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**ADVANCED FUEL PROPERTIES -
A Computer Program for
Estimating Property Values**



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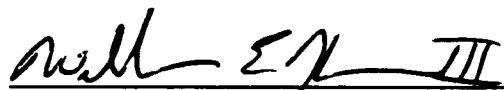
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1.0 INTRODUCTION

The successful development and production of fuels needed for the high performance aircraft of the future must overcome two technical hurdles. The source of raw materials is changing from relatively light, paraffinic petroleum to hydrocarbons from other sources that may be much more aromatic and contain higher levels of contaminants. In addition, the performance specifications of the engine and fuel system may extend to regions beyond that attainable by the fuels of today.

2.0 OBJECTIVES

The overall objective of this program is to develop a tool that will accurately predict the bulk fuel properties of a complex mixture of hydrocarbons and, thereby, aid in the design of fuels based on satisfying a set of specified fuel properties.

The objective of Phase I was to be able to predict desired physical and thermochemical properties of pure organic compounds based solely upon the knowledge of their molecular structures.

The objective of Phase II was to thoroughly test the properties developed in Phase I, and develop a method for obtaining the mixture properties from the pure component properties.

The objective of Phase III was to implement the methods developed in Phase II and test the overall performance of the calculations.

3.0 BACKGROUND

3.1 Aircraft Fuels. The changing quality of petroleum and the possible introduction of fuels derived from tar sand, oil shale, and coal will place new demands on analytical techniques and specification development. Fuels for future applications may require properties beyond those needed today. To solve these problems, a greater understanding of the relationship of fuel structure at the molecular level and the bulk fuel properties is needed.

3.2 Predictive Techniques. To cope with the complexity of current fuels and the large numbers of potential components of future fuels, the use of mathematical techniques is valuable in studying the structure-property

relationships of fuel components. Graph theory, group additivity, and multivariate statistics are all important tools.

The application of mathematical techniques depends on accurate experimental data. In addition, the broad base of current knowledge which has resulted in what is termed "empirical correlations" is also a valuable technique to augment the more fundamental approach.

3.3 Overall Approach. The strategy used was to make maximum use of available data, and use both theories based solely on structure and empirical relationships derived from experiment to predict properties of single compounds. Published methods for estimating properties from structure or empirical correlations were used where available. In addition, for some properties, graph theory was used to develop structure-property correlations by statistical analysis.

The methods used to obtain properties of mixtures had largely been coded into a program called DETHERM-SDC¹. This program is available commercially, but is exceedingly difficult to use. DETHERM-SDC contains its own data base of pure compounds, which are used along with interaction parameters, to estimate the properties of mixtures. That data base is extensive for vapor-liquid equilibrium data, but very limited for physical properties.

We used the pure-component estimations developed in this program to provide the input to DETHERM, to vastly increase the variety of compounds which could be included in mixtures. We integrated the programs into a common, user-friendly, interface, to increase the usability of the mixture calculations.

3.4 Historical Perspective. Predicting the physical properties of gases and liquids has long been a major goal of physical chemists. By the early 1950s, accurate structure-based theories had been developed for gas densities, thermodynamics, and transport properties²; reliable experimental data for gases and liquids were also available from the American Petroleum Institute³, National Bureau of Standards⁴ and JANAF Tables⁵; and the Hougen-Watson Tables permitted predictions of liquid and gas compressibilities and thermodynamic functions⁶. Since the 1950s, increasingly complex correlations for a wide range of properties have been developed^{7,8}, but they still use inputs of both experimental and structure-based data. Apparently, now it is possible to predict most of the properties of gases and liquids using only their molecular structures.

3.5 Interrelationships of Properties. The phase diagrams (P-T curve shown in Figure 3.5-1) of all pure compounds have separate regions for solid, liquid, vapor, and supercritical fluid phases. For temperatures greater than the critical point (C) or for pressures greater than the critical point with temperatures greater than those on the fusion curve, only a supercritical fluid phase is present. Comparisons of these P-T curves for several substances led to formulation of the law of corresponding states.² According to this empirical law, if the temperature, pressure, and volume are scaled by the critical temperature (T_c), pressure (P_c), and volume (V_c), all substances obey the same equation of state.

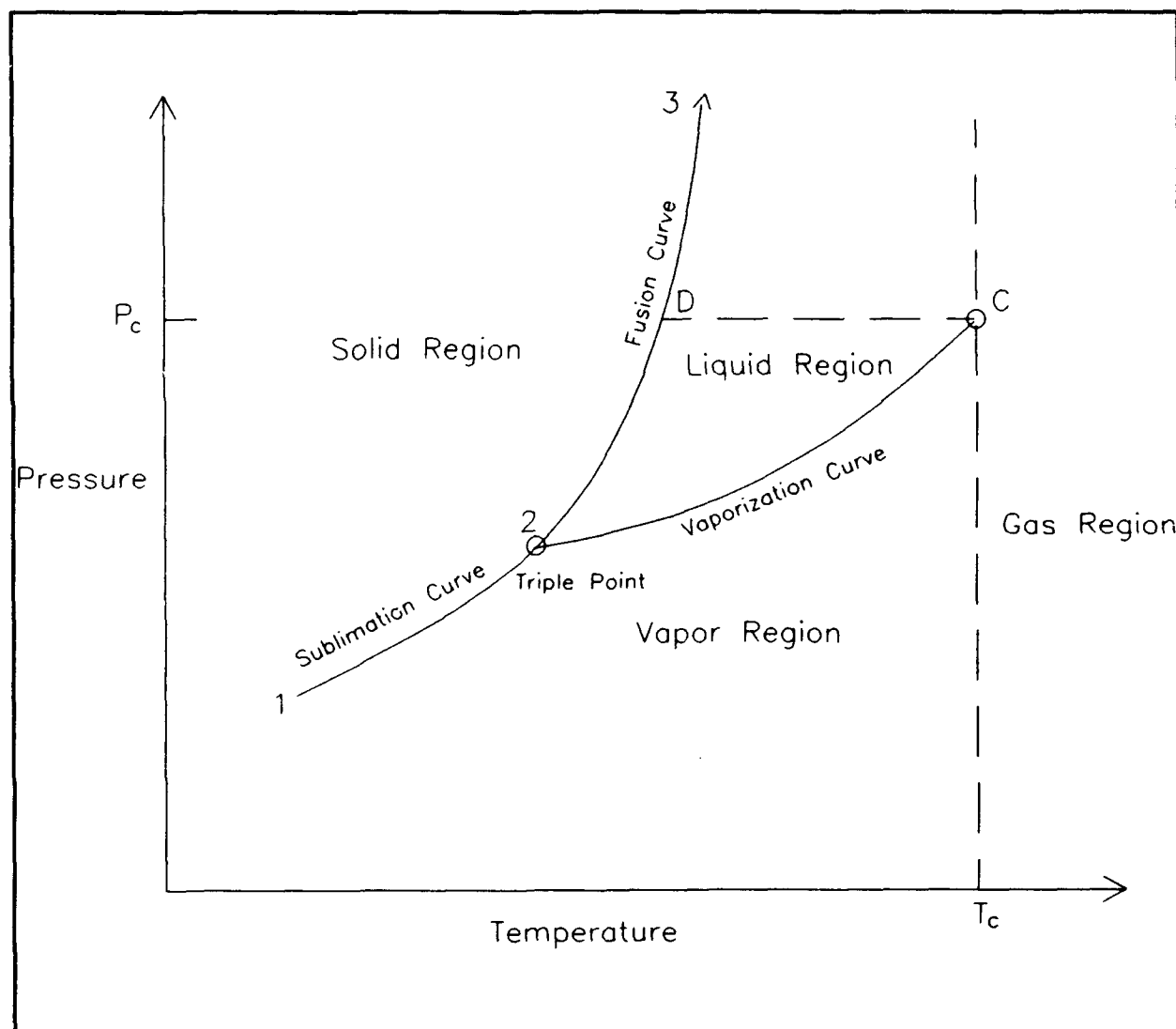


Figure 3.5-1
P-T Curves for a Pure Compound

Nearly all of the correlations available for the properties of real gases and liquids are based upon the law of corresponding states. For nonspherical and polar molecules, correction factors are also added into the property correlations to consider the shape of the molecules. The most widely used of these "structural parameters" are the acentric factor, ω , the Rackett parameter, Z_{RA} , and the COSTALD parameters, ϕ_{SRK} and V^* . Careful analysis of the API and AIChE methods for predicting the properties of pure liquids and gases^{7,8} shows that all the properties can be predicted given values of T_c , P_c , Z_{RA} , ω , ϕ_{SRK} , V^* , and two physical properties: the normal boiling point and liquid density at one temperature. (Note: these correlations also contain parameters which can be calculated directly from molecular structure.) The strategy taken was to develop highly accurate structure-based correlations for these eight key properties since they are used in many other predictive methods.

Mixture properties can also be obtained from the eight key properties listed above. Some of the methods used to determine the properties of pure compounds can be extended to a mixture of compounds by applying mixture rules. The mixture rules adjust parameters found in equations of state so that the equations account for the interactions between compounds. The pure component properties, pure component coefficients, as well as binary interaction parameters for each compound pair in the mixture are determined when AFP begins to perform mixture calculations.

4.0 PHASE I TASK REVIEW

This section reviews the work of Phase I of the Advanced Fuel Properties (AFP) project by task as outlined in the original proposal and subsequent contract modifications. Each section defines the objectives for the task and describes what was actually completed.

4.1 Definition of Fuel Candidates

4.1.1 Objective

Define the types of hydrocarbon structures to be included in the data base and models of this project.

4.1.2 Work Completed

Data for aliphatics, olefinics, naphthenics, aromatics, and heteroatomics have been assembled in the AFP data base. Originally, the proposal estimated we would build a data base containing 2,500 molecules, but the actual current total has reached 4,576. The hydrocarbon classes include

normal alkanes through C₁₀₀, all branched alkane isomers up through C₁₂, cyclopentanes, cyclohexanes, other cycloalkanes, alpha-olefins, other olefins, diolefins, acetylenes, cycloalkenes, decalins, normal and branched alkylbenzenes, tetralins, indans, indenenes, diphenyls, biphenyls, other benzene derivatives such as styrenes, polyaromatics, and multicyclic compounds containing strained and saturated rings. These classes of compounds were chosen because of availability of good data and their presence in many fuel mixtures.

The nonhydrocarbon classes included some of the elements, normal and branched alcohols, aromatic alcohols, polyols, aldehydes and ketones, ethers, epoxides and peroxides, normal and branched carboxylic acids, aromatic carboxylic acids, anhydrides, various kinds of esters, halogenated compounds, amines and imines, nitriles, nitrates, polyfunctional compounds, a few phosphorous compounds, and aromatic rings containing oxygens and nitrogens. Some of these compounds occur in trace amounts in jet fuels derived from petroleum feedstocks but they are more prevalent in fuels derived from coal. However, most of them were included in the data base because their structures will help define the structure-based models.

The numbers of entries for each compound category are presented in Table 4.1-1. Nearly all the categories have several compounds. Some, like branched alkanes, have hundreds. This data set was used to develop new correlative property prediction models based upon graph theory indices.

The compound classifications in Table 4.1-1 were made using the FAMILY subroutine which uses the SMILES strings (see Entry of Structural Data in Section 4.3.1.2.2) for each compound. This process is straightforward for simple structures, but is open to interpretation when more than one functional group is present in a molecule. The details of how this classification works are described in Section 4.4.2.2.5.

Table 4.1-1
AFP Data Base Family Counts

FAMILY #	NAME	# OF COMPOUNDS
1	n-PARAFFINS	101
2	METHYLALKANES	121
3	CYCLOALKANES	39
4	OTHER ALKANES	688
5	ALPHA-OLEFINS	99
6	OTHER ALKANES	165
7	DIOLEFINS	32
8	ALKYNES	90
9	N-ALKYLBENZENES	97
10	OTHER ALKYLBENZENES	86
11	OTHER MONOAROMATICS	40
12	OTHER POLYAROMATICS	227
13	MULTICYCLIC HYDROCARBON RINGS	24
15	ALDEHYDES	23
16	KETONES	67
17	N-ALCOHOLS	18
18	OTHER ALIPHATIC ALCOHOLS	40
19	AROMATIC ALCOHOLS	57
20	POLYOLS	37
21	N-ALIPHATIC ACIDS	19
22	OTHER ALIPHATIC ACIDS	36
23	AROMATIC CARBOXYLIC ACIDS	38
24	ANHYDRIDES	9
25	FORMATES & ACETATES	27
26	N-ALKYL ESTERS	51
27	UNSATURATED ALIPHATIC ESTERS	16
28	AROMATIC ESTERS	48
29	ESTERS	37
30	EPOXIDES & PEROXIDES	28
31	ALIPHATIC CHLORIDES	52
32	AROMATIC CHLORIDES	14
33	C,H,Br COMPOUNDS	15
34	C,H,I COMPOUNDS	6
35	C,H,F COMPOUNDS	22
36	C, MULTIHALOGEN	28
37	ALIPHATIC AMINES	25
38	AROMATIC AMINES	29
39	OTHER AMINES & IMINES	35
40	NITRILES	29
41	C,H,NO ₂ COMPOUNDS	36

Table 4.1-1 (cont.)
APP Data Base Family Counts

FAMILY #	NAME	# OF COMPOUNDS
42	MULTIFUNCTIONAL C,H,N,O	94
43	C,H,S COMPOUNDS	310
44	POLYFUNCTIONAL C,H,O	90
45	POLYFUNCTIONAL C,H,O,N	0
46	POLYFUNCTIONAL C,H,O,S,Cl	34
47	POLYFUNCTIONAL C,H,O, HALIDES	39
48	POLYFUNCTIONAL C,H,O,N, HALIDES	13
54	ELEMENTS	39
100	DECALINS	29
101	TETRALINS	41
102	CYCLOOLEFINS	99
104	DIPHENYLS	78
105	BIPHENYLS	22
106	CYCLOPENTANES	115
107	CYCLOHEXANES	153
108	ANTHRACENES	78
109	PHENANTHRACENES	156
110	INDANS	181
111	INDENES	71
112	ALKYL RADICALS	18
114	MISCELLANEOUS	74
115	PHOSPHOROUS COMPOUNDS	5
116	NITROGEN AROMATIC RINGS	56
118	OLEFINS WITH>2 DOUBLE BONDS	2
119	OXYGEN AROMATIC RINGS	9
120	CHARGED SPECIES	6

4.2 Definition of Properties

4.2.1 Objective

Define a list of fuel properties to be modeled during the course of this project.

4.2.2 Work Completed

The list of properties for which single component estimations are available is given in Table 4.2-1. The list of properties that can be determined by mixture calculations is given in Table 4.2-2. Not all properties are available for all compounds. Some are available only as database lookups.

Table 4.2-1
Fuel Properties in AFP System

Single Valued Properties:

x	*	1.	Critical Temperature
x	*	2.	Critical Pressure
x	*	3.	Critical Volume
x	*	4.	Critical Compressibility
x	*	5.	Acentric Factor
x	*	6.	Rackett Parameters
x	*	7.	Normal Boiling Temperature
x	*	8.	Melting Temperature
x	*	9.	Liquid Molar Volume at 25 C
x		10.	Enthalpy of Formation at 25 C
x		11.	Gibbs Free Energy of Formation at 25 C
x		12.	Absolute Entropy at 25 C
x		13.	Standard Enthalpy of Combustion at 25 C
x		14.	Enthalpy of Fusion at the Melting Temperature
x		15.	Triple Point Temperature
x		16.	Triple Point Pressure
x	*	17.	Solubility Parameter at 25 C
x		18.	Dipole Moment
x		19.	Radius of Gyration
x	*	20.	Flash Point
x	*	21.	Lower Flammability Limit
x	*	22.	Upper Flammability Limit
x	*	23.	Autoignition Temperature

x Indicates data present in AFP data base
* Indicates predictive method programmed

Table 4.2-1 (cont.)
Fuel Properties in AFP System

Ideal Gas Properties:

x	*	24.	Enthalpy of Formation at 298K
x	*	25.	Absolute Enthalpy at 298K
x	*	26.	Gibbs Free Energy of Formation at 298K
	*	27.	Enthalpy vs. Temperature
	*	28.	Absolute Entropy vs. Temperature
	*	29.	Gibbs Free Energy vs. Temperature
	*	30.	Helmholtz Free Energy vs. Temperature
	*	31.	Internal Energy vs. Temperature
x	*	32.	Isobaric Heat Capacity vs. Temperature
	*	33.	Isochoric Heat Capacity vs. Temperature
	*	34.	Enthalpy of Formation vs. Temperature
	*	35.	Gibbs Free Energy of Formation vs. Temperature
	*	36.	Formation Equilibrium Constant vs. Temperature

Residual Properties:

	*	37.	Enthalpy vs. Temperature and Pressure
	*	38.	Entropy vs. Temperature and Pressure
	*	39.	Gibbs Free Energy vs. Temperature and Pressure
x	*	40.	Isobaric Heat Capacity vs. Temperature and Pressure
	*	41.	Isochoric Heat Capacity vs. Temperature and Pressure
	*	42.	Fugacities vs. Temperature and Pressure

Real Gas Properties:

	*	43.	Molar Volume vs. Temperature and Pressure
x	*	44.	Compressibility vs. Temperature and Pressure
x	*	45.	2nd Virial Coefficient vs. Temperature and Pressure
	*	46.	Gas Density vs. Temperature and Pressure
	*	47.	Enthalpy vs. Temperature and Pressure
	*	48.	Entropy vs. Temperature and Pressure
	*	49.	Gibbs Free Energy vs. Temperature and Pressure
	*	50.	Isobaric Heat Capacity vs. Temperature and Pressure
	*	51.	Isochoric Heat Capacity vs. Temperature and Pressure
	*	52.	Enthalpy of Formation vs. Temperature and Pressure
	*	53.	Gibbs Free Energy of Formation vs. Temperature and Pressure
	*	54.	Heat of Combustion vs. Temperature and Pressure
x		55.	Entropy for a real gas at 398 K
x		56.	Density for a real gas at 293 K
x		57.	Density for a real gas at 298 K
x.		58.	Heat capacity for a real gas at 298 K
x	*	59.	Gibbs free energy of formation of an ideal gas at 298 K

X Indicates data present in AFP data base
* Indicates predictive method programmed

Table 4.2-1 (cont.)
Fuel Properties in AFP System

Liquid Properties:

x	*	60.	Saturated Molar Volumes vs. Temperature
	*	61.	Compressed Molar Volumes vs. Temperature and Pressure
x	*	62.	Liquid Densities vs. Temperature and Pressure
	*	63.	Enthalpy vs. Temperature and Pressure
	*	64.	Entropy vs. Temperature and Pressure
	*	65.	Gibbs Free Energy vs. Temperature and Pressure
x	*	66.	Isobaric Heat Capacity vs. Temperature and Pressure
	*	67.	Isochoric Heat Capacity vs. Temperature and Pressure
	*	68.	Enthalpy of Formation vs. Temperature and Pressure
	*	69.	Gibbs Free Energy of Formation vs. Temperature and Pressure
x	*	70.	Surface Tension vs. Temperature and Pressure
x		71.	Entropy of a liquid at 298 K
x		72.	Density for a liquid at 293 K
x		73.	Density for a liquid at 298 K
x		74.	Heat capacity for a liquid at 298 K
x		75.	Gibbs free energy of formation for a liquid at 298 K

Liquid-Gas Phase Transition Properties:

x	*	76.	Vapor Pressures vs. Temperature
x		77.	Boiling Point Correction
x	*	78.	Enthalpy of Vaporization vs. Temperature

Solid Properties:

x		79.	Solid Heat Capacity vs. Temperature
x		80.	Solid Density vs. Temperature

Transport Properties:

x	*	81.	Liquid Viscosity vs. Temperature and Pressure
x	*	82.	Vapor Viscosity vs. Temperature and Pressure
x	*	83.	Liquid Thermal Conductivity vs. Temperature and Pressure
x	*	84.	Vapor Thermal Conductivity vs. Temperature and Pressure

x Indicates data present in AFP data base

* Indicates predictive method programmed

Table 4.2-2
Mixture Properties in AFP System

(Equilibrium Calculations)

Boiling temperature at system pressure
Dew temperature at system pressure
Boiling pressure at system temperature
Dew pressure at system temperature
Vapor-liquid compositions (weight and mole %)

(Thermophysical Properties)

Density	Entropy
Specific Heat	Thermal Conductivity
Adiabatic Exponent	Viscosity
Compressibility factor	Pseudo critical quantities
Enthalpy	Proposed nominal widths
Calorific value	Surface tension (liquids)
Heat of vaporization/condensation	

The data base contains experimental data for the properties marked with x's. It does not contain experimental data for all the properties because many of them are interrelated. For example, the Gibbs free energies, internal energies, and Helmholtz free energies can all be calculated from the corresponding entropies and enthalpies. Most of the gas phase and residual thermodynamic properties are not stored in the data base because they can be calculated from equations of state. Methods have been programmed for prediction of the properties marked with asterisks. These programs are described in Section 4.4.

Even for the properties which are stored in the data base, there are many gaps in the data set due to missing data. The actual numbers of experimental values are shown in Table 4.2-3 for the critical temperature, critical pressure, critical volume, critical compressibility, normal boiling point, melting point, and acentric factor, respectively. The most data are available for normal boiling points but even for this easily measured property over 2,000 compounds have missing values. These gaps in the literature are a major reason why it is so important to develop accurate methods to estimate the properties of fuels.

Table 4.2-3
Examples of Counts For Experimental Properties

T_c - 1148 VALUES
 P_c - 1155 VALUES
 V_c - 1155 VALUES
 Z_c - 1141 VALUES
 T_b - 2351 VALUES
 T_n - 1880 VALUES
 ω - 922 VALUES

4.3 Data Base Development

Objective

Develop a data base of experimentally measured properties for hydrocarbon fuels.

Development of the data base is divided into the three subtasks described in Sections 4.3.1 through 4.3.3.

4.3.1 Literature Review

4.3.1.1 Objective

Make a comprehensive and critical review of the scientific literature in order to identify and collect the most accurate experimental data and predictive methods for the properties of pure-component fuels.

4.3.1.2 Work Completed

This task involved three parts: selection of data sources for the data base, selection of methods for entering and manipulating molecular structures, and selection of literature methods for the prediction of properties.

4.3.1.2.1 Selection of Data Sources

All the property data were taken from critically evaluated data compilations from reliable sources. These included:

1. The American Institute of Chemical Engineers DIPPR Data base⁹
2. The National Institute for Petroleum and Energy Research Data base on C10 - C16 Molecules¹⁰
3. Texas A&M's Thermodynamic Research Center's Hydrocarbon Tables¹¹
4. Texas A&M's Thermodynamic Research Center's Nonhydrocarbon Tables¹²
5. The JANAF Thermodynamic Tables⁵
6. The National Bureau of Standards Thermodynamic Tables⁴.

Since AlliedSignal is a corporate sponsor of the AIChE DIPPR project, access was available for the most recent data tape from them. Less complete data tapes are also available from the National Bureau of Standards, National Standards Reference Data System in Gaithersburg MD. The Reference Data Office was also the source of the JANAF and NBS Thermodynamic Tables. The NIPER data base was provided by WL/POSF, Wright-Patterson AFB. AlliedSignal subcontracted with Dr. Kenneth Marsh, Director of Texas A&M's Thermodynamic Research Center, for a tape of the TRC Hydrocarbon Tables. The current version of the Advanced Fuel Properties Data Base contains data from DIPPR, NIPER, and the TRC Hydrocarbon Tables. The TRC Nonhydrocarbons, JANAF Tables, and NBS Tables are on the computer but were never loaded into the data base because of time and budgetary constraints.

4.3.1.2.2 Entry of Structural Data

In addition to property data, the data base must contain the structure for each compound. After reviewing the literature, we selected SMILES (Simplified Molecular Input Line System) strings as the method for entering structural data. The AFP program incorporates the MedChem¹³ software package for structural searching. The MedChem software uses SMILES strings as its method for structural input.

SMILES strings are computer readable strings of characters which describe a molecular structure as a 2-D representation where hydrogens are generally omitted. The Medchem Software Manual contains a paper which describes the methods of correcting chemical compounds into their SMILES strings.¹⁴ This paper is also included in AFP user manual. SMILES strings are easy to learn and are constructed using the following six basic rules:

1. Atoms are represented by their atomic symbols and are generally enclosed in square brackets when in the elemental state.

2. Single, double, triple, and aromatic bonds are represented by the symbols '-', '=', '#', and ':', respectively, with single and aromatic bonds being generally omitted.
3. Branches are specified by enclosures in parentheses.
4. Cyclic structures are represented by breaking one bond in each ring and identifying the atom on either side of the break with the same number.
5. Disconnected structures are written as individual structures separated by a '.'.
6. Atoms in an aromatic compound use lower case letters.

One of the drawbacks to SMILES strings is that optical isomers, and cis and trans isomers of double bonds and rings, cannot be distinguished. These isomers are distinguished by an isomer counter in the data base. When there is an ambiguity about which compound is to be selected, the program gives the user a choice. Daylight Chemical Information Systems, which provided the module for manipulating SMILES strings, was working on extensions to SMILES strings which would distinguish isomers. Inclusion of these improvements would require revision of the AFP system.

To enter SMILES strings for each of the compounds, lists of compound names for the TRC Hydrocarbon and Nonhydrocarbon, DIPPR, and NIPER data sets were obtained. Over 8,000 SMILES strings were written for these compounds. As noted above, many of these compounds were never actually added to the database. However, the data sets have been provided to the Air Force.

A reliable method for finding obscure structures is to use a computer search. If the CAS (Chemical Abstracts Service) registry number is available for the compound, a computer search output includes a line printer version of the structure. SMILES strings can be written from these structures. This was the primary method of obtaining structures for the more complex inorganic compounds.

4.3.1.2.3 Selection of Literature Models

Numerous papers were reviewed during Phase I as part of the search for the best methods to predict fuel properties. Fortunately, the following four books, which include careful reviews of the literature up through 1987, were also found:

1. Reid, Prausnitz, and Poling. The Properties of Gases and Liquids.¹⁵
2. Edmister and Lee. Applied Hydrocarbon Thermodynamics.¹⁶
3. Danner and Daubert. Manual for Predicting Chemical Process Design Data from the AIChE.⁸
4. Technical Data Book - Petroleum Refining from the American Petroleum Institute.

All of these books provided recommendations for predictive methods for various properties. The first book also contained quantitative comparisons of several of the methods. These books, taken as a collection, provided a very valuable guide to the enormous literature on the prediction of fuel properties and nearly all of the methods programmed during Phase I were covered in one or more of these reviews.

4.3.2 Data Compilation

4.3.2.1 Objective

Compile the fuel property data collected during Task 3.1 into a computer data base that can provide easy management, access, and analysis of the data of either structure or property based parameters.

4.3.2.2 Work Completed

The data for all the measured values of all the pertinent properties of 4,576 fuel candidate chemical compounds have been compiled and stored in a data base in the AFP system.

The software tool used to manage the storage of this data is called a Data Base Management System (DBMS). The Digital Equipment Corporation (DEC) product VAX Rdb/VMS was the DBMS used for the Advanced Fuels Properties data base. It was chosen because it is a relational DBMS, it is marketed and supported by a reputable vendor, and it is one of the leaders in its field.

4.3.2.2.1 Relational Data Base Concepts

The relational model of data storage offers several advantages over other data models:

1. The structure of the data base is easier to understand.
2. Data can be combined and compared in a wide variety of ways.
3. Relationships among data can be established dynamically.
4. The data base structure can be modified without necessarily rebuilding the entire data base.

Refer to Figure 4.3.2-1 for the following explanation of the concepts of the relational data model.

Nomenclature

Relation — Record — Field — Key

Key — Field(s) to

Uniquely ID

a Record

		Field, Column					
		A	B	C	D	E	F
Record, Row	1						
	2						
	3						
	4						
		Relation, Table					

Figure 4.3.2-1
Relational Data Model

In a relational data base, data reside in two-dimensional data structures known as relations or tables. One or many relations may exist in a data base. Each relation is made up of rows and columns. The rows are called records and are a collection of fields (columns). Each record must be uniquely identified by one or more fields in the record. This concept is often referred to as the key.

Every record in a relation has the same set of fields in the same order as all the others. The width of the relation is fixed by the list of fields that comprise a record. The length of the table is limited only by the physical constraints of the system and can change at any time by adding to or deleting records from the table.

While each relation in a data base can be viewed as an independent entity, they can also be related to other relations by one or more common fields. When the relations are joined together by these common fields, they form a new larger "logical" relation containing all the information from both relations. For instance, if a relation X contains fields A, B, and C and relation Y contains fields A, D, and E, when they are joined, the resulting relation would contain fields A, B, C, D, and E. It is in this simple operation that the real power of the relational data model resides.

4.3.2.2.2 Design of the AFP Data Base

The goal of the AFP data base is to store all the measured values of all the pertinent properties of all the fuel candidates. Each measured value should carry with it an indication of quality, an indication of the source of the value, any references the data source might quote, and any notes or footnotes the measurement might carry.

Some of the problems this goal presents include:

1. Fuels are chemicals, and it is difficult to uniquely identify a chemical that will be valid, not only for existing chemicals, but also for new chemicals and mixtures.
2. The list of properties has grown, over the life of the project, from 39 to 120.
3. The number of measurements for a property may be 0, 1, or an unlimited number.
4. The number of references and notes for a measurement may be 0, 1, or an unlimited number.
5. Some of the data do not have associated quality indicators.

The problem of the chemical's unique identity was overcome by using the MedChem SMILES string plus a secondary field that is a sequential counter of

the number of nonunique occurrences of the SMILES string because of isomers. This solved the uniqueness problem but caused a potential disk storage problem because the SMILES string is currently a 240-byte character string, and the counter is a 4-byte integer. As the unique identifier (SMILES/counter), it would be carried through all relations in the data base that were related to the fuel candidate. Therefore, a 4-byte integer field called the ASID (for AlliedSignal Identifier) was created to solve the disk problem. The ASID is a computer assigned number that is the sequential order of the fuel candidate entry into the data base. It has no chemical meaning, but can be cross referenced to a SMILES string/isomer counter combination and, thus, a chemical. It saves 240 bytes of storage every time a unique fuel candidate ID is needed within the data base.

While either the SMILES string/isomer counter or the ASID each can uniquely identify a fuel candidate, neither is very practical for retrieving data because neither would be known to a chemist looking for information from the data base. For this reason, the COMPONENTS and SYNONYMS relations are in the data base. The COMPONENTS relation contains many of the various methods the chemical industry has of identifying chemical compounds. The SYNONYMS relation contains many of the names, both formal and informal, by which a given compound is known.

These are the fields in the COMPONENTS relation. There is one record in this relation for each fuel candidate in the data base.

ASID	The AlliedSignal Identifier
SMILES1	The first 60 characters of the 240-character SMILES string (Note: this field was partitioned to make it easier to display on a terminal)
SMILES2	The second 60 characters of the SMILES string
SMILES3	The third 60 characters of the SMILES string
SMILES4	The fourth 60 characters of the SMILES string
ISCOUNT	A sequential count of nonunique occurrences of SMILES strings caused by isomers
PSUID	The DIPPR unique identifier
NAMED	The chemical name as found in DIPPR
STRUCTD	The chemical structure as found in DIPPR
FORMULA	The chemical formula
FAMDCODE	The chemical family code as found in DIPPR
FAMKCODE	The chemical family code as assigned by the FAMILY routine
CASNUM	The Chemical Abstracts Services (CAS) chemical identifier
NAMEC	The chemical name as found in CAS
APIID	The American Petroleum Institute identifier for this chemical
NAMEA	The chemical name as found in the API tables
TRCID	The TRC identifier for this chemical
NAMET	The chemical name as found in the TRC tables
NIPERID	The NIPER identifier for this chemical
NAMEN1	The first 60 characters for the chemical name as found in NIPER

NAMEN2	The second 60 characters of the NIPER name
NAMEI	The chemical name according to IUPAC nomenclature rules
DECHEMAID	The DECHEMA identifier for this chemical
NAMEDECH	The chemical name as found in DECHEMA

The COMPONENTS relation can be maintained using the AFPDBU program. The AFPDBU program was written to allow amending and updating of the data base. This program was not originally designed into AFP, and it should be used with great care. This separate program can be used to add any property, or compound into the database. It is a dangerous program because AFP does not have the means to check the validity of information being put into the data base. Therefore, if the AFPDBU program is not used carefully, inaccurate information will propagate into the database.

These are the fields in the SYNONYMS relation. There is one record for each name for each chemical in the data base, although there may be many records for any given ASID. There is usually at least one. Only two fields appear in the SYNONYMS relation. They are:

ASID	The AlliedSignal Identifier
SYNONYM	A synonym for the chemical identified by this ASID.

The SYNONYMS relation can be maintained using the AFPDBU program.

The problems with a loosely determined number of properties to be stored and having an undetermined number of measurements for each property were overcome by storing the measurements as records in a relation as opposed to storing them as fields in a record. Any number of measurements for any number of properties can be stored using this structure.

The relations ALLMSVP (ALL Measurements for Single Value Properties) and ALLMMVP (ALL Measurements for Multiple Value Properties) store all the property measurement values. The difference between the two is that ALLMMVP includes fields for the pressure and temperature at which the values were measured. ALLMSVP contains values for properties that are not dependent upon temperature and pressure.

There is one record in the ALLMSVP relation for each measurement for each property for each ASID. If there is no measurement for a given property for a certain ASID, then there is no record in this relation with this particular ASID/PROPCODE combination. If there is only one measurement for a given ASID/PROPCODE combination, then PROPCOUNT will be 1. If there are five measurements for a given ASID/PROPCODE combination, then there will be five

records each with a different PROPCOUNT going from 1 to 5. The list of fields in the ALLMSVP relation:

ASID	The AlliedSignal Identifier
PROPCODE	The property code (see relation TABLE_PROPERTIES)
PROPCOUNT	A sequentially assigned counter for the number of measurements for this property for this ASID
PROPVALUE	The measurement value
DSRCECODE	A code indicating the source of the measurement (see relation TABLE_DATASOURCES)
DQUALCODE	Alphanumeric data quality indicator (carryover from DIPPR)
DQUALNUM	Numeric data quality indicator
DATEIS	Date this measurement was issued
DATEREV	Date this measurement was last revised.

There is no tool provided to modify the ALLMSVP relation. There is no need to modify it. It is supplied strictly as a reference.

Relation ALLMMVP is identical to relation ALLMSVP except that relation ALLMMVP also contains the fields PROPTEMP and PROPPRES, the temperature and pressure at which the measurement was performed. The list of fields in the ALLMMVP relation:

ASID	The AlliedSignal Identifier
PROPCODE	The property code (see relation TABLE_PROPERTIES)
PROPCOUNT	A sequentially assigned counter for the number of measurements for this property for this ASID
PROPTEMP	The temperature(Deg K) at which the value was measured.
PROPPRES	The pressure(Pascals) at which the value was measured.
PROPVALUE	The measurement value
DSRCECODE	A code indicating the source of the measurement (see relation TABLE_DATASOURCES)
DQUALCODE	Alphanumeric data quality indicator (carryover from DIPPR)
DQUALNUM	Numeric data quality indicator
DATEIS	Date this measurement was issued
DATEREV	Date this measurement was last revised.

There is no tool provided to modify the ALLMMVP relation. There is no need to modify it. It is supplied strictly as a reference.

Relations TABLE_PROPERTIES and TABLE_DATASOURCES are essentially look-up tables and contain the correct translation between the property code and the name of the property and also between the data source code and a text string describing the data source.

There is one record in relation TABLE_PROPERTIES for each property in the AFP data base. Table 4.3.2-1 lists the the TABLE_PROPERTIES relation for each property in AFP data base. Relation TABLE_PROPERTIES contains the following fields:

PROPCODE	The property code
PROPERTY	The property name
PROPTYPE	The type of property (1=Single Value, 2=Multiple Value)
UNITCODE	The units class * 100 + the specific units code
UNIT	The textual description of the units.

There is no tool provided to modify the TABLE_PROPERTIES relation. There is no need to modify it. It is supplied strictly as a reference.

There is one record in relation TABLE_DATASOURCES for each data source in the AFP data base. Relation TABLE_DATASOURCES contain the following fields:

DSRCECODE	The data source code
DSOURCE	The data source name.

There is no tool provided to modify the TABLE_DATASOURCES relation. There is no need to modify it. It is supplied strictly as a reference.

The problem of having multiple references, notes, and footnotes for a given measurement was overcome in much the same manner as the synonym list. Relations ALLMSVP_XTRNLS and ALLMMVP_XTRNLS store the external references and footnotes for the ALLMSVP and ALLMMVP measurements respectively.

There is one record in relation ALLMSVP_XTRNLS for each external reference for each measured value for each property for each ASID. The actual text for the reference/footnote/note is stored external to the data base in files associated with the data source. This relation merely contains the pointers to the text location. The list of fields in the ALLMSVP_XTRNLS relation:

ASID	The AlliedSignal Identifier
PROPCODE	The property code
PROPCOUNT	The sequential counter for measurements (see ALLMSVP)
XTRNLCODE	An alphanumeric code to identify the reference/footnote
XTRNLTYPE	Code identifying this as a reference, footnote, or note.

There is no tool provided to modify the ALLMSVP_XTRNLS relation. There is no need to modify it. It is supplied strictly as a reference.

Relation ALLMMVP_XTRNLS is identical to relation ALLMSVP_XTRNLS. There is no tool provided to modify the ALLMMVP_XTRNLS relation. There is no need to modify it. It is supplied strictly as a reference.

With the relations mentioned above, all the data for the AFP project can be stored. There remains the problem of retrieval. When asking for any

measurement for a given property, all measurements must be searched. And once a measurement is located and retrieved, it may not be a representative measurement, that is, the accuracy of any arbitrarily retrieved measurement is not known. To overcome these problems, the BESTMSVP and the BESTMVP relations were added to the data base. The BESTMSVP relation contains the best measurements for each single value property for each ASID. The BESTMVP relation contains the regression coefficients and a regression equation code for each of the multiple value properties for each ASID. These equations and coefficients are currently not stored in ALLMVP.

There is a record in BESTMSVP for each fuel candidate in the data base. If there is no measurement for a given property in the ALLMSVP relation, then both the property value AND the cross reference back to the ALLMSVP relation will be zero. If the cross-reference field is nonzero, then the property value is actual. The quality indicator is the decimal fractional representation of the quality. For example, if a value is accurate to ± 5 percent, then the quality indicator will be 0.05. The AFP system only handles equal plus and minus errors. The fields in the BESTMSVP relation:

ASID	The AlliedSignal Identifier
BMV001	The best measured value for property code 1
BQN001	The numeric quality indicator for property code 1
BIX001	The cross reference back to the ALLMSVP relation for property code 1 - contains the value of PROPCOUNT
BMV002	The best measured value for property code 2
BQN002	The numeric quality indicator for property code 2
BIX002	The cross reference back to the ALLMSVP relation for property code 2 - contains the value of PROPCOUNT, etc.

There is a field for the value, the quality, and the propcount for each of the single value properties. The single value properties currently have property codes 1-26, 42-68, 70, and 71.

The BESTMSVP relation can be maintained with the AFPDBU program.

The criteria used to load the BESTMSVP relation from the ALLMSVP relation are as follows:

1. Choose the measurement with the smallest nonzero quality indicator.
2. If there is more than one value with the same quality indicator, then choose by data source. The priority scheme is DIPPR, NIPER, and, lastly, TRC. This order was selected because the DIPPR data were selected by a committee of the American Institute of Chemical Engineers and contained error bars and references telling where the numbers came from. The NIPER data were collected in the last five years and also contained error information. The information in the TRC tables rarely included error bars or detailed references to where the values came from. However, the TRC tables, the standard reference source for thermodynamic data for the chemical and petroleum industries, have been updated

regularly, and are generally considered to be reliable. In practice, the situation where the quality codes were the same for more than one value rarely occurred in building the data base. This rule was, therefore, used only in a few dozen cases.

3. If more than one value has the same quality indicator and the same data source code, then keep the first one encountered. This situation only occurred in the DIPPR data where several experimental values were sometimes reported for the same property. By convention, the DIPPR committee stored the recommended value first in their data file and this rule picks it out. This rule was applied in very few cases.

There is one record in the BESTMMVP relation for each regression equation for each property for each ASID in the data base. If no regression equation has been fitted to the ALLMMVP data for a given ASID/property, then no record will exist in BESTMMVP for that ASID/property. Table 4.3.2-2 lists the equation codes that are used by each property code. The fields in the BESTMMVP relation:

ASID	The AlliedSignal Identifier
PROPCODE	The property code
REQNCODE	The regression equation code
REQCOEFA	Coefficient A for the regression equation
REQCOEFB	Coefficient B for the regression equation
REQCOEFC	Coefficient C for the regression equation
REQCOEFD	Coefficient D for the regression equation
REQCOEFE	Coefficient E for the regression equation
REQCOEFF	Coefficient F for the regression equation
REQCOEFG	Coefficient G for the regression equation
REQCOEFH	Coefficient H for the regression equation
REQCOEFI	Coefficient I for the regression equation
REQCOEFJ	Coefficient J for the regression equation
REQTEMPU	The upper limit for valid temperature range
REQTEMPL	The lower limit for valid temperature range
REQPRESU	The property value estimated at upper temperature
REQPRESL	The property value estimated at lower temperature
REQQCODE	The quality code
REQNUMCS	The number of coefficients actually used.

The quality code is alphanumeric in BESTMMVP. It uses the DIPPR interpretation for quality codes.

The BESTMMVP relation can be maintained with the AFPDBU program.

The final piece of the AFP data base is relation BTRMMVP. This relation contains temperature and pressure dependent data from TRC that had no regression equation fitted to it. The description of each record is identical to the ALLMMVP record description. The data in BTRMMVP are not also contained in ALLMMVP.

There is no tool provided to modify the BTRMMVP relation. There is no need to modify it. It is supplied strictly as a reference.

If the structure of the data base is changed, then it is likely that many of the routines used to access the data base will no longer function properly. Therefore, it is recommended that AlliedSignal be consulted to actually perform such changes.

The following is a list of the single value properties, the propcode, the units code, and the units in which they are stored. The units code is a combination of the units class and units code. It can be determined as follows: (units class * 100) + particular units code. The values match those used in the units conversion methods within the AFP program. A value of -1 means the property is unitless, and a value of -2 means it is a percent.

Table 4.3.2-1
TABLE PROPERTIES for Each Property in the AFP Data Base

Prop Code	Property	Units Code	Units
1	MOLECULAR WEIGHT	2303	kg/kmol
2	CRITICAL TEMPERATURE	102	Degrees Kelvin (K)
3	CRITICAL PRESSURE	201	Pascals
4	CRITICAL VOLUME	1004	m**3/kmol
5	CRITICAL COMPRESSIBILITY FACTOR	-1	unitless
6	MELTING POINT (AT 1 ATM)	102	Degrees Kelvin (K)
7	TRIPLE POINT TEMPERATURE	102	Degrees Kelvin (K)
8	TRIPLE POINT PRESSURE	201	Pascals
9	NORMAL BOILING POINT (@ 1 ATM)	102	Degrees Kelvin (K)
10	LIQUID MOLAR VOLUME (@ 298K)	1004	m**3/kmol
11	IDEAL GAS ENTHALPY OF FORMATION (298K)	501	J/kmol
12	IDEAL GAS GIBBS ENERGY OF FORM. (298K)	501	J/kmol
13	IDEAL GAS ABSOLUTE ENTROPY (@ 298K)	601	J/K kmol
14	ENTHALPY OF FUSION AT MELTING POINT	501	J/kmol
15	STANDARD ENTHALPY OF COMBUSTION (298K)	501	J/kmol
16	ACENTRIC FACTOR	-1	unitless
17	RADIUS OF GYRATION	1106	meter
18	SOLUBILITY PARAMETER (@ 298K)	-1	unitless
19	DIPOLE MOMENT	2401	C-m
20	VAN DER WAALS VOLUME	1004	m**3/kmol
21	VAN DER WAALS AREA	1202	meter**2
22	REFRACTIVE INDEX (298K 1ATM)	-1	unitless
23	FLASH POINT	102	Degrees Kelvin (K)
24	LOWER FLAMMABILITY LIMIT	-2	Volume % in Air
25	UPPER FLAMMABILITY LIMIT	-2	Volume % in Air
26	AUTOIGNITION TEMPERATURE	102	Degrees Kelvin (K)
42	RACKETT PARAMETER	1004	m**3/kmol
43	REAL GAS ENTHALPY OF FORMATION (@298K)	501	J/kmol
44	REAL GAS GIBBS OF FORMATION (@298K)	501	J/kmol
45	REAL GAS ABSOLUTE ENTROPY (@298K)	601	J/K kmol
46	REAL GAS HEAT CAPACITY (298K & CONST P.)	401	J/K kmol
47	LIQUID ENTHALPY OF FORMATION (@298K)	501	J/kmol
48	LIQUID GIBBS OF FORMATION (@298K)	501	J/kmol
49	LIQUID ABSOLUTE ENTROPY (@298K)	601	J/K kmol
50	LIQUID HEAT CAPACITY (298K & CONST P.)	401	J/K kmol
51	SOLID 1 ENTHALPY OF FORMATION (@298K)	501	J/kmol
52	SOLID 1 GIBBS OF FORMATION (@298K)	501	J/kmol
53	SOLID 1 ABSOLUTE ENTROPY (@298K)	601	J/K kmol
54	SOLID 1 HEAT CAPACITY (298K & CONST P.)	401	J/K kmol

55 SOLID 2 ENTHALPY OF FORMATION (@298K)	501 J/kmol
56 SOLID 2 GIBBS OF FORMATION (@298K)	501 J/kmol
57 SOLID 2 ABSOLUTE ENTROPY (@298K)	601 J/K kmol
58 SOLID 2 HEAT CAPACITY (298K & CONST P.)	401 J/K kmol
59 REFRACTIVE INDEX (293K 1ATM)	-1 unitless
60 BOILING POINT PRESSURE CORRECTION	2601 K/Pa
61 REAL GAS DENSITY (293K 1ATM)	302 kg/m**3
62 REAL GAS DENSITY (298K 1ATM)	302 kg/m**3
63 LIQUID DENSITY (293K 1ATM)	302 kg/m**3
64 LIQUID DENSITY (298K 1ATM)	302 kg/m**3
65 SOLID DENSITY (293K 1ATM)	302 kg/m**3
66 SOLID DENSITY (298K 1ATM)	302 kg/m**3
67 SOLID 2 DENSITY (293K 1ATM)	302 kg/m**3
68 SOLID 2 DENSITY (298K 1ATM)	302 kg/m**3
70 I.G. ENTHALPY OF FORMATION (OK)	501 J/kmol
71 CRITICAL DENSITY	302 kg/m**3

The following is a list of the multiple value properties, the propcode, the units code, and the units in which they are stored. The units code is a combination of the units class and units code. It can be determined as follows: (units class * 100) + particular units code. The values match those used in the units conversion methods within the AFP program. A value of -1 means the property is unitless, and a value of 0 means none is defined.

Prop Code	Property	Units Code	Units
27	SOLID DENSITY	302	kg/m**3
28	LIQUID DENSITY	302	kg/m**3
29	VAPOR PRESSURE (@ SATURATION PRESSURE)	201	Pascals
30	ENTHALPY OF VAPORIZATION (@ SAT. PRESS.)	501	J/kmol
31	SOLID HEAT CAPACITY	401	J/K kmol
32	LIQUID HEAT CAPACITY	401	J/K kmol
33	IDEAL GAS HEAT CAPACITY	401	J/K kmol
34	SECOND VIRIAL COEFFICIENT	-1	unitless
35	LIQUID VISCOSITY	702	N s/m**2
36	VAPOR VISCOSITY	702	N s/m**2
37	LIQUID THERMAL CONDUCTIVITY	2202	kg m/s**3 K
38	VAPOR THERMAL CONDUCTIVITY	2202	kg m/s**3 K
39	SURFACE TENSION	901	N/m
40	SOLID VAPOR PRESSURE	201	Pascals
41	LIQUID VAPOR PRESSURE	201	Pascals
69	SOLID 2 HEAT CAPACITY	401	J/K kmol
72	SOLID 3 HEAT CAPACITY	401	J/K kmol
73	ENTHALPY OF TRANSITION SOLID3 TO SOLID2	501	J/kmol
74	ENTHALPY OF TRANSITION SOLID3 TO SOLID1	501	J/kmol
75	ENTHALPY OF TRANSITION SOLID3 TO LIQUID	501	J/kmol
76	ENTHALPY OF TRANSITION SOLID3 TO GAS	501	J/kmol
77	ENTHALPY OF TRANSITION SOLID2 TO SOLID1	501	J/kmol
78	ENTHALPY OF TRANSITION SOLID2 TO LIQUID	501	J/kmol
79	ENTHALPY OF TRANSITION SOLID2 TO GAS	501	J/kmol
80	ENTHALPY OF TRANSITION SOLID1 TO LIQUID	501	J/kmol
81	ENTHALPY OF TRANSITION SOLID1 TO GAS	501	J/kmol
82	ENTHALPY OF TRANSITION LIQUID TO GAS	501	J/kmol
83	ENTROPY OF TRANSITION SOLID3 TO SOLID2	601	J/K kmol
84	ENTROPY OF TRANSITION SOLID3 TO SOLID1	601	J/K kmol
85	ENTROPY OF TRANSITION SOLID3 TO LIQUID	601	J/K kmol
86	ENTROPY OF TRANSITION SOLID3 TO GAS	601	J/K kmol
87	ENTROPY OF TRANSITION SOLID2 TO SOLID1	601	J/K kmol

88	ENTROPY OF TRANSITION SOLID2 TO LIQUID	601 J/K kmol
89	ENTROPY OF TRANSITION SOLID2 TO GAS	601 J/K kmol
90	ENTROPY OF TRANSITION SOLID1 TO LIQUID	601 J/K kmol
91	ENTROPY OF TRANSITION SOLID1 TO GAS	601 J/K kmol
92	ENTROPY OF TRANSITION LIQUID TO GAS	601 J/K kmol
93	DELTA ENTHALPY OF TRANS SOLID3 TO SOLID2	501 J/kmol
94	DELTA ENTHALPY OF TRANS SOLID3 TO SOLID1	501 J/kmol
95	DELTA ENTHALPY OF TRANS SOLID3 TO LIQUID	501 J/kmol
96	DELTA ENTHALPY OF TRANS SOLID3 TO GAS	501 J/kmol
97	DELTA ENTHALPY OF TRANS SOLID2 TO SOLID1	501 J/kmol
98	DELTA ENTHALPY OF TRANS SOLID2 TO LIQUID	501 J/kmol
99	DELTA ENTHALPY OF TRANS SOLID2 TO GAS	501 J/kmol
100	DELTA ENTHALPY OF TRANS SOLID1 TO LIQUID	501 J/kmol
101	DELTA ENTHALPY OF TRANS SOLID1 TO GAS	501 J/kmol
102	DELTA ENTHALPY OF TRANS LIQUID TO GAS	501 J/kmol
103	TRANS CRYOSCOPIC CONST SOLID3 TO SOLID2	0
104	TRANS CRYOSCOPIC CONST SOLID3 TO SOLID1	0
105	TRANS CRYOSCOPIC CONST SOLID3 TO LIQUID	0
106	TRANS CRYOSCOPIC CONST SOLID3 TO GAS	0
107	TRANS CRYOSCOPIC CONST SOLID2 TO SOLID1	0
108	TRANS CRYOSCOPIC CONST SOLID2 TO LIQUID	0
109	TRANS CRYOSCOPIC CONST SOLID2 TO GAS	0
110	TRANS CRYOSCOPIC CONST SOLID1 TO LIQUID	0
111	TRANS CRYOSCOPIC CONST SOLID1 TO GAS	0
112	TRANS CRYOSCOPIC CONST LIQUID TO GAS	0
113	SOLID2 DENSITY	302 kg/m**3
114	EQUATION OF STATE	0
115	REAL GAS HEAT CAPACITY	401 J/K kmol
116	SOLID1 ENTROPY	601 J/K kmol
117	SOLID2 ENTROPY	601 J/K kmol
118	SOLID3 ENTROPY	601 J/K kmol
119	LIQUID ENTROPY	601 J/K kmol
120	REAL GAS ENTROPY	601 J/K kmol
121	BWR EQUATION VALUES	0

The following is a list of the equation codes that are used with the various multiple value properties in relation BESTMMVP.

Table 4.3.2-2
Equation Codes Used by Each Property Code

Propcode	Property	Equation Code
27	SOLID DENSITY	100
28	LIQUID DENSITY	100
28	LIQUID DENSITY	105
29	VAPOR PRESSURE (@ SATURATION PRESSURE)	100
29	VAPOR PRESSURE (@ SATURATION PRESSURE)	101
30	ENTHALPY OF VAPORIZATION (@ SAT. PRESS.)	100
30	ENTHALPY OF VAPORIZATION (@ SAT. PRESS.)	106
31	SOLID HEAT CAPACITY	100
32	LIQUID HEAT CAPACITY	100
33	IDEAL GAS HEAT CAPACITY	100
33	IDEAL GAS HEAT CAPACITY	103
33	IDEAL GAS HEAT CAPACITY	107
34	SECOND VIRIAL COEFFICIENT	104
35	LIQUID VISCOSITY	100
35	LIQUID VISCOSITY	101
36	VAPOR VISCOSITY	100
36	VAPOR VISCOSITY	102

36	VAPOR VISCOSITY	300
37	LIQUID THERMAL CONDUCTIVITY	100
38	VAPOR THERMAL CONDUCTIVITY	100
38	VAPOR THERMAL CONDUCTIVITY	102
39	SURFACE TENSION	100
39	SURFACE TENSION	106
121	BWR EQUATION VALUES	304

The following are the equations associated with the equation codes.

Eqn Code	Equation
100	$Y = A + (B \cdot T) + (C \cdot T^{**2}) + (D \cdot T^{**3}) + (E \cdot T^{**4})$
101	$Y = \exp(A + (B/T) + (C \cdot \ln(T)) + (D \cdot T^{**E}))$
102	$Y = (A \cdot T^{**B}) / (1 + (C/T) + (D/T^{**2}))$
103	$Y = A + B \cdot \exp(-C/T^{**D})$
104	$Y = A + (B/T) + (C/T^{**3}) + (D/T^{**8}) + (E/T^{**9})$
105	$Y = A / (B^{**}(1 + (1 - T/C)^{**D}))$
106	$Y = A \cdot ((1 - Tr)^{**}(B + (C \cdot Tr) + (D \cdot Tr^{**2}) + (E \cdot Tr^{**3})))$

Where:

Y = The property value in the units specified above.
T = The temperature in Degrees Kelvin.
Tr = The reduced temperature.
A, B, C, D, E = The equation coefficients
** Indicates exponentiation
* Indicates multiplication

4.3.3 Obtaining Missing Data

4.3.3.1 Objective

Experimentally measure the properties of pure hydrocarbons which were not included in the literature data base but are judged to be important in determining structure-property relationships.

4.3.3.2 Work Completed

Because of the enormous size of the literature data base, we did not feel that any critical data points were missing. To demonstrate the extent of the data base, 30 hydrocarbons were arbitrarily selected and the values for 18 properties were requested for each compound. The compounds selected were:

Ethane	Toluene
Propylene	1,3-Dimethylbenzene
Butane	Ethylbenzene
Octane	m-Ethyltoluene
2-Methylpentane	Naphthalene

Neopentane	1-Ethyl-naphthalene
Cyclohexane	1,3-Dimethylnaphthalene
Methylcyclohexane	1-Ethyl-3-methylnaphthalene
Trans-1,3-dimethylcyclohexane	Trans-decahydronaphthalene
Ethylcyclohexane	1-Ethyl-cis-decahydronaphthalene
Trans-1-ethyl-3-methylcyclohexane	1,3-Dimethyldecahydronaphthalene
1-Ethyl-3methyldecahydronaphthalene	Vinylcyclohexane
2,2-Dimethylbutane	Cyclopentane
2,2-Dimethylpentane	Methylcyclopentane
2,2-Dimethylhexane	Benzene.

The properties that were selected for testing and the number of compounds, out of the 30 listed above, for which values were retrieved are:

Triple Point Temperature	22
Triple Point Pressure	22
Liquid Molar Volume at 298K	22
Melting Point at Standard Pressure	23
Flash Point	19
Upper Flammability Limit	22
Lower Flammability Limit	22
Entropy at 298K for an Ideal Gas	22
Enthalpy of Formation at 298K for an Ideal Gas	22
Enthalpy of Formation at 298K for a Liquid	22
Enthalpy of Combustion at 298K	22
Critical Volume	22
Critical Temperature	22
Critical Pressure	22
Critical Compressibility	22
Normal Boiling Point	26
Autoignition Temperature	22
Acentric Factor	22.

Three of the compounds (vinylcyclohexane, 1,3-dimethyldecahydronaphthalene, and 1-Ethyl-3-methyldecahydronaphthalene) were not in the data base. One compound (1-ethylnaphthalene) was found in the data base but did not have values for any of the test properties, four compounds (trans-1-ethyl-3-methylcyclohexane, 1-ethyl-3-methylnaphthalene, and 1-ethyl-cis-decahydronaphthalene) have only the normal boiling point, and one compound (1,3-dimethylnaphthalene) had only the normal boiling point and the melting point at standard pressure. This example demonstrates the extent of data that is available in the data base. Therefore, no work was done on this task.

4.4 Compilation, Evaluation, and Selection of Structure-Property Relationships

4.4.1 Objective

Collect and assess known structure-property relationships for pure hydrocarbons in order to develop accurate structure based predictive methods for the properties listed in Section 4.2.

4.4.2 Work Completed

The methods, recommended by the American Petroleum Institute (API) and American Institute of Chemical Engineers (AIChE), for predicting the properties of small fuel molecules were carefully evaluated. All of these predictive methods were hierarchical and depended on only two experimental inputs: the normal boiling point and specific gravity at room temperature^{7,8}. Using these two experimental inputs, the critical temperature and pressure could be calculated followed by the acentric factor, critical volume, and various specialized parameters appearing in equations of state (Figure 4.4-1). Densities and thermodynamic properties were then calculated from the equations of state at any temperature and pressure (Figure 4.4-2).

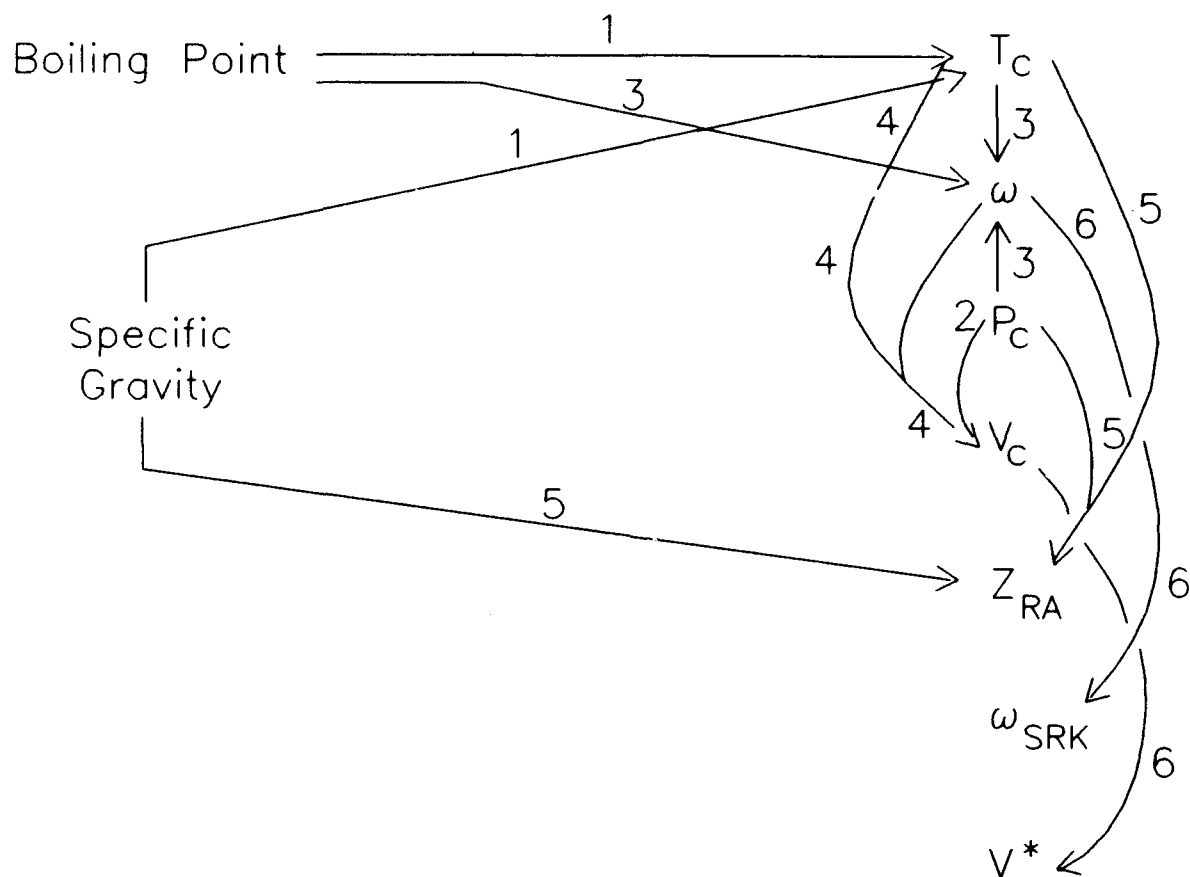
Based upon this analysis, our strategy in developing structure-based predictive methods has been to focus on the key single valued properties, such as the normal boiling point, critical properties, and acentric factor, and then program in established equations of state for the temperature and pressure dependence of properties. We have automated the user structural inputs required by many of the API and AIChE methods using the MedChem software and SMILES strings. We have also programmed several methods for many of the properties so that we could compare the accuracies of the various prediction schemes.

The methods developed under this task are presented in the following subsections:

1. Data base Access Routines
2. Methods for Structural Inputs
3. Methods for Single Valued Properties
4. Introduction to the Methods for Thermodynamic Properties
5. Methods for Ideal Gases
6. Methods for Residual Properties
7. Methods for Real Gases
8. Methods for Liquids
9. Methods for Phase Transitions
10. Methods for Transport Properties
11. Methods for Solids
12. Methods for Error Tracking.

Each method described in this section has been programmed as a separate subroutine which can be called independently. A discussion of how the properties determined by these subroutines compare with experimental values has been presented in detail in previous test reports. These two reports demonstrated the reliability and accuracy of the estimation routines for both pure compounds and mixtures.^{17,18}

API Prediction of Critical Properties and Tabulated Parameters



Numbers indicate the logical sequence for predicting properties

Figure 4.4-1
API Prediction of Critical Properties from the Normal Boiling Point and Specific Gravity

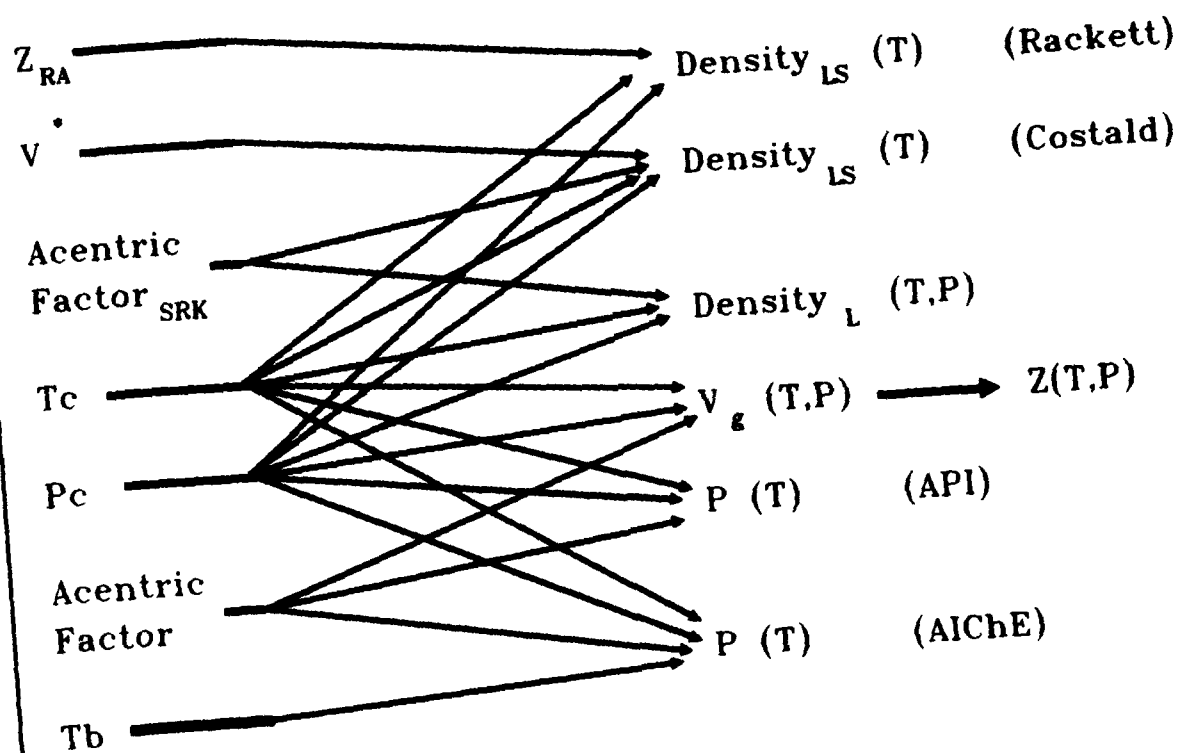


Figure 4.4-2
Prediction of the Densities and Vapor Pressures of Pure Components

4.4.2.1 Data Base Access Routines

4.4.2.1.1 Single-Valued Property Access Routines

All the single-valued property access routines are identical in function. They access the BESTMSVP relation, count the number of records in the relation with the desired ASID, and, if there is a record for the ASID, retrieve the property value, quality indicator, and reference back to the ALLMSVP relation for the desired ASID.

Inputs to the routines are:

ASID	An integer array of the AlliedSignal identifiers
SMILES	A character array of SMILES strings
NCMPDS	An integer field indicating the number of ASIDs in the ASID array.

Outputs from the routines are:

VALUE	A real array of property values that have been retrieved
ERROR	A real array of the quality indicators for the property values
IER	An integer array of error codes.

All the routines use the RDB\$INTERPRET function to send commands to Rdb/VMS and retrieve data from the data base. They all function as follows:

There is a DO loop that loops through the ASID array from element 1 to the NCMPDS element. Inside this loop:

- RDB\$INTERPRET is used to count the records in relation BESTMSVP having the current ASID.
- Error signals are put into the current element of IER if there is an Rdb error or if no records are found for this ASID.
- The property value, the quality indicator, and the cross reference back to the ALLMSVP relation are retrieved using RDB\$INTERPRET.
- Error signals are put into the current element of IER if there is an Rdb error or if both the property value and the cross reference value are zero. The latter indicates no value for this property.
- The retrieved values are loaded into the output arrays.

Once the loop has finished, the routine is complete.

If IER is nonzero, then an error has occurred. Currently, the only possible error code suffixes are:

001	Indicates an Rdb error
501	Indicates no data for this property or ASID.

4.4.2.1.2 Multiple-Valued Property Access Routines

All the multiple-valued property access routines are identical in function. They access the BESTMMVP relation, count the number of records in the relation with the desired ASID, and, if there is a record for the ASID, retrieve the property value regression equation and coefficients, quality indicator, and valid temperature and pressure ranges.

Inputs to the routines are:

ASID	An integer array of AlliedSignal identifiers
SMILES	A character array of SMILES strings
NCMPDS	An integer field indicating the number of ASIDs in the ASID array.

Outputs from the routines are:

VALUE	A two dimensional real array containing the equation code, the number of coefficients, the 10 coefficients, and the temperature and pressure limits for each ASID
ERROR	A real array of the quality indicators for the equation.
IER	An integer array of error codes.

All the routines use the RDB\$INTERPRET function to send commands to Rdb/VMS and retrieve data from the data base. They all function as follows:

There is a DO loop that loops through the ASID array from element 1 to the NCMPDS element. Inside this loop:

- RDB\$INTERPRET is used to count the records in relation BESTMMVP having the current ASID.
- Error signals are put into the current element of IER if there is an Rdb error or if no records are found for this ASID.
- The equation code, the number of coefficients, the 10 coefficients, the temperature and pressure limits, and the quality indicator are retrieved using RDB\$INTERPRET.
- Error signals are put into the current element of IER if there is an Rdb error.
- The retrieved values are loaded into the output arrays.

Once the loop has finished, the routine is complete.

If IER is nonzero, then an error has occurred. Currently, the only possible error code suffixes are:

001	Indicates an Rdb error
501	Indicates no data for this property or ASID.

4.4.2.2 Methods for Structural Inputs

The structural methods in the AFP Property Prediction System are used to supply structural information to subroutines requiring group decompositions, atom counts, the Z number, and molecular formulas. They were also used to classify molecules into families (see Table 4.4-1) and to check the SMILES strings entered under Task 4.3.1. The structural methods are based upon MedChem software.

4.4.2.2.1 MedChem Software

MedChem software is a system for the storage and retrieval of chemical information and structure. It is a product of Daylight Chemical Information Systems, Inc. Its capabilities include:

- * - Computer-readable chemical structure representation as a SMILES string.
- Graphical representation of SMILES strings.
- * - Substructure searching of SMILES strings using SMARTS strings.
- THOR (Thesaurus Oriented Retrieval) data base system provides MedChem's POMONA89, a 21,565-compound data base and the capability for the user to include additional chemical structures and information.
- MERLIN routine for substructure searching of the compounds in a THOR data base.

The capabilities marked with an asterisk were determined to be useful and/or cost effective and, therefore, are the only capabilities used by the Advanced Fuel Properties system.

4.4.2.2.2 Substructure Searching

The Advanced Fuel Properties system uses SMILES and SMARTS strings (fragments of SMILES strings representing pieces of molecules) to do substructure searching for chemical family classification and for property estimation, e.g., to search for Benson's groups in the estimation of the ideal gas heat of formation of a compound.

Substructure Searching Using GCL Files - Whenever possible, MedChem's GENIE Control Language, GCL, was used to do substructure searching. GCL is a command language that allows one to write a substructure search routine using SMARTS strings and execute the search on any SMILES string.

In the Advanced Fuel Properties system software, a GCL search is executed by calling the subroutine COUNT and passing the name of the GCL file to be executed. When a substructure search on a SMILES string is successful, the subroutine INCGRP is called to set the necessary variable. GCL file substructure searching is used in the Benson's thermodynamic property estimation routine and other group decomposition routines.

Substructure Searching Using SMARTS Searching Directly - When GCL files could not be used (for example, when the type of search to be done required more decision-making or faster execution, a FORTRAN routine was preferred) direct substructure searching using SMARTS strings was done. This was accomplished by sending a SMARTS string along in a call to the subroutines FIND, SRCH, or COUNT. Each has different schemes for marking atoms as found in a SMILES string when matched by a SMARTS substructure. Subroutine FIND is used in the chemical family classification routines, subroutine SRCH is used in the atom-by-atom testing routines described below, and subroutine COUNT is used for multiatom searching in the group decomposition routines.

4.4.2.2.3 Group Decompositions

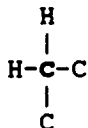
One way of predicting properties from chemical structures is to break the structure into parts and sum the contribution of each of the parts to the property value. The Advanced Fuel Properties software uses two methods of group decomposition for property prediction: atomic groups and multiatom groups.

Atomic Group Decompositions - In atomic group decompositions, the contribution to the property value is obtained by summing the contribution of one atom at a time. The contribution of each atom may or may not contain information about the hybridization or neighbors of that atom.

Example:

A Csp³ carbon is one example of an atomic group that includes hybridization.

An example of an atomic group definition that includes neighbors is:



where the bolded carbon is the only atom counted for this group, the other atoms are only used to define the group.

Multiatom Group Decompositions - In multiatom group decompositions, a group contains more than one atom and a given group may be contained within another group for which there is also a contribution. Therefore, a hierarchical search for groups, and a marking of atoms once a group has been found, is necessary in multiatom group decompositions.

Example:

The search for the propyl group, $\text{-CH}_2\text{CH}_2\text{CH}_3$, must precede a search for a methyl, -CH_3 , or an ethyl, $\text{-CH}_2\text{CH}_3$ group.

Benson's Group Additivity:

The Advanced Fuel Properties software uses a number of tables of group contributions for properties. One of the major tables is the one developed by S. W. Benson, published in his book Thermochemical Kinetics¹⁹. Benson's tables use both atomic and multiatom group decompositions in estimating the ideal gas entropy, enthalpy, and the heat capacity of a molecule.

Example: Calculation of the heat of formation of methylcyclohexane using Benson's group additivity method

Group	Benson's notation	Contribution of Group to Heat of Formation	
Methyl	C-(H)3(C)	-10.20 kcal/mole	(atomic group)
Methylenes in ring	C-(H)2(C)2	5 x -4.93 kcal/mole	(atomic group)
Substituted ring carbon	C-(H)(C)3	-1.90 kcal/mole	(atomic group)
Ring correction	C1CCCCC1	0.00 kcal/mole	(multiatom group)

		-36.75 kcal/mole (measured value)	
		-36.99 kcal/mole)	

4.4.2.2.4 Atom-by-Atom Counting

Once a SMILES string is initialized with the MedChem software, there is a great deal of information about the molecule in the MedChem arrays. Some of this information was used to determine certain properties of the molecule. The molecular weight (subroutine MW2), the Z number (ZNUMB), the number of carbons (CNUM), and the molecular formula (MOLCFM), for example, were

determined by accessing the atomic number of each character in the SMILES string and the hydrogen count of the molecule.

4.4.2.2.5 Chemical Family Classification

The Advanced Fuel Properties software uses a chemical family classification scheme to aid in property estimation and method development. The scheme, embodied in the subroutine FAMLY2 and used for Table 4.1-1, was based originally upon the classifications of chemical compounds used in the DIPPR and TRC data bases. New chemical families were created when it was found that the number of compounds in a given family began to get too large and there was a chemically significant manner in which to subdivide the family.

The chemical family classification scheme is illustrated in Figure 4.4-3. A molecule is classified into a family by searching for a substructure within the molecule that characterizes the family. If the molecule contains the substructure, the search is completed. If not, another substructure search is done. This process continues until a family is found in which the molecule belongs.

The scheme is hierarchical. Therefore, a compound which contains two different functional groups may be classified into a family which only recognizes one of them as significant. Figure 4.4-4 illustrates the subdivision of the "Various hydrocarbon families" indicated in Figure 4.4-3. Again, this hydrocarbon family classification scheme was generally based upon the DIPPR and TRC chemical family schemes and will not classify a compound with more than one functional group in more than one family.

4.4.2.3 Methods for Single-Valued Properties

The methods for the single-valued properties are summarized in Table 4.4-1. For each property, the subroutines available for that property are listed along with a brief explanation of the method and a literature reference if it's appropriate. Many of these methods use group additivity along with experimental inputs to make their predictions. Some are simple correlations between one property and another such as method ZRA2 which calculates the Rackett parameter from the acentric factor.

Following each method is its priority for the priority system described in Section 5. Data base lookup methods have the highest priority because they return experimental (or interpolated or assessed) values. The rest of the

methods are prioritized according to recommendations in the reviews^{7, 45, 8, 15, 16} listed in Section 4.3.1 and the results of our own testing described in the two AFP test reports.^{17, 18}

The calling sequences for the single value property routines are identical to those for single-valued property data lookups. Inputs are:

ASID	An integer array of AlliedSignal identifiers
SMILES	A character array of SMILES strings
NCMPDS	An integer field indicating the number of ASIDs in the ASID array.

Outputs are:

VALUE	A real array of property values
ERROR	A real array of the quality indicators for the property values
IER	An integer array of error codes.

Table 4.4-1
Sources of the Methods for Single-Valued Properties.

Critical Temperature:

TC1 - data base lookup (priority 1)	
TC2 - Joback's method ⁴⁰ (priority 2)	Error = 0.008
TC3 - MW method ²¹ (priority 6)	
TC4 - Jalowka and Daubert's method ²² (priority 5)	
TC5 - Fedor's method ²³ (priority 4)	
TC6 - AIChE 2C and API 4Al.1 ^{24,25} (priority 3)	Error = 0.105

Critical Pressure:

PC1 - data base lookup (priority 1)	
PC2 - Joback's method ⁴⁰ (priority 2)	Error = 0.052
PC3 - MW method ²¹ (priority 5)	
PC4 - Jalowka and Daubert's method ²² (priority 4)	
PC5 - AIChE 2F and API 4Al.1 ^{26,25} (priority 3)	Error = 0.045

Critical Volume:

VC1 - data base lookup (priority 1)	
VC2 - Joback's method ⁴⁰ (priority 2)	Error = 0.023
VC3 - MW method ²¹ (priority 4)	
VC4 - API 4Al.1 ²⁵ (priority 3)	Error = 0.034

Critical Compressibility:

ZC1 - data base lookup (priority 1)	
ZC2 - calculated from PC, VC, and TC (priority 2)	
ZC3 - from acentric factor ²⁷ (priority 3)	

Acentric Factor:

ACENF1 - data base lookup (priority 1)	
ACENF2 - Lee-Kesler ²⁸ (priority 2)	
ACENF3 - from PVAPS ²⁹ (priority 3)	
ACENF4 - Clapeyron Eq'n ³⁰ (priority 4)	

Characteristic Volumes:

VSTAR2 - substituted with VC ³¹ (priority 2)	
VSTAR4 - HBT method with liquid density at 25C ³² (priority 1)	

Soave-Redlich-Kwong Parameter:

ACSRK2 - substituted with acentric factor ³³ (priority 1)	
--	--

Table 4.4-1 (cont.)
Sources of the Methods for Single-Valued Properties

Critical Density:

RHOC1 - AFP data base lookup (priority 1)
RHOC2 - From VC (priority 2)

Rackett Parameter:

ZRA1 - data base lookup (priority 1)
ZRA2 - from acentric factor³⁴ (priority 3)
ZRA3 - substituted with ZC³⁵ (priority 4)
ZRA4 - calculated from liquid density at 25 C³⁶ (priority 2)

Normal Boiling Point:

TNBP1 - data base lookup (priority 1)
TNBP2 - Joback's method²⁰ (priority 2)

Melting Temperature:

TMPSP1 - data base lookup (priority 1)
TMPSP2 - Joback's method²⁰ (priority 2)

Liquid Molar Volume at 25 C:

LMV251 - data base lookup from DIPPR (priority 1)
LMV252 - data base lookup from TRC (priority 2)

Enthalpy of Formation at 25 C:

HF251 - data base lookup (priority 1)

Gibbs Free Energy of Formation at 25 C:

GF251 - data base lookup (priority 1)

Absolute Entropy at 25 C:

S251 - data base lookup (priority 1)

Standard Enthalpy of Combustion at 25 C:

HC251 - data base lookup (priority 1)

Molecular Weight:

MN1 - AFP data base lookup (priority 1)
MN2 - calculated from SMILES string (priority 2)

Table 4.4-1 (cont.)
Sources of the Methods for Single-Valued Properties

Enthalpy of Fusion at T_m :

HFTMP1 - data base lookup (priority 1)

Triple Point Temperature:

TTP1 - data base lookup (priority 1)

Triple Point Pressure:

PTP1 - data base lookup (priority 1)

Solubility Parameter:

SP251 - data base lookup (priority 1)

SP252 - from MVLQ and HVSAT (priority 2)³⁷

Dipole Moment:

DM1 - data base lookup (priority 1)

Radius of Gyration:

RG1 - data base lookup (priority 1)

Flash Point:

FP1 - data base lookup (priority 1)

FP2 - AIChE procedure 11D³⁸

Lower Flammability Limit:

FLLW1 - data base lookup (priority 1)

FLLW2 - AIChE procedure 11B³⁹ (priority 2)

Upper Flammability Limit:

FLUP1 - data base lookup (priority 1)

FLUP2 - AIChE procedure 11C⁴⁰

Autoignition Temperature:

TAI1 - data base lookup (priority 1)

TAI2 - graph theory correlation method (priority 2)

MOLECULE HAS:		FAMILY CLASSIFICATION
TRIPLE BONDS	---->	ALKYNES
ALIPHATIC RINGS		
DECALIN STRUCTURE	---->	DECALIN FAMILY
Bi- OR Tri-CYCLIC RINGS	---->	MULTICYCLIC
HYDROCARBON RINGS		
DOUBLE BONDS	---->	CYCLOOLEFINS
CYCLOPENTANE STRUCTURE	---->	CYCLOPENTANE FAMILY
CYCLOHEXANE STRUCTURE	---->	CYCLOHEXANE FAMILY
OTHER	---->	CYCLOALKANES FAMILY
DOUBLE BONDS		
1 DOUBLE BOND AND MORE THAN 1 METHYL	---->	OTHER ALKENES FAMILY
1 DOUBLE BOND AND 1 METHYL GROUP	---->	ALPHA-OLEFINS FAMILY
2 DOUBLE BONDS	---->	DIOLEFINS
MORE THAN 2 DOUBLE BONDS	---->	OLEFINS WITH > 2 BONDS
DOUBLE		
METHANE	---->	n-PARAFFINS
2 METHYL GROUPS	---->	n-PARAFFINS
BRANCHING IN MOLECULE		
1 METHYL BRANCH	---->	METHYLALKANES
MORE THAN 1 BRANCH	---->	OTHER ALKANES
MORE THAN 6 AROMATIC CARBONS		
MORE THAN 2 FUSED RINGS		
ANTHRACENE STRUCTURE	---->	ANTHRACENE FAMILY
PHENANTHRENE STRUCTURE	---->	PHENANTHRENE FAMILY
OTHER	---->	OTHER POLYAROMATICS
2 FUSED RINGS		
NAPHTHALENE STRUCTURE	---->	NAPHTHALENE FAMILY
BIPHENYL RINGS		
1 BIPHENYL RING	---->	BIPHENYL FAMILY
MORE THAN ONE BIPHENYL RING	---->	OTHER POLYAROMATICS
PENDANT PHENYL RINGS		
2 PHENYL RINGS	---->	DIPHENYL FAMILY
MORE THAN 2	---->	OTHER POLYAROMATICS
6 AROMATIC CARBONS		
TETRALIN STRUCTURE	---->	TETRALIN FAMILY
INDAN STRUCTURE	---->	INDAN FAMILY
INDENE STRUCTURE	---->	INDENE FAMILY
DOUBLE OR TRIPLE BONDS OR ALIPHATIC RINGS	---->	OTHER MONOAROMATICS
BENZENE	---->	n-ALKYL BENZENE
ONLY 1 METHYL GROUP	---->	n-ALKYL BENZENE
MORE THAN 1 METHYL GROUP	---->	ALKYLBENZENES

Figure 4.4-3
Hydrocarbon Family (C and H only) Classification

Molecules are classified into chemical families using substructure searching. A molecule will be a member of only one family. The hierarchical scheme for classifying molecules is as follows:

<u>MOLECULE CONTAINS:</u>	<u>FAMILY CLASSIFICATION</u>
1 atom or 2 identical atoms	Element family
Atoms other than H, C, N, O, S, P, or halogens	Miscellaneous
C and H only	Various hydrocarbon families
Phosphorous	Phosphorous family
Sulfur	Sulfur family
Halogen	Various halogen families
Nitrogen	Various nitrogen families
Oxygen	Various oxygen families

NOTE: Because of the fact that the scheme above is hierarchical and that each molecule belongs to only one chemical family, molecules have certain functional groups in common that may be placed in different chemical families.

EXAMPLE:	CCCN=O	----->	a nitrogen family
	CCCN=O	----->	a halogen family
	Cl		

Figure 4.4-4
Chemical Family Classification Scheme

4.4.2.4 Introduction to the Methods for Thermodynamic Properties

AFP is intended to provide useful thermodynamic information about organic compounds. The principal thermodynamic functions needed are enthalpy, H , entropy, S , Gibbs free energy, G , internal energy, U , and Helmholtz free energy, A . The state variables employed are temperature, T , pressure, P , molar volume, V , phase (solid, liquid, ideal gas, real gas), and mixture composition. A discussion of the various thermodynamic functions is given below. This discussion is useful for its information on thermodynamic functions as they apply to AFP, and it also helps to alleviate confusion concerning the reference state used to determine these properties.

4.4.2.4.1 Internal Energy

Internal energy, U , is the potential and kinetic energy of the particles within a system. There is no way to fix an absolute value on internal energy. Therefore, the reference state is arbitrary. Internal energy is defined by:

$$\begin{aligned}\Delta U &= Q - W \\ \text{or} \\ dU &= \delta Q - \delta W\end{aligned}$$

for changes where the overall kinetic and potential energy of the system do not change (i.e., the system does not accelerate). Here Q is the heat and W is the work. Since the internal energy is a function of state, and its zero point is arbitrary, we will define U relative to the zero point in the enthalpy function described below. The value of internal energy of any material can be calculated by subtracting the pressure times the volume from the enthalpy, as shown below.

4.4.2.4.2 Enthalpy

H is chosen so that changes in heat correspond to changes in the enthalpy function. Thus, changes in H are directly measurable for a

reversible process. The relation between enthalpy and internal energy is:

$$H=U+PV.$$

Like internal energy, the enthalpy function can have its zero point chosen at any convenient reference condition. For AFP, we have chosen a convenient set of reference conditions, consistent with our ability to calculate thermodynamic departure functions, or residual properties. We choose the reference enthalpy to be the heat of formation at 298.15 for all substances in their reference state.

The ideal gas state (zero pressure) will be chosen as the reference state for all compounds. For elements, the state chosen as reference state in the JANAF tables will be selected. This is usually the most stable form of the compound at any temperature. Graphite is the reference state for carbon. The rhombic form of crystalline sulfur is chosen for 0 to 368.54K, the monoclinic form from 368.54 to 388.36K, the liquid from 388.36 to 717.75K, and the ideal gas state above that point. The ideal gas forms of diatomic oxygen, hydrogen, deuterium, chlorine, fluorine, and nitrogen are chosen. At present, these are the only elements defined in AFP for thermodynamic calculations.

4.4.2.4.3 Entropy

Absolute entropies are used, that is, the entropy of a substance is zero at 0 K. As is done in the JANAF tables, this applies to the crystalline, as well as the ideal gas state. The entropy at any other temperature is found by integrating the heat capacity at constant pressure over the natural log of temperature from 0 K to the temperature of interest.

4.4.2.4.4 Gibbs Free Energy

Gibbs free energy, G , is a convenient function because it can be used as a criterion for equilibrium in a system at constant pressure. For a system at constant P , equilibrium occurs when G is minimized. Values for Gibbs free energy can be calculated using the reference conditions described above for

enthalpy and entropy. The definition of G is:

$$G=H-TS.$$

Thus, we can calculate or estimate enthalpy and entropy for any compound or element at any temperature. H will be relative to the elements in the reference state at 298.15K, and S will be relative to zero at 0 K.

4.4.2.4.5 Helmholtz Free Energy

Helmholtz's free energy, A , is a convenient function which describes equilibrium for changes in a system at constant volume. The minimum in A at constant volume is the criterion for equilibrium. Values for the Helmholtz free energy can be calculated using the reference conditions described above for enthalpy and entropy. The definition of A is:

$$A=H-PV-TS.$$

Thus, we can calculate or estimate enthalpy and entropy for any compound or element at any temperature. H will be relative to the elements in the reference state at 298.15K, and S will be relative to zero at 0 K.

4.4.2.4.6 Data Flow for Thermodynamic Properties

The data flow for calculations of thermodynamic properties of fluids is illustrated in Figure 4.4-5. Two groups of inputs are needed: (1) critical temperatures, critical pressures, and acentric factors are required for calculations of nonideal gas pressure effects using equations of state, and (2) ideal gas enthalpies of formation at 298K, ideal gas absolute entropies at 298K, and ideal gas heat capacities as a function of temperature are required to calculate ideal gas properties.

Using an equation of state, the gas and liquid molar volumes, densities, and compressibilities can be calculated from the first set of inputs. The molar volumes can then be used to calculate residual thermodynamic properties for either the gas or liquid phase. Directly from these residual thermodynamic properties, the properties associated with the liquid-gas phase transition such as boiling points, vapor pressures, and heats of vaporization can be calculated.

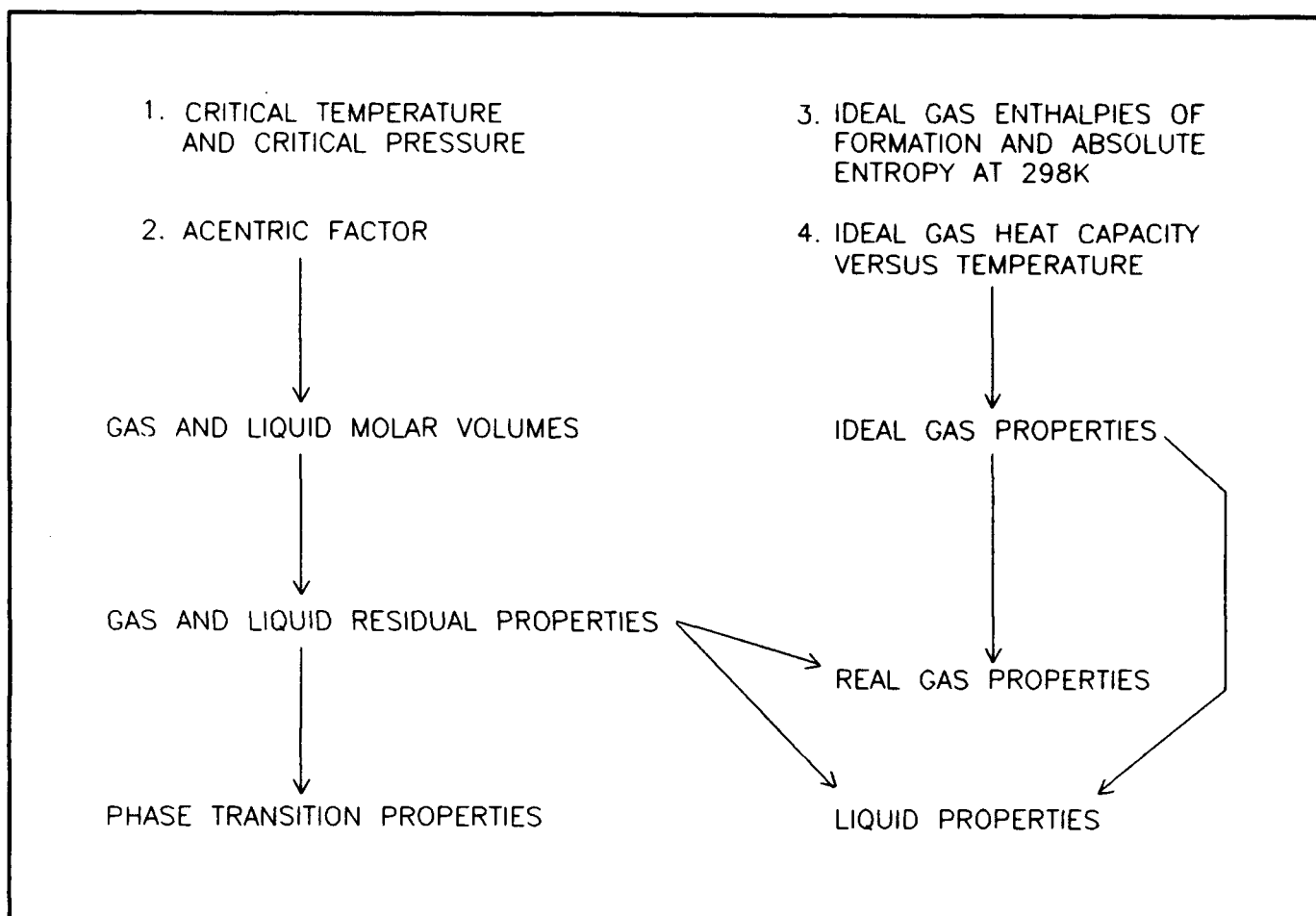


Figure 4.4-5
Data Flow for Fluid Thermodynamic Calculations

Starting with the second set of inputs, the ideal gas thermodynamic properties can be calculated by simply integrating the heat capacity for relative enthalpies and the heat capacity divided by temperature for relative entropies. The values of the enthalpy of formation and absolute entropy at 298K are used to calculate ideal gas enthalpies of formation and absolute entropies at any temperature.

By combining the ideal gas thermodynamic properties with the gas phase residual properties, the real gas properties can be calculated at any temperature and pressure. Similarly, the combination of ideal gas properties and the liquid phase residual properties gives liquid properties at any temperature and pressure.

4.4.2.5 Methods for Ideal Gases

The calculation of ideal gas thermodynamic properties is complicated by the great variety of ways in which temperature dependent heat capacities are stored in the literature. In the DIPPR data base alone two equations are used to describe ideal gas heat capacities:

$$C_p^{\text{ideal}} = A + B \cdot T + C \cdot T^2 + D \cdot T^3 + E \cdot T^4$$

$$C_p^{\text{ideal}} = A + B \cdot (C / (T \cdot \sinh(C/T)))^2 + D \cdot (E / (T \cdot \cosh(E/T)))^2.$$

Benson's¹⁹ group additivity method for predicting ideal gas heat capacities produces values at temperatures of 300K, 400K, 500K, 600K, 800K, 1000K, and 1500K. Heat capacities at other temperatures are estimated by interpolating among these values. The ideal gas heat capacity data in the TRC tables are also tabulated at individual temperatures, but they are different than those from Benson's method. Thus, a set of ideal gas subroutines is required for every source of data or predicted values.

4.4.2.5.1 Relative Enthalpy

The enthalpy change of an ideal gas is dependent on the change in temperature. Therefore, the ideal gas enthalpy or relative enthalpy, can be determined from the heat capacity by:

$$H^{\text{ideal}}(T) - H^{\text{ideal}}(298) = \int C_p^{\text{ideal}} dT.$$

HID provides the enthalpy of an ideal gas at temperature T value. This is the enthalpy of formation at 298.15, plus the enthalpy of heating or cooling the ideal gas to temperature T. It differs from the enthalpy of

formation at T in that it is referred to the elements at 298.15 instead of T. It is the enthalpy for path BCD in Figure 4.4-7.

The relative enthalpy is not very useful for thermodynamic calculations, therefore, the ideal gas enthalpy of formation is also calculated as described in Figure 4.4-6.

$$\Delta H_f^0(T) = \{H^0(T) - H^0(298)\}_{\text{cpd}} - \sum v_i \{H^0(T) - H^0(298)\}_{\text{elem}} + \Delta H_f^0(298)$$

where,

- * $\Delta H_f^0(298)$ is calculated using method HF25I (Table 4.4-1)
- * $\{H^0(T) - H^0(298)\}_{\text{cpd}}$ is calculated using method HID
- * $\{H^0(T) - H^0(298)\}_{\text{elem}}$ is calculated for all of the elements (based initially on Table 18 from TRC¹¹)
- * v_i are stoichiometric coefficients or atom counts from method ATMCNT

Figure 4.4-6
Ideal Gas Enthalpy of Formation

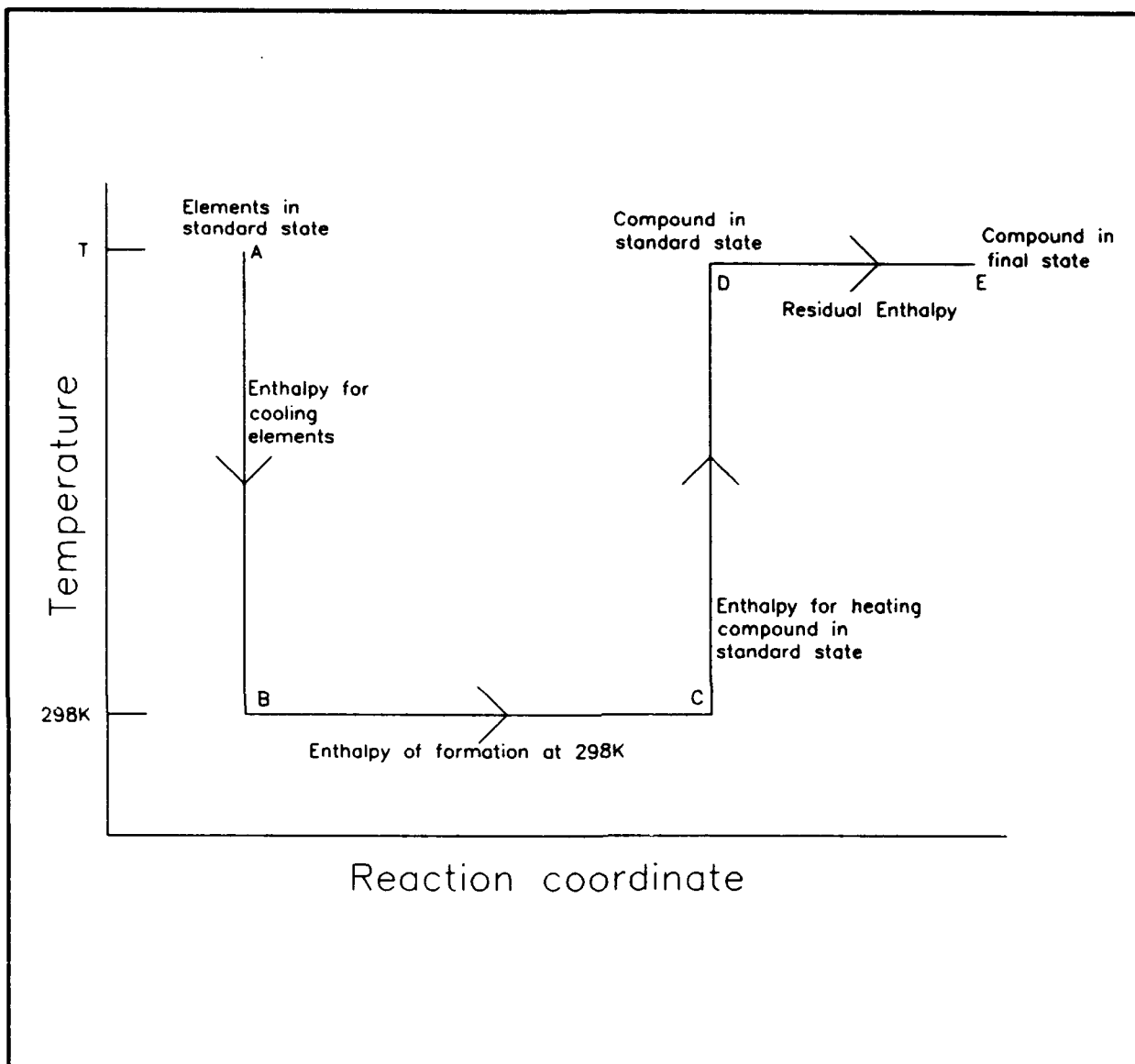


Figure 4.4-7
Enthalpy of Formation of a Compound at Any Temperature

4.4.2.5.2 Enthalpy of Formation

This quantity is the enthalpy of reaction for the formation of a compound from its elements at standard conditions, i.e., the specified temperature and one atmosphere. The enthalpy of formation of the elements in

their reference state is zero at all temperatures. The enthalpy of formation of any compound at any temperature is found as follows. The enthalpy of taking the elements from the temperature of interest to 298.15 is found. The heat of formation of the compound in its standard state at 298.15 is added. The enthalpy of taking the compound from 298.15 to the temperature of interest is added, then the residual enthalpy for the phase at the temperature of interest is added. This path is shown graphically in Figure 4.4-7.

The superscript circle in Figure 4.4-6 is used to indicate that these are ideal gas standard state enthalpies. Real gas and liquid thermodynamic properties are used for the elements and are looked up from a data table. The stoichiometric coefficients, ν_i , are the counts for each atom in the compound and are automatically calculated in the AFP prediction system using the structural method ATMCNT.

4.4.2.5.3 Enthalpy of Formation for an Ideal Gas at 298K

HF25I provides the enthalpy of formation of the ideal gas at 298.15K. This is the enthalpy for converting the elements in their reference states to the compound in the ideal gas state at 298.15 K. Methods include a database lookup and an estimation by Benson's¹⁹ method. HF25I is the enthalpy change upon taking path BC in Figure 4.4-7.

4.4.2.5.4 Enthalpy of Formation of an Ideal Gas

HFID provides the enthalpy of formation of an ideal gas at temperature T. It is the enthalpy of converting the elements at T to the ideal gas compound at T. It corresponds to the enthalpy change for path ABCD in Figure 4.4-7. In practice, it is the difference between the values returned by HID and HELM.

4.4.2.5.5 Entropy of an Ideal Gas

The zero point for entropies is always taken as absolute zero. The entropy of an element is calculated as the integral of C_p/T from 0 K to the temperature of interest. If a phase transformation occurs, e.g., sulfur, the entropy of the transition is included in the calculation, as below.

$$S = \int_0^{T_{trans}} \frac{C_p(1)}{T} dT + \Delta S_{trans} + \int_{T_{trans}}^T \frac{C_p(2)}{T} dT$$

4.4.2.5.6 Entropy of Formation

The entropy of formation ΔS of a compound can be calculated by taking the difference between the entropy of the reference state and the elements, and adding the residual entropy for the appropriate state. This is tantamount to integrating the entropy of the elements from T to 0 K , transforming at 0 K to the ideal gas state ($\Delta S = 0$), integrating the entropy from 0 back to T for the products, then adding the residual entropy for the final state. The calculation is illustrated in Figure 4.4-8.

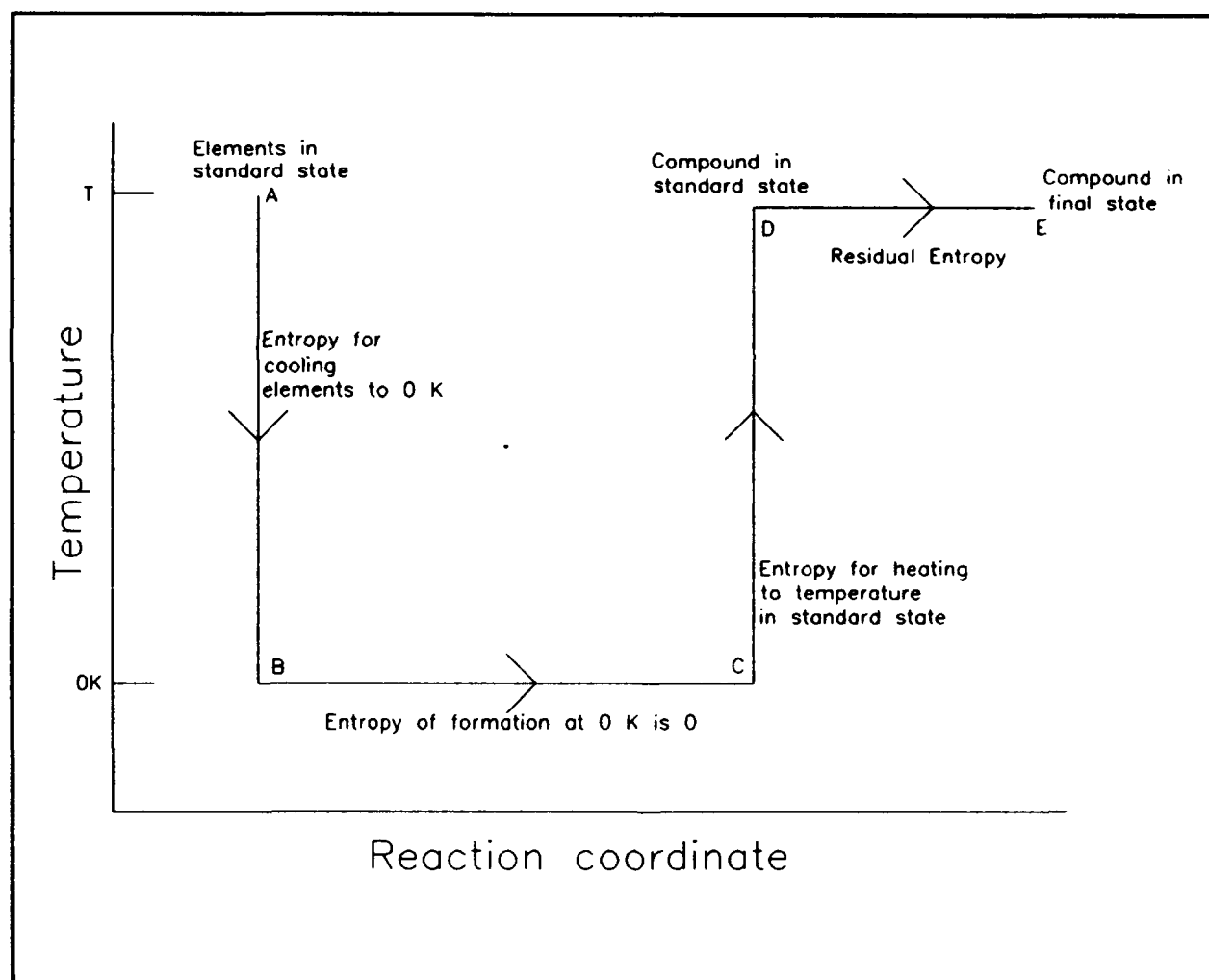


Figure 4.4-8
Calculation of Entropy of a Compound

The ideal gas predictive methods are summarized in Table 4.4-2. For most properties there are only two methods: one based upon the two DIPPR equations and one based upon Benson's method. The highest priority is given to the lookup of experimental data followed by Benson's group additivity method.

Many of these ideal gas thermodynamic properties are both temperature and pressure dependent since ideal gas entropies, Gibbs free energies, and Helmholtz free energies change with pressure. Pressure effects are frequently forgotten when dealing with ideal gases but follow from the ideal gas equation of state, $P*V=R*T$. The pressure dependence for the ideal gas entropy, for example, is given by:

$$S^{ideal}(T,P) = S^{ideal}(T,1 \text{ atm.}) - R*\ln(P)$$

where the pressure, P , is given in atmospheres. The pressure dependence of other quantities can easily be calculated by substituting the pressure corrected entropy in their definitions.

The calling sequences for the ideal gas property routines are more complicated than for the single value properties. Inputs are:

ASID	An integer array of AlliedSignal identifiers
SMILES	A character array of SMILES strings
NCMPDS	An integer field indicating the number of ASIDs in the ASID array
TEMP	A real array of temperatures
NTEMP	An integer field indicating the length of the TEMP array
PRESS	A real array of pressures
NPRESS	An integer field indicating the length of the PRESS array.

Outputs are:

VALUE	A real 3D array of property values
ERROR	A real 3D array of the relative errors corresponding to the property values
IER	An integer 3D array of error codes.

The new inputs and changed outputs reflect the fact that ideal gas properties are different for each compound, temperature, and pressure.

Table 4.4-2
Sources for the Methods for Ideal Gas Properties

Relative Enthalpy:

HID2 - calculated from DIPPR data (priority 1)
HID3 - Benson's method¹⁹ (priority 2)

Absolute Entropy:

SID2 - calculated from DIPPR data (priority 1)
SID3 - Benson's method¹⁹ (priority 2)

Gibbs Free Energy:

GID2 - calculated from HID2 and SID2 (priority 1)
GID3 - calculated from HID3 and SID3 (priority 2)

Helmholtz Free Energy:

AID2 - calculated from HID2 and SID2 (priority 1)
AID3 - calculated from HID3 and SID3 (priority 2)

Internal Free Energy:

UID2 - calculated from HID2 (priority 1)
UID3 - calculated from HID3 (priority 2)

Isobaric Heat Capacity:

CPID2 - data base lookup (priority 1)
CPID3 - Benson's method¹⁹ (priority 2)

Isochoric Heat Capacity:

CVID2 - calculated from CPID2 (priority 1)
CVID3 - calculated from CPID3 (priority 2)

Table 4.4-2 (cont.)
Sources for the Methods for Ideal Gas Properties

Enthalpy of Formation at 298 K:

HF25I1 - data base lookup (priority 1)
HF25I2 - Benson's method¹⁹ (priority 2)

Absolute Entropy at 298 K:

S25ID1 - data base lookup (priority 1)
S25ID2 - Benson's method¹⁹ (priority 2)

Gibbs Free Energy of Formation at 298 K:

GF25I1 - data base lookup (priority 1)
GF25I2 - calculated from HF25I1 and S25ID1 (priority 2)
GF25I3 - calculated from HF25I2 and S25ID2 (priority 3)

Enthalpy of Formation:

HFID2 - DIPPR data base equations (priority 1)
HFID3 - Benson's method¹⁹ (priority 2)

Gibbs Free Energy of Formation:

GFID2 - DIPPR data base equations (priority 1)
GFID3 - Benson's method¹⁹ (priority 2)

Formation Equilibrium Constant:

KI1D2 - calculated from GFID2 (priority 1)
KI1D3 - calculated from GFID3 (priority 2)

4.4.2.6 Methods for Residual Properties

The AFP property prediction system calculates residual thermodynamic properties using any one of the following equations of state. Residual or departure, properties describe real gases relative to the ideal gas reference state.

1. Ideal Gas Equation: $P * V = R * T$
2. Second Virial Equation: $P = R * T * ((1/V) + (B/V^2))$ where B is a function of temperature that must be retrieved or predicted.
3. Peng-Robinson Equation: $P = (R * T)/(V - b) - a/(V * (V + b) + b * (V - b))$ where a and b are given in Figure 4.4-9.
4. Redlich-Kwong Equation: $P = (R * T)/(V - b) - a/(V * (V + b))$ where a and b are given in Figure 4.4-9.
5. Soave Equation: $P = (R * T)/(V - b) - a/(V * (V + b))$ where a and b are given in Figure 4.4-9.
6. Van der Waals Equation: $P = (R * T)/(V - b) - a/V^2$ where a and b are given in Figure 4.4-9.

Experimental values for the second virial equation are available in the DIPPR data base and have been used to calculate gas phase residual properties. Second virial coefficients are not valid for the liquid phase so these methods have not been programmed.

Equations 3-6 are all cubic equations in the molar volume as shown in Figure 4.4-9.¹⁶ They can be solved using the algebraic solution for cubic equations¹¹ or by iterative root solvers¹². We now use the algebraic solver.

$$P = \frac{RT}{V - b} - \frac{a}{V^2 + ubV + wb^2}$$

EQUATION	u	w	b	a
PENG-ROBINSON	2	-1	$\frac{0.07780 RT_c}{P_c}$	$\frac{0.45724 R^2 T_c^2}{P_c} [1 + f_\omega(1-t_r^{1/2})]^2$
REDLICH KWONG	1	0	$\frac{0.08664 RT_c}{P_c}$	$\frac{0.42748 R^2 T_c^{2.5}}{P_c T^{0.5}}$
SOAVE	1	0	$\frac{0.08664 RT_c}{P_c}$	$\frac{0.42748 R^2 T_c^2}{P_c} [1 + f_\omega(1-t_r^{1/2})]^2$
VAN DER WAALS	0	0	$\frac{RT_c}{8P_c}$	$\frac{27 R^2 T_c^2}{64 P_c}$

General	$t_r = T/T_c$
PENG-ROBINSON	$f_\omega = 0.37464 + 1.54226\omega - 0.26992\omega^2$
SOAVE	$f_\omega = 0.48 + 1.574\omega - 0.176\omega^2$

Figure 4.4-9
Cubic Equations of State

Cubic equations of state are tricky to solve because there are non-physical and multiple roots which must be trapped out of the calculations. This is illustrated in Figure 4.4-10 which is a plot of the Peng-Robinson equation¹⁶. For temperatures above the critical point (e.g., $T_r = 2.7$), the high molar volume (low density) root (point C on Figure 4.4-10) is clearly the physical solution for the supercritical fluid. However, for reduced pressures greater than P_c , there are two nonphysical roots (points A and B on Figure 4.4-10) at very small or negative molar volumes. Similarly, for temperatures below the critical point (e.g., $T_r = 0.9$), there are three regions of concern. For reduced pressures below P_c , there is only one large molar volume root which is the pure gas phase. Between reduced pressures P_1 and P_2 , there are three roots: the largest is the vapor phase, the middle is nonphysical, and the smallest is the liquid. This is the two-phase region of the phase diagram. For reduced pressures greater than P_2 , only one small molar volume root exists for the liquid phase. The AFP software finds all of these roots and correctly assigns them for each case.

* The reduced temperature and reduced pressure (t_r and p_r) are defined as the temperature and pressure divided by the critical temperature and critical pressure, respectively.

Values of the Peng Robinson Equation

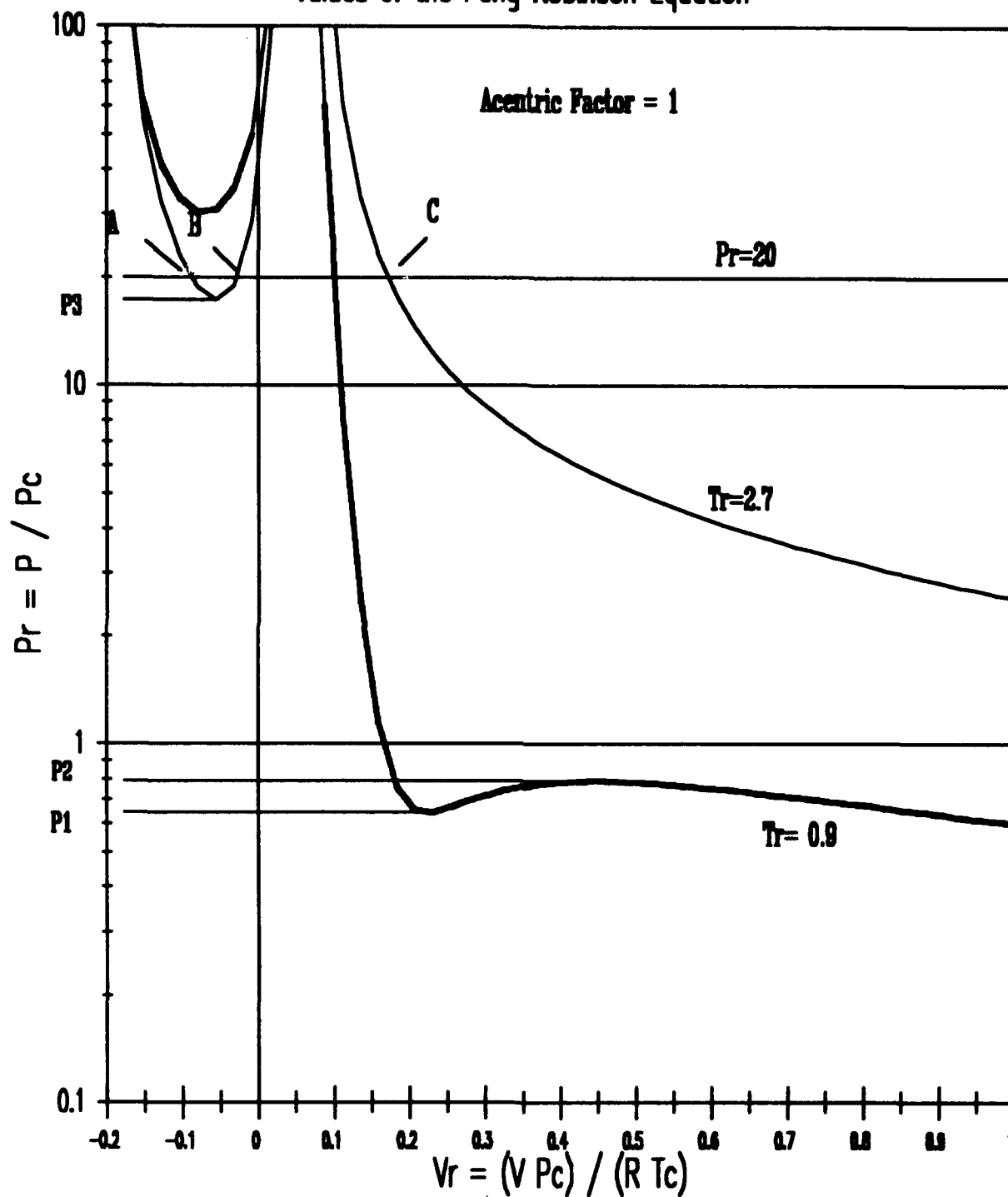


Figure 4.4-10
 P_r vs V_r Plot for Peng-Robinson Equation

Once the values of P , T , V_g , and V_l are known, we can calculate residual properties by inserting either gas or liquid phase molar volumes into the appropriate equations for the given equation of state. These equations are tabulated in Reid, Prausnitz, and Poling¹⁵ and Edmister and Lee¹⁶. They are derived by inserting the equations of state listed above into the following thermodynamic relations:

$$\text{Residual Enthalpy: } H^{res} = \int_0^P (V - T * (\partial V / \partial T)_P) dP$$

$$\text{Residual Entropy: } S^{res} = \int_0^P ((R/P) - (\partial V / \partial T)_P) dP$$

$$\text{Residual Internal Energy: } U^{res} = (R * T) - (P * V) +$$

$$\int_0^P (V - T * (\partial V / \partial T)_P) dP$$

$$\text{Residual Gibbs Free Energy: } G^{res} = \int_0^P (V - (R * T) / P) dP$$

$$\text{Residual Helmholtz Free Energy: } A^{res} = (R * T) - (P * V) +$$

$$\int_0^P (V - (R * T) / P) dP$$

$$\text{Residual Isobaric Heat Capacity: } C_p^{res} = - \int_0^P (T * (\partial^2 V / \partial T^2)_P) dP$$

$$\text{Residual Isochoric Heat Capacity: } C_v^{res} = \int_{\infty}^V (\partial^2 P / \partial T^2)_V dV$$

$$\text{Fugacities: } \ln(f/P) = G^{res} / (R * T).$$

The methods for residual properties are summarized in Table 4.4-3. For most of the properties, there are five methods corresponding to equations of state numbered 2 through 6 in Section 4.4.2.6. Residual properties are zero for ideal gases by definition.

The residual enthalpy of a real gas or liquid will be used as an example to describe the values determined by the residual property methods. HRES returns the enthalpy for the state change from the compound as an ideal gas to the compound as a real gas or liquid. It calculates the residual, or departure, enthalpy by performing the integration of Equation 6. HRES corresponds to the enthalpy change of segment DE in Figure 4.4-7. Two checks on this estimate are that HRES for a liquid should approximately equal the enthalpy of vaporization, and HRES for a real gas should be near zero at low pressures.

The calling sequences for the residual property routines are slightly more complicated than for the ideal gas properties. Inputs are:

ASID	An integer array of AlliedSignal identifiers
SMILES	A character array of SMILES strings
NCMPDS	An integer field indicating the number of ASIDs in the ASID array
TEMP	A real array of temperatures
NTEMP	An integer field indicating the length of the TEMP array
PRESS	A real array of pressures
NPRESS	An integer field indicating the length of the PRESS array
STATE	An integer field indicating the state for calculation; 1 is for gases, 2 is for liquids, 3 is for solids.

Outputs are:

VALUE	A real 3D array of property values
ERROR	A real 3D array of the relative errors for the property values
IER	An integer 3D array of error codes.

The same subroutine will be used for all the phases.

Table 4.4-3
Summary of Methods for Residual Properties

Isobaric Heat Capacity:

- CPRES2 - 2nd virial equation (priority 4)
- CPRES3 - Peng-Robinson equation (priority 1)
- CPRES4 - Van der Waals equation (priority 5)
- CPRES5 - Redlich-Kwong equation (priority 3)
- CPRES6 - Soave equation (priority 2)

Isochoric Heat Capacity:

- CVRES3 - Peng-Robinson equation (priority 1)
- CVRES4 - Van der Waals equation (priority 4)
- CVRES5 - Redlich-Kwong equation (priority 3)
- CVRES6 - Soave equation (priority 2)

Fugacities:

- FUGAC2 - 2nd virial equation (priority 4)
 - FUGAC3 - Peng-Robinson equation (priority 1)
 - FUGAC4 - Van der Waals equation (priority 5)
 - FUGAC5 - Redlich-Kwong equation (priority 3)
 - FUGAC6 - Soave equation (priority 2)
-

Table 4.4-3 (cont.)
Summary of the Methods for Residual Properties

Enthalpy:

- HRES2 - 2nd virial equation (priority 4)
- HRES3 - Peng-Robinson equation (priority 1)
- HRES4 - Van der Waals equation (priority 5)
- HRES5 - Redlich-Kwong equation (priority 3)
- HRES6 - Soave equation (priority 2)

Entropy:

- SRES2 - 2nd virial equation (priority 4)
- SRES3 - Peng-Robinson equation (priority 1)
- SRES4 - Van der Waals equation (priority 5)
- SRES5 - Redlich-Kwong equation (priority 3)
- SRES6 - Soave equation (priority 2)

Internal Energy:

- URES3 - Peng-Robinson equation (priority 1)
- URES4 - Van der Waals equation (priority 4)
- URES5 - Redlich-Kwong equation (priority 3)
- URES6 - Soave equation (priority 2)

Gibbs Free Energy:

- GRES2 - 2nd virial equation (priority 4)
- GRES3 - Peng-Robinson equation (priority 1)
- GRES4 - Van der Waals equation (priority 5)
- GRES5 - Redlich-Kwong equation (priority 3)
- GRES6 - Soave equation (priority 2)

Helmholtz Free Energy:

- ARES2 - 2nd virial equation (priority 4)
- ARES3 - Peng-Robinson equation (priority 1)
- ARES4 - Van der Waals equation (priority 5)
- ARES5 - Redlich-Kwong equation (priority 3)
- ARES6 - Soave equation (priority 2)

4.4.2.7 Methods for Real Gases

Given the methods for ideal gas and residual thermodynamic properties, a large number of methods for real gases can be constructed. These methods are summarized in Table 4.4-4. There are currently 10 methods for most thermodynamic properties because there are 2 choices for the ideal gas properties (see Table 4.4-2) and 5 choices for the residual properties (see Table 4.4-3). The real gas thermodynamic methods do not have priorities of their own because they call priority level routines for the ideal gas and residual contributions.

The molar heat of combustion method uses the structural method ATMCNT to find the number of elements in the compound and then uses HFRG methods to calculate the change in enthalpy during the combustion reaction. (Methods for heats of combustion per unit mass and unit volume are also available.)

HC returns the enthalpy of combustion for a compound. The reactant and products are all at the same temperature. There are several options for the type of calculation. In every case the calculation is carried out as:

$$\Delta H_c = \sum_{\text{products}} v_i \Delta H_{fi} - \sum_{\text{reactants}} v_j \Delta H_{fj} + \Delta H_{mix}(\text{products}) - \Delta H_{mix}(\text{reactants})$$

where the v_i are mole numbers, ΔH_f are the heats of formation, and ΔH_{mix} are the heats of mixing.

The reactants are the compound of interest, plus oxygen as diatomic ideal gas. Both are at the temperature and pressure of interest. The compound to be burned is in the initial state (liquid, real gas, ideal gas) specified by the user. The products are estimated by AFP using the routine CPRDCT. Principal products will be CO_2 and H_2O , plus other compounds formed from heteroatoms in the reactant.

The two main options for this calculation are the initial state of the reactants, and the final state of the water in the products. The net heat of combustion is found for water as vapor in the product. The net heat is smaller than the gross heat of combustion, which is based on liquid water as the product.

Table 4.4-4
Summary of Methods for Real Gas Properties

Molar Volume:

- MVRG3 - Peng-Robinson equation (priority 1)
- MVRG4 - ideal gas equation (priority 5)
- MVRG5 - Van der Waals equation (priority 4)
- MVRG6 - Redlich-Kwong equation (priority 3)
- MVRG7 - Soave equation (priority 2)

Compressibility:

- CMPR2 - 2nd virial equation (priority 4)
- CMPR3 - Peng-Robinson equation (priority 1)
- CMPR4 - ideal gas equation (priority 6)
- CMPR5 - Van der Waals equation (priority 5)
- CMPR6 - Redlich-Kwong equation (priority 3)
- CMPR7 - Soave equation (priority 2)

2nd Virial Coefficient:

- BRG2 - data base lookup (priority 1)
- BRG4 - ideal gas equation (priority 3)
- BRG5 - Van der Waals equation (priority 2)

Density:

- RHORG3 - Peng-Robinson equation (priority 1)
- RHORG4 - ideal gas equation (priority 5)
- RHORG5 - Van der Waals equation (priority 4)
- RHORG6 - Redlich-Kwong equation (priority 3)
- RHORG7 - Soave equation (priority 2)

Table 4.4-4 (cont.)
Summary of Methods for Real Gas Properties

Enthalpy:

HRG - 10 methods (2 ideal gases * 5 residuals)

Entropy:

SRG - 10 methods (2 ideal gases * 5 residuals)

Internal Energy:

URG - 10 methods (2 ideal gases * 5 residuals)

Gibbs Free Energy:

GRG - 10 methods (2 ideal gases * 5 residuals)

Helmholtz Free Energy:

ARG - 10 methods (2 ideal gases * 5 residuals)

Isobaric Heat Capacity:

CPRG - 10 methods (2 ideal gases * 5 residuals)

Isochoric Heat Capacity:

CVRG - 10 methods (2 ideal gases * 5 residuals)

Enthalpy of Formation:

HFRG - 10 methods (2 ideal gases * 5 residuals)

Gibbs Free Energy of Formation:

GFRG - 10 methods (2 ideal gases * 5 residuals)

Molar Heat of Combustion:

HCRG - 10 methods (2 ideal gases * 5 residuals)

The calling sequences for the real gas methods are the same as for the ideal gas properties.

Inputs are:

ASID	An integer array of AlliedSignal identifiers
SMILES	A character array of SMILES strings
NCMPDS	An integer field indicating the number of ASIDs in the ASID array
TEMP	A real array of temperatures
NTEMP	An integer field indicating the length of the TEMP array
PRESS	A real array of pressures
NPRESS	An integer field indicating the length of the PRESS array.

Outputs are:

VALUE	A real 3D array of property values
ERROR	A real 3D array of the relative errors for the property values
IER	An integer 3D array of error codes.

4.4.2.8 Methods for Liquid Properties

The ideal gas and second virial coefficient equations of state are only valid for the gas phase. Thus, by combining the various ideal gas and residual property methods to obtain liquid property methods, one obtains eight liquid thermodynamic methods. This is due to having two ideal gas methods and four equations of state (Peng-Robinson, Redlich-Kwong, Soave, and van der Waals). Since DIPPR and the TRC tables contained experimental data for liquid heat capacities, liquid phase thermodynamics could be calculated by integrating over the heat capacities.

Because of the enormous amount of work required to use equations of state to calculate liquid properties, several researchers have developed equations that are used for liquids only. The Rackett³⁶ and Hankinson-Brost-Thomson⁴³ equations have currently been programmed for liquid densities at saturation pressure. These equations are:

$$\text{Rackett Equation}^{36}: V_s = ((R * T_c) / P_c) * Z_{RA}^{(1 + (1 - T_r)^{2/3})}$$

$$\text{Hankinson-Brost-Thomson}^{43}: V_s = V^* * V_R^{(0)} * (1. - \omega_{SRK} * V_R^{(0)})$$

where $V_R^{(0)}$ and $V_R^{(0)}$ are known functions of $T_r = T/T_c$.

For the liquid densities under compression, the Tait-Hankinson-Brost-Thomson⁴⁴ and Density Correlation⁴⁵ equations:

$$\text{Tait-HBT}^{44}: V = V_s * (1 - c * \ln((\beta + P) / (\beta + P_{vap}))) \text{ where } c \text{ is a known function of } \omega_{SRK} \text{ and } \beta \text{ is a function of } T_r \text{ and } \omega_{SRK}.$$

$$\text{Density Correlation}^{45}: V_1 = V_2 * C_2 / C_1 \text{ where the correlation coefficients are known functions of the reduced temperature and pressure.}$$

The methods for liquids are summarized in Table 4.4-5. The methods that use ideal gas and residual properties to calculate liquid thermodynamic properties do not have priorities because they call priority subroutines for the ideal gas and residual properties.

HRG and HLQ return the enthalpy at T of the real gas or liquid relative to the elements in their reference states at 298.15 K. This corresponds to path BCDE in Figure 4.4-7, and is obtained in practice by adding HID and HRES for the appropriate state.

HFRG and HFLQ return the enthalpy of formation at T of the real gas or liquid, relative to the elements in their reference states at the same temperature. This corresponds to path ABCDE in Figure 4.4-7. It is obtained in practice by subtracting the result of HELM from the value returned by HRG or HLQ.

The calling sequences for these methods are the same as for the ideal gas properties.

Inputs are:

ASID	An integer array of AlliedSignal identifiers
SMILES	A character array of SMILES strings
NCMPDS	An integer field indicating the number of ASIDs in the ASID array
TEMP	A real array of temperatures
NTEMP	An integer field indicating the length of the TEMP array
PRESS	A real array of pressures
NPRESS	An integer field indicating the length of the PRESS array.

Outputs are:

VALUE	A real 3D array of property values
ERROR	A real 3D array of the quality indicators for the property values
IER	An integer 3D array of error codes.

Table 4.4-5
Summary of Methods for Liquid Properties

Enthalpy:

HLQ2 - 8 methods (2 ideal gases * 4 residuals)

Entropy:

SLQ2 - 8 methods (2 ideal gases * 4 residuals)

Internal Energy:

ULQ2 - 8 methods (2 ideal gases * 4 residuals)

Gibbs Free Energy:

GLQ2 - 8 methods (2 ideal gases * 4 residuals)

Helmholtz Free Energy:

ALQ2 - 8 methods (2 ideal gases * 4 residuals)

Isobaric Heat Capacity:

CPLQ2 - 8 methods (2 ideal gases * 4 residuals)

Isochoric Heat Capacity:

CVLQ2 - 8 methods (2 ideal gases * 4 residuals)

Enthalpy of Formation:

HFLQ2 - 8 methods (2 ideal gases * 4 residuals)

Gibbs Free Energy of Formation:

GFLQ2 - 8 methods (2 ideal gases * 4 residuals)

Molar Heat of Combustion:

HCLQ2 - 8 methods (2 ideal gases * 4 residuals)

Surface Tension:

ST2- data base lookup (priority 1)

ST3- Brock & Bird⁴⁶ (priority 2)

Error < 0.05

Table 4.4-5 (cont.)
Summary of Methods for Liquid Properties

Saturated Molar Volumes:

MVLQS2 - Hankinson-Brost-Thomson equation⁴³ (priority 2)
MVLQS3 - Rackett Equation³⁶ (priority 3)
MVLQS4 - data base lookup (priority 1)

Compressed Molar Volumes:

MVLQ2 - Tait-HBT⁴⁴ (priority 1)
MVLQ3 - Density Correlation⁴⁵ (priority 2)
MVLQ4 - Peng-Robinson equation (priority 3)
MVLQ5 - Soave equation (priority 4)

Densities:

RHOLQ2 - calculated from MVLQ3 (priority 3)
RHOLQ3 - calculated from MVLQ3 (priority 2)
RHOLQ4 - calculated from MVLQ3 (priority 1)

4.4.2.9 Methods for Phase Transitions

The properties of the liquid-gas phase transition may be calculated by comparing the fugacities for each of the two phases. These fugacities are equal at the equilibrium phase transition temperature and pressure. To calculate the boiling point at a given pressure, the temperature is varied until the fugacities are equal. The temperature where they are equal is the boiling point. Similarly, to calculate the vapor pressure at a given temperature, the pressures of the two phases are varied until the fugacities are equal. The resulting pressure is the vapor pressure. Once the equilibrium temperature and pressure are known, the enthalpy and entropy of vaporization can be calculated by subtracting the residual enthalpy and entropy of the liquid phase from the residual enthalpy and entropy of the gas phase.

Since these calculations require an accurate equation of state, only the Peng-Robinson, Soave, and Lee-Kesler are implemented. An example of these calculations using the Peng-Robinson equation is presented in Table 4.4-6 for methylcyclohexane. The Peng-Robinson equation is quite accurate for calculations of the molar liquid volumes at 298K and 293K, boiling point at 1 atm, the enthalpy and entropy of vaporization at the boiling point and 1 atm, the vapor pressure at 298K, the enthalpy and entropy of vaporization at 298K and the vapor pressure (at 298K), and for the entropies of the gas and liquid phases at 298K and 1 atm.

Table 4.4-6
Comparison Between Peng-Robinson Predictions and Experiment

	<u>P-R EQ'N</u>	<u>EXPT.</u>	<u>UNITS</u>
$V_1(298)$	0.12422	0.12818	m ³ /kmol
$V_1(293)$	0.12365	0.12762	m ³ /kmol
T_b	373.96	374.08	K
$\Delta H_{vap}(t_b, 1 \text{ atm})$	3.105E7	3.11E7	J/kmol
$\Delta S_{vap}(T_b, 1 \text{ atm})$	8.302E4	8.322E4	J/kmol K
P_b	6563	6133	Pa
$\Delta H_{vap}(298, P_b)$	3.436E7	3.536E7	J/kmol
$\Delta S_{vap}(298, P_b)$	1.152E5	1.186E5	J/kmol K
$S_{gas}(298, 1 \text{ atm})$	3.425E5	3.433E5	J/kmol K
$S_{liq}(298, 1 \text{ atm})$	2.509E5	2.479E5	J/kmol K

In addition to the equation of state methods, there are specialized methods for calculating phase transition properties. These methods include the Riedel¹⁷ method for determining vapor pressure and the Vetere¹⁸ method using the Watson¹⁹ relation for determining the enthalpy of vaporization. The liquid-gas phase transition methods are summarized in Table 4.4-7. We have not implemented the equation of state methods for determining vapor pressure or boiling point.

The calling sequences for the phase transition methods vary from one method to another because some properties are only temperature dependent, such as vapor pressures, while others are both temperature and pressure dependent. The calling sequences for the vapor pressure methods do not contain the PRESS and NPRESS variables found in the real gas and liquid methods. The calling sequences for the enthalpy and entropy of vaporization are the same as for the real gas and liquid methods.

Table 4.4-7
Summary of the Methods for Liquid-Gas Phase Transition

Vapor Pressures:

PVAPS2 - data base lookup (priority 1)
PVAPS3 - Riedel's method¹⁷ (priority 2)

Boiling Point Correction:

DTDPB1 - data base lookup (priority 1)

Enthalpy of Vaporization:

HVSAT2 - data base lookup (priority 1)
HVSAT3 - Watson¹⁹ relation using Vetere¹⁸

4.4.2.10 Methods for Transport Properties

The methods available for transport properties are summarized in Table 4.4-8. Since Phase I, predictive methods were programmed for liquid viscosity, liquid thermal conductivity, and vapor thermal conductivity.

The Przewdziecki and Sridhar⁵⁰ liquid viscosity method does not determine the viscosities of alcohols accurately. The Sato-Riedel⁵¹ liquid thermal conductivity method is reliable for most organic liquids. Ely and Hanley⁵² report this method for determining the vapor thermal conductivity has a maximum error of 15 percent for hydrocarbons.

The calling sequences for these properties are the same as for thermodynamic properties of real gases or liquids.

Table 4.4-8
Summary of Methods for Transport Properties

Liquid Viscosity:

NULQ2 - data base lookup (priority 1)
NULQ3 - Przewdziecki and Sridhar⁵⁰ (priority 2)

Vapor Viscosity:

NUVAP2 - API method 11B1-6⁵³ (priority 3)
NUVAP3 - AIChE method 8A⁵⁴ (priority 2)
NUVAP4 - data base look up (priority 1)

Liquid Thermal Conductivity:

LTC2 - data base look up (priority 1)
LTC3 - Sato-Riedel method⁵¹ (priority 2)

Vapor Thermal Conductivity:

VAPTC2 - data base look up (priority 1)
VAPTC3 - Ely and Hanley⁵² (priority 2) Error < 15%

4.4.2.11 Methods for Solid Properties

There are experimental data in the DIPPR data base and TRC Hydrocarbon tables for the heat capacity and density of solids. Only the data base lookup methods have been programmed. It was determined that thermodynamic properties of solids were not necessary, since for aviation applications, fuels must be fluids. The methods for solids are summarized in Table 4.4-9. Their calling sequence is the same as for real gases or liquids.

Solid properties of hydrocarbons are notoriously difficult to estimate because there is little data on the solid states, there may be multiple crystalline states plus an amorphous state.

Table 4.4-9
Summary of Methods for Solids

Solid Heat Capacity:

CPS1 - data base lookup (priority 1)

Solid Density:

RHOS1 - data base lookup (priority 1)

4.4.2.12 Methods for Error Tracking

In order to assess the accuracy of the predictive methods, experimental and known predictive errors were propagated through some of the subroutines programmed during Phase I. This method of propagating errors tends to overestimate errors, because errors that should cancel occur in different subroutines but they are added rather than subtracted. To overcome this problem, in some cases relative errors for the properties are determined by numerically calculating partial derivatives of the answers with respect to the input experimental data. For example, if the experimental errors were in T_c and P_c , the absolute error in the resulting thermodynamic functions would be:

$$\text{error in } f = |\delta f / \delta T_c| * (\text{error in } T_c) + |\delta f / \delta P_c| * (\text{error in } P_c).$$

These error calculations were programmed for densities but were not extended to other properties. We determined that quoting relative error for each method would be easier, and in most cases more accurate. The relative error calculations are not based on any particular criteria and the results obtained are approximate.

For group additivity and graph theory methods, the errors quoted are fixed. The errors vary by family, so for each family of compounds, a different error value is quoted. In general, these were determined as the mean error or the standard deviation error by comparing predicted values with experimental values. In many cases, no error is returned. In these cases, the error is unknown.

To summarize briefly the methods which are employed to estimate errors, all of the following are used at various times:

Quality code from data base

No error returned

Partial derivative with respect to T_c , P_c , acentric factor

Sum of relative errors in critical temperature, pressure, and volume

Propagated from acentric factor error alone

Fixed error

Fixed error dependent on chemical family

Maximum of fixed error or error in boiling point

Propagated errors from component routines.

4.5 New Model Development

4.5.1 Objective

Develop new property predictive methods based solely on the structure of the molecule of interest.

4.5.2 Work Completed

The development of new models for the prediction of physical and thermochemical properties was based upon the use of simple groups, graph theory parameters, and structural descriptors such as the number of non-hydrogen atoms in the molecule and the molecular weight. This approach was chosen since it is well known that each of these types of parameters can be used to predict properties. The intent was to allow statistical analysis to provide the best choice of graph theory parameters, group contributions, structural descriptors, or any combination to be used for the new method.

Three types of groups were defined: zero order groups (atoms), zero order groups with hybridization, and bonds. The groups considered for each class are shown in Table 4.5-1.

The graph theory parameters that were used are shown in Table 4.5-1. This table also lists the structural descriptors used in the new methods development. The graph theory parameters chosen were done because of available software (MOLCONN5⁵⁵) that can automatically derive these parameters from a SMILES string. Other types of parameters were also considered. These parameters consisted of transformed or derived variables. For example, the square root of the first order path connectivity index was considered; examples of some of these "transformed" or derived parameters are shown in Table 4.5-2.

Table 4.5-1
Graph Theory Parameters and Structural Descriptors
for New Methods Development

<u>Connectivity Indices</u>		
<u>Symbol</u>	<u>Name</u>	<u>Order</u>
$0-20 \chi_p$	Simple Path	0 - 20
$0-20 \chi_v$	Valence Path	0 - 20
$3 \chi_c$	Simple Cluster	3
$3 \chi_v$	Valence Cluster	3
$4 \chi_{pc}$	Simple Path/Cluster	4
$4 \chi_{cc}$	Valence Path/Cluster	4
$0-20 \chi_{ch}$	Simple Chain	3 - 20
$0-20 \chi_{ph}$	Valence Chain	3 - 20

Other Parameters

Total Topological State Index
 Wiener Number
 Total Wiener
 Shannon Index
 Kappa Zero Index
 Kappa Simple Indices (first to third order)
 Kappa Indices (first to third order)

Structural Descriptors

Atom Count, nonhydrogen
 Atom Count, hydrogen
 Molecular Weight

The group contribution method was tried but it proved to be unsuccessful. Instead, the graph theory methods have been developed, since they can be extended to computer analysis using modern decomposition techniques and statistical regression packages. A graph theory method has been applied to autoignition temperature. Section 5.2 discusses this application in further detail.

At this point, it is necessary to define the various graph theory parameters. The connectivity indices are based on the encoding of structural information according to the connectivity of the nonhydrogen atoms in a molecule. The first parameter that needs to be defined is δ . Delta is the number of nonhydrogen atoms attached to the atom of interest. Therefore, a methylene ($-\text{CH}_2-$) group has a δ of 2.

Table 4.5-2
Transformed and Derived Parameters
for New Methods Development

Transformed Parameters

Reciprocal Zero-Order Path Index
Reciprocal First-Order Path Index
Reciprocal Second-Order Path Index
Reciprocal Atom Count
Reciprocal Molecular Weight

Derived Parameters

Sum Zeroth-Order Simple and Valence Connectivity Indices
Sum First-Order Simple and Valence Connectivity Indices
Sum Second-Order Simple and Valence Connectivity Indices
Difference Zeroth-Order Simple and Valence Connectivity Indices
Difference First-Order Simple and Valence Connectivity Indices
Difference Second-Order Simple and Valence Connectivity Indices

The simple path connectivity χ_p of order m is given by:

$$\chi_p = \sum_{i=1}^{N_s} \left(\prod_{k=1}^{m+1} (\delta_k)^{-0.5} \right)$$

where N_s is the number of paths of order m , and δ_k are the delta values for the atoms in the path. As an example, the first order (simple) path

connectivity index for dimethyl ether would be given by:

$$\begin{aligned} {}^1\chi_p &= (1*2)^{-0.5} + (2*2)^{-0.5} + (2*2)^{-0.5} + (2*1)^{-0.5} \\ &= 2.414. \end{aligned}$$

However, it should be noted that this value would be the same for n-pentane. To account for heteroatoms and multiply bonded carbon atoms, one can use what is referred to as the valence connectivity indices and these are designated by a trailing superscript, v. The difference between the simple connectivity indices and the valence indices is in the definition of δ . Whereas for the simple indices, δ is just the number of nonhydrogen atoms attached to the atom of interest, for the valence indices, δ^v (the valence delta) replaces δ . δ^v is defined as:

$$\delta^v = Z^v - h$$

where Z^v is the number of valence electrons in the atom of interest and h is the number of hydrogens on that atom. The effect that this would have on our previous example of dimethyl ether, for the first-order valence path connectivity index, is given by:

$$\begin{aligned} {}^1\chi_p &= (1*2)^{-0.5} + (2*6)^{-0.5} + (6*2)^{-0.5} + (2*1)^{-0.5} \\ &= 1.992. \end{aligned}$$

This example, together with the previous example shows the value of the valence connectivity indices and why they were considered in the new methods development.

Additionally, other types of molecular fragments can be considered as being part of a molecule and were also considered as part of the graph theory based new method development. These fragments are most easily depicted as:



Figure 4.5-1
Different Types of Molecular Fragments Used in Graph Theory

These fragments are referred to as a path (a), cluster (b), path/cluster (c), and a chain (d).

The topological state index encodes information (using the valence delta described above) about each atom in a molecule and how it relates to all of the paths in the molecule in which it is involved. The total topological state index is the sum of all of the topological state indices for each atom in the molecule. The molecular shape indices (Kappa and Simple Kappa indices) are included to account for properties that may have a molecular shape dependence. The Kappa indices are based on the number of one, two, and three bond fragments in a molecule, relative to the minimum and maximum number of fragments possible for real or hypothetical molecules having the same number of atoms as the molecule of interest.

The overall concept is to encode structural information into a series of parameters that in some combinations will provide property predictive capabilities. Further, more detailed information on the various graph theory parameters, graph theory in general, and graph theory in property prediction can be found in several books^{56,57,58}.

4.6 Codification of Modeling Program

4.6.1 Objective

Develop the necessary code to make the AFP system an integrated user friendly system.

4.6.2 Work completed

The AFP system is based on a series of menus that allows the user to select the various input and output options that are available. The main menu allows the user to select from options for:

- Single Compound Information
- Multiple Compound Information
- Mixture Information
- Error Code Translation
- Exit Program.

Selecting either of the first two options brings up a menu with the following selections:

- Select Compounds
- Property Information
- Temperature(s) Selection
- Pressure(s) Selection
- Choose for Output Units

Output Results
Return to Previous Menu.

It should be mentioned that for all but the main menu, the last selection is always to return to previous menu, which in this case would take the user back to the main menu.

The methods available for compound selection include the input of a molecular structure using the SMILES notation described earlier, input of the name of the compound of interest, or supplying the name of a file that contains a list of SMILES strings, compound names, and/or ASID numbers.

In the case of the SMILES string entry, the SMILES string can be put in exactly, or only a partial SMILES string or strings need be entered. In the latter case, the system will search the entire AFP data base for compounds that contain the group(s) designated. Two examples show how the searching works. First, to find all compounds that contain a benzene ring, the SMILES string that would be input would be c1ccccc1*, the asterisk designating that this is to be a subgroup search as opposed to wanting to choose benzene. The other example is to specify "all" compounds (in the AFP data base) that have both a cyclohexane ring and an ethyl group, the SMILES input would be C1CCCCC1,C-[C&H3]. In this case, the comma designates that the search is to be for all molecules that contain the specified groups. In either case, after the computer has found all of the compounds that meet the search criteria, the user is allowed to select the compound(s) of interest.

The search by compound name is similar to the SMILES entry in that either an exact match can be sought or wildcards can be used. In either case, all of the names available in the AFP data base will be searched for matches. The syntax for the wildcard name searches is that anywhere that an asterisk is located, any number of characters may be substituted. For example, to find all compounds that have dimethylcyclohexane in their name, the search name would be entered as *DIMETHYLCYCLOHEXANE*. This method of searching is not trivial since the matching must be exact where there are no asterisks, including the possibility for spaces and/or hyphens. All searches are done in uppercase so misses due to mismatched cases are not a problem.

Property selection is accomplished by providing the user with a long scrollable list of all of the available properties in alphabetical order. Each property can be selected or deselected by putting the cursor on the property of interest and pressing enter. A property is designated as selected when an asterisk appears on the far right side of the screen across from the

property description. The asterisk disappears upon deselection. As many or as few properties as desired can be selected.

Currently, temperature and pressure selection can be done by entering individual values or the number of values, the initial value, and an incremental value. The current limit on the number of temperatures and pressures is 30 for each.

The output of the AFP system defaults to SI units; however, the user can choose to change this to one of many different units that are available for each property. Again, the selection of the units is done by presenting the user with a menu showing the possible output units available. For example, for the density of a liquid, the possible units that could be selected are:

kg/m³,
g/cm³,
oz/in³,
lb/in³,
lb/ft³, or
lb/gal.

The method that was developed to handle the different units was designed for flexibility; therefore, the effort necessary to add new units (up to a maximum of 10 different units, current limit) is minimal.

The results can be output immediately to the computer screen or they can be sent to a file for later viewing or printing. The output first lists the compounds selected and assigns them a number. Following this, the system outputs the property values for all temperature and pressure combinations for each compound for every property selected.

The ability to output results graphically exists when a property is being determined at multiple pressures or temperatures. In order to use the graphical output option the user should know the type of graphics device they will be using. AFP can display graphics to the following devices:

1. VT240/VT241
2. Tektronics
3. HP7550 plotter, to logical PLOT
4. HP7550 plotter to a file you name.

Once the output has been chosen, the type of plot is then defined either to be property versus temperature or property versus pressure. The number of compounds that will be displayed on each plot is also an option of graphical output.

For more information concerning the AFP integrated user friendly system, consult the user manual⁹⁹.

5.0 PHASE II TASK REVIEW

5.1 Model Testing and Verification

5.1.1 Objective

Demonstrate the reliability and accuracy of estimation routines within single component routines. Provide a frequency of success for returning a property estimate. Provide an overall accuracy figure for each estimation method. And demonstrate that all routines provide correct results in all available units.

5.1.2 Work Completed

A property testing strategy was developed that weighted each property according to the following criteria:

1. Importance of the estimation
2. CPU cost per data point X number of datapoints per compound
3. Feasibility of reliable experimental data for comparison.

Each property was placed into one of four categories. Crucial single-point methods included T_c , P_c , V_c , T_b and the acentric factor, since these properties are used to determine other properties. Medium importance single-point method included combustion properties such as flammability limits, flash point, and autoignition temperature. The most important multivalued-methods category included properties such as density, viscosity, heat of combustion, and enthalpy of formation. And the fourth category of properties included all the methods which did not fit into one of the first three categories. The extent of testing decreased as the importance of the property decreased.

The test compounds were selected by sorting them into families (e.g., straight chain, alkenes, aromatic compounds) and then drawing a random sampling from each family. All classes of compounds were represented proportional to the size of their family.

The results of the tests were presented in the form of plots. A set of plots was created for hydrocarbon and for nonhydrocarbons; and two plots were generated for each property. The first of which was a plot of the property versus molecular weight. This plot was used as an initial check of the property values since molecular weight is usually the strongest correlation variable with any property. If the plot did not scale with molar weight, it was a good indication that the property values were incorrect.

The second plot was a mean error between look-up value and the estimated value. Many of the properties tested only had one or two look-up values, since the data base cannot store values for every property at every pressure and temperature condition. The relative error was obtained by dividing the difference between the estimate and look up values by the look-up value. Average error was computed as the average of the absolute values of the errors.

The results of the test plan are detailed in first Software Test Report for the Advanced Fuels Properties System¹⁷. In general all of the predictions provide a reasonably accurate estimate of the properties, with a better than 50 percent chance of success determining the property.

5.2 Application of Graph Theory to the Model of Autoignition Temperature

5.2.1 Objective

Develop a correlation between graph theory indices and autoignition temperature. The graph theory model will determine the autoignition temperature for the following families of hydrocarbons: normal alkanes, methylalkanes, other branched alkanes, cyclopentanes, cyclohexanes, other cycloalkanes, decalins, tetralins, saturated multicyclic compounds, alpha alkenes, other noncyclic alkenes, cycloalkenes, dialkenes, alkynes, normal alkylbenzenes, other alkylbenzenes, indanes, indenenes, other phenyl containing molecules, diphenyls, naphthalenes, anthracenes, phenanthrenes, and other polyaromatics. This correlation was programmed as a new method in the prediction system.

5.2.2 Work Completed

5.2.2.1 Introduction

Prior to the development of the AFP system, there were no adequate models for the prediction of the autoignition temperature for carbon-containing compounds. This was our first successful application of graph theory to the development of predictive models. During the earlier part of this research contract, several attempts had been made to use graph theory for predictions of such properties as boiling point, using SAS as the analysis system.⁶⁰

Two major difficulties were encountered. First, we attempted to create global models. That is, we tried to make one model which would predict boiling point for all carbon-containing compounds. This proved to be an inappropriate approach, as no model is sufficiently robust to handle the differences from chemical family to chemical family. Thus, in the successful effort, we found it necessary to assemble compounds into groups of families, and perform the multilinear regression over these groups.

Second, development of good models using graph theory parameters awaited the development of robust computer programs which could perform the regression analysis over large data sets with many parameters, and guarantee with reasonable confidence that the prediction would apply to new molecules outside the original training set. A chief problem in any multilinear regression analysis is that the model can successfully reproduce the data of the training set, but cannot interpolate or extrapolate predictions to new situations. Thus, algorithms were required which would develop the model on part of the training set, and test it on another part. Additionally, the skills of an experienced statistician were found more valuable here than the skills of an experienced chemist.

5.2.2.2 Statistical Approach

We used a partial least squares (PLS) computer program for the data analysis⁶¹. In the PLS approach, we generate the graph theory parameters for all of the molecules in a given training set, as well as the known experimental values for the autoignition temperature. Then, the program performs a regression over part of the training set, using as inputs the graph theory parameters, and using autoignition temperature as the property to be fitted.

After the initial regression analysis, the newly developed model is tested over the portion of the training set which was not used in the model development, and the residuals are calculated. This process is repeated over different combinations of the data until the sum of the squares of the residuals is minimized. Thus, a good model is developed, which is demonstrably able to do reasonable interpolations and extrapolations.

5.2.2.3 Training Set Family Groupings

Chemicals were lumped for developing individual models into groups of families with similar functional groups. The PLS program was applied, and

models were generated by group. The selected groups are listed below. The family number is listed, and then the family name.

Group A

1	n-PARAFFINS
2	METHYLALKANES
4	OTHER ALKANES

Group B

3	CYCLOALKANES
13	MULTICYCLIC HYDROCARBON RINGS
100	DECALINS
106	CYCLOPENTANES
107	CYCLOHEXANES

Group C

5	ALPHA-OLEFINS
6	OTHER ALKENES
7	DIOLEFINS
102	CYCLOOLEFINS
118	OLEFINS WITH>2 DOUBLE BONDS

Group D

8	ALKYNES
---	---------

Group E

9	N-ALKYLBENZENES
10	OTHER ALKYLBENZENES
11	OTHER MONOAROMATICS
101	TETRALINS
104	DIPHENYLS
105	BIPHENYLS
110	INDANS
111	INDENES

Group F

12	OTHER POLYAROMATICS
103	NAPHTHALENES
108	ANTHRACENES
109	PHENANTHRENES

Group G

15	ALDEHYDES
16	KETONES

Group H

17	N-ALCOHOLS
18	OTHER ALIPHATIC ALCOHOLS
19	AROMATIC ALCOHOLS
20	POLYOLS

Group I

21	N-ALIPHATIC ACIDS
22	OTHER ALIPHATIC ACIDS
23	AROMATIC CARBOXYLIC ACIDS

No attempt was made to estimate autoignition temperature for the remaining compounds.

5.2.2.4 Results

In the equations below, the following symbols are used for graph theory parameters. These are the graphs described in the paper by Kier and Hall⁵⁶:

XPA _n = SIMPLE CHI PATH	$n\chi_p$
XCA _n = SIMPLE CHI CLUSTER	$n\chi_c$
XPCA _n = SIMPLE CHI PATH CLUSTER	$n\chi_{pc}$
XCHA _n = SIMPLE CHI CHAIN	$n\chi_{ch}$
XPVA _n = VALENCE CHI PATH	$n\chi_{pv}$
XCVAn = VALENCE CHI CLUSTER	$n\chi_{cv}$
XPCVAn = VALENCE CHI PATH CLUSTER	$n\chi_{pcv}$
XCHVAn = VALENCE CHI CHAIN	$n\chi_{chv}$
AKAPAn = KAPPA INDICES	$n\chi$
SIA = SHANNON INDEX	i
WWA = WIENER'S NUMBER	w
WTA = TOTAL WIENER'S NUMBER	TW
TOPOL = TOTAL TOPOLOGICAL INDEX	τ_i
NAA = TOTAL NONHYDROGEN ATOMS	T_{nonH}
HTOTA = TOTAL HYDROGEN ATOMS	T_H
NEDGE = NUMBER OF EDGES OF LENGTH 1	ϵ^1
NXP _n = NUMBER OF EDGES OF LENGTH n	ϵ^n
MW = MOLECULAR WEIGHT	$MW.$

We computed the autoignition temperature (TAI2) coefficients for group A compounds, the straight and branched alkanes. Based on 43 compounds checked, the average relative error was 5.5 percent, the standard deviation of the error was 7.2 percent, and the maximum error 16 percent. The equation is as follows:

$$\begin{aligned} TAI2 = & 812.3815 - 0.3289608 \cdot MW - 0.4895888 \cdot TOPOL - 84.41458 \cdot SIA \\ & + 0.3014608 \cdot WWA + 3.006436 \cdot NXP2 + 1.223477 \cdot NXP3 + 6.427660 \cdot NXP4 \\ & + 14.84061 \cdot NXP5 - 17.83366 \cdot NXP6 + 5.900274 \cdot NXP7 + 54.73765 \cdot NXP8 \\ & + 1.310108 \cdot AKAPA0 - 23.40906 \cdot AKAPA2 - 12.63088 \cdot AKAPA3 - \\ & 1.369623 \cdot XPA0 - 18.36610 \cdot XPA1 + 12.14030 \cdot XPA2 - 10.40851 \cdot XPA3 - \\ & 14.44044 \cdot XPA4 + 84.46376 \cdot XPA5 - 215.8954 \cdot XPA6 - 5.999813 \cdot XPA7 + \\ & 20.34099 \cdot XCA3 - 72.08473 \cdot XCA4 + 17.07761 \cdot XPCA4. \end{aligned}$$

The TAI2 equation for group B compounds (cyclic saturated hydrocarbons) was developed using 19 compounds. The mean error was 2.8 percent; the standard deviation on the error was 3.6 percent; the maximum error was 7.6 percent.

$$\begin{aligned} TAI2 = & 863.79579 - 0.77700 \cdot MW + 0.32534 \cdot TOPOL + 23.21796 \cdot SIA + \\ & 0.29725 \cdot WWA + 1.00410 \cdot NXP2 - 3.65689 \cdot NXP3 - 1.15581 \cdot NXP4 + \\ & 1.01384 \cdot NXP5 + 3.64149 \cdot NXP6 + 3.59086 \cdot NXP7 + 5.39268 \cdot NXP8 + \\ & 10.50428 \cdot AKAPA0 - 48.09767 \cdot AKAPA2 + 35.36966 \cdot AKAPA3 - \\ & 6.81160 \cdot XPA0 - 30.05850 \cdot XPA1 + 15.24721 \cdot XPA2 - 33.55259 \cdot XPA3 - \\ & 40.69580 \cdot XPA4 + 2.22056 \cdot XPA7. \end{aligned}$$

The TAI2 equation for group C compounds (olefins) was developed from 31 compounds. The mean error was 8 percent, the standard deviation 10 percent,

the maximum error 27 percent. The equation is:

$$\begin{aligned} \text{TAI2} = & 762.48520 - 0.13145 \cdot \text{MW} + 0.31590 \cdot \text{TOPOL} - 47.39448 \cdot \text{SIA} - \\ & 0.04662 \cdot \text{WWA} + 1.49863 \cdot \text{NXP2} + 1.02209 \cdot \text{NXP3} + 1.64973 \cdot \text{NXP4} - \\ & 0.44376 \cdot \text{NXP5} + 0.14186 \cdot \text{NXP6} + 0.36381 \cdot \text{NXP7} + 1.72277 \cdot \text{NXP8} - \\ & 2.47021 \cdot \text{AKAPA0} - 6.89365 \cdot \text{AKAPA2} - 5.36838 \cdot \text{AKAPA3} - 2.71817 \cdot \text{XPA0} \\ & - 4.09791 \cdot \text{XPA1} + 3.87924 \cdot \text{XPA2} - 0.47577 \cdot \text{XPA3} + 6.95309 \cdot \text{XPA4} - \\ & 9.93097 \cdot \text{XPA5} - 1.67503 \cdot \text{XPA6} - 7.71992 \cdot \text{XPA7} - 4.05674 \cdot \text{AKAPA4} - \\ & 6.93425 \cdot \text{AKAPA5} - 2.94337 \cdot \text{XPVA0} - 5.11676 \cdot \text{XPVA1} + 2.94862 \cdot \text{XPVA2} \\ & - 2.94852 \cdot \text{XPVA3}. \end{aligned}$$

There were not enough data points to develop an autoignition temperature equation for alkynes, group D.

The TAI2 equation for group E was developed from 31 aromatic compounds. The mean relative error was 3 percent. The maximum error was 7.7 percent, with a standard deviation of 3.8 percent. The equation for group E is:

$$\begin{aligned} \text{TAI2} = & 858.66065 - 0.09097 \cdot \text{MW} + 1.48266 \cdot \text{TOPOL} - 25.63339 \cdot \text{SIA} + \\ & 0.15696 \cdot \text{WWA} + 1.84197 \cdot \text{NXP2} - 2.44759 \cdot \text{NXP3} - 1.25330 \cdot \text{NXP4} - \\ & 0.14878 \cdot \text{NXP5} + 0.15791 \cdot \text{NXP6} - 1.83598 \cdot \text{NXP7} - 0.48432 \cdot \text{NXP8} - \\ & 2.79588 \cdot \text{AKAPA0} - 3.98814 \cdot \text{AKAPA2} + 31.80411 \cdot \text{AKAPA3} + 4.47312 \cdot \text{XPA0} \\ & + 0.48529 \cdot \text{XPA1} + 17.48220 \cdot \text{XPA2} - 6.72397 \cdot \text{XPA3} - 7.45271 \cdot \text{XPA4} - \\ & 5.08232 \cdot \text{XPA5} + 11.81087 \cdot \text{XPA6} - 72.01668 \cdot \text{XPA7} + 79.78305 \cdot \text{XCA3} \\ & - 204.43701 \cdot \text{XCA4} - 15.74205 \cdot \text{XPCA4} + 1.77688 \cdot \text{NAA} - \\ & 23.60440 \cdot \text{HTOTA} + 0.01851 \cdot \text{WWTA} + 1.18244 \cdot \text{NEDGE} + 0.50618 \cdot \text{NXP9} + \\ & 2.68946 \cdot \text{AKAPA1} - 2.11757 \cdot \text{AKAPA6}. \end{aligned}$$

The TAI2 equation for group E compounds was applied to group F compounds, i.e., polyaromatics. This was found to be accurate for four compounds within 10 percent. There was insufficient data to develop a model for the F compounds, but it makes sense that aromatics and polyaromatics should have similar behavior.

Group G (aldehydes and ketones): We were unable to develop a model for this group. There is no significant correlation in this group whatsoever. Camphor is a noticeable outlier in the graph theory indices configuration, but removing it from the analysis doesn't help. Therefore, there is no model for this group.

Group H (alcohols) is much better behaved. After an initial analysis with all members, we omitted compounds with molecular weight higher than 140, since they were obvious outliers. The analysis with these omitted showed 2-propyn-1-ol to have an unusually low autoignition temperature of 388.15K, unpredictable by the model. The model says it should be something like 700K. 2-propyn-1-ol is a very unstable and hazardous material. We refit once again this compound omitted, and developed a good model. The following equation is for the autoignition temperature for group H compounds:

$$\begin{aligned}
 \text{TAI2} = & 758.40962 - 0.05371 \cdot \text{MW} + 1.71138 \cdot \text{NAA} - 8.44428 \cdot \text{HTOTA} + \\
 & 1.38540 \cdot \text{TOPOL} - 1.26656 \cdot \text{SIA} + 0.11361 \cdot \text{WWA} + 0.10032 \cdot \text{WTA} + \\
 & 1.88863 \cdot \text{NEDGE} + 1.93389 \cdot \text{NXP2} + 1.61538 \cdot \text{NXP3} + 1.40121 \cdot \text{NXP4} + \\
 & 1.32115 \cdot \text{NXP5} + 5.23979 \cdot \text{NXP6} + 11.44402 \cdot \text{NXP7} + 32.48766 \cdot \text{NXP8} + \\
 & 1.19586 \cdot \text{AKAPA0} - 4.83978 \cdot \text{AKAPA2} - 4.07854 \cdot \text{AKAPA3} - 5.21263 \cdot \text{AKAPA6} \\
 & + 5.68704 \cdot \text{XPA2} + 7.28380 \cdot \text{XPA3} + 7.31011 \cdot \text{XPA4} + 7.11370 \cdot \text{XPA5} + \\
 & 57.20570 \cdot \text{XPA6} + 109.45318 \cdot \text{XPA7} - 22.14355 \cdot \text{XPVA2} - 29.27790 \cdot \text{XPVA3} \\
 & - 50.79082 \cdot \text{XPVA4} - 78.50304 \cdot \text{XPVA5} - 156.22630 \cdot \text{XPVA6} + \\
 & 16.33810 \cdot \text{XPVA7} + 10.21372 \cdot \text{XCA3} - 12.88337 \cdot \text{XCA4} + 18.73434 \cdot \text{XPCA4} \\
 & - 17.71056 \cdot \text{XPCVA}.
 \end{aligned}$$

Similar to group G, we were unable to develop a model for the group I compounds (carboxylic acids).

5.2.2.5 Implementation

The above equations are stored in text form in the file AFP\$DATA:EVALEQ.EQN. We have written a FORTRAN subroutine which interprets the equations and evaluates them. The MOLCONN software is used to evaluate the graph theory parameters. Each equation is stored along with the chemical families for which the equation is valid.

5.3 Evaluation of DECHEMA

5.3.1 Objective

Perfect the use of Dechema as a component of the AFP code by introducing little or no changes in the Dechema code. We will develop "scripts" which will be used to drive Dechema; this will allow the AFP system and Dechema to run in a shell. We will identify the compounds that exist in Dechema's data base so that AFP will know whether it has to supply additional pure substance data to make the program run. We will develop a scheme for inserting the data into Dechema's data base, allowing the program to calculate mixture properties in more cases.

5.3.2 Work Completed

5.3.2.1 Choice of Program

At the point in this project where we began to develop methods for mixtures, we realized that there was in existence a program which had been created in Germany which would estimate the properties of hydrocarbon mixtures.¹ This program, DETHERM, included a data base of approximately 500 compounds with extensive thermal and physical property data, which could be used for mixture calculations. We have frequently referred to this program as

DECHEMA, although strictly speaking, DECHEMA is the name of the organization which developed the program. For many of these compounds, it also contained fitted binary interaction parameters, which could be used to estimate mixture properties. It also included a much larger data base of vapor-liquid equilibrium data, principally vapor pressures as a function of temperature for pure compounds and mixtures.

Although the subroutine library was extensive within DETHERM, the data base of 500 compounds was not large enough to be meaningful for fuel mixtures. We realized that we could generate the properties of the individual compounds as needed, supply them to the DETHERM data base, and estimate mixture properties directly. Thus, we traded off a technical problem, locating mixture models and programming them, for a programming problem, integrating the DETHERM program into the AFP system.

DETERM can be used by itself, but it has a formidable user interface which is difficult to handle even by one experienced with the program. Thus, it made sense to weave it into the AFP user interface which is designed to be much more user friendly.

5.3.2.2 Advantages of Approach

The principal advantage of using DETHERM was that the FORTRAN code for performing mixture calculations using many published methods was already developed. A rule of thumb in scientific programming is that if a code already exists, it is more cost effective to buy it than develop it yourself. The code could estimate mixture properties for most of the properties required in the AFP system. Using the code was expected to shorten the development time for the AFP system.

5.3.2.3 Disadvantages of Approach

The code was difficult to understand because all of the comments within the code were in German. The FORTRAN code was typical of nonstructured code for which it is very difficult to decipher the logic. We had to dig into the code in a few places to correct bugs and to hook the program into our AFP system. DETHERM did not have all of the estimates which were desired in the final software product, and adding additional mixture calculations to it proved very difficult.

5.3.2.4 Technical Evaluation

Before we linked DETHERM to AFP, we spent considerable time evaluating how it worked, and how well it worked. The first part of this evaluation was running the program with its native interface. Later, we supplied it data using a temporary interface, and evaluated how well DETHERM would run using data supplied by us.

One of the critical issues in performing mixture calculations is knowledge or estimates of binary interaction parameters (BIPs). Mixture properties are functions of the properties of the individual components, but also of the interactions between those components. Estimation of the pure component properties is handled effectively within AFP, but estimates of interaction parameters were needed.

We investigated how LETHERM performs, obtains, and uses BIPs for vapor-liquid equilibria (VLE) calculations. There are two methods: equilibrating the fugacity of each component in the gas and vapor phases, or equilibrating the activity coefficients of each component in each phase. Methods involving equilibrating the activity coefficients (van Laar⁶², NRTL⁶³, Margules⁶⁴) are applicable to strongly interacting compounds like polar compounds, and alcohols. Methods which equilibrate the fugacity, also known as equation of state methods, are better for hydrocarbons. These include the LKP^{65,66}, Peng-Robinson⁶⁷, and Benedict-Webb-Rubin^{68,69,70} (BWR) models.

The method of Gilmont for estimating binary interaction parameters is available in DETHERM. Unfortunately, it applies to the van Laar equation, and is, therefore, not the best choice. As AFP is optimized for hydrocarbons, we prefer to get the BIPs appropriate for the LKP model. We have used a correlation for the LKP BIPs from the printed DECHEMA tables⁷¹.

The equation for correlated binary interaction parameters for the LKP model is:

$$K_{ij} = 0.93722 + 0.4372Q - 0.007202Q^2 \quad \text{where}$$

$$Q = T_c((j)V_c(j)/T_c(i)V_c(i)).$$

Here, $T_c(i)$ and $V_c(i)$ are the critical temperature and critical volume for component i . Component i is the one with the lower boiling point. The fit is quite good over the range of $1 < Q < 20$.

Under certain cases, DETHERM will not use the LKP method, but instead choose the Chao-Seader method. This, in particular, is triggered by the inclusion of N₂, O₂, CH₃, C₂H₆, or other low-boiling compounds. This method does not use interaction parameters, only the solubility parameter and liquid molar volume. These values are supplied by AFP in the material properties for the pure components.

5.3.2.5 Test Calculations

As part of our evaluation of the DETHERM software, we have used DETHERM to estimate several properties of toluene, methylcyclohexane, and n-heptane mixtures. The experimental and estimated results are given in Tables 5.3-1 - 5.3-4. The results of the estimations agree quite well with the experimental measurements. We have also synthesized within DETHERM a custom fuel which is a blend of normal alkanes. Estimates of typical aviation fuel properties were then obtained. The results were compared with the property values expected for a typical aviation gas turbine fuel. These results are shown in Table 5.3-5 along with property value limits for JP-4 and JP-7. This showed that the program would be quite useful for fuel design.

Table 5.3-1
Mixture Properties for
33 Toluene/33 Methylcyclohexane/33 n-Heptane*

	METHOD	CALCULATED	OBSERVED ⁷²
Density @ 15.6°C (g/cc)	IDEAL @ 15°C	0.7778	0.7762
Surface Tension (dynes/cm @ 25°C)	SUGDEN SINGLE	23.19	21.2
Viscosity, Kinematic (cSt @ -20°C)	MOLAR AVERAGE	1.0369	1.098
Boiling Point (°C)	LKP	100.85	100.8

* Liquid volume percents

Pressure of experimental boiling point determination not reported.

Table 5.3-2
Mixture Properties for
16 Toluene/42 Methylcyclohexane/42 n-Heptane*

	METHOD	CALCULATED	OBSERVED ⁷²
Density @ 15.6°C (g/cc)	IDEAL @ 15°C	0.7575	0.7527
Surface Tension (dynes/cm @ 25°C)	SUGDEN SINGLE	22.32	20.4
Viscosity, Kinematic (cSt @ -20°C)	MOLAR AVERAGE	1.0352	1.147
Boiling Point (°C)	LKP	99.13	100.0

* Liquid volume percents

Pressure of experimental boiling point determination not reported.

Table 5.3-3
Mixture Properties for
42 Toluene/16 Methylcyclohexane/42 n-Heptane*

	METHOD	CALCULATED	OBSERVED ⁷²
Density @ 15.6°C (g/cc)	IDEAL @ 15°C	0.7705	0.7775
Surface Tension (dynes/cm @ 25°C)	SUGDEN SINGLE	23.17	21.6
Viscosity, Kinematic (cSt @ -20°C)	MOLAR AVERAGE	0.9581	1.022
Boiling Point (°C)	LKP	101.25	101.0

* Liquid volume percents

Pressure of experimental boiling point determination not reported.

Table 5.3-4
Mixture Properties for
42 Toluene/42 Methylcyclohexane/16 n-Heptane*

	METHOD	CALCULATED	OBSERVED ⁷²
Density @ 15.6C (g/cc)	IDEAL @ 15°C	0.7925	0.7994
Surface Tension (dynes/cm @ 25°C)	SUGDEN SINGLE	24.11	22.3
Viscosity, Kinematic (cSt @ -20°C)	MOLAR AVERAGE	1.1217	1.163
Boiling Point (°C)	LKP	102.89	101.8

* Liquid volume percents

Pressure of experimental boiling point determination not reported.

Table 5.3-5
Normal Alkane Custom Fuel Design
Fuel Property Comparison

Composition			
<u>Synthetic Fuel</u>			
Component	Wt%		
n-Hexane	10		
n-Octane	10		
n-Decane	30		
n-Dodecane	25		
n-Tetradecane	25		
Properties ⁷³			
	<u>Synthetic</u>		
	<u>Fuel</u>	<u>JP-4</u>	<u>JP-7</u>
Boiling Point (°C) @ 1 atm	128.3	190*	196*
Vapor Pressure @ 38°C (kPa)	8.23	14-21	---
Density @ 15°C (kg/m3)	768	751-802	779-806
Viscosity @ -20°C (cSt)	1.65	---	8.0*
Heat content (MJ/kg)	44.23	42.8**	43.5**
* Maximum value			
** Minimum value			

6.0 PHASE III TASK REVIEW

6.1 Integration of AFP and DECHEMA

6.1.1 Objective

We will develop a procedure to be added to AFP which will generate the data in format required for Dechema's data base. This routine will function by checking whether Dechema has the needed data, and if not, calling the appropriate methods in AFP to generate the data. This data will be given the appropriate format, then inserted into the data base. Lists of properties generated during these executions will only be retained for the duration of the calculation session, then discarded from the data base. The methods were coded and the necessary shell routines were added to AFP so that Dechema will run from AFP.

6.1.2 Work Completed

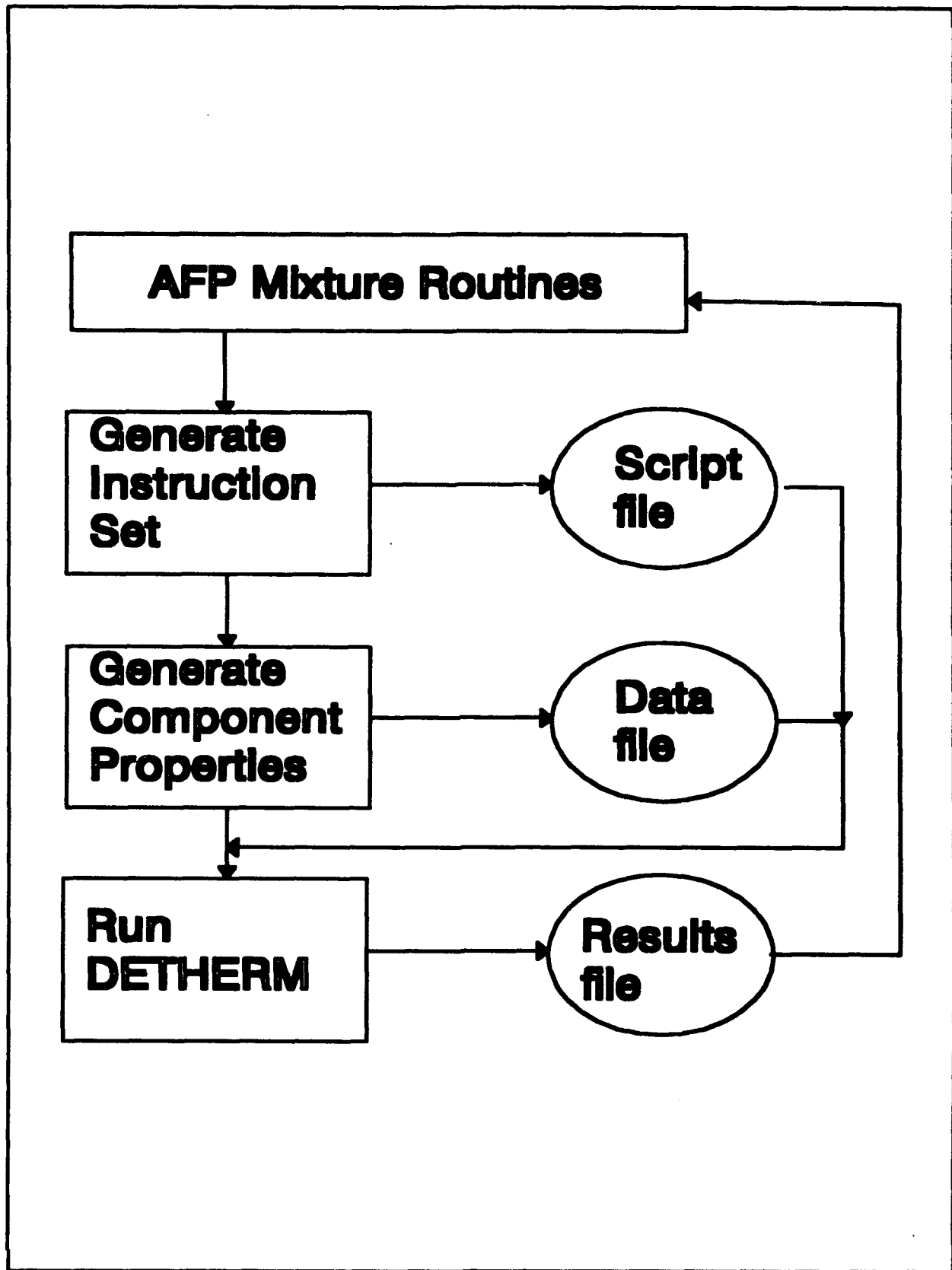
The following paragraphs describe the work completed in this task.

6.1.2.1 Philosophy

After extensive evaluation of the structure of the DETHERM-SDC code, we realized it would be exceedingly difficult to incorporate the FORTRAN code directly into the AFP system. This is principally because the program flow in DETHERM is intertwined. There is no clear "top-down" structure. There is extensive use of common blocks, which may be modified anywhere, and output is not concentrated into a few routines.

Therefore, we determined that a more effective approach would be to treat the DETHERM program as a self-contained package. We would provide material properties to its data base via intermediate data files, and provide an instruction set (script file) which emulates what the user would type to use DETHERM interactively. DETHERM is run as a separate process, and then provides its results back to AFP, once again through a data file.

The program flow may be diagrammed as shown on the next page.



6.1.2.2 Data Estimation

DETERM-SDC normally stores its material property data in a data base of approximately 500 compounds. We do not use this data, but instead, we build the data base from our own data. AFP estimations and lookups are used for pure component properties which are crucial to the mixture calculation.

The first step, then, in performing a mixture calculation, is to add the data to this data base for the compounds one wishes to study. We have set up a routine which calls many AFP pure component estimations and stores the data in the DETERM data base. It also estimates the interaction parameters for the LKP model, and stores those in the data base.

The following properties are looked up or estimated for each of the compounds.

Properties from AFP for use in Mixture Calculations		
FUNCTION	TEMPERATURE (K)	TEMPERATURE (K)
COUNT OF ATOMS IN MOLECULE		
MOLECULAR WEIGHT		
LIQUID DENSITY		
CRITICAL TEMPERATURE		
CRITICAL PRESSURE		
CRITICAL COMPRESSIBILITY FACTOR		
VAPOR PRESSURE AT SATURATION PRESSURE	9 Temperatures from $0.4T_b$ to $0.975T_b$	
NORMAL BOILING POINT TEMPERATURE		
ACENTRIC FACTOR		
SOLUBILITY PARAMETER	298	
COEFFICIENTS FOR LIQUID HEAT CAPACITY EQUATIONS		

Properties from AFP for use in Mixture Calculations		
FUNCTION	TEMPERATURE (K)	TEMPERATURE (K)
COEFFICIENTS FOR IDEAL GAS HEAT CAPACITY EQUATIONS		
IDEAL GAS ENTROPY	298	
IDEAL GAS HEAT OF FORMATION	298	
CRITICAL VOLUME		
CRITICAL DENSITY		
ENTHALPY OF VAPORIZATION AT SATURATION PRESSURE	Boiling point	
SURFACE TENSION	288	298
LIQUID VISCOSITY	293	373
VAPOR VISCOSITY	298	473
LIQUID THERMAL CONDUCTIVITY	273	323
GAS (VAPOR) THERMAL CONDUCTIVITY	298	478
GIBBS IDEAL GAS ENERGY OF FORMATION	298	
HEAT OF COMBUSTION-LIQUID AND VAPOR	298	
BWR COEFFICIENTS		
PARACHOR		
IDEAL GAS ENTHALPY OF FORMATION AT 25°C		
IDEAL GAS ENTROPY AT 25°C		
IDEAL GAS ENTHALPY		
UNIFAC GROUPS		

Properties from AFP for use in Mixture Calculations		
FUNCTION	TEMPERATURE (K)	TEMPERATURE (K)
RIEDEL EQUATION COEFFICIENTS		

For the physical properties, e.g., thermal conductivity and viscosity, DETHERM requires values at two temperatures, and it interpolates or extrapolates from those values. For some compounds, the two temperatures are in nonphysical regimes. For example, liquid properties are required below the freezing point or above the critical point. We have done our best to perform reasonable extrapolations into these nonphysical regimes, but for some cases, the estimations will fail.

Several routines were created for the sole purpose of generating equation coefficients for DETHERM.

6.1.2.3 Heat Capacity Coefficients

The heat capacity equations are used to calculate thermal properties over a range of temperatures. Two basic forms of the heat capacity equation may be used, the quadratic form or the NASA form of the equation. The quadratic form is:

$$C_p = A + 2 B T + 3 C T^2$$

where T is in °C.

The NASA form is:

$$C_p = R (A + B T + C T^2 + D T^3 + E T^4)$$

where T is in Kelvin and R is the gas constant. The coefficients A, B, C, D, and E are obviously different for each equation. We estimate the heat capacities for the liquid and vapor over a range of temperatures, and then use a singular value decomposition routine to perform the least-squares fit to get the heat capacity equations.

The full quadratic fit requires at least three C_p values. If only two C_p values are found, a linear fit will be tried:

$$C_p = A + 2 B T; C=0.$$

If only one C_p value is found, a constant fit will be used:

$$C_p = A; B=0, C=0.$$

The full NASA fit requires at least five C_p values. If only four C_p values are found, a third order fit will be tried:

$$C_p = R (A + B T + C T^2 + D T^3); E=0.$$

If less than four C_p values are found, the quadratic coefficients will be used for the NASA fit, appropriately transformed to the correct units.

6.1.2.4 BWR Coefficients

DETERM uses the Benedict-Webb-Rubin (BWR) equation of state to describe pure components.⁷⁰

The BWR equation used in DETERM is:

$$P = RT/V + (B_0RT - A_0 - C_0/T^2)/V^2 + (bRT - a)/V^3 + \alpha\alpha/V^6 + c(1 + \gamma/V^2)/(V^3 T^2) \exp(-\gamma/V^2).$$

The units are pressure, P , in atmospheres, volume, V , in liters, temperature, T , in Kelvin, and the gas constant, R in liter-atm/degree-mole. a , A_0 , b , B_0 , c , C_0 , α , and γ are the BWR constants.

AFP uses two methods for obtaining the BWR constants. First, it tries to look up the values in the data base, and second, it estimates them from a corresponding states method as follows:

$$\begin{aligned} A_0 &= 0.31315(R^2 T_c^2)/P_c \\ B_0 &= 0.13464(R T_c)/P_c \\ C_0 &= 0.1692(R^2 T_c^4)/P_c \\ a &= 0.059748(R^3 T_c^3)/P_c^2 \\ b &= 0.04307(R^2 T_c^2)/P_c^2 \\ c &= 0.059416(R^3 T_c^5)/P_c^2 \\ \alpha &= 0.0016081(R^3 T_c^3)/P_c^3 \\ \gamma &= 0.042113(R^2 T_c^2)/P_c^2 \end{aligned}$$

where: $R = 0.08206$ liter-atm/mole K, P_c is the critical pressure in atmospheres, and T_c is the critical temperature in K. These parameters were

developed for the LKP (Lee-Kesler-Plöcker) equation of state, which is essentially a modified BWR equation, using the principle of corresponding states.^{65, 66, 74}

6.1.2.5 Riedel Equation

DETERM uses the Riedel equation for vapor pressures of a pure component. The equation is:

$$P_v = \exp(R_1 + R_2/T + R_3T^2 + R_4 \ln(T))$$

Two methods are used to obtain the coefficients, R_i , for the equation. The most general method is to estimate the vapor pressure at a range of temperatures, and then fit the individual pressures to the equation using singular-value decomposition. This is a linear least squares method which is quite robust.

The more direct route retrieves the coefficients for the vapor pressure equation stored in the AFP data base, and recasts them into the Riedel form. The equation stored in the data base is slightly different, but a simple transformation is all that is required to use the coefficients in the Riedel equation.

6.1.2.6 Parachor

The parachor parameter is a correlation factor which is used in DETERM for calculating surface tension. A discussion of the parachor and its use is given in Reid, Prausnitz, and Poling⁷⁵. A group contribution method for accurate estimations of the parachor was developed by Quayle⁷⁶. AFP uses Quayle's group method for estimating the parachor.

6.1.2.7 UNIFAC Groups

Detherm uses the UNIFAC method for performing liquid-liquid equilibrium calculations. The UNIFAC groups are used for estimating liquid-liquid interaction parameters. A discussion of the use of the UNIFAC groups can be found in Reid, Prausnitz, and Poling⁷⁷. For each molecule, the count of each of the groups is required. A table of the groups as used by DETHERM follows. Note that the groups as used by DETHERM are numbered slightly differently from many other sources.

UNIFAC GROUPS USED IN DETHERM

1	CH ₃	30	>CHNH ₂	52	CCl ₄	81	Si
2	CH ₂	31	CH ₃ NH-	53	cCl	82	SiH ₂ O
3	CH	32	-CH ₂ NH-	54	CH ₃ NO ₂	83	SiHO
4	C	33	>CHNH-	55	-CH ₂ NO ₂	84	SiO
5	CH ₂ =CH	34	CH ₃ N<	56	>CHNO ₂	85	>N-
6	HC=CH	35	-CH ₂ N	57	cNO ₂	86	Amide
7	CH ₂ =C	36	cNH ₂	58	CS ₂	87	CON(Me) ₂
8	CH=C	37	c ₅ H ₅ N	59	CH ₃ SH	88	CONMeCH ₂
9	cH	38	1-c ₅ H ₄ N	60	CH ₂ SH	89	CON(CH ₂) ₂
10	c	38	2-c ₅ H ₄ N	61	Furfural	174	HCF ₃
11	cCH ₃	38	3-c ₅ H ₄ N	62	(CH ₂ OH) ₂	175	HXCF ₂
12	cCH ₂	39	2,3-c ₅ H ₃ N	63	I	176	HXCF
13	cCH	39	1,5-c ₅ H ₃ N	64	Br		
14	-OH	39	2,4-c ₅ H ₃ N	65	CH#C		
15	CH ₃ OH	39	1,3-c ₅ H ₃ N	66	C#C		
16	H ₂ O	39	1,2-c ₅ H ₃ N	67	Me ₂ SO		
17	C-OH	39	1,4-c ₅ H ₃ N	68	Acrylonitrile		
18	CH ₃ CO	40	CH ₃ C#N	70	C=C		
19	CH ₂ CO	41	-CH ₂ C#N	70	Cl(C=C)		
20	CH=O	42	-COOH	71	cF		
21	CH ₃ COO	43	HCOOH	72	Dimethylformamide		
22	CH ₂ COO	44	-CH ₂ Cl	73	Diethylformamide		
23	CHOO	45	>CHCl	74	-CF ₃		
24	CH ₃ O-	46	>C(Cl)-	75	>CF ₂		
25	-CH ₂ O-	47	CH ₂ Cl ₂	76	>C(-)F		
26	>CHO-	48	-CHCl ₂	77	-COO		
27	FCH ₂ O-	49	>CCl ₂	78	SiH ₃		
28	CH ₃ NH ₂	50	CHCl ₃	79	SiH ₂		
29	-CH ₂ NH ₂	51	-CCl ₃	80	SiH.		

6.1.2.8 LKP Interaction Coefficients

As discussed in the section on Evaluation of DECHEMA, the LKP interaction coefficients are calculated for each pair of components in the mixture.

The equation for correlated binary interaction parameters for the LKP model is:

$$K_{ij} = 0.93722 + 0.4372Q - 0.007202Q^2 \text{ where} \\ Q = T_c(j)V_c(j)/T_c(i)V_c(i).$$

Here, $T_c(i)$ and $V_c(i)$ are the critical temperature and critical volume for component i . Component i is the one with the lower boiling point.

6.1.2.9 Storage of Component Data

After the user has selected the components of a mixture, all of the properties of the pure components, as well as the interaction coefficients, are generated by lookup or estimation.

These estimations are subject to the usual AFP priority system, so that different methods can be selected for estimating properties. That is a significant part of the power of this approach; the user can explore alternative means of estimating pure component properties to observe the effect on the mixture as a whole.

The estimation of the entire list of properties can be a lengthy process, especially if large molecules are concerned. Also, compounds which are entirely unknown to the AFP system will add considerably to the time for the calculation. During the estimation process, an on-screen report is displayed, showing the progress of the calculation, and any errors which have arisen.

At the end of the estimation procedure, the pure component properties are stored in the data base for DETHERM. These are coded files, and not easily retrievable by the user. If errors have arisen, the user will be asked whether calculations should be continued. In general, it is possible to continue mixture calculations, even if one or more errors occur during

estimation of pure component properties. The mixture calculations will, of course, be compromised. After the data are stored, the program proceeds to selecting the mixture calculations to be run.

6.1.2.10 Creating the Script File and Spawning the Mixture Calculation

The native DETHERM user interface is a user-unfriendly command driven procedure. To allow the casual user to make use of the program, a method was developed in which the user selects options for running the program in the usual AFP menu system. These menus are arranged so that mutually incompatible options cannot be selected. Furthermore, the choices offered are a set which is compatible with the methods which are available for estimating interaction coefficients. For example, there are several different models available for estimating interactions, but only the LKP for vapor-liquid equilibria, and UNIFAC for liquid-liquid equilibria were used. Most of the functionality within DETHERM in our options selection process was preserved.

The options for performing mixture calculations, and interpretation of the results back, have been described in detail in the AFP USER'S MANUAL⁹⁹.

After all of the options are selected, an instruction file is written. AFP is then suspended, while DETHERM is started up, using the VAX LIB\$SPAWN procedure. Normally, DETHERM performs its calculations without feedback to the user, until it is complete. This usually takes a minute or less. Finally, DETHERM writes an output file of the results. This file is available for later printing. Additionally, AFP displays the results back a page at a time, at the console.

6.1.2.11 Mixture Calculation Methods

The purpose of this section is to define the methods used to determine the thermophysical properties of mixtures obtained by AFP and offer suggestions concerning the accuracy of these methods when this information is known.

The following pages discuss the methods used to determine mixture properties. The methods used by DETHERM to determine these properties are outlined in the DETHERM users manual¹. This information was enhanced by other thermodynamic text as well as original sources when they were available.

The thermophysical properties of gaseous and liquid mixtures are calculated using the Dechema Data Calculation system SDC. AFP will call this program when output results are activated from the Mixture Information Menu.

The following is a list of the thermophysical properties that are determined as a result of instructing AFP to do a mixture calculation.

DENSITY	VISCOSITY
HEAT CAPACITY	PSEUDO CRITICAL QUANTIFIER
ENTHALPY	ADIABATIC EXPONENT
CALORIFIC VALUE	COMPRESSIBILITY FACTOR
HEAT OF VAPORIZATION OR CONDENSATION	SURFACE TENSION
THERMAL CONDUCTIVITY	ENTROPY

In order to determine whether or not the fluid mixture exists in the liquid, vapor, or both states, DETHERM computes the vapor-liquid equilibria of the system. A vapor-liquid mixture will exist in equilibrium if the fugacity of each component i is the same in both the liquid and the gas phases.

$$f_i^G = f_i^L$$

In general, there are two methods for computing the fugacity of a gas (f_i^G) and the fugacity of the liquid (f_i^L). Consequently, these methods are also used to determine vapor-liquid equilibrium conditions. Fugacities are determined through an equation of state or by using activity coefficients along with an appropriate correlation model.

Given an equation of state where $p=p(v,t,n_i,\dots)$ the fugacity can be determined from the following equation:

$$\ln(f_i) = \frac{1}{RT} \int_v^p \left[\left(\frac{\partial p}{\partial n_i} \right)_{t,v,n_{i-1}} - \frac{RT}{V} \right] dv - \ln\left(\frac{V}{n_i RT}\right)$$

where,

f_i	=	fugacity
R	=	gas constant
T	=	absolute temperature
V	=	total volume
P	=	total pressure
n_i	=	number of moles of species i .

Equations of state are used to determine the fugacity of simple or "normal" liquids, that is, mixtures of low boiling substances that are composed of components that do not interact with each other. Equations of state can also be used for mixtures containing supercritical components and high pressure vapor-liquid equilibria.

Calculating the fugacities of the liquid and vapor using activity coefficients models involve the following equations:

$$\begin{aligned} f_i^G &= \phi_i y_i P \\ f_i^L &= \gamma_i \lambda_i f_i^\circ \end{aligned}$$

where,

f_i^G	=	fugacity of the gas
ϕ_i	=	fugacity coefficient
y_i	=	mole fraction of component i in the gas phase
P	=	pressure of the system
f_i^L	=	fugacity of the liquid
γ_i	=	activity coefficient
λ_i	=	mole fraction in liquid phase (component i)
f_i°	=	standard fugacity.

The fugacity coefficient, ϕ_i , depends on temperature and pressure and in a multicomponent mixture, on all mole fractions in the vapor phase, not just y_i . The fugacity coefficient is normalized such that as $P \rightarrow 0$, $\phi_i \rightarrow 1$; therefore, for a mixture of ideal gases $\phi_i = 1$.

The standard fugacity, f_i° , is the fugacity of component i at the temperature of the mixture, and at some arbitrarily chosen pressure and composition. Usually this arbitrarily defined standard state is based on the fugacity of pure liquid i at system temperature and pressure. When f_i° is defined as that of a pure liquid at system temperature and pressure, the limiting relation that $\gamma_i \rightarrow 1$ as $\lambda_i \rightarrow 1$ is true.⁷⁸

Activity coefficient methods are used when the liquid phase of a mixture contains strongly polar or hydrogen bonding substances. These methods also work well with weak electrolytes and, in general, mixtures at low pressures. Activity coefficient methods fail, however, if the mixture contains some supercritical components.

6.1.2.11.1 Equation of State Methods

DETERM determines liquid fugacities using the three equations of state listed below.

1. Lee-Kesler-Plöcker (LKP)
2. Redlich-Kwong-Soave (RKS)
3. Peng-Robinson (PR)

The advantages of these semiempirical equations of state are that they are relatively simple, they have a limited number of parameters, they can be extrapolated beyond the range of experimental data, and they describe critical phenomena and phase changes.

These equations can be used for calculating mixture properties, if mixture rules for the equation parameters are introduced. The mixture rules are satisfied if one interaction parameter for each binary compound pair in the mixture is given. For example, for a mixture composed of three compounds, A, B, and C, the mixture rules will be satisfied if three interaction parameters are given: K_{AB} , K_{AC} , K_{BC} .

These equations of state will all give similar fugacities, since fugacity is more dependent on the interaction parameters than on the type of equation used. In some cases the LKP equation may show slightly worse convergence behavior during boiling and dew point calculations.

The equations of state and the methods used for obtaining the activity coefficients used by DETERM will be discussed in the following paragraphs. These calculation methods play an essential role in determining the thermophysical properties of mixtures.

The Lee-Kesler-Plöcker equation of state is based on the general principle of corresponding states. As discussed previously, this is the only method implemented in AFP because it is the only one for which we can estimate interaction coefficients. This equation of state is of the Benedict-Webb-Rubin form and is based on Pitzers extended theory of corresponding states. Lee and Kesler⁶⁵ introduced a modified method of the three-parameter principle of corresponding states. This method determines the compressibility factor of a fluid from the compressibility factors of a "simple fluid" (Ar, Kr, CH₄) and of a "reference fluid" (n-octane).

$$Z(P, T) = \frac{PV}{RT} = Z^{(0)} + \frac{\omega}{\omega^{(r)}} (Z^{(r)} - Z^{(0)})$$

where,

- Z = Compressibility factor
- P = Pressure
- v = Specific volume (volume/mole)
- R = Gas constant
- T = Temperature
- ω = Acentric factor of the fluid
- $\omega^{(r)}$ = Acentric factor of the reference fluid
- $Z^{(0)}$ = Compressibility of the simple fluid
- $Z^{(r)}$ = Compressibility of the reference fluid.

The simple and reference compressibilities, $Z^{(0)}$ and $Z^{(r)}$, are determined via the modified Benedict-Webb-Rubin equation,

$$Z^{(0, r)} = \frac{P_r V_r}{T_r} = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^3} + \frac{C_4}{T_r^3 V_r^2} \left(\beta + \frac{\gamma}{V_r} \right) \exp \left(-\frac{\gamma}{V_r^2} \right)$$

where,

$$B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3}$$

$$C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3}$$

$$D = d_1 + \frac{d_2}{T_r}$$

All of the constants in the above equations must be determined for both the simple and the reference states.

T_r , P_r , and V_r are the reduced temperature, pressure and volume respectively. The values of b_1 through b_4 , c_1 through C_4 , d_1 , d_2 , β , γ , and ω for the simple and reference fluids were determined from experimental data of argon, krypton, methane, and n-octane⁶.

Plöcker proposed the following mixing rules for pseudocritical temperature, T_{cM} , pseudocritical molar volume V_{cM} , and the acentric factor of the mixture, ω_M . These rules make the above equations applicable to mixtures.

$$T_{cM} = \frac{1}{V_{cM}^2} \sum_j \sum_k Z_j Z_k V_{cjk}^2 T_{cjk}$$

$$V_{cM} = \sum_j \sum_k Z_j Z_k V_{cjk}$$

$$\omega_M = \sum_j Z_j \omega_j$$

where,

$$T_{cjk} = (T_{cj} T_{ck})^{1/2} K_{jk} \quad K_{jj} = 1$$

and

$$V_{cjk} = \frac{1}{8} (V_{cj}^{1/2} + V_{ck}^{1/2})^3$$

Here K_{jk} is an adjustable binary parameter, independent of temperature, density, and composition.

The pseudocritical pressure P_{cm} is found to be:

$$P_{cm} = (0.2905 - 0.085\omega_M) \frac{RT_{cm}}{V_{cm}}$$

The Redlich-Kwong-Soave equation of state was derived when Soave replaced the $a/(T^{0.5})$ term of the Redlich-Kwong equation with a more general temperature dependent term of $a(T)$.⁷⁹

$$Z = \frac{v}{v-b} - \frac{a(T)}{RT(v+b)}$$

where,

$$\begin{aligned} a(T) &= 0.42747 (R^2 T_c^2 / P_c) \{1 + m(1 - (T/T_c)^{1/2})^2\} \\ m &= 0.48 + 1.574\omega - 0.176\omega^2 \\ b &= 0.08664 RT_c / P_c \\ T_c &= \text{critical temperature} \\ P_c &= \text{critical pressure} \\ \omega &= \text{acentric factor} \\ v &= \text{volume per mole.} \end{aligned}$$

When doing mixture calculations, the following mixing rules for parameters a and b apply:

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2} (1 - K_{ij})$$

$$K_{ii} = 0$$

$$b = \sum_i x_i b_i$$

As seen in the above equations, a and b are expressed as simple functions of mole fractions when the RKS equation of state is extended to mixtures.

K_{ij} is an experimental correction factor, which is determined through experimental data for each binary combination present in the mixture. Each K_{ij} parameter is independent of system temperature, pressure, and composition.

We have not implemented an estimation method for RKS interaction coefficients, so the results presented in the output are very approximate.

The Peng-Robinson equation of state is a modification of the attractive term of the van-der-Waals equation of state.⁶⁷

$$Z = \frac{v}{v-b} - \frac{a}{RT} \left[\frac{1}{(v+b) + \frac{b}{v}(v-b)} \right]$$

The constant b is determined by the critical pressure, P_c , and critical temperature, T_c , and the constant a depends on the reduced temperature and the acentric factor ω .

$$a = \frac{0.45724 R^2 T_c^2}{P_c} [1 + \chi (1 - \sqrt{T/T_c})^2]$$

$$\chi = 0.37464 + 1.54266\omega - 0.26992\omega^2$$

$$b = 0.07780 \frac{RT_c}{P_c}$$

In order to use this equation of state in mixture calculations parameters, a and b must be adjusted to fit the mixture rules. The following equations are obtained by redefining the constants a and b to make the Peng-Robinson equation of state applicable to mixtures.

$$a = \sum_i \sum_j x_i x_j (1 - K_{ij}) a_i^{1/2} a_j^{1/2}$$

$$K_{ii} = 0$$

$$b = \sum_j x_j b_j$$

K_{ij} is an empirically determined binary interaction coefficient which describes the interaction of the binary formed by the interactions between component i and component j . Notice that the constants a and b are the same form for both the Peng-Robinson and the Redlich-Kwong-Soave equations of state when they are extended to mixtures. Neither form is estimated in AFP, so the results are approximate.

6.1.2.11.2 Activity Coefficient Methods

Vapor liquid equilibria can be determined using activity coefficients. Activity coefficients are related to the Gibbs excess free energy of mixing, ΔG^E , by the following equation.

$$\Delta G^E = RT \sum_i x_i \ln(\gamma_i)$$

Where x_i is the mole fraction of component i , R is the gas constants, and T is the system temperature. G^E consists of an enthalpic and an entropic term as shown in this equation.

$$\Delta G^E = \Delta H^E - T \Delta S^E$$

Where ΔH^E and ΔS^E are the enthalpy and entropy of mixing, respectively. An equation which describes both of these terms exceeds the possibilities of the chemical theory and, therefore, correlations which emphasize either the enthalpic or the entropic terms exist.

Interaction parameters for most correlations are available in literature and can be retrieved from a data base. For the most part, these interaction

DETERM can determine the activity coefficient using enthalpic or entropic correlation methods. Enthalpic methods used by DETERM include:

1. Chao-Seader
2. van Laar
3. Margules.

Entropic methods used to determine activity coefficient are:

1. Wilson
2. NRTL
3. UNIQUAC
4. UNIFAC.

The Chao-Seader method, also known as the regular solution theory, is an activity coefficient correlation method that emphasizes the enthalpic term. A regular solution is a solution in which the entropy of mixing is considered to be ideal. This assumption sets $G^E = H^E$ which assumes that $S^E = 0$. This approximation leads to the conclusion that at constant composition $\ln \gamma$ varies as $1/T$ and G^E are independent of temperature.

$$RT \ln \gamma_i = V_i (\delta_i - \frac{\sum_j x_j v_j \delta_j}{\sum_j x_j v_j})^2$$

This theory leads to the following expression for the activity coefficient γ_i^{80} :

where, R = gas constant
 T = temperature
 γ_i = activity coefficient (species i)
 V_i = molar volume (species i)
 δ = solubility parameter (species i)
 x_i = liquid composition (species i).

To use this equation, two constants are required: the solubility parameters, δ_i , and the liquid molar volume V_i . There are no interaction parameters used in this correlation. Solubility parameters and molar volume are provided by AFP, so this method is relatively accurate for hydrocarbons.

The regular solution method is an extreme approximation and is not appropriate for solutions with hydrogen bonding compounds or compounds with strong intermolecular interactions. In practice the Chao-Seader method is only used for mixtures of hydrocarbons and light gases like hydrogen or nitrogen.

The van Laar equation was developed under the assumption that the entropy of mixing vanishes. Although this assumption is not fulfilled by many mixtures, in practice the van Laar equation works quite well for many systems. The van Laar equation for a binary system is⁶²:

$$\ln(\gamma_1) = A_{12} \left(\frac{A_{21}x_2}{A_{12}x_1 + A_{21}x_2} \right)^2$$

where, γ_i = activity coefficient
 x_1, x_2 = mole fractions of each component
 A_{12}, A_{21} = binary parameters.

DETERM uses a multicomponent van Laar equation, which is only valid if higher order interactions are neglected. Since these higher order interactions are neglected two interaction parameters A_{ij} and A_{ji} are needed for each binary combination of components. These parameters are calculated using the Gilmont approximation.⁸¹

The van Laar equation does not give good results for unsymmetrical systems, and multifunctional compounds.

The Margules equation is a method used to obtain the activity coefficient which was developed from a Taylor expansion for $\ln \gamma$.⁶¹ DETHERM uses the three suffix or two parameter form of this correlation.

$$\ln \gamma_1 = [A_{12} + 2(A_{21} - A_{12})x_1]x_2^2$$

The A_{ij} parameters are not available as implemented in AFP.

The activity coefficients calculated using the Margules equation are less accurate than those obtained via the van Laar equation. However, the Margules equation can describe mixtures containing unsymmetrical compounds.

Entropic methods for computing activity coefficients are more modern than the enthalpic methods. These methods are based on the concept of local composition.⁸² The concept of local composition is a means for describing the entropy of mixing.

The Wilson equation is an entropic method derived to describe the activity coefficients of normal mixtures.⁸³ It was obtained by substituting local volume fractions for volume fraction in the Flory and Huggins equations for Gibbs free energy of mixing. The activity coefficient γ_i , of a multi-component system can be found from:

$$\ln(\gamma_i) = -\ln\left(\sum_j x_j \Lambda_{ij}\right) + 1 - \frac{\sum_k x_k \Lambda_{ki}}{\sum_j x_j \Lambda_{kj}}$$

where,

$$\Lambda_{ij} = \frac{V_j^l}{V_i^l} \exp\left(\frac{\lambda_{ij}}{RT}\right)$$

$$A_{ii} = A_{jj} = 1.$$

V_i^L and V_j^L are the molar volumes of the pure liquids i and j .

A_{ij} , A_{ji} and λ_{ij} , and λ_{ji} are binary interactions parameters. The value of A_{ij} depends on the size and energy of the molecules in the mixture. DETHERM needs only two of these interaction parameters in order to perform mixture calculations. These binary interaction parameters are not implemented in AFP.

The above two parameter Wilson equation has two disadvantages. It cannot compute activity coefficients for a system with restricted mutual solubility, and it cannot determine the maximum or the minimum of the activity coefficient.

The NRTL (NonRandom Two Liquids) equation was developed by Renon and Prausnitz⁶³ in order to overcome the disadvantages of the Wilson equation. They introduced a "nonrandomness" parameter which makes the NRTL equation applicable to partially miscible systems."

The derivation of the NRTL equation was based on a two-liquid mixture theory. According to this theory, the mixture components i and j exist as two types of cells, one with molecule i as the central molecule, the other having molecule j as the central molecule. The activity coefficients are obtained using the following equation.

$$\ln(\gamma_i) = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_l G_{li} x_l} + \frac{\sum_j x_j G_{ij}}{\sum_l G_{lj} x_l} (\tau_{ij} - \frac{\sum_n x_n \tau_{nj} G_{nj}}{\sum_l G_{lj} x_l})$$

where,

$$G_{ij} = \exp (-\alpha_{ij}\tau_{ij})$$

$$\alpha_{ij} = \alpha_{ji}, \quad \tau_{ii} = \tau_{jj} = 0, \quad G_{ii} = G_{jj} = 1.$$

The parameters of the Wilson and the NRTL equations can be determined from activity coefficient data for binary mixtures. By correlating activity coefficient data for the species 1 - species 2 mixture using either of the models, the 1-2 parameters can be determined. Similarly, from the data of the species 2 - species 3, and the species 1 - species 3 binary mixtures, the 2-3 and 1-3 parameters can be found. These coefficients can then be used to estimate the activity coefficient for the ternary 1-2-3 mixture without the need for experimental data for the three-component system.

The NRTL equation contains three interaction parameters per binary, but the reduction of experimental data for a large number of binary systems indicates that α_{ij} varies from about 0.20 to 0.47. For moderately nonideal systems, the NRTL model does not offer any advantages over the van Laar or Margules equations. However, for strongly nonideal mixtures and for partially immiscible systems, the NRTL equation is more appropriate for calculating the activity coefficients.

The activity coefficients can also be determined using the **UNIQUEAC**, **UNiversal QUAsiChemical, model** developed by Abrams, and Prausnitz.⁸⁵ The UNIQUEAC model is based on statistical mechanical theory. This model accounts for the fact that local compositions result from both the size and energy differences between the molecules in the mixture.

The size differences between the molecules are accounted for in the combination part of the activity coefficient, while the energy differences are accounted for in the residual part of the activity coefficient. The overall equation for the activity coefficient is then:

$$\ln \gamma_i = \ln \gamma_i (\text{combinatorial}) + \ln \gamma_i (\text{residual})$$

where,

$$\ln \gamma_i (\text{combinatorial}) = \ln \left(\frac{\phi_i}{x_i} \right) + \frac{Z}{2} q_i \ln \left(\frac{\theta_i}{\phi_i} \right) + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j$$

$$\ln \gamma_i (\text{residual}) = -q_i \left[1 - \ln \left(\sum_j \theta_j \tau_{ji} \right) \right] - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}}$$

$$l_i = (r_i - q_i) \frac{Z}{2} - (r_i - 1)$$

$$\ln \tau_{ij} = \frac{-(U_{ij} - U_{jj})}{RT}$$

where,

- r_i = volume parameter for species i
- q_i = molecular surface area parameter for species i
- θ_i = area fraction of specie i $\approx x_i q_i / \sum x_j q_j$
- ϕ_i = segment or volume fraction of species i $\approx x_i r_i / \sum x_j r_j$
- Z = average coordination number (usually taken to be 10)
- x_i = mole fraction of component i
- U_{ij} = average interaction energy for a species i - species j interaction.

The UNIQUAC equation contains only two adjustable parameters, τ_{12} and τ_{21} (or equivalent, $(U_{12} - U_{12}^0)$ and $(U_{21} - U_{11}^0)$) for each binary pair. The surface area parameters r_i and q_i can be evaluated from the molecular structure of the mixture compounds. This two-parameter activity coefficient model has a better theoretical basis than the other two-parameter models, namely the van Laar and the Wilson equations.

The values of r and q are evaluated by a group contribution method. The underlying idea of the group contribution method is that a molecule can be considered a collection of functional groups, and the volume R_i and the surface area Q_i of group i will be approximately the same in any molecule in which that group occurs. For example, the contribution to the total volume and surface area of a molecule from a methyl ($-\text{CH}_3$) group would be the same whether the methyl group is at the end of an ethane, propane, or decane molecule. Therefore, the parameters r and q are obtained by adding the R and Q parameters of all of the molecules functional groups. The advantage of the group contribution approach is that there are a relatively small number of functional groups, and from this small number of functional groups virtually any compound can be defined.⁸⁶

The UNIQUAC model is not used directly in our implementation, but the UNIFAC method is available.

The UNIFAC, (UNIQUAC Functional-group Activity Coefficient) model, developed by Fredenslund, Jones and Prausnitz⁸⁷, is based on the UNIQUAC model. It is a group contribution model that can be used to estimate solution behavior when there is no experimental data available. For this reason the UNIFAC model is known as a predictive activity coefficient model. In the UNIFAC model, both the combinatorial and the residual terms found in the UNIQUAC models are determined from group contribution methods, whereas in the UNIQUAC model, the residual term is determined from two adjustable parameters which fit experimental data.

The first step in applying the UNIFAC model is to identify the functional groups present in each of the molecules of the mixture. Next the activity coefficients for each species is obtained through:

$$\ln \gamma_i = \ln \gamma_i(\text{combinatorial}) + \ln \gamma_i(\text{residual}).$$

The combinatorial term is determined in the same manner as it was in the UNIQUAC model. The residual term is also derived from the group contribution method. When using the UNIFAC model, it may help to envision the mixture as a mixture of functional groups rather than a mixture of molecules. The residual contribution to the logarithm of the activity coefficient from group k in the mixture, $\ln \Gamma_k$, is computed in a similar way as the residual contribution term in the UNIQUAC method.

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_n \Theta_n \Psi_{nk} \right) - \sum_n \frac{\Theta_n \Psi_{kn}}{\sum_n \Theta_n \Psi_{nn}} \right]$$

where,

$$\begin{aligned} \Theta_n &= \text{surface area fraction of group } n = X_n Q_n / \sum X_n Q_n \\ X_n &= \text{mole fraction of group } n \text{ in mixture} \\ \Psi_{mn} &= \exp [(-U_{mn} - U_{nn}) / (kT)] = \exp [-a_{mn} / T] \\ U_{mn} &= \text{measure of interaction energy between functional groups } m \text{ and } n. \end{aligned}$$

The sums in the above equations are taken over all of the groups in the mixture.

The residual contribution to the activity coefficient of species i is computed from:

$$\ln \gamma_i(\text{residual}) = \sum_k v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}].$$

Here v_{ik} is the number of k groups present in species i and $\ln \Gamma_k^{(i)}$ is the residual contribution to the activity coefficient of group k in a pure fluid of species i molecules. The Γ_k^i term is included to ensure that in the limit of pure species i , which is still a mixture of groups (unless species i molecules consist of only a single functional group), $\ln \gamma_i$ (residual) goes to zero.

The parameter R_i and Q_i are available in tables and are based on the geometry of the functional group. This leaves the a_{mn} and a_{nm} the only unknown parameters in the UNIFAC model. According to the group contribution model, the functional groups m and n will have the same value of a_{mn} and a_{nm} , since they will interact in the same manner. That is, it is assumed that the interaction between an alcohol (-OH) group and a methyl (-CH₃) group will be the same, regardless of whether these groups occur in ethanol-n-butane, or propanol-decane mixtures. The parameters a_{mn} and a_{nm} for many group-group interactions are determined by regression analysis of activity coefficient data. These parameters are then used to predict activity coefficient in mixture (binary or multicomponent) for which no experimental data are available.

UNIFAC groups are provided by AFP. Thus, this method is available for calculations.

Now that the methods for determining activity coefficients have been discussed, the calculation methods for thermophysical properties will be explained. The conditions for which these calculation methods are accurate will be given when they are known.

6.1.2.11.3 The Caloric Properties of Gas and Liquid

AFP provides pure component polynomial coefficients for representing the specific heat (C_p) and the enthalpy of ideal gases and liquids. The ideal gases or liquid assumption is true only at zero pressure. There are three sets of polynomial coefficients stored for gases. One set of coefficients would be used in the following equation:

$$C_p = A + BT + CT^2.$$

The other two sets of polynomial coefficients, the NASA-coefficients, describe a 4th degree polynomial. One set of coefficients describe the

temperature range from $300 \leq T \leq 1000$ K and the other set of coefficients applies when $T \geq 1000$ K. These coefficients are used in this equation:

$$C_p = A + BT + CT^2 - DT^3 + ET^4.$$

The NASA coefficients are used, when they are available, for computing the caloric properties of a gas.

The caloric properties of a liquid are always determined using the second order polynomial coefficients.

The pressure dependence of the caloric properties are described using departure functions ΔC_p , ΔH , and ΔS . Therefore, the equations for the real caloric properties are given by:

$$C_p^{\text{real}} = C_p^{\text{ideal}} + \Delta C_p$$

$$H^{\text{real}} = H^{\text{ideal}} + \Delta H$$

$$S^{\text{real}} = S^{\text{ideal}} + \Delta S.$$

The departure functions are determined using the following equations of state:

Benedict-Webb-Rubin^{68, 69, 70}
 Lee-Kesler-Plöcker^{65, 66}
 Peng-Robinson⁶⁷.

The departure functions could also be determined from correlation tables developed by:

Yen-Alexander⁸⁸
 Lydersen⁸⁹.

6.1.2.11.4 The Enthalpy of Gas

Enthalpy (H) is chosen so that changes in heat correspond to changes in the enthalpy function. Thus, changes in H are directly measurable for a reversible process. The zero point of the enthalpy function can be chosen arbitrarily at any convenient reference condition. The reference enthalpy used by AFP to determine pure component enthalpies is different than the reference enthalpy used when mixture calculations are performed.

For mixture calculations, the reference enthalpy is the pure liquid compounds at 0°C, while the reference enthalpy used in pure component calculations is that of the elements in their most stable state at 298K. In order to compare enthalpies of pure compounds determined by AFP to those of mixtures, the enthalpies of the pure liquid components at 0°C (proportional to their concentration in the mixture) must be subtracted from the mixture enthalpy. The TEST output of mixture calculations gives the absolute enthalpy. This mixture output gives the same enthalpy values as the pure component calculations, done by AFP, since the same reference state is used.

Table 6.2-1 shows the methods that DETHERM uses to determine enthalpies.

Table 6.2-1
Methods for Determining the Enthalpy of Gas

Real Gases

$$H_{real} = H^{IG} + \Delta H$$

H^{IG} gas coefficients (valid only at low pressures)

ΔH (departure function)

Benedict-Webb-Rubin^{68, 69, 70}

Yen-Alexander⁸⁸

Lydersen⁸⁹

Lee-Kesler-Plöcker^{65, 66}

Redlich-Kwong-Soave⁷⁹

$$H_{Gas} = H_{liquid} + \Delta H(\text{condensation})$$

The enthalpies determined from the gas coefficients is determined independent of pressure. This is the ideal gas enthalpy of the mixture.

The enthalpy of real gases are found by:

$$H^{real} = H^{IG} + \Delta H$$

where,

$$H^{IG} = H^{IG}(T_2, T_2) - H^{IG}(T_1, P_1)$$

$$\Delta H = (H - H^{IG})_{T_2, P_2} - (H - H^{IG})_{T_1, P_1}$$

$$(H - H^{IG})_{T, P} = RT(Z - 1) + \int_{Y=0}^{Y=Y(T, P)} [T \left(\frac{\partial P}{\partial T} \right)_Y - P] dY$$

$$Z = PV/RT$$

In the above equations the IG superscript stands for ideal gas. The gas enthalpy of the gas is being measured from state 2 to state 1. Z is the compressibility factor, P is the pressure, T is the temperature, $\underline{V}$ is the volume per mole, R is the gas constant.

The Benedict-Webb-Rubin equation of state is⁷⁰:

$$\frac{PV}{RT} = 1 + (B - \frac{A}{RT}) \frac{1}{Y} + (b - \frac{a}{RT}) \frac{1}{Y^2} + \frac{aa}{RTY^3} \frac{\beta}{RT^3Y} (1 + \frac{Y}{Y^2}) \exp(-\frac{Y}{Y^2}).$$

This equation should be solved for P, then the partial derivative should be taken with respect to T at constant $\underline{V}$. This can then be substituted into the above equation in order to determine the departure function of the gas at a given T and P.

Yen-Alexander⁸⁹ developed graphs of $(H^0 - H)/T_c$ versus reduced pressure, P_r , at varying reduced temperatures, T_r , for four values of critical compressibility ($Z_c = 0.23, 0.25, 0.27, 0.29$). These curves were then fitted to an analytical expression using a nonlinear estimation program. The equations that were developed represent the charts to within ± 0.1 BTU/(lbmole R).

Mixture properties are calculated using pseudocritical pressures, temperatures, and compressibilities. The use of charts, and therefore the Yen-Alexander fitted equations, generally do not provide accurate enthalpies for nonpolar systems.

Lydersen developed a method for determining departure functions by dividing compounds into four groups according to their critical compressibilities.

Group I	Z_c	=	0.24 to 0.25
Group II	Z_c	=	0.26 to 0.28
Group III	Z_c	=	0.28 to 0.30
Group IV	Z_c	=	0.232 (water)

He then developed extensive graphs and tables of thermodynamic properties using a corresponding states correlation based on critical compressibility. Enthalpy departures from the ideal gas state is one of the thermodynamic properties that Lydersen determined. In order to make the Lydersen method programmable, the graphs and tables have been fit to equations. Some of this equation fitting was done by Dr. L.O. Hirschfelder of the Naval Research Laboratories.

The Lee-Kesler-Plöcker equation of state was described earlier. The enthalpy departure function for the LKP equation of state is developed in Reid, Prausnitz, and Poling and reads:⁹⁰

$$\frac{H^0-H}{RT_c} = \left(\frac{H^0-H}{RT_c} \right)^{(0)} + \frac{\omega}{\omega^R} \left(\left(\frac{H^0-H}{RT_c} \right)^{(R)} - \left(\frac{H^0-H}{RT_c} \right)^{(0)} \right).$$

In this equation, ω^R is the reference acentric factor which can be chosen arbitrarily.

The departure function enthalpy from the Peng-Robinson⁶⁷ or Redlich-Kwong-Soave⁷⁹ equations of state are determined by substituting the equations of state into the following equation:

$$\text{Dept function} = \underline{H} (T,P) - \underline{H}^{IG} (T,P)$$

$$H(T, P) - \underline{H}^{IG}(T, P) = RT(Z-1) + \int_{P^\infty}^P [T(\frac{\partial P}{\partial T})_T - P] dP.$$

In the above equation the underscored variables represent properties per mole. The equation of state should be solved for pressure, P , and then substituted into the departure function. The following equation shows the departure function for the Peng-Robinson equation after taking the partial derivative and performing the integration.

$$H(T, P) - \underline{H}^{IG} = RT(Z-1) + \frac{T \frac{da}{dT} - a}{2\sqrt{2}b} \ln \left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right]$$

where $Z = PV/RT$ and $B = Pb/RT$.

DETERM determines the enthalpy of mixtures by using the molar average of the ideal gas enthalpies of the pure compounds, and the departure functions are calculated for the whole mixture.

The following recommendations can be made concerning the accuracy of the enthalpy calculation methods. At atmospheric pressure, the ideal values can be used; when the pressure is above atmospheric pressures, a method which accounts for the pressure changes should be selected. The Benedict-Webb-Rubin, Lee-Kesler-Plöcker, Peng-Robinson, and Redlich-Kwong-Soave equations of state determine the enthalpy of hydrocarbon mixture very accurately. If non-hydrocarbons are present, the Benedict-Webb-Rubin equation of state is not applicable, and the Redlich-Kwong-Soave, equation of state should not be used

if the mixture contains hydrogen. The errors introduced by using one of these equations of state are normally a few Joules per gram.

6.1.2.11.5 The Specific Heat of the Gas (C_p)

For an ideal gas mixture, the ideal heat capacity is given by:

$$C_{p_m}^0 = \sum_i y_i C_{p_i}^0.$$

Therefore, for either a pure gas or a gas mixture at constant composition the heat capacity for a real gas is related to that of a gas in the ideal state at the same temperature and composition by:

$$C_p = C_p^0 + \Delta C_p.$$

ΔC_p is the residual heat capacity, and the 0 symbol is used to represent the ideal gas state. For a pressure-explicit equation of state, the residual or departure function, for specific heat is most convenient determined by⁹¹:

$$\Delta C_p = T \int_v \left(\frac{\partial^2 P}{\partial T^2} \right) dv - \frac{T \left(\frac{\partial P}{\partial T} \right)_v^2}{\left(\frac{\partial P}{\partial v} \right)_T} - R.$$

DETERM can determine the specific heat of a gas using five different methods. When the method of gas coefficients is used, the specific heat that is determined will be that of an ideal gas. This specific heat was determined by a method that did not account for the pressure dependence of C_p .

The Benedict-Webb-Rubin⁷⁰, Peng-Robinson,⁶⁷ or the Redlich-Kwong-Soave⁷⁹ equations of state are used to determine the departure function, or residual, specific heat. By solving these equations of state for P and then substituting them into the above, equation values of ΔC_p can be determined. These values are then added to the ideal gas specific heat which is determined by the gas coefficients to obtain the specific heat of the real gas.

Calculating the residual specific heat, using the Lee-Kesler-Plöcker method^{65,66} and adding it to the ideal gas specific heat, is the final method DETHERM uses to obtain the heat capacity of a real gas. For this method:

$$C_p - C_p^\circ - \Delta C_p = (\Delta C_p)^\circ + \omega (\Delta C_p)^1.$$

The simple fluid contribution $(\Delta C_p)^{(0)}$ and the deviation function $(\Delta C_p)^{(1)}$ can be found in tables as functions of reduced temperature and pressure (T_r and P_r). Examples of these tables are Table 5-8 and Table 5-9 in Reid, Prausnitz, and Poling⁹². Mixtures require pseudocritical rules given in equations 4-6.3 to 4-6.7 of the same reference. These rules tend to break down when highly polar components are present.

The specific heats of mixture are determined by taking the mole-average of the ideal gas specific heats of the pure compounds, and the departure functions are calculated for the whole mixture.

At pressures below or at atmospheric pressure, the C_p° values obtained from the gas coefficients can be used. Mixtures of hydrocarbons are accurately described by any of the equations of state. Just as in the enthalpy calculations the Benedict-Webb-Rubin cannot be applied if any non-hydrocarbons are present, and the Redlich-Kwong-Soave equation should not be used if the mixture contains hydrogen.

6.1.2.11.6 Enthalpy of the Liquid

The enthalpy of an ideal liquid can be determined from the liquid coefficient described in the caloric properties of gas and liquid. This method assumes that the enthalpy of the liquid is independent of pressure. When the enthalpy of a liquid is pressure dependent departure functions are used to account for this dependency. Estimation of the departure function usually takes place in several steps.

$$H^L - H^o = (H^L - H^{SL}) + (H^{SL} - H^{SV}) + (H^{SV} - H^o)$$

where,

H^L = liquid enthalpy at T and P
 H^o = ideal-gas enthalpy at T and P^o
 H^{SL} = saturated liquid enthalpy at T and P_{vp}
 H^{SV} = saturated vapor enthalpy at T and P_{vp} .

The $H^{SV} - H^o$ term is the enthalpy of an ideal gas and can be determined from the liquid coefficient. The $H^{SL} - H^{SV}$ term is the heat of condensation at 0°C, and the $H^L - H^{SL}$ represents the departure function of the liquid enthalpy. The $H^L - H^{SL}$ term represents the effect of pressure on the liquid enthalpy; this term is usually relatively small compared to the other two terms.

DETERM determines the liquid enthalpy of a mixture using six different methods. The enthalpies of these mixtures are calculated by taking the molar average of the ideal enthalpies of the pure compounds. The departure functions are calculated for the whole mixture.

The liquid enthalpy determined by the liquid coefficients is the enthalpy of an ideal liquid. This enthalpy is calculated independent of pressure. The other methods account for the pressure dependence of a liquid enthalpy. These methods all calculate the real enthalpy of a liquid by determining three quantities, the enthalpy of an ideal gas, the heat of condensation at 0°C and the departure function. The ideal gas enthalpy is calculated from the gas coefficients. The heat of condensation is set equal to the mole fraction average of the pure component values of $-\Delta H_v$, that is,

$$-\Delta H_v - \Delta H_c - H^{SL} - H^{SV} = \sum_j X_j \Delta H_{vj}.$$

The departure functions are determined through the use of the Yen-Alexander⁸⁸, the Lydersen⁸⁹, the Lee-Kesler-Plöcker^{65,66}, the Peng-Robinson⁶⁷, or the Redlich-Kwong-Soave⁷⁹ equation of state. Each of these methods of obtaining the departure function has already been discussed.

At low pressures, the liquid enthalpy values computed from the liquid coefficients should be used. At high pressures, no satisfactory recommendation can be given. The Yen-Alexander method computes the enthalpy of a nonpolar liquid to within 25J/g; for this reason this method is widely used. The Lee-Kesler-Plöcker method sometimes is unable to generate

enthalpies of phase changes with the desired accuracy. Good results are obtained when the Redlich-Kwong-Soave or the Peng-Robinson equation of state are used, but if the mixture contains hydrogen the Redlich-Kwong-Soave equation of state cannot be used.

6.1.2.11.7 The Specific Heat of the Liquid

DETERM determines the specific heat of a liquid in four ways. Pressure independent specific heat of a liquid is determined from the liquid coefficients discussed in the Caloric Properties of Gases and Liquid (Section 6.1.2.11.3). The other three methods determine the heat capacity of a liquid by first determining the specific heat of an ideal gas and then adding on the departure function. The specific heat of the ideal gas is determined by the gas coefficients. The departure function is determined by the Lee-Kesler-Plöcker^{65,66}, the Peng-Robinson⁶⁷, or the Redlich-Kwong-Soave⁷⁹ equations of state. These equations of state have all been discussed in previous sections. The departure functions are determined for the whole mixture. The specific heat of mixtures is calculated by taking the molar average of the ideal gas specific heats of the pure components.

Liquid heat capacities are not strong functions of temperature except when the reduced temperature, T_r , is above 0.7. At high reduced temperatures, they are large and strong functions of temperature. Near the normal boiling point, liquid organic compounds have heat capacities between 1.2 and 2J/(g.K). In this temperature range, the effect of pressure on the liquid heat capacity is small.⁹³

At low pressures, the value for the specific heat of a liquid determined by the liquid coefficients, is the most accurate. At higher pressures the values obtained by the Peng-Robinson or the Redlich-Kwong-Soave equation of state are preferred over the liquid coefficient and Lee-Kesler-Plöcker methods. The liquid coefficient method does not account for pressure, and the Lee-Kesler-Plöcker equation may encounter accuracy problems when predicting the temperature derivative of the enthalpy of condensation. As usual, if the mixture contains hydrogen, the Redlich-Kwong-Soave method cannot be applied.

6.1.2.11.8 Density of Gases

The density of gases are determined by the ideal gas law or by an equation of state. The equations of state are solved for specific volume, $\underline{v}$, which has the units of length³/mass. Density is the inverse of specific volume and is given in both mole volume and mass/volume units. The density of gas is determined using 5 different equations of state.

The first equation of state used to determine the density of a gas is the ideal gas law. This equation is accurate up to a pressure of about 2 atm and even higher pressure if the mixture contains small molecules which do not interact.

$$(\rho) = \frac{1}{v} = \frac{P}{RT}$$

In the above equation, ρ is the molar density, v is the volume per mole of mixture, P is pressure, R is the gas constant, and T is the absolute temperature. The mass density is the product of the molecular weight of the mixture and the molar density.

The Beattie-Bridgeman equation of state⁹ is the second equation of state used to determine the density of a gas. This equation of state is a truncated virial equation. This equation is only applicable for supercritical gases (reduced temperature >1) at low and medium pressures (reduced pressure <10).

The Beattie-Bridgeman equation of state solved for pressure reads:

$$P = \frac{RT(1-e)}{v^2} (v+B) - \frac{A}{v^2}$$

where,

P = pressure
 R = gas constant
 T = absolute temperature
 v = volume per mole
 A = $A_0 (1-a/v)$,
 B = $B_0 (1-b/v)$,
 c = C/vT^2 .

The constants A_0 , B_0 , a , b , and c are constants which depend on the mixture composition. The density of a real gas is determined from the above equation by solving it for volume, and then recognizing that density (given in moles/volume) is the inverse of v ($1/v$).

The Benedict-Webb-Rubin equation of state is the third method used to determine the density of a gas. This equation of state has been discussed earlier in this report. The Benedict-Webb-Rubin equation in terms of density reads:

$$P = RT + (\beta_0 RT - A_0 - C_0/T^2) \rho^2 + (bRT - a) \rho^3 + a\alpha \rho^6 + (c \frac{\rho^3}{T^2}) (1 + \gamma \rho^2) \exp(-\gamma \rho^2).$$

When this equation is solved for density it can have up to six roots. The lowest of these roots is the vapor density, and the highest root is the liquid density.

The Lee-Kesler-Plöcker and the Peng-Robinson are the other two equations of state used to determine the density of a gas. To determine the density of a gas from these equations of state, substitute $1/\rho$ wherever v occurs in these equations.

When the density of a hydrocarbon gas mixture is desired, the Peng-Robinson, the Lee-Kesler-Plöcker, and the Benedict-Webb-Rubin give the most accurate results. For nonhydrocarbons, the Lee-Kesler-Plöcker is most likely to generate the best results. The equations of state should obtain a density that has errors of 2 to 3 percent, unless the density is determined near the critical point or the fluid is highly polar.

6.1.2.11.9 Density of a Liquid

The Peng-Robinson, Lee-Kesler-Plöcker, and Benedict-Webb-Rubin equation of state are all used to determine the density of a liquid in basically the same way as they were used to determine the density of a gas. In addition to these three equations, a volume average of pure component densities and the Yen-Woods⁹⁵ method are also used to determine the density of a liquid.

The volume average of pure component densities calculates the density of a liquid as though it were independent of pressure. This method determines the density of each component as if it was not in a mixture. Once all of the pure component densities have been determined, a volume average is taken. The data base contains the densities of pure components at 20 and 25°C. If the mixture is being studied at temperatures other than 20 to 25°C, the temperature dependence of the pure component densities are determined using a reduced equation of state developed by Watson.⁹⁶

The Watson correlations read:

$$\rho = \frac{\rho_1}{\omega_1} \omega$$

where ω is called the expansion factor and the subscript 1 refers to a reference state with known density and expansion factor. The value of ω is determined as a function of reduced temperature and reduced pressure. The value of ρ_1 and ω_1 for temperatures of 20 and 25°C are in the data base. This method generates good results for conditions of reduced temperature ≤ 0.65 and pressure < 10 bar.

The Yen-Woods method uses the principle of corresponding states. In fact, this method was developed in order to transform the graphical and tabular corresponding states methods into programmable analytical expressions. For mixtures, the liquid density is determined using pseudocritical properties. In the following equations, ρ_r is the reduced density, T_r is the

reduced temperature, Z_c is the pseudocritical compressibility, and ΔP_r is the increase in reduced pressure, the subscript c denotes a pseudocritical property, and the subscript s denotes a saturated state.

For saturated liquids, the density determined by Yen-Woods is calculated using:

$$\rho_{rs} = \frac{\rho_s}{\rho_c} = 1 + A(1-T_r)^{1/3} + B(1-T_r)^{2/3} + D(1-T_r)^{4/3}$$

$$\begin{aligned} A &= 17.4425 - 214.578 Z_c + 989.625 Z_c^2 - 1522.06 Z_c^3 \\ &\quad \text{if } Z_c \leq 0.26 \\ B &= -3.28257 + 13.6377 Z_c + 107.4844 Z_c^2 - 384.211 Z_c^3 \\ &\quad \text{if } Z_c > 0.26 \\ C &= 60.2091 - 402.063 Z_c + 501.0 Z_c^2 + 641.0 Z_c^3 \\ &\quad \text{if } Z_c > 0.26 \\ D &= 0.93 - B. \end{aligned}$$

This method is valid when the reduced temperature, T_r , is between 0.3 and 1, and the reduced pressure is less than 30. An average deviation of 2.8 percent of experimental data is reported from tests made on 15 binary, 1 ternary, and 1 quaternary mixture at saturation state."

At low temperatures and pressures, the volume averages for liquid density give accurate results. At higher temperatures, the Yen-Woods method is reliable as long as the reduced pressure is below 30. The Peng-Robinson, Lee-Kesler-Plöcker, and Benedict-Webb-Rubin give good results for hydrocarbon mixtures near the saturation line. If the mixture is not near the vapor-liquid saturation line, the Benedict-Webb-Rubin equation will not give good results. This equation of state is also only reliable for hydrocarbon mixtures.

6.1.2.11.10 Viscosity of the Liquid

The viscosities of pure component liquids at 20 and 100°C and at atmospheric pressure are provided by AFP for mixture calculations. The

temperature dependence of viscosity is determined using these two viscosity data points and the Andrade correlation." Viscosities of liquids decrease with increasing temperature either under isobaric conditions or as saturated liquids.

The Andrade equation reads:

$$\ln \eta_i = A+B/T.$$

In this equation, η_i is the viscosity of the liquid, T is temperature, and A and B are constants which are determined by the viscosities at 20 and 100°C.

The viscosity of a liquid mixture is determined by taking the molar average of the logarithms of the pure component viscosities. This is not a very accurate method. If the mixture consists of chemically similar substances, the error of this calculation should not exceed 15 percent. For mixtures containing polar compounds, DETHERM is usually able to determine the liquid viscosity at least to the correct order of magnitude.

6.1.2.11.11 Viscosity of the Gas

The viscosity of pure gaseous components at 25 and 200°C and at atmospheric pressure are provided by AFP for mixture calculations. The Sutherland equation is used along with these two viscosity-temperature data points in order to determine the viscosity of pure component gases at other temperatures. The Sutherland viscosity equation is:"

$$\frac{M}{M_o} = \frac{(T)^{1/2}}{T_o} \frac{1+C/T_o}{1+C/T}$$

where T_o is the temperature of known viscosity M_o , and T is the temperature at which the viscosity M is being determined. C is a constant that can be determined by substituting the known viscosities at the temperature of 25 and 200°C. Once C has been determined, the viscosity of the pure fluid can be obtained at any temperature.

The viscosities of gaseous mixture are determined in three different ways. The molar average of the pure components viscosities and the Wilke" equation generate viscosities of gases without taking into account the effect of pressure on viscosity.

The Wilke method for estimating the viscosity of a gas at low pressure is a kinetic theory approach which neglects second order effects. This equation reads:

$$\eta_m = \frac{\sum_i y_i \eta_i}{\sum_j y_j \phi_{ij}}$$

where,

$$\phi_{ij} = \frac{[1 + (\frac{\eta_i}{\eta_j})^{1/2} (\frac{M_j}{M_i})^{1/4}]^2}{[8(1 + \frac{M_i}{M_j})]^{1/2}}$$

η_m = viscosity of the mixture
 y_i = pure component viscosity of component i
 y_i = mole fractions of component i
 ϕ_{ij} = $\phi_{ij} \eta_j M_i / \eta_i M_j$
 M_i = molecular weight of component i.

The viscosity of a gas is a strong function of pressure near the critical point and at reduced temperatures of about 1 to 2 at high pressures. The pressure correction of Dean and Stiel¹⁰⁰ is used to adjust the Wilke determined viscosity to reflect the effect of pressure on the viscosity of a gas. The Dean-Stiel method calculates the viscosity of nonpolar gas mixtures at moderate and elevated pressures. With the use of pure component

viscosities and pseudocritical constants, this method has been extended to mixtures. The viscosity of a real gas mixture at moderate pressures as given by Dean-Stiel is:

$$T_r < 1.5 \quad = \quad \mu^* \xi = 34.0 \times 10^{-5} T_r^{0.9}$$

$$T_r < 1.5 \quad = \quad \mu^* \xi = 166.8 \times 10^{-5} [0.1338 T_r - 0.0932]^{0.9}$$

$$\xi = \frac{T_{cm}^{1/6}}{(\sum x_i M_i)^{1/2} P_{cm}^{2/3}}$$

where,

μ^*	=	viscosity of the gas, moderate pressure
T_r	=	reduced temperature (T/T_c)
ξ	=	viscosity parameter
T_{cm}	=	pseudocritical temperature of a mixture
x_i	=	mole fraction of component i
M_i	=	molecular weight of component i
P_{cm}	=	pseudocritical pressure of the mixture.

For real gases at high pressure, Dean and Stiel proposed the following equation:

$$(\mu - \mu^*) \xi = 10.8 \times 10^{-5} (e^{1.439 \rho_r} - e^{-1.11 \rho_r})^{1.858}$$

where,

μ	=	viscosity of the real gas at high pressure
ρ_r	=	reduced density = ρ/ρ_c .

For the 80 experimental points presented by Dean and Stiel, the above equation reproduced the experimental points with an average deviation of 1.05 percent.

The Wilke method has been extensively tested. In most cases only non-polar mixtures were compared, and very good results were obtained. The results were less satisfactory if one of the components in the system was hydrogen. The Wilke's method will predict viscosities larger than experimental viscosities for an N_2-H_2 system, but for a system containing N_2-NH_3 , it will underestimate the viscosity. The results tend to become less accurate in cases where $M_1 \gg M_2$ and $N_1 \gg N_2$. At low and moderate pressures, the values computed by the Wilke method and the values computed by the Wilke-Dean and Stiel are within 3 to 4 percent of each other. These calculated viscosities will not be the same at high pressures, especially if nonpolar compounds are present.

6.1.2.11.12 Thermal Conductivity of the Liquid

AFP provides thermal conductivity of pure liquid components at atmospheric pressure and at 0 and 50°C for mixture calculations. The temperature dependence of the pure component thermal conductivity is assumed to be linear. The thermal conductivity of liquid mixtures is computed by taking the weight average of the pure component data. The effect of pressure on thermal conductivity is not taken into account. This assumption will give accurate thermal conductivities as long as the pressure of the system is below 50 to 60 bar.

6.1.2.11.13 Thermal Conductivity of the Gas

AFP provides thermal conductivities of gaseous pure compounds at atmospheric pressure and at 25 and 200°C. The thermal conductivity at other temperatures are determined using the Sutherland's equation.⁹⁸ Sutherland developed the following relationship for calculating thermal conductivity k , from the heat capacities at constant pressure C_p and the viscosity of gases.

$$\frac{k}{k_0} = \frac{C_p \mu}{C_{p0} \mu_0} = \frac{C_p}{C_{p0}} \left(\frac{T}{T_0} \right)^{1/2} \left(\frac{1+C/T_0}{1+C/T} \right)$$

In this equation, the 0 subscript indicates known values of thermal conductivity, heat capacity, and viscosity at a given temperature. Given two known thermal conductivities at two unique temperatures, the constant C can be determined. Once this constant is known, the value of thermal conductivity can be determined at any temperature.

The thermal conductivity of gaseous mixtures is computed by three methods. The first two methods determine the thermal conductivity neglecting the effect of pressure on this property. The simplest way of calculating the thermal conductivity is to take the molar average of the thermal conductivities of the pure components.

$$k_m = \sum_i x_i k_i$$

In this equation, k_m is the thermal conductivity of the mixture, k_i is the thermal conductivity of the component i , and x_i is the mole fraction of i in the mixture.

The Lindsay-Bromley equation for thermal conductivity of a mixture is:¹⁰¹

$$k_m = \sum_i \frac{k_i}{\frac{1}{x_i} \sum_j A_{ij} x_j}$$

when $A_{ij} = A_{ji}$

$$A_{12} = \frac{1}{4} \left[1 + \left(\frac{\mu_1}{\mu_2} \left(\frac{M_2}{M_1} \right)^{3/4} \frac{(1 + \frac{S_1}{T})}{(1 + \frac{S_2}{T})} \right)^{1/2} \right]^2 \frac{(1 + \frac{S_{12}}{T})}{(1 + \frac{S_1}{T})}$$

S	=	1.5 T _b
k _m	=	thermal conductivity of the mixture
k _i	=	thermal conductivity of component i
x _i	=	mole fraction of component i in the mixture
A ₁₂	=	interaction constant (dimensionless)
M ₁ /M ₂	=	viscosity ratio between component 1 and 2
M ₁	=	molecular weight of component 1
S	=	Sutherland constant
T	=	absolute temperature
T _b	=	boiling point at 1 atmospheric.

The Sutherland constant, S_{12} , is dependent on the type of molecule in the mixture. When one of the components is strongly polar $S_{12} = 0.733 (S_1 S_2)^{1/2}$ otherwise $S_{12} = S_1 S_2)^{1/2}$.

The effects of pressure on thermal conductivity is taken into account by the third estimation method. The third method for determining thermal conductivity adjusts the thermal conductivity determined by Lindsay-Bromley with the pressure correction term of Stiel and Thodos.¹⁰² Stiel and Thodos assumed that the excess thermal conductivity ($\lambda - \lambda^0$) is dependent on T_c , P_c , V_c , M , and ρ . Using dimensional analysis they obtained a correlation between $\lambda - \lambda^0$, Z_c , T_1 and ρ . From data on 20 nonpolar substances, which included inert gases, diatomic gases, CO₂, and hydrocarbons, the following analytical expressions were developed.

$$(\lambda - \lambda^0) \Gamma Z_c^{-5} = 1.22 \times 10^{-2} [\exp (0.535 \rho_r) - 1] \quad \rho_r < 0.5$$

$$(\lambda - \lambda^0) \Gamma Z_c^{-5} = 1.14 \times 10^{-2} [\exp (0.67 \rho_r) - 1.069] \quad \rho_r < 2.0$$

$$(\lambda - \lambda^0) \Gamma Z_c^{-5} = 2.60 \times 10^{-3} [\exp (1.155 \rho_r) + 2.016] \quad \rho_r < 2.8$$

where,

$(\lambda - \lambda^0)$	=	excess thermal conductivity
λ^0	=	low pressure thermal conductivity at the same temperature.
Z_c	=	critical compressibility = $P_c V_c / RT$
ρ	=	reduced density $\rho / \rho_c = V_c / V$
Γ	=	$210 (T_c M^2 / P_c^4)^{1/6} . K^{-1}$
	=	reduced inverse thermal conductivity
M	=	molecular weight.

In order to apply the Stiel and Thodos method to mixtures, mixing and combining rules must be available that would determine the critical properties of the mixture, T_{cm} , P_{cm} , V_{cm} , and M_m .

6.1.2.11.14 Diffusion of Coefficients of the Gas

The diffusion coefficients are only calculated and displayed in the output if the FULL or TEST output format is specified.

The diffusion coefficients for a binary mixture of A and B are defined:

$$J_A = -C D_{AB} \quad dx_A/dz$$

$$J_B = -C D_{BA} \quad dx_B/dz$$

where,

C	=	total molar concentration
z	=	direction of diffusion
J_A	=	net mole flow of A across the boundaries of a hypothetical plane
x_A	=	mole fraction of A
D_{AB}	=	diffusion coefficient.

The diffusion coefficient, therefore, represents the proportionality between the flux of A relative to a plane of no net molar flow and the gradient C (dx_A/dz).

The diffusion coefficient of the pure components of a mixture are calculated using two methods, the Hirschfelder-Bird-Spotz¹⁰³ and the Fuller-Schettler-Giddings.¹⁰⁴

Hirschfelder, Bird, and Spotz evaluated a set of integrals, $\Omega_n^1(T)$ developed by Chapman and Cowling.¹⁰⁵ This set of integrals relates the coefficients of viscosity, diffusion, thermal diffusion, and heat conductivity. The integrals involve the law of force between pairs of spherical nonpolar molecules. Evaluation of these integrals lead to predictions of temperature dependent transport properties that are more accurate than values provided by the Sutherland approximation. The data provided by the solution of the integral set generate a corresponding states relationship which can be applied to extremely hot or cold mixtures. For details concerning the solution of the integrals and the calculation of the diffusion coefficient from this data, see Hirschfelder-Bird-Spotz.¹⁰³

Fuller, Schettler, and Giddings developed the following equation for estimating the diffusion coefficient.

$$D_{AB} = \frac{0.00143 T^{1.75}}{P M_{AB}^{1/2} [(\sum v)_A^{1/3} + (\sum v)_B^{1/3}]^2}$$

where,

D_{AB} = binary diffusion coefficient, cm^2/s
 T = temperature K
 M_{AB} = $2((1/M_A) + (1/M_B))^{-1}$
 $\sum v$ = sum of atomic diffusion volumes
 P = pressure, bar.

The atomic parameters are determined by a regression analysis of experimental data. When using this method an average absolute error of about 4 percent can be expected. AFP does not estimate atomic diffusion volumes, therefore, this method does not function here.

The Hirschfelder-Bird-Spotz theoretically based model is applicable for pressures less than 20 atm. The Fuller-Schettler-Giddings method is purely empirical, for nonpolar mixtures at moderate temperatures the method will introduce errors between 5 and 10 percent.

6.1.2.11.15 Surface Tension

The surface tensions of pure components against air at 15.56 and 25°C are estimated by AFP and then provided to DETHERM. The surface tensions of other pure components at other temperatures are calculated using the values provided and the Mitra and Sanyal method.¹⁰⁶ Mitra and Sanyal developed the following relationship between surface tension and the viscosity of liquids.

$$\log(S) = A - \frac{B}{T_c - T}$$

In this expression, S is the surface tension of the liquid, T_c is the critical temperature, T is the temperature of the liquid, and A and B are constants. In order to find the surface tension at a given temperature T , the known surface tensions at 15.56 and 25°C are substituted into the above equation. This will give two independent equations with two unknowns (A , B). Once constants A and B have been determined, the surface tension of a pure liquid can be calculated at any temperature.

The surface tension of mixtures is computed by using the Macleod-Sugden^{107,108} method and the Sugden¹⁰⁹ surface tension of pure components method.

In 1923, Macleod suggested the following relation between surface tension (σ) and liquid and vapor densities (ρ_L and ρ_v , respectively).¹⁰⁸

$$\sigma^{1/4} = [P] (\rho_L - \rho_v)$$

Sugden^{109,110} defined the temperature independent parameter $[P]$ as the parachor and suggested that this parameter could be determined from the structure of a molecule. Since surface tension is proportional to $[P]^4$ in this correlation, this estimation procedure is very sensitive to the parachor values used.

The Sugden method calculates a parachor-like quantity from the surface tension of the pure components. This quantity is then used to determine the surface tension of the mixture.

Both methods lead to similar results. If the mixture contains non-associating components, the error is close to 0.5 percent, and if the components in the mixture are associating ones then the error may increase to 3.5 percent. The accuracy of the calculated surface tension depends on the parachor estimated by AFP or the pure component surface tensions.

6.1.2.11.16 Entropy

Entropy, S , is a state function. In a system in which there are flows of both heat (Q) and work (W and Pdv/dt) across the system boundaries, the heat flow, but not the work flow, causes a change in the entropy of the system. The rate of entropy change is Q/T , where T is the absolute temperature of the system at the point of the heat flow. The entropy of the

system may also change as a result of mass flows across the boundary. According to the second law of thermodynamics the entropy production of a process must always be greater than or equal to zero.¹¹¹

Since entropy is a state function, it can be calculated using departure functions. The entropy of an ideal gas is determined from the gas coefficients described under Caloric Properties of the Gas and Liquid (see Section 6.1.2.11.3). Entropy of real gases are determined by adding the entropy of an ideal gas to the entropy departure function. The departure functions are defined using an equation of state. The entropy departure function is obtained from the Lydersen, the Lee-Kesler-Plöcker, and the Peng-Robinson equation of state. The use of these equations to determine departure functions has already been discussed.

At atmospheric pressures, the entropy determined by the gas coefficients can be used. At higher pressures, mixtures of hydrocarbons are very accurately described by the Lee-Kesler-Plöcker or the Peng-Robinson equations of state. These equations of state usually estimate the entropy within a few J/(g.K).

The entropy of a liquid is determined using the same methods as the entropy of a gas. However, the heat of vaporization is added to the entropy determined from the sum of the gas coefficients and the departure function.

6.1.2.11.17 Heat of Vaporization/Condensation

The heat of vaporization of a mixture is determined by taking a molar average of the heats of vaporization of the pure components of the mixture.

$$\Delta H_{mix}^{vap} = \sum_i x_i \Delta H_i^{vap}$$

where,

ΔH_{mix}^{vap} = heat of vaporization of the mixture

x_i = mole fraction of species i

ΔH_i^{vap} = heat of vaporization of pure i.

The sum is taken over all the components in the mixture. The heat of vaporization of the pure components is determined at saturation pressure.

6.1.2.11.18 Compressibility Factor

The compressibility factor (Z) is defined:

$$Z = PV/RT.$$

Units for each of the variables, pressure, P, volume per mole $\underline{V}$, temperature, T, and the gas constant, R, should be chosen such that the compressibility factor is a unitless quantity.

The compressibility factor can be determined once the state of the system has been defined. For example, if by specifying the temperature, pressure, and composition of a mixture system satisfies the degrees of freedom of the system, then the volume per mole of mixture can be determined through an equation of state. Once the volume per mole of a mixture has been found, the compressibility factor can be determined. The compressibility factor is most often correlated as a function of reduced pressure and reduced temperature.

DETERM determines the compressibility factor using the Peng-Robinson, Lee-Kesler-Plöcker, Benedict-Webb-Rubin, and the Beattie-Bridgeman equations of state.

6.1.2.11.19 Pseudocritical Values

The method of corresponding states suggests that reduced properties of all fluids are essentially the same if they are compared at equal reduced temperatures and pressures. The reduced temperature, T_r , and pressure, P_r , are obtained by scaling the systems temperature and pressure. The scaling factors used when applying the corresponding states method to pure gases and liquids are the critical properties of the fluid. For mixtures, the

corresponding states correlations are applied using pseudocritical properties as scaling factors. The pseudocritical properties are not the same as the true critical properties, and they do not relate to critical phenomena in mixtures. However, at the pseudocritical point the following equations are satisfied.

$$\left(\frac{\partial p}{\partial V}\right)_{T_c} = 0 \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_{T_c} = 0$$

The corresponding states method is applied to mixtures with the assumption that PVT behavior of the mixture will correspond to the PVT behavior of the pure component when the reduced properties are determined using the pseudocritical point.

The pseudocritical temperature, volume, and compressibility factor are determined by taking the mole fraction average of the pure component properties. This method is referred to as Kay's rule¹¹².

$$T_{cm} = \sum_j y_j T_{cj}$$

This equation applies to a mixture of n components, where y_j is the mole fraction of the j component, T_{cj} is the critical temperature of the j component, and T_{cm} is the pseudocritical temperature of the mixture. The pseudocritical properties determined by Kay's method are accurate to within 20 percent for all components.

$$0.5 < T_{cj}/T_{cm} < 2.0$$

The pseudocritical pressure is determined using the modified Prausnitz-Gunn equation¹¹³.

$$P_{cm} = \frac{R \left(\sum_j y_j Z_{cj} \right)}{\sum_j y_j V_{cj}}$$

In this equation, R is the gas constant, y_i is the mole fraction (vapor or liquid) of component j , and $Z_{c,j}$, $T_{c,j}$, $V_{c,j}$ are the critical compressibility, temperature, and volume (per mole) of species j .

Note that these methods used for determining pseudocritical properties do not contain any interaction parameters, and therefore, cannot truly reflect the properties of a mixture. However, good results are usually obtained when the pseudocritical quantities calculated by these methods are used in corresponding states calculations to determine mixture properties.

6.1.2.11.20 Adiabatic Exponent

The adiabatic exponent is the ratio of the heat capacity at constant pressure, C_p , to the heat capacity at constant volume, C_v .

For ideal gases, C_v can be expressed, $C_v = C_p - R$, and in this case the adiabatic exponent is calculated by:

$$\gamma = \frac{C_p}{C_v} = \frac{C_p}{C_p - R}$$

where R is the gas constant. The adiabatic exponent is a dimensionless quantity.

The adiabatic exponent, γ , derives its name from the following expression:

$$PV^\gamma = \text{constant}.$$

This expression is the relationship between pressure and volume at any time during an adiabatic process involving an ideal gas. The accuracy of the adiabatic exponent is directly related to the accuracy of the heat capacities and the assumption of ideal gases. As the gases become complex the contribution to the specific heats of gases from the rotational and vibrational motions of the molecule become more significant, and the

assumption that internal energy is dependent only on temperature becomes less valid.

6.1.2.11.21 Calorific Value

The calorific value of a mixture is determined by taking the weight average of the standard heat of combustion of each component in the mixture. The standard heat of combustion is the difference in enthalpy of a compound and its combustion products at 298K and 1 atm. The combustion products are considered to be in their gaseous state, and the typical products of a hydrocarbon combustion are CO_2 and H_2O . When studying large organic compounds, the heat of formation is sometimes difficult to obtain, in this case the standard heat of combustion can be used to determine the standard heat of reaction.

The calorific value of a mixture is determined by taking the weight average of the standard heat of combustion of each component in the mixture. The standard heats of combustion are estimated by AFP.

6.2 Quality Assessment of Integrated Product

6.2.1 Objective

To test the ability of AFP to estimate the properties of hydrocarbon mixtures. The emphasis of mixture testing was centered around physical properties, vapor-liquid equilibrium (VLE) behavior, and energy content since these are important properties of aircraft and missile fuels.

6.2.2 Strategy

The AFP program estimates mixture properties by first obtaining properties of the individual components of the mixture. These properties are obtained from the data base or through estimation based on the molecular structure of each component. The default priority scheme seeks the individual component data from the data base first and then resorts to estimation methods if the data was not found in the data base. The program can be forced to obtain the individual component data from strictly database lookups or estimation methods.

Three sets of mixture properties were tested:

1. A comparison between estimated and experimental vapor-liquid equilibrium behavior of three binary mixtures.
 - a. Hexane + P-xylene
 - b. Benzene + Cyclohexane
 - c. Naphthalene + Dodecane
2. A comparison between estimated and experimental vapor-liquid equilibrium behavior of two ternary mixtures.
 - a. Toluene + n-Octane + Ethylbenzene
 - b. Hexane + Benzene + P-xylene
3. An estimation of physical properties for two fuels
 - a. JP-8 surrogate fuel
 - b. RJ-7 surrogate fuel.

The vapor-liquid equilibrium calculations were carried out using both forced AFP database lookups and forced AFP estimation methods. Each fuel set is computed using both forced AFP estimations and the default priority scheme.

6.2.3 Results

The vapor-liquid equilibrium calculations use the Lee-Kesler-Plöcker equation of state. This equation of state uses the T_c , P_c , V_c , and the acentric factor of the individual components in order to perform mixture calculations. The binary interaction parameter, K_{ij} , is obtained through a correlation involving T_c and V_c . This correlation causes some error in almost all of the vapor-liquid equilibrium calculations performed by the AFP. The accuracy of vapor-liquid equilibrium calculations depends then, on the accuracy of the correlation done to obtain the binary interaction parameter.

When doing forced estimates of the individual properties, the best available estimate is used for T_b , T_c , P_c , and V_c . These are usually group contribution methods. If the Joback method fails to provide an accurate normal boiling point, the error becomes compounded in the binary interaction parameter. In cases such as this, the estimation methods produce a grossly inaccurate description of the vapor-liquid equilibrium behavior.

The specific results of this mixture testing are presented in Test Results: AFP Hydrocarbon Mixture Property Calculations¹⁸. The test report

was submitted October 31, 1992, and revised January 14, 1993. Consult this report to obtain the details concerning the testing of mixtures.

6.3 Documentation

6.3.1 Objective

A manual will be written, documenting how to use the program, its data structure, and predictive methods.

6.3.2 Work Completed

Complete documentation of the AFP program is provided in the user manual⁹. This manual provides detailed instruction on how to run the AFP program from the initial execution step to the exiting of the program. The user's manual was designed to be a reference manual, that is, details concerning any of the AFP menu options can easily be located in the manual, but this manual was not meant to be read cover to cover. Several example calculations, which detail the menu selections and the inputs needed to obtain proper output, are also included in the manual. These examples are provided to show how AFP can be applied to obtain the property values of pure compounds and mixtures.

6.4 Delivery and Training

6.4.1 Objective

Two personnel will travel to Dayton for installation of the program, and training of users. Two trips will be required. The first will be to execute the actual installation. This will require one skilled in the VAX art, and one skilled in the operation and testing of the program. The second trip will be for training.

6.4.2 Work Completed

The AFP system has been provided to the Wright Laboratories for its exclusive use on a VAX computer.

Several training sessions have been carried out over the life of the project.

7.0 SOFTWARE DESIGN

7.1 Approach

The Advanced Fuel Properties System is based on a user friendly menu driven concept. Additionally, the software has the capability to have available on-line help to explain the operation of each menu. The system was designed for ease of use, expendability, modification, and incorporation into the Phase II and III software. The concept was to construct modular software routines that would do a minimal number of tasks, with the target being one task for each routine. This approach was successful and is one of the things that makes the AFP software system easy to expand, modify, and incorporate into the latter phases of the project.

Since it was evident in the early stages of the project that several methods would be necessary to obtain a desired property, a method that would afford the necessary flexibility and expandability was needed. This concept developed into the priority scheme approach. The basis for the priority scheme is a driver routine (a FORTRAN subroutine) for each property. This routine will call each of the different methods available to obtain a good property value for each compound. The system is diagrammed in Figure 7.1-1, using as an example the request to obtain the critical temperature (method name TC) for 10 compounds. This is accomplished by having a file on disk (named DEFAULTS.PRI) that is accessed and contains the order in which each different method should be called. This order depends on the accuracy of the property values provided by each method. An example of part of the DEFAULTS.PRI file is shown in Figure 7.1-2.

The fields in the DEFAULTS.PRI file are: Record number, subroutine name, property number, whether the property is temperature dependent (T or F), whether the property is pressure dependent (T or F), number of estimation methods, and the method numbers, in order of decreasing priority.

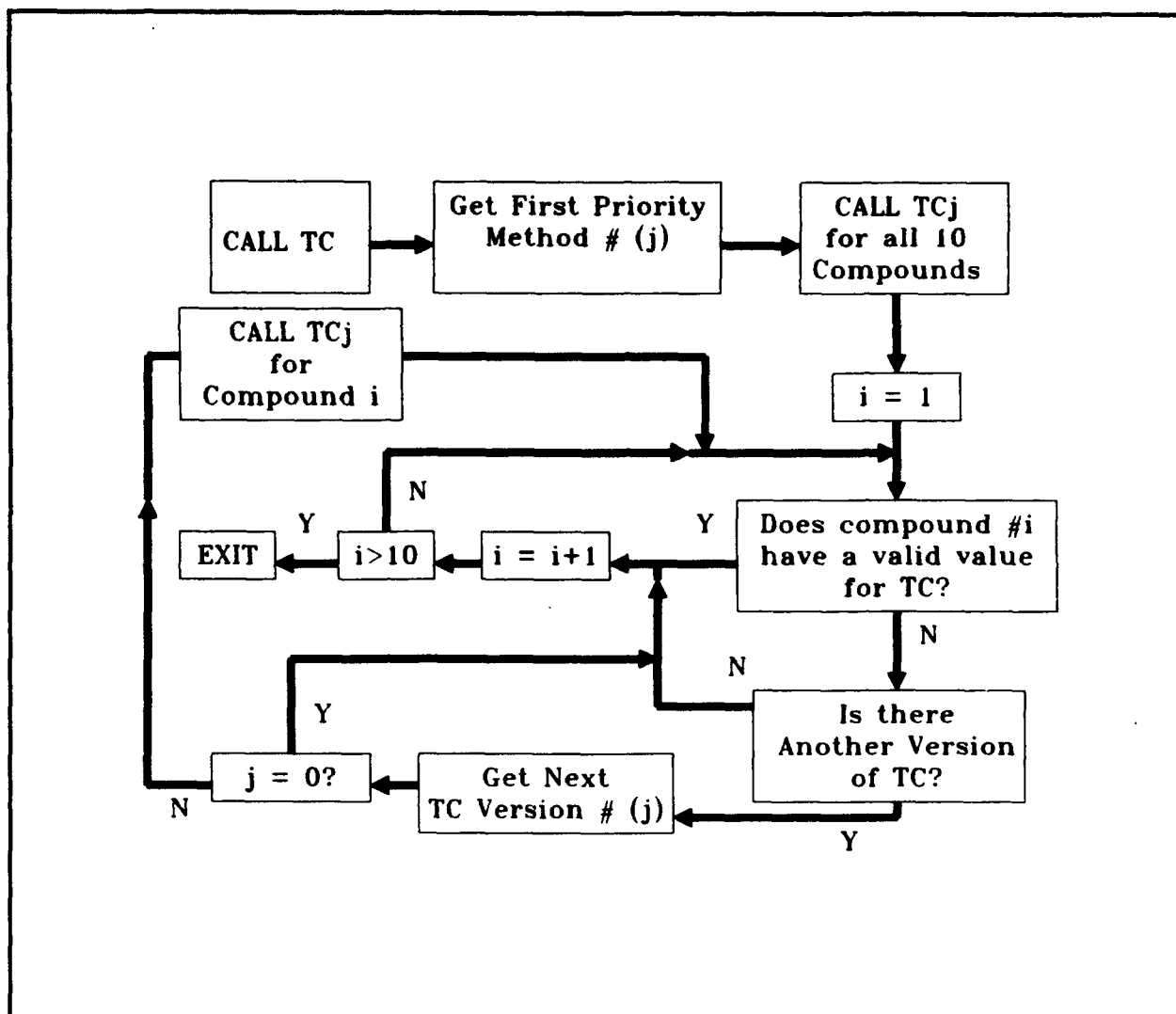


Figure 7.1-1
Diagram of Priority Scheme for an Example of Obtaining the Critical Temperature (Method Name TC) for 10 Compounds.

6	TC	7	F	F	6	1	2	6	5	4	3
7	PC	8	F	F	5	1	2	5	4	3	
10	ACENF	11	F	F	4	1	2	3	4		
13	TMPSP	18	F	F	2	1	2				
33	FUGAC	56	T	T	5	3	6	5	2	4	
34	GF25I	57	F	F	3	1	2	3			
35	CMPR	58	T	T	6	3	7	6	2	5	4
40	NUVAP	64	T	F	3	4	3	2			

Figure 7.1-2
Selections from the DEFAULTS.PRI File that is Used by
the Priority Scheme in the AFP System (Details in the Text)

The priority scheme also had to be flexible so that if the user wanted to use specific methods, the default priority scheme could be overridden. This is accomplished by allowing the user to select the priority order for any property. After modifying the priority scheme, the user can save the customized priority scheme in a user file. This saved priority scheme file can later be reloaded into the AFP system (overriding the default priority scheme) so that a user can use the same customized priority scheme at different times with minimal effort.

The priority scheme was also designed with sufficient flexibility so that an expert system could be added. The expert system would be able to modify the priority scheme during program operation. Although this is not implemented at this time, the extension would not be difficult because of the design of the current AFP priority scheme.

To keep control of the hundreds of software routines that were necessary to accomplish this modular concept, a systematic subroutine naming convention was implemented. Two naming conventions were used in the project. The first

was used to name routines that generated values for properties and the second was for utility routines. The convention used for the former was to use up to five characters that described the property; the first character(s) related to the type of property (T for temperature, H for enthalpy, S for entropy, NU for viscosity, etc.), and the remainder of the characters to specify the exact property. For example, TNBP would be the normal boiling point; T for temperature and NBP for normal boiling point and HF25I would be enthalpy (H) of formation (F) at 298.15K (25 for 25°C) for an ideal gas (I). This naming scheme is how the priority routines are named. The names of the various routines that obtain the property values via different methods are named the same except for a trailing character. Specifically, a 1 is added to any routine that is used to look up a value from the data base, 2 through 9 and A through Y are available for any alternate methods by which the property can be obtained. Trailing zeros and Z's are reserved for special usage.

The naming convention for utility routines is much simpler in that each the names of the routines are chosen to be descriptive of its function. This is adhered to as much as is allowable within the FORTRAN77 standard of six character names.

In addition to a systematic routine naming convention, every utility routine and base property determination routine is assigned a unique method number. The base method number is modified for the various property determination routines by adding 10,000 times the value of the trailing to the base method number. For example, the method number for CPID (heat capacity at constant pressure for an ideal gas) is 81; therefore, the method number for CPID3 would be $3 \times 10000 + 81$ or 30081. This number is used in a number of ways, but the most important usage is in the reporting of subroutine errors. A subroutine error is when the subroutine is requested to do an illegal function, it cannot obtain a value for what has been requested, or any other type of error that may occur. As the result of any error condition, the routine will pass back an error code. This error code has embedded within its method number and a code for the error condition so that the calling routine can handle the condition properly. Additionally, if this error code is output for a requested value, one can determine what subroutine caused the error condition. The encoding scheme is to take the full method number multiplied by 1,000 and add the error code to obtain the resulting full error code. In addition, if the error condition is actually only a warning, the error code will be negated.

The final aspect of the approach taken was that the main program or its utility routines should be the only routines that interact with the user. The main program should also control selection of properties, compounds, units, and options.

7.2 Documentation and Subroutines

The subroutine that AFP calls in order to determine the properties of pure components, are documented in the user's manual.⁵⁹ This documentation is in the form of subroutine flow charts. The properties listed in the AFP property menu, which can be determined by more than one method, has been generated. These flow charts can be found in Appendix IV of the user's manual. Each flow chart details the sequence of subroutines that are called by the most general subroutine in order to obtain the value of a property. These flow charts were developed by mapping the call sequence of the most general subroutine until the program assigned the property a value.

7.3 FORTRAN77 Standard Compliance

The software has been written in general to the FORTRAN77 standard. Those places where this was not done are listed below, along with a brief explanation of the reasons and consequences for the action.

1. The use of INCLUDE statements is probably the largest deviation from the FORTRAN77 standard. This was done as a method for efficient code generation. The INCLUDE statement allows common code to be kept in a file and then included into the individual routines at compile time. This was done to keep items such as array size declarations in one place so that if they need to be changed during program development, the change need only be done to one file before recompilation with the changes.
2. The use of nonstandard subroutine and variable names was done only where it was necessary to accommodate the requirements of commercial software packages.
3. The use of VAX extensions to FORTRAN77 standards was also only done when required by commercial software packages being used by the AFP system.
4. A very few subroutines (approximately 6) which were created to form the interface between the mixture routines and the pure component routines contain a number of FORTRAN extensions which are generally acceptable to a wide variety of compilers. These

extensions include names of more than six characters, and lower case source. All of this code also contains many calls to the VAX-specific screen management utilities, so this code would have to be modified in any case to transport the AFP system to another platform.

5. The final nonconformity to FORTRAN77 was in the use of the READONLY parameter in OPEN statements. This was necessary because some of the data files that the AFP system needs are stored in an area that is read only to most of the users, and even though the files are only going to be read, the VAX requires that the files be opened with the READONLY qualifier.

7.4 Graphical Input/Output

The ability to input molecular structures using a graphical users interface was not incorporated into the AFP program. Compounds need to be input using SMILES strings or using the compound name. A graphical input method could be implemented if the state of the art methods become more economical.

Graphical output is an option of the AFP Output Format Selection Menu. Graphical output is available when a property is being tested at multiple temperatures or pressures. The user is also given a choice of how the graphical output should be displayed. AFP uses CGS graphics and can display these graphics to the following devices:¹⁴

1. VT240/VT241 (Terminal)
2. Tektronics (Terminal)
3. HP7550 Plotter, to logical PLOT
4. HP7550 Plotter, to file you name.

Plots of property values versus temperature, and property values versus pressure are available if the compound is being tested at multiple temperatures and pressures. The user also has option of displaying as many as 6 compounds on a plot.

Two example plots, generated from graphical output, are shown in Figures 7.4-1, 7.4-2. These plots show the pressure and temperature dependence of the density of toluene, decane, water and methanol when they are in the real gas state. Note that, the output units displayed as the graph axis can be set in the AFP Choose Units for Output menu option.

REAL GAS DENSITY (RHORG)
VS. TEMPERATURE PLOT
PRESSURE = 5.000 ATM

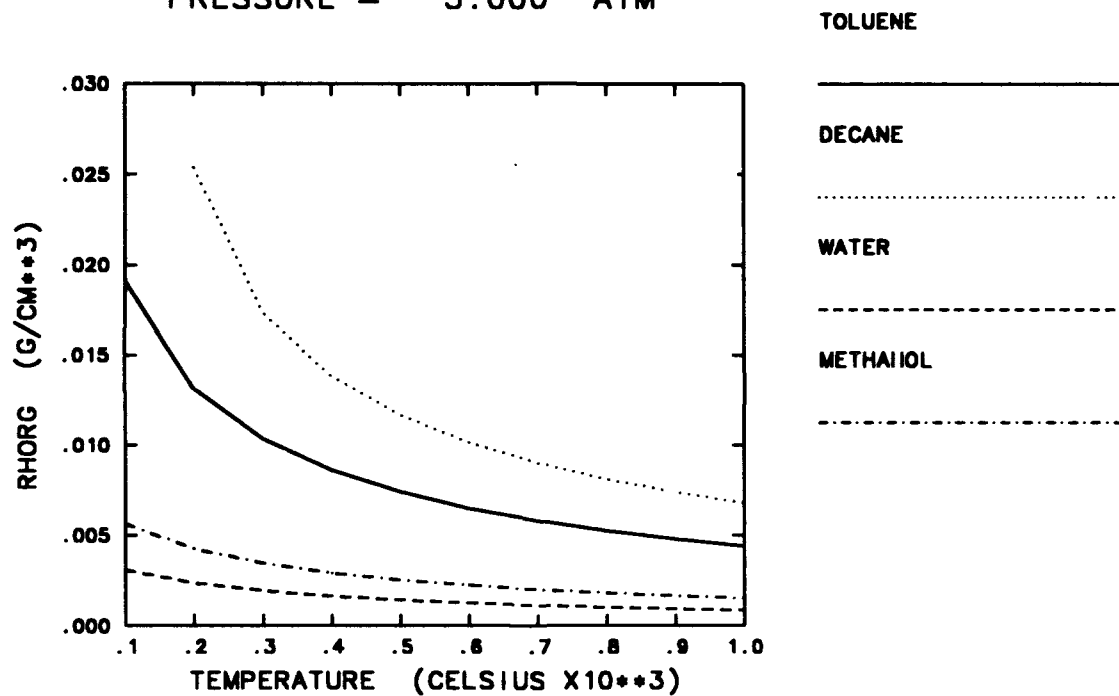


Figure 7.4-1

Example of the Graphical Output Generated by AFP. This plot shows the temperature dependence of the density of four real gases.

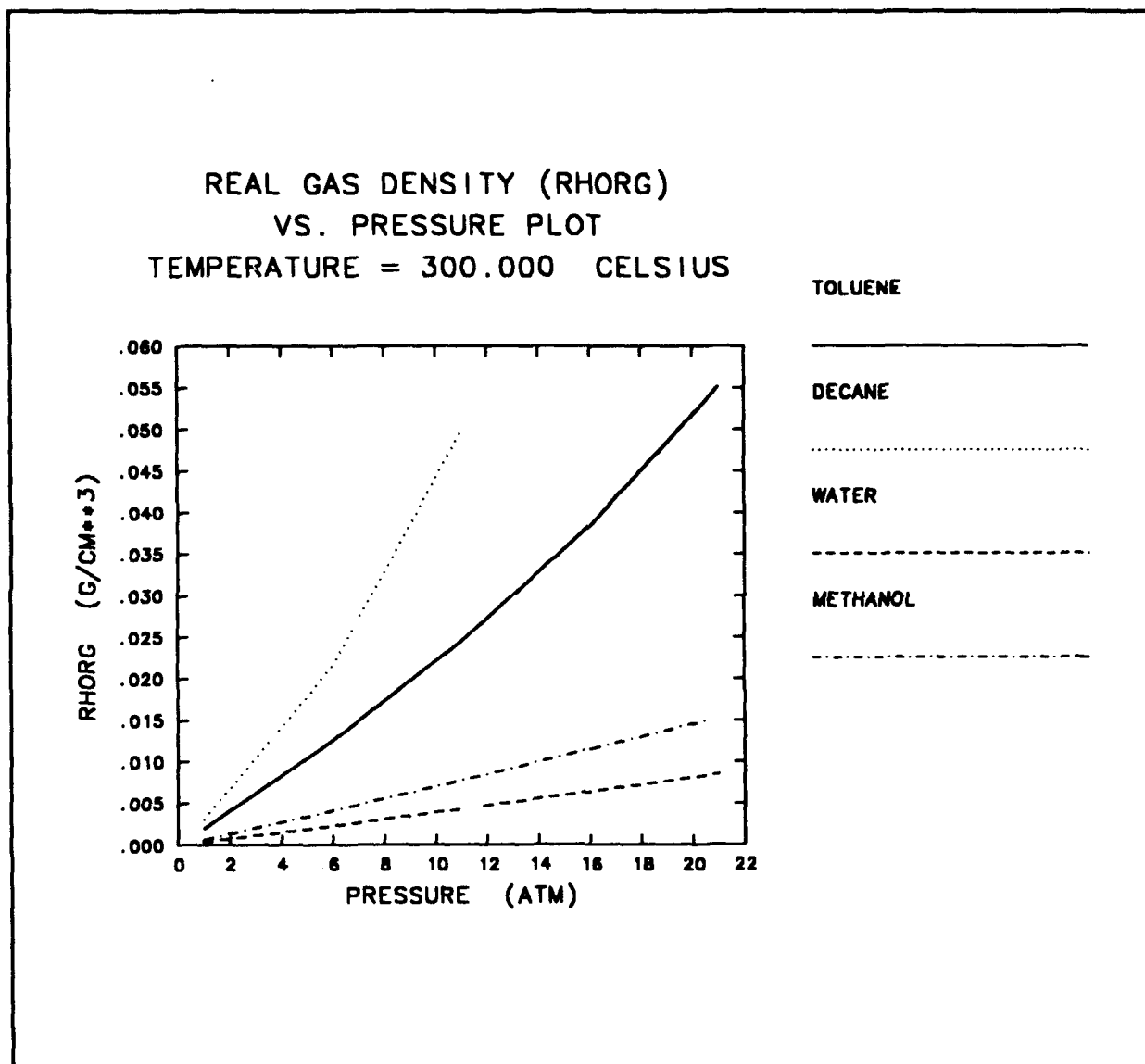


Figure 7.4-2 Example of the Output Generated by AFP. This example shows the pressure dependence of the density of four real gases.

8.0 CONCLUSIONS

8.1 Conclusions

The AFP system is a powerful tool for estimating the properties of a wide variety of pure organic compounds. It has robust algorithms for estimating many thermodynamic and physical properties of hydrocarbons, aldehydes, ketones, alcohols, acids, esters, and amines. Critical properties, boiling and vaporization behavior, density, enthalpy, entropy and free energy, flammability properties, heat capacity, thermal conductivity and viscosity are some of the properties estimated. The AFP system is also a powerful tool for estimating the properties of mixtures of compounds. Using estimates of the properties of pure compounds, and the estimates of the LKP interaction parameter, AFP can estimate the vapor-liquid equilibria of mixtures of hydrocarbons and similar compounds. Using the UNIFAC method, AFP can estimate the liquid-liquid equilibria for many systems, including polar compounds. In addition, the AFP system can estimate for mixtures most of the thermodynamic and physical properties available for pure compounds.

For most properties of pure compounds, the system has multiple means of estimating the properties, using a priority scheme. Several different models for estimating a given property are available, and chosen in order on the basis of accuracy. If the first priority method is unable to estimate the property, lower priority methods are used until an estimate is achieved, or the list is exhausted. This leads to a high probability of obtaining an estimate for a property, even for different kinds of compounds, including compounds containing heteroatoms. For mixtures, results from the different methods are presented simultaneously.

AFP encompasses a large part of the state-of-the-art in estimating properties of compounds. It uses equation of state methods, group contribution methods, graph theoretical methods, and activity coefficient methods for obtaining values. With the exception of the autoignition temperature, which was modeled explicitly for this project, the system is essentially a computerization of available data and available estimation methods. Because the code is expandable, modular and flexible, it is possible to add new methods for estimations at any time.

We recommend that the AFP system continue to be developed and improved. Particularly valuable would be the development of an improved boiling point routine. For lack of adequate theory, we were unable to develop any flammability properties for mixtures. Additional theoretical development, and subsequent addition to the code would be desirable. Additional software engineering would be very desirable to improve the appearance of the output of the mixture data.

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