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Computation of Fifteen Thermodynamic Properties Along Arbitrary Paths from Fundamental Equations of State Correlations

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COMPUTATION OF FIFTEEN THERMODYNAMIC PROPERTIES ALONG ARBITRARY PATHS FROM FUNDAMENTAL EQUATIONS OF STATE CORRELATIONS

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ABSTRACT

In this work, a set of fifteen thermodynamic properties for thirty pure compounds has been estimated using fundamental equations of state (FEOS). A computer program was written which allows to input any two of four fundamental thermodynamic properties entropy, pressure, temperature and density to fix a state point and then use the FEOS to generate any other property at that given state. The program further applies the FEOS to trace thermodynamic processes like isochoric, isobaric, isenthalpic, isothermal and isentropic state changes to find the final state of the compound. The program subsequently displays the initial, final and intermediate state points in a 2-dimensional plot with any two of fifteen thermodynamic properties along any two axes.

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LIST OF SYMBOLS

Upper Case Symbols

1.	A_i	Substance specific model parameter
2.	B_i	Substance specific model parameter
3.	C_p	Specific heat of at constant pressure
4.	C_v	Specific heat of at constant volume
5.	M	Molecular mass
6.	P	Pressure
7.	R	Universal gas constant
8.	T	Temperature
9.	Z	Compressibility factor

Lower Case Symbols

10.	a	Specific Helmholtz energy
11.	g	Specific Gibbs energy
12.	h	Specific enthalpy
13.	u	Specific internal energy
14.	n_i	Substance specific model constants
15.	s	Specific entropy
16.	v	Specific volume
17.	y_i	Substance specific model constant

Upper Case Greek Symbols

18.	θ_i	Model parameter

Lower Case Greek Symbols

19. α	Dimensionless Helmholtz energy
20. β	Inverse of temperature
21. δ	Inverse reduced volume
22. ρ	Density
23. σ	Model parameter
24. τ	Inverse reduced temperature

Subscripts

25. i	Index of summation
26. 0	Reference state
27. c	Critical

Superscripts

28. 0	Ideal gas property

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CHAPTER I

INTRODUCTION

1.1 MOTIVATION FOR WORK

To design any heat engine or refrigerator one usually first decides on what temperatures the unit should work between. The working fluid selection would then impose pressure changes that the fluid would undergo to produce desired effects. Then a suitable thermodynamic cycle, such as the Stirling cycle, is selected. Upon selection of a process change, an equation of state (EOS) is necessary to describe any intermediate state between the initial and final state. As the name suggests, EOS are equations that relate different states of a particular fluid through a mathematical model usually determined from numerous experiments. Most widely used EOS, such as the van der Waals EOS and its improvements (Peng-Robinson, Redlich- Kwong etc.) are known as cubic equations of state, which have serious limitations for application in process design. Usually, these

EOS are only valid in regions where underlying experiments for their correlations have been performed. The focus of this study is to apply a more general class of EOS called fundamental equations of state (FEOS), which allow for not only highly accurate correlations but also for determination of thermodynamic properties without restriction. One of the key tasks of thermodynamics is the description of thermodynamic properties by means of FEOS.

Thermodynamic consistency is essential to ensure stability during process simulation. FEOS allow derivation of all thermodynamic properties from a single mathematical expression, thus ensuring their thermodynamic consistency. The structure of the FEOS is complicated and tracing thermodynamic paths from them is computationally challenging. This study used FEOS from the work by Tillner-Roth [1] to trace thermodynamic properties along various paths for a set of thirty pure compounds in their fluid phase. For example, in a Stirling cycle [2] the working fluid undergoes the thermodynamic processes; isothermal expansion, isochoric heat removal, isothermal compression and isochoric heat addition. This work computes a set of fifteen thermodynamic properties along each of the state changes in the cycle, for all thirty pure compounds from a database. Under real conditions the processes may not be strictly isothermal or isochoric. The algorithm is developed such that, a function of temperature or volume maybe be input, as a modification to the source code, and the program can trace the path along the given function to simulate more realistic operating conditions.

1.2 REVIEW OF PREVIOUS WORK

For the study in this thesis the FEOS of each of the thirty compounds was required. The book compiled by Tillner-Roth [1] contained the FEOS for each of the pure compounds and the empirical constants associated with each correlation. We first discuss what a FEOS is and how it is different from a thermal EOS.

The simplest EOS is the ideal gas law $Pv = RT$[3], where P is pressure, v is molar volume, R is the universal gas constant and T is temperature. One explicit form of the EOS is $P=f(T,v)$. With $v = 1/\rho$, where ρ is molar density , we can also express the EOS as $P= f(T,\rho)$. More realistic EOS such as the van der Waals EOS are also expressed as function of temperature and density. Similarly, many subsequent EOS such as Peng-Robinson, Redlich –Kwong , Benedict-Webb -Rubin were expressed as $P=f(T,\rho)$. The problem with these EOS is that properties like enthalpy or internal energy cannot be obtained without additional quantities like specific heats. These quantities are obtained from experiments and correlations are usually valid only for the conditions under which the experiments were performed. Extrapolation into state regions not backed by experimental data are most likely to fail for the above mentioned EOS.

An EOS where properties like enthapy and internal energy are correlated simultaneously would allow to compute any other thermodynamic property. Fundamental equations of state (FEOS) provide such means, therefore they constitute much more advanced correlation. FEOS for pure substances are exclusively in terms of the Helmholtz energy $a(T,\rho)/RT \equiv \alpha(T,\rho)$ where $\alpha(T,\rho)$ is some complex algebraic, exponential or logarithmic expression or a combination of all. The Helmholtz energy is a thermodynamic potential which allows for the calculation of any other thermodynamic property by differentiation with respect to T and ρ. A P,ρ,T relationship is called a thermal equation of state. A FEOS contains an EOS.

1.3 FUNDEMENTAL EQUATIONS OF STATE FOR IDEAL FLUIDS

In this section the FEOS for pure substances are discussed in further detail, as outlined in the work by Tillner-Roth[1].

As indicated before, the thermal EOS for all real gases approaches

$$Pv = RT \tag{1}$$

for ρ →0 or v → ∞. The ideal gas state is a fictitious state which nevertheless plays a significant role in FEOS correlation. Furthermore, internal energy u and enthalpy h depend on temperature only. This limiting behavior is called the ideal gas state which has to be fulfilled by every EOS or FEOS. From an operational point of view the measurable ideal gas heat capacities $C^0{}_p(T)$ or $C^0{}_v(T) = C^0{}_p(T) - R$ are augmented to the thermal EOS (1).

Integration yields other ideal gas properties such as enthalpy[1]:

$$h^0(T) = h_0(T_0) + \int_{T_0}^{T} C^0{}_p(T)\, dT \tag{2}$$

internal energy

$$u^0 (T) = u_0 (T_0) + \int_{T_0}^{T} C^0_v (T) \, dT \tag{3}$$

and entropy

$$s^0(T, P) = s_0 (T_0, P_0) + \int_{T_0}^{T} (C^0_p (T) /T)dT - R \ln (P/ P_0) \tag{4}$$

or

$$s^0(T, v) = s_0 (T_0, v_0) + \int_{T_0}^{T} (C^0_v (T) /T)dT + R \ln (v/ v_0) \tag{5}$$

The Gibbs energy can be derived from (3) and (4),

$$\begin{aligned} g^0 (T, P) &= h^0 (T) - T s^0 (T, P) \\ &= h_0 - T s_0 + \int_{T_0}^{T} C^0_p (T) \, dT - \int_{T_0}^{T} (C^0_p (T) /T)dT + R \ln (P/ P_0) \end{aligned} \tag{6}$$

For an ideal gas s_0, u_0 and h_0 are the values of an arbitrary reference state T_0 and P_0 or v_0 which can be freely chosen and $h^0(T)$, $u^0(T)$, $s^0(T, P)$, $s^0(T, v)$, $g^0(T, P)$ indicate these are properties of the ideal gas with respect to the assumed reference state.

Correlations for $C^0_p(T)$ or $C^0_v(T)$ are usually quadratic or cubic polynomials for small temperature intervals. For larger temperature intervals however, extrapolation of quadratic or cubic polynomials might not be accurate. Hence correlations for $C^0_p(T)$ or $C^0_v(T)$ are functions of type [4]

$$C^0_v/R = C_0 + \sum_{i=1}^{n} C_i \frac{(\theta_i\tau)^2 \exp(\theta_i\tau)}{(\exp(\theta_i\tau) - 1)^2} \tag{7}$$

with critical temperature T_c and inverse reduced temperature $\tau = T_c/T$. The coefficients C_i, θ_i and n are usually fitted to experimental heat capacity data. Correlation (7) is based on Einstein's theory of the contributions of molecular vibrations to heat capacity, therefore, often called Einstein terms. The advantage of this correlation is improved extrapolation capability towards higher temperatures.

A FEOS combines the first and second law of thermodynamics. It can be expressed in various forms. Two of those are h(s,P) and u(s,v). For what follows, references [4,5] give further details. The mathematical expression for the first law of thermodynamics is

$$dq = du + dw \tag{8}$$

The definition of reversible work in thermodynamics is ,

$$dw = Pdv \tag{9}$$

The mathematical expression for the second law of thermodynamics involves reversible heat

$$dq = T\,ds \tag{10}$$

Combining (9) and (10) into (8),

$$du = Tds - Pdv \tag{11}$$

which is u(s,v).

To obtain an expression for enthalpy,

$$du + d(Pv) = Tds - Pdv + d(Pv) \tag{12}$$

$$d(u + Pv) = Tds + v\,dP \tag{13}$$

by definition $h \equiv u + Pv$,

$$dh = Tds + v\,dP \tag{14}$$

which is h(s,P) .

Expressions (11) and (14) are FEOS neither of which are explicit in T. Therefore, they cannot be directly derived from, $C^0{}_p(T)$ or $C^0{}_v$ (T) as a function of temperature. To compute them from $C^0{}_p(T)$ or $C^0{}_v$ (T) some mathematical manipulation is necessary.

From (11) and (14) it follows that,

$$T = \left(\frac{\partial h^0}{\partial s}\right)_P \text{and} \quad v = \left(\frac{\partial h^0}{\partial P}\right)_s$$

which transforms the ideal-gas law into,

$$P\left(\frac{\partial h^0}{\partial P}\right)_s = R\left(\frac{\partial h^0}{\partial s}\right)_P \tag{15}$$

Analogously, using internal energy, the ideal gas law can be written as:

$$-v\left(\frac{\partial u^0}{\partial v}\right)_s = R\left(\frac{\partial u^0}{\partial s}\right)_v \tag{16}$$

Upon replacing one of the partial derivatives by Eq (15) in the total differential of the enthalpy, it follows

$$dh^0 = \left(\frac{\partial h^0}{\partial s}\right)_P ds + \left(\frac{\partial h^0}{\partial P}\right)_s dP = \left(\frac{\partial h^0}{\partial s}\right)_P ds + \frac{R}{P}\left(\frac{\partial h^0}{\partial s}\right)_P dP$$

$$= \left(\frac{\partial h^0}{\partial s}\right)_P d\left(s + R\ln\frac{P}{P_0}\right) \tag{17}$$

Accordingly the total differential of internal energy $u^0(s,v)$, can be expressed as :

$$du^0 = \left(\frac{\partial u^0}{\partial s}\right)_v d\left(s - R\ln\frac{v}{v_0}\right) \tag{18}$$

The fundamental equations of state $h^0(s,p)$ and $u^0(s,v)$, therefore , depend only on one independent variable,

$$h^0 = h^0\left(s + R\ln\frac{P}{P_0}\right) \tag{19}$$

or

$$u^0 = u^0\left(s - R\ln\frac{v}{v_0}\right) \tag{20}$$

by which the ideal gas law is automatically fulfilled. Hence instead of having isobars and as a consequence having multiple lines, we can collapse all of them into one line when enthalpy is plotted versus σ, which can be defined as

$$\sigma = s + R \ln\frac{P}{P_0}\,. \tag{21}$$

Similarly all the isochors also collapse into one line when plotting internal energy versus entropy.

An expression for $h^0(s,p)$ can be derived analytically for an ideal gas with constant heat capacity.

$$s - s_0 = C_P^0 \ \ln\frac{T}{T_0} - R \ln\frac{P}{P_0} \tag{22}$$

Solving for temperature leads to

$$T^0(s,P) = T_0 \left(\frac{P}{P_0}\right)^{\frac{R}{C_P^0}} \ \exp\left(\frac{s-s_0}{C_P^0}\right) \tag{23}$$

This is then consequently put into the enthalpy equation along with the substitution for σ after which the enthalpy becomes

$$h^0(\sigma) - h_0 = T_0\, C_P^0 \left[\exp\left(\frac{\sigma}{C_P^0}\right) - 1\right] \tag{24}$$

A similar equation could be established for the internal energy of an ideal gas with a constant heat capacity.

Even for a linear temperature dependence of the heat capacity the FEOS cannot be deduced analytically. It can only be established through the empirical extension of the above equation. In short the solution can be combined as a polynomial with both exponential and algebraic terms. The empirical constants result from regression analysis as was pioneered by Wagner [6].

1.4 FUNDEMENTAL EQUATIONS OF STATE FOR REAL FLUIDS

FEOS for many compounds have been developed from experimental data where the Helmholtz energy is represented as a function just like the function for enthalpy and entropy in the previous section. The Helmholtz energy is split into two parts.

$$a^{r}(T, v) = a(T, v) - a^{0}(T, v)$$

The ideal part of the FEOS $a^{0}(T, v)$ consists of terms like

1. $\ln(\tau)$, where $\tau = T_c/T$
2. $\ln(1-\exp(-n_i\tau))$, where n_i, is a constant depending on the model
3. $\tau \ln(\tau) - \tau$

4. τ^{n_i}

A general form of a correlation is,

$$\alpha^0 = \ln\delta + y_0 + y_1\tau + y_2\ln(\tau) + \sum_{i=4}^{X1} y_i^0 f_i\ (\tau) + \ldots \quad (25)$$

where

$\delta = v_c/v$, where v_c is critical volume and v is volume

y_0, y_1, y_2… are substance specific constants

$\tau = T_c/T$, where T_c is critical volume and T is the temperature

$f_i\ (\tau)$ are functions of temperature as outlined in detail by Tillner-Roth[1]

X1, X2... = 1, 2, …, n , where n is the total number of terms in the expression

The residual term , $\alpha^r(T, v)$, of the Helmhotlz energy is usually of the form

$$\alpha^r = \sum_{i=1}^{IP} y_i\delta^{d_i}\tau^{t_i} + \sum_{i=IP+1}^{IE} y_i\delta^{d_i}\tau^{t_i}\exp(-\delta^{e_i}) + \sum_{i=IE+IP+1}^{IG} y_i\tau^{t_i}\exp(-\delta^2) - 1) \quad (26)$$

where IP,IE IG are the numbers of purely polynomial, polynomial and exponential, and Gaussian terms.

These above correlation models are the results of decades of research. For example, the third term in the residual function whose shape corresponds to a two-dimensional Gaussian was introduced by Setzmann and Wagner [7] in their equation of state for methane. These terms have the largest impact near the critical point $v = v_c$ and $T = T_c$. The larger the distance of the state point from the critical point the lower the influence of such terms .The intention of Gaussian terms is to model the critical region if enough precise measurements are available. Since critical point measurements are very rare and not available for all substances such terms have not been used often.

The above remarks indicate a high level of sophistication for FEOS correlation in terms of the reduced Helmholtz energy. The involved terms are purely empirical and their accuracy is limited by the uncertainty of available experimental data. The development of new terms through new optimization schemes have led to FEOS correlations of outstanding quality. Genetic algorithms developed by Span[4] optimize the functional form of an analytical FEOS correlation by automatically selecting the most influential terms from a bank of terms so that a given data set is represented with the smallest standard deviation possible. As it is not the intention of this work to ponder the optimization and regression analysis the reader is referred to the original literature in the book by Span [4]. Table 1 contains a list of substances used in this thesis. The FEOS for these particular substances are obtained from the work of Tillner-Roth [1] and references therein.

Substances	Validity Range		
	Pmax/MPa	Tmin/K	Tmax/K
Methane	1000	90	625
Ethane	69	90	523
Propane	100	85	600
n-butane	70	134	500
Isobutane	35	113	600
Ethylene	260	103	450
Propylene	200	100	600
Methanol	800	175	570
Ammonia	1000	195	700
Argon	1000	83	700
Fluorine	20	53	300
Helium	100	2	1500
Neon	700	25	700
Oxygen	82	54	300
Nitrogen	1000	63	2000
Trichloromonofluromethane (R11)	200	163	525
Dichlorodifluromethane (R12)	200	116	525
Monochlorodifluromethane (R22)	200	155	525

Difluromethane (R32)	70	136	435
Trichlorotrifluroethane (R113)	200	236	525
2,2-Dichloro-1,1,1-trifluroethane (R123)	40	166	525
2-Chloro-1,1,1,2-tetrafluroethane (R124)	40	100	440
Pentafluroethane (R125)	70	172	440
1,1,1,2-Tetrafluroethane (R134a)	70	170	455
1,1,1-Trifluoroethane (R143a)	35	161	430
1,1-Difluroethane (R152a)	35	154	435

Table 1: Substances used in this work with their range of validity [1].

CHAPTER II

THE PROGRAM

2.1 INTRODUCTION TO THE PROGRAM

From the previous section it follows that very accurate FEOS correlations are available. The objective is to find thermodynamic properties of substances using these FEOS under various state changes. Such state changes involve nonlinear equations including polynomial, exponential and logarithmic terms. Analytical solutions to the problem are not possible. Numerical solution using series approximations and concepts of interval shrinking are necessary. This section discusses how to use the FEOS to develop equations for practical process design involving pure substances. Properties to be considered are

1. Thermal properties
    a. P,v,T data
    b. Compressibility factor $Z \equiv \frac{Pv}{RT}$ (27)
2. Caloric properties

   a. Internal energy u
   b. Entropy s
   c. Enthalpy $h \equiv u + Pv$ (28)
   d. Gibbs energy $g \equiv u + Pv - Ts$ (29)

3. Mechanical coefficients
   a. Isothermal compressibility $\beta_T \equiv -v^{-1}(\frac{\partial v}{\partial P})_T$ (30)
4. Adiabatic coefficients
   a. Speed of sound $w^2 \equiv \frac{-v^2}{M}(\frac{\partial P}{\partial v})_s$ (31)
   b. Joule-Thompson coefficient $\mu_{JT} \equiv (\frac{\partial T}{\partial P})_h$ (32)
5. Caloric coefficients
   a. Isochoric heat capacity $C_v \equiv (\frac{\partial u}{\partial T})_v$ (33)
   b. Isobaric heat capacity $C_p \equiv (\frac{\partial h}{\partial T})_P$ (34)

From the combined first law and second law of thermodynamics one has for the Helmholtz energy the following expression

$$da = -sdT - Pdv \tag{35}$$

Comparing (35) with the purely mathematical result

$$da = \frac{\partial a(T,v)}{\partial T}dT + \frac{\partial a(T,v)}{\partial v}dv \tag{36}$$

yields P and s in terms of partial derivatives a(T,v) which can be used to devise an algorithm. Pressure is therefore the partial derivative of Helmholtz energy with respect to v at constant T. Analytical and numerical methods may be used to compute the partial derivates for equations (25) and (26). Similarly entropy is the partial derivative of the Helmholtz energy with respect to temperature at constant volume. Usually Jacobi transformation [8] is used to compute other thermodynamic properties.

The following is an example given by Lustig [8,9].

According to equation (31) the definition of speed of sound is

$$w \equiv [-\rho M(\partial v/\partial P)_s/v]^{-1/2} \tag{32}$$

The derivative $(\partial v/\partial P)_s$ must be expressed as partial derivates of the Helmholtz energy with respect to T and v. Jacobi transformation accomplishes such tasks. For the problem at hand the method yields, with $\beta \equiv 1/T$ [9]

$$\left(\frac{\partial p}{\partial v}\right)_s \equiv \frac{\partial(p,s)}{\partial(v,s)} = \frac{\frac{\partial(p,s)}{\partial(v,\beta)}}{\frac{\partial(v,s)}{\partial(v,\beta)}} = \frac{\left(\frac{\partial p}{\partial v}\right)_\beta \left(\frac{\partial s}{\partial T}\right)_v - \left(\frac{\partial p}{\partial \beta}\right)_v \left(\frac{\partial s}{\partial v}\right)_\beta}{\left(\frac{\partial s}{\partial \beta}\right)_v} \tag{30}$$

The result is then

$$w(T, v) = \frac{v^2}{M}\left[\frac{\left(\frac{\partial^2 a}{\partial \beta\, \partial v}\right)^2}{\frac{\partial^2 a}{\partial \beta^2}} - \frac{\partial^2 a}{\partial v^2}\right] \tag{31}$$

where, again, $\beta \equiv 1/T$

The above mathematical tools are used to manipulate different thermodynamic properties along different paths into expressions which contain derivatives with respect to (T, v) only.

Property	Helmholtz energy derivatives
Derivatives	$\alpha_\delta \equiv \frac{\partial \alpha}{\partial \delta}, \alpha_\tau \equiv \frac{\partial \alpha}{\partial \tau}, \alpha_{\delta\delta} \equiv \frac{\partial^2 \alpha}{\partial \delta^2}, \alpha_{\delta\tau} \equiv \frac{\partial^2 \alpha}{\partial \delta\, \partial \tau}$
Pressure, P	$RT\delta\alpha_\delta/v$
Volume, v	v (Independent variable)
Temperature, T	T (Independent variable)
Compressibility factor, Z	$1 + \delta\alpha_\delta^r$
Internal energy, u	$RT\tau\alpha_\tau$
Enthalpy, h	$RT(\tau\alpha_\tau + \delta\alpha_\delta)$
Entropy, s	$R(\tau\alpha_\tau - \alpha)$
Gibbs energy, g	$RT(\alpha + \delta\alpha_\delta)$
Isothermal compressibility, β_T	$1/((1+\delta(2\alpha_\delta^r + \delta\alpha_{\delta\delta}^r))(1/v)RT)$

Speed of sound, w^2	$RT(2\delta\alpha_\delta + \delta^2\alpha_{\delta\delta} + (\delta\alpha_\delta - \tau\alpha_{\delta\tau})^2/(C_v/R))$
Joule-Thompson coefficient, μ_{JT}	$\dfrac{-(\delta\alpha_\delta^r + \delta 2\,\alpha_{\delta\delta}^r + \delta\tau\alpha_{\delta\tau}^r)100v}{((1+\delta\alpha_\delta^r - \delta\tau\alpha_{\delta\tau}^r)^2 - \tau^2\alpha_{\tau\tau}(1+2\alpha_\delta^r+\delta^2\alpha_{\delta\delta}^r))R}$
Isochoric heat capacity, C_v	$-R\,\tau^2\alpha_{\tau\tau}$
Isobaric heat capacity, C_p	$R(\left(\frac{C_v}{R}\right) + (\delta\alpha_\delta - \tau\alpha_{\delta\tau})^2 / (2\delta\alpha_\delta + \delta^2\alpha_{\delta\delta}))$

Table 2: The thermodynamic properties computed in this work and their respective Helmholtz energy derivates [1]. Note that τ is proportional to inverse of temperature and δ is proportional to the density.

2.2 INPUTS TO THE PROGRAM

In the previous section we have established that we can compute any thermodynamic property from the FEOS given by $a/RT = \alpha = f(T, v)$. Any thermodynamic state for a pure compound in a single phase can be fixed with any two properties. In this program the properties that were used to fix a state, in addition to temperature and volume, are pressure and entropy. Hence, given any two of the above mentioned properties the program computes a set of 15 thermodynamic properties which includes pressure, volume, temperature, enthalpy, entropy, internal energy, isochoric heat capacity, isobaric heat capacity, speed of sound, isothermal compressibility , Joule-Thompson coefficient.

The objective of the program is not only to find all properties at one particular state but to trace a thermodynamic process as 2- dimensional plot with any two of the fifteen properties as abscissa and ordinate. Hence, the program should find all properties at a given initial state and then select certain paths at certain constant given property based on user inputs. A spreadsheet file is created for each specific compound. In that file any specified path of the state change is input.

Initially, the program asks for the substance. The user can input the name of the compound like methane or R134a. Based on the substance entered the program will chose a corresponding spreadsheet file along with constants such as the critical temperature and critical volume.

The program asks the user to input any two of the four thermodynamic properties pressure, temperature, volume and entropy to compute all thermodynamic properties at that state and asks for the number of state points desired to reach the final state: Obviously, the more points the smoother the curve. Then the program asks to select a certain path for the process: Isothermal, isochoric, isobaric, isentropic or isenthalpic. Finally the program computes all 15 thermodynamic properties at all the intermediate state points from initial to final state. Depending on the user specified input a 2-dimensional plot of any of the 15 properties versus any other can be plotted.

2.3 ALGORITHM

As established by now, a Helmholtz energy correlation as a function of temperature and density allows to compute any thermodynamic property as derivatives. If only one of temperature or density is given along with some other property like pressure or entropy, the problem becomes highly nonlinear with more than 30-40 terms, and analytical solutions are impossible. Even numerical solutions are difficult because the mathematical form of correlations change with substances. A general algorithm for different types of correlation is necessary, which is accomplished by iteration using an initial guess.

Assuming a state point is given by pressure and temperature and the required property is volume, the task is accomplished by using the ideal gas law to guess an initial value for the volume. The pair of volume and temperature are input to the specific Helmholtz energy correlation. Pressure then follows from a differentiation of the correlation according to Table 2. Based on if pressure is higher or lower than the required value the program corrects for the initial value of volume. The procedure is repeated until a user specified convergence criterion is satisfied.

A problem with the proposed algorithm is limited convergence under certain circumstances. A nested iteration scheme is employed. If during the overall iteration the user defined convergence criteria in nested iterations is not met, they are relaxed to progress towards overall convergence.

After computing any thermodynamic property at a given state point the program computes the corresponding properties at a final state point of a given process and also at each specified amount of point in between. The user is asked to input a specific thermodynamic process. The current choices are isochoric, isothermal, isobaric, isentropic and isenthalpic state changes, as most thermodynamic cycles consists of a combination of these. For example, if the process is isothermal the program asks the user for the number of state points and properties to be computed. The more state points between the initial and final state the smoother the resulting curves for the process. The program also requires an input for final state variable like pressure, volume and temperature excluding the property which is being held constant during the process. For example, in an isothermal process the final state property can be any one of pressure, volume or entropy. The program will construct an isothermal path, then use pressure, for example, as a final state point and then partition the path into regular intervals based on user input. Finally, the 15 thermodynamic properties along the path are computed.

The program also allows to plot any property versus any other property. That is, for the above example, the user could plot the Joule-Thompson coefficient (32) versus the isothermal compressibility (30) at constant temperature.

2.4 USED METHODS IN THE PROGRAM

The above is an overview of the overall algorithm. This section explains individual MATLAB functions. A driver program and subroutines (functions) compute the thermodynamic property from the specific Helmholtz energy. In the following, subsection titles are identical to MATLAB function names.

1. **main_code.m**

   A driver program runs the overall code and will invoke different subroutines to perform specific tasks. The driver asks the user for all inputs including the substance, initial and final state points, the particular process and the properties to be displayed. It then searches the data banks for the respective FEOS correlation constants and applies them in further subroutines.

2. **display_properties.m**

   Displays a set of 15 thermodynamic properties at a given state point. Input arguments are volume, pressure, temperature, critical volume, critical temperature and molecular mass.

3. **compute_properties.m**

   Computes a set of 15 thermodynamic properties at a given state point. Input arguments are volume, pressure, temperature, critical volume, critical temperature and molecular mass. Output is a 1x15 vector of the 15 properties at each state point.

4. **first_do_res .m and first_do_id.m**

First order partial derivative of the specific Helmholtz energy with respect to reduced density. Output is the numerical value of the derivative.

5. **first_tau_res.m and first_tau_id.m**

   First order partial derivative of the specific Helmholtz energy with respect to inverse reduced temperature. Output is the numerical value of the derivative.

6. **first_do_first _tau_res .m**

   Second order mixed partial derivative of the specific Helmholtz energy with respect to reduced density and inverse reduced temperature are computed. Details are as above.

7. **sec_do_res.m and sec_do_id.m**

   Second order partial derivative of the specific Helmholtz energy with respect to reduced density are computed. Details are as above.

8. **sec_tau_res.m and sec_tau_id.m**

   Second order partial derivative of specific Helmholtz energy with respect to inverse reduced temperature. Details are as above.

9. **find_vol_tp.m**

   Volume of a given state if temperature and pressure are specified.

10. **find_vol_st.m**

    Volume of a given state if entropy and temperature are specified

11. **Find_temp_vp.m**

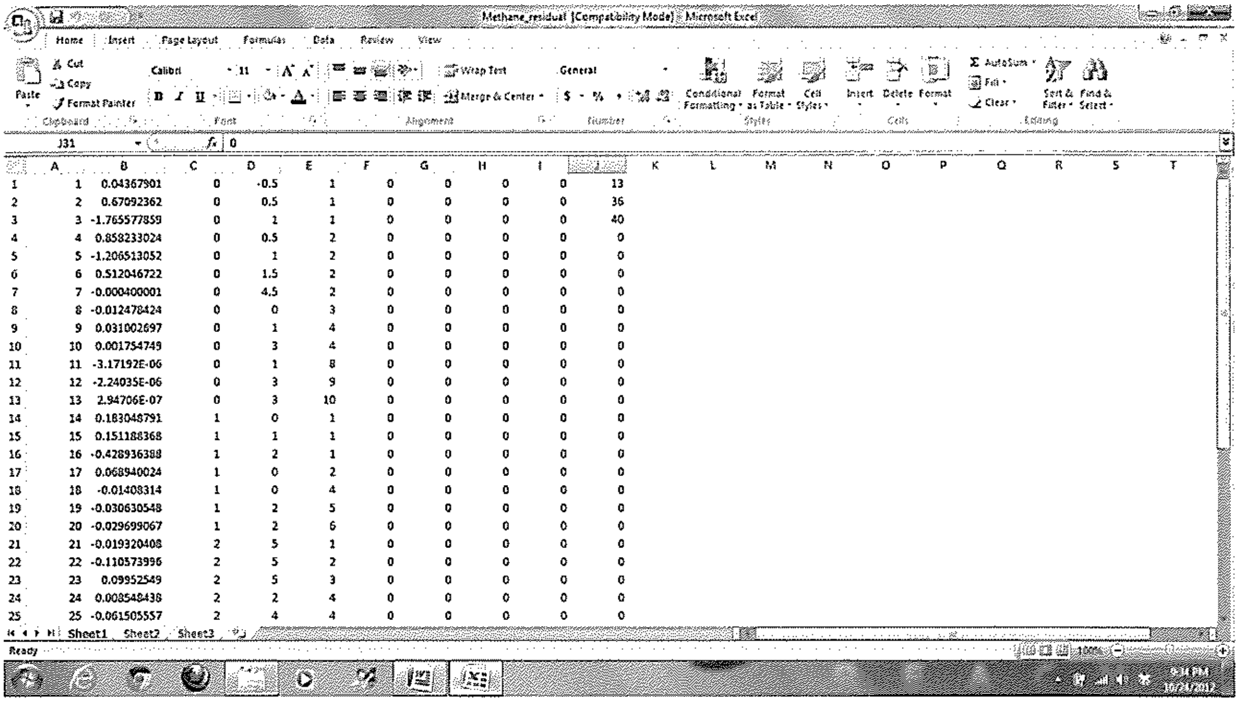
    Temperature of a given state if volume and pressure are specified.

12. **Find_temp_sv.m**

    Temperature of a given state if entropy and volume are specified.

For modules 9-12, the iterative algorithm is based on directional search of roots. Starting with an initial guess for whichever property, the program computes the deviation from the target property. Based on that error it narrows the guess to converge to a specified tolerance.

Data spreadsheets are Microsoft Excel data sheets which contain all model parameters for a specific compound. Every compound will have two such data sheets, one for the ideal and one for the residual part of the FEOS correlation according to equations (25) and (26). A sample screenshot of the data sheet for methane is shown in Figure 1.



J31 = 0

	A	B	C	D	E	F	G	H	I	J
1	1	0.04367901	0	-0.5	1	0	0	0	0	13
2	2	0.67092362	0	0.5	1	0	0	0	0	36
3	3	-1.765577859	0	1	1	0	0	0	0	40
4	4	0.858233024	0	0.5	2	0	0	0	0	0
5	5	-1.206513052	0	1	2	0	0	0	0	0
6	6	0.512046722	0	1.5	2	0	0	0	0	0
7	7	-0.000400001	0	4.5	2	0	0	0	0	0
8	8	-0.012478424	0	0	3	0	0	0	0	0
9	9	0.031002697	0	1	4	0	0	0	0	0
10	10	0.001754749	0	3	4	0	0	0	0	0
11	11	-3.17192E-06	0	1	8	0	0	0	0	0
12	12	-2.24035E-06	0	3	9	0	0	0	0	0
13	13	2.94706E-07	0	3	10	0	0	0	0	0
14	14	0.183048791	1	0	1	0	0	0	0	0
15	15	0.151188368	1	1	1	0	0	0	0	0
16	16	-0.428936388	1	2	1	0	0	0	0	0
17	17	0.068940024	1	0	2	0	0	0	0	0
18	18	-0.01408314	1	0	4	0	0	0	0	0
19	19	-0.030630548	1	2	5	0	0	0	0	0
20	20	-0.029699067	1	2	6	0	0	0	0	0
21	21	-0.019320408	2	5	1	0	0	0	0	0
22	22	-0.110573996	2	5	2	0	0	0	0	0
23	23	0.09952549	2	5	3	0	0	0	0	0
24	24	0.008548438	2	2	4	0	0	0	0	0
25	25	-0.061505557	2	4	4	0	0	0	0	0

Figure 1: Model constants in the residual part of the methane FEOS correlations. Each column represents a constant from equation (26). For example, row 13 column D is the value of the model parameter t for the thirteenth term in the residual part of methane FEOS correlation.

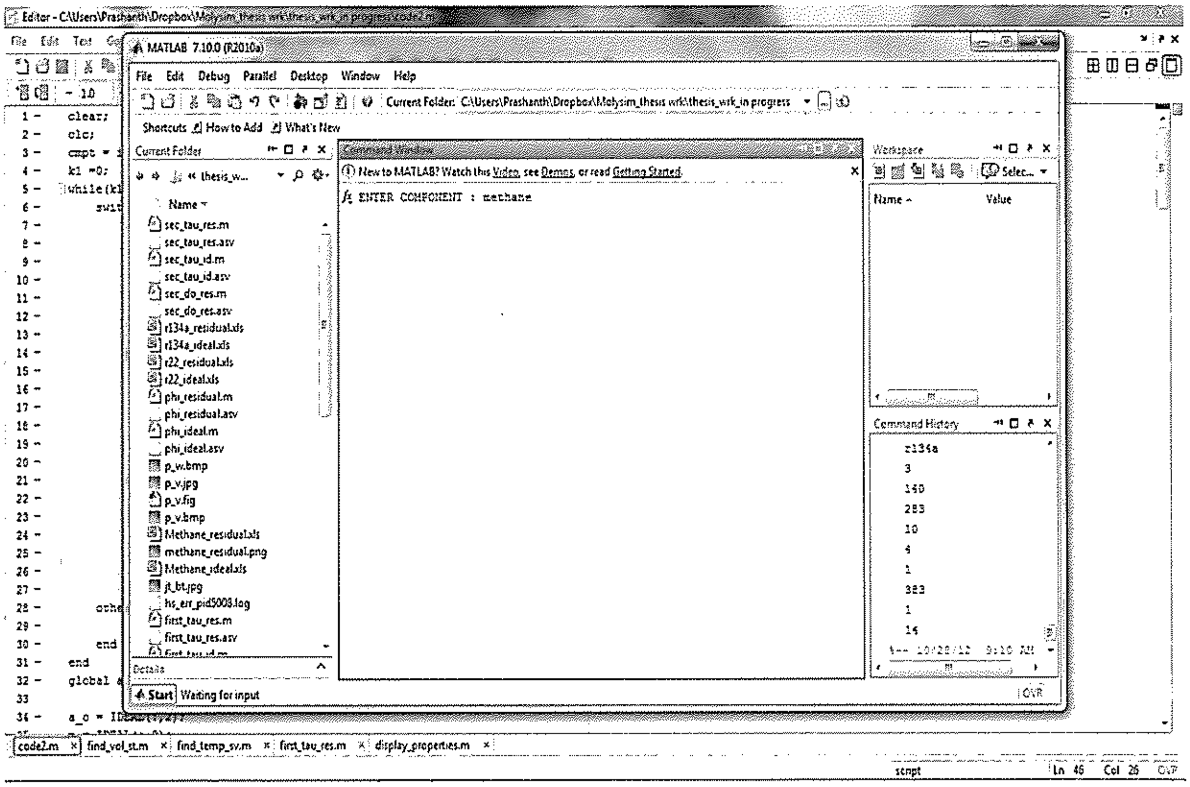
2.5 ESTIMATION OF STATE POINTS

Again, the user can choose different paths for a given substance to proceed from one state point to another: Constant temperature, constant pressure, constant volume, constant entropy and constant enthalpy. The objective of the program is to compute the set of thermodynamic properties along the path and plot them as a curve as chosen by the user. The computation of properties at intermediate state points becomes relevant. For example, an isothermal process with initial state defined and a final pressure requested at a number of intermediate states defined by the user, the program partitions the process. This information is then stored as a pressure vector. For each pressure in the vector other thermodynamic properties are computed and they are also stored as respective vectors. Hence, the program populates 15 vectors of each thermodynamic property at each state.

CHAPTER III

RESULTS AND DISCUSSION

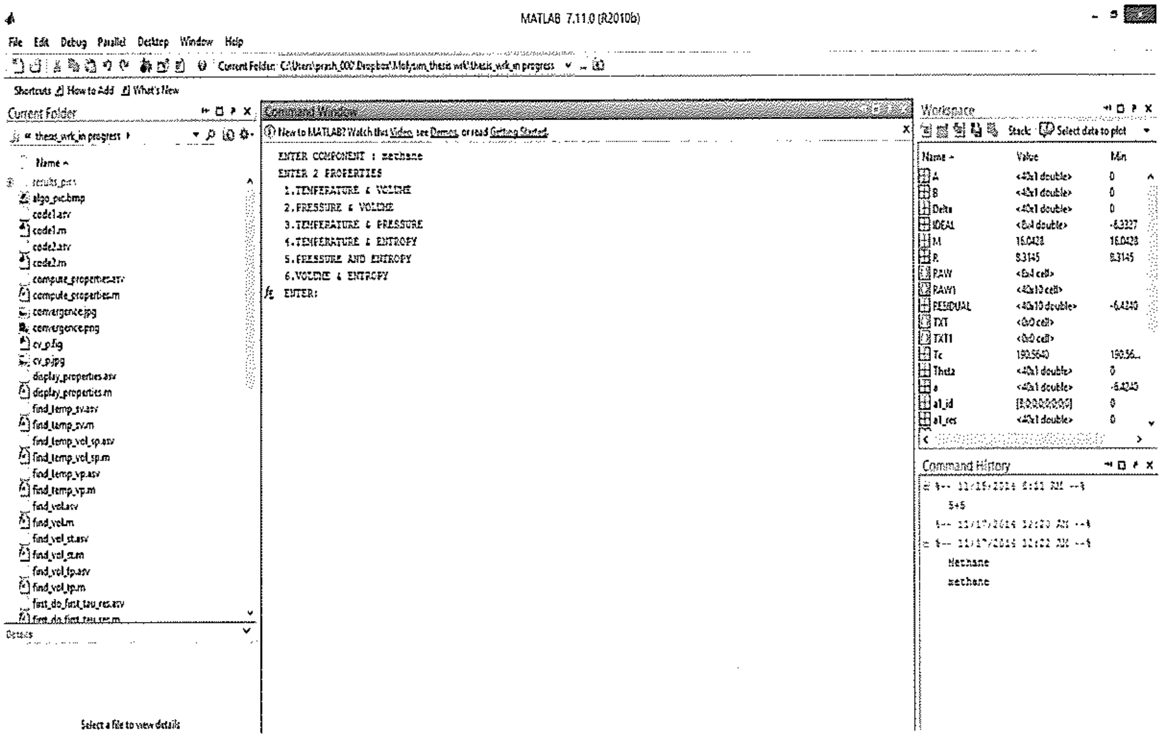
In this section some results are shown as screenshots generated by the program. The screen shots are taken at consecutive input screens and resulting output screens.



```
ENTER COMPONENT : methane
```

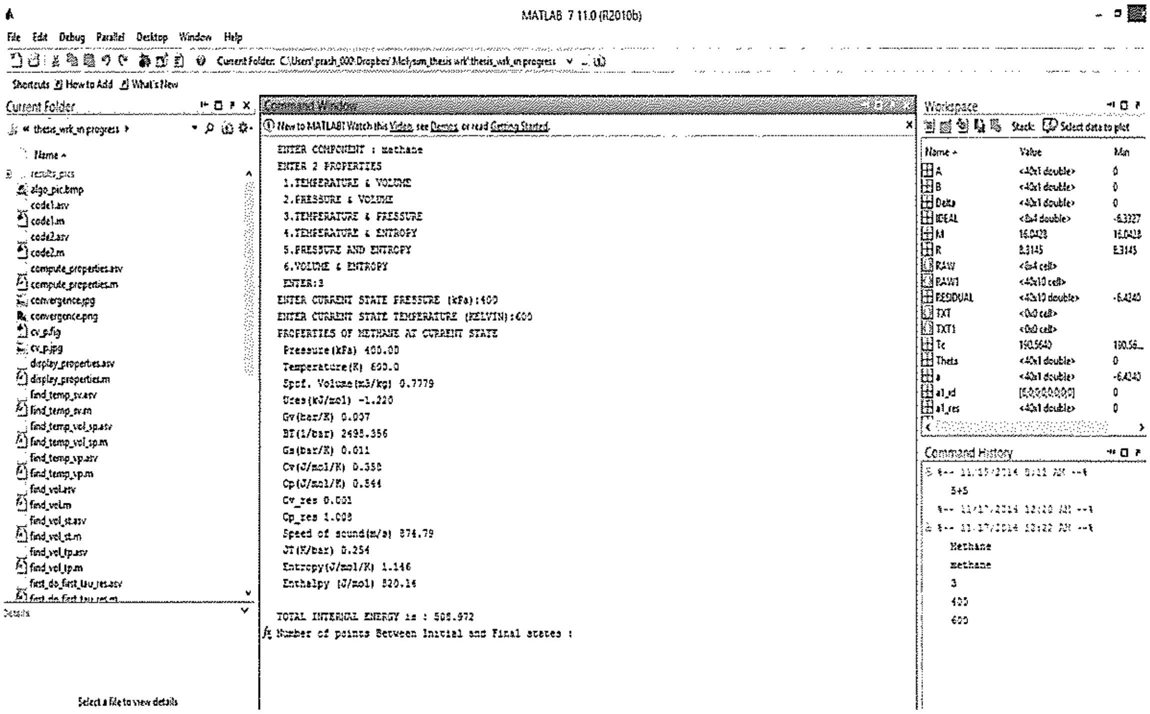
```
r134a
3
140
283
10
4
1
383
1
14
%-- 10/28/12  9:10 AM
```

Figure 2: Initial run screen. Input is the substance, here methane.



```
ENTER COMPONENT : methane
ENTER 2 PROPERTIES
 1.TEMPERATURE & VOLUME
 2.PRESSURE & VOLUME
 3.TEMPERATURE & PRESSURE
 4.TEMPERATURE & ENTROPY
 5.PRESSURE AND ENTROPY
 6.VOLUME & ENTROPY
fx ENTER:
```

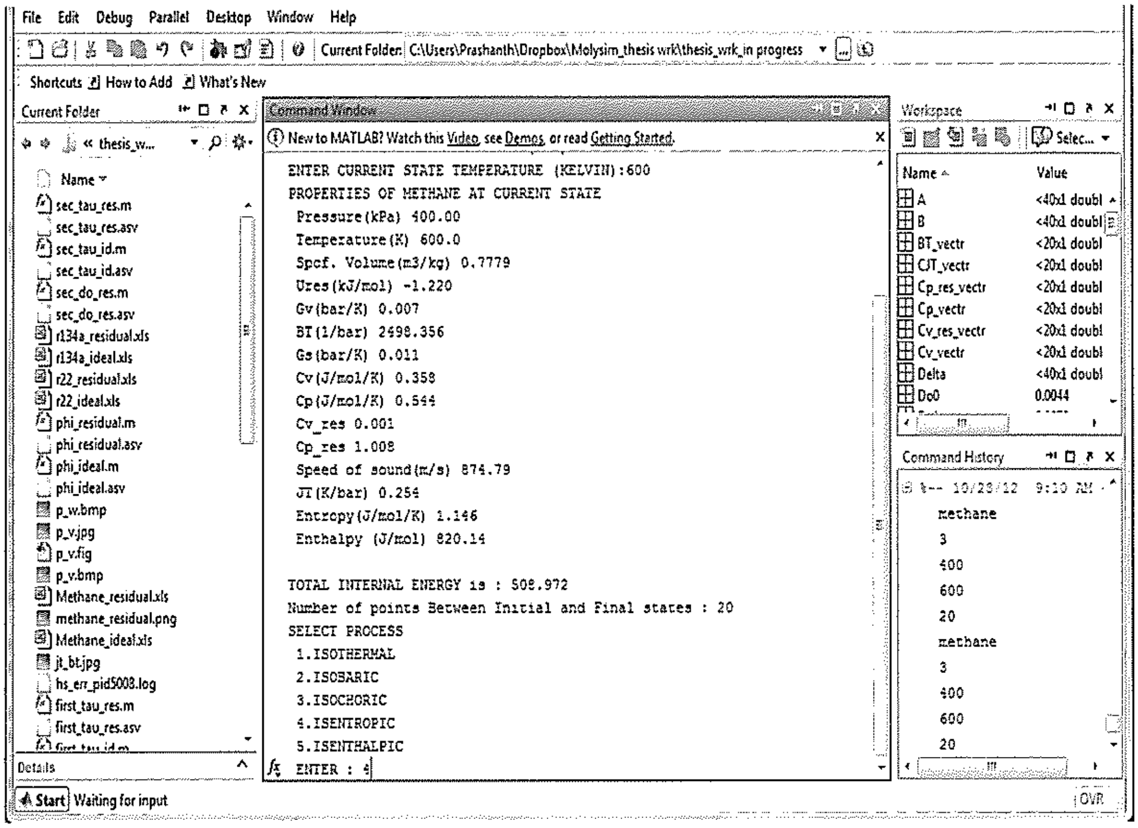
Figure 3: Second run screen. Input initial state variables.



```
ENTER COMPONENT : methane
ENTER 2 PROPERTIES
 1.TEMPERATURE & VOLUME
 2.PRESSURE & VOLUME
 3.TEMPERATURE & PRESSURE
 4.TEMPERATURE & ENTROPY
 5.PRESSURE AND ENTROPY
 6.VOLUME & ENTROPY
 ENTER:3
ENTER CURRENT STATE PRESSURE (kPa):400
ENTER CURRENT STATE TEMPERATURE (KELVIN):600
PROPERTIES OF METHANE AT CURRENT STATE
 Pressure(kPa) 400.00
 Temperature(K) 600.0
 Spcf. Volume(m3/kg) 0.7779
 Ures(kJ/mol) -1.220
 Gv(bar/K) 0.007
 BT(1/bar) 2495.356
 Gs(bar/K) 0.011
 Cv(J/mol/K) 0.350
 Cp(J/mol/K) 0.544
 Cv_res 0.001
 Cp_res 1.008
 Speed of sound(m/s) 374.79
 JT(K/bar) 0.254
 Entropy(J/mol/K) 1.146
 Enthalpy (J/mol) 520.14

TOTAL INTERNAL ENERGY is : 508.972
fx Number of points Between Initial and Final states :
```

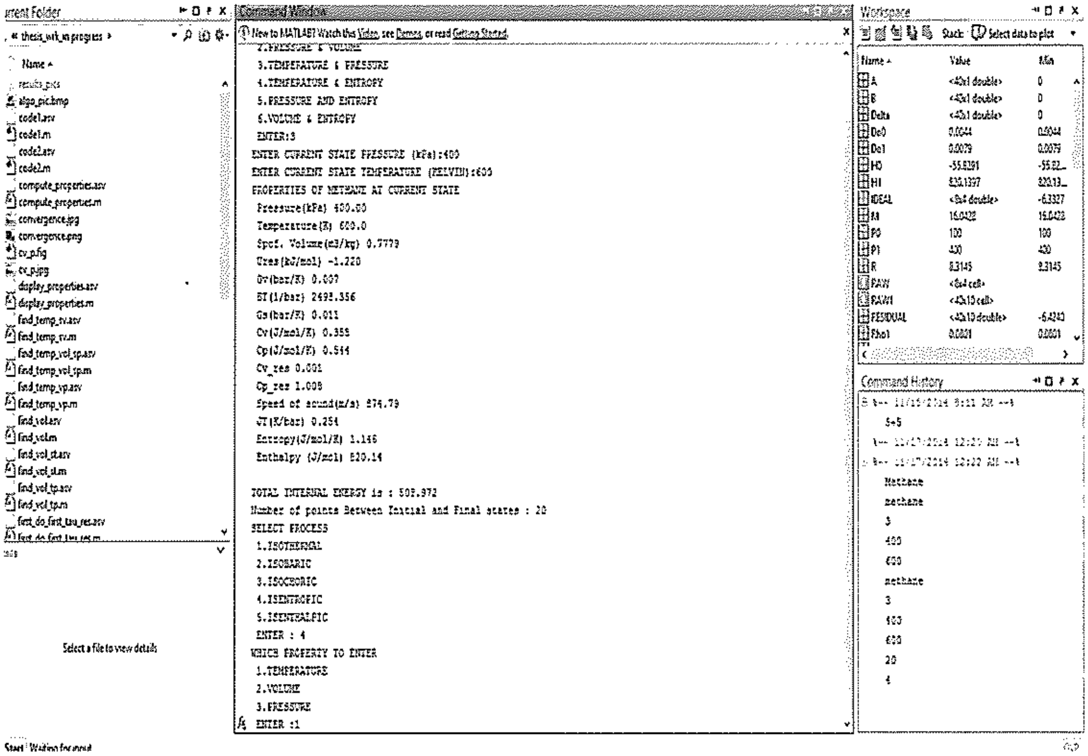
Figure 4: Property data for the given state point. In the current example for methane at state point 400 kPa and 600 K the thermodynamic properties are computed.



```
ENTER CURRENT STATE TEMPERATURE (KELVIN):600
PROPERTIES OF METHANE AT CURRENT STATE
 Pressure(kPa) 400.00
 Temperature(K) 600.0
 Spcf. Volume(m3/kg) 0.7779
 Ures(kJ/mol) -1.220
 Gv(bar/K) 0.007
 BT(1/bar) 2498.356
 Gs(bar/K) 0.011
 Cv(J/mol/K) 0.358
 Cp(J/mol/K) 0.544
 Cv_res 0.001
 Cp_res 1.008
 Speed of sound(m/s) 874.79
 JT(K/bar) 0.254
 Entropy(J/mol/K) 1.146
 Enthalpy (J/mol) 820.14

TOTAL INTERNAL ENERGY is : 508.972
Number of points Between Initial and Final states : 20
SELECT PROCESS
 1.ISOTHERMAL
 2.ISOBARIC
 3.ISOCHORIC
 4.ISENTROPIC
 5.ISENTHALPIC
 ENTER : 4
```

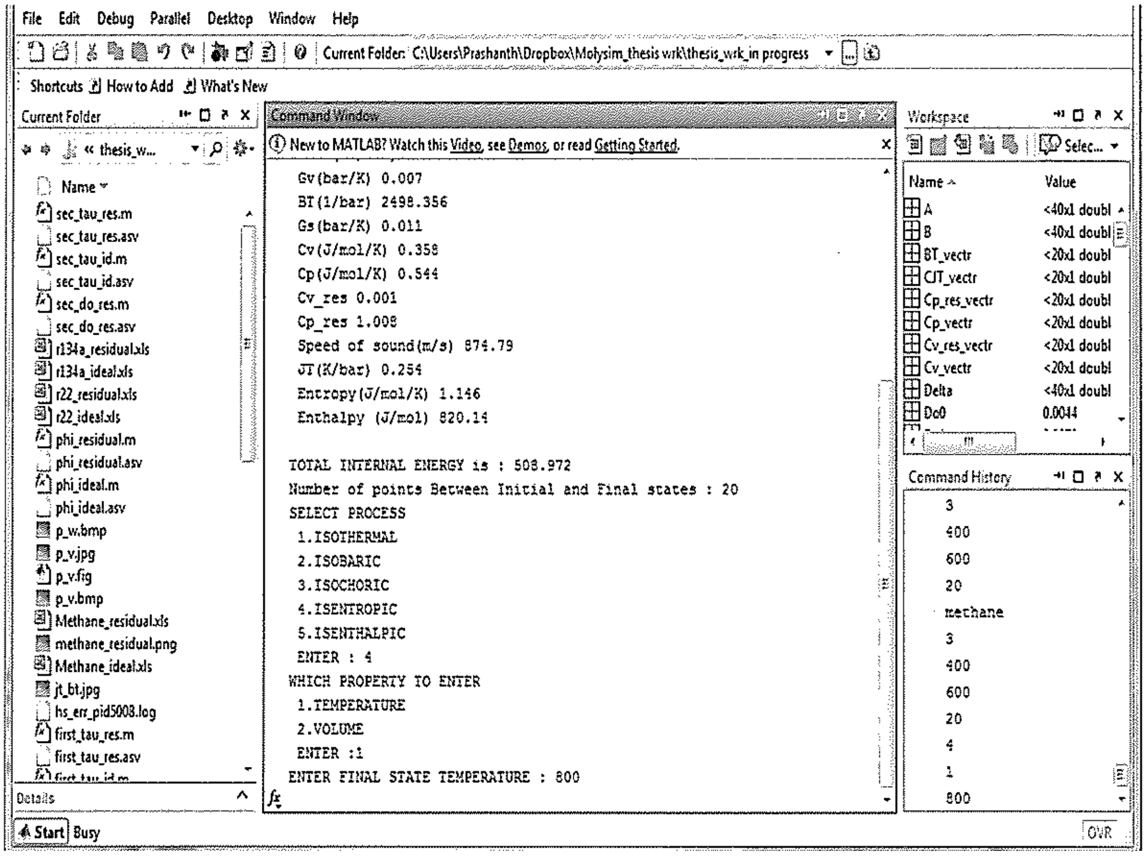
Figure 5: Selection of paths for the program to trace. In the current example, the user selects an isentropic process.



```
 2.PRESSURE & VOLUME
 3.TEMPERATURE & PRESSURE
 4.TEMPERATURE & ENTROPY
 5.PRESSURE AND ENTROPY
 6.VOLUME & ENTROPY
 ENTER:3
ENTER CURRENT STATE PRESSURE (kPa):400
ENTER CURRENT STATE TEMPERATURE (KELVIN):600
PROPERTIES OF METHANE AT CURRENT STATE
 Pressure(kPa) 400.00
 Temperature(K) 600.0
 Spcf. Volume(m3/kg) 0.7779
 Ures(kJ/mol) -1.220
 Gv(bar/K) 0.007
 BT(1/bar) 2495.356
 Gs(bar/K) 0.011
 Cv(J/mol/K) 0.355
 Cp(J/mol/K) 0.544
 Cv_res 0.001
 Cp_res 1.005
 Speed of sound(m/s) 574.79
 JT(K/bar) 0.254
 Entropy(J/mol/K) 1.146
 Enthalpy (J/mol) 520.14

TOTAL INTERNAL ENERGY is : 507.972
Number of points Between Initial and Final states : 20
SELECT PROCESS
 1.ISOTHERMAL
 2.ISOBARIC
 3.ISOCHORIC
 4.ISENTROPIC
 5.ISENTHALPIC
 ENTER : 4
WHICH PROPERTY TO ENTER
 1.TEMPERATURE
 2.VOLUME
 3.PRESSURE
 ENTER :1
```

Figure 6: Upon selection of a process, a final state point is selected. In the current example, the user selects temperature.



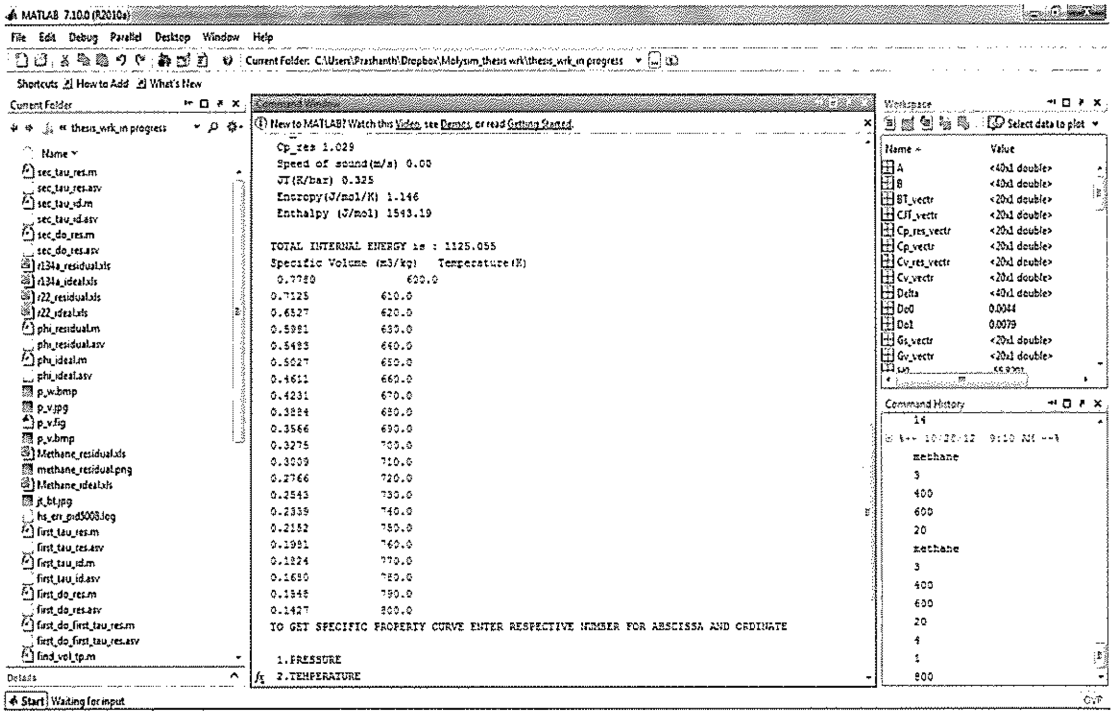
```
  Gv(bar/K) 0.007
  BT(1/bar) 2498.356
  Gs(bar/K) 0.011
  Cv(J/mol/K) 0.358
  Cp(J/mol/K) 0.544
  Cv_res 0.001
  Cp_res 1.008
  Speed of sound(m/s) 874.79
  JT(K/bar) 0.254
  Entropy(J/mol/K) 1.146
  Enthalpy (J/mol) 820.14

 TOTAL INTERNAL ENERGY is : 508.972
 Number of points Between Initial and Final states : 20
 SELECT PROCESS
  1.ISOTHERMAL
  2.ISOBARIC
  3.ISOCHORIC
  4.ISENTROPIC
  5.ISENTHALPIC
  ENTER : 4
 WHICH PROPERTY TO ENTER
  1.TEMPERATURE
  2.VOLUME
  ENTER :1
 ENTER FINAL STATE TEMPERATURE : 800
```

Name	Value
A	<40x1 doubl
B	<40x1 doubl
BT_vectr	<20x1 doubl
CJT_vectr	<20x1 doubl
Cp_res_vectr	<20x1 doubl
Cp_vectr	<20x1 doubl
Cv_res_vectr	<20x1 doubl
Cv_vectr	<20x1 doubl
Delta	<40x1 doubl
Do0	0.0044

```
3
400
600
20
methane
3
400
600
20
4
1
800
```

Figure 7: Upon defining a final state point, the program computes properties at each state point along the selected process. In the example, for 20 state points between T= 600 K and T = 800 K the program computes properties.



```
 Cp_res 1.029
 Speed of sound(m/s) 0.00
 JT(K/bar) 0.325
 Entropy(J/mol/K) 1.146
 Enthalpy (J/mol) 1543.19

TOTAL INTERNAL ENERGY is : 1125.055
Specific Volume (m3/kg)   Temperature(K)
 0.7780           600.0
0.7125          610.0
0.6527          620.0
0.5981          630.0
0.5483          640.0
0.5027          650.0
0.4611          660.0
0.4231          670.0
0.3884          680.0
0.3566          690.0
0.3275          700.0
0.3009          710.0
0.2766          720.0
0.2543          730.0
0.2339          740.0
0.2152          750.0
0.1981          760.0
0.1824          770.0
0.1680          780.0
0.1546          790.0
0.1427          800.0
TO GET SPECIFIC PROPERTY CURVE ENTER RESPECTIVE NUMBER FOR ABSCISSA AND ORDINATE

 1.PRESSURE
 2.TEMPERATURE
```

```
  14
%-- 10/22/12  9:10 AM --%
  methane
  3
  400
  600
  20
  methane
  3
  400
  600
  20
  4
  1
  800
```

Figure 8: Screenshot for T, v data for points between the initial and final state points along an isentropic process.

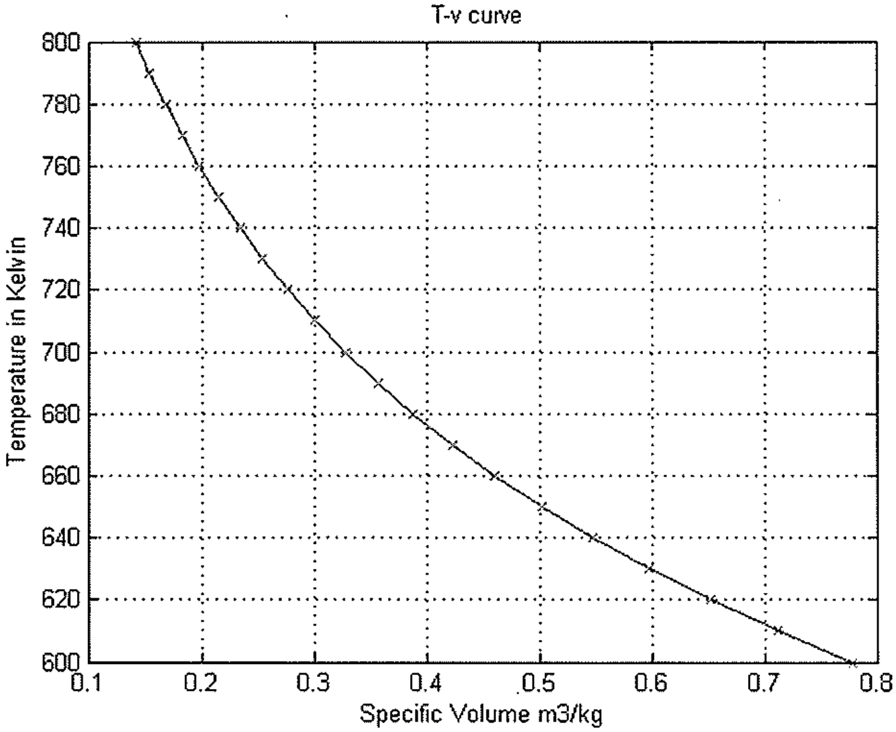
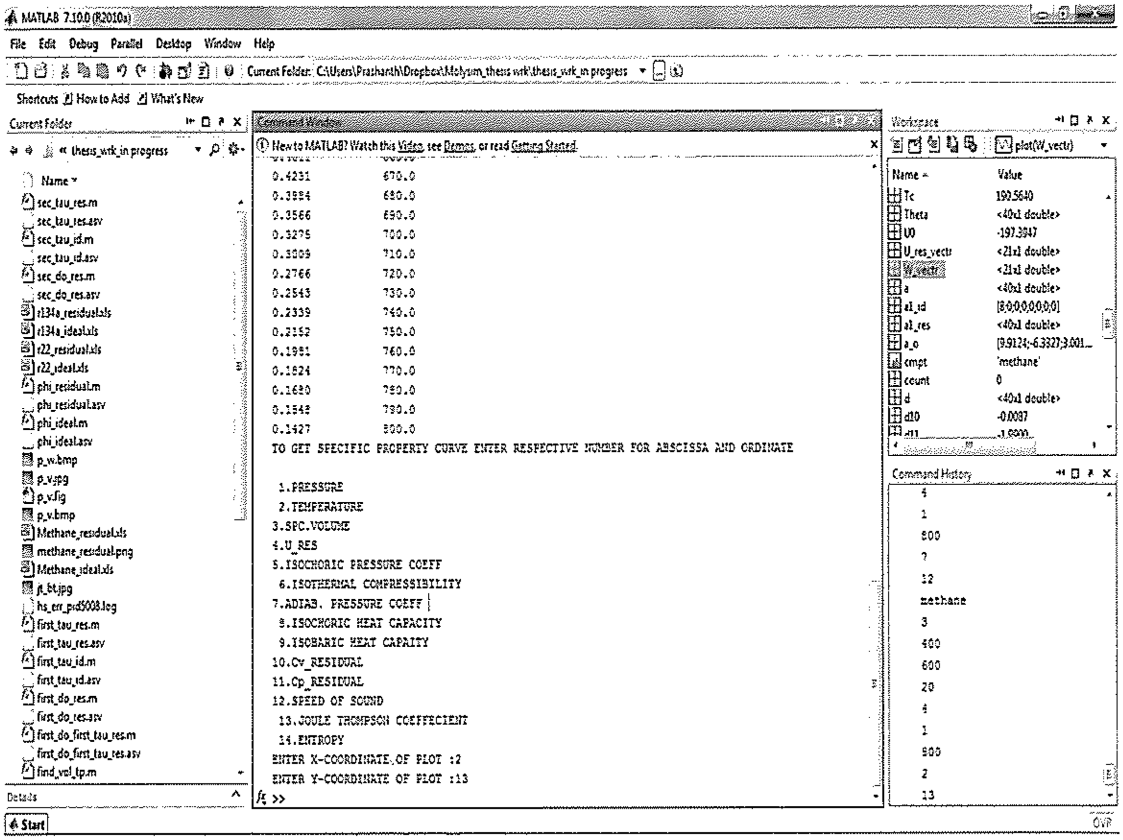


Figure 9: Representation of a T, v curve for an isentropic process.



```
0.4231          670.0
0.3984          680.0
0.3566          690.0
0.3275          700.0
0.3009          710.0
0.2766          720.0
0.2543          730.0
0.2339          740.0
0.2152          750.0
0.1981          760.0
0.1824          770.0
0.1680          780.0
0.1548          790.0
0.1427          800.0
TO GET SPECIFIC PROPERTY CURVE ENTER RESPECTIVE NUMBER FOR ABSCISSA AND ORDINATE

 1.PRESSURE
 2.TEMPERATURE
3.SPC.VOLUME
4.U_RES
5.ISOCHORIC PRESSURE COEFF
 6.ISOTHERMAL COMPRESSIBILITY
7.ADIAB. PRESSURE COEFF
 8.ISOCHORIC HEAT CAPACITY
 9.ISOBARIC HEAT CAPAITY
10.Cv_RESIDUAL
11.Cp_RESIDUAL
12.SPEED OF SOUND
 13.JOULE THOMPSON COEFFECIENT
 14.ENTROPY
ENTER X-COORDINATE OF PLOT :2
ENTER Y-COORDINATE OF PLOT :13
>>
```

Name	Value
Tc	190.5640
Theta	<40x1 double>
U0	-197.3947
U_res_vectr	<21x1 double>
W_vectr	<21x1 double>
a	<40x1 double>
a1_id	[8;0;0;0;0;0;0;0]
a1_res	<40x1 double>
a_o	[9.9124;-6.3327;3.001...
cmpt	'methane'
count	0
d	<40x1 double>
d10	-0.0087

```
4
1
800
7
12
methane
3
400
600
20
4
1
800
2
13
```

Figure 10: Screenshot of the property input screen to generate a 2-dimensional plot of any two properties.

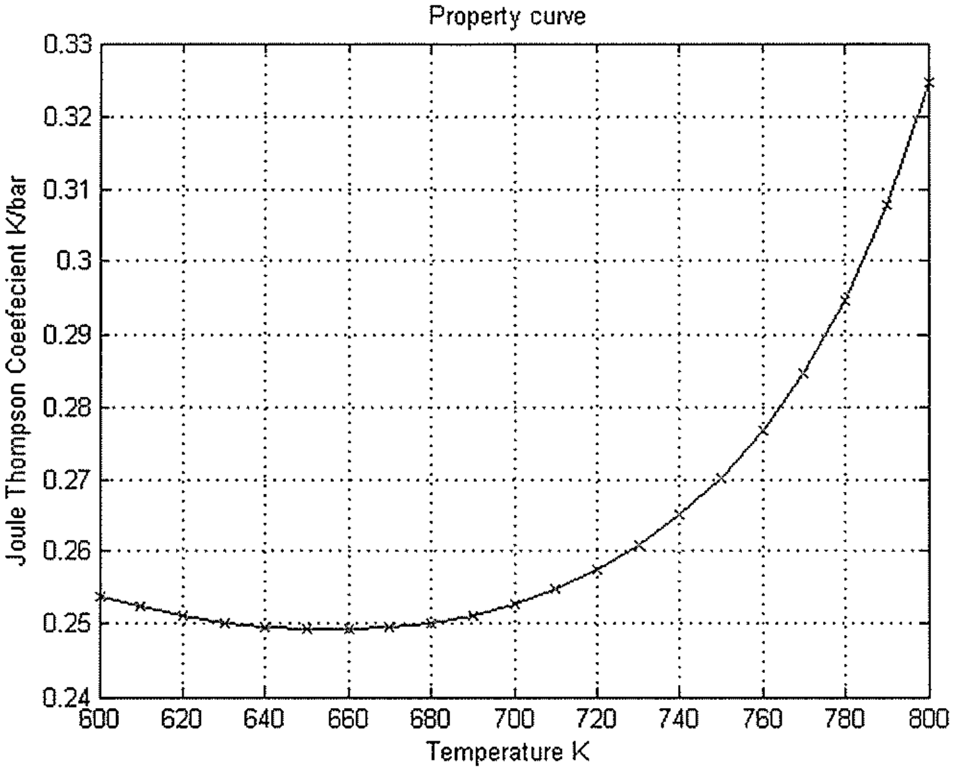


Figure 11: Example of 2- dimensional property plot where the x and y-coordinate can be any of the 15 properties computed in this work. The present case is a plot of the Joule-Thompson coefficient versus temperature for methane at constant entropy.

CHAPTER IV

CONCLUSION AND FUTURE WORK

The objective of this study was to use highly accurate fundamental equations of state correlations to trace thermodynamic paths which are common in technological processes. Owing to the complexity of these correlations, analytical methods for tracing state changes are impossible. Iterative methods, of which the suggested ones are an example, are the only alternatives. The results are accurate to the combined accuracy of the correlations and the algorithms used. Anyone interested in arbitrary state changes as for the investigation of new working fluids, can directly use the results of this work.

Future work may involve addition of more compounds to the data bank. Such new correlations can be included in spreadsheets to be imported into the program directly. Another important future work is the inclusion of phase equilibrium and the development of phase transition envelopes. The program written in this study excludes state points inside the vapor-liquid phase envelope. Property values returned by the program at such state points will not be accurate, as conditions for phase equilibrium are not included. Since there are no strictly isothermal or adiabatic paths in real processes the paths traced by the program might not be an accurate representation of the processes. To mitigate this issue a modification can be made in the source code to set properties as function of other properties to present a more realistic simulation of a path of a process.

The source code is available upon request to prashanth.87@gmail.com. A CD copy of the source code is available from the Department of Chemical Engineering at Cleveland State University upon request.

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