SPECIFIC VOLUME AND COMPRESSIBILITY FACTOR; Vc , Zc 3) ACENTRIC FACTOR AND MOLECULAR WEIGHT; OMEGA , MWEIGHT
L	comp	dimless	name of the compound
	flag	dimless	type: 1 to get data from databank type: 0 to turn off databank
L	tc	k	critical temperature , k
L	pc	atm	critical pressure , atm
L	vc	cm^3/gmol	critical molar volume , cm^3/gmole
L	zc	dimless	critical compressibility factor
L	omega	dimless	acentric factor , dimless
L	mweight	g/gmole	molecular weight , g/gmole
			PROGRAM DATBANK1.TK 10-3-1984 DATA FOR MORE THAN 100 COMPOUNDS: 1) IDEAL GAS MOLAL HEAT CAPACITY; Cp = ALPHA + BETA*T + GAMMA*T^2 + THETA*T^3 2) NUMBER OF ATOMS IN A COMPOUND; C , H , O , N , S , Cl 3) ENTHALPY AND ENTROPY OF FORMATION AT 25 c; DHf@25c , DSf@25c type: 0 to turn off databank
L	trangek	k	temperature range of Cp data , k
L	mformul	dimless	molecular formula , dimless
L	nec	dimless	number of carbon atoms ,dimless
L	neh	dimless	number of hydrogen atoms , dimless
L	neo	dimless	number of oxygen atoms , dimless
L	nen	dimless	number of nitrogen atoms , dimless
L	nes	dimless	number of sulfur atoms , dimless
L	necl	dimless	number of chlorine atoms , dimless
L	alpha	cal/gmole	first term of Cp data, cal/gmole/k
L	beta	cal/gmole	second term of Cp data, cal/gmole/k^2
L	gamma	cal/gmole	third term of Cp data, cal/gmole/k^3
L	theta	cal/gmole	fourth term of Cp data, cal/gmole/k^4
L	dhf25c	cal/gmole	enthalpy of formation@25 c, cal/gmole
L	ds25c	cal/gmole	standard entropy @25 c, cal/gmole/k

Figure III.4a
Variable sheet of the merged CRITICAL.TK and DATBANK1.TK.

```
S Rule
- ----
                    "maps a compound to its critical properties.
I 0/flag    + tc = mapc1(comp)
I 0/flag    + pc = mapc2(comp)
I 0/flag    + vc = mapc3(comp)
I 0/flag    + zc = mapc4(comp)
I 0/flag    + omega = mapc5(comp)
I 0/flag    + mweight = mapc6(comp)
                  "maps a compound to its heat capacity data.
I 0/flag    + alpha = mapcp1(comp)
I 0/flag    + beta = mapcp2(comp)
I 0/flag    + gamma = mapcp3(comp)
I 0/flag    + theta = mapcp4(comp)
I trangek = mapcpr(comp)
I mformula = mapcpf(comp)
I 0/flag    + dhf25c= maphf25(comp)
I 0/flag    + ds25c = maps25(comp)
I 0/flag    + nec = mapnc(comp)
I 0/flag    + neh = mapnh(comp)
I 0/flag    + neo = mapno(comp)
I 0/flag    + nen = mapnn(comp)
I 0/flag    + nes = mapns(comp)
I 0/flag    + necl = mapncl(comp)
```

Figure III.4b
Rule sheet of the merged CRITICAL.TK and DATBANK1.TK.

St	Input	Name	Output	Unit	Comment
L	'methane	comp		dimless	name of the compound
	1	flag		dimless	type: 1 to get data from databank
					type: 0 to turn off databank
L		tc		k	critical temperature , k
L		pc		atm	critical pressure , atm
L		vc		cm^3/gmol	critical molar volume , cm^3/gmole
L		zc		dimless	critical compressibility factor
L		omega		dimless	acentric factor , dimless
L		mweight		g/gmole	molecular weight , g/gmole

Figure III.5
Variable sheet.

St	Input	Name	Output	Unit	Comment
L	'methane	comp		dimless	name of the compound
	1	flag		dimless	type: 1 to get data from databank type: 0 to turn off databank
L		tc	190.6	k	critical temperature , k
L		pc	45.4	atm	critical pressure , atm
L		vc	99	cm^3/gmol	critical molar volume , cm^3/gmole
L		zc	.288	dimless	critical compressibility factor
L		omega	.007	dimless	acentric factor , dimless
L		mweight	16.04	g/gmole	molecular weight , g/gmole

Figure III.6a
Variable sheet.

St	Input	Name	Output	Unit	Comment
L		trangek	'r273_150	k	temperature range of Cp data , k
L		mformul	'ch4	dimless	molecular formula , dimless
L		nec	1	dimless	number of carbon atoms ,dimless
L		neh	4	dimless	number of hydrogen atoms , dimless
L		neo	0	dimless	number of oxygen atoms , dimless
L		nen	0	dimless	number of nitrogen atoms , dimless
L		nes	0	dimless	number of sulfur atoms , dimless
L		necl	0	dimless	number of chlorine atoms , dimless
L		alpha	4.75	cal/gmole	first term of Cp data, cal/gmole/k
L		beta	.012	cal/gmole	second term of Cp data, cal/gmole/k^2
L		gamma	.00000303	cal/gmole	third term of Cp data, cal/gmole/k^3
L		theta	-2.63E-9	cal/gmole	fourth term of Cp data, cal/gmole/k^4
L		dhf25c	-17889	cal/gmole	enthalpy of formation@25 c, cal/gmole
L		ds25c	44.5	cal/gmole	standard entropy @25 c, cal/gmole/k

Figure III.6b
Variable sheet.

St	Input	Name	Output	Unit	Comment
L	'methane	comp		dimless	name of the compound
	1	flag		dimless	type: 1 to get data from databank
					type: 0 to turn off databank
LG	190.6	tc		k	critical temperature , k
LG	45.4	pc		atm	critical pressure , atm
LG	99	vc		cm^3/gmol	critical molar volume , cm^3/gmole
LG	.288	zc		dimless	critical compressibility factor
LG	.007	omega		dimless	acentric factor , dimless
LG	16.04	mweight		g/gmole	molecular weight , g/gmole

Figure III.7
Variable sheet.

St	Input	Name	Output	Unit	Comment
	'methane	comp		dimless	name of the compound
	1	flag		dimless	type: 1 to get data from databank
					type: 0 to turn off databank
	190.6	tc		k	critical temperature , k
	45.4	pc		atm	critical pressure , atm
	99	vc		cm^3/gmol	critical molar volume , cm^3/gmole
	.288	zc		dimless	critical compressibility factor
	.007	omega		dimless	acentric factor , dimless
	16.04	mweight		g/gmole	molecular weight , g/gmole

Figure III.8
Variable sheet.

```
                                        1) CRITICAL TEMPERATURE AND PRESSURE;
                                                Tc  ,  Pc
                                        2) CRITICAL SPECIFIC VOLUME AND
                                           COMPRESSIBILITY FACTOR;  Vc , Zc
                                        3) ACENTRIC FACTOR AND MOLECULAR
                                           WEIGHT;  OMEGA  ,  MWEIGHT

'methane   comp        dimless    name of the compound
1          flag        dimless    type: 1  to get data from databank
                                  type: 0 to turn off databank
190.6      tc          k          critical temperature , k
45.4       pc          atm        critical pressure , atm
99         vc          cm^3/gmol  critical molar volume , cm^3/gmole
.288       zc          dimless    critical compressibility factor
.007       omega       dimless    acentric factor , dimless
16.04      mweight     g/gmole    molecular weight , g/gmole

                                        PROGRAM   DATBANK1.TK   10-3-1984
                                        DATA FOR MORE THAN 100 COMPOUNDS:
                                        1) IDEAL GAS MOLAL HEAT CAPACITY;
                                          Cp = ALPHA + BETA*T + GAMMA*T^2
                                               + THETA*T^3
                                        2) NUMBER OF ATOMS IN A COMPOUND;
                                                C , H , O , N , S , Cl
                                        3) ENTHALPY AND ENTROPY OF FORMATION
                                             AT 25 c;  DHf@25c , DSf@25c
                                        type: 0  to turn off databank
'r273_150  trangek     k          temperature range of Cp data , k
'ch4       mformul     dimless    molecular formula , dimless
1          nec         dimless    number of carbon atoms ,dimless
4          neh         dimless    number of hydrogen atoms , dimless
0          neo         dimless    number of oxygen atoms , dimless
0          nen         dimless    number of nitrogen atoms , dimless
0          nes         dimless    number of sulfur atoms , dimless
0          necl        dimless    number of chlorine atoms , dimless
4.75       alpha       cal/gmole  first term of Cp data, cal/gmole/k
.012       beta        cal/gmole  second term of Cp data, cal/gmole/k^2
.00000303  gamma       cal/gmole  third term of Cp data, cal/gmole/k^3
-2.63E-9   theta       cal/gmole  fourth term of Cp data, cal/gmole/k^4
-17889     dhf25c      cal/gmole  enthalpy of formation@25 c, cal/gmole
44.5       ds25c       cal/gmole  standard entropy @25 c, cal/gmole/k
```

Figure III.9
Variable sheet for methane.

```
                                        1) CRITICAL TEMPERATURE AND PRESSURE;
                                                Tc  ,  Pc
                                        2) CRITICAL SPECIFIC VOLUME AND
                                           COMPRESSIBILITY FACTOR;  Vc , Zc
                                        3) ACENTRIC FACTOR AND MOLECULAR
                                           WEIGHT;  OMEGA  ,  MWEIGHT

'ammonia   comp          dimless   name of the compound
1          flag          dimless   type: 1  to get data from databank
                                   type: 0 to turn off databank
405.6      tc            k         critical temperature , k
111.3      pc            atm       critical pressure , atm
72.5       vc            cm^3/gmol critical molar volume , cm^3/gmole
.242       zc            dimless   critical compressibility factor
.25        omega         dimless   acentric factor , dimless
17.03      mweight       g/gmole   molecular weight , g/gmole

                                        PROGRAM   DATBANK1.TK   10-3-1984
                                        DATA FOR MORE THAN 100 COMPOUNDS:
                                        1) IDEAL GAS MOLAL HEAT CAPACITY;
                                          Cp = ALPHA + BETA*T + GAMMA*T^2
                                               + THETA*T^3
                                        2) NUMBER OF ATOMS IN A COMPOUND;
                                                C , H , O , N , S , Cl
                                        3) ENTHALPY AND ENTROPY OF FORMATION
                                             AT 25 c;  DHf@25c , DSf@25c
                                        type: 0  to turn off databank
'r273_150  trangek       k         temperature range of Cp data , k
'nh3       mformul       dimless   molecular formula , dimless
0          nec           dimless   number of carbon atoms ,dimless
3          neh           dimless   number of hydrogen atoms , dimless
0          neo           dimless   number of oxygen atoms , dimless
1          nen           dimless   number of nitrogen atoms , dimless
0          nes           dimless   number of sulfur atoms , dimless
0          necl          dimless   number of chlorine atoms , dimless
6.5846     alpha         cal/gmole first term of Cp data, cal/gmole/k
.0061251   beta          cal/gmole second term of Cp data, cal/gmole/k^2
2.3663E-6  gamma         cal/gmole third term of Cp data, cal/gmole/k^3
-1.598E-9  theta         cal/gmole fourth term of Cp data, cal/gmole/k^4
-11040     dhf25c        cal/gmole enthalpy of formation@25 c, cal/gmole
-23.69     ds25c         cal/gmole standard entropy @25 c, cal/gmole/k
```

Figure III.10
Variable sheet for ammonia.

Loading RESIDUAL.TK

After obtaining data from CRITICAL and DATBANK1 programs, you are ready to load the RESIDUAL program into the computer memory to solve the residual properties of methane. Type '/sl'.

When the computer asks for the filename, type 'b:residual.tk' and push the 'Return' key.

The computer responds: loading residual.tk . Wait until the program is loaded into the memory. If you have performed the above steps correctly, the screen should be like Figure III.11a.

Figure III.11a is the variable sheet of the RESIDUAL program. Type '=r' to go to the rule sheet of the RESIDUAL program. the Screen should be like Figure III.11b.

Figure III.11b is the rule sheet of the RESIDUAL program. Type '=v' to go back to the variable sheet. In order to calculate the residual properties of methane, perform the following steps:

8) Type '/sl' to load the data file for methane that you saved in the previous steps(e.g., steps 1 through 5). When the computer asks for the filename, type 'b:methane'. The computer responds: loading b:methane.tk. Wait until the program is loaded into the memory. Note that you want to merge the RESIDUAL and

METHANE programs together. Therefore, you should not erase the RESIDUAL program from memory. After loading the METHANE program into the memory, the upper portion of the variable sheet is like Figure III.11a, and the lower portion of the variable sheet is like Figure III.8.

9) In the status column of the variable type, type '1' to indicate there is a list associated with this variable. also, in the input column of this variable type any character to indicate this variable is an input variable. If this step is already performed, skip this step.

10) Push '>' twice to go to the variable type list subsheet. Variable type has six choices. These choices are:

```
'pitzer_correlation
'van_der_waals
'redlich_kwong
'path_on
'states_off
'rules_off
```

The first choice calculates the residual properties of a compound using the Pitzer correlation. The second choice uses the van der Waals equation of state to calculate the residual properties of a compound, and the third choice uses Redlich Kwong equation of state. The fourth choice(e.g., path_on) calculates the change in the properties of a compound for the path from the initial state to the final state. The fifth choice turns off the rules containing the equations of state, and the sixth

choice(e.g., rules_off) turns off all of the rule sheet. Suppose the initial state of the methane is best described by the van der Waals equation of state, and the final state of the methane by the Redlich Kwong equation of state. The first entry on the variable type list subsheet is for the type of equation of state to be used for the initial state of the gas. The second entry on this subsheet is for the type of the equation of state to be used for the final state of the gas. The third entry can be used to find the changes in the properties of the gas from the initial state to the final state by typing 'path_on. Since we want to use van der Waals for the initial state and Redlich Kwong for the final state, enter the names one at a time on the variable type subsheet as shown below:

```
'van_der_waals
'redlich_kwong
'path_on
```

After entering all three names, the variable type list subsheet should be like Figure III.12.

Figure III.12 is the completed variable type list subsheet. Type '<' twice to go back to the variable sheet.

11) In the status column of the variable t type '1' to indicate that you have a list of temperatures. Also, in the input column of this variable type any number to

indicate that variable t is an input variable(e.g., type '1'). If this step is already performed, skip this step.

12) push '>' twice to go to the variable t list subsheet. The first entry on this subsheet is for the initial temperature of the gas, and the second entry is for the final state of the gas. Therefore, enter the initial and final temperatures on the first and second lines respectively as shown in Figure III.13. Note that the temperatures have to be in Kelvin, not in degrees Fahrenheit.

Figure III.13 is the completed subsheet for the variable t. type '<' twice to go back to the variable sheet.

13) In the status column of the variable p type '1' to indicate you have a list associated with this variable. Also, in the input column of this variable type any number to indicate that this variable is an input variable. If this step is already performed, skip this step.

14) Push '>' twice to go to the variable p list subsheet. The first entry on this subsheet is the initial pressure of the gas, and the second entry is the final pressure of the gas. Therefore, enter the initial and the final pressures on the first and the second lines respectively as shown in Figure III.14. Note that the pressure should be entered in atmosphere not in psia.

Figure III.14 is the completed subsheet for the variable

p. Press '<' twice to go back to the variable sheet.

15) In the status column of the variable z type 'lg'. L indicates that there is a list associated with this variable, and the g indicates that this variable has iterative solution. Also, in the input column of this variable type any number to indicate that this variable is an input variable(e.g., type '1').

16) Press '>' twice to go to the variable z list subsheet. The first entry is for the initial state of the gas, and the second entry is for the final state of the gas. Therefore, enter the initial guesses for the initial and the final states on the first and second lines respectively as shown in figure III.15. The best guess for variable z, the compressibility factor, is the ideal gas law value of one.

Figure III.15 is the completed subsheet for the variable z. Press '<' twice to go back to the variable sheet.

17) In the input column of the variable r type '82.05', the value of the gas constant in cm©3*atm/gmole*K.

18) If the upper portion of the variable sheet is like Figure III.16 after the completion of the above steps, you are ready to execute the program. Type '/l !' and wait until the program stops executing. Note that the execution step may take a few minutes.

19) After the program stops execution, press '>' while

the cursor is on the row of the variable z to go to the variable z subsheet. The subsheet is like Figure III.17a. The first entry on this subsheet is for the initial state of the gas via van der Waals equation of state and the second entry is for the final state of the gas via Redlich Kwong equation of state. Therefore, according to the z subsheet, the compressibility factor of methane at 40 F and 300 psia is 0.948 and at 200 F and 1500 psia is 0.940.
Press '<' twice to go back to the variable sheet.

20) Press '>' twice while the cursor is on the row of the variable vres to go to the variable vres list subsheet. The subsheet should be like Figure III.17b.
The first entry on this subsheet is for the initial state of the gas and the second entry is for the final state of the gas. Therefore, according to vres subsheet, the residual molar volume of methane at 40 F and 300 psia is 57.82 cm©3/gmole, and at 200 F and 1500 psia is 17.56 cm©3/gmole. The third entry is for the change in the molar specific volume of the gas from the initial state to the final state. Therefore, the change in the volume of the methane from 40 F and 300 psia to 200 F and 1500 psia is -781.7 cm©3/gmole.
Press '<' twice to go back to the variable sheet.

21) Press '>' twice while the cursor is on the row of the variable ures to go to the variable ures list subsheet. The subsheet is like Figure III.17c.

The first entry in this sheet is the residual internal energy of methane for the initial state, the second entry is for the final state, and the third entry is for the change in the internal energy of the gas for the path from the initial to the final state. Therefore, the residual internal energy of methane at 40 F and 300 psia is 51.97 cal/gmole, at 200 F and 1500 psia is 214.97 cal/gmole, and the total change from the initial to the final state is 447.27 according to the ures subsheet.

Press '<' twice to go back to the variable sheet.

22) Press '>' twice while the cursor is on the row of the variable hres to go to the variable hres subsheet. The subsheet should be like Figure III.17d.

The first entry in this table is for the residual enthalpy of methane for the initial state, the second entry is for the final state, and the third entry is for the change in the enthalpy of the gas from the initial state to the final state. Therefore, the residual enthalpy of methane at 40 F and 300 psia is 80.55 cal/gmole, at 200 F and 1500 psia is 257.55 cal/gmole, and the total change in the enthalpy from the initial state to the final state is 609.09 cal/gmole. The real change in the enthalpy of methane from 40 F and 200 psia to 200 F and 1500 psia is 622 cal/gmole according to the pressure enthalpy diagram of methane (Ref. 8). This represents two percent error in the enthalpy of the methane. Methane is a small

nonpolar molecule compared to other organic molecules. This explains why the error is small. This example shows that this program can describe the residual properties of nonpolar and small organic molecules.

Press '<' twice to go back to the variable sheet.

23) Press '>' twice while the cursor is on the row of the variable sres to go to the variable sres subsheet. The subsheet should be like Figure III.18e.

The first entry in this subsheet is for the residual entropy of methane for the initial state, the second entry is for the final state, and the third entry is for the total change in the entropy of methane from the initial state to the final state. Therefore, the residual entropy of methane at 40 F and 300 psia is 0.188 cal/gmole/k, at 200 F and 1500 psia is 0.553 cal/gmole/k, and the total change in the entropy of the gas from the initial to the final state is -1.115 cal/gmole*K according to the variable sres list subsheet.

Press '<' twice to go back to the variable sheet.

24) In order to get a copy of the solution in tabular format, type '=t' to go to the table sheet of the TK!Solver. Type the title of the table on the row title. The rest of information for the table is already entered in the table sheet. The completed table sheet is like Figure III.18a. Press '!' to see the table for the residual properties of the methane. The table should be

like Figure III.18b.

To get a hard copy of the table, you can either press PrtSc to get a copy of the screen or you can change to printer mode on the first row of the table sheet. Type '/qy' to go to the DOS system and leave the TK!Solver program or you can go to the next page to do the second example.

```
==================== VARIABLE SHEET ========================================
St Input     Name    Output    Unit       Comment
-- -----     ----    ------    ----       -------
                                          PROGRAM  RESIDUAL.TK  10-3-1984
                                          CALCULATES THE RESIDUAL VOLUME (VRES),
                                          RESIDUAL INTERNAL ENERGY ( URES),
                                          RESIDUAL ENTHALPY (HRES), AND
                                          RESIDUAL ENTROPY AS A FUNCTION OF T&P
                                          BY THE FOLLOWING EQUATIONS OF STATE.
                                          1) PITZER CORRELETION
                                          2) VAN DER WAALS
                                          3) REDLICH KWONG

L  'input    type              dimless    name of the equation of state
L            t                 k          temperature , k
L            p                 atm        pressure , atm
   82.05     r                 atm*cm^3/  gas constant , cm^3*atm/gmole/k
L            z                 dimless    compressibility factor , dimless
L            vres              cm^3/gmol  residual specific volume , cm^3/gmole
L            ures              cal/gmole  residual internal energy , cal/gmole
L            hres              cal/gmole  residual enthalpy , cal/gmole
L            sres              cal/gmole  residual entropy , cal/gmole/k
```

Figure III.11a
Variable sheet of RESIDUAL.TK.

```
! tr = t/tc
! pr = p/pc
    "compressibility factor, residual volume, and residual internal energy
! z  = vmole!p/t/r
! vres = r!t/p - vmole
! ures = hres - p!(r!t/p - vmole)!1.987/82.05

                    "Pitzer correlation
! b0 = .1445 - .33/tr - .1385/tr^2 - .0121/tr^3
! b1 = .073 + .46/tr - .5/tr^2 - .097/tr^3 - .0073/tr^8
! b!pc/r/tc = b0 + omega!b1
! db0= .33/tr^2 + 2!.1385/tr^3 + 3!.0121/tr^4
! db1=-.46/tr^2 + 2!.5000/tr^3 + 3!.0970/tr^4 + 8!.0073/tr^9
! db!pc/r/tc = db0 + omega!db1
! p!vmole/r/t = 1 + b!p/r/t
! hres = tr!p!(db - b/tr)!1.987/82.05
! sres = (p!db/tc)!1.987/82.05

                    "van der Waals
! avan = 27!r^2!tc^2/64/pc
! bvan = r!tc/8/pc
! (p + avan/vmole^2 ) ! (vmole - bvan ) = r!t
! hres = 1.987!t!(1 - vmole/(vmole-bvan) + 2!avan/r/t/vmole)
! sres = 1.987!ln(r!t/p/(vmole - bvan))

                    "Redlich Kwong
! ared = .4441!r^2!tc^2.5/pc
! bred = .0903!r!tc/pc
! cred = ln( (vmole+bred) /vmole)
! p = r!t/(vmole - bred) - ared/t^.5/vmole/(vmole + bred)
! hres = (r!t-p!vmole + 3!ared!cred/2/bred/t^.5)!1.987/82.05
! sres = 1.987!(ln(r!t/p/(vmole-bred)) + ared!cred/2/bred/t^1.5/82.05)

          "ideal gas change in properties from state i to state f
! tf = element('t,2,0)
! ti = element('t,1,0)
! pf = element('p,2,1)
! pi = element('p,1,1)
! ut = ht - 1.987!(tf-ti)
! ht =alpha!(tf-ti)+beta!(tf^2-ti^2)/2+gamma!(tf^3-ti^3)/3+theta!(tf^4-ti^4)/4
! sp = -1.987!ln( element('p,2,1) / element('p,1,1) )
! st=alpha!ln(tf/ti)+beta!(tf-ti)+gamma!(tf^2-ti^2)/2 +theta!(tf^3-ti^3)/3 +sp

                    "total change in properties from state i to state f
! vres = element('vres,1,0) - element('vres,2,0) + r!tf/pf - r!ti/pi
! ures = element('ures,1,0) - element('ures,2,0) + ut
! hres = element('hres,1,0) - element('hres,2,0) + ht
! sres = element('sres,1,0) - element('sres,2,0) + st
```

Figure III.11b
Rule sheet of RESIDUAL.TK.

```
==================== LIST: type ================================================
Comment:                  list for type of equation of state
Display Unit:             dimless
Storage Unit:             dimless
Element Value
------- -----
1       'van_der_waals
2       'redlich_kwong
3       'path_on
```

Figure III.12
Subsheet of list type.

```
==================== LIST: t ===================================================
Comment:                  list for temperature of initial and final states
Display Unit:             k
Storage Unit:             k
Element Value
------- -----
1       277.7777778
2       366.6666667
```

Figure III.13
Subsheet of list t.

```
==================== LIST: p ================================================
Comment:                 list for pressure of initial and final states
Display Unit:            atm
Storage Unit:            atm
Element Value
------- -----
1       20.40816327
2       102.0408163
```

Figure III.14
Subsheet of list p.

```
==================== LIST: z ================================================
Comment:                 list for compressibility factor
Display Unit:            dimless
Storage Unit:            dimless
Element Value
------- -----
1       1
2       1
```

Figure III.15
Subsheet of list z.

St	Input	Name	Output	Unit	Comment
L	'input	type		dimless	name of the equation of state
L	1	t		k	temperature , k
L	1	p		atm	pressure , atm
	82.05	r		atm*cm^3/	gas constant , cm^3*atm/gmole/k
LG	1	z		dimless	compressibility factor , dimless
L		vres		cm^3/gmol	residual specific volume , cm^3/gmole
L		ures		cal/gmole	residual internal energy , cal/gmole
L		hres		cal/gmole	residual enthalpy , cal/gmole
L		sres		cal/gmole	residual entropy , cal/gmole/k

Figure III.16
Variable sheet of RESIDUAL.TK.

```
==================== LIST: z ================================================
Comment:                  list for compressibility factor
Display Unit:             dimless
Storage Unit:             dimless
Element Value
------- -----
1       .9482226172
2       .94044125
```

Figure III.17a
Subsheet of list z.

```
==================== LIST: vres ================================================
Comment:                  list for residual volume for I @ F states
Display Unit:             cm^3/gmole
Storage Unit:             cm^3/gmole
Element Value
------- -----
1       57.8245497
2       17.55988494
3       -781.6940019
```

Figure III.17b
Subsheet of list vres.

```
==================== LIST: ures ================================================
Comment:                  list for residual internal energy for I @F states
Display Unit:             cal/gmole
Storage Unit:             cal/gmole
Element Value
------- -----
1       51.97179394
2       214.1725426
3       447.2744789
```

Figure III.17c
Subsheet of list ures.

```
==================== LIST: hres ==============================================
Comment:                  list for residual enthalpy for I @ F states
Display Unit:             cal/gmole
Storage Unit:             cal/gmole
Element Value
------- -----
1       80.55003276
2       257.5650626
3       609.08242
```

Figure III.17d
Subsheet of list hres.

```
==================== LIST: sres ==============================================
Comment:                  list for residual entropy for I @ F states
Display Unit:             cal/gmole/k
Storage Unit:             cal/gmole/k
Element Value
------- -----
1       .1881217532
2       .5531478136
3       -1.115203002
```

Figure III.17e
Subsheet of list sres.

```
==================== TABLE SHEET ============================================
Screen or Printer:          Screen
Title:                      residual properties of methane
Vertical or Horizontal:     Vertical
List      Width First Header
----      ----- ----- ------
type      20    1     type
t         5     1     t,k
p         5     1     p,atm
vres      10    1     v,cm^3/gmole
ures      10    1     u,cal/gmole
hres      10    1     h,cal/gmole
sres      10    1     s,cal/gmole/k
```

Figure III.18a
Table sheet of RESIDUAL.TK.

residual properties of methane

type	t,k	p,atm	v,cm^3/gmo	u,cal/gmol	h,cal/gmol	s,cal/gmol
van_der_waals	277.8	20.41	57.8245497	51.9717939	80.5500328	.188121753
redlich_kwong	366.7	102.0	17.5598849	214.172543	257.565063	.553147814
path_on			-781.69400	447.274479	609.08242	-1.1152030

Figure III.18b
Residual properties of methane.

EXAMPLE TWO

PROBLEM STATEMENT: calculate the residual properties of ammonia from the initial state of 60 degrees Fahrenheit and 100 psia to the final state of 240 degrees Fahrenheit and 300 Psia. Both the initial and the final states of the gas are best described by Pitzer correlation. Also, calculate the total change in the properties of the ammonia from the initial to the final state.

Assuming you have done the first example and the variable sheet is like figure III.16, perform the following steps in order to solve the second example:

1) Load the data file you saved for ammonia in step 6) of the previous example into the memory by typing '/s 1'. When the computer asks for the filename, type 'b:ammonia.tk' and push the 'Return' key. The computer responds: loading the b:ammonia.tk. Wait until the data file for ammonia is loaded into the memory. Note that you do not need to delete any program from the memory. The computer simply updates the methane data file that you used in the previous example to the ammonia data file. Also, note that you want to merge the RESIDUAL and AMMONIA programs together, therefore, you should not attempt to erase RESIDUAL program from the memory.

2) Make sure there is an 1 in the status column of the variable type. Also, type any character in the input

column of this variable to indicate that variable type is an input variable. Dive to the variable type list subsheet by pressing '>' twice while the cursor is on the row of the variable type. Since both the initial and final states of the gas are described by Pitzer correlation, type the name of the equations of state as shown below:

'pitzer_correlation
'pitzer_correlation
'path_on

After completing the variable type subsheet, the subsheet should be like Figure III.19.
Note that the third entry in Figure III.19 (e.g., 'path_on) indicates that you want to find the change in the properties of ammonia from the initial to the final state. Press '<' twice to go back to the variable sheet.
3) Make sure there is an 1 in the status column of the variable t. Also, type any number in the input column of this variable to indicate that variable t is an input variable. Dive to the variable t list subsheet by pressing '>' twice while the cursor is on the row of this variable. Enter the initial and final temperatures of the gas one at a time on this subsheet as shown below. Note that the temperatures should be in Kelvin, not in degrees Fahrenheit.

(60+460)/1.8
(240+460)/1.8

After the completion of this step, the variable t subsheet should be like Figure III.20.

Press '<' twice to go back to the variable sheet.

4) Make sure there is an 1 in the status column of the variable p. Also, type any number in the input column of this variable to indicate that variable p is an input variable. Dive to the variable p list subsheet by pressing '>' twice while the cursor is on the row of this variable. Enter the initial and the final pressures of the gas one at a time on this subsheet as shown below. Note that the pressures should be in atmosphere not in psia.

100/14.7
300/14.7

After the completion of this step, the variable p subsheet should be like Figure III.21.

Press '<' twice to go back to the variable sheet.

5) Make sure the value of 82.05 cm©3*atm/gmole*K for the gas constant is in the input column of the variable r.

6) Make sure the characters lg are on the status column of the variable z. L indicates that there is a list associated with this variable, and g indicates that the solution to this variable involves an iterative procedure. Dive to the variable z list subsheet to enter the initial guesses for the compressibility factor of the initial and

final states of the ammonia. The best initial guess for compressibility factor of any gas at any state is the ideal gas value for z which is 1. After the completion of the z list subsheet, the subsheet should be like Figure III.15 of the previous example.

7) If the upper portion of the variable sheet is like Figure III.16 of the previous example, you are ready to execute the program. Type '/L !' and wait until the computer stops execution. The execution may take a few minutes. After the program stops execution, you can dive to the list subsheets of the variables z, vres, ures, hres, and sres as you did in steps 20 through 24 of the example one to see the solution for the residual properties of ammonia for both the initial and the final states.

8) In order to get a copy of the solution in tabular format, type'=t' to go to the table sheet. Enter the title of the table on the row title. The rest of the information is already entered on the table sheet. The completed table sheet should be like Figure III.22a. Push '!' to see the table for the residual and the total change in the properties of ammonia in tabular format. The table should be like Figure III.22b.

According to the table 22a, the residual enthalpy of ammonia at 60 F and 100 psia is 130.5 cal/gmole, at 240 F and 300 psia is 197.1 cal/gmole, and the total change in

the enthalpy of ammonia from the initial to the final state is 820.5 cal/gmole. The real change for the enthalpy of ammonia from 60 F and 100 psia to 240 F and 300 psia is 850 cal/gmole from the pressure enthalpy diagram of ammonia (Ref. 7). This represents less than four percent error in the calculation of enthalpy of ammonia. Ammonia is a polar molecule but it is relatively small molecule compared to other organic molecules. Despite the fact that ammonia is a polar molecule, this example indicates how well Pitzer correlation describes the residual properties of ammonia.

To get a hard copy of the table sheet, you can press PrtSc or you can change to printer mode on the first row of the table sheet. Type '/q' to quit and go to the DOS system.

```
==================== LIST: type ================================================
Comment:                  list for type of equation of state
Display Unit:             dimless
Storage Unit:             dimless
Element Value
------- -----
1       'pitzer_correla
2       'pitzer_correla
3       'path_on
```

Figure III.19
Subsheet of list type.

```
==================== LIST: t ===================================================
Comment:                  list for temperature of initial and final states
Display Unit:             k
Storage Unit:             k
Element Value
------- -----
1       288.8888889
2       388.8888889
```

Figure III.20
Subsheet of list t.

```
==================== LIST: p ===================================================
Comment:                  list for pressure of initial and final states
Display Unit:             atm
Storage Unit:             atm
Element Value
------- -----
1       6.802721088
2       20.40816327
```

Figure III.21
Subsheet of list p.

```
==================== TABLE SHEET ============================================
Screen or Printer:          Screen
Title:                      residual properties of ammonia
Vertical or Horizontal:     Vertical
List      Width First Header
----      ----- ----- ------
type      20    1     type
t         5     1     t,k
p         5     1     p,atm
vres      10    1     v,cm^3/gmole
ures      10    1     u,cal/gmole
hres      10    1     h,cal/gmole
sres      10    1     s,cal/gmole/k
```

Figure III.22a
Table sheet of RESIDUAL.TK.

residual properties of ammonia

type	t,k	p,atm	v,cm^3/gmo	u,cal/gmol	h,cal/gmol	s,cal/gmol
pitzer_correlation	288.9	6.803	235.223482	91.7658772	130.516851	.317651114
pitzer_correlation	388.9	20.41	117.185915	139.156015	197.072022	.357829753
path_on			-1802.8441	640.960633	820.495599	.408375740

Figure III.22b
Residual properties of ammonia.

IV. Program FRENERGY.TK: Free Energy Calculations

1. Theory

Program FRENERGY.TK calculates the standard free energy, enthalpy, and entropy of formation for a compound at the pressure of one atmosphere and any temperature. This program can also calculate the standard free energy, enthalpy, and entropy for a reaction at the pressure of one atmosphere and any temperature. Standard free energy of formation is the change in the free energy when a compound is formed from its elements at constant temperature. These elements are hydrogen(H2), oxygen(O2), nitrogen(N2), carbon as graphite(C), sulfur(S2), and chlorine(Cl2). This means that the compound should consist of these elements.

Figure IV.1 shows the steps that are involved in the calculation of free energy of formation for a compound at temperature t.

Step 1) The elements are transferred from temperature t to the temperature of 298.15 Kelvin at constant pressure of one atmosphere, as shown in Figure IV.1. Note that heat capacity data is needed for all of the elements to

accomplish the first step.

Step 2) The elements react to form the compound at 298.15 Kelvin and one atmosphere. For this step, enthalpy and entropy data are needed to calculate the standard free energy of formation for the compound at 298.15 Kelvin.

Step 3) The compound is heated to the desired temperature, t, at constant pressure of one atmosphere. Note that heat capacity data is needed for the compound to accomplish the third step.

Therefore, the standard free energy of formation for a compound at temperature t (e.g., dgt) is the sum of the free energy changes for each of the above steps, as given by the following equations:

dgt = dg(1) + dg(2) + dg(3) Eq.(IV.1)

where

dg(2) = dgf25c Eq.(IV.2)

Symbols dg(1), dg(2), and dg(3) are the free energy changes for steps 1), 2), and 3), respectively. Symbol dgt is the standard free energy of formation for a compound at temperature t, and dgf25c is the free energy of formation for the compound at 25 degrees Celsius(e.g., 298.15 K). However, free energy is given by:

dgt = dht - t * dst Eq.(IV.3)

Symbols dht and dst are the standard enthalpy and entropy of formation for the compound at temperature t, respectively. The enthalpy of formation for the compound at temperature t is given by

$$dht = dhf25c + \int_{298}^{t} dcp(t) * dt \qquad \text{Eq.(IV.4)}$$

where

$$dcp(t) = cp(t)compound - \sum_{i} ai * cp(t)Ei \qquad \text{Eq.(IV.5)}$$

Symbol dhf25c is the standard entropy of formation for the compound at 25 degrees Celsius. Symbol ai is the stoichiometric coefficient for element i in the formation reaction. Symbol cp(t)compound is the heat capacity for the compound for which we want to find the heat of formation, and cp(t)Ei is the heat capacity of each element in the formation reaction. The summation includes all of the elements in the formation reaction. The lower limit for the integral is 298.15 Kelvin, and the upper limit is the temperature t in degrees Kelvin. Symbol dCp(t) is the average heat capacity for the elements and the compound for the formation reaction which is given by equation (IV.6).

a1*E1 + a2*E2 + a3*E3 + ... ---> 1 mole Compound Eq.(IV.6)

Symbol ai is the stoichiometric coefficient for element i in the formation reaction, and Ei represents

element i in the formation reaction. The entropy of formation for the compound at temperature t (e.g., dst) is given by:

$$dst = dsf25c + \int_{298}^{t} (dcp(t) / t) * dt \qquad \text{Eq.(IV.7)}$$

where

$$dsf25c = ds25c(compound) - \sum_{i} ai * ds25ci(element) \qquad \text{Eq.(IV.8)}$$

Symbol dcp(t) is given by equation (IV.5), and the formation reaction is given by equation (IV.6). Symbol dsf25c is the entropy of formation for the compound at 298.15 Kelvin. The lower limit for the integral is 298.15 Kelvin, and the upper limit for the integral is the temperature t in Kelvin. Symbol ds25c(compound) is the standard entropy of the compound at 298.15 Kelvin. Note that ds25c is an absolute entropy based on the fact that the entropy of any compound is zero at zero Kelvin, but, dsf25c is the entropy of formation for a compound based on its elements at 298.15 Kelvin. Symbol ds25ci is the standard entropy for the elements at 298.15 Kelvin. The summation includes all of the elements for the formation reaction which is given by equation (IV.6).

Program FRENERGY.TK also calculates the standard free energy for a reaction given by equation (IV.9) at any temperature.

$$a1*R1 + a2*R2 + a3*R3 +.. + a4*P1 + a5*P2 + a6*P3 +..=0$$

Eq.(IV.9)

Symbol ai is the stoichiometric number for each reactant and product. The stoichiometric number is the negative of the stoichiometric coefficient for a reactant, and for the products the stoichiometric number and the stoichiometric coefficient have the same value. Symbol ri is the reactant i, and Pi is the product i. The program calculates the standard free energy, enthalpy, and entropy for a reaction at any temperature t, by the following equations:

$$dgrxn = \sum_i ai*dgt,i \qquad \text{Eq.(VI.10)}$$

$$dhrxn = \sum_i ai*dht,i \qquad \text{Eq.(IV.11)}$$

$$dsrxn = \sum_i ai*dst,i \qquad \text{Eq.(IV.12)}$$

Symbol ai is the stoichiometric number for the reactant i and the product i. Symbols dgt, dht, and dst are the standard free energy, enthalpy, and entropy of formation for the reactants and the products at temperature t, respectively. Symbols dgrxn, dhrxn, and dsrxn are the standard free energy, enthalpy, and entropy for the reaction at temperature t, respectively.

Program FRENERGY.TK also calculates the equilibrium constant for a reaction by the following formula:

keq = exp (-dgrxn / (r*t)) Eq.(IV.13)

Symbol keq is the equilibrium constant. Symbol r is the gas constant, and t is the temperature.

Program FRENERGY.TK obtains data from the data file DATBANK1.TK. DATBANK1.TK contains heat capacity data in the form shown below:

cp = a + b*t + c* t^2 + d*t^3 [t] = K Eq.(IV.14)

The data file provides the coefficients a, b, c, and d in the above equation. The data file also provides the applicable temperature range for the heat capacity data.

The data file DATBANK1.TK also provides the enthalpy of formation at 25 degrees Celsius(e.g. dhf25c), and the standard entropy at 25 degrees Celsius(e.g. ds25c) for a compound and its elements.

There are two limitations in using the FRENERGY.TK program:

1) There should be heat capacity data and heat of formation data for the compound in the data file DATBANK1.TK, in order to find the standard free energy of formation for a compound at any temperature.

2) The compound should consist of only the elements hydrogen, oxygen, nitrogen, carbon as graphite, sulfur, and chlorine.

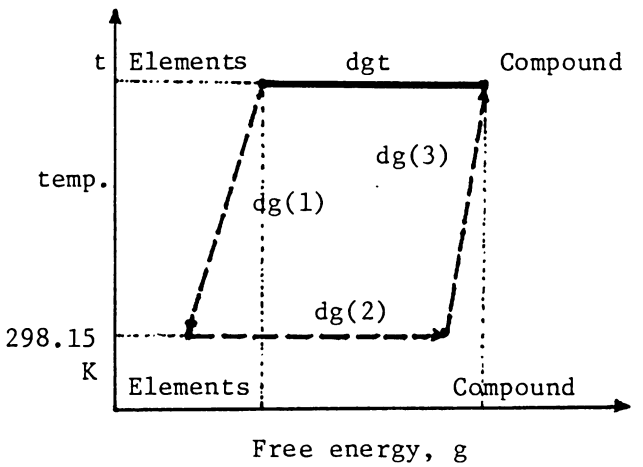


Figure IV.1
Steps involved in free energy calculations.

2. Instructions

Program FRENERGY.TK calculates the standard free energy, enthalpy, and entropy of formation for a compound at the pressure of one atmosphere and any temperature. This program can also calculate the standard free energy, enthalpy, and entropy of a reaction at the pressure of one atmosphere and any temperature.

In the following instructions, if a phrase is typed in double emphasized format and it is in quotation marks, it indicates that the phrase should be typed by the user.

In order to use the FRENERGY program you need these additional programs :

1) A DOS diskette (version 2.0 or 2.1).

2) The TK!Solver diskette.

3) The disk containing The FRENERGY and DATBANK1 programs.

4) A formatted storage diskette to save your solution. The formatted storage diskette and the disk containing the FRENERGY and DATBANK1 programs may be the same diskette.

In the following instructions it is assumed that your personal computer has a double disk drive. It is also assumed that the disk containing FRENERGY and DATBANK1 programs and the storage diskette are the same diskette.

Load the TK!Solver program into the memory of the computer as described in Appendix 1. After loading the TK!Solver program, the screen should be like Figure IV.2.

Loading DATBANK1.TK

You need to transfer the DATBANK1 program from the storage diskette to the memory of the computer. Type '/sl'.
When the computer asks for the filename , type 'b:datbank1.tk' and push the 'Return' key. The computer responds : loading the b:datbank1.tk. Wait until the program is loaded into the computer memory.
If you have executed the above steps correctly, the screen should be like Figure IV.3.

Selecting data from DATBANK1.TK

Before loading the FRENERGY program into the computer memory, let's use an example to illustrate how to get data from DATBANK1. We want to obtain heat capacity data, molecular data(e.g. Number of different atoms in a compound), enthalpy of formation, and standard entropy data for compounds water vapor, carbon monoxide, hydrogen, and carbon dioxide. The temperature range of interest for heat capacity data is 273 to 1800 Kelvin.
In order to get data from the databank for the above compounds, perform the following steps :
1) In the status column of the variable comp type '1' to indicate you have a list of compounds. Also type any character in the input column of variable comp to indicate

this is an input variable(e.g., type ''input').If the above commands are already in the variable sheet, skip this step.

2) Press '>' twice while the cursor is on the row of the variable comp in order to go to the variable comp list subsheet. Enter the name of each compound one at a time as shown below :

```
'water
'carbonmonoxide
'hydrogen
'carbondioxide
```

Note that in the databank there is heat capacity data for two different temperature ranges, namely low range and high range for the above compounds. The low temperature range is 273 to 1800 K and the high range is 273 to 3800 Kelvin. You need data for the low temperature range, because the temperature range of interest for heat capacity is 273 to 1800 K. After the completion of the second step the subsheet comp should be like Figure IV.4. Press '<' twice to return to the variable sheet.

3) In the input column of the variable flag type '1' to indicate you want to get data from the data bank.

4) If the variable sheet is like Figure IV.5 after the completion of the above steps, you are ready to execute the program. Type '/1!' and wait until the computer stops execution. This may take as long as one minute.

5) You can go to the subsheet of any of the variables

trangek, mformula, nec, neh, neo, nen, nes, necl, alpha, beta, gamma, theta, dhf25c, or ds25c and see the data for each compound.

Let's try variable dhf25c. Press '>' twice while the cursor is on the row of the variable dhf25c to go to the dhf25c subsheet. The screen should be like Figure IV.6. Each entry corresponds to one compound. As you see in Figure IV.6, the standard enthalpy of formation for water is -57798 cal/gmole, carbon monoxide is -26416 cal/gmole, hydrogen is zero, and carbon dioxide is -94051 cal/gmole.

6) In order to get a copy of the data in tabular format, go to the table sheet by typing '=t'. The instructions for the table sheet are already typed in the table sheet. The table sheet is like Figure IV.7.

7) Press '!' . The screen is like Figure IV.8 . This is the heat capacity data in tabular format. You can get a hard copy of the table by pressing PrtSc.

8) Push any key. The screen is like Figure IV.9 . This is the molecular, enthalpy of formation, and standard entropy data in a tabular format. You can get a hard copy of the table by pressing PrtSc.

Type '=v' to go back to the variable sheet.

Loading FRENERGY.TK

After obtaining data from the databank you are ready to load FRENERGY program into the memory. Let's load

FRENERGY program into the computer memory to calculate free energy and equilibrium constants for chemical reactions.

Type '/sl'. When the computer asks for the filename, type 'b:frenergy.tk' and push the 'Return' key.

The computer responds: loading the b:frenergy.tk. Wait until the program is loaded into the computer memory.

If you have executed the above steps correctly, the variable sheet should be like Figure IV.10 .

Figure IV.10 is the variable sheet of the merged FRENERGY and DATBANK1 programs.

Type '=r' to go to the rule sheet. The rule sheet (see reference 20) should be like Figure IV.11.

Figure IV.11 is the rule sheet of the merged FRENERGY and DATBANK1 programs.

```
==================== VARIABLE SHEET ============================================
St Input     Name    Output    Unit      Comment
-- -----     ----    ------    ----      -------


==================== RULE SHEET ================================================
S Rule
- ----
```

Figure IV.2
Variable and rule sheets of TK!Solver.

```
==================== VARIABLE SHEET ============================================
St Input     Name    Output    Unit      Comment
-- -----     ----    ------    ----      -------
                                         PROGRAM   DATBANK1.TK   10-3-1984
                                         DATA FOR MORE THAN 100 COMPOUNDS:
                                         1) IDEAL GAS MOLAL HEAT CAPACITY;
                                           Cp = ALPHA + BETA*T + GAMMA*T^2
                                              + THETA*T^3
                                         2) NUMBER OF ATOMS IN A COMPOUND;
                                                 C , H , O , N , S , Cl
                                         3) ENTHALPY AND ENTROPY OF FORMATION
                                             AT 25 c;  DHf@25c , DSf@25c
L            comp            dimless     name of the compound
             flag            dimless     type: 1  to get data from databank
                                         type: 0  to turn off databank
L            trangek         k           temperature range of Cp data , k
L            mformul         dimless     molecular formula , dimless
L            nec             dimless     number of carbon atoms ,dimless
L            neh             dimless     number of hydrogen atoms , dimless
L            neo             dimless     number of oxygen atoms , dimless
L            nen             dimless     number of nitrogen atoms , dimless
L            nes             dimless     number of sulfur atoms , dimless
```

Figure IV.3
Variable sheet of DATBANK1.TK.

```
==================== LIST: comp ================================================
Comment:                  variable sheet list for compound
Display Unit:             dimless
Storage Unit:             dimless
Element Value
------- -----
1       'water
2       'carbonmonoxide
3       'hydrogen
4       'carbondioxide
```

Figure IV.4
Subsheet of list comp.

St	Input	Name	Output	Unit	Comment
L	'input	comp		dimless	name of the compound
	1	flag		dimless	type: 1 to get data from databank type: 0 to turn off databank
L		trangek		k	temperature range of Cp data , k
L		aformul		dimless	molecular formula , dimless
L		nec		dimless	number of carbon atoms ,dimless
L		neh		dimless	number of hydrogen atoms , dimless
L		neo		dimless	number of oxygen atoms , dimless
L		nen		dimless	number of nitrogen atoms , dimless
L		nes		dimless	number of sulfur atoms , dimless
L		necl		dimless	number of chlorine atoms , dimless
L		alpha		cal/gmole	first term of Cp data, cal/gmole/k
L		beta		cal/gmole	second term of Cp data, cal/gmole/k^2
L		gamma		cal/gmole	third term of Cp data, cal/gmole/k^3
L		theta		cal/gmole	fourth term of Cp data, cal/gmole/k^4
L		dhf25c		cal/gmole	enthalpy of formation@25 c, cal/gmole
L		ds25c		cal/gmole	standard entropy @25 c, cal/gmole/k

Figure IV.5
Variable sheet of DATBANK1.TK.

```
==================== LIST: dhf25c ============================================
Comment:                 variable sheet list for enthalpy of formation@25c
Display Unit:            cal/gmole
Storage Unit:            cal/gmole
Element Value
------- -----
1       -57798
2       -26416
3       0
4       -94051
```

Figure IV.6
Subsheet of list dhf25c.

```
Screen or Printer:          Screen
Title:                      Cp, dHf25c, dSf25c, C, H, O, N, S, Cl data
Vertical or Horizontal:     Vertical
List      Width First Header
----      ----- ----- ------
comp      25    1     compound
mformula  6     1     m. formula
alpha     6     1     alpha
beta      7     1     beta
gamma     7     1     gamma
theta     7     1     theta
trangek   15    1     temp. range
comp      25    1     compound
mformula  6     1     m. formula
nec       3     1     C
neh       3     1     H
neo       3     1     O
nen       3     1     N
nes       3     1     S
necl      3     1     Cl
dhf25c    10    1     dhf25c
```

Figure IV.7
Table sheet of DATBANK1.TK.

Cp, dHf25c, dSf25c, C, H, O, N, S, Cl data

compound	a. for	alpha	beta	gamma	theta	temp. range
water	h2o	7.7	.000459	2.52E-6	-9.E-10	r273_1800k
carbonmonoxide	co	6.726	.000400	1.28E-6	-5.E-10	r273_1800k
hydrogen	h2	6.952	-.00046	9.56E-7	-2.E-10	r273_1800k
carbondioxide	co2	5.316	.014285	-8.4E-6	1.78E-9	r273_1800k

Figure IV.8
Table showing the heat capacity data.

Cp, dHf25c, dSf25c, C, H, O, N, S, Cl data

compound	a. for	C	H	O	N	S	Cl	dhf25c	ds25c
water	h2o	0	2	1	0	0	0	-57798	45.106
carbonmonoxide	co	1	0	1	0	0	0	-26416	47.301
hydrogen	h2	0	2	0	0	0	0	0	31.211
carbondioxide	co2	1	0	2	0	0	0	-94051	51.061

Figure IV.9
Table showing heat of formation data.

St	Input	Name	Output	Unit	Comment
L	'input	comp		dimless	name of the compound
	1	flag		dimless	type: 1 to get data from databank
					type: 0 to turn off databank
L		trangek		k	temperature range of Cp data , k
L		mformul		dimless	molecular formula , dimless
L		nec		dimless	number of carbon atoms ,dimless
L		neh		dimless	number of hydrogen atoms , dimless
L		neo		dimless	number of oxygen atoms , dimless
L		nen		dimless	number of nitrogen atoms , dimless
L		nes		dimless	number of sulfur atoms , dimless
L		necl		dimless	number of chlorine atoms , dimless
L		alpha		cal/gmole	first term of Cp data, cal/gmole/k
L		beta		cal/gmole	second term of Cp data, cal/gmole/k^2
L		gamma		cal/gmole	third term of Cp data, cal/gmole/k^3
L		theta		cal/gmole	fourth term of Cp data, cal/gmole/k^4
L		dhf25c		cal/gmole	enthalpy of formation@25 c, cal/gmole
L		ds25c		cal/gmole	standard entropy @25 c, cal/gmole/k
					PROGRAM FRENERGY.TK 10-3-1984
					CALCULATES:
					1) FREE ENERGY, ENTHALPY, ENTROPY
					AT 1 ATM. AND ANY TEMPERATURE :
					A) FOR COMPOUNDS
					B) FOR A REACTION
					2) EQUILIBRIUM CONSTANT OF A REACTION
		t		k	temperature , k
L		mu		dimless	stoichiometric number of the compound
		option		dimless	type: 'r_p' to find properties of
					reactants and products
					type: 'rxn' for properties of reaction
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L		dgt		cal/gmole	DG of formation at T@1atm ,cal/gmole
L		dht		cal/gmole	DH of formation at T@1atm ,cal/gmole
L		dst		cal/gmole	DS of formation at T@1atm ,cal/gmole/k
		dgrxn		cal/gmole	DG of reaction at T@1atm ,cal/gmole
		dhrxn		cal/gmole	DH of reaction at T@1atm ,cal/gmole
		dsrxn		cal/gmole	DS of reaction at T@1atm ,cal/gmole/k
		keq		dimless	equilibrium constant for the reaction

Figure IV.10
Variable sheet of the merged DATBANK1 and FRENERGY.TK.

```
S Rule
- ----
                "maps a compound to its heat capacity data.
  0/flag    + alpha = mapcp1(comp)
  0/flag    + beta = mapcp2(comp)
  0/flag    + gamma = mapcp3(comp)
  0/flag    + theta = mapcp4(comp)
  trangek = mapcpr(comp)
  mformula = mapcpf(comp)
  0/flag    + dhf25c= maphf25(comp)
  0/flag    + ds25c = maps25(comp)
  0/flag    + nec = mapnc(comp)
  0/flag    + neh = mapnh(comp)
  0/flag    + neo = mapno(comp)
  0/flag    + nen = mapnn(comp)
  0/flag    + nes = mapns(comp)
  0/flag    + necl = mapncl(comp)
           "Cp for the formation of the compound from its elements
t dalpha = alpha -(nec*2*4.03+neh*6.952 + neo*6.085 + nen*6.903 + nes*6.499 + n
t dbeta = beta -(nec*2*1.14e-3+neh*-4.576e-4 + neo*.3631e-2 + nen*-3.753e-4 + n
t dgamma = gamma -(neh*9.563e-7 - neo*1.709e-6 + nen*1.93e-6 - nes*3.888e-6 - n
t dtheta = theta -(-neh*2.079e-10+neo*3.133e-10-nen*6.861e-10+nes*.952e-9 + nec
                    "DH, DS, and DG of formation for compound at T@1atm
t dht = dhf25c + poly(t,dtheta/4,dgamma/3,dbeta/2,dalpha,0) - poly(298,dtheta/4
t dsf25 = ds25c - nec*1.3609 - (neh*31.211+neo*49.003+nen*45.767+nes*27.62+nec
t dst = dsf25 + dalpha*ln(t/298) + dbeta*(t-298) + dgamma*(t^2-298^2)/2 + dthet
t dgt = dht -t*dst
                    "DG, DH, and DS for the reaction at T@1atm
t dgrxn = dot('dgt,'mu)
t dhrxn = dot('dht,'mu)
t dsrxn = dot('dst,'mu)
                    "Equilibrium constant for the reaction at T
t ln(keq) = -dgrxn/t/r
```

Figure IV.11
Rule Sheet of the merged DATBANK1 and FRENERGY.TK.

Example One

PROBLEM STATEMENT: calculate free energy of formation, enthalpy of formation, entropy of formation, and equilibrium constant of the following reaction :

$$H2O + CO \text{ -------> } H2 + CO2$$

The temperature of interest is 800 K. The free energy, enthalpy, and entropy of formation that the program calculates are standard values. This means that the pressure at which the above properties are calculated is one atmosphere. You also need to provide the stoichiometric number for each compound of the above reaction. The stoichiometric number is just the stoichiometric coefficient of each compound with a negative sign if the compound is a reactant and a positive sign if the compound is a product. If you look in the variable sheet you see that the stoichiometric number is denoted by the variable mu. Therefore, the stoichiometric number for each compound in the above reaction is :

mu(H2O) = -1
mu(CO) = -1
mu(H2) = +1
mu(CO2) = +1

You have every input variable you need to solve the problem. In order to find the properties of the above

reaction you should do the following steps :

1) In the input column of the variable flag type '1'. This enables the program to get data from the databank. If there is already a 1 in this column, skip this step.

2) In the input column of variable t type '800' which is the temperature of interest.

3) In the input column of the variable option type ''r_p' . This indicates that you want to find the properties of each compound. Note that you need to calculate the properties of each compound in a reaction before you can calculate properties of the reaction.

4) If the lower portion of the variable sheet is like Figure IV.12 after the completion of the above steps, you are ready to execute the program to find the properties of each compound in the above reaction. Type '/1!' and wait until the computer stops executing. The execution of the program may take as long as one minute.

5) When the computer stops executing, press '>' twice while the cursor is on the row of the variable dgt to go into the variable dgt list subsheet. The screen should be like Figure IV.13 .

Each value in the dgt list subsheet corresponds to one of the compounds of the above reaction. For instance, the standard free energy of formation of water vapor at 800 Kelvin is -48657.12777cal/gmole according to the dgt Subsheet. Press '<' twice to go back to the variable

sheet.

6) Repeat step 5) for the variable dht. The variable dht Subsheet looks like Figure IV.14.

Each value of the above table corresponds to one of the compounds in the above reaction. For instance, the standard enthalpy of formation of carbon dioxide at 800 Kelvin is -94337.55264 cal/gmole according to dht subsheet.

7) Repeat step 5) for the variable dst. The screen should be like Figure IV.15.

Each value of the above subsheet corresponds to one of the compounds in the above reaction. For instance, The standard entropy of formation of hydrogen at 800 Kelvin is zero according to dst subsheet. Press '<' twice to go back to the variable sheet.

8) In order to obtain a copy of your solution in tabular format go to the table sheet by typing '=t'. The information needed for the table sheet is already preloaded in this sheet. Type '!' and push the 'Return' key twice. The screen should be like Figure IV.16.

Figure IV.16 is the dgt, dht, and dst of each compound at 800 Kelvin in tabular format. To get a hard copy of this table press PrtSc or change to the printer mode on the first row of the table sheet. Press '=v' to return to the variable sheet.

9) Now you are ready to calculate the properties of the

reaction itself. Blank the input column of the variable comp by typing '/b' while the cursor is on this field. This indicates that you do not want to find the properties of each compound but are interested in the chemical reaction itself.

10) In the input column of the variable flag type '0' to indicate that you want the rule sheet of the DATBANK1.TK to be turned off.

11) In the status column of the variable mu type '1' to indicate you have a list of values for mu. Also in the input column of the variable mu type any character to indicate mu is an input variable.

12) Press '>' twice to go to the variable mu list subsheet. Enter the value of mu for each compound one at a time. After the completion of the subsheet mu the screen should be like Figure IV.17.

13) In the input column of the variable option type ''rxn' to indicate you want to find the properties of the reaction.

14) If the upper portion of the variable sheet is like Figure IV.18a and the lower portion of the variable sheet is like Figure IV.18b at the completion of the previous steps then you are ready to execute your program. Type '!' and wait until the computer stops execution.

15) After the computer executes the program, the lower portion of the variable sheet is like Figure IV.19.

According to the variable sheet the standard free energy of the above reaction at 800 K is -2170.330 calories per mole, the standard enthalpy at 800 K is -8862.807 calories per mole, the standard entropy at 800 K is -8.365597 calories per mole, and the equilibrium constant for the above reaction is 3.9170187 at 800 Kelvin. You can get a hard copy of the variable sheet by typing PrtSc or typing '/p'.

Type '/qy' to quit TK!Solver and return to the DOS system, or turn to the next page to do example two.

St	Input	Name	Output	Unit	Comment
	800	t		k	temperature , k
L	'input	mu		dimless	stoichiometric number of the compound
	'r_p	option		dimless	type: 'r_p' to find properties of reactants and products type: 'rxn' for properties of reaction
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L		dgt		cal/gmole	DG of formation at T@lata ,cal/gmole
L		dht		cal/gmole	DH of formation at T@lata ,cal/gmole
L		dst		cal/gmole	DS of formation at T@lata ,cal/gmole/k
		dgrxn		cal/gmole	DG of reaction at T@lata ,cal/gmole
		dhrxn		cal/gmole	DH of reaction at T@lata ,cal/gmole
		dsrxn		cal/gmole	DS of reaction at T@lata ,cal/gmole/k
		keq		dimless	equilibrium constant for the reaction

Figure IV.12
Lower portion of the variable sheet.

LIST: dgt

Comment:	DG of formation at T for Reactants and Products
Display Unit:	cal/gmole
Storage Unit:	cal/gmole

Element	Value
1	-48657.12777
2	-43612.27301
3	0
4	-94439.73064

Figure IV.13
Subsheet of list dgt.

```
==================== LIST: dht ================================================
Comment:                  DH of formation at T for Reactants and Products
Display Unit:             cal/gmole
Storage Unit:             cal/gmole
Element Value
------- -----
1       -58887.01821
2       -26587.72718
3       0
4       -94337.55264
```

Figure IV.14
Subsheet of list dht.

```
==================== LIST: dst ================================================
Comment:                  DS of formation at T for Reactants and Products
Display Unit:             cal/gmole/k
Storage Unit:             cal/gmole/k
Element Value
------- -----
1       -12.78736305
2       21.28068228
3       0
4       .1277225084
```

Figure IV.15
Subsheet of list dst.

standard energy of formation data

compound	dg(t)	dh(t)	ds(t)
water	-48657.12777	-58887.01821	-12.78736305
carbonmonoxide	-43612.27301	-26587.72718	21.28068228
hydrogen	0	0	0
carbondioxide	-94439.73064	-94337.55264	.1277225084

Figure IV.16
dgt, dht, dst of each compound.

========== LIST: au ==========

Comment: list for stoichiometric number of React. & Prod.
Display Unit: dimless
Storage Unit: dimless

Element	Value
1	-1
2	-1
3	1
4	1

Figure IV.17
Subsheet of list mu.

St	Input	Name	Output	Unit	Comment
L		comp		dimless	name of the compound
	0	flag		dimless	type: 1 to get data from databank type: 0 to turn off databank
L		trangek		k	temperature range of Cp data , k
L		mformul		dimless	molecular formula , dimless
L		nec		dimless	number of carbon atoms ,dimless
L		neh		dimless	number of hydrogen atoms , dimless
L		neo		dimless	number of oxygen atoms , dimless
L		nen		dimless	number of nitrogen atoms , dimless
L		nes		dimless	number of sulfur atoms , dimless

Figure IV.18a
Upper portion of the variable sheet.

St	Input	Name	Output	Unit	Comment
	800	t		k	temperature , k
L	'input	mu		dimless	stoichiometric number of the compound
	'rxn	option		dimless	type: 'r_p' to find properties of reactants and products type: 'rxn' for properties of reaction
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L		dgt		cal/gmole	DG of formation at T@1atm ,cal/gmole
L		dht		cal/gmole	DH of formation at T@1atm ,cal/gmole
L		dst		cal/gmole	DS of formation at T@1atm ,cal/gmole/k
		dgrxn		cal/gmole	DG of reaction at T@1atm ,cal/gmole
		dhrxn		cal/gmole	DH of reaction at T@1atm ,cal/gmole
		dsrxn		cal/gmole	DS of reaction at T@1atm ,cal/gmole/k
		keq		dimless	equilibrium constant for the reaction

Figure IV.18b
Lower portion of the variable sheet.

St	Input	Name	Output	Unit	Comment
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L		dgt		cal/gmole	DG of formation at T@1atm ,cal/gmole
L		dht		cal/gmole	DH of formation at T@1atm ,cal/gmole
L		dst		cal/gmole	DS of formation at T@1atm ,cal/gmole/k
		dgrxn	-2170.330	cal/gmole	DG of reaction at T@1atm ,cal/gmole
		dhrxn	-8862.807	cal/gmole	DH of reaction at T@1atm ,cal/gmole
		dsrxn	-8.365597	cal/gmole	DS of reaction at T@1atm ,cal/gmole/k
		keq	3.9170187	dimless	equilibrium constant for the reaction

Figure IV.19
Lower portion of the variable sheet.

Example Two

PROBLEM STATEMENT: Find the variation of equilibrium constant as a function of temperature for the following reaction :

$$3\ H2 + CO \text{ ---------> } CH4 + H2O$$

The above reaction is one of the many reactions involved in the production of synthetic natural gas. The temperature range of interest is 300 to 700 Kelvin with intervals of 100 Kelvin. The stoichiometric number for each compound of the above reaction is :

mu(H2) = -3
mu(CO) = -1
mu(CH4)= +1
mu(H2O) = +1

You have every input variable you need to solve the problem. In order to find the properties of the above reaction do the following steps :

1) In the status column of the variable comp type '1' to indicate you have a list of compounds. If there is an 1 in this column, skip this step.

2) In the input column of the variable comp type any character to indicate variable comp is an input variable(e.g., type ''input').

3) Press '>' twice while the cursor is on the row of

the variable comp to go to the variable comp list subsheet. Enter the name of each compound one at a time on this subsheet as shown below :

'hydrogen
'carbonmonoxide
'methane
'water

Note that in the databank there is heat capacity data for two different temperature ranges, namely low range and high range for compounds hydrogen, carbon monoxide, and water vapor. The low temperature range is 273 to 1800 K and the high range is 273 to 3800 K. Since the temperature range of interest is 300 to 700 Kelvin, you use the data for the low temperature range. After the completion of this step the subsheet comp should be like Figure IV.20.
Press '<' twice to go back to the variable sheet.
4) After the completion of the above steps the upper portion of the variable sheet should be like Figure IV.21. If there are any numerical values in the output field of any variable from the previous example, the computer resets all of the output fields of the variable sheet automaticaly before executing your program.
5) Go to the lower part of the variable sheet. In the input column of the variable t type the temperature in Kelvin(e.g., type '500').
6) In the status column of the variable mu type '1' to indicate you have a list of values for mu. In the input

column of this variable type any character to indicate this is an input variable(e.g., type ''input').

7) Press '>' twice to go to the variable mu list subsheet. Enter the value of mu for each compound one at a time. after the completion of the subsheet mu the screen should be like Figure IV.22.

Press '<' twice to go back to the variable sheet.

8) In the input column of the variable option type ''r_p'. This indicates you want to find the properties of each compound. The lower portion of the variable sheet should be like Figure IV.23.

9) If the upper portion of the variable sheet is like Figure IV.21 and the lower portion is like Figure IV.23, you are ready to execute the program. Type '/ 1 !' and wait until the computer stops execution. The execution step may take as long as one minute.

10) You can of course look at the contents of the dgt, dht, and dst subsheets, but we are more interested in the variation of equilibrium constant.

11) Now let's find the equilibrium constant. Go to the upper portion of the variable sheet. In the input column of the variable comp type '/b' to blank this field. This indicates that you do not want to find the properties of each compound but the reaction itself.

12) In the input column of the variable flag type '0' to indicate that you want to turn off the rule sheet of

the DATBANK1.TK. After the completion of this step the upper portion of the screen should be like Figure IV.24a .

13) Go to the lower portion of the variable sheet. In the input column of the variable option type ''rxn' to indicate you want to find the properties of the reaction. After the completion of this step, the lower portion of the screen should be like Figure IV.24b .

14) If the upper portion of the variable sheet is like Figure IV.24a and the lower portion is like Figure IV.24b, you are ready to execute the program. Type '!' and wait until the computer stops execution.

15) After the program stops execution the lower portion of the variable sheet is like Figure IV.25. As you see, the value of equilibrium constant(Keq) is 1.1629E10 at 500 K for the above reaction. This number is very large, and it is impossible to plot the variation of equilibrium constant with temperature on one graph. But we can plot natural logarithm of the equilibrium constant as a function of temperature. Therefore, let's go to the rule sheet by typing '=r' and type the rule to find the natural logarithm of equilibrium constant.

16) Type the rule '0/arxn(option) + lkeq = ln(keq)' on any blank rule line in the rule sheet. After you enter the rule, the rule sheet should be like Figure IV.26. Type '=v' to go back to the variable sheet.

17) Now press '!' to execute the program one more time.

You do not have to make any modifications to the variable sheet. The variable sheet should be like Figure IV.25 before you execute the program. After the program is executed, the variable sheet is like Figure IV.27.

As you can see, the natural logarithm of the equilibrium constant is 23.176803 according to the variable sheet. This value is much easier to plot.

18) Now you need to save the values for temperature and equilibrium constant in a list sheet so that you can plot them later. Note that you cannot declare variables t and keq as list variables because the program may find the properties of each compound at one temperature and calculate the properties of the reaction at another temperature. Type two new names for variables temperature and equilibrium constant different from t and keq (type 'temp' for temperature and type 'lnkeq' for logarithm of equilibrium constant). Declare both of these variables as list variables by typing 'l' in the status column of these variables. Also, type any character in the input column of these two variables so that the program does not treat them as output variables during execution(e.g., type ''input').

After the completion of this step, the lower portion of the variable sheet is like Figure IV.28.

19) Press '>' twice to go to the variable temp list subsheet. Enter temperatures 300 to 700 with intervals of

100 one at a time. After the completion of this step, the temp list subsheet should be like Figure IV.29.

Press '<' twice to go back to the variable sheet.

20) Press '>' twice to go to the variable lnkeq list subsheet. Enter the natural logarithm of the equilibrium constant calculated by the program(e.g., lnkeq = 23.176803) on the row corresponding to its temperature in the variable temp subsheet(e.g., row No. 3). After the completion of this step, the variable lnkeq subsheet should be like Figure IV.30.

Press '<' to go back to the variable sheet.

21) Repeat steps 2, 5, 8-9, 11-14, 20) for temperatures 300, 400, 600, 700 . After the completion of this step, the variable temp list subsheet should be like Figure IV.29, and the variable lnkeq list subsheet should be like Figure IV.31 .

22) In order to obtain a copy of the solution in graphical format go to the plot sheet by typing '=p'. Enter the title of the plot on the row beginning with the word title. Then enter the rest of the information on this sheet as shown in Figure IV.32. Figure IV.32 is the completed plot sheet for the variation of natural logarithm of equilibrium constant with temperature.

23) Now press '!' to see the plot on your screen. The screen should be like Figure IV.33. As you can see, the natural logarithm of the equilibrium constant decreases

with increasing temperature. Since the reaction is exothermic, this relationship is correct.

You can get a hard copy of the plot by pressing PrtSc or you can change to the printer mode on the first line of the plot sheet.

To quit the program type '/q y'. The A prompt indicates that you are out of the TK!solver program and back in the DOS system.

```
==================== LIST: comp ================================================
Comment:                variable sheet list for compound
Display Unit:           dimless
Storage Unit:           dimless
Element Value
------- -----
1       'hydrogen
2       'carbonmonoxide
3       'methane
4       'water
```

Figure IV.20
Subsheet of list comp.

St	Input	Name	Output	Unit	Comment
L	'input	comp		dimless	name of the compound
	1	flag		dimless	type: 1 to get data from databank type: 0 to turn off databank
L		trangek		k	temperature range of Cp data , k
L		mformul		dimless	molecular formula , dimless
L		nec		dimless	number of carbon atoms ,dimless
L		neh		dimless	number of hydrogen atoms , dimless
L		neo		dimless	number of oxygen atoms , dimless
L		nen		dimless	number of nitrogen atoms , dimless
L		nes		dimless	number of sulfur atoms , dimless
L		necl		dimless	number of chlorine atoms , dimless
L		alpha		cal/gmole	first term of Cp data, cal/gmole/k
L		beta		cal/gmole	second term of Cp data, cal/gmole/k^2
L		gamma		cal/gmole	third term of Cp data, cal/gmole/k^3
L		theta		cal/gmole	fourth term of Cp data, cal/gmole/k^4
L		dhf25c		cal/gmole	enthalpy of formation@25 c, cal/gmole
L		ds25c		cal/gmole	standard entropy @25 c, cal/gmole/k

Figure IV.21
Upper portion of the variable sheet.

```
==================== LIST: nu ================================================
Comment:                  list for stoichiometric number of React. & Prod.
Display Unit:             dimless
Storage Unit:             dimless
Element Value
------- -----
1       -3
2       -1
3       1
4       1
```

Figure IV.22
Subsheet of list mu.

St	Input	Name	Output	Unit	Comment
	500	t		k	temperature , k
L	'input	nu		dimless	stoichiometric number of the compound
	'r_p	option		dimless	type: 'r_p' to find properties of reactants and products type: 'rxn' for properties of reaction
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L		dgt		cal/gmole	DG of formation at T&1atm ,cal/gmole
L		dht		cal/gmole	DH of formation at T&1atm ,cal/gmole
L		dst		cal/gmole	DS of formation at T&1atm ,cal/gmole/k
		dgrxn	-2170.330	cal/gmole	DG of reaction at T&1atm ,cal/gmole
		dhrxn	-8862.807	cal/gmole	DH of reaction at T&1atm ,cal/gmole
		dsrxn	-8.365597	cal/gmole	DS of reaction at T&1atm ,cal/gmole/k
		keq	3.9170187	dimless	equilibrium constant for the reaction

Figure IV.23
Lower portion of the variable sheet.

St	Input	Name	Output	Unit	Comment
L		comp		dimless	name of the compound
	0	flag		dimless	type: 1 to get data from databank type: 0 to turn off databank
L		trangek		k	temperature range of Cp data , k
L		aformul		dimless	molecular formula , dimless
L		nec		dimless	number of carbon atoms ,dimless
L		neh		dimless	number of hydrogen atoms , dimless
L		neo		dimless	number of oxygen atoms , dimless
L		nen		dimless	number of nitrogen atoms , dimless
L		nes		dimless	number of sulfur atoms , dimless
L		necl		dimless	number of chlorine atoms , dimless
L		alpha		cal/gmole	first term of Cp data, cal/gmole/k
L		beta		cal/gmole	second term of Cp data, cal/gmole/k^2
L		gamma		cal/gmole	third term of Cp data, cal/gmole/k^3
L		theta		cal/gmole	fourth term of Cp data, cal/gmole/k^4
L		dhf25c		cal/gmole	enthalpy of formation@25 c, cal/gmole
L		ds25c		cal/gmole	standard entropy @25 c, cal/gmole/k

Figure IV.24a
Upper portion of the variable sheet.

St	Input	Name	Output	Unit	Comment
	500	t		k	temperature , k
L	'input	mu		dimless	stoichiometric number of the compound
	'rxn	option		dimless	type: 'r_p' to find properties of reactants and products type: 'rxn' for properties of reaction
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L		dgt		cal/gmole	DG of formation at T@data ,cal/gmole
L		dht		cal/gmole	DH of formation at T@data ,cal/gmole
L		dst		cal/gmole	DS of formation at T@data ,cal/gmole/k
		dgrxn		cal/gmole	DG of reaction at T@data ,cal/gmole
		dhrxn		cal/gmole	DH of reaction at T@data ,cal/gmole
		dsrxn		cal/gmole	DS of reaction at T@data ,cal/gmole/k
		keq		dimless	equilibrium constant for the reaction

Figure IV.24b
Lower portion of the variable sheet.

St	Input	Name	Output	Unit	Comment
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L		dgt		cal/gmole	DG of formation at T@1atm ,cal/gmole
L		dht		cal/gmole	DH of formation at T@1atm ,cal/gmole
L		dst		cal/gmole	DS of formation at T@1atm ,cal/gmole/k
		dgrxn	-23026.15	cal/gmole	DG of reaction at T@1atm ,cal/gmole
		dhrxn	-51230.98	cal/gmole	DH of reaction at T@1atm ,cal/gmole
		dsrxn	-56.40965	cal/gmole	DS of reaction at T@1atm ,cal/gmole/k
		keq	1.1629E10	dimless	equilibrium constant for the reaction

Figure IV.25
Lower portion of the variable sheet.

S	Rule
	dgrxn = dot('dgt,'mu)
	dhrxn = dot('dht,'mu)
	dsrxn = dot('dst,'mu)
	"Equilibrium constant for the reaction at T
	ln(keq) = -dgrxn/t/r
#	0/arxn(option) + lkeq = ln(keq)

Figure IV.26
Rule sheet of FRENERGY.TK.

St	Input	Name	Output	Unit	Comment
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L		dgt		cal/gmole	DG of formation at T@latm ,cal/gmole
L		dht		cal/gmole	DH of formation at T@latm ,cal/gmole
L		dst		cal/gmole	DS of formation at T@latm ,cal/gmole/k
		dgrxn	-23026.15	cal/gmole	DG of reaction at T@latm ,cal/gmole
		dhrxn	-51230.98	cal/gmole	DH of reaction at T@latm ,cal/gmole
		dsrxn	-56.40965	cal/gmole	DS of reaction at T@latm ,cal/gmole/k
		keq	1.1629E10	dimless	equilibrium constant for the reaction
		lkeq	23.176803		

Figure IV.27
Lower portion of the variable sheet.

St	Input	Name	Output	Unit	Comment
L		dgt		cal/gmole	DG of formation at T@latm ,cal/gmole
L		dht		cal/gmole	DH of formation at T@latm ,cal/gmole
L		dst		cal/gmole	DS of formation at T@latm ,cal/gmole/k
		dgrxn	-23026.15	cal/gmole	DG of reaction at T@latm ,cal/gmole
		dhrxn	-51230.98	cal/gmole	DH of reaction at T@latm ,cal/gmole
		dsrxn	-56.40965	cal/gmole	DS of reaction at T@latm ,cal/gmole/k
		keq	1.1629E10	dimless	equilibrium constant for the reaction
		lkeq	23.176803		
L	'input	temp			
L	'input	lnkeq			

Figure IV.28
Lower portion of the variable sheet.

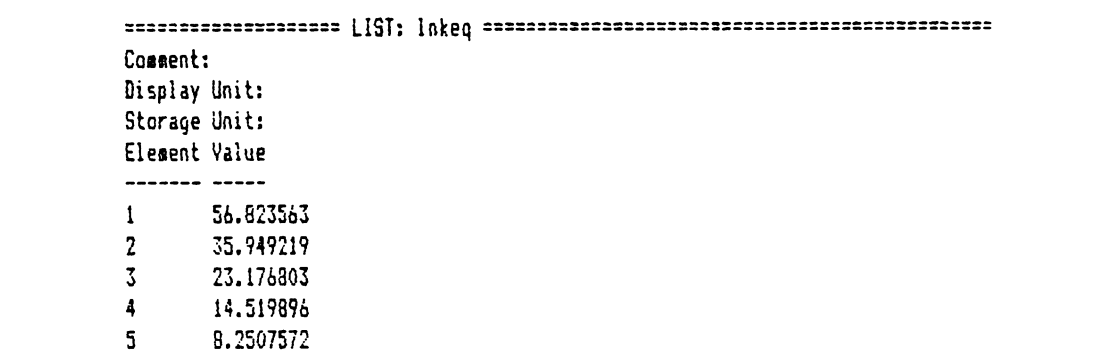
```
==================== LIST: temp ================================================
Comment:
Display Unit:
Storage Unit:
Element Value
------- -----
1       300
2       400
3       500
4       600
5       700
```

Figure IV.29
Subsheet of list temp.

```
==================== LIST: lnkeq ===============================================
Comment:
Display Unit:
Storage Unit:
Element Value
------- -----

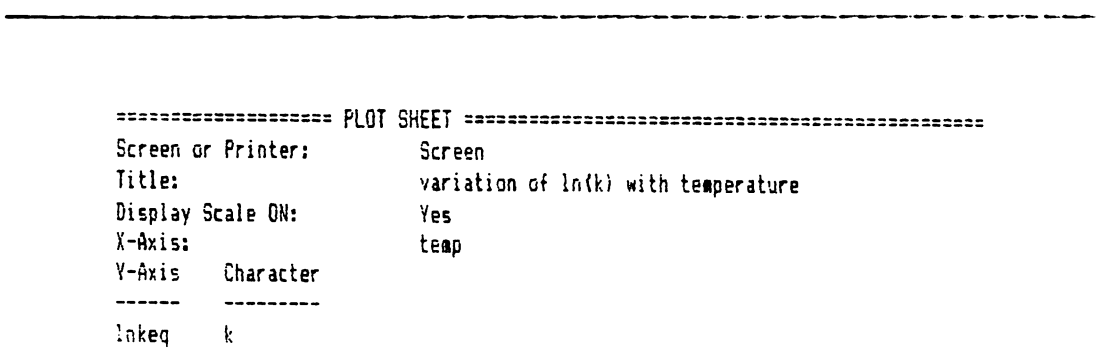

3       23.176803
```

Figure IV.30
Subsheet of list lnkeq.



```
==================== LIST: lnkeq ================================================
Comment:
Display Unit:
Storage Unit:
Element Value
------- -----
1       56.823563
2       35.949219
3       23.176803
4       14.519896
5       8.2507572
```

Figure IV.31
Subsheet of list lnkeq.



```
==================== PLOT SHEET ================================================
Screen or Printer:          Screen
Title:                      variation of ln(k) with temperature
Display Scale ON:           Yes
X-Axis:                     temp
Y-Axis    Character
------    ---------
lnkeq     k
```

Figure IV.32
Plot sheet of FRENERGY.TK.

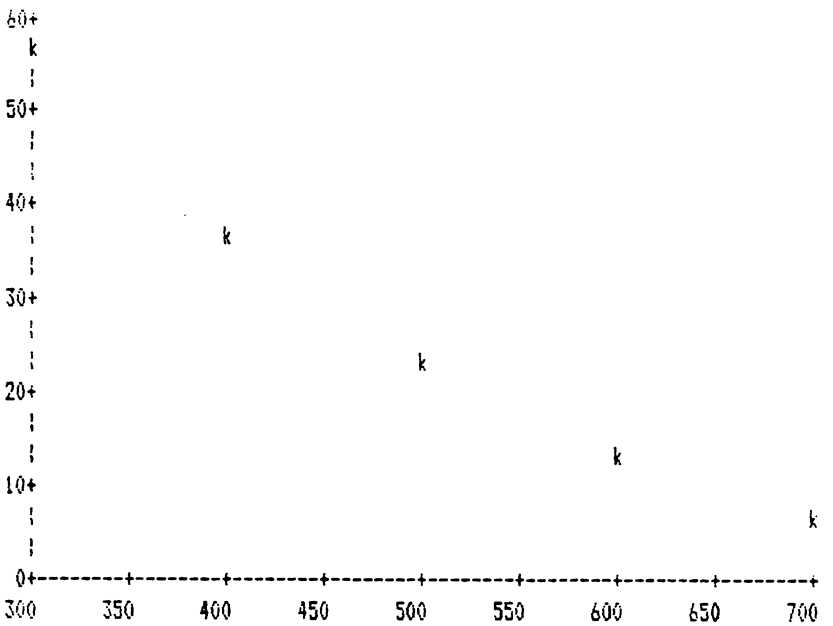


Figure IV.33
Variation of equilibrium constant with temperature.

V. Program CHON.TK: Equilibrium Composition Calculations

1. Theory

Program CHON.TK calculates the equilibrium composition for a system consisting of the elements carbon, hydrogen, oxygen, and nitrogen. The program also calculates the heat requirements and the heating value of the product stream for this system. The program also calculates the equilibrium composition for an adiabatic reactor. The feed to this reactor is carbon as graphite, water, hydrogen, oxygen, and nitrogen gas.

Equilibrium composition of a system consisting of the elements carbon, hydrogen, oxygen, and nitrogen has been previously calculated on a main frame computer by Baron R. E. and asscciates at MIT and the results are published by the MIT press (Ref. 18). Program CHON.TK attempts to duplicate the MIT results using the TK!Solver program.

There are three reactions that take place in the reactor as shown below:

$C + H2O \text{ ------> } CO + H2$ Reaction(V.1)

$CO + H2O \text{ ------> } CO2 + H2$ Reaction(V.2)

C + 2 H2 ------> CH4 Reaction(V.3)

In the first reaction, carbon reacts with water to form carbon monoxide and hydrogen gas. In the second reaction, carbon monoxide reacts with water to form carbon dioxide and hydrogen gas. In the third reaction, carbon reacts with hydrogen to form methane. Therefore, the products of this reactor are hydrogen, water, methane, carbon monoxide, carbon dioxide, and nitrogen assuming all of the oxygen fed to the reactor is consumed completely. Note that carbon as graphite is in the solid state. Also, note that no allowance has been made for the production of higher hydrocarbons. Also, it is assumed that nitrogen does not react at all, so there is no ammonia or nitrogen oxides produced.

Assuming all gases are ideal and the activity coefficient of carbon is one, the corresponding equilibrium constants for the above reactions are given by the following equations:

k1 = yco * yh2 * p / yh2o Eq.(V.1)

k2 = yco2 * yh2 / yco / yh2o Eq.(V.2)

k3 = ych4 / yh2^2 / p Eq.(V.3)

Symbols k1, k2, and k3 are the equilibrium constants for the above reactions, respectively. Symbols yco, yh2, yh2o, yco2, and ych4 are the mole fractions of carbon

monoxide, hydrogen, water, carbon dioxide, and methane, respectively. Symbol p is the pressure of the reactor in atmospheres. The equilibrium constants can be calculated by the following equation:

$$kj = \exp\left\{ - \left[\sum_{prod.} vi*dgt,prod - \sum_{react.} vi*dgt,reac \right]/r/t \right\} \quad \text{Eq.(V.4)}$$

where

kj = equilibrium constant for reaction j,
vi = stoichiometric coefficient for component i of reaction j,
dgti,prod = standard free energy of formation for product i at temperature t,
dgti,reac = standard free energy of formation for reactant i at temperature t,
r = gas constant
t = temperature at which the reaction takes place.

An elementary phase rule analysis shows that a system consisting of the elements carbon as graphite, hydrogen, oxygen, and nitrogen has four degrees of freedom. The variables that are specified are temperature, pressure, H/O ratio in the feed(horf), and N2/O2 ratio (n2o2r). Rearranging the equilibrium constants gives the following equations:

yh2o = yh2 / h2h2orp Eq.(V.5)

ych4 = k3 * p * yh2^2 Eq.(V.6)

yco = k1 / p / h2h2orp Eq.(V.7)

yco2 = k1 * k2 / p / h2h2orp^2 Eq.(V.8)

If these values are now substituted into the additional

equation requiring the sum of the product gas mole fractions to equal unity, a simple quadratic results:

coef1 * yh2^2 + coef2 * yh2 + coef3 = 0 Eq.(V.9)

where

coef1 = k3 * p * (1+2*n2o2r*(2-horf)/2) Eq.(V.10)

coef2 = (1+1/h2h2orp) * (1+n2o2r*(2-horf)/2) Eq.(V.11)

coef3 = k1 * k2/p/ h2h2orp^2 + k1/p/h2h2orp - 1 Eq.(V.12)

The correct root may be selected by noting that yh2 must lie between zero and one. The H/O ratio of the product gas is then calculated and compared to the desired value. Note that a guess should be provided for the variable h2h2orp, which is the ratio of hydrogen to water in the product stream.

Non-adiabatic reactor: The control volume for the non-adiabatic reactor is shown in Figure V.1a.
All of the reactants enter the control volume at 298.15 Kelvin. Carbon enters as a solid, water as liqiud, and hydrogen, oxygen, and nitrogen enter as a gas at one atmosphere. The gaseous products leave the reactor at the temperature and pressure of the reactor. The following equations are used to calculate the heat requirement of the reactor.

dhmolc = hptt + hptfrx - h2of*dhfh2o,1 Eq.(V.13)

$$hptt = pcr * \int_{298}^{t} cpavgp(t) * dt \qquad \text{Eq.(V.14)}$$

$$hptfrx = pcr * \sum_{i} yi * dhf,i \qquad \text{Eq.(V.15)}$$

where

dhmolc = heat requirement for the reactor per mole carbon fed,
hptt = enthalpy change due to temperature change from the reactant to the product,
hptfrx = enthalpy change due to the formation of the product,
pcr = moles of product per mole of carbon fed,
h2of = moles of water fed per mole of carbon,
dhfh2o,1 = heat of formation of liquid water at 298.15 Kelvin,
cpavgp(t) = molar average heat capacity for the product stream,
yi = mole fraction of product i,
dhf,i = enthalpy of formation for product i at 298.15 Kelvin.

Note that the compression work for the reactants from one atmosphere to the pressure of the reactor is ignored in the above calculations.

Adibatic reactor: For the adiabatic reactor, the constraint of thermal neutrality (i.e., dhmolc=0) means that the enthalpy of the gaseous products, calculated at the temperature and pressure of the reactor, must be equal to the enthalpy of the entering reactants. The control volume for the adiabatic reactor is shown in Figure V.1b. Solid carbon enters at 298.15 Kelvin and the reactor pressure. Water enters as dry saturated steam at the pressure of the reactor. Gaseous reactants enter at reactor pressure and at the temperature that the

reactants would reach if they were compressed adiabatically from 298.15 Kelvin and 1 atmosphere. The following equation is used as a constraint for the thermal neutrality of the reactor:

hptt + hptfrx - h2of*(dhh2o,g+hsteamf)-hftt = 0 Eq.(V.16)

where

hftt = cpavgf*298.15* [exp(r*ln(p)/cpavgf) - 1] Eq.(V.17)

and

dhh2o,g = enthalpy of formation for water vapor at 298.15 Kelvin,
hftt = enthalpy change for the reactants,
cpavgf = molar average heat capacity for the reactants,
hsteamf = enthalpy change for steam from 212 F to reactor pressure as a saturated vapor.

Symbols hptt and hptfrx are given by equations (V.14) and (V.15). Program CHON.TK also calculates the heating value of the product stream. The product gas heating value(Btu/scf) is the heat that would be released by burning 1 standard cubic foot of water-free product gas if the reactants and the products were at 298.15 Kelvin and the water produced by combustion remained as a vapor. The following equation calculates the heating value of the product stream:

$$hvaluep = \sum_{i} yi * dhc,i \qquad \text{Eq.(V.18)}$$

Symbols yi and dhc,i are the mole fraction and heat of combustion at 298.15 Kelvin for the products methane,

carbon monoxide, and carbon dioxide. Symbol hvaluep is the heating value of the product stream.

Program CHON.TK does not use the data files CRITICAL.TK or DATBANK1.TK. This program contains heat capacity and heat of formation data for compounds water, methane, carbon monoxide, carbon dioxide, hydrogen, oxygen, nitrogen, and solid carbon.

There are three limitaions in using program CHON.TK. First of all, the reactants should consist of only the elements carbon, hydrogen, oxygen, and nitrogen. Secondly, it is assumed that the gaseous reactants and products are all ideal gases. In other words, no adjustments have been made for nonideality of the gaseous reactants and products. The above assumption may introduce as much as five percent error in the calculations of the equilibrium composition and the heat requirement of the reactor at high pressure and low temperature. However, the error may be as low as one percent at low pressure and high temperature. Third, no allowance has been made for the production of higher hydrocarbons, ammonia, and nitricoxides in the reactor.

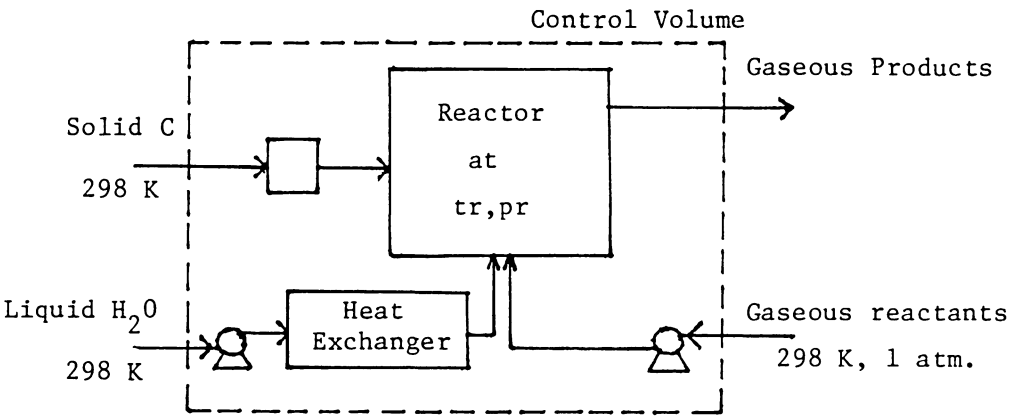


Figure V.1a
Control volume for non-adiabatic reactor.

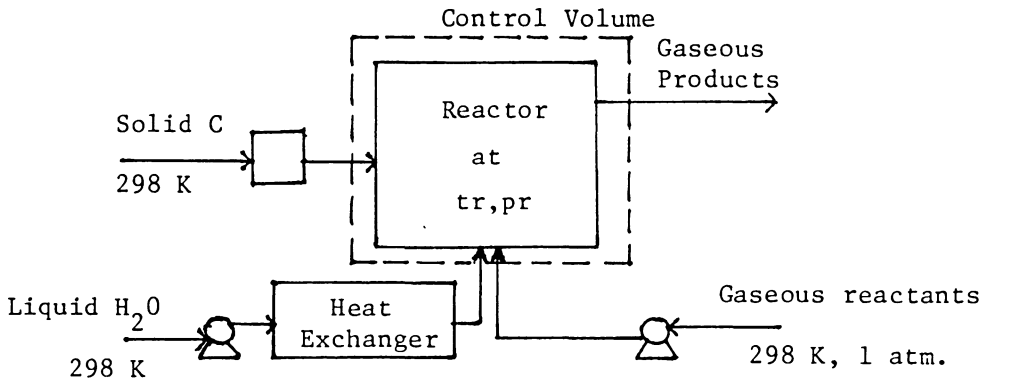


Figure V.1b
Control volume for adiabatic reactor.

2. Instructions

Program CHON.TK calculates the equilibrium composition for a system consisting of elements carbon-hydrogen-oxygen-nitrogen. The system can either be adiabatic or non-adiabatic. The molar ratio of hydrogen to oxygen and the ratio of oxygen to nitrogen in the feed completely specifies the feed composition. The products of the system(e.g., reactor) are hydrogen, water, methane, carbon monoxide, carbon dioxide, and nitrogen. It should be noted that no allowance has been made for the production of higher hydrocarbons, ammonia, or nitrogen oxides. The main variables in this system are the temperature and the pressure of the reactor.

In the following instructions, if a phrase is typed in double emphasized format and it is in quotation marks, it indicates that the phrase should be typed by the user.

In order to use the program CHON.TK, you need the following additional programs:

1) A DOS diskette. The DOS diskette can either be version 2.0 or version 2.1.

2) The TK!Solver diskette.

3) The diskette containing the program CHON.TK.

4) A storage diskette in order to save the solution. The diskette containing the CHON.TK and the storage diskette

may be the same diskette.

Load the TK!Solver diskette into the memory of the computer as described in Appendix 1. After loading the TK!Solver diskette, the screen should be like Figure V.2.

LOADING CHON.TK

To load CHON.TK into the memory, type '/ s 1'.

When the computer asks for the filename, type 'b:chon.tk' and press 'Return' key. Computer responds: loading the b:chon.tk. Wait until the load is completed. After the load is completed, the memory indicator on the right corner of the screen shows 133, indicating that 133K bytes of free memory is available. The program CHON.TK takes up 55K bytes of memory. Note that you do not need to load any of the databanks CRITICAL.TK or DATBANK1.TK in order to use CHON.TK. The program CHON.TK provides its own data. After loading CHON.TK, the variable sheet is like Figure V.3a.

Figure V.3a is the variable sheet of the program CHON.TK.

Type '=r' to go to the rule sheet. The rule sheet is like Figures V.3b and V.3c.

Figures V.3b and V.3c are the rule sheet of the CHON.TK.

Type '=v' to return to the variable sheet.

```
==================== VARIABLE SHEET ============================================
St Input     Name    Output    Unit      Comment
-- -----     ----    ------    ----      -------



==================== RULE SHEET ================================================
S Rule
- ----
```

Figure V.2
Variable and rule sheets of TK!Solver.

```
St Input     Name    Output    Unit      Comment
-- -----     ----    ------    ----      -------

L  'watervap comp              dimless   list of compounds , dimless
           t                   k         reactor temperature , k
   1.987   r                   cal/gmole gas constant , cal/gmole/k
L          dgt                 cal/gmole DGf(1 atm) at temp. t ,cal/gmole
L          dht                 cal/gmole DHf(1 atm) at temp. t ,cal/gmole
L          dst                 cal/gmole DSf(1 atm) at temp. t ,cal/gmole/k
           option              dimless   control variable , dimless
           p                   atm       reactor pressure , atm
           horf                dimless   ratio H/O in feed , dimless
           n2o2r               dimless   ratio N2/O2 in feed , dimless
           h2h2orp             dimless   ratio H2/H2O in product , dimless
           yh2                 dimless   product mole fraction of H2 , dimless
           yh2o                dimless   product mole fraction of H2O , dimless
           ych4                dimless   product mole fraction of CH4 , dimless
           yco                 dimless   product mole fraction of CO , dimless
           yco2                dimless   product mole fraction of CO2 , dimless
           yn2                 dimless   product mole fraction of N2 , dimless
           pcr                 dimless   ratio moles product/mole C , dimless
           dhmolc              btu/lbmol DH feed-->product , btu/lbmole c
           hvaluep             btu/scf   product heating value , btu/scf
           hsteamf             btu/lb    DH steam (212F,sat vap)-->(p,sat vap)
```

Figure V.3a
Variable sheet of CHON.TK.

```
S Rule
- ----
                        "DGT, DHT, DST for each compound
! n = mapl(comp)
! dalpha = m8(n) -(m2(n)*2*-1.5718+m3(n)*7.201 + m4(n)*5.7816+m5(n)*6.4443)/2
! dbeta = m9(n) -(m2(n)*2*7.666e-3*2+m3(n)*-5.2697e-4*2 + m4(n)*.21942e-2*2+ m5
! dgamma = m10(n) -(m2(n)*2*-4.0177e-6*3+m3(n)*4.5653e-7*3 + m4(n)*-.76772e-6*3
! dtheta = m11(n) -(m2(n)*2*8.6122e-10*4+m3(n)*-.7378e-10*4+m4(n)*1.1546e-10*4+
! dht = m13(n) + poly(t,dtheta/4,dgamma/3,dbeta/2,dalpha,0) - poly(298,dtheta/4
! dsf25c = m12(n) - m2(n)*1.3609 - (m3(n)*31.211+m4(n)*49.003+m5(n)*45.767)/2
! dst = dsf25c + dalpha*ln(t/298) + dbeta*(t-298) + dgamma*(t^2-298^2)/2 + dthe
! dgt = dht -t*dst

                        "equilibrium constants K1, K2, K3
! k1 = exp(-1*(mdgt(2) - mdgt(1) )/r/t)
! k2 = exp(-1*(mdgt(3) - mdgt(1) - mdgt(2) )/r/t)
! k3 = exp(-1*(mdgt(4) )/r/t)

                        "Equilibrium composition
! coef1 = k3 * p * (1 + 2*n2o2r*(2-horf)/2)
! coef2 = (1+1/h2h2orp) * (1+n2o2r*(2-horf)/2)
! coef3 = k1*k2/p/h2h2orp^2  +  k1/p/h2h2orp  - 1
! coef1 * yh2^2  +  coef2 * yh2  +  coef3 = 0
! yh2o = yh2 / h2h2orp
! ych4 = k3 * p * yh2^2
! yco  = k1 / p / h2h2orp
! yco2 = k1 * k2 / p / h2h2orp^2
! 0/n2o2r + yn2 = 1 - yh2 - yh2o - ych4 - yco - yco2
! horf = (2*yh2 + 2*yh2o + 4*ych4) / (2*yco2 + yco + yh2o)
! pcr  = 1 / (ych4 + yco2 + yco)

                        "Feed composition
! h2of = pcr*step(horf,2)*(yh2o+yco+2*yco2)  +  pcr*step(1.999999999,horf)*(yh2
! h2f  = step(horf,2)*h2of*(horf - 2)/2
! o2f  = step(2,horf)*h2of*(2 - horf)/2
! n2t = n2o2r*o2f
! h2t = h2f + h2of
! o2t = o2f + h2of/2
```

Figure V.3b
Upper part of the rule sheet of CHON.TK.

```
3 Rule
- ----
                    *enthalpy of Product stream
$ alphat = 1$m8(8) + h2t$m8(5) + o2t$m8(6) + n2t$m8(7)
$ betat  = 1$m9(8) + h2t$m9(5) + o2t$m9(6) + n2t$m9(7)
$ gammat = 1$m10(8)+ h2t$m10(5)+ o2t$m10(6)+ n2t$m10(7)
$ thetat = 1$m11(8)+ h2t$m11(5)+ o2t$m11(6)+ n2t$m11(7)
$ hptfrx = pcr$(yh2o$mdht(1) + ych4$mdht(4) + yco$mdht(2) + yco2$mdht(3) )
$ hptt = alphat$(t-298)+betat$(t^2-298^2)/2 +gammat$(t^3-298^3)/3 +thetat$(t^4-
$ dhmolc = ( (hptt+hptfrx) - h2of$(-68317))$1.8

$ cpavgf = (7.6$o2f + 7.3$n2t + 7.1$h2f)/(o2f+n2t+h2f)
$ - dhmolc + (hptt+hptfrx) - h2of$(-57253+hsteamf$10) - cpavgf$(o2f+n2t+h2f)$29

                    *Heating value of Product stream
$ hvaluep = -1$(yh2$-57798 + ych4$-212800 + yco$-67636)$1.8/(1-yh2o)/379.5
```

Figure V.3c
Lower part of the rule sheet of CHON.TK.

EXAMPLE ONE

PROBLEM STATEMENT: Calculate the equilibrium composition for a reactor with the hydrogen to oxygen ratio(e.g., H/O ratio) of 3.0 in a bed of solid carbon. The temperature of the reactor is 2000 degrees Fahrenheit and the pressure is 100 atmospheres. There is no nitrogen in the feed. Also calculate the heat requirement of the reactor along with the heating value of the product stream.

The solution to this problem involves three stages. Stage one calculates the standard free energy of formation of water, carbon monoxide, carbon dioxide, and methane at temperature 2000 degrees Fahrenheit. Stage two calculates the equilibrium composition of the product stream, and stage three calculates the heat requirement of the reactor along with the heating value of the product stream. The solution is divided into three stages in order to minimize the number of equations that have iterative solutions and save execution time.

In order to solve this problem, perform the following steps:

STAGE ONE.....

1) In the input column of the variable t type the temperature of the reactor(e.g., type '(2000+460)/1.8'). Note that the temperature has

to be in Kelvin, not in degrees Fahrenheit.

2) In the input column of the variable option type ''dgt_on'. This option turns on the part of the rule sheet that calculates the standard free energy of formation for each compound and turns off the rest of the rule sheet.

Variable option has eight choices as shown below:

'dgt_on
'keq_on
'equilibria_on
'k_equilibria_on
'adiabatic_on
'molesfed_on
'dhmolc_on
'rules_off

Option dgt_on turns on the part of the rule sheet that involves the calculation of standard free energy of formation of compounds. Option keq_on turns on the part of the rule sheet that calculates the equilibrium constant for each reaction. Option 'equilibria_on turns on the part of the rule sheet that involves the calculation of the equilibrium composition for the product stream. Option k_equilibria_on turns on rules for both equilibrium constants and equilibrium composition calculations. Option adiabatic_on turns on rules for the calculation of the equilibrium composition for an adiabadic reactor. Option molesfed_on turns on the rules for the calculation of moles fed to the reactor. Option dhmolc_on turns on rules for the calculation of heat requirement of the reactor and the

heating value of the product stream. Option rules_off turns off all of the rule sheet as the name indicates.

3) If the upper portion of the variable sheet is like Figure V.4a after the completion of the above steps, you are ready to execute the program. Note that there is no change in the lower portion of the variable sheet. Type '/1 !' and wait until the computer completes execution. The execution step may take as long as a minute.

4) After the execution is completed, dive to the variable dgt subsheet dy using the dive command(e.g., Press '>' twice). The screen should be like Figure V.4b.

Figure V.4b is the variable dgt subsheet. According to this subsheet, the standard free energy of formation for water vapor is -41096.6 cal/gmole, carbon monoxide is -55602.9 cal/gmole, carbon dioxide is -94726.1 cal/gmole, and for methane is 14392.8 cal/gmole at 2000 F.

Press '<' twice to return to the variable sheet.

You can also see the enthalpy of formation and the entropy of formation of each compound by diving to the variables dht and dst subsheets, respectively.

STAGE TWO....

5) In order to find the equilibrium composition, change the option to k_equilibria_on by typing ''k_equilibria_on' in the input column of the

variable option.

6) In the input column of the variable p type the pressure of the reactor in atmospheres(e.g. type '100').

7) In the input column of the variable horf(e.g., H/O ratio in the feed) type the hydrogen to oxygen ratio in the feed stream(e.g., type '3').

8) In the input column of the variable n2o2r(e.g., N2/O2 ratio) type the nitrogen to oxygen ratio. Since there is no nitrogen in the feed, type '0'.

9) In the status column of the variable h2h2orp(e.g., H2/H2O ratio product) type 'g' to indicate that this variable has an iterative solution. Note that the number 1 appears in the input column of this variable after you enter g in the status column. The value 1 is the default value for the first guess.

10) In the status column of the variable yh2 type 'g' to indicate that this variable has an iterative solution. Note that the value 0.2 appears in the input column after you enter g in the status column. The value 0.2 is the default value for the first guess for the variable yh2.

11) If the variable sheet is like Figure V.5 after the completion of the above steps, you are ready to execute the program. Type '!' and wait until the program completes execution. The execution step may take a few minutes. This stage of the program involves iterative solution.

After the program completes the execution, the lower portion of the variable sheet is like Figure V.6a. This figure shows the equilibrium composition of the product stream. In Figure V.6b, the solution to the same problem is shown from a publication by MIT (Ref. 19).

According to Figure V.6a, The mole fraction of hydrogen in the product stream is 0.4473, for water is 0.0749, for methane is 0.0998, for carbon monoxide is 0.3497, and for carbon dioxide is 0.0283. Also, the ratio of moles of product per mole of carbon is 2.093. Comparing the above mole fractions with the mole fractions in Figure V.6b indicates that the errors in the above values do not exceed 3 percent. This problem illustrates how accurately this program predicts the equilibrium composition of the CARBON-HYDROGEN-OXYGEN systems.

STAGE THREE.....

12) In order to find the heating requirement of the reactor, change the option to dhmolc_on by typing ''dhmolc_on' in the input column of the variable option.

13) Transfer the values in the output columns to the input column of their respective variables by typing 'g' in the status column of each variable. After performing this command, the variable sheet is like Figure V.7.

Type 'g' one more time in the status column of the

above variables to erase the g's. Note that typing g once transfers the values from the output to the input column, and typing g again erases the g's from the status column. After performing the above command, the screen is like Figure V.8.

14) If the variable sheet is like Figure V.8 after the completion of the above steps, you are ready to execute the program. Type '!' and wait until the execution is completed. The execution step may take as long as a minute. After the execution is completed, the variable sheet is like Figure V.9.

According to Figure V.9, the heat requirement of the reactor(e.g., dhmolc) is 89823 cal/gmol carbon fed assuming no shaft work is done by the system. Also, the heating value of the product stream based on 298K and 1 atm is 363 Btu per standard cubic feet. Again, comparing the above values with the corresponding values in Figure V.6b indicates that there is less than 3 percent error in the values of dhmolc and hvaluep.

15) You can get a hard copy of the variable sheet by typing PrtSc or you can use the /p command of the TK!Solver program. Type '/q' to quit TK!Solver and return to the DOS system, or do step 16 before going to the next example.

16) Delete the values in the input column of the variables option through pcr by using '/b' command. After doing

this step, the lower portion of the variable sheet is like Figure V.10.

Turn to the next page to do example two.

St	Input	Name	Output	Unit	Comment
L	'watervap	comp		dimless	list of compounds , dimless
	1366.6667	t		k	reactor temperature , k
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L		dgt		cal/gmole	DGf(1 atm) at temp. t ,cal/gmole
L		dht		cal/gmole	DHf(1 atm) at temp. t ,cal/gmole
L		dst		cal/gmole	DSf(1 atm) at temp. t ,cal/gmole/k
	'dgt_on	option		dimless	control variable , dimless
		p		atm	reactor pressure , atm
		horf		dimless	ratio H/O in feed , dimless
		n2o2r		dimless	ratio N2/O2 in feed , dimless
		h2h2orp		dimless	ratio H2/H2O in product , dimless

Figure V.4a
Upper portion of the variable sheet.

LIST: dgt

Comment:	dgt for h2o, co, co2, ch4
Display Unit:	cal/gmole
Storage Unit:	cal/gmole

Element	Value
1	-41096.62382
2	-55602.95575
3	-94726.05503
4	14392.79098

Figure V.4b
Subsheet of list dgt.

St	Input	Name	Output	Unit	Comment
L	'watervap	comp		dimless	list of compounds , dimless
	1366.6667	t		k	reactor temperature , k
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L		dgt		cal/gmole	DGf(1 atm) at temp. t ,cal/gmole
L		dht		cal/gmole	DHf(1 atm) at temp. t ,cal/gmole
L		dst		cal/gmole	DSf(1 atm) at temp. t ,cal/gmole/k
	'k_equili	option		dimless	control variable , dimless
	100	p		atm	reactor pressure , atm
	3	horf		dimless	ratio H/O in feed , dimless
	0	n2o2r		dimless	ratio N2/O2 in feed , dimless
G	1	h2h2orp		dimless	ratio H2/H2O in product , dimless
G	.2	yh2		dimless	product mole fraction of H2 , dimless
		yh2o		dimless	product mole fraction of H2O , dimless
		ych4		dimless	product mole fraction of CH4 , dimless
		yco		dimless	product mole fraction of CO , dimless
		yco2		dimless	product mole fraction of CO2 , dimless
		yn2		dimless	product mole fraction of N2 , dimless
		pcr		dimless	ratio moles product/mole C , dimless
		dhmolc		btu/lbmol	DH feed-->product , btu/lbmole c
		hvaluep		btu/scf	product heating value , btu/scf
		hsteamf		btu/lb	DH steam (212F,sat vap)-->(p,sat vap)

Figure V.5
Variable sheet.

St	Input	Name	Output	Unit	Comment
L	'watervap	comp		dimless	list of compounds , dimless
	1366.6667	t		k	reactor temperature , k
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L		dgt		cal/gmole	DGf(1 atm) at temp. t ,cal/gmole
L		dht		cal/gmole	DHf(1 atm) at temp. t ,cal/gmole
L		dst		cal/gmole	DSf(1 atm) at temp. t ,cal/gmole/k
	'k_equili	option		dimless	control variable , dimless
	100	p		atm	reactor pressure , atm
	3	horf		dimless	ratio H/O in feed , dimless
	0	n2o2r		dimless	ratio N2/O2 in feed , dimless
		h2h2orp	5.9736930	dimless	ratio H2/H2O in product , dimless
		yh2	.44725276	dimless	product mole fraction of H2 , dimless
		yh2o	.07487040	dimless	product mole fraction of H2O , dimless
		ych4	.09963879	dimless	product mole fraction of CH4 , dimless
		yco	.34972140	dimless	product mole fraction of CO , dimless
		yco2	.02830466	dimless	product mole fraction of CO2 , dimless
		yn2		dimless	product mole fraction of N2 , dimless
		pcr	2.0926419	dimless	ratio moles product/mole C , dimless
		dhmolc		btu/lbmol	DH feed-->product , btu/lbmole c
		hvaluep		btu/scf	product heating value , btu/scf
		hsteamf		btu/lb	DH steam (212F,sat vap)-->(p,sat vap)

Figure V.6a
Variable sheet showing the equilibrium composition.

comparison of the results with the reference

type	yh2	yh2o	ych4	yco	yco2	pcr	dhmolc	hvaluep
chon_tk	.4472	.0749	.0998	.3497	.0283	2.093	89823	363
Reference	.4449	.0771	.1014	.3465	.0298	2.092	89640	367

Figure V.6b
Comparison of the results with the reference.

St	Input	Name	Output	Unit	Comment
L	'watervap	comp		dimless	list of compounds , dimless
	1366.6667	t		k	reactor temperature , k
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L		dgt		cal/gmole	DGf(1 atm) at temp. t ,cal/gmole
L		dht		cal/gmole	DHf(1 atm) at temp. t ,cal/gmole
L		dst		cal/gmole	DSf(1 atm) at temp. t ,cal/gmole/k
	'dhmolc_o	option		dimless	control variable , dimless
	100	p		atm	reactor pressure , atm
	3	horf		dimless	ratio H/O in feed , dimless
	0	n2o2r		dimless	ratio N2/O2 in feed , dimless
G	5.9736930	h2h2orp		dimless	ratio H2/H2O in product , dimless
G	.44725276	yh2		dimless	product mole fraction of H2 , dimless
G	.07487040	yh2o		dimless	product mole fraction of H2O , dimless
G	.09983879	ych4		dimless	product mole fraction of CH4 , dimless
G	.34972140	yco		dimless	product mole fraction of CO , dimless
G	.02830466	yco2		dimless	product mole fraction of CO2 , dimless
		yn2		dimless	product mole fraction of N2 , dimless
G	2.0926419	pcr		dimless	ratio moles product/mole C , dimless
		dhmolc		btu/lbmol	DH feed-->product , btu/lbmole c
		hvaluep		btu/scf	product heating value , btu/scf
		hsteamf		btu/lb	DH steam (212F,sat vap)-->(p,sat vap)

Figure V.7
Variable sheet.

St	Input	Name	Output	Unit	Comment
L	'watervap	comp		dimless	list of compounds , dimless
	1366.6667	t		k	reactor temperature , k
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L		dgt		cal/gmole	DGf(1 atm) at temp. t ,cal/gmole
L		dht		cal/gmole	DHf(1 atm) at temp. t ,cal/gmole
L		dst		cal/gmole	DSf(1 atm) at temp. t ,cal/gmole/k
	'dhmolc_o	option		dimless	control variable , dimless
	100	p		atm	reactor pressure , atm
	3	horf		dimless	ratio H/O in feed , dimless
	0	n2o2r		dimless	ratio N2/O2 in feed , dimless
	5.9736930	h2h2orp		dimless	ratio H2/H2O in product , dimless
	.44725276	yh2		dimless	product mole fraction of H2 , dimless
	.07487040	yh2o		dimless	product mole fraction of H2O , dimless
	.09983879	ych4		dimless	product mole fraction of CH4 , dimless
	.34972140	yco		dimless	product mole fraction of CO , dimless
	.02830466	yco2		dimless	product mole fraction of CO2 , dimless
		yn2		dimless	product mole fraction of N2 , dimless
	2.0926419	pcr		dimless	ratio moles product/mole C , dimless
		dhmolc		btu/lbmol	DH feed-->product , btu/lbmole c
		hvaluep		btu/scf	product heating value , btu/scf
		hsteamf		btu/lb	DH steam (212F,sat vap)-->(p,sat vap)

Figure V.8
Variable sheet.

St	Input	Name	Output	Unit	Comment
	.09983879	ych4		dimless	product mole fraction of CH4 , dimless
	.34972140	yco		dimless	product mole fraction of CO , dimless
	.02830466	yco2		dimless	product mole fraction of CO2 , dimless
		yn2		dimless	product mole fraction of N2 , dimless
	2.0926419	pcr		dimless	ratio moles product/mole C , dimless
		dhmolc	89823.168	btu/lbmol	DH feed-->product , btu/lbmole c
		hvaluep	362.72973	btu/scf	product heating value , btu/scf
		hsteamf		btu/lb	DH steam (212F,sat vap)-->(p,sat vap)

Figure V.9
Variable sheet.

St	Input	Name	Output	Unit	Comment
L	'watervap	comp		dimless	list of compounds , dimless
	1366.6667	t		k	reactor temperature , k
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L		dgt		cal/gmole	DGf(1 atm) at temp. t ,cal/gmole
L		dht		cal/gmole	DHf(1 atm) at temp. t ,cal/gmole
L		dst		cal/gmole	DSf(1 atm) at temp. t ,cal/gmole/k
		option		dimless	control variable , dimless
		p		atm	reactor pressure , atm
		horf		dimless	ratio H/O in feed , dimless
		n2o2r		dimless	ratio N2/O2 in feed , dimless
		h2h2orp		dimless	ratio H2/H2O in product , dimless
		yh2		dimless	product mole fraction of H2 , dimless
		yh2o		dimless	product mole fraction of H2O , dimless
		ych4		dimless	product mole fraction of CH4 , dimless
		yco		dimless	product mole fraction of CO , dimless
		yco2		dimless	product mole fraction of CO2 , dimless
		yn2		dimless	product mole fraction of N2 , dimless
		pcr		dimless	ratio moles product/mole C , dimless
		dhmolc	89823.168	btu/lbmol	DH feed-->product , btu/lbmole c
		hvaluep	362.72973	btu/scf	product heating value , btu/scf
		hsteamf		btu/lb	DH steam (212F,sat vap)-->(p,sat vap)

Figure V.10
Variable sheet.

EXAMPLE TWO

PROBLEM STATEMENT: Calculate the equilibrium composition for a reactor with the hydrogen to oxygen ratio (e.g., H/O ratio) of 1.0 in a bed of solid carbon. The temperature of the reactor is 2500 degrees Fahrenheit and the pressure is 50 atmospheres. The nitrogen to oxygen ratio in the feed(e.g. N2/O2 ratio feed) is 1.5. Also calculate the heat requirement of the reactor along with the heating value of the product stream.

In order to solve this problem, perform the following steps:

STAGE ONE.....

1) In the input column of the variable t type the temperature of the reactor(e.g., type '(2500+460)/1.8'). Note that the temperature has to be in Kelvin not in degrees Fahrenheit.

2) In the input column of the variable option type ''dgt_on'. This option turns on the part of the rule sheet that calculates the standard free energy of formation for each compound and turns off the rest of the rule sheet.

3) If the upper portion of the variable sheet is like Figure V.11a after the completion of the above steps, you are ready to execute the program. Note that there is no

change in the lower portion of the variable sheet. Type '/l !' and wait until the computer completes execution. The execution step may take as long as a minute.

4) After the execution is completed, dive to the variable dgt subsheet by using the dive command(e.g., Press '>' twice). The screen should be like Figure V.11b.

Figure V.11b is the variable dgt subsheet. According to this subsheet, the standard free energy of formation for water vapor is -37290.1 cal/gmole, carbon monoxide is -61301.1 cal/gmole, carbon dioxide is -94756.1 cal/gmole, and for methane is 21818.5 cal/gmole at 2500 F.

Press '<' twice to return to the variable sheet.

You can also see the enthalpy of formation and the entropy of formation of each compound by diving to the variables dht and dst subsheet, respectively.

STAGE TWO....

5) In order to find the equilibrium composition, change the option by typing ''k_equilibria_on' in the input column of the variable option.

6) In the input column of the variable p type the pressure of the reactor in atmospheres (e.g., type '50').

7) In the input column of the variable horf type the hydrogen to oxygen ratio in the feed (e.g., type '1').

8) In the input column of the variable n2o2r(e.g., N2/O2

ratio) type the nitrogen to oxygen ratio which is 1.5. Therefore, type '1.5'.

9) In the status column of the variable h2h2orp(e.g., H2/H2O ratio product) type 'g' to indicate that this variable has an iterative solution. Note that the number 1 appears in the input column of this variable after you enter g in the status column. The value 1 is the default value for the first guess.

10) In the status column of the variable yh2 type 'g' to indicate that this variable has iterative solution. Note that the value 0.2 appears in the input column after you enter g in the status column. The value 0.2 is the default value for the first guess for the variable yh2.

11) If the variable sheet is like Figure V.12 after the completion of the above steps, you are ready to execute the program. Type '!' and wait until the program completes execution. The execution step may take a few minutes. This stage of the program involves an iterative solution.

After the program completes execution, the lower portion of the variable sheet is like Figure V.13a. This figure shows the equilibrium composition of the product stream. In Figure V.13b, the solution to the same problem is shown from a publication by MIT (Ref. 19).

According to Figure V.13a, The mole fraction of hydrogen in the product stream is 0.2570, for water is 0.0044, for

methane is 0.0041, for carbon monoxide is 0.5294, for carbon dioxide is 0.0028, and for nitrogen is 0.2023. Also, the ratio of the moles of product per mole of carbon is 1.864. Comparing the above mole fractions with the mole fractions in Figure V.13b indicates that the error in the above values do not exceed 3 percent. This problem illustrates how accurately this program predicts the equilibrium composition of the CARBON-HYDROGEN-OXYGEN-NITROGEN systems.

STAGE THREE.....

12) In the input column of the variable option type ''dhmolc_on' to calculate the heat requirement of the reactor.

13) Transfer the values in the output columns to the input columns of their respective variable by typing 'g' in the status column of each variable as you did in the previous example. Type 'g' one more time in the status column of the above variables to erase the g's. After the completion of this step the screen is like Figure V.14.

14) If the variable sheet is like Figure V.14 after the completion of the above steps, you are ready to execute the program. Type '!' and wait until the execution is completed. The execution step may take as long as a minute. After the execution is completed, the variable sheet is like Figure V.15.

According to Figure V.14, the heat requirement of the reactor(e.g., dhmolc) is 47732 cal/gmol carbon fed assuming no shaft work is done by the system. Also, the heating value of the product stream based on 298K and 1 atm is 245 Btu per standard cubic foot. Again, comparing the above values with the corresponding values in Figure V.13b indicates that there is less than 3 percent error in the values of dhmolc and hvaluep.

15) You can get a hard copy of the variable sheet by typing PrtSc or you can use the /p command of the TK!Solver program. Type '/q' to quit TK!Solver and return to the DOS system, or do step 16 of example one before going to the next example.

Turn to the next page to do example three.

St	Input	Name	Output	Unit	Comment
L	'watervap	comp		dimless	list of compounds , dimless
	1644.4444	t		k	reactor temperature , k
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L		dgt		cal/gmole	DGf(1 atm) at temp. t ,cal/gmole
L		dht		cal/gmole	DHf(1 atm) at temp. t ,cal/gmole
L		dst		cal/gmole	DSf(1 atm) at temp. t ,cal/gmole/k
	'dgt_on	option		dimless	control variable , dimless
		p		atm	reactor pressure , atm
		horf		dimless	ratio H/O in feed , dimless
		n2o2r		dimless	ratio N2/O2 in feed , dimless
		h2h2orp		dimless	ratio H2/H2O in product , dimless

Figure V.11a
Variable sheet.

========== LIST: dgt ==========

Comment:	dgt for h2o, co, co2, ch4
Display Unit:	cal/gmole
Storage Unit:	cal/gmole

Element	Value
1	-37290.12345
2	-61301.06056
3	-94756.14883
4	21818.55617

Figure V.11b
Subsheet sheet of list dgt.

St	Input	Name	Output	Unit	Comment
L	'watervap	comp		dimless	list of compounds , dimless
	1644.4444	t		k	reactor temperature , k
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L		dgt		cal/gmole	DGf(1 atm) at temp. t ,cal/gmole
L		dht		cal/gmole	DHf(1 atm) at temp. t ,cal/gmole
L		dst		cal/gmole	DSf(1 atm) at temp. t ,cal/gmole/k
	'k_equili	option		dimless	control variable , dimless
	50	p		atm	reactor pressure , atm
	1	horf		dimless	ratio H/O in feed , dimless
	1.5	n2o2r		dimless	ratio N2/O2 in feed , dimless
G	1	h2h2orp		dimless	ratio H2/H2O in product , dimless
G	.2	yh2		dimless	product mole fraction of H2 , dimless
		yh2o		dimless	product mole fraction of H2O , dimless
		ych4		dimless	product mole fraction of CH4 , dimless
		yco		dimless	product mole fraction of CO , dimless
		yco2		dimless	product mole fraction of CO2 , dimless
		yn2		dimless	product mole fraction of N2 , dimless
		pcr		dimless	ratio moles product/mole C , dimless
		dhmolc		btu/lbmol	DH feed-->product , btu/lbmole c
		hvaluep		btu/scf	product heating value , btu/scf
		hsteamf		btu/lb	DH steam (212F,sat vap)-->(p,sat vap)

Figure V.12
Variable sheet.

St	Input	Name	Output	Unit	Comment
	1644.4444	t		k	reactor temperature , k
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L		dgt		cal/gmole	DGf(1 atm) at temp. t ,cal/gmole
L		dht		cal/gmole	DHf(1 atm) at temp. t ,cal/gmole
L		dst		cal/gmole	DSf(1 atm) at temp. t ,cal/gmole/k
	'k_equili	option		dimless	control variable , dimless
	50	p		atm	reactor pressure , atm
	1	horf		dimless	ratio H/O in feed , dimless
	1.5	n2o2r		dimless	ratio N2/O2 in feed , dimless
		h2h2orp	58.694170	dimless	ratio H2/H2O in product , dimless
		yh2	.25699383	dimless	product mole fraction of H2 , dimless
		yh2o	.00437852	dimless	product mole fraction of H2O , dimless
		ych4	.00415764	dimless	product mole fraction of CH4 , dimless
		yco	.52941846	dimless	product mole fraction of CO , dimless
		yco2	.00278919	dimless	product mole fraction of CO2 , dimless
		yn2	.20226235	dimless	product mole fraction of N2 , dimless
		pcr	1.8644010	dimless	ratio moles product/mole C , dimless
		dhmolc		btu/lbmol	DH feed-->product , btu/lbmole c
		hvaluep		btu/scf	product heating value , btu/scf
		hsteamf		btu/lb	DH steam (212F,sat vap)-->(p,sat vap)

Figure V.13a
Variable sheet.

comparison of the results with the reference

type	yh2	yh2o	ych4	yco	yco2	yn2	pcr	dhmolc	hvaluep
chon_tk	.2569	.0044	.0041	.5294	.0028	.2023	1.864	47732	245
Reference	.2566	.0045	.0043	.5291	.0029	.2023	1.864	47690	255

Figure V.13b
Comparison of results with the reference.

St	Input	Name	Output	Unit	Comment
--	-----	----	------	----	-------
	'dhmolc_o	option		dimless	control variable , dimless
	50	p		atm	reactor pressure , atm
	1	horf		dimless	ratio H/O in feed , dimless
	1.5	n2o2r		dimless	ratio N2/O2 in feed , dimless
	58.694170	h2h2orp		dimless	ratio H2/H2O in product , dimless
	.25699383	yh2		dimless	product mole fraction of H2 , dimless
	.00437852	yh2o		dimless	product mole fraction of H2O , dimless
	.00415764	ych4		dimless	product mole fraction of CH4 , dimless
	.52941846	yco		dimless	product mole fraction of CO , dimless
	.00278919	yco2		dimless	product mole fraction of CO2 , dimless
	.20226235	yn2		dimless	product mole fraction of N2 , dimless
	1.8644010	pcr		dimless	ratio moles product/mole C , dimless
		dhmolc		btu/lbmol	DH feed-->product , btu/lbmole c
		hvaluep		btu/scf	product heating value , btu/scf
		hsteamf		btu/lb	DH steam (212F,sat vap)-->(p,sat vap)

Figure V.14
Variable sheet.

St	Input	Name	Output	Unit	Comment
--	-----	----	------	----	-------
	'dhmolc_o	option		dimless	control variable , dimless
	50	p		atm	reactor pressure , atm
	1	horf		dimless	ratio H/O in feed , dimless
	1.5	n2o2r		dimless	ratio N2/O2 in feed , dimless
	58.694170	h2h2orp		dimless	ratio H2/H2O in product , dimless
	.25699383	yh2		dimless	product mole fraction of H2 , dimless
	.00437852	yh2o		dimless	product mole fraction of H2O , dimless
	.00415764	ych4		dimless	product mole fraction of CH4 , dimless
	.52941846	yco		dimless	product mole fraction of CO , dimless
	.00278919	yco2		dimless	product mole fraction of CO2 , dimless
	.20226235	yn2		dimless	product mole fraction of N2 , dimless
	1.8644010	pcr		dimless	ratio moles product/mole C , dimless
		dhmolc	47732.263	btu/lbmol	DH feed-->product , btu/lbmole c
		hvaluep	245.56322	btu/scf	product heating value , btu/scf
		hsteamf		btu/lb	DH steam (212F,sat vap)-->(p,sat vap)

Figure V.15
Variable sheet.

EXAMPLE THREE

PROBLEM STATEMENT: Calculate the hydrogen to oxygen ratio and the equilibrium composition of the product of an adiabatic reactor at 1000 F and for pressures of 1, 10, 100 atmospheres. The feed to the above reactor is carbon, water vapor, oxygen, and nitrogen. The ratio of nitrogen to oxygen in the feed is 1.5. Also, calculate the heating value of the product stream in units of Btu per standard cubic foot.

Since the reactor is adiabatic, the solution to the above problem involves only two stages. In the first stage, the standard free energy of formation for each compound is calculated. In the second stage, the equilibrium composition and the heating value of the product stream are calculated by setting dhmolc, the heat requirement of the reactor, equal to zero(e.g., reactor is adiabatic). Also, note that you need to provide initial guesses for three variables for the adiabatic reactor. These variables are h2h2orp, ratio H2/H2O in the product, yh2, mole fraction of hydrogen in the product, and horf, ratio H/O in the feed.

In order to solve the above problem, perform the following steps:

STAGE ONE....

1) In the input column of the variable t type the temperature of the reactor (e.g., type '(1000+460)/1.8'). Note that the temperature should be in Kelvin not in Fahrenheit.

2) In the input column of the variable option type 'dgt_on'. Option dgt_on turns on the rule sheet for dgt calculation and turns off the rest of the rule sheet.

3) If the variable sheet is like Figure V.16a after completing the above steps, you are ready to execute the program. Press '/1!' and wait until the program stops execution. The execution step may take as long as a minute. After program execution is completed, dive to the variable dgt subsheet to see the standard free energy of formation for each compound. The dgt subsheet is like Figure V.16b.

According to Figure V.16b, the standard free energy of formation for water is -48492 cal/gmole, for carbon monoxide is -43911 cal/gmole, for carbon dioxide is -94565 cal/gmole, and for methane is -204 cal/gmole at 1000 F.

Press '< ' twice to return to the variable sheet.

STAGE TWO.....

4) In the input column of the variables dgt, dht, and dst type any character to indicate these variables are input variables for the second stage(e.g., type ''input').

5) In the input column of the variable option type

''adiabatic_on'. This option turns on the rules for the adiabatic reactor.

6) In the status column of the variable p type '1' to indicate that this variable has an associated list. Also, in the input column of this variable type any number to indicate that this variable is an input variable(e.g., type '1').

Dive to the variable p subsheet by pressing '>' twice. Enter each pressure in this subsheet. The completed p subsheet is shown in Figure V.17.

Press '<' twice to return to the variable sheet.

7) In the status column of the variable horf type 'lg' to indicate there is a list associated with the variable, and there exists iterative solution for this variable. Note that the value of 1 appears in the input column for variable horf. The value 1 is the default first guess for this variable.

Dive to the variable horf subsheet by pressing '>' twice. Enter the first guess for horf value for each pressure. Note that the initial guesses should be close to the final solution for the adiabatic reactor or the program may not converge to the desired solution. The completed variable horf subsheet is shown in Figure V.18.

Press '<' twice to return to the variable sheet.

8) In the input column of the variable n2o2r type the ratio of N2/O2 in the feed which is 1.5. Therefore, type

'1.5'.

9) In the status column of the variable h2h2orp type '1g'. L indicates that this variable has an associated list, and g indicates that this variable has an iterative solution. Note that the value of 1 appears in the input column for variable h2h2orp. The value 1 is the default first guess for this variable.

Dive to the variable h2h2orp subsheet by pressing '>' twice. Enter the first guess for h2h2orp value for each pressure. Note that the initial guesses should be close to the final solution for the adiabatic reactor or the program may not converge to the desired solution. The completed variable h2h2orp subsheet is shown in Figure V.19.

Press '<' twice to return to the variable sheet.

10) In the status column of the variable yh2 type '1g' to indicate there is a list associated with the variable and that there exists iterative solution for this variable. Note that the value of 0.2 appears in the input column for variable yh2. The value 0.2 is the default first guess for this variable.

Dive to the variable yh2 subsheet by pressing '>' twice. Enter the first guess for yh2 value for each pressure. Note that the initial guesses should be close to the final solution for the adiabatic reactor or the program may not converge to the desired solution. The

completed variable yh2 subsheet is shown in Figure V.20.
Press '<' twice to return to the variable sheet.
11) In the status column of the variables yh2o, ych4, yco, yco2, yn2, pcr, and hvaluep type '1' to indicate there is a list associated with each one of the above variables.
12) Since the reactor is adiabatic, type '0' in the input column of the variable dhmolc, the heat requirement of the reactor.
13) Variable hsteamf, the difference between the saturation enthalpy of steam from 212 F to saturated steam at the pressure of the reactor, is used exclusively with the adiabatic reactor case. In the status column of this variable type '1' to indicate there is a list associated with this variable. Also, type any number in the input column to indicate that this variable is an input variable.
Dive to the variable hsteamf subsheet by pressing '>' twice. Enter the value for hsteamf corresponding to each pressure of the reactor in this subsheet. The values for hsteamf can be obtained from a steam table. The completed subsheet is like Figure V.21.
Press '<' twice to return to the variable sheet.
14) If the variable sheet is like Figure V.22 after the completion of the above steps, you are ready to execute the program. Type '/lb'. The computer asks for the first element of the block. Type '1' and press

'Return' in response to this question. Then, the computer asks for the last element of the block. Type '3' and press 'Return' in response to this question and the computer begins execution. Note that in the above instructions, the block option of the list solver is used. The duration of the execution step depends on the initial guesses. It is also possible that the solution may not converge. If the solution does not converge for a set of initial guesses, go back to the variables horf, h2h2orp, and yh2 subsheets and change the initial guesses until the solution converges.

15) After the computer executes the program and the final solution is reached successfully, dive to the variable yh2 subsheet by pressing '>' twice. This subsheet shows the mole fraction of hydrogen in the product stream. The subsheet is like Figure V.23.

According to Figure V.23, the mole fraction of hydrogen for the reactor pressure of 1 atm is 0.2263, for 10 atm is 0.1076, for 100 atm is 0.0394. Press '<' twice to return to the variable sheet.

You can go to the subsheet of the variables yh2o, ych4, ycO, and yco2, to see the mole fractions of water, methane, carbon monoxide, and carbon dioxide, respectively, for each reactor pressure. You can also go to the subsheet of the variables pcr and hvaluep to see the values for moles of product per mole of carbon fed(e.g.,

pcr), and heating value of the product stream, respectively.

16) In order to get a copy of solution in tabular format, type '=t' to go to the table sheet. Type the title of the table on the row title. Enter the rest of the information on the table sheet as shown in Figure V.24a. Figure V.24a is the completed table sheet.

Press '!' to see the table for the variation of pcr, horf, and hvaluep with pressure. The screen is like figure V.24b. Press '!' again to see the mole fraction of each compound in the product stream for different pressures. The screen should be like Figure V.24c. You can get a hard copy of either table by pressing PrtSc. You can also get a hard copy of the tables by changing to Printer mode on the first row of the table sheet.

Figure V.25 shows the solution to the above problem from a publication by MIT (Ref. 19).

Comparing the values indicates that there is a significant difference between the two solutions. For instance, there is an 8 percent difference in the values of pcr for each pressure. And there is as much as 50 percent difference in the mole fraction of nitrogen. The fact that the percent errors do not change with pressure suggests that nonideality of the gases due to the pressure is not responsible for these errors. The results also indicate that nitrogen has the highest error and carbon monoxide

has the lowest error. It is suggested that the reason for this discrepency is the fact that this program calculates heat capacity of the product and the feed stream based on molar average heat capacity, but the publication by MIT is based on weighted average heat capacity of each stream. The solution to the adiabatic reactor is very sensitive to the enthalpy of both product and feed streams. Threrefore, the results of this program for the adiabatic reactor should be treated as estimates, not as absolute values.

17) Type '/q' to quit TK!solver and go back to the DOS system.

St	Input	Name	Output	Unit	Comment
L	'watervap	comp		dimless	list of compounds , dimless
	811.11111	t		k	reactor temperature , k
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L		dgt		cal/gmole	DGf(1 atm) at temp. t ,cal/gmole
L		dht		cal/gmole	DHf(1 atm) at temp. t ,cal/gmole
L		dst		cal/gmole	DSf(1 atm) at temp. t ,cal/gmole/k
	'dgt_on	option		dimless	control variable , dimless
		p		atm	reactor pressure , atm
		horf		dimless	ratio H/O in feed , dimless
		n2o2r		dimless	ratio N2/O2 in feed , dimless
		h2h2orp		dimless	ratio H2/H2O in product , dimless
		yh2		dimless	product mole fraction of H2 , dimless

Figure V.16a
Variable sheet.

========== LIST: dgt ==========

Comment:	dgt for h2o, co, co2, ch4
Display Unit:	cal/gmole
Storage Unit:	cal/gmole

Element	Value
1	-48492.12482
2	-43910.88076
3	-94565.28962
4	-204.182937

Figure V.16b
Subsheet of list dgt.

```
==================== LIST: p ================================================
Comment:
Display Unit:              atm
Storage Unit:              atm
Element Value
------- -----
1       1
2       10
3       100
```

Figure V.17
Subsheet of list p.

```
==================== LIST: horf =============================================
Comment:
Display Unit:              dimless
Storage Unit:              dimless
Element Value
------- -----
1       1
2       1.7
3       1.8
```

Figure V.18
Subsheet of list horf.

```
==================== LIST: h2h2orp ============================================
Comment:
Display Unit:              dimless
Storage Unit:              dimless
Element Value
------- -----
1       1
2       .2
3       .1
```

Figure V.19
Subsheet of list h2h2orp.

```
==================== LIST: yh2 ================================================
Comment:
Display Unit:              dimless
Storage Unit:              dimless
Element Value
------- -----
1       .2
2       .1
3       .05
```

Figure V.20
Subsheet of list yh2.

```
==================== LIST: hsteamf ============================================
Comment:
Display Unit:              btu/lb
Storage Unit:              btu/lb
Element Value
------- -----
1       0
2       43.8
3       18.7
```

Figure V.21
Subsheet of list hsteamf.

St	Input	Name	Output	Unit	Comment
L	'watervap	comp		dimless	list of compounds , dimless
	811.11111	t		k	reactor temperature , k
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L	'input	dgt		cal/gmole	DGf(1 atm) at temp. t ,cal/gmole
L	'input	dht		cal/gmole	DHf(1 atm) at temp. t ,cal/gmole
L	'input	dst		cal/gmole	DSf(1 atm) at temp. t ,cal/gmole/k
	'adiabati	option		dimless	control variable , dimless
L	1	p		atm	reactor pressure , atm
LG	1	horf		dimless	ratio H/O in feed , dimless
	1.5	n2o2r		dimless	ratio N2/O2 in feed , dimless
LG	1	h2h2orp		dimless	ratio H2/H2O in product , dimless
LG	.2	yh2		dimless	product mole fraction of H2 , dimless
L		yh2o		dimless	product mole fraction of H2O , dimless
L		ych4		dimless	product mole fraction of CH4 , dimless
L		yco		dimless	product mole fraction of CO , dimless
L		yco2		dimless	product mole fraction of CO2 , dimless
L		yn2		dimless	product mole fraction of N2 , dimless
L		pcr		dimless	ratio moles product/mole C , dimless
	0	dhmolc		btu/lbmol	DH feed-->product , btu/lbmole c
L		hvaluep		btu/scf	product heating value , btu/scf
L	0	hsteamf		btu/lb	DH steam (212F,sat vap)-->(p,sat vap)

Figure V.22
Variable sheet.

```
==================== LIST: yh2 ================================================
Comment:
Display Unit:                dimless
Storage Unit:                dimless
Element Value
------- -----
1       .2263083068
2       .1076081955
3       .03944030045
```

Figure V.23
Subsheet of list yh2.

```
==================== TABLE SHEET ==============================================
Screen or Printer:           Screen
Title:                       adiabatic reactor, t=1000f, n2/o2=1.5
Vertical or Horizontal:      Vertical
List      Width First Header
----      ----- ----- ------
p         4     1     p(atm)
pcr       25    1     mol prod./mol c
horf      20    1     h/o
hvaluep   20    1     btu/scf
p         10    1     p(atm)
yh2       7     1     yh2
yh2o      7     1     yh2o
ych4      7     1     ych4
yco       7     1     yco
yco2      7     1     yco2
yn2       7     1     yn2
```

Figure V.24a
Table sheet of CHON.TK.

adiabatic reactor, t=1000f, n2/o2=1.5

p(at	mol prod./mol c	h/o	btu/scf
1	2.89497099	1.535246983	181.1158417
10	2.586227655	1.712503337	258.9653241
100	2.362099952	1.788373186	323.5870882

Figure V.24b
Heating value as a function of pressure.

adiabatic reactor, t=1000f, n2/o2=1.5

p(atm)	yh2	yh2o	ych4	yco	yco2	yn2
1	.226308	.229026	.058133	.058978	.228316	.199239
10	.107608	.350310	.131435	.018972	.236257	.155418
100	.039440	.409848	.176564	.006056	.240733	.127359

Figure V.24c
Product composition as a function of pressure.

comparison of the results with the reference

type	p	yh2	yh2o	ych4	yco	yco2	yn2	pcr	hvaluep
chon_tk	1	.2263	.229	.0581	.059	.2283	.1992	2.895	181
Reference	1	.2415	.2557	.0686	.059	.2459	.129	2.676	206
chon_tk	10	.1076	.3503	.1314	.019	.2363	.1554	2.586	259
Reference	10	.1116	.3794	.1467	.0189	.2531	.0899	2.387	285
chon_tk	100	.0394	.4098	.1765	.0061	.2407	.1273	2.3621	323
Reference	100	.0409	.441	.197	.006	.2546	.0602	2.184	358

Figure V.25
Comparison of results with the reference.

VI. Data File CRITICAL.TK: Critical Data

1. Theory

Data file CRITICAL.TK contains critical data for more than 50 compounds. The data includes critical temperature(tc), critical pressure(pc), critical volume(vc), critical compressibility factor(zc), acentric factor(omega), and molecular weight(mweight) of the compound. For the name of the compounds in CRITICAL.TK data file and their corresponding critical properties see CRITICAL.TK documentation in Appendix 4 (pages 281-282).
The following equations are used to relate a compound to its corresponding critical properties:

tc = mapc1 (comp)	+0/flag	Eq.(VI.1)
pc = mapc2 (comp)	+0/flag	Eq.(VI.2)
vc = mapc3 (comp)	+0/flag	Eq.(VI.3)
zc = mapc4 (comp)	+0/flag	Eq.(VI.4)
omega = mapc5 (comp)	+0/flag	Eq.(VI.5)
mweight = mapc6 (comp)	+0/flag	Eq.(VI.6)

Variable comp is the name of the compound. Functions mapc1, mapc2, mapc3, mapc4, mapc5, and mapc6 are user

function variables that relate a compound to its tc, pc, vc, zc, omega, and mweight, respectively. The variable flag is a control variable. It can have the values of zero and one. If the value of the variable flag is one, the data file is turned on. If the value of the variable flag is zero, the data file is turned off.

The critical data and the acentric factor for all of the compounds in this data file is duplicated from reference (6). However, the original source of the data for the critical properties and acentric factor of each compound can be found in references (14) and (15), respectively.

2. Instructions

Program CRITICAL.TK contains critical data for more than 50 compounds. The data includes critical temperature, critical pressure, critical volume, critical compressibility factor, acentric factor, and molecular weight. This program can be used to obtain critical data for many organic compounds, and also provides critical data for programs ESTATE.TK and RESIDUAL.TK. In the following instructions, if a phrase is typed in double emphasized format and it is in quotation marks, it indicates that the phrase should be typed.

In order to use the program CRITICAL.TK, you need the following additional programs:

1) A DOS diskette. The DOS diskette can either be version 2.0 or version 2.1 .

2) The TK!Solver diskette.

3) The diskette containing the program CRITICAL.TK.

4) A storage diskette in order to save the solution. The diskette containig the CRITICAL.TK and the storage diskette may be the same diskette.

Load the TK!Solver diskette into the memory of the computer as described in Appendix 1. After loading the TK!Solver diskette, the screen should be like Figure VI.1.

LOADING CRITICAL.TK

To load CRITICAL .TK into the memory, type '/ s 1'.
When the computer asks for the filename, type 'b:critical.tk'.
Computer responds: loading the b:critical.tk. Wait until the load is completed. After the load is completed, the memory indicator on the right corner of the screen shows 162 indicating that 162K bytes of free memory is available. The program CRITICAL.TK takes up 25K bytes of memory.
After loading CRITICAL.TK, the screen is like Figure VI.2a. Figure VI.2a is the variable sheet of the program CRITICAL.TK. Type '=r' to go to the rule sheet. The rule sheet is like Figure VI.2b.
Figure VI.2b is the rule sheet of the CRITICAL.TK. Type '=v' to return to the variable sheet.

EXAMPLE ONE

PROBLEM STATEMENT: Obtain data for compounds nitrogen, oxygen, and air. This data should include critical temperature, critical pressure, critical volume, critical compressibility factor, acentric factor, and molecular weight of each compound.
In order to do this problem, perform the following steps:

1) Type '=l' to go to the list sheet. Dive to the subsheet of the the list compnd by pressing '>'. List compnd has the list of all the compounds for CRITICAL.TK databank. Search for the name of the compounds nitrogen, oxygen, and air. The name of the compound nitrogen is on the row with the element number 41, and the name of the compound oxygen is on the row with the element number 42, as shown in Figure VI.3.

The name of the compound air is not in the compnd subsheet. This means that there is no data for the compound air.

Press '<' to return to the list sheet.

In order to learn how to expand this program and include more data in the CRITICAL.TK databank, let's enter the critical data for air in the databank. The critical data for air is shown below :

```
tc(air) = -140.7 C
pc(air) = 37.2 Atm.
vc(air) = 82.86 cm^3/gmole
zc(air) = .284
omega(air) = .03
m.w.(air) = 29 g/gmole
```

EXPANDING CRITICAL.TK

2) Type '=f' to go to the function sheet of the CRITICAL.TK program. Dive to the list sheet of the function mapc1 by pressing '>' while the cursor is on

the row of mapc1. Function mapc1 relates a compound to its respective critical temperature. Go to the end of the list by using the search command(':' command). The end of the list for function mapc1 is like Figure VI.4a.

Type ''air' in the column with the heading 'Domain' and the row which is next to the name 'water'. Note that the element number '60' appears in the element column. Then, type the critical temperature of the air in the column with the heading 'Range' and the row with the element number '60. Since the critical temperature of the air is -140.7 C, type '(273.15-140.7)'. Note that the temperature should be in Kelvin, not in degrees Centigrade. After the completion of the above commands, the screen is like Figure VI.4b.

Press '<' to return to the function sheet.

3) Now, let's enter the critical pressure of the air. Dive to the list sheet of the function mapc2 by typing '>' while the cursor is on the row of function mapc2. Function mapc2 relates a compound to its respective critical pressure. Go to the end of the list by using the search command. The end of the list is like Figure VI.5a.

As you can see, the name of the compound 'air' is already on the row with the element number '60'. All you need to do, is to enter the critical pressure of the air on the column 'Range' and the row '60'. Since the critical pressure of air is 37.2 atm., type '37.2'. Note that

the pressure should be in atmosphere. The screen should be like Figure VI.5b.

Press '<' to return to the function sheet.

In a similar manner, critical volume of Air(82.86 cm^3/gmole) can be added to user function mapc3, critical compressibility factor(0.284) to mapc4, acentric factor(0.03) to mapc5, molecular weight(29) to mapc6.

After, you have entered all the data for compound air on user functions mapc1, mapc2, mapc3, mapc4, mapc5, mapc6, type '=v' to return to the variable sheet.

Now, let's obtain data for compounds nitrogen, oxygen, and air.

4) Make sure there is an '1' in the status column of the variable comp. also, type any character in the input column of this variable to indicate that this is an input variable. Dive to the variable comp subsheet by pressing '>' twice while the cursor is on the row of the variable comp. Enter the name of each compound in the comp subsheet; after entering the name of all the compounds, the variable comp subsheet is like Figure VI.6.

Press '<' twice to return to the variable sheet.

5) In the input column of the variable flag type '1', to indicate that you want to get data from the databank.

10) Make sure there is an '1' in the status column of the variables tc, pc, vc, zc, omega, and mweight to indicate that there is a list associated with each of the above

variables.

11) If the variable sheet is like Figure VI.7 after the completion of the above steps, you are ready to execute the program. Type '/l!' and wait until computer stops execution. After execution is completed, dive to the variable tc subsheet. The tc subsheet is like Figure VI.8. Figure VI.8 shows the critical temperature of each compound. According to the tc subsheet, critical temperature of nitrogen is 126.2 K, for oxygen is 154.6 K, and for air is 132.45 K. Press '<' to return to the variable sheet.

You can dive to the subsheet of the variables pc, vc, zc, omega, and mweight to see the critical pressure, critical volume, critical compressibility factor, acentric factor, and molecular weight of each compound, respectively.

12) To get a copy of the data in tabular format, type '=t' to go to the table sheet. The table sheet is already completed and it is like Figure VI.9a. Press '!' to see the table for the critical data of compounds nitrogen, oxygen, and air. The table is like Figure VI.9b.

To get a hard copy of the table, you can press PrtSc, or you can change to printer mode on the first row of the table sheet.

Type '/q' to quit TK!Solver program and return to the DOS system.

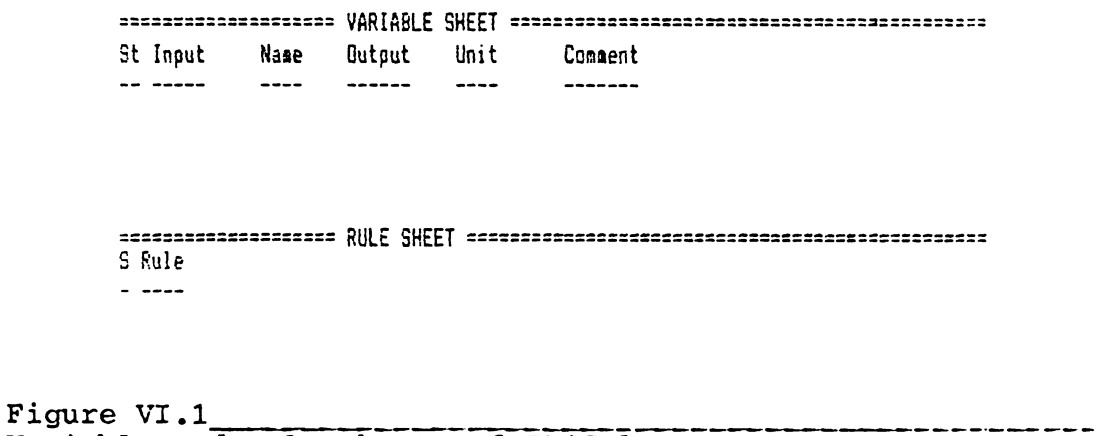


Figure VI.1
Variable and rule sheets of TK!Solver.

```
==================== VARIABLE SHEET ==========================================
St Input     Name     Output     Unit       Comment
-- -----     ----     ------     ----       -------
                                            PROGRAM  CRITICAL.TK  10-3-1984
                                            CRITICAL DATA FOR MORE THAN 50
                                            COMPOUNDS.
                                            1) CRITICAL TEMPERATURE AND PRESSURE;
                                                    Tc  ,  Pc
                                            2) CRITICAL SPECIFIC VOLUME AND
                                               COMPRESSIBILITY FACTOR;  Vc , Zc
                                            3) ACENTRIC FACTOR AND MOLECULAR
                                               WEIGHT;  OMEGA  ,  MWEIGHT

L            comp               dimless    name of the compound
             flag               dimless    type: 1 to get data from databank
                                           type: 0 to turn off databank
L            tc                 k          critical temperature , k
L            pc                 atm        critical pressure , atm
L            vc                 cm^3/gmol  critical molar volume , cm^3/gmole
L            zc                 dimless    critical compressibility factor
L            omega              dimless    acentric factor , dimless
L            mweight            g/gmole    molecular weight , g/gmole
```

Figure VI.2a
Variable sheet of CRITICAL.TK.

```
==================== RULE SHEET ==============================================
S Rule
- ----
                "maps a compound to its critical properties.
1 0/flag    + tc = mapc1(comp)
1 0/flag    + pc = mapc2(comp)
1 0/flag    + vc = mapc3(comp)
1 0/flag    + zc = mapc4(comp)
1 0/flag    + omega = mapc5(comp)
1 0/flag    + mweight = mapc6(comp)
```

Figure VI.2b
Rule sheet of CRITICAL.TK.

Element	Value
39	'krypton
40	'neon
41	'nitrogen
42	'oxygen
43	'xenon
44	'ammonia
45	'carbondioxide
46	'carbondisulfid

Figure VI.3
Subsheet of user function compnd.

```
==================== USER FUNCTION: mapc1 ====================================
Element Domain      Range
------- ------      -----
54      'nitricoxid 180
55      'nitrousoxi 309.6
56      'sulfur     1314
57      'sulfurdiox 430.8
58      'sulfurtrio 491
59      'water      647.1
```

Figure VI.4a
Subsheet of user function mapc1.

```
==================== USER FUNCTION: mapc1 ====================================
Element Domain      Range
------- ------      -----
54      'nitricoxid 180
55      'nitrousoxi 309.6
56      'sulfur     1314
57      'sulfurdiox 430.8
58      'sulfurtrio 491
59      'water      647.1
60      'air        132.43
```

Figure VI.4b
Subsheet of user function mapc1.

```
==================== USER FUNCTION: mapc2 ====================================
Element Domain      Range
------- ------      -----
54      'nitricoxid 64
55      'nitrousoxi 71.5
56      'sulfur     116
57      'sulfurdiox 77.8
58      'sulfurtrio 81
59      'water      217.6
60      'air
```

Figure VI.5a
Subsheet of user function mapc2.

```
==================== USER FUNCTION: mapc2 ====================================
Element Domain      Range
------- ------      -----
54      'nitricoxid 64
55      'nitrousoxi 71.5
56      'sulfur     116
57      'sulfurdiox 77.8
58      'sulfurtrio 81
59      'water      217.6
60      'air        37.2
```

Figure VI.5b
Subsheet of user function mapc2.

```
==================== LIST: comp ================================================
Comment:                  variable sheet list for compound
Display Unit:             dimless
Storage Unit:             dimless
Element Value
------- -----
1       'nitrogen
2       'oxygen
3       'air
```

Figure VI.6
Subsheet of list comp.

```
==================== VARIABLE SHEET ============================================
St Input     Name    Output    Unit       Comment
-- -----     ----    ------    ----       -------
                                          PROGRAM   CRITICAL.TK   10-3-1984
                                          CRITICAL DATA FOR MORE THAN  50
                                          COMPOUNDS.
                                          1) CRITICAL TEMPERATURE AND PRESSURE;
                                                Tc  ,  Pc
                                          2) CRITICAL SPECIFIC VOLUME AND
                                             COMPRESSIBILITY FACTOR;  Vc , Zc
                                          3) ACENTRIC FACTOR AND MOLECULAR
                                             WEIGHT;  OMEGA  ,  MWEIGHT

L  'input    comp              dimless    name of the compound
   1         flag              dimless    type: 1 to get data from databank
                                          type: 0 to turn off databank
L            tc                k         critical temperature , k
L            pc                atm       critical pressure , atm
L            vc                cm^3/gmol critical molar volume , cm^3/gmole
L            zc                dimless   critical compressibility factor
L            omega             dimless   acentric factor , dimless
L            mweight           g/gmole   molecular weight , g/gmole
```

Figure VI.7
Variable sheet of CRITICAL.TK.

```
==================== LIST: tc ==================================================
Comment:                    variable sheet list for critical temperature
Display Unit:               k
Storage Unit:               k
Element Value
------- -----
1       126.2
2       154.6
3       132.43
```

Figure VI.8
Subsheet of list tc.

```
==================== TABLE SHEET ==========================================
Screen or Printer:          Screen
Title:                      critical property data
Vertical or Horizontal:     Vertical
List      Width First Header
----      ----- ----- ------
comp      20    1     compound
mweight   8     1     mweight
tc        8     1     tc,k
pc        8     1     pc,atm
vc        8     1     vc,cm3/gmol
zc        8     1     zc
omega     8     1     omega
```

Figure VI.9a
Table sheet of CRITICAL.TK.

critical property data

compound	mweight	tc,k	pc,atm	vc,cm3/g	zc	omega
nitrogen	28.02	126.2	33.5	89.5	.29	.04
oxygen	32	154.6	49.8	73.4	.288	.021
air	29	132.45	37.2	82.86	.284	.03

Figure VI.9b
Table showing the critical property data.

VII. Data File DATBANK1.TK: Heat Capacity Data

1. Theory

Data file DATBANK1.TK contains heat capacity and heat of formation for more than hundred compounds. The data includes ideal heat capacity data in the form shown below:

$$cp = a + b*t + c*t^2 + d*t^3 \qquad \text{Eq.(VII.1)}$$

The program provides the coefficients a, b, c, and d in the above equation. The applicable temperature range for the heat capacity data(trangek) is also included. The data also includes standard enthalpy of formation at 25 degrees Centigrade(dhf25c), standard entropy at 25 degrees Centigrade(ds25c). Molecular formula(mformula), number of carbon atoms(nec), hydrogen atoms(neh), oxygen atoms(neo), nitrogen atoms(nen), sulfur stoms(nes), and chlorine atoms(necl) in the compound. For the name of the compounds in DATBANK1.TK data file and their corresponding properties see DATBANK1.TK documentation in Appendix 4 (pages 289-294).

The following equations are used to relate a compound to its corresponding properties:

alpha = mapcp1 (comp)	+0/flag	Eq.(VII.2)
beta = mapcp2 (comp)	+0/flag	Eq.(VII.3)
gamma = mapcp3 (comp)	+0/flag	Eq.(VII.4)
theta = mapcp4 (comp)	+0/flag	Eq.(VII.5)
trangek = mapcpr (comp)		Eq.(VII.6)
mformula = mapcpf (comp)		Eq.(VII.7)
dhf25c = maphf25 (comp)	+0/flag	Eq.(VII.8)
ds25c = maps25 (comp)	+0/flag	Eq.(VII.9)
nec = mapnc (comp)	+0/flag	Eq.(VII.10)
neh = mapnh (comp)	+0/flag	Eq.(VII.11)
neo = mapno (comp)	+0/flag	Eq.(VII.12)
nen = mapnn (comp)	+0/flag	Eq.(VII.13)
nes = mapns (comp)	+0/flag	Eq.(VII.14)
necl = mapncl (comp)	+0/flag	Eq.(VII.15)

Variable comp is the name of the compound. Functions mapcp1, mapcp2, mapcp3, and mapcp4 are user function variables for the first, second, third, and fourth coefficients of the heat capacity data, respectively. Functions mapcpr and mapcpf relate a compound to its applicable temperature range of the heat capacity data and the molecular formula of the compound, respectively. Functions maphf25 and maps25 relate a compound to its enthalpy of formation and standard entropy, respectively. Functions mapnc, mapnh, mapno, mapnn, mapns, and mapncl relate a compound to its number of carbon, hydrogen,

oxygen, nitrogen, sulfur, and chlorine atoms, respectively.

The variable flag is a control variable. It can have the values of zero and one. If the value of the variable flag is one, the data file is turned on. If the value of the variable flag is zero, the data file is turned off.

The heat capacity data for all of the compounds is duplicated from reference (13); however, the original source of the data can be found in reference (16). The heat of formation and entropy of formation for all of the compounds is duplicated from reference (5); however, the original source of the data can be found in reference (17).

2. Instructions

Program DATBANK1.TK contains data for more than 110 compounds. The data includes heat capacity data as an ideal gas with its applicable temperature range, enthalpy of formation, standard entropy, and molecular formula of a compound.

The data also includes number of carbon atoms, hydrogen atoms, oxygen atoms, nitrogen atoms, sulfur atoms, and chlorine atoms in a compound. This program can be used to obtain heat capacity data for many organic compounds, and also provides data for programs FRENERGY.TK, and RESIDUAL.TK. In the following instructions, if a phrase is typed in double emphasized format and it is in quotation marks, it indicates that the phrase should be typed by the user.

In order to use the program DATBANK1.TK, you need the following additional programs:

1) A DOS diskette. The DOS diskette can either be version 2.0 or version 2.1.

2) The TK!Solver diskette.

3) The diskette containing the program DATBANK1.TK.

4) A storage diskette in order to save the solution. The diskette containig the DATBANK1.TK and the storage diskette may be the same diskette.

Load the TK!Solver diskette into the memory of the

computer as described in Appendix 1. After loading the TK!Solver diskette, the screen should be like Figure VII.1.

LOADING DATBANK1.TK

To load DATBANK1.TK into the memory, type '/ s 1'.
When the computer asks for the filename, type 'b:datbank1.tk'.
Computer responds: loading the b:datbank1.tk. Wait until the load is completed. After the load is completed, the memory indicator on the right corner of the screen shows 123, indicating that 123K bytes of free memory is available. The program DATBANK1.TK takes up 60K bytes of memory.
After loading DATBANK1.TK, the screen is like Figure VII.2a. Figure VII.2a is the variable sheet of the program DATBANK1.TK. Type '=r' to go to the rule sheet.
The rule sheet is like Figure VII.2b.
Figure VII.2b is the rule sheet of the DATBANK1.TK. Type '=V' to return to the variable sheet.

EXAMPLE ONE

PROBLEM STATEMENT: Obtain data for compounds hydrogen, water, methane, carbon monoxide, carbon dioxide, nitrogen,

oxygen, and solid graphite(e.g. carbon). This data should include heat capacity as an ideal gas, standard enthalpy and entropy at 25C, number of carbon atoms, hydrogen atoms, oxygen atoms, nitrogen atoms, sulfur atoms, and chlorine atoms for each compound. The temperature range of the heat capacity data should be from 273 K to 1800 K.

In order to do this problem, perform the following steps:

1)Type '=1' to go to the list sheet. Dive to the subsheet of the list compound by pressing '>'. List compound has the list of all the compounds for DATBANK1.TK databank. Search for the name of the compounds hydrogen, water, methane, carbon monoxide, carbon dioxide, nitrogen, oxygen, and carbon. the name of the compound methane is on the row with the element number 1, as shown in figure VII.3a. The name of the compounds nitrogen, oxygen, hydrogen, carbon monoxide, carbon dioxide, and water are on the rows with the element numbers 34, 35, 37, 38, 39, and 40, respectively, as shown in Figure VII.3b.

Note that the name of the compounds N2, O2, H2, CO, CO2, and H2O also appear on the rows with the element numbers 42, 43, 45, 46, 47, and 48, respectively, as shown in figure VII.3c. Some of the compound's names appear in the databank twice, because, there is heat capacity data for these compounds for two different temperature ranges. These compounds are:

low temperature range (273k_1800k)	high temperature range (273k_3800k)
nitrogen	nitrogen_high_range
oxygen	oxygen_high_range
air	air_high_range
hydrogen	hydrogen_high_range
carbonmonoxide	carbonmonoxide_high_range
carbondioxide	carbondioxide_high_range
water	water_high_range
nitricoxide	nitricoxide_high_range

For the lower temperature range, the name of the compound is used, and for the higher temperature range, the name of the compound with the suffix '_high_range' is used. you only need to type the name of the compound without the suffix '_high_range', to get heat capacity data for temperature range of 273K_1800K.

The name of the compound carbon is not in the compound subsheet. this means that there are no data for the compound carbon.

Press '<' to return to the list sheet.

In order to learn how to expand this program and include more data in the DATBANK1.TK databank, let's enter the data for carbon in the databank. The data for carbon is shown below :

```
cp =-1.5718 + 1.5332e-2*t - 1.20531e-5*t^2 +
    3.44488e-9*t^3    [cp] = cal/gmole/k  [t] = K
temperature range of cp: 273k_1800k
mformula = c
dsf25c = 1.3609 cal/gmole/k
dhf25c = 0 cal/gmole
nc = 1
nh = 0
no = 0
nn = 0
ns = 0
ncl = 0
```

```
EXPANDING DATBANK1.TK
---------------------
```

2) Type '=f' to go to the function sheet of the DATBANK1.TK program. Dive to the list sheet of the function mapcp1 by pressing '>' while the cursor is on the row of mapcp1. Function mapcp1 relates a compound to its respective first coefficient of the heat capacity equation. Go to the end of the list by using the search command(':' command). The end of the list for function mapcp1 is like Figure VII.4a.

Type ''carbon_graphite' in the column with the heading 'Domain' and the row which is next to the name 'trimethylamine'. Note that the element number '119' appears in the element column. The name 'carbon_graphite' would be in the element number '119' of any function with the domain list 'compound'. Then, type '-1.5718', the value for the first coefficient of the heat capacity of carbon in the column with the heading 'Range' and the row

with the element number '119. Note that the temperature unit of cp data should be in degrees Kelvin. After the completion of the above commands, the screen is like Figure VII.4b.

Press '<' to return to the function sheet.

3) Dive to the list subsheet of the function mapcp2 by typing '>' while the cursor is on the row of function mapcp2, in order to enter the second coefficient of the cp equation for carbon. Function mapcp2 relates a compound to its respective second coefficient of the cp data. Go to the end of the list by using the search command. The end of the list is like figure VII.5a.

As you can see, the name of the compound 'carbon_graphite' is already on the row with the element number '119'. All you need to do, is to enter the second coefficient of the cp equation in the column 'Range' and the row '119'. therefore, type '1.5332e-2'. The screen should be like Figure VII.5b.

Press '<' to return to the function sheet.

In a similar manner, the third coefficient of cp equation(-1.20531e-5) can be added to user function mapcp3, fourth coefficient of cp equation(3.44488e-9) to mapcp4, applicable temperature range of cp data(R273_1800) to mapcpr, molecular formula(c) to mapcpf, standard enthalpy at 25 C(1.3609) to maps25, standard enthalpy of formation at 25 C(0) to maphf25, number of carbon atoms(1)

to mapnc, number of hydrogen atoms(0) to mapnh, number of oxygen atoms(0) to mapno, number of nitrogen atoms(0) to mapnn, number of sulfur atoms(0) to mapns, and number of chlorine(0) atoms to mapncl.

After, You have entered all the data for compound carbon on user functions mapcp1, mapcp2, mapcp3, mapcp4, mapcpr, mapcpf, maps25, maphf25, mapnc, mapnh, mapno, mapnn, mapns, and mapncl, type '=v' to return to the variable sheet.

Now, let's obtain data for compounds hydrogen, water, methane, carbon monoxide, carbon dioxide, nitrogen, oxygen, and carbon.

4) Make sure there is an 1 in the status column of the variable comp. Also, type any character in the input column of this variable to indicate that this is an input variable. Dive to the variable comp subsheet by pressing '>' twice while the cursor is on the row of the variable comp. Enter the name of each compound in the comp subsheet. After entering the name of all the compounds, the variable comp subsheet is like Figure VII.6.

Press '<' twice to return to the variable sheet.

5) In the input column of the variable flag type '1' to indicate that you want to get data from the databank.

6) Make sure there is an 1 in the status column of the variables trangek, mformula, nec, neh, neo, nen, nes, necl, alpha, beta, gamma, theta, dhf25c, and ds25c to

indicate that there is a list associated with each of the above variables.

7) If the variable sheet is like Figure VII.7a after the completion of the above steps, you are ready to execute the program.Type '/1!' and wait until computer stops execution. After execution is completed, dive to the variable dhf25c subsheet. The dhf25c subsheet is like Figure VII.7b.

Figure VII.7b shows the enthalpy of formation at 25c for each compound. According to the dhf25c subsheet, enthalpy of formation at 25c for hydrogen is zero, for water is -57798 cal/gmole, for methane is -17889 cal/gmole, for carbon monoxide is -26416 cal/gmole, for carbon dioxide is -94051 cal/gmole, for nitrogen is zero, for oxygen is zero, and for carbon is zero. Press '<' to return to the variable sheet.

You can also dive to the subsheet of the variables trangek through ds25c to see the data for each compound.

8) To get a copy of the data in tabular format, type '=t' to go to the table sheet. The table sheet is already completed and it is like Figure VII.8a.

Press '!' to see the table for the heat capacity data for all the compounds. the table is like Figure VII.8b.

Press 'Return' key to see the table for the standard enthalpy and entropy at 25c, and the number of different atoms for each compound in tabular format. The table is

like Figure VII.8c.

To get a hard copy of each table, you can press PrtSc, or you can change to printer mode on the first row of the table sheet.

Type '/q' to quit TK!Solver program and return to the DOS system.

```
==================== VARIABLE SHEET ========================================
St Input     Name    Output    Unit      Comment
-- -----     ----    ------    ----      -------


==================== RULE SHEET ============================================
S Rule
- ----
```

Figure VII.1
Variable sheet of TK!Solver.

```
==================== VARIABLE SHEET ========================================
St Input     Name    Output    Unit      Comment
-- -----     ----    ------    ----      -------
                                         PROGRAM   DATBANK1.TK   10-3-1984
                                         DATA FOR MORE THAN 100 COMPOUNDS:
                                         1) IDEAL GAS MOLAL HEAT CAPACITY;
                                           Cp = ALPHA + BETA*T + GAMMA*T^2
                                               + THETA*T^3
                                         2) NUMBER OF ATOMS IN A COMPOUND;
                                                 C , H , O , N , S , Cl
                                         3) ENTHALPY AND ENTROPY OF FORMATION
                                             AT 25 c;  DHf@25c , DSf@25c
L            comp            dimless     name of the compound
             flag            dimless     type: 1  to get data from databank
                                         type: 0  to turn off databank
L            trangek         k           temperature range of Cp data , k
L            mformul         dimless     molecular formula , dimless
L            nec             dimless     number of carbon atoms ,dimless
L            neh             dimless     number of hydrogen atoms , dimless
L            neo             dimless     number of oxygen atoms , dimless
L            nen             dimless     number of nitrogen atoms , dimless
L            nes             dimless     number of sulfur atoms , dimless
```

Figure VII.2a
Variable sheet of DATBANK1.TK.

```
$ Rule
- ----
                    'maps a compound to its heat capacity data.
# 0/flag    + alpha = mapcp1(comp)
# 0/flag    + beta = mapcp2(comp)
# 0/flag    + gamma = mapcp3(comp)
# 0/flag    + theta = mapcp4(comp)
# trangek = mapcpr(comp)
# mformula = mapcpf(comp)
# 0/flag    + dhf25c= maphf25(comp)
# 0/flag    + ds25c = maps25(comp)
# 0/flag    + nec = mapnc(comp)
# 0/flag    + neh = mapnh(comp)
# 0/flag    + neo = mapno(comp)
# 0/flag    + nen = mapnn(comp)
# 0/flag    + nes = mapns(comp)
# 0/flag    + necl = mapncl(comp)
```

Figure VII.2b
Rule sheet of DATBANK1.TK.

LIST: compound Element	Value	LIST: compound Element	Value	LIST: compound Element	Value
1	'methane	34	'nitrogen	42	'nitrogen_high_
2	'ethane	35	'oxygen	43	'oxygen_high_ra
3	'propane	36	'air	44	'air_high_range
4	'n_butane	37	'hydrogen	45	'hydrogen_high_
5	'i_butane	38	'carbonmonoxide	46	'carbonmonoxide
6	'n_pentane	39	'carbondioxide	47	'carbondioxide_
7	'n_hexane	40	'water	48	'water_high_ran

Figure VII.3
Subsheet of the list compound.

```
==================== USER FUNCTION: mapcp1 ====================================
Element Domain      Range
------- ------      -----
114     'ammonia    6.5846
115     'hydrazine  3.89
116     'methylamin 2.9956
117     'dimethylam -.275
118     'trimethyla -2.098
```

Figure VII.4a
Subsheet of user function mapcp1.

```
==================== USER FUNCTION: mapcp1 ====================================
Element Domain      Range
------- ------      -----
114     'ammonia    6.5846
115     'hydrazine  3.89
116     'methylamin 2.9956
117     'dimethylam -.275
118     'trimethyla -2.098
119     'carbon_gra -1.5718
```

Figure VII.4b
subsheet of user function mapcp1.

```
==================== USER FUNCTION: mapcp2 ====================================
Element Domain      Range
------- ------      -----
114     'ammonia    .0061251
115     'hydrazine  .03554
116     'methylamin .036101
117     'dimethylam .066152
118     'trimethyla .096187
119     'carbon_gra
```

Figure VII.5a
Subsheet of user function mapcp2.

```
==================== USER FUNCTION: mapcp2 ====================================
Element Domain      Range
------- ------      -----
114     'ammonia    .0061251
115     'hydrazine  .03554
116     'methylamin .036101
117     'dimethylam .066152
118     'trimethyla .096187
119     'carbon_gra .015332
```

Figure VII.5b
Subsheet of user function mapcp2.

```
==================== LIST: comp ==============================================
Comment:                    variable sheet list for compound
Display Unit:               dimless
Storage Unit:               dimless
Element Value
------- -----
1       'hydrogen
2       'water
3       'methane
4       'carbonmonoxide
5       'carbondioxide
6       'nitrogen
7       'oxygen
8       'carbon_graphit
```

Figure VII.6
Subsheet of list comp.

```
==================== VARIABLE SHEET ==========================================
St Input     Name    Output    Unit       Comment
-- -----     ----    ------    ----       -------
L  'input    comp               dimless   name of the compound
   1         flag               dimless   type: 1  to get data from databank
                                          type: 0  to turn off databank
L            trangek            k         temperature range of Cp data , k
L            @formul            dimless   molecular formula , dimless
L            nec                dimless   number of carbon atoms ,dimless
L            neh                dimless   number of hydrogen atoms , dimless
L            neo                dimless   number of oxygen atoms , dimless
L            nen                dimless   number of nitrogen atoms , dimless
L            nes                dimless   number of sulfur atoms , dimless
L            necl               dimless   number of chlorine atoms , dimless
L            alpha              cal/gmole first term of Cp data, cal/gmole/k
L            beta               cal/gmole second term of Cp data, cal/gmole/k^2
L            gamma              cal/gmole third term of Cp data, cal/gmole/k^3
L            theta              cal/gmole fourth term of Cp data, cal/gmole/k^4
L            dhf25c             cal/gmole enthalpy of formation@25 c, cal/gmole
L            ds25c              cal/gmole standard entropy @25 c, cal/gmole/k
```

Figure VII.7a
Variable sheet of DATBANK1.TK.

```
==================== LIST: dhf25c ============================================
Comment:                  variable sheet list for enthalpy of formation@25c
Display Unit:             cal/gmole
Storage Unit:             cal/gmole
Element Value
------- -----
1       0
2       -57798
3       -17889
4       -26416
5       -94051
6       0
7       0
8       0
```

Figure VII.7b
Subsheet of list dhf25c.

List	Width	First	Header
comp	25	1	compound
mformula	6	1	m. formula
alpha	6	1	alpha
beta	7	1	beta
gamma	7	1	gamma
theta	7	1	theta
trangek	15	1	temp. range
comp	25	1	compound
mformula	6	1	m. formula
nec	3	1	C
neh	3	1	H
neo	3	1	O
nen	3	1	N
nes	3	1	S
necl	3	1	Cl
dhf25c	10	1	dhf25c
ds25c	10	1	ds25c

Figure VII.8a
Table sheet of DATBANK1.TK.

Cp, dHf25c, dSf25c, C, H, O, N, S, Cl data

compound	n. for	alpha	beta	gamma	theta	temp. range
hydrogen	h2	6.952	-.00046	9.56E-7	-2.E-10	r273_1800k
water	h2o	7.7	.000459	2.52E-6	-9.E-10	r273_1800k
methane	ch4	4.75	.012	3.03E-6	-2.6E-9	r273_1500K
carbonmonoxide	co	6.726	.000400	1.28E-6	-5.E-10	r273_1800k
carbondioxide	co2	5.316	.014285	-8.4E-6	1.78E-9	r273_1800k
nitrogen	n2	6.903	-.00038	1.93E-6	-7.E-10	r273_1800k
oxygen	o2	6.085	.003631	-1.7E-6	3.1E-10	r273_1800k
carbon_graphite	c	-1.572	.015332	-1.2E-5	3.44E-9	r273_1800k

Figure VII.8b
Table showing the heat capacity data.

Cp, dHf25c, dSf25c, C, H, O, N, S, Cl data

compound	n. for	C	H	O	N	S	Cl	dhf25c	ds25c
hydrogen	h2	0	2	0	0	0	0	0	31.211
water	h2o	0	2	1	0	0	0	-57798	45.106
methane	ch4	1	4	0	0	0	0	-17889	44.5
carbonmonoxide	co	1	0	1	0	0	0	-26416	47.301
carbondioxide	co2	1	0	2	0	0	0	-94051	51.061
nitrogen	n2	0	0	0	2	0	0	0	45.767
oxygen	o2	0	0	2	0	0	0	0	49.003
carbon_graphite	c	1	0	0	0	0	0	0	1.360[9]

Figure VII.8c
Table showing the heat of formation data.

Appendix 1: Loading The TK!Solver Program

In order to load the TK!Solver program, you need a DOS diskette and the disk containing the TK!Solver program. In the following instructions, it is assumed that your personal computer has a double disk drive. In the following instructions, if a phrase is typed in double emphasized format and it is in quotation marks, this indicates that the phrase should be typed by the user.

In order to load TK!Solver program, perform the following steps:

1) Insert the DOS diskette in drive A and turn on the PC. Make sure the display switch is on.

2) The computer will ask you for the date and time. In response to these questions push the 'Return' key twice. Then the computer will give the A prompt(e.g., A>). After this step, the screen is like Figure A.1.

3) Remove the DOS diskette from drive A and insert the TK!Solver diskette instead. Type 'tk' and press the 'Return' key once. The screen should be like Figure A.2. Figure A.2 shows the license agreement for TK!Solver program. Press the 'Return' key one more time and the screen should be like Figure A.3.

Figure A.3 shows the variable and the rule sheet of the

TK!Solver program. If you have an instruction diskette for TK!Sclver program, remove the TK!Sclver program from drive A and insert the Instruction diskette instead.

Loading a *.TK program into memory: Load the TK!Solver diskette as outlined above. The TK!Sclver diskette should be in drive A, and the diskette containing the *.TK (e.g. CRITICAL.TK, ESTATE.TK, etc.) should be in drive B. Type '/sl'.

When the computer asks for the filename, type 'b:xxxx.tk' and push the 'Return' key. The computer responds: Loading the b:xxxx.tk. Wait until the program is loaded into memory.

Saving a *.TK program: After you solve a model using TK!Solver program, you need to save the model. In order to save a model, type '/ss'. When the computer asks for the filename, type 'b:yyyy.tk', assuming that the storage diskette is in drive B.

The computer responds: Saving the b:yyyy.tk. Wait until the model is saved.

Dive command of TK!Solver: The Dive command is used to get to the subsheet of a variable. For a complete explanation of this command see reference (1).

```
Current date is Tue  1-01-1980
Enter new date:
Current time is  0:00:08.45
Enter new time:


The IBM Personal Computer DOS
Version 2.10 (C)Copyright IBM Corp 1981, 1982, 1983

A>
```

Figure A.1
Screen showing the A> command.

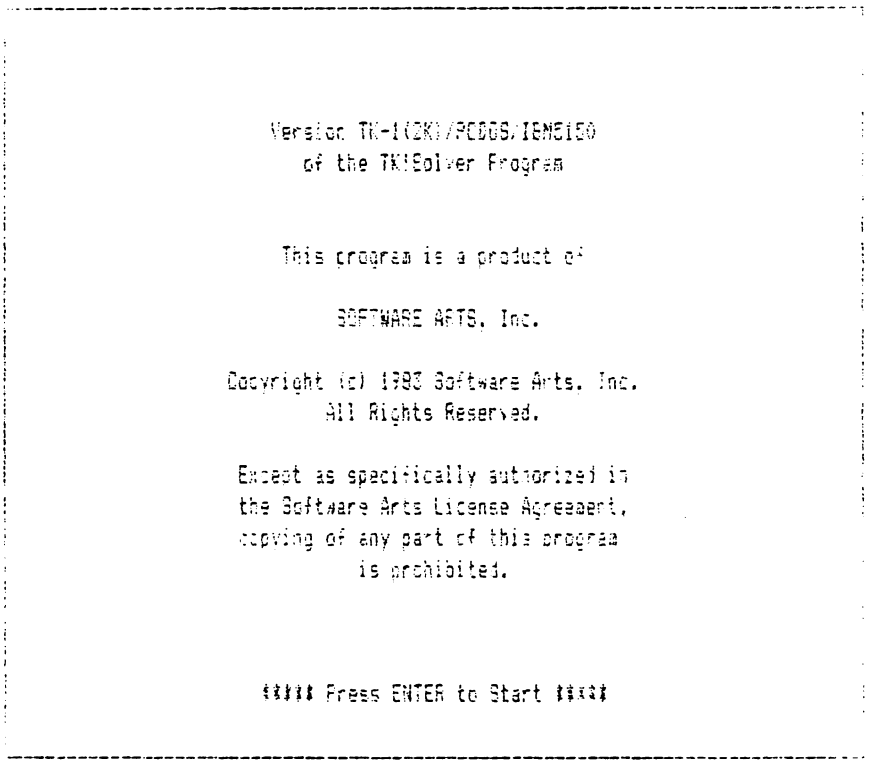


Figure A.2
Screen showing the license agreement of TK!Solver.

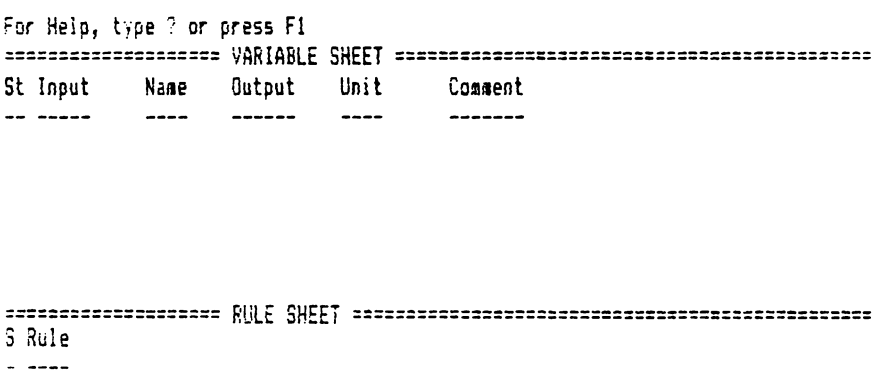


Figure A.3
Variable and rule sheets of TK!Solver.

Appendix 2: Description Of Variables

Variable	Description
	A
aber	: Constant for Berthelot equation of state.
adie	: Constant for Dietericie equation of state.
alist	: A user function variable to turn on rule sheet for free energy calculation of a compound.
alpha	: First coefficient of the heat capacity data,cal/gmole/t.
alphat	: First term for the heat capacity of the product stream,cal/gmole/t.
ared	: Constant for Redlich Kwong equation of state.
arxn	: A user function variable to turn on rule sheet for free energy calculation of a reaction.
avan	: Constsnt for van der Waals equation of state.
	B
b, b0, b1	: Constants for Pitzer correlation(b =b0 +omega*b1).
bb	: Constant for Pitzer correlation.
bber	: Constant for Berthelot equation of state.
bdie	: Constant for Dietericie equation of state.
berth	: User function variable to turn on Berthelot equation.
beta	: Second coefficient of the heat capacity data,cal/gmole/t^2.
betat	: Second term for the heat capacity of the product stream,cal/gmole/t^2.
bred	: Constant for Redlich Kwong equation of state.
bvan	: Constant for van der Waals equation.
	C
comp	: Name of the compound.
cpavgf	: Molar average heat capacity for the feed stream,cal/gmole/t.

Variable	Description
	D
dalpha	: First term for the molar average heat capacity for the formation of a compound,cal/gmole/t.
db,db0,db1	: Dervative of Pitzer correlation constants with respect to temperature(db=db0+db1).
dbeta	: Second term for the molar average heat capacity for the formation of a compound,cal/gmole/t^2.
dgamma	: Third term for the molar average heat capacity for the formation of a compound,cal/gmole/t^3.
dgrxn	: Standard free enrgy for a reaction at temperature t,cal/gmole.
dgt	: Standard free energy of formation for a compound at temperature t,cal/gmole.
dhf25c	: Standard enthalpy of formation at 25 C,cal/gmole.
dhmolc	: Enthalpy change for the reactor per mole carbon fed,btu/mole C.
dhrxn	: Standard enthalpy for a reaction at temperature t,cal/gmole.
dht	: Standard enthalpy of formation for a compound at temperature t,cal/gmole.
dieter	: User function variable to turn on Dieterici equation.
ds25c	: Standard entropy for a compound at 25 C,cal/gmole/t.
dsf25c	: Standard entropy of formation at 25 C,cal/gmole/t.
dsrxn	: Standard entropy for a reaction at temperature t,cal/gmole/t.
dst	: Standard entropy of formation for a compound at temperature t,cal/gmole/t.
dtheta	: Fourth term for the molar average heat capacity for the formation of a compound,cal/gmole/t^4.
	F
flag	: A control variable to turn on the data file.
	G
gamma	: Third coefficient for the heat capacity equation,cal/gmole/t^3.
gammat	: Third term for the molar average heat capacity for the product stream,cal/gmole/t^3.
	H
h2f	: Moles of hydrogen fed per mole of carbon, lbmol/lbmol C.
h2h2orp	: Molar ratio of hydrogen to water in the product stream.
h2of	: Moles of water fed per mole of carbon,lbmol/lbmol C.
horf	: Molar ratio of atomic hydrogen to atomic oxygen in the feed.

Variable	Description
hptfrx	: Enthalpy change due to formation of products at reactor temperature,btu/mol C.
hptt	: Enthalpy change from reactants to products due to temperature,btu/mol C.
hres	: Residual enthalpy,cal/gmole.
hsteamf	: Enthalpy change of steam from 212 F to reactor pressure as saturated vapor,btu/lb.
h2t	: Total moles of hydrogen fed per mole carbon, lbmol/lbmol C.
hvaluep	: Heating value of the product stream,btu/scf.
	I
ideal	: User function variable to turn on ideal gas equation.
	K
k1, k2, k3	: Equilibrium constants for each reaction.
keq	: Equilibrium constant for a reaction.
	M
mapc1,2,3, 4,5,6	: User function variables to relate a compound to its critical properties.
mapcp1,2, 3,4	: User function variables to relate a compound to its corfficients of the heat capacity equation.
mapcpf	: User function variable to relate a compound to its molecular formula.
mapcpr	: User function variable to relate a compound to its applicable temperature range of Cp data.
mapnc	: User function variable to relate a compound to its number of carbon atoms.
mapncl	: User function variable to relate a compound to its number of chlorine atoms.
mapnh	: User function variable to relate a compound to its number of hydrogen atoms.
mapnn	: User function variable to relate a compound to its number of nitrogen atoms.
mapno	: User function variable to relate a compound to its number of oxygen atoms.
mapns	: User function variable to relate a compound to its number of sulfur atoms.
maphf25c	: User function variable to relate a compound to its standard entropy of formation at 25 C.
maps25c	: User function variable to relate a compound to its standard entropy at 25 C.
mcadia	: User function variable to turn on rule sheet for the adiabatic reactor case.

Variable	Description
mcchon	: User function variable to turn on rule sheet for the non-adiabatic case.
mcdgt	: User function variable to turn on rule sheet for free energy calculations at temperature t.
mcdh	: User function variable to turn on rule sheet for the calculation of heat requirements of reactor.
mceq	: User function variable to turn on rule sheet for equilibrium constant calculations.
mck	: User function variable to turn on rule sheet for equilibrium composition calculations.
mformula	: Molecular formula for the compound.
mweight	: Molecular weight for a compound,g/gmole.
	N
nec	: Number of carbon atoms in a compound.
necl	: Number of chlorine atoms in a compound.
neh	: Number of hydrogen atoms in a compound.
nen	: Number of nitrogen atoms in a compound.
neo	: Number of oxygen atoms in a compound.
nes	: Number of sulfur atoms in a compound.
n2f	: Moles of nitrogen fed per mole of carbon lbmol/lbmol C.
n2o2r	: Molar ratio of nitrogen to oxygen.
	O
o2f	: Moles of oxygen fed per mole of carbon,lbmol/lbmol C.
omega	: Acentric factor for a compound.
option	: A control variable to turn on different parts of rule sheet.
o2t	: Total moles of atomic oxygen fed per mole of carbon, lnmol/lbmol C.
	P
p	: Pressure,atm.
pc	: Critical pressure,atm.
pcr	: Moles of product per mole carbon fed.
pf	: Final pressure,atm.
pi	: Initial pressure,atm.
pitzer	: User function variable to turn on Pitzer correlation.
pr	: Reduced pressure.
	R
r	: Gas constant.
reducedr	: User function variable to turn on rule sheet for the reduced properties of a compound.

Variable	Description
	T
redwg	: User function variable to turn on Redlich Kwong equation.
	S
sres	: Residual entropy,cal/gmole/t.
stater	: User function variable to turn on rule sheet for state property calculations.
t	: Temperature,K.
tc	: Critical temperature,K.
tf	: Final temperature,K.
theta	: Fourth coefficient for the heat capacity equation,cal/gmole/t^4.
thetat	: Molar average heat capacity for the product stream,cal/gmole/t^4.
ti	: Initial temperature,K.
tr	: Reduced temperature,K.
trangek	: Applicable temperature range for Cp data,K.
type	: Type of equation of state.
	U
ures	: Residual internal energy,cal/gmole.
	V
vander	: User function variable to turn on van der Waals equation.
vc	: Critical volume,cm 3/gmole.
vmass	: Specific volume on mass basis,cm^3/g.
vmole	: Molar specific volume,cm^3/gmole.
vres	: Residual volume,cm^3/gmole.
	Y
ych4	: Mole fraction of Methane in product stream.
yco	: Mole fraction of carbon monoxide in product stream.
yco2	: Mole fraction of carbon dioxide in product stream.
yh2	: mole fraction of hydrogen in product stream.
yh2o	: Mole fraction of water in product stream.
yn2	: Mole fraction of nitrogen in product stream.
	Z
z	: Compressibility factor.
zc	: Critical compressibility factor.

Appendix 3: References

1) " TK!Solver Package, " Software Arts,Inc., 1983, Page III.16.

2) Milos Konopasek and Sundaresan Jayaraman, " THE TK!SolverBOOK: A Guide to Problem-Solving in Science, Engineering, Business, and Education ," Osborn/McGraw-Hill, 1984, Chap. 3.

3) Ibid., Page 275.

4) Smith J. M. and Van Ness H. C., " Introduction to Chemical Engineering Thermodynamics ," McGraw-Hill Book Company, Third Ed., 1975, Pages 172-184.

5) Ibid., pages 120-121.

6) Ibid., pages 569-570.

7) Ibid., page 524.

8) ibid., page 190.

9) Ibid., pages 80-94.

10) Kenneth Wark, " Thermodynamics ," McGraw-Hill Book Company, Third Ed., 1977, Page 534.

11) Prausnitz J. M., " Molecular Thermodynamics of Fluid-Phase Equilibria ," Prentice-Hall, Inc., 1969, Pages 39-42.

12) Ibid., page 127.

13) Hougen O. A., Watson K. M., and Ragatz R. A., " Chemical Process principles ," Volume II, Jhon Wileyand Sons, Inc., New York, Second Ed., Pages XXVI-XXIX of Appendix.

14) J. F. Mathews, " Chemical Reviews ," 72:71(1972).

15) C. A. Passat and R. P. Danner, " Industrial Engineering Chemistry Process Design and Development ," 12:365(1974).

16) K. A. Kobe and associates; " Thermochemistry for the Petrochemical Industry ," Petroleum Refiner, Jan. 1949 through Nov. 1954.

17) " Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Texas A&M University, College Station, Texas.

18) Baron R. E., Porter J. H., and Hammond O. H., " Chemical Equilibria In Carbon-Hydrogen-Oxygen Systems ," The MIT Press, Cambridge,Massachusets, 1976, pages ix-xii.

19) Ibid., pages 16, 70, 88.

20) The heat capacity data for carbon which is used on the rule sheet of FRENERGY.TK is not the same as the data which is used on page 229 of DATBANK1.TK instructions. The heat capacity data for carbon on the rule sheet of FRENERGY.TK is in the form of cp = a + b*t + c*t'-2, and the heat capacity data on page 229 of DATBANK1.TK instructions is in the form of cp= a + b*t + c*t^2 + d*t^3. However, both heat capacity equations give the same results for compound carbon.

Appendix 4: Documentation

Program ESTATE.TK

(1c) Comment: PROGRAM ESTATE.TK 10-3-1984 133/!

========== VARIABLE SHEET ==========

St	Input	Name	Output	Unit	Comment
					PROGRAM ESTATE.TK 10-3-1984 CALCULATES VOLUMETRIC PROPERTIES OF COMPOUNDS BY SIX EQUATIONS OF STATE: 1) IDEAL GAS LAW 2) PITZER CORRELATION 3) VAN DER WAALS 4) REDLICH KWONG 5) DIETERICI 6) BERTHELOT
L		type		dimless	name of equation of state , dimless
		t		k	temperature , k
		p		atm	pressure , atm
L		vmole		cm^3/gmol	molar specific volume , cm^3/gmole
L		vmass		cm^3/g	mass specific volume , cm^3/g
	82.05	r		atm*cm^3/	gas constant , cm^3*atm/gmole/k
L		z		dimless	compressibility factor , dimless

```
==================== RULE SHEET ================================================
S Rule
- ----

* tr = t/tc
* pr = p/pc
                        "Ideal gas law
* p*vmole = r*t
                        "Pitzer correlation
* p*vmole/r/t = 1 + bb*pr/tr
* bb = .083 - .422/tr^1.6 + omega*(.139 - .172/tr^4.2)
                        "van der Waals
* (p + 27*r^2*tc^2/64/pc/vmole^2 ) * (vmole - r*tc/8/pc ) = r*t
                        "Redlich Kwong
* p = r*t/(vmole - bred) - .4278*r^2*tc^2.5/pc/t^.5/vmole/(vmole + bred)
* bred = .0867*r*tc/pc
                        "Dieterici
* p = r*t*exp(-4*r^2*tc^2/r/t/vmole/pc/exp(2)) / (vmole - r*tc/pc/exp(2))
                        "Berthelot
* p = r*t/(vmole - r*tc/8/pc) - 27*r^2*tc^3/64/pc/t/vmole^2
* vmass = vmole/mweight
* z     = vmole*p/t/r
```

```
(1f) From:                                                          133/!

==================== UNIT SHEET ================================================
From      To        Multiply By  Add Offset
----      --        -----------  ----------
```

```
( )                                                                 133/!

==================== GLOBAL SHEET ===============================================
Variable Insert ON:          No

Intermediate Redisplay ON:   Yes
Automatic Iteration ON:      No
Comparison Tolerance:        .0001
Typical Value:               1
Maximum Iteration Count:     10

Page Breaks ON:              No
Page Numbers ON:             Yes
Form Length:                 66
Printed Page Length:         60
Printed Page Width:          80
Left Margin:                 0
Printer Device or Filename:  PRN
Printer Setup String:
Line End:                    CR&LF

Color Display ON:            No
```

(1n) Name: typee 128/!

========== LIST SHEET ==========

Name	Elements	Unit	Comment
typee	6	dimless	domain list for functions IDEAL through BERTH
aaaa	6	dimless	range list for function IDEAL
bbbb	6	dimless	range list for function PITZER
cccc	6	dimless	range list for function VANDER
dddd	6	dimless	range list for function REDWG
eeee	6	dimless	range list for function DIETER
ffff	6	dimless	range list for function BERTH
type		dimless	list for type of equation of state
vmole		cm^3/gmol	list for variable VMOLE
vmass		cm^3/g	list for variable VMASS
z		dimless	list for variable Z

Subsheet of variables on the list sheet

typee	aaaa	bbbb	cccc	dddd	eeee	ffff
ideal_gas	1	0	0	0	0	0
pitzer_correlation	0	1	0	0	0	0
van_der_waals	0	0	1	0	0	0
redlich_kwong	0	0	0	1	0	0
dieterici	0	0	0	0	1	0
berthelot	0	0	0	0	0	1

(1n) Name: ideal 128/!

========== USER FUNCTION SHEET ==========

Name	Domain	Mapping	Range	Comment
ideal	typee	Table	aaaa	maps TYPEE into AAAA
pitzer	typee	Table	bbbb	maps TYPEE into BBBB
vander	typee	Table	cccc	maps TYPEE into CCCC
redwg	typee	Table	dddd	maps TYPEE into DDDD
dieter	typee	Table	eeee	maps TYPEE into EEEE
berth	typee	Table	ffff	maps TYPEE into FFFF

```
(t) Title:                                                          133/1

==================== PLOT SHEET ================================================
Screen or Printer:          Screen
Title:
Display Scale ON:           Yes
X-Axis:
Y-Axis    Character
------    ---------
```

```
(t) Title:                                                          133/1

==================== TABLE SHEET ===============================================
Screen or Printer:          Screen
Title:
Vertical or Horizontal:     Vertical
List      Width First Header
----      ----- ----- ------
```

Program RESIDUAL.TK

(11s) Status: L 113/!

VARIABLE SHEET

St	Input	Name	Output	Unit	Comment
					PROGRAM RESIDUAL.TK 10-3-1984 CALCULATES THE RESIDUAL VOLUME (VRES), RESIDUAL INTERNAL ENERGY (URES), RESIDUAL ENTHALPY (HRES), AND RESIDUAL ENTROPY AS A FUNCTION OF T&P BY THE FOLLOWING EQUATIONS OF STATE. 1) PITZER CORRELETION 2) VAN DER WAALS 3) REDLICH KWONG
L	'input	type		dimless	name of the equation of state
L		t		k	temperature , k
L		p		atm	pressure , atm
	82.05	r		atm*cm^3/	gas constant , cm^3*atm/gmole/k
L		z		dimless	compressibility factor , dimless
L		vres		cm^3/gmol	residual specific volume , cm^3/gmole
L		ures		cal/gmole	residual internal energy , cal/gmole
L		hres		cal/gmole	residual enthalpy , cal/gmole
L		sres		cal/gmole	residual entropy , cal/gmole/k

```
RULE SHEET
S Rule
- ----
                        "reduced T @ P
* tr = t/tc
* pr = p/pc
    "compressibility factor, residual volume, and residual internal energy
* z  = vmole*p/t/r
* vres = r*t/p - vmole
* ures = hres - p*(r*t/p - vmole)*1.987/82.05

                        "Pitzer correlation
* b0 = .1445 - .33/tr - .1385/tr^2 - .0121/tr^3
* b1 = .073 + .46/tr - .5/tr^2 - .097/tr^3 - .0073/tr^8
* b*pc/r/tc = b0 + omega*b1
* db0= .33/tr^2 + 2*.1385/tr^3 + 3*.0121/tr^4
* db1=-.46/tr^2 + 2*.5000/tr^3 + 3*.0970/tr^4 + 8*.0073/tr^9
* db*pc/r/tc = db0 + omega*db1
* p*vmole/r/t = 1 + b*p/r/t
* hres = tr*p*(db - b/tr)*1.987/82.05
* sres = (p*db/tc)*1.987/82.05

                        "van der Waals
* avan = 27*r^2*tc^2/64/pc
* bvan = r*tc/8/pc
* (p + avan/vmole^2 ) * (vmole - bvan ) = r*t
* hres = 1.987*t*(1 - vmole/(vmole-bvan) + 2*avan/r/t/vmole)
* sres = 1.987*ln(r*t/p/(vmole - bvan))

                        "Redlich Kwong
* ared = .4441*r^2*tc^2.5/pc
* bred = .0903*r*tc/pc
* cred = ln( (vmole+bred) /vmole)
* p = r*t/(vmole - bred) - ared/t^.5/vmole/(vmole + bred)
* hres = (r*t-p*vmole + 3*ared*cred/2/bred/t^.5)*1.987/82.05
* sres = 1.987*(ln(r*t/p/(vmole-bred)) + ared*cred/2/bred/t^1.5/82.05)

            "ideal gas change in properties from state i to state f
* tf = element('t,2,0)
* ti = element('t,1,0)
* pf = element('p,2,1)
* pi = element('p,1,1)
* ut = ht - 1.987*(tf-ti)
* ht =alpha*(tf-ti)+beta*(tf^2-ti^2)/2+gamma*(tf^3-ti^3)/3+theta*(tf^4-ti^4)/4
* sp = -1.987*ln( element('p,2,1) / element('p,1,1) )
* st=alpha*ln(tf/ti)+beta*(tf-ti)+gamma*(tf^2-ti^2)/2 +theta*(tf^3-ti^3)/3 +sp

                "total change in properties from state i to state f
* vres = element('vres,1,0) - element('vres,2,0) + r*tf/pf - r*ti/pi
* ures = element('ures,1,0) - element('ures,2,0) + ut
* hres = element('hres,1,0) - element('hres,2,0) + ht
* sres = element('sres,1,0) - element('sres,2,0) + st
```

```
(1f) From:                                                          113/!

==================== UNIT SHEET ================================================
From       To         Multiply By  Add Offset
----       --         -----------  ----------
```

```
( )                                                                 113/!

==================== GLOBAL SHEET ===============================================
Variable Insert ON:          No

Intermediate Redisplay ON:   Yes
Automatic Iteration ON:      No
Comparison Tolerance:        .005
Typical Value:               1
Maximum Iteration Count:     10

Page Breaks ON:              No
Page Numbers ON:             No
Form Length:                 66
Printed Page Length:         60
Printed Page Width:          80
Left Margin:                 0
Printer Device or Filename:  PRN
Printer Setup String:
Line End:                    CR&LF

Color Display ON:            No
```

(1n) Name: typer 113/!

========== LIST SHEET ==========

Name	Elements	Unit	Comment
typer	6	dimless	domain list of functions PITZER through REDUCEDR
aaaa	6	dimless	range list of function PITZER
bbbb	6	dimless	range list of function VANDER
cccc	6	dimless	range list of function REDWG
dddd	6	dimless	range list of function STATER
eeee	6	dimless	range list of function REDUCEDR
type		dimless	list for type of equation of state
z		dimless	list for compressibility factor
t		k	list for temperature of initial and final states
p		atm	list for pressure of initial and final states
vres		cm^3/gmol	list for residual volume for I @ F states
ures		cal/gmole	list for residual internal energy for I @F states
hres		cal/gmole	list for residual enthalpy for I @ F states
sres		cal/gmole	list for residual entropy for I @ F states

Subsheet of variables on the list sheet

typer	aaaa	bbbb	cccc	dddd	eeee
pitzer_correlation	1	0	0	0	1
van_der_waals	0	1	0	0	1
redlich_kwong	0	0	1	0	1
path_on	0	0	0	1	0
states_off	0	0	0	1	0
rules_off	0	0	0	0	0

(1n) Name: pitzer 113/!

========== USER FUNCTION SHEET ==========

Name	Domain	Mapping	Range	Comment
pitzer	typer	Table	aaaa	maps TYPER to AAAA; f(TYPER)=AAAA
vander	typer	Table	bbbb	maps TYPER to BBBB; f(TYPER)=BBBB
redwg	typer	Table	cccc	maps TYPER to CCCC; f(TYPER)=CCCC
stater	typer	Table	dddd	maps TYPER to DDDD; f(TYPER)=DDDD
reducedr	typer	Table	eeee	maps TYPER to EEEE; f(TYPER)=EEEE

(t) Title: 113/!

```
==================== PLOT SHEET ================================================
Screen or Printer:          Screen
Title:
Display Scale ON:           Yes
X-Axis:
Y-Axis    Character
------    ---------
```

(s) Screen or Printer: Screen 113/!

```
==================== TABLE SHEET ===============================================
Screen or Printer:          Screen
Title:                      residual properties
Vertical or Horizontal:     Vertical
List      Width First Header
----      ----- ----- ------
type      20    1     type
vres      10    1     v,cm^3/gmole
ures      10    1     u,cal/gmole
hres      10    1     h,cal/gmole
sres      10    1     s,cal/gmole/k
```

Program FRENERGY.TK

(1c) Comment: PROGRAM FRENERGY.TK 10-3-1984 128/!

VARIABLE SHEET

St	Input	Name	Output	Unit	Comment
					PROGRAM FRENERGY.TK 10-3-1984
					CALCULATES:
					1) FREE ENERGY, ENTHALPY, ENTROPY
					AT 1 ATM. AND ANY TEMPERATURE :
					A) FOR COMPOUNDS
					B) FOR A REACTION
					2) EQUILIBRIUM CONSTANT OF A REACTION
		t		k	temperature , k
L		mu		dimless	stoichiometric number of the compound
		option		dimless	type: 'r_p' to find properties of reactants and products
					type: 'rxn' for properties of reaction
	1.987	r		cal/gmole	gas constant , cal/gmole/k
L		dgt		cal/gmole	DG of formation at T@1atm ,cal/gmole
L		dht		cal/gmole	DH of formation at T@1atm ,cal/gmole
L		dst		cal/gmole	DS of formation at T@1atm ,cal/gmole/k
		dgrxn		cal/gmole	DG of reaction at T@1atm ,cal/gmole
		dhrxn		cal/gmole	DH of reaction at T@1atm ,cal/gmole
		dsrxn		cal/gmole	DS of reaction at T@1atm ,cal/gmole/k

VARIABLE SHEET

St	Input	Name	Output	Unit	Comment
		keq		dimless	equilibrium constant for the reaction

```
(1r) Rule:          "Cp for the formation of the compound from its element 128/!

==================== RULE SHEET ================================================
S Rule
- ----
           "Cp for the formation of the compound from its elements
* dalpha = alpha -(nec*2*4.03+neh*6.952 + neo*6.085 + nen*6.903 + nes*6.499 + n
* dbeta = beta -(nec*2*1.14e-3+neh*-4.576e-4 + neo*.3631e-2 + nen*-3.753e-4 + n
* dgamma = gamma -(neh*9.563e-7 - neo*1.709e-6 + nen*1.93e-6 - nes*3.888e-6 - n
* dtheta = theta -(-neh*2.079e-10+neo*3.133e-10-nen*6.861e-10+nes*.952e-9 + nec

                     "DH, DS, and DG of formation for compound at T@1atm
* dht = dhf25c + poly(t,dtheta/4,dgamma/3,dbeta/2,dalpha,0) - poly(298,dtheta/4
* dsf25 = ds25c - nec*1.3609 - (neh*31.211+neo*49.003+nen*45.767+nes*2*7.62+nec
* dst = dsf25 + dalpha*ln(t/298) + dbeta*(t-298) + dgamma*(t^2-298^2)/2 + dthet
* dgt = dht -t*dst
                     "DG, DH, and DS for the reaction at T@1atm
* dgrxn = dot('dgt,'mu)
* dhrxn = dot('dht,'mu)
* dsrxn = dot('dst,'mu)
                     "Equilibrium constant for the reaction at T
* ln(keq) = -dgrxn/t/r
```

(1f) From: 128/!

```
==================== UNIT SHEET ================================================
From       To         Multiply By  Add Offset
----       --         -----------  ----------
```

( ) 128/!

```
==================== GLOBAL SHEET ==============================================
Variable Insert ON:          Yes

Intermediate Redisplay ON:   Yes
Automatic Iteration ON:      No
Comparison Tolerance:        .005
Typical Value:               1
Maximum Iteration Count:     10

Page Breaks ON:              No
Page Numbers ON:             No
Form Length:                 66
Printed Page Length:         60
Printed Page Width:          80
Left Margin:                 0
Printer Device or Filename:  PRN
Printer Setup String:
Line End:                    CR&LF

Color Display ON:            No
```

(1n) Name: dummy 128/!

========== LIST SHEET ==========

Name	Elements	Unit	Comment
dummy	2	dimless	domain list for function ARP and ARXN
ggg	2	dimless	range list for function ARP
jjj	2	dimless	range list for reaction ARXN
mu		dimless	list for stoichiometric number of React. & Prod.
dgt		cal/gmole	DG of formation at T for Reactants and Products
dst		cal/gmole	DS of formation at T for Reactants and Products
dht		cal/gmole	DH of formation at T for Reactants and Products

Subsheet of variables on the list sheet

dummy	jjj	ggg
r_p	0	1
rxn	1	0

(1n) Name: mm1 128/!

========== USER FUNCTION SHEET ==========

Name	Domain	Mapping	Range	Comment
mm1	number	Table	mu	maps compound to its MU; f(NUMBER)=MU
m1	number	Table	dgt	maps compound to its DGT; f(NUMBER)=DGT
arp	dummy	Table	ggg	maps DUMMY to GGG; f(DUMMY)=GGG
arxn	dummy	Table	jjj	maps DUMMY to JJJ; f(DUMMY)=JJJ

```
(s) Screen or Printer: Screen                                          128/!

==================== PLOT SHEET ================================================
Screen or Printer:          Screen
Title:
Display Scale ON:           Yes
X-Axis:
Y-Axis    Character
------    ---------
```

```
(s) Screen or Printer: Screen                                          128/!

==================== TABLE SHEET ================================================
Screen or Printer:          Screen
Title:                      standard energy of formation data
Vertical or Horizontal:     Vertical
List      Width First Header
----      ----- ----- ------
comp      25    1     compound
dgt       13    1     dg(t)
dht       13    1     dh(t)
dst       13    1     ds(t)
```

Program CHON.TK

```
(1c) Comment: PROGRAM   CHON.TK  11/ 1/ 1984                          98 /!

==================== VARIABLE SHEET ============================================
St Input      Name     Output     Unit        Comment
-- -----      ----     ------     ----        -------
                                               PROGRAM   CHON.TK  11/ 1/ 1984
                                               CHEMICAL EQUILIBRIA IN CARBON-
                                               HYDROGEN-OXYGEN-NITROGEN SYSTEMS.
                                               FEED : C, H2O, H2, O2, N2
                                               PRODUCT : H2, H2O, CH4, CO, CO2, N2
                                               ALSO CALCULATES THE EQUILIBRIUM
                                               COMPOSITION FOR AN ADIABATIC REACTOR.

L  'watervap comp                 dimless     list of compounds , dimless
               t                  k           reactor temperature , k
   1.987       r                  cal/gmole   gas constant , cal/gmole/k
L              dgt                cal/gmole   DGf(1 atm) at temp. t ,cal/gmole
L              dht                cal/gmole   DHf(1 atm) at temp. t ,cal/gmole
L              dst                cal/gmole   DSf(1 atm) at temp. t ,cal/gmole/k
               option             dimless     control variable , dimless
               p                  atm         reactor pressure , atm
               horf               dimless     ratio H/O in feed , dimless
               n2o2r              dimless     ratio N2/O2 in feed , dimless
               h2h2orp            dimless     ratio H2/H2O in product , dimless


VARIABLE SHEET
St Input      Name     Output     Unit        Comment
-- -----      ----     ------     ----        -------
               yh2                dimless     product mole fraction of H2 , dimless
               yh2o               dimless     product mole fraction of H2O , dimless
               ych4               dimless     product mole fraction of CH4 , dimless
               yco                dimless     product mole fraction of CO , dimless
               yco2               dimless     product mole fraction of CO2 , dimless
               yn2                dimless     product mole fraction of N2 , dimless
               pcr                dimless     ratio moles product/mole C , dimless
               dhmolc             btu/lbmol   DH feed-->product , btu/lbmole c
               hvaluep            btu/scf     product heating value , btu/scf
               hsteamf            btu/lb      DH steam (212F,sat vap)-->(p,sat vap)
```

```
RULE SHEET
S Rule
- ----
                          "DGT, DHT, DST for each compound
* n = map1(comp)
* dalpha = m8(n) -(m2(n)*2*-1.5718+m3(n)*7.201 + m4(n)*5.7816+m5(n)*6.4443)/2
* dbeta = m9(n) -(m2(n)*2*7.666e-3*2+m3(n)*-5.2697e-4*2 + m4(n)*.21942e-2*2+ m5
* dgamma = m10(n) -(m2(n)*2*-4.0177e-6*3+m3(n)*4.5653e-7*3 + m4(n)*-.76772e-6*3
* dtheta = m11(n) -(m2(n)*2*8.6122e-10*4+m3(n)*-.7378e-10*4+m4(n)*1.1546e-10*4+
* dht = m13(n) + poly(t,dtheta/4,dgamma/3,dbeta/2,dalpha,0) - poly(298,dtheta/4
* dsf25c = m12(n) - m2(n)*1.3609 - (m3(n)*31.211+m4(n)*49.003+m5(n)*45.767)/2
* dst = dsf25c + dalpha*ln(t/298) + dbeta*(t-298) + dgamma*(t^2-298^2)/2 + dthe
* dgt = dht -t*dst

                          "equilibrium constants K1, K2, K3
* k1 = exp(-1*(mdgt(2) - mdgt(1) )/r/t)
* k2 = exp(-1*(mdgt(3) - mdgt(1) - mdgt(2) )/r/t)
* k3 = exp(-1*(mdgt(4) )/r/t)

                          "Equilibrium composition
* coef1 = k3 * p * (1 + 2*n2o2r*(2-horf)/2)
* coef2 = (1+1/h2h2orp) * (1+n2o2r*(2-horf)/2)
* coef3 = k1*k2/p/h2h2orp^2  +  k1/p/h2h2orp  - 1
* coef1 * yh2^2  +  coef2 * yh2  +  coef3 = 0
* yh2o = yh2 / h2h2orp
* ych4 = k3 * p * yh2^2
* yco  = k1 / p / h2h2orp
* yco2 = k1 * k2 / p / h2h2orp^2
* 0/n2o2r + yn2 = 1 - yh2 - yh2o - ych4 - yco - yco2
* horf = (2*yh2 + 2*yh2o + 4*ych4) / (2*yco2 + yco + yh2o)
* pcr  = 1 / (ych4 + yco2 + yco)
```

```
RULE SHEET
S Rule
- ----
  "Rule sheet continued
                        "Feed composition
* h2of = pcr*step(horf,2)*(yh2o+yco+2*yco2)   +  pcr*step(1.999999999,horf)*(yh2
* h2f  = step(horf,2)*h2of*(horf - 2)/2
* o2f  = step(2,horf)*h2of*(2 - horf)/2
* n2t = n2o2r*o2f
* h2t = h2f + h2of
* o2t = o2f + h2of/2

                        "enthalpy of Product stream
* alphat = 1*m8(8) + h2t*m8(5) + o2t*m8(6) + n2t*m8(7)
* betat  = 1*m9(8) + h2t*m9(5) + o2t*m9(6) + n2t*m9(7)
* gammat = 1*m10(8)+ h2t*m10(5)+ o2t*m10(6)+ n2t*m10(7)
* thetat = 1*m11(8)+ h2t*m11(5)+ o2t*m11(6)+ n2t*m11(7)
* hptfrx = pcr*(yh2o*mdht(1) + ych4*mdht(4) + yco*mdht(2) + yco2*mdht(3) )
* hptt = alphat*(t-298)+betat*(t^2-298^2)/2 +gammat*(t^3-298^3)/3 +thetat*(t^4-
* dhmolc = ( (hptt+hptfrx) - h2of*(-68317))*1.8

* cpavgf = (7.6*o2f + 7.3*n2t + 7.1*h2f)/(o2f+n2t+h2f)
* - dhmolc + (hptt+hptfrx) - h2of*(-57253+hsteamf*10) - cpavgf*(o2f+n2t+h2f)*29

                        "Heating value of Product stream
* hvaluep = -1*(yh2*-57798 + ych4*-212800 + yco*-67636)*1.8/(1-yh2o)/379.5
```

(1f) From: 98 /!

========== UNIT SHEET ==========

From	To	Multiply By	Add Offset

( ) 98 /!

========== GLOBAL SHEET ==========

Variable Insert ON:	No
Intermediate Redisplay ON:	Yes
Automatic Iteration ON:	No
Comparison Tolerance:	.005
Typical Value:	1
Maximum Iteration Count:	10
Page Breaks ON:	No
Page Numbers ON:	No
Form Length:	66
Printed Page Length:	60
Printed Page Width:	132
Left Margin:	0
Printer Device or Filename:	PRN
Printer Setup String:	
Line End:	CR&LF
Color Display ON:	No

LIST SHEET

Name	Elements	Unit	Comment
comp	4	dimless	list of compounds h2o, co, co2, ch4
num	4	dimless	list num
number	10	dimless	list number
nec	8	dimless	number of carbon atoms
neh	8	dimless	number of hydrogen atoms
neo	8	dimless	number of oxygen atoms
nen	8	dimless	number of nitrogen atoms
ds25c	8	cal/gmole	standard entropy @25c
dhf25c	8	cal/gmole	enthalpy of formation @25c
alpha	8	cal/gmole	a term of the cp= a + b*t + c*t^2 + d*t^3
beta	8	cal/gmole	b term of the cp= a + b*t + c*t^2 + d*t^3
gamma	8	cal/gmole	c term of the cp= a +b*t + c*t^2 + d*t^3
theta	8	cal/gmole	d term of the cp= a + b*t + c*t^2 + d*t^3
dst		cal/gmole	dst for h2o, co, co2, ch4
dgt		cal/gmole	dgt for h2o, co, co2, ch4
dht		cal/gmole	dht for h2o, co, co2, ch4
cho1	8	dimless	range list for function MCDGT
cho2	8	dimless	range list for function MCK
cho3	8	dimless	range list for function MCKEQ
cho4	8	dimless	range list for function MCDH
cho5	8	dimless	range list for function MCADIA
cho6	8	dimless	range list for function MCCHON
cho	8	dimless	domain list for functions MCDGT through MCCHON

Subsheet of variables on the list sheet

number	num	comp
1	1	watervapor
2	2	carbonmono
3	3	carbondiox
4	4	methane
5		
6		
7		
8		
9		
10		

Subsheet of variables on the list sheet (continued)

cho	cho1	cho2	cho3	cho4	cho5	cho6
dgt_on	1	0	0	0	0	0
keq_on	0	1	0	0	0	0
equilibria_on	0	0	1	0	0	0
k_equilibria_on	0	1	1	0	0	0
adiabatic_on	0	1	1	1	1	0
molesfed_on	0	0	0	1	0	1
dhmolc_on	0	0	0	1	0	1
rules_off	0	0	0	0	0	0

Subsheet of variables on the list sheet (continued)

alpha	beta	gamma	theta	dhf25c	ds25c	nec	neh	neo	nen
7.424	.00126276	1.76835E-6	-6.0924E-10	-57798	45.106	0	2	1	0
6.249	.00185422	-4.4328E-8	-1.4761E-10	-26416	47.301	1	0	1	0
5.8515	.0127314	-6.9756E-6	1.38832E-9	-94051	51.061	1	0	2	0
2.3689	.020688	-6.5391E-6	6.0336E-10	-17889	44.5	1	4	0	0
7.201	-.00105394	1.36959E-6	-2.9512E-10	0	31.211	0	2	0	0
5.7816	.0043884	-2.30316E-6	4.6184E-10	0	49.003	0	0	2	0
6.4443	.00109036	5.4579E-7	-2.8526E-10	0	45.767	0	0	0	2
-1.5718	.015332	-1.20531E-5	3.44488E-9	0	1.3609	1	0	0	0

USER FUNCTION SHEET

Name	Domain	Mapping	Range	Comment
map1	comp	Table	num	maps compound to its number; f(COMP)=NUM
m2	number	Table	nec	maps compound to its C atoms; f(NUMBER)=N
m3	number	Table	neh	maps compound to its H atoms; f(NUMBER)=N
m4	number	Table	neo	maps compound to its O atoms; f(NUMBER)=N
m5	number	Table	nen	maps compound to its N atoms; f(NUMBER)=N
m8	number	Table	alpha	compound to its a of cp data; f(NUMBER)=A
m9	number	Table	beta	compound to its b of cp data; f(NUMBER)=B
m10	number	Table	gamma	compound to its c of cp data; f(NUMBER)=G
m11	number	Table	theta	compound to its d of cp data; f(NUMBER)=T
m12	number	Table	ds25c	compound to its standard entropy @25c
m13	number	Table	dhf25c	compound to its enthalpy of formation@25c
mdgt	number	Table	dgt	compound to its DGT at temp.=T
mdst	number	Table	dst	compound to its DST at temp.=T
mdht	number	Table	dht	compound to its DHT at temp.=T
mcdgt	cho	Table	cho1	maps CHO to CHO1; f(CHO)=CHO1
mck	cho	Table	cho2	maps CHO to CHO2; f(CHO)=CHO2
mceq	cho	Table	cho3	maps CHO to CHO3; f(CHO)=CHO3
mcdh	cho	Table	cho4	maps CHO to CHO4; f(CHO)=CHO4
mcadia	cho	Table	cho5	maps CHO to CHO5; f(CHO)=CHO5
mcchon	cho	Table	cho6	maps CHO to CHO6; f(CHO)=CHO6

```
(s) Screen or Printer: Screen                                          98 /!

==================== TABLE SHEET ================================================
Screen or Printer:          Screen
Title:
Vertical or Horizontal:     Vertical
List      Width First Header
----      ----- ----- ------
```

```
(s) Screen or Printer: Screen                                          98 /!

==================== PLOT SHEET =================================================
Screen or Printer:          Screen
Title:
Display Scale ON:           Yes
X-Axis:                     lnhorf
Y-Axis    Character
------    ---------
```

Program CRITICAL.TK

```
(1c) Comment: PROGRAM   CRITICAL.TK   10-3-1984                    127/!

==================== VARIABLE SHEET ============================================
St Input      Name     Output     Unit       Comment
-- -----      ----     ------     ----       -------
                                             PROGRAM   CRITICAL.TK   10-3-1984
                                             CRITICAL DATA FOR MORE THAN  50
                                             COMPOUNDS.
                                             1) CRITICAL TEMPERATURE AND PRESSURE;
                                                      Tc  ,  Pc
                                             2) CRITICAL SPECIFIC VOLUME AND
                                                COMPRESSIBILITY FACTOR;  Vc , Zc
                                             3) ACENTRIC FACTOR AND MOLECULAR
                                                WEIGHT;  OMEGA  ,  MWEIGHT

L             comp              dimless    name of the compound
              flag              dimless    type: 1 to get data from databank
                                           type: 0 to turn off databank
L             tc                k          critical temperature , k
L             pc                atm        critical pressure , atm
L             vc                cm^3/gmol  critical molar volume , cm^3/gmole
L             zc                dimless    critical compressibility factor
L             omega             dimless    acentric factor , dimless
L             mweight           g/gmole    molecular weight , g/gmole


(1r) Rule:                "maps a compound to its critical properties.    127/!

==================== RULE SHEET ================================================
S Rule
- ----
                "maps a compound to its critical properties.
* 0/flag     + tc = mapc1(comp)
* 0/flag     + pc = mapc2(comp)
* 0/flag     + vc = mapc3(comp)
* 0/flag     + zc = mapc4(comp)
* 0/flag     + omega = mapc5(comp)
* 0/flag     + mweight = mapc6(comp)
```

```
(1f) From:                                                          127/!

==================== UNIT SHEET ================================================
From       To         Multiply By  Add Offset
----       --         -----------  ----------
```

```
( )                                                                 127/!

==================== GLOBAL SHEET ===============================================
Variable Insert ON:          No

Intermediate Redisplay ON:   Yes
Automatic Iteration ON:      No
Comparison Tolerance:        .005
Typical Value:               1
Maximum Iteration Count:     10

Page Breaks ON:              No
Page Numbers ON:             No
Form Length:                 66
Printed Page Length:         60
Printed Page Width:          80
Left Margin:                 0
Printer Device or Filename:  PRN
Printer Setup String:
Line End:                    CR&LF

Color Display ON:            No
```

(1n) Name: compnd 127/!

========== LIST SHEET ==========

Name	Elements	Unit	Comment
compnd	59	dimless	list for compound
atc	59	k	list for critical temperature
apc	59	atm	list for critical pressure
avc	59	cm^3/gmol	list for critical specific volume
azc	59	dimless	list for critical compressibility factor
aomega	59	dimless	list for acentric factor
amwght	59	g/gmole	list for molecular weight
comp		dimless	variable sheet list for compound
number	6	dimless	number list
tc		k	variable sheet list for critical temperature
pc		atm	variable sheet list for critical pressure
vc		cm^3/gmol	variable sheet list for critical specific volume
zc		dimless	variable sheet list for critical compressibility
omega		dimless	variable sheet list for acentric factor
mweight		g/gmole	variable sheet list for molecular weight

(1n) Name: map1 127/!

========== USER FUNCTION SHEET ==========

Name	Domain	Mapping	Range	Comment
map1	comp	Table	number	maps comp to its number; f(COMP)=NUMBER
mc2	number	Table	tc	maps comp to its Tc; f(NUMBER)=TC
mc3	number	Table	pc	maps comp to its Pc; f(NUMBER)=PC
mc4	number	Table	vc	maps comp to its Vc; f(NUMBER)=VC
mc5	number	Table	zc	maps comp to its Zc; f(NUMBER)=ZC
mc6	number	Table	omega	maps comp to its Omega; f(NUMBER)=OMEGA
mc7	number	Table	mweight	maps comp to its Mweight; f(NUMBER)=Mweig
mapc1	compnd	Table	atc	maps compnd to its ATc; f(COMPND)=ATC
mapc2	compnd	Table	apc	maps compnd to its APc; f(COMPND)=APC
mapc3	compnd	Table	avc	maps compnd to its AVc; f(COMPND)=AVC
mapc4	compnd	Table	azc	maps compnd to its AZc; f(COMPND)=AZC
mapc5	compnd	Table	aomega	maps compnd to its AOmega; f(COMPND)=AOME
mapc6	compnd	Table	amwght	maps compnd to its AMW; f(COMPND)=AMW

```
(s) Screen or Printer: Screen                                          127/!

==================== PLOT SHEET ================================================
Screen or Printer:          Screen
Title:
Display Scale ON:           Yes
X-Axis:
Y-Axis    Character
------    ---------
```

```
(s) Screen or Printer: Screen                                          127/!

==================== TABLE SHEET ===============================================
Screen or Printer:          Screen
Title:                      critical property data
Vertical or Horizontal:     Vertical
List      Width First Header
----      ----- ----- ------
comp      20    1     compound
mweight   8     1     mweight
tc        8     1     tc,k
pc        8     1     pc,atm
vc        8     1     vc,cm3/gmol
zc        8     1     zc
omega     8     1     omega
```

List of the compounds in data file CRITICAL.TK with their respective properties

Subsheet of variables on the list sheet (critical property data)

compnd	atc	apc	avc	azc	aomega	amwght
methane	190.6	45.4	99	.288	.007	16.04
ethane	305.4	48.2	148	.285	.091	30.07
propane	369.8	41.9	203	.281	.145	44.09
n_butane	425.2	37.5	255	.274	.193	58.12
i_butane	408.1	36	263	.283	.176	58.12
n_pentane	469.6	33.3	304	.262	.251	72.15
i_pentane	460.4	33.4	306	.273	.227	72.15
neo_pentane	433.8	31.6	303	.269	.197	72.15
n_hexane	507.4	29.3	370	.264	.296	86.17
n_heptane	540.2	27	432	.263	.351	100.2
n_octane	568.8	24.5	492	.259	.394	114.22
ethylene	282.4	49.7	129	.276	.086	28.05
propylene	365	45.6	181	.275	.148	42.08
butene_1	419.6	39.7	240	.277	.187	56.1
pentene_1	464.7	40	missing	missing	.245	70.13
aceticacid	594.5	57.1	171	.2	.45	60.05
acetone	508.2	46.4	209	.232	.318	58.08
acetonitrile	547.9	47.7	173	.184	.321	41.054
acetylene	308.3	60.6	113	.271	.184	26.04
benzene	562.1	48.3	259	.271	.21	78.11

Subsheet of variables on the list sheet (critical property data)

compnd	atc	apc	avc	azc	aomega	amwght
butadiene13	425	42.7	221	.27	.181	54.09
chlorobenzene	632.4	44.6	308	.265	.255	112.56
cyclohexane	553.4	40.2	308	.273	.214	84.16
freon12	385	40.7	217	.279	.158	120.925
diethylether	467.7	35.9	280	.262	.283	74.12
ethanol	516.2	63	167	.248	.635	46.07
ethyleneoxide	469	71	140	.259	.157	44.052
methanol	512.6	79.9	118	.224	.556	32.04
methylchloride	416.2	65.9	139	.268	.158	50.49
methylethylketone	535.6	41	267	.249	.337	72.1
toluene	591.7	40.6	316	.264	.257	92.13
freon11	471.2	43.5	248	.279	.295	137.382
freon113	487.2	33.7	304	.257	.249	175.382
argon	150.8	48.1	74.9	.291	0	39.944
bromine	584	102	127	.27	.132	159.83
chlorine	417	76	124	.275	.074	70.91
helium	5.2	2.24	57.3	.301	0	4
hydrogen	33.2	12.8	65	.305	0	2.016
krypton	209.4	54.3	91.2	.287	0	83.8
neon	44.4	27.2	41.7	.311	0	20.183

Subsheet of variables on the list sheet (critical property data)

compnd	atc	apc	avc	azc	aomega	amwght
nitrogen	126.2	33.5	89.5	.29	.04	28.02
oxygen	154.6	49.8	73.4	.288	.021	32
xenon	289.7	57.6	118	.286	0	131.3
ammonia	405.6	111.3	72.5	.242	.25	17.03
carbondioxide	304.2	72.8	94	.274	.225	44.01
carbondisulfide	552	78	160	.28	.123	76.14
carbonmonoxide	132.9	34.5	93.1	.295	.041	28.01
carbontetrachlori	556.4	45	276	.272	.193	153.84
chloroform	536.4	54	239	.293	.214	119.39
hydrazine	653	145	missing	missing	.337	32.052
hydrogenchloride	324.6	82	81	.25	.266	36.47
hydrogencyanide	456.8	53.2	139	.197	.399	27.03
hydrogensulfide	373.2	88.2	98.5	.284	.1	34.08
nitricoxide	180	64	58	.25	.6	30.01
nitrousoxide	309.6	71.5	97.4	.274	.16	44.02
sulfur	1314	116	missing	missing	.07	32
sulfurdioxide	430.8	77.8	122	.268	.273	64.07
sulfurtrioxide	491	81	130	.26	.51	80.07
water	647.1	217.6	56	.23	.348	18.016

Program DATBANK1.TK

(1c) Comment: PROGRAM DATBANK1.TK 10-3-1984 88 /!

VARIABLE SHEET

St	Input	Name	Output	Unit	Comment
					PROGRAM DATBANK1.TK 10-3-1984 DATA FOR MORE THAN 100 COMPOUNDS: 1) IDEAL GAS MOLAL HEAT CAPACITY: Cp = ALPHA + BETA*T + GAMMA*T^2 + THETA*T^3 2) NUMBER OF ATOMS IN A COMPOUND; C , H , O , N , S , Cl 3) ENTHALPY AND ENTROPY OF FORMATION AT 25 c; DHf@25c , DSf@25c
L		comp		dimless	name of the compound
		flag		dimless	type: 1 to get data from databank type: 0 to turn off databank
L		trangek		k	temperature range of Cp data , k
L		mformul		dimless	molecular formula , dimless
L		nec		dimless	number of carbon atoms ,dimless
L		neh		dimless	number of hydrogen atoms , dimless
L		neo		dimless	number of oxygen atoms , dimless
L		nen		dimless	number of nitrogen atoms , dimless
L		nes		dimless	number of sulfur atoms , dimless

VARIABLE SHEET

St	Input	Name	Output	Unit	Comment
L		necl		dimless	number of chlorine atoms , dimless
L		alpha		cal/gmole	first term of Cp data, cal/gmole/k
L		beta		cal/gmole	second term of Cp data, cal/gmole/k^2
L		gamma		cal/gmole	third term of Cp data, cal/gmole/k^3
L		theta		cal/gmole	fourth term of Cp data, cal/gmole/k^4
L		dhf25c		cal/gmole	enthalpy of formation@25 c, cal/gmole
L		ds25c		cal/gmole	standard entropy @25 c, cal/gmole/k

```
(1r) Rule:              "maps a compound to its heat capacity data.        88 /!

==================== RULE SHEET ================================================
S Rule
- ----
                "maps a compound to its heat capacity data.
* O/flag     + alpha = mapcp1(comp)
* O/flag     + beta = mapcp2(comp)
* O/flag     + gamma = mapcp3(comp)
* O/flag     + theta = mapcp4(comp)
* trangek = mapcpr(comp)
* mformula = mapcpf(comp)
* O/flag     + dhf25c= maphf25(comp)
* O/flag     + ds25c = maps25(comp)
* O/flag     + nec = mapnc(comp)
* O/flag     + neh = mapnh(comp)
* O/flag     + neo = mapno(comp)
* O/flag     + nen = mapnn(comp)
* O/flag     + nes = mapns(comp)
* O/flag     + necl = mapncl(comp)
```

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(if) From:                                                          88 /!

==================== UNIT SHEET ================================================
From      To        Multiply By  Add Offset
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( )                                                                 88 /!

==================== GLOBAL SHEET ===============================================
Variable Insert ON:          No

Intermediate Redisplay ON:   Yes
Automatic Iteration ON:      No
Comparison Tolerance:        .005
Typical Value:               1
Maximum Iteration Count:     10

Page Breaks ON:              No
Page Numbers ON:             No
Form Length:                 66
Printed Page Length:         60
Printed Page Width:          80
Left Margin:                 0
Printer Device or Filename:  PRN
Printer Setup String:
Line End:                    CR&LF

Color Display ON:            No
```

LIST SHEET

Name	Elements	Unit	Comment
compound	118	dimless	list for compound
nalpha	118	cal/gmole	list for first term of Cp
nbeta	118	cal/gmole	list for second term of Cp
ngamma	118	cal/gmole	list for third term of Cp
ntheta	118	cal/gmole	list for fourth term of Cp
trange	118	k	list for applicable temperature range of Cp
formula	118	dimless	list for molecular formula of compound
ds25	114	cal/gmole	list for stansard entropy @25 c
dhf25	114	cal/gmole	list for enthalpy of formation@25 c
nc	118	dimless	list for number of carbon atoms
nh	118	dimless	list for number of hydrogan atoms
no	118	dimless	list for number of oxygen atoms
nn	118	dimless	list for number of nitrogen atoms
ns	118	dimless	list for number of sulfur atoms
ncl	118	dimless	list for number of chlorine atoms
comp		dimless	variable sheet list for compound
trangek		k	variable sheet list for temperature range of Cp
mformula		dimless	variable sheet list for molecular formula
nec		dimless	variable sheet list for number of carbon atoms
neh		dimless	variable sheet list for number of hydrogen atoms
neo		dimless	variable sheet list for number of oxygen atoms
nen		dimless	variable sheet list for number of nitrogen atoms
nes		dimless	variable sheet list for number of sulfur atoms
necl		dimless	variable sheet list for number of chlorine atoms
number	10	dimless	list number
ds25c		cal/gmole	variable sheet list for standard entropy @25c
dhf25c		cal/gmole	variable sheet list for enthalpy of formation@25c
alpha		cal/gmole	variable sheet list for first term of Cp data
beta		cal/gmole	variable sheet list for second term of Cp data
gamma		cal/gmole	variable sheet list for third term of Cp data
theta		cal/gmole	variable sheet list for fourth term of Cp data

USER FUNCTION SHEET

Name	Domain	Mapping	Range	Comment
map1	comp	Table	number	maps comp to its number; f(COMP)=NUMBER
m2	number	Table	nec	maps comp to its NEC; f(NUMBER)=NEC
m3	number	Table	neh	maps comp to its NEH; f(NUMBER)=NEH
m4	number	Table	neo	maps comp to its NEO; f(NUMBER)=NEO
m5	number	Table	nen	maps comp to its NEN; f(NUMBER)=NEN
m6	number	Table	nes	maps comp to its NES; f(NUMBER)=NES
m7	number	Table	necl	maps comp to its NECL; f(NUMBER)=NECL
m8	number	Table	alpha	maps comp to its ALPHA; f(NUMBER)=ALPHA
m9	number	Table	beta	maps comp to its BETA; f(NUMBER)=BETA
m10	number	Table	gamma	maps comp to its GAMMA; f(NUMBER)=GAMMA
m11	number	Table	theta	maps comp to its THETA; f(NUMBER)=THETA
m12	number	Table	ds25c	maps comp to its DS25C; f(NUMBER)=DS25C
m13	number	Table	dhf25c	maps comp to its DHF25C; f(NUMBER)=DHF25C
m14	number	Table	trangek	maps comp to its TRANGEK; f(NUMBER)=TRANG
m15	number	Table	mformula	maps comp to its MFORMULA; f(NUMBER)=MFOR
mapcp1	compound	Table	nalpha	maps compound to its NALPHA; f(COMPOUND)=
mapcp2	compound	Table	nbeta	maps compound to its NBETA; f(COMPOUND)=N
mapcp3	compound	Table	ngamma	maps compound to its NGAMMA; f(COMPOUND)=
mapcp4	compound	Table	ntheta	maps compound to its NTHETA; f(COMPOUND)=
mapcpr	compound	Table	trange	maps compound to its TRANGE; f(COMPOUND)=
mapcpf	compound	Table	formula	maps compound to its FORMULA; f(COMPOUND)
maps25	compound	Table	ds25	maps compound to its DS25; f(COMPOUND)=DS
maphf25	compound	Table	dhf25	maps compound to its DHF25; f(COMPOUND)=D
mapnc	compound	Table	nc	maps compound to its NC; f(COMPOUND)=NC
mapnh	compound	Table	nh	maps compound to its NH; f(COMPOUND)=NH
mapno	compound	Table	no	maps compound to its NO; f(COMPOUND)=NO
mapnn	compound	Table	nn	maps compound to its NN; f(COMPOUND)=NN
mapns	compound	Table	ns	maps compound to its NS; f(COMPOUND)=NS
mapncl	compound	Table	ncl	maps compound to its NCL; f(COMPOUND)=NCL

(s) Screen or Printer: Screen 88 /!

========== PLOT SHEET ==========

Screen or Printer: Screen
Title:
Display Scale ON: Yes
X-Axis:

Y-Axis	Character

(s) Screen or Printer: Screen 88 /!

========== TABLE SHEET ==========

Screen or Printer: Screen
Title: Cp, dHf25c, dSf25c, C, H, O, N, S, Cl data
Vertical or Horizontal: Vertical

List	Width	First	Header
comp	25	1	compound
mformula	6	1	m. formula
alpha	6	1	alpha
beta	7	1	beta
gamma	7	1	gamma
theta	7	1	theta
trangek	15	1	temp. range
comp	25	1	compound
mformula	6	1	m. formula
nec	3	1	C
neh	3	1	H
neo	3	1	O
nen	3	1	N
nes	3	1	S
necl	3	1	Cl
dhf25c	10	1	dhf25c

TABLE SHEET

List	Width	First	Header
ds25c	10	1	ds25c

List of the compounds in data file DATBANK1.TK with their respective properties

Subsheet of variables on the list sheet (heat capacity data)

compound	nalpha	nbeta	ngamma	ntheta	trange
methane	4.75	.012	.00000303	-2.63E-9	r273_1500K
ethane	1.648	.04124	-.0000153	1.74E-9	r273_1500K
propane	-.966	.07279	-.00003755	7.58E-9	r273_1500K
n_butane	.945	.08873	-.0000438	8.36E-9	r273_1500K
i_butane	-1.89	.09936	-.00005495	1.192E-8	r273_1500K
n_pentane	1.618	.1085	-.00005365	1.01E-8	r273_1500K
n_hexane	1.657	.1319	-.00006844	1.378E-8	r273_1500K
ethylene	.944	.03735	-.00001993	4.22E-9	r273_1500K
propylene	.753	.05691	-.0000291	5.88E-9	r273_1500K
butene_1	-.24	.0865	-.0000511	1.207E-8	r273_1500K
i_butene	1.65	.07702	-.00003981	8.02E-9	r273_1500K
cis_2_butene	-1.778	.08078	-.00004074	7.89E-9	r273_1500K
trans_2_butene	2.34	.0722	-.00003403	6.07E-9	r273_1500K
cyclopentane	-12.957	.13087	-.00007447	1.641E-8	r273_1500K
methylcyclopentane	-12.114	.1538	-.00008915	2.003E-8	r273_1500K
cyclohexane	-15.935	.16454	-.00009203	1.927E-8	r273_1500K
methylcyclohexane	-15.07	.18972	-.00010989	2.409E-8	r273_1500K

Subsheet of variables on the list sheet (heat of formation data)

compound	formula	dhf25	ds25	nc	nh	no	nn	ns	ncl
methane	ch4	-17889	44.5	1	4	0	0	0	0
ethane	c2h6	-20236	54.85	2	6	0	0	0	0
propane	c3h8	-24820	64.51	3	8	0	0	0	0
n_butane	c4h10	-30150	74.12	4	10	0	0	0	0
i_butane	c4h10		70.42	4	10	0	0	0	0
n_pentane	c5h12	-35000	83.4	5	12	0	0	0	0
n_hexane	c6h14	-39960	92.83	6	14	0	0	0	0
ethylene	c2h4	12496	52.45	2	4	0	0	0	0
propylene	c3h6	4879	63.8	3	6	0	0	0	0
butene_1	c4h8	-30	73.04	4	8	0	0	0	0
i_butene	c4h8		70.17	4	8	0	0	0	0
cis_2_butene	c4h8		71.9	4	8	0	0	0	0
trans_2_butene	c4h8		70.86	4	8	0	0	0	0
cyclopentane	c5h10		70	5	10	0	0	0	0
methylcyclopentane	c6h12			6	12	0	0	0	0
cyclohexane	c6h12	-29430	71.28	6	12	0	0	0	0
methylcyclohexane	c7h14	-36990		7	14	0	0	0	0

Subsheet of variables on the list sheet (heat capacity data)

compound	nalpha	nbeta	ngamma	ntheta	trange
benzene	-8.65	.11578	-.0000754	1.854E-8	r273_1500K
toluene	-8.213	.13357	-.0000823	1.92E-8	r273_1500K
ethylbenzene	-8.398	.15935	-.00010003	2.395E-8	r273_1500K
styrene	-5.968	.14354	-.0000915	2.203E-8	r273_1500K
cumene	-9.452	.18686	-.00011869	2.88E-8	r273_1500K
acetylene	5.21	.022008	-.00001559	4.349E-9	r273_1500K
methylacetylene	4.21	.04073	-.00002192	4.713E-9	r273_1500K
dimethylacetylene	3.54	.05838	-.0000276	4.974E-9	r273_1500K
propadiene	2.43	.04693	-.00002781	6.484E-9	r273_1500K
butadiene_1_3	-1.29	.0835	-.00005582	1.424E-8	r273_1500K
isoprene	-.44	.10418	-.00006762	1.693E-8	r273_1500K
nitrogen	6.903	-.0003753	.00000193	-6.861E-10	r273_1800k
oxygen	6.085	.003631	-1.709E-6	3.133E-10	r273_1800k
air	6.713	.0004697	.000001147	-4.696E-10	r273_1800k
hydrogen	6.952	-.0004576	9.563E-7	-2.079E-10	r273_1800k
carbonmonoxide	6.726	.0004001	.000001283	-5.307E-10	r273_1800k
carbondioxide	5.316	.014285	-8.362E-6	1.784E-9	r273_1800k
water	7.7	.0004594	-.000002521	-8.587E-10	r273_1800k

Subsheet of variables on the list sheet (heat of formation data)

compound	formula	dhf25	ds25	nc	nh	no	nn	ns	ncl
benzene	c6h6	19820	64.34	6	6	0	0	0	0
toluene	c7h8	11950		7	8	0	0	0	0
ethylbenzene	c8h10	7120	82.48	8	10	0	0	0	0
styrene	c8h8	35220		8	8	0	0	0	0
cumene	c9h12			9	12	0	0	0	0
acetylene	c2h2	54194	59.3	2	2	0	0	0	0
methylacetylene	c3h4			3	4	0	0	0	0
dimethylacetylene	c4h6			4	6	0	0	0	0
propadiene	c3h4			3	4	0	0	0	0
butadiene_1_3	c4h6			4	6	0	0	0	0
isoprene	c5h8			5	8	0	0	0	0
nitrogen	n2	0	45.767	0	0	0	2	0	0
oxygen	o2	0	49.003	0	0	2	0	0	0
air	air	0		0	0	2	6	0	0
hydrogen	h2	0	31.211	0	2	0	0	0	0
carbonmonoxide	co	-26416	47.301	1	0	1	0	0	0
carbondioxide	co2	-94051	51.061	1	0	2	0	0	0
water	h2o	-57798	45.106	0	2	1	0	0	0

Subsheet of variables on the list sheet (heat capacity data)

compound	nalpha	nbeta	ngamma	ntheta	trange
nitrogen_high_range	6.529	.001488	-2.271E-7	0	r273_3800k
oxygen_high_range	6.732	.001505	-1.791E-7	0	r273_3800k
air_high_range	6.557	.001477	-2.148E-7	0	r273_3800k
hydrogen_high_range	6.424	.001039	-7.804E-8	0	r273_3800k
carbonmonoxide_high_range	6.48	.001566	-2.387E-7	0	r273_3800k
carbondioxide_high_range	18.036	-4.474E-5	na	na	r273_3800k
water_high_range	6.97	.003464	-4.833E-7	0	r273_3800k
sulfur	6.499	.005298	-3.888E-6	9.52E-10	r273_1800k
sulfurdioxide	6.157	.01384	-9.103E-6	2.057E-9	r273_1800k
sulfurtrioxide	3.918	.03483	-.00002675	7.744E-9	r273_1800k
hydrogensulfide	7.07	.003128	.000001364	-7.867E-10	r273_1800k
carbondisulfide	7.39	.01489	-.00001096	2.76E-9	r273_1800k
carbonylsulfide	6.222	.01536	-.00001058	2.56E-9	r273_1800k
fluorine	6.115	.005864	-4.186E-6	9.797E-10	r273_2000k
chlorine	6.8214	.0057095	-5.107E-6	1.547E-9	r273_1500k
bromine	8.051	.002462	-2.128E-6	6.406E-10	r273_1500k
iodine	8.504	.0013135	-1.0684E-6	3.125E-10	r273_1800k

Subsheet of variables on the list sheet (heat of formation data)

compound	formula	dhf25	ds25	nc	nh	no	nn	ns	ncl
nitrogen_high_range	n2	0	45.767	0	0	0	2	0	0
oxygen_high_range	o2	0	49.003	0	0	2	0	0	0
air_high_range	air	0		0	0	2	6	0	0
hydrogen_high_range	h2	0	31.211	0	2	0	0	0	0
carbonmonoxide_high_range	co	-26416	47.301	1	0	1	0	0	0
carbondioxide_high_range	co2	-94051	51.061	1	0	2	0	0	0
water_high_range	h2o	-57798	45.106	0	2	1	0	0	0
sulfur	s2	0	54.41	0	0	0	0	2	0
sulfurdioxide	so2	-70960	59.4	0	0	2	0	1	0
sulfurtrioxide	so3	-94450	61.24	0	0	3	0	1	0
hydrogensulfide	h2s	-4815	49.15	0	2	0	0	1	0
carbondisulfide	cs2		56.84	1	0	0	0	2	0
carbonylsulfide	cos		55.34	1	0	1	0	1	0
fluorine	f2	0	48.6	0	0	0	0	0	0
chlorine	cl2	0	53.286	0	0	0	0	0	2
bromine	br2	0	58.639	0	0	0	0	0	0
iodine	i2	0	62.28	0	0	0	0	0	0

Subsheet of variables on the list sheet (heat capacity data)

compound	nalpha	nbeta	ngamma	ntheta	trange
hydrogenfluoride	7.201	-.001178	.000001576	-3.76E-10	r273_2000k
hydrogenchloride	7.244	-.00182	.00000317	-1.036E-9	r273_1500k
hydrogenbromide	7.169	-.001604	.000003314	-1.161E-9	r273_1500k
hydrogeniodide	6.702	.0004546	.000001216	-4.813E-10	r273_1900k
methylchloride	3.05	.02596	-.00001244	2.3E-9	r273_1500k
methylenechloride	4.2	.03419	-.0000235	6.068E-9	r273_1500k
chloroform	7.61	.03461	-.00002668	7.344E-9	r273_1500k
carbontetrachloride	12.24	.034	-.00002995	8.828E-9	r273_1500k
phosgene	10.35	.01653	-8.408E-6	0	r273_1000k
thiophosgene	10.8	.01859	-.00001045	0	r273_1000k
cyanogen	9.82	.014858	-6.571E-6	0	r273_1000k
hydrogencyanide	6.34	.008375	-2.611E-6	0	r273_1500k
cyanogenchloride	7.97	.010745	-5.265E-6	0	r273_1000k
cyanogenbromide	8.82	.009084	-4.367E-6	0	r273_1000k
cyanogeniodide	9.69	.007213	-3.265E-6	0	r273_1000k
acetonitrile	5.09	.027634	-9.111E-6	0	r273_1200k
acrylicnitrile	4.55	.041039	-1.6939E-5	0	r273_1000k

Subsheet of variables on the list sheet (heat of formation data)

compound	formula	dhf25	ds25	nc	nh	no	nn	ns	ncl
hydrogenfluoride	hf		41.47	0	1	0	0	0	0
hydrogenchloride	hcl		44.617	0	1	0	0	0	1
hydrogenbromide	hbr		47.437	0	1	0	0	0	0
hydrogeniodide	hi		49.314	0	1	0	0	0	0
methylchloride	ch3cl		55.97	1	3	0	0	0	1
methylenechloride	ch2cl2		64.68	1	2	0	0	0	2
chloroform	chcl3		70.86	1	1	0	0	0	3
carbontetrachloride	ccl4		73.95	1	0	0	0	0	4
phosgene	cocl2		69.13	1	0	1	0	0	2
thiophosgene	csc12			1	0	0	0	1	2
cyanogen	c2n2		57.86	2	0	0	2	0	0
hydrogencyanide	hcn		48.23	1	1	0	1	0	0
cyanogenchloride	cncl		56.31	1	0	0	1	0	1
cyanogenbromide	cnbr		59.05	1	0	0	1	0	0
cyanogeniodide	cni		61.26	1	0	0	1	0	0
acetonitrile	ch3cn			2	3	0	1	0	0
acrylicnitrile	ch2chcn			3	3	0	1	0	0

Subsheet of variables on the list sheet (heat capacity data)

compound	nalpha	nbeta	ngamma	ntheta	trange
nitricoxide_high_range	6.461	.002358	-7.705E-7	8.729E-11	r273_3800k
nitricoxide	7.008	-.0002244	.000002328	-1.E-9	r273_1500k
nitrousoxide	5.758	.014004	-8.508E-6	2.526E-9	r273_1500k
nitrogendioxide	5.48	.01365	-.00000841	1.88E-9	r273_1500k
nitrogentetroxide	7.9	.0446	-.0000271	0	r273_600k
formaldehyde	5.447	.009739	.000001703	-2.078E-9	r273_1500k
acetaldehyde	4.19	.03164	-.00000515	-3.8E-9	r273_1000k
methanol	4.55	.02186	-.00000291	-1.92E-9	r273_1000k
ethanol	4.75	.05006	-.00002479	4.79E-9	r273_1500k
ethyleneoxide	-1.12	.04925	-.00002389	3.149E-9	r273_1000k
ketene	4.11	.02966	-.00001793	4.22E-9	r273_1500k
cyclopropane	-6.481	.08206	-.00005577	1.561E-8	r273_1000k
i_pentane	-2.273	.12434	-.00007097	1.586E-8	r273_1500k
neo_pentane	-3.865	.13305	-.00008018	1.883E-8	r273_1500k
o_xylene	-3.789	.14291	-.00008354	1.88E-8	r273_1500k
m_xylene	-6.533	.14905	-.00008831	2.005E-8	r273_1500k
p_xylene	-5.334	.1422	-.00007984	1.703E-8	r273_1500k

Subsheet of variables on the list sheet (heat of formation data)

compound	formula	dhf25	ds25	nc	nh	no	nn	ns	ncl
nitricoxide_high_range	no	21570	50.339	0	0	1	1	0	0
nitricoxide	no	21570	50.339	0	0	1	1	0	0
nitrousoxide	n2o	19513	52.58	0	0	1	2	0	0
nitrogendioxide	no2	7930	57.47	0	0	2	1	0	0
nitrogentetroxide	n2o4	2190	72.73	0	0	4	2	0	0
formaldehyde	ch2o		52.26	1	2	1	0	0	0
acetaldehyde	c2h4o	-39760		2	4	1	0	0	0
methanol	ch4o	-48050	56.8	1	4	1	0	0	0
ethanol	c2h6o	-56030	67.4	2	6	1	0	0	0
ethyleneoxide	c2h4o			2	4	1	0	0	0
ketene	c2h2o			2	2	1	0	0	0
cyclopropane	c3h6			3	6	0	0	0	0
i_pentane	c5h12			5	12	0	0	0	0
neo_pentane	c5h12			5	12	0	0	0	0
o_xylene	c8h10			8	10	0	0	0	0
m_xylene	c8h10			8	10	0	0	0	0
p_xylene	c8h10			8	10	0	0	0	0

Subsheet of variables on the list sheet (heat capacity data)

compound	nalpha	nbeta	ngamma	ntheta	trange
carbonsuboxide	8.203	.03073	-.00002081	5.182E-9	r273_1500k
acetone	1.625	.06661	-.00003737	8.307E-9	r273_1500k
i_propylalcohol	.7936	.08502	-.00005016	1.156E-8	r273_1500k
n_propylalcohol	-1.307	.09235	-.000058	1.414E-8	r273_1500k
allylalcohol	.5203	.07122	-.00004259	9.948E-9	r273_1500k
chloroethene	2.401	.0427	-.00002751	6.797E-9	r273_1500k
dichloroethene_11	5.899	.04383	-.00003182	8.516E-9	r273_1500k
cis_12_dichloroethene	4.336	.04691	-.00003397	9.01E-9	r273_1500k
trans_12_dichloroethene	5.661	.04295	-.00003022	7.891E-9	r273_1500k
trichloroethene	9.2	.04517	-.000036	1.01E-8	r273_1500k
tetrachloroethene	15.11	.03799	-.00003179	9.089E-9	r273_1500k
ammonia	6.5846	.0061251	2.3663E-6	-1.5981E-9	r273_1500k
hydrazine	3.89	.03554	-.00002304	5.99E-9	r273_1500k
methylamine	2.9956	.036101	-1.6446E-5	2.9505E-9	r273_1500k
dimethylamine	-.275	.066152	-3.4826E-5	7.151E-9	r273_1500k
trimethylamine	-2.098	.096187	-5.5488E-5	1.2432E-8	r273_1500k

Subsheet of variables on the list sheet (heat of formation data)

compound	formula	dhf25	ds25	nc	nh	no	nn	ns	ncl
carbonsuboxide	c3o2			3	0	2	0	0	0
acetone	c3h6o		72.7	3	6	1	0	0	0
i_propylalcohol	c3h8o		73.4	3	8	1	0	0	0
n_propylalcohol	c3h8o			3	8	1	0	0	0
allylalcohol	c3h6o			3	6	1	0	0	0
chloroethene	c2h3cl			2	3	0	0	0	1
dichloroethene_11	c2h2cl2			2	2	0	0	0	2
cis_12_dichloroethene	c2h2cl2			2	2	0	0	0	2
trans_12_dichloroethene	c2h2cl2			2	2	0	0	0	2
trichloroethene	c2hcl3			2	1	0	0	0	3
tetrachloroethene	c2cl4			2	0	0	0	0	4
ammonia	nh3	-11040	-23.69	0	3	0	1	0	0
hydrazine	n2h4			0	4	0	2	0	0
methylamine	ch5n			1	5	0	1	0	0
dimethylamine	c2h7n			2	7	0	1	0	0
trimethylamine	c3h9n			3	9	0	1	0	0

The vita has been removed from the scanned document