THERMODYNAMIC PROPERTY ESTIMATION PACKAGE FOR P-V-T

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ABSTRACT

A personal computer based thermodynamic property estimation package for pure and ideal gases has been developed. It is a user-friendly, menu-driven package written in FORTRAN, comprising of a computational module, named the ***PVT Module****, for evaluating pressure, volume or temperature and an executive module, named* ***TPACK*** *(version 1.0). Ten equations of state have been used, in addition to the generalized compressibility charts of Hougen-Watson. In this package any one of the equations/tables can be selected for the evaluation of the properties, by the user during operation. The rapid polynomial technique has been employed for using the tables. The values returned by the package have been compared with the experimental data for* CH_4 *and* CO_2*. The source code for the computational module runs to about 3800 programming lines and the executive program to about 4500 lines. The entire executable version of TPACK occupies about 610 k bytes of memory. The average executing time for a property is less than 1.7 seconds. The entire package can be stored on a standard 2 Mb diskette and used independently for property estimations or can be incorporated into other design or simulation packages. Here the features of the package, along with the flow charts for the computational and executive modules have been presented.*

INTRODUCTION

Computers have been a major tool in specific aspects of the design of chemical plants for over 30 years. Originally most of the available computer aided design (CAD) packages were dedicated to solving isolated problems, such as distillation column or heat exchanger design. More recently, however packages have been developed for almost all phases of plant design viz., process simulation, pipe drafting, material control, critical path scheduling and structural design. Over a hundred flow-sheeting systems have been developed among which a few, such as ASPEN, ASPEN PLUS, CHEMTRAN, CONCEPT, DESIGN 2000, FLOWPACK II, FLOWTRAN and PROCESS have achieved wide acceptance. These packages have improved design efficiency enormously and enabled the process engineer to look at many alternative design strategies.

The importance of property estimation packages in process simulation cannot be over emphasised. On an average 70-80 per cent of computer time is utilised for accessing data and estimating properties during any simulation. There now exists a plethora of application software ranging from quite simple in-house developed, problem-specific programs through so-called fully integrated, conception-to-grave design packages. But although the number of commercial data packages available in the market is considerable, it is difficult to have any idea of the accuracy before hand, and it is not possible to improve upon these packages, which are more or less black boxes, since the source code would not be available. Therefore the trend has been for the user to develop for himself the packages to meet the specific requirements wherever possible.

Prediction of thermodynamic properties of pure components and solutions has been a subject of considerable practical and theoretical interest since long. Extensive experimental work has been done in this field by numerous investigators in the past. However, correlation of such data has not been achieved to the required degree of accuracy and many of these equations (even the purely empirical equations) are, for some limited specific range only . To this day the best of correlations for pure components yield a maximum deviation of around 4 per cent (outside the critical region) whereas experimental measurements are sometimes available with a reliability of 99 per cent and higher.

One of the major chores of a process engineer is to select a good thermodynamic correlation for his system from which he can proceed to find design parameters. This selection is vital for a good process design and simulation. For a particular property there are quite a number of available correlations but with attendant difficulty in selecting the right one to match all possible combinations of temperature, pressure, polarity etc. Further all such correlations are developed with different system attributes like the acentric factor, boiling point etc. Presently there is an increased emphasis on modelling, simulation and synthesis for process development and scale-up. A chemical engineer therefore has to necessarily place greater emphasis on the calculation of thermodynamic properties from the available and published correlations and data at any point of interest in no time. It was difficult to imagine the possibility of computer aided design or process simulation in developing countries a decade or so ago because of the high cost and limited capabilities of both hardware and software, but the scene has now changed due to the soaring capabilities and plummeting prices of computer hardware.

The present work was therefore taken up with a view to develop user-friendly, property estimation packages (using available methods and correlations) which could be used on ordinary PC systems and which could be the starting step for integration with full-fledged simulation packages to be developed later.

DESCRIPTION AND FEATURES OF PACKAGE

TPACK (Version 1.0)

The package described here, named TPACK (version 1.0), is capable of working on the **PVT Module**, designed for calculation of any one of pressure, volume or temperature, given the other two, and also on any other computational module that would be developed later.
Although the computational module (PVT) is an integral part of the overall package, TPACK, it can also be operated independently, with the menu-driven facility. While the computational module is written in FORTRAN the executive program of TPACK has been written in C.

PVT Module

Designated as PEVOT2 the PVT module is a user-friendly FORTRAN program for calculating any one of the following properties given the values of the other two - (i) Pressure (ii) Volume (iii) Temperature

PEVOT2 when invoked from the executive program displays an option-menu with the help of MENU MODULE which asks the user to specify the critical properties of the substance (gas) whose properties are desired. If the user strikes the "ESC" key the substance is assumed to be methane and its critical values are defaulted. The next menu displayed asks for the property to be estimated. Accordingly the control is transferred to the appropriate module.

If the property to be estimated is, for example, volume it gives two options i.e., a tabulated set or a single value. If a tabulated set is opted, the user has to specify the output file name into which the values are to be directed, number of values, initial temperature and pressure and the increments in temperature and pressure.

The modules for calculation of single values of pressure, temperature or volume are similar. These modules first ask for the other two properties. Then the list of methods available is displayed among which the user has to select any one, after which the desired property is calculated using the selected method and the values are displayed.

The methods available[1-7], in the package, for PVT calculations are:

1. Ideal Gas Law: $PV = RT$
2. Virial Equation (Truncated): $Z = 1 + \frac{BP}{RT}$
3. Van der Waal's Equation: $[P + a/V^2](V - b) = RT$
4. Dieterici Equation: $\{P e^{(a/VRT)}\}(V - b) = RT$
5. Berthlot's Equation: $[P + a/TV^2](V - b) = RT$
6. Soave-Redlich-Kwong Equation:

For Volume :

$$Z = \frac{1}{(1-h)} - \frac{a}{bRT^{1.5}}\left\{\frac{h}{1+h}\right\}$$

Where $h = \frac{bP}{ZRT}$

For Temperature and Pressure:

$$P = \frac{RT}{(v+b)} - \frac{a}{\{T^{0.5}V(V+b)\}}$$

7. Peng-Robinson Equation:

$$P = \frac{RT}{(V-b)} - \frac{aT}{\{V(V+b)+b(V-b)\}}$$

8. Beattie-Bridgeman Equation:

$$PV^2 = RT[V + B_o\{1 - \frac{b}{V}\}][1 - \frac{c}{VT^2}] - A_o[1 - \frac{a}{V}]$$

9. Benedict-Webb-Rubin Equation:

$$P = RT\rho + [B_oRT - A_o - \frac{C_o}{T^2}]\rho^2 + [bRT - a]\rho^3 + a\alpha\rho^6$$

$$+c\rho^3 \frac{(1 + \gamma\rho^2)}{T^2} e^{-\gamma\rho^2}$$

10. Barner-Adler modification:

$$P = \frac{RT}{V - b} - \frac{afa}{V(V - b)} + \frac{cfc}{V(V - b)^2} + \frac{dfd}{V(V - b)^3} + \frac{efe}{V(V - b)^4}$$

11. Generalized Compressibility Charts.

The flowchart for the PEVOT2 module is given in figure A-1.

While using generalized Hougen-Watson[6] charts the rapid polynomial technique has been employed for the purposes of interpolation. This technique has been preferred as it combines the advantages of the Least square method and the Cubic spline technique.

For the evaluation of temperature or volume from the explicit equations for pressure, Newton-Raphson method has been used in many cases. In others the secant method has been used.

The error criterion taken for the calculation of PVT is 0.001. The number of iterations has been limited to 100.

Executive Program (TPACK)

The computational module (PVT module) is in itself self-contained and is rendered menu-driven by enabling each of these packages to call MENU subroutine common to all packages. All the computations achievable by the larger package TPACK (version 1.0) can be carried out using any computational package without need of the EXECUTIVE program. However, an executive program has been included for the purpose of combining any other modules, to be developed later, into a single-whole, so that the user can have the option at any time to change from one computational package to another. The executive program is given the name TPACK, which is also the name used for the entire package involving the executive and any other computational modules.

The executive program is written in C language where it gives the user a set of predefined options viz.,

PVT Module;	Other Modules;
DOS Shell;	Quit

These options are displayed on the screen in a WINDOW using MENU module which in turn returns an integer number which is the representation of the user's choice. Depending upon the number returned the control is transferred to the appropriate module. DOS Shell command enables the user to come out of the program to execute DOS commands and return to the program on typing EXIT.

The flowchart for the EXECUTIVE module is given in figure A-2.

MENU Module

MENU Module is a subroutine used in the executive program and the three computational programs for displaying "POP MENUS". This utilizes functions of C language like clrscr, window, text colour, text background etc., which are not available in FORTRAN, used for the computational programs.

When this program is invoked from the executive program, with the help of an interfacing program, it reads the number of strings and the maximum length among all strings that are sent by the executive program and accordingly allots a window area on the screen. This also reads the colours for background, foreground, high-lighting and pop cursor of the window as selected in the executive program. The character strings are written in the window and the predefined alphabet can be high-lighted.

MENU module has a subroutine - WORKBOX which when invoked reads the character string and the default values with the help of the interfacing program and creates a window and writes the character string and default values. It then waits for the user to input the required values. Hitting the ESC key, on the other hand, causes the default values to be taken for calculation. "Quit" commands have also been provided for cancelling an entry.

When more than one menu is displayed on the screen, the "active" menu is distinguished by the presence of a double-lined border while the other menus are all single-lined.

DISCUSSION OF RESULTS, CONCLUSIONS AND RECOMMENDATIONS

To show the format in which the packages display the results on the video monitor screen, a sample output for one of the computations is presented, as a screen dump, in figure A-3.

Plots of evaluated and experimental values

i) For methane, over a narrow range of temperatures from 90 K to 190 K, and pressures of 0.1 to 45 atmospheres, the values returned by the package have been presented in fig.1-6. In all of the figures the continuous line shows the experimental values [2,10].

Figs. 1 and 2 are the plots of pressure evaluated from known values of temperature and volume. As can be seen the Van der Waals, Dieterici, Berthlot, SRK, and Peng-Robinson equations show good agreement with the experimental values.

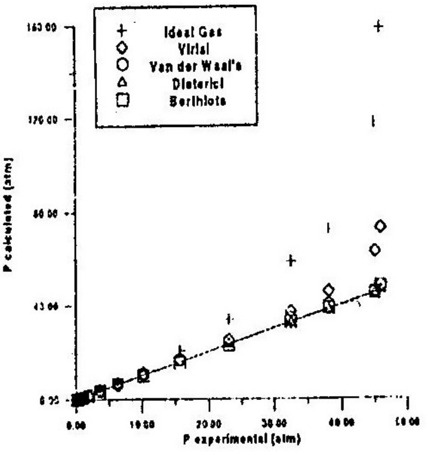


Fig. 1: Methane: P from T and V

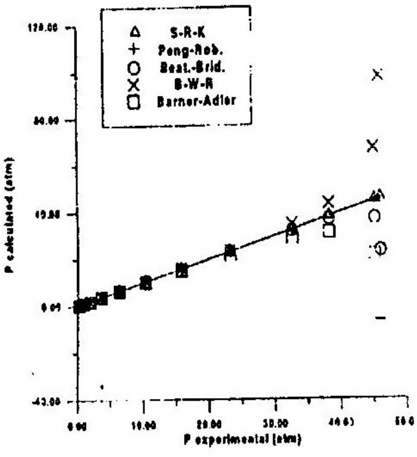
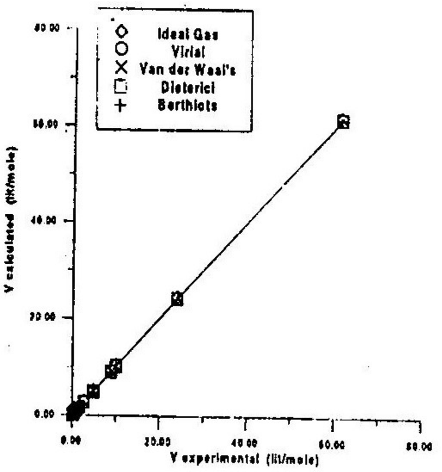


Fig. 2: Methane: P from T and V

Figs. 3 and 4 show the success of the various methods in evaluating volume from known values of pressure and temperature. In the range tested all the methods show good agreement with experimental values.



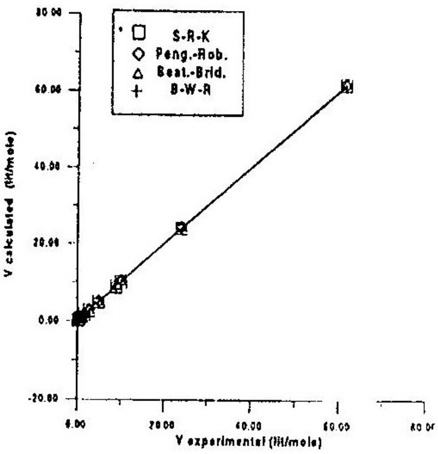
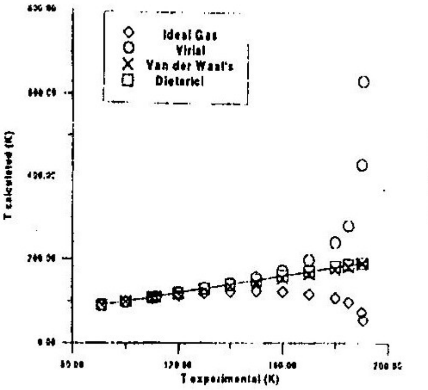


Fig. 3: Methane: V from P and T

Fig. 4: Methane: V from P and T

Figs. 5 and 6 show temperature calculated from known values of pressure and volume. It can be seen that only the Van der Waals, Dieterici, SRK, Peng-Robinson and Beattie-Bridgeman equations give results which are consistent with experimental values.



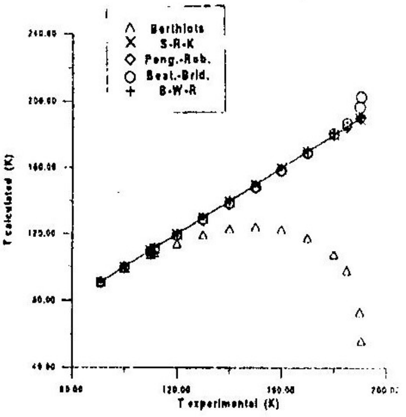


Fig. 5: Methane: T from P and V

Fig. 6: Methane: T from P and V

ii) For carbon-di-oxide [8,9], over a temperature range of 170 K to 300 K and pressure range of 0.2 to 75 atmospheres the values predicted by the TPACK have been presented in Figs. 7 and 8. Here, only the Dieterici, SRK, Peng-Robinson and Barner-Adler equations meet the tolerance criteria.

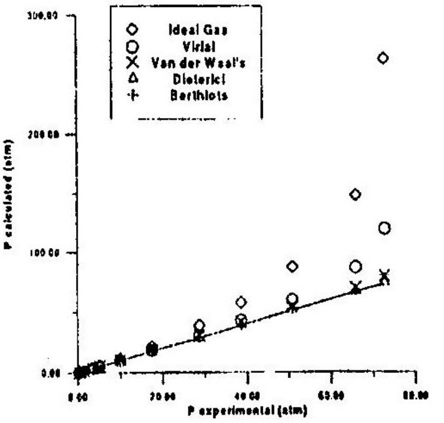


Fig. 7: CO_2: P from T and V

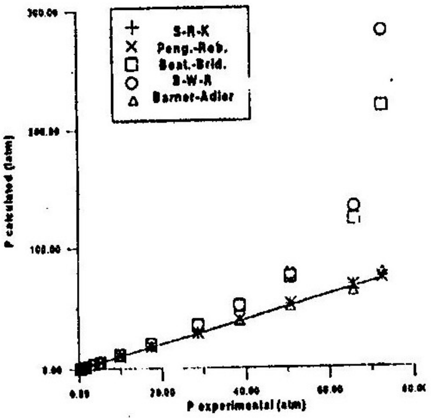


Fig. 8: CO_2: P from T and V

The packages TPACK and PEVOT2 have been tested thoroughly under various conditions and have been found to be rugged and free from bugs. Further, from the results and the plots it can be seen that these packages give outputs of property values which are reliable to the extent of the reliability of the equations and estimation methods themselves.

Error and convergence analysis

Based on experimental data for methane, the relative error involved in different kinds of computations, using the Tpack and PVT modules, has been evaluated over a wide range of temperature and pressure. Methane has been selected for this purpose as it is a simple molecule which is spherical and non-polar, at the same time being polyatomic. It can be representative of typical compounds used commercially. Further, experimental data is readily available. In the PVT module the pressure range investigated, using the modules, is 1 - 500 atms., and the temperature is 90 - 370 Kelvin.

Equations are recommended based on two criteria, viz., (i) relative error and (ii) Ease of convergence. A relative error of ±6% has been used as the cut-off point. In all the computational modules a limit of 100 iterations is used for convergence purposes. When convergence is not achieved within this limit, the system terminates the computation.

Based on the above criteria, recommendations are made for the various equations, as presented in table 1 :

Table 1.

Equation	Recommendation
Ideal gas law	Recommended in the temperature range of 70 - 170 K and at pressures below 10 atm.
Virial	Recommended for pressures up to 40 atm.
Van der waals	Applicable for pressures up to 400 atm and temperatures of 200K.
Dieterici	This equation may be recommended for molal densities less than 3.25.
Berthelot	Recommended for molal densities less than 3.0 in calculation of volume and pressure, but is not recommended for calculation of temperature.
Soave-Redlich-Kwong (SRK)	Consistent in the whole of the gaseous region and is recommended for all the three calculations.
Peng-Robinson	In the calculation of pressure and temperature it is applicable only up to a pressure of 180 atm and temperatures up to 180 K. In calculations of volume this range can be extended up to 250 atm.
Beattie-Bridgeman	In calculation of temperature and pressure it is recommended for pressures up to 30 atm., and at temperature upto 180 K. In the calculation of

	volume the range of pressure may be extended up to 100 atm. It was found that this equation converges faster in the range of its applicability than SRK equation.
Benedict-Webb-Rubin (BWR)	Its consistency in calculation of pressure and temperature is limited to temperatures of about 200 K. This equation gives consistent results for volume calculations except for some scarce points.
Barner-Adler	This equation was tested only for low pressures as it was found that its range of applicability is very limited; only up to 20 atm and for temperatures up to 180 K.
Generalized Charts	In the range of data tables it was found that the error was less than 2.0 per cent.

NOMENCLATURE:

A_0	constant
B	second virial coefficient
B_0	constant
C_0	constant
P	pressure [atm]
R	universal gas constant = 0.08206 [lit.atm/gmole.K]
T	temperature [K]
V	volume [lit/gmole]
Z	compressibility factor
a,b,c, d,e	constants
a	constant
r	constant
g	constant
f_a,f_c, f_d,f_e	temperature functions equal to unity at $T = T_c$

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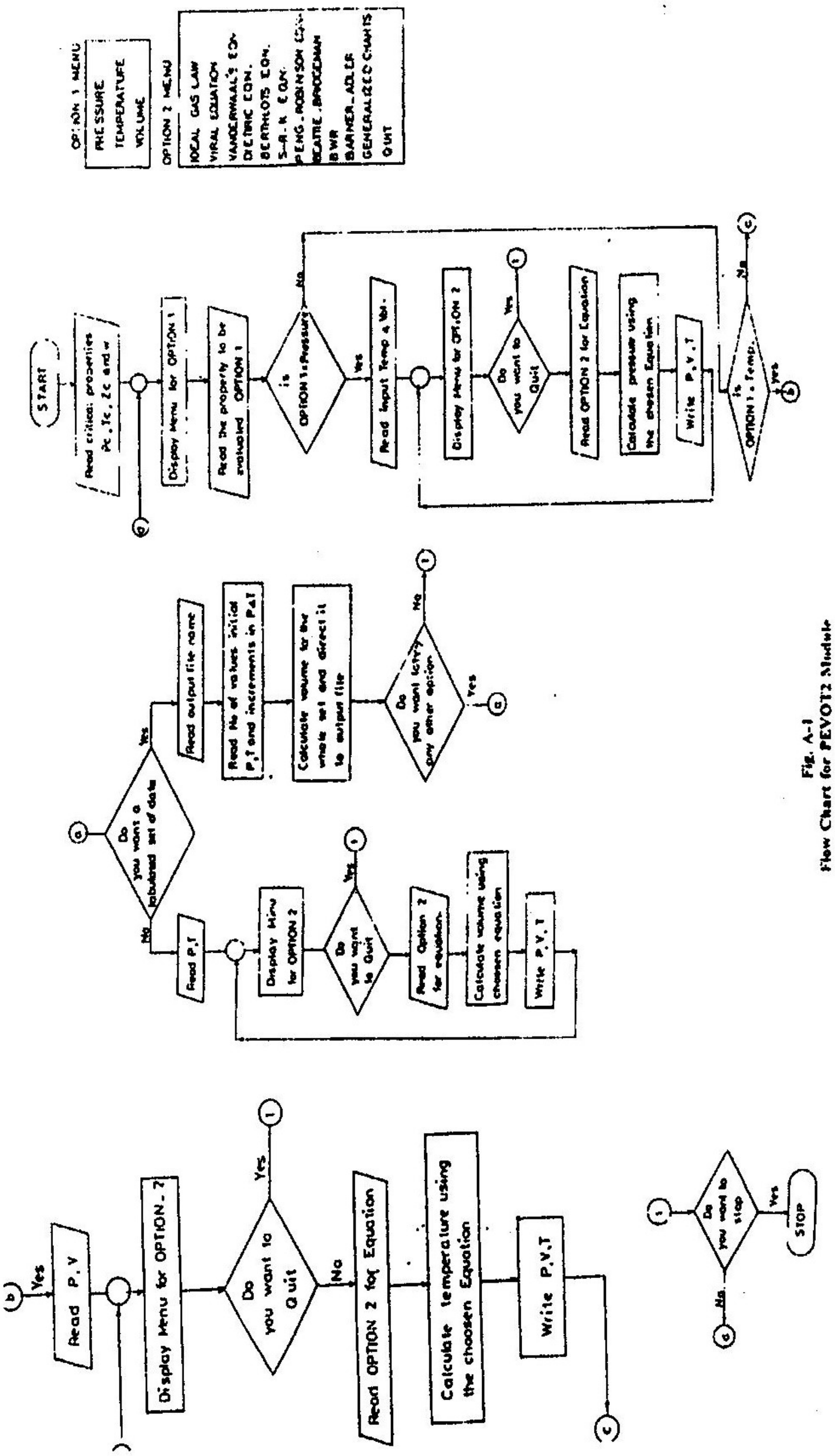


Fig. A-1
Flow Chart for PEVOT2 Module

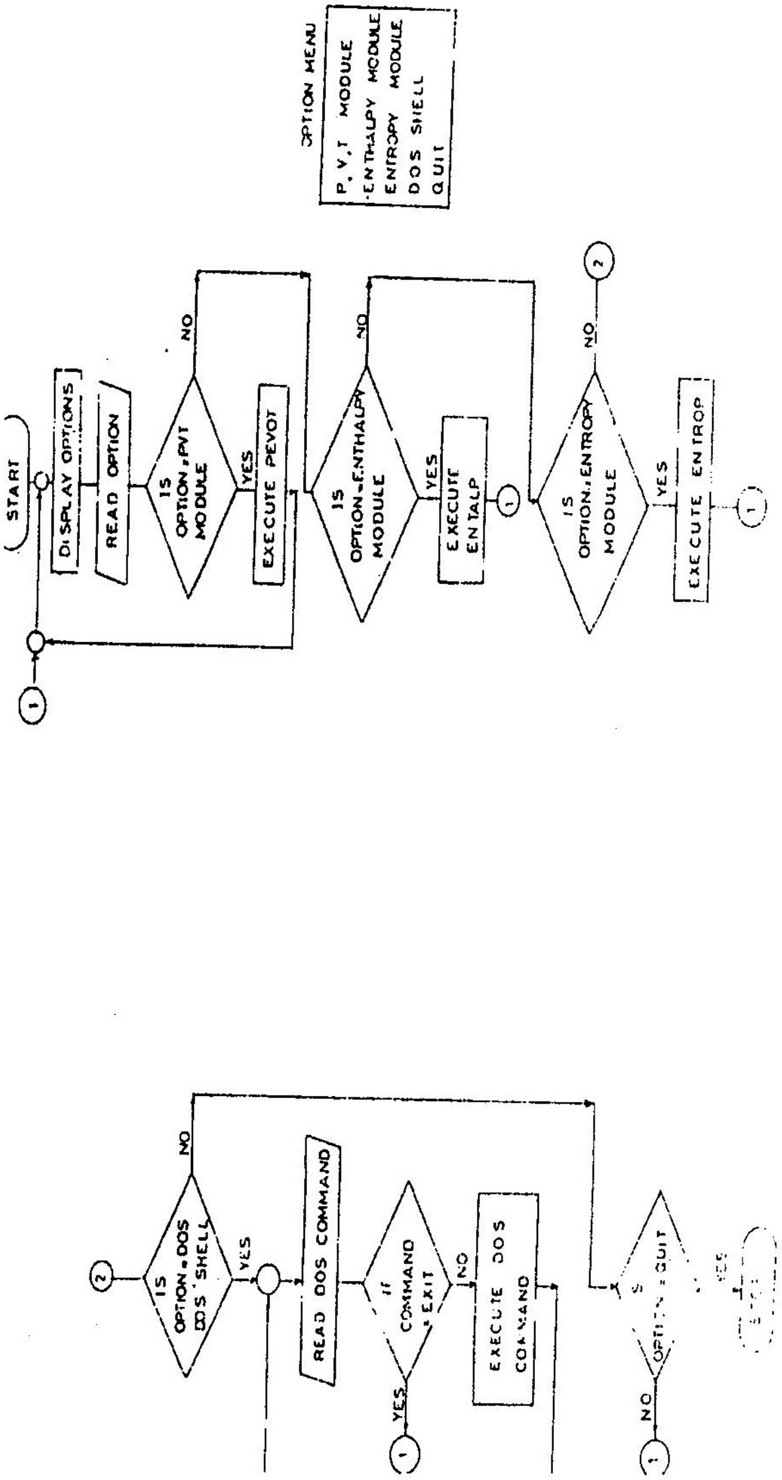
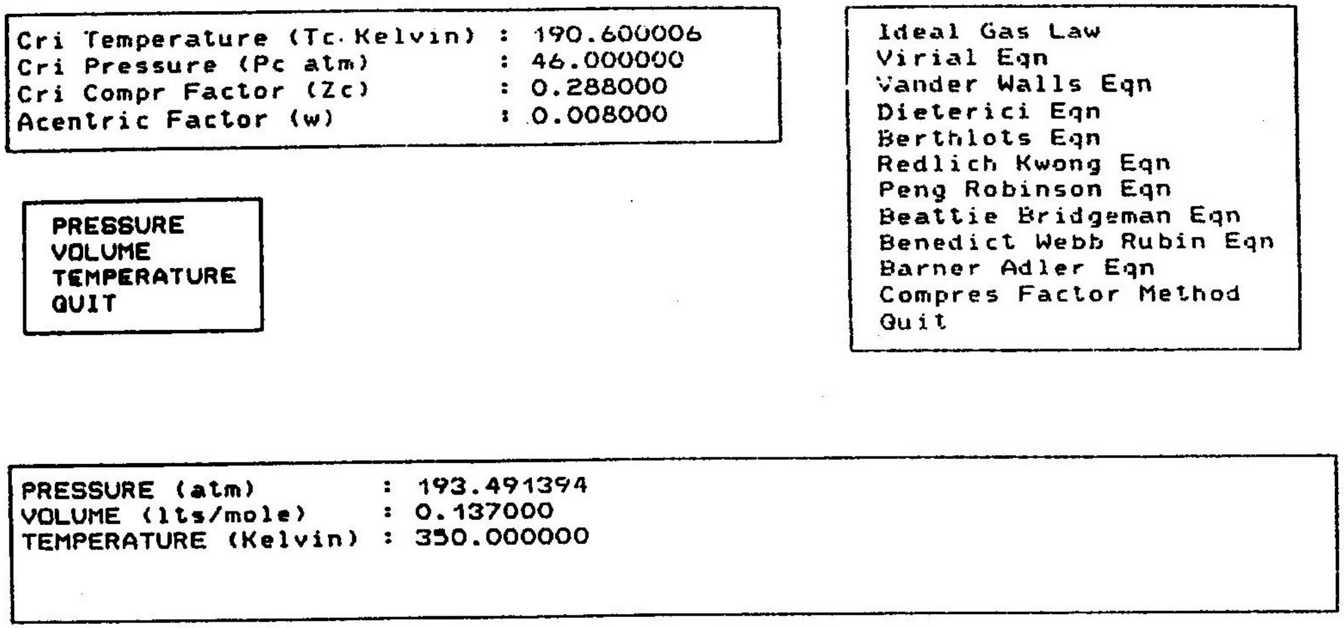


Fig. A-2
Flow Chart for EXECUTIVE Module



```
Cri Temperature (Tc Kelvin) : 190.600006
Cri Pressure (Pc atm)       : 46.000000
Cri Compr Factor (Zc)       : 0.288000
Acentric Factor (w)         : 0.008000
```

```
Ideal Gas Law
Virial Eqn
Vander Walls Eqn
Dieterici Eqn
Berthlots Eqn
Redlich Kwong Eqn
Peng Robinson Eqn
Beattie Bridgeman Eqn
Benedict Webb Rubin Eqn
Barner Adler Eqn
Compres Factor Method
Quit
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PRESSURE
VOLUME
TEMPERATURE
QUIT
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```
PRESSURE (atm)        : 193.491394
VOLUME (lts/mole)     : 0.137000
TEMPERATURE (Kelvin)  : 350.000000
```

Fig. A-3
Sample Data Display