REPORT ORO-5249-2

DEVELOPMENT OF WORKING FLUID THERMODYNAMIC PROPERTIES INFORMATION FOR GEOTHERMAL CYCLES - PHASE I

MASTER

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Annual Report

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ABSTRACT

During the first year (Phase I) of this research program, the following elements of research have been performed: (1) the collection and processing of data for pure components, (2) the evaluation of the generalized MBWR equation of state for halocarbon saturated thermodynamic properties, (3) the determination of pure component parameters for the MBWR equation for ten halocarbons, isobutane and, over a limited range, for ammonia and water (4) the investigation of modifications of the MBWR equation for improved prediction of properties of hydrogen bonding and polar fluids. With the results of the present work, MBWR parameters have now been determined for twenty-seven pure fluids, making the use of the MBWR equation in geothermal cycle calculations feasible for most candidate working fluids. From this research, it has been concluded that the MBWR equation can be used to correlate the thermodynamic properties of many of the hydrocarbons and halocarbons which are presently potential candidate working fluids for geothermal binary cycles. However, for ammonia and water, the MBWR equation cannot accurately describe behavior in the complete range of fluid states. In anticipation of future needs to describe complex fluids (such as flourinol-water mixtures) which have been proposed as working fluids, efforts have been initiated to develop an equation of state capable of describing the behavior of hydrogen bonding and polar as well as nonpolar fluids.

TABLE OF CONTENTS

		Page
1.	SUMMARY AND OVERVIEW	1
2.	LITERATURE SURVEY AND DATA COLLECTION	3
3.	THE MBWR EQUATION OF STATE	3
4.	USE OF THE MBWR EQUATION FOR HALOCARBONS	4
5.	MBWR CORRELATIONS FOR TEN HALOCARBONS	4
6.	MBWR CORRELATION FOR ISOBUTANE	5
7.	MBWR CORRELATION FOR WATER	6
8.	MBWR CORRELATION FOR AMMONIA	7
9.	DEVELOPMENT OF A NEW EQUATION OF STATE	7
10.	CONCLUSIONS AND PLANS	9
11.	REFERENCES	10

APPENDICES

A.	PROJECT WORK STATEMENT	A-1
B.	MODIFIED BWR EQUATION OF STATE PARAMETERS FOR TWENTY-SEVEN COMPOUNDS	B-1
C.	CORRELATION OF THE THERMODYNAMIC PROPERTIES OF TEN HALOCARBONS USING A MODIFIED BWR EQUATION OF STATE	C-1
D.	THERMODYNAMIC PROPERTIES OF ISOBUTANE USING A MODIFIED BWR EQUATION OF STATE	D-1
E.	REPORT DISTRIBUTION LIST	E-1

1. SUMMARY AND OVERVIEW

The objective of this research project is development of working fluid thermodynamic properties information for geothermal cycles. The work statement for the project is presented in Appendix A. The project was proposed as a three year research program to be carried out in three phases of one year each. Phase I has emphasized the correlation of pure fluid thermodynamic properties, Phase II will emphasize the correlation of mixture thermodynamic properties and Phase III will emphasize finalization of the correlation and development of user oriented documentation, including properties tables, diagrams and computer programs. The project was initiated under ERDA contract E-(40-1)-5249 on September 1, 1976. The results of the Phase I effort (September 1, 1976 through December 31, 1977) are presented in this report.

The project effort during the first year centered on providing correlations of the thermodynamic properties of halocarbons (halogenated hydrocarbons). The MBWR (Modified Benedict-Webb-Rubin) equation[1], previously had been used for correlations of hydrocarbon thermodynamic behavior, including mixture behavior, and had found widespread use in the geothermal industry. Early project efforts therefore were aimed at determining the feasibility of using the MBWR equation for halocarbons. This feasibility was proven quickly by use of the generalized MBWR equation[1], which required only the critical temperature, critical density and acentric factor for characterization of a fluid.

Efforts were then initiated to determine MBWR parameters for ten halocarbons. The ten halocarbons were selected on the basis of their potential as geothermal cycle working fluids and also to be assured that reasonable ranges of characterization parameters (such as critical temperature, critical density, acentric factor and dipole moment) were covered. The results were quite good, as noted in this report. At the outset of the project it was planned that water would be included in the correlation effort. The correlation of water properties was not to meet a need to develop a new equation of state for pure water, but because of the need for correlation of the thermodynamic properties of the working fluid - water mixtures which occur in direct contact geothermal cycles. Provided a single correlation framework could be found for describing the behavior of such diverse fluids as hydrocarbons, halocarbons and water, it was felt that ammonia and even alcohols also could be correlated in this framework. Ammonia was included in the Phase I effort and alcohols may be included in subsequent work. As is noted herein, the MBWR equation was found to be incapable of describing the thermodynamic behavior of ammonia and water for the full range of fluid states. Therefore, the MBWR correlations of the behavior of ammonia and water are for restricted ranges of state conditions. Promising results in initial efforts to develop a new equation of state which can describe the behavior of water and ammonia, as well as the hydrocarbons and halocarbons have been obtained. It is anticipated that the objectives of Phase II of the project effort, correlation of mixture thermodynamic

property behavior, will be met using a new equation of state correlation.

The various elements of the Phase I project are discussed in greater detail in the following sections and in the appendices of this report.

2. LITERATURE SURVEY AND DATA COLLECTION

Data have been collected for and processed into the data base for 35 pure components. This includes ten halocarbons, water, ammonia, eighteen hydrocarbons, and five miscellaneous fluids. Data for other fluids and updated property values for the above fluids will subsequently be processed into the data base. The data points already processed include information on density, vapor pressure and enthalpy departure.

3. THE MBWR EQUATION OF STATE

The MBWR (Modified Benedict-Webb-Rubin) equation of state utilized in this research is the following equation:

$$P = \rho RT + \left(B_o RT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4}\right)\rho^2 + \left(bRT - a - \frac{d}{T}\right)\rho^3 + \alpha\left(a + \frac{d}{T}\right)\rho^6 + \frac{c\rho^3}{T^2}(1 + \gamma\rho^2)\exp(-\gamma\rho^2) \quad (1)$$

In this equation, P is the absolute pressure, T is the absolute temperature, ρ is the molar density, R is the universal gas constant and B_o, A_o, C_o, D_o, E_o, b, a, d, α, c and γ are the eleven MBWR equation of state parameters. The relations for the derived properties, enthalpy, entropy and fugacity and computation

methodology have been presented previously.[1,2] Nevertheless, for the sake of completeness, the pertinent relations also are presented in Appendix B, along with MBWR parameters for the twenty-seven pure fluids studied.

4. USE OF THE MBWR EQUATION FOR HALOCARBONS

To test the feasibility of using the MBWR equation for halocarbons, the generalized MBWR equation was used to predict thermodynamic properties of eight pure component halocarbons. An optimum acentric factor was determined for each halocarbon for use in the generalized MBWR correlation previously used for light hydrocarbons.[1] The acentric factor was determined from vapor pressure data and then was applied to predict other saturated properties. The overall property average absolute percentage deviations were 1.6 percent for vapor pressures, 2.48 percent for liquid densities, and 2.38 percent for vapor specific volumes. For other thermodynamic properties, the average absolute deviations were 1.75 Btu/lb for liquid enthalpies, 1.21 Btu/lb for vapor enthalpies, 0.05 Btu/lb°R for liquid entropies, and 0.05 Btu/lb°R for vapor entropies. This work, which demonstrated that the MBWR equation can be used for halocarbons with small dipole moments, was discussed in detail[3] in the semiannual report on this project.

5. MBWR CORRELATIONS FOR TEN HALOCARBONS

With the feasibility of using the MBWR equation for correlation of halocarbon thermodynamic properties established by the application of the generalized MBWR equation, it was reasonably straightforward to determine MBWR parameters for selected

halocarbons. Density, enthalpy departure and vapor pressure values were utilized simultaneously for each fluid in multi-property regression analysis to determine the eleven MBWR parameters. The halocarbons selected are R-11, R-12, R-13, R-14, R-22, R-23, R-113, R-114, R-142B and R-152A. The average absolute deviations of predicted properties from values reported[4] by ASHRAE (American Society of Heating, Refrigeration and Aircondition ing Engineers) are 0.49 percent for density, 0.46 percent for vapor pressure and 1.02 joules/gram (0.44 Btu/lb) for enthalpy. The regions of state conditions covered by the reported values of density and enthalpy include the saturated liquid and saturated vapor and the superheated gas. A more detailed description of the MBWR correlations of the thermodynamic properties of the ten halocarbons is presented in Appendix C.

6. MBWR CORRELATION FOR ISOBUTANE

Because of the consideration and/or use of isobutane as the working fluid in a number of geothermal binary cycle projects, the MBWR parameters for isobutane (reported[1] in 1973) have been redetermined with more careful scrutiny of the experimental data. The impetus for this redetermination of isobutane MBWR parameters was provided by a study in early 1977 by the Brown University group under Professor Joseph Kestin's direction. In this study, isobutane property values calculated using various correlations were compared with experimental data. It was noted that in the high density gas phase pressures calculated using experimental densities were larger than desirable. With the help of the Brown University group, a new literature search for isobutane

experimental data was carried out, the data were scrutinized for sources of error and revised MBWR parameters were determined, with heavy weighting on the data considered most accurate. A summary of this research study is presented in Appendix D.

7. MBWR CORRELATION FOR WATER

The equation of state for water developed by Keenan, et.al.[5] is more than adequate for accurate computations of pure water properties. However, there is a need for the capability of computing the properties of the mixtures of working fluids and water which occur in direct contact heat exchange binary cycles. The development of a good mixture correlation require formulation of an equation of state expression capable of describing each constituent occuring in the mixtures of interest as well as formulation of the composition dependence of the equation. Because the MBWR equation can be used for predictions of mixture behavior and presently is being used for computation of the properties of a number of working fluids, we determined MBWR parameters for water.

The resultant parameter values are presented in Appendix B. It should be noted that with the use of these parameter values the thermodynamic behavior of water is described by the MBWR equation only over a limited range of conditions. The MBWR equation is not capable of accurate description of water properties over the full range of state conditions for which fluid phase experimental data for water are available. The applicable range for use of the reported MBWR parameters for water is 273°K to 1528°K (492°R to 2750°R) and 0 MPA to 17.24 MPA

(0 psia to 2500 psia). In this range the average absolute deviations of predicted properties from experimental[6,7] or reported[5] values is 0.57 percent for density (260 points), 0.67 percent for vapor pressure (64 points), and 3.23 joules/gm (1.39 Btu/lb) for enthalpy (260 points).

8. MBWR CORRELATION FOR AMMONIA

MBWR parameters also have been determined for ammonia. The parameters determined for ammonia are reported in Appendix B. As was also noted for water, an excellent correlation of the thermodynamic properties of ammonia already exists, namely the ammonia equation of state developed by Haar and Gallagher[8]. Nevertheless, the MBWR parameters for ammonia may be useful to those using the MBWR equation in design work. Also similar to the situation for water, the MBWR equation is capable of accurate description of the thermodynamic behavior of ammonia in only a restricted range. The applicable range for use of the reported MBWR parameters for ammonia is 290°K to 572°K (522 °R to 1031 °R) and 0 MPA to 6.76 MPA (0 psia to 980 psia). The average absolute deviations of ammonia thermodynamic properties predicted using the MBWR equation from the property values reported by Haar and Gallagher[8] are 0.52 percent for density (146 points), 0.47 percent for vapor pressure (41 points) and 3.72 joules/gm (1.60 Btu/lb) for enthalpy (97 points).

9. DEVELOPMENT OF A NEW EQUATION OF STATE

It has been noted that the MBWR equation cannot accurately describe the thermodynamic behavior of ammonia and water for the complete range of fluid states. This points up the need

for development of a new equation of state which can describe ammonia, water and other hydrogen bonding fluids such as alcohols and alcohol-water mixtures which are potential working fluids in geothermal cycles. The new equation should satisfy the need for description of a wide variety of fluids ranging from nonpolar fluids (such as hydrocarbons) through polar fluids (such as halocarbons with large dipole moments) and finally hydrogen bonding fluids (such as alcohols and water).

Initial efforts in this project were directed toward providing useful working fluid thermodynamic properties information at the earliest possible date. It was logical to use the MBWR equation as the basis for the initial correlation effort because the thermodynamic behavior of a number of hydrocarbons already had been correlated using the MBWR equation. Because of our success in correlating the behavior of halocarbons using the MBWR equation, it was logical to search for modifications to the MBWR equation for prediction of water properties over wider ranges of state conditions than was possible with the eleven parameter equation. Among a number of equation forms considered, the following thirty-two parameter modification of the MBWR equation was found to yield the best results:

$$Z = 1 + \sum_{i=1}^{6} A_i \rho^i + \sum_{i=7}^{12} A_i \rho^{i-6} T^{-1}$$

$$+ \sum_{i=12}^{18} \sum_{j=19}^{24} A_i A_j \rho^{i-12} T^{17-j}$$

$$+ A_{25} \rho T^{-3} + A_{26} \rho^2 T^{-3} (1 + A_{27} \rho^2) \exp(-A_{27} \rho^2) \qquad (2)$$

$$+ (A_{28} + A_{30} T^{-1})(-\rho^2 + A_{29} \rho^5) T^{-1} + A_{31} \rho T^{-7} + A_{32} \rho T^{-5}$$

In this equation $Z = P/\rho RT$ is the compressibility factor, where P is absolute pressure, T is absolute temperature, ρ is molar density, R is the universal gas constant and A_1 - A_{32} are the thirty-two equation of state parameters. Because Equation (2) is nonlinear in some of the parameters, it does not mesh conveniently with the perturbation methods and the multiparameter corresponding states method for mixture correlation which will be considered in the Phase II effort. For this reason, studies of equation of state forms which are entirely linear in the parameters have been initiated.

10. CONCLUSIONS AND PLANS

In the first year of this project, significant progress has been made toward the goal of using one method for prediction of the thermodynamic properties of hydrocarbons, halocarbons, water, and ammonia. The feasibility of using the MBWR equation for

fluids with small to moderate dipole moments has been shown. With this established, the determination of tentative sets of parameters for twelve pure components has been completed. Research has been initiated to improve the prediction for the hydrogen bonding fluids such as water and ammonia. The program plan is to develop an equation of state functional form which can be used for describing the wide range of potential working fluids for geothermal cycles (including mixture working fluids).

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APPENDIX A

Work Statement

The following is a work statement which outlines the sequence of planned research tasks for the following project, proposed to ERDA on March 5, 1975: "Development of Working Fluid Thermodynamic Properties Information for Geothermal Cycles," Principal Investigator, Kenneth E. Starling, The University of Oklahoma.

Phase I - Correlation of Pure Fluid Thermodynamic Properties (first year)

(1) Literature survey and data collection. Available thermodynamic property data will be collected for working fluids which have been or are considered to be candidate working fluids for geothermal conversion processes. These fluids include the refrigerants R-11, R-12, R-21, R-22,R-32, R-113, R-114, R-C318, R-717(ammonia) and water. Other candidate working fluids have been studied previously, including ethane(R-170), n-butane (R-600), propane(R-290), isobutane(R-600a), ethylene(R-1150), propylene(R-1270), n-pentane, isopentane and n-hexane. The data will then be punched on IBM cards and then transferred to magnetic tape or disk (for subsequent retrieval in regression calculations).

(2) Preliminary MBWR equation of state parameter values will then be determined for each fluid using the generalized MBWR equation developed by Han and Starling (Reference: K.E. Starling, Fluid Thermodynamic Properties for Light Petroleum Systems, Gulf Publishing Company, Houston, Texas, 1973). Because acentric factors for the refrigerants are not well established, vapor pressure data will be used to determine pseudo acentric factors for each fluid consistent with the generalized MBWR equation.

(3) The ability of the generalized MBWR equation to describe the thermodynamic behavior of the fluids under study in the gaseous and liquid regions will be tested, using the critical temperature, critical density and pseudo acentric factor determined above to characterize each fluid.

(4) Available thermodynamic property data (PVT, vapor pressure, enthalpy, heat capacity and velocity of sound data) will then be used simultaneously in multiproperty regression analysis to determine tentative MBWR equation of state parameters for each of the fluids studied.

(5) The MBWR equation will be modified, if necessary, to obtain predictions of thermodynamic properties which are of acceptable accuracy for geothermal energy conversion calculations. The anticipated uncertainties are 0.5% to 1% for densities, 0.5% to 1% for vapor pressures, and 1 to 2 Btu/lb.

for enthalpies, depending upon the accuracy of the available data. We feel that it is highly probable that modification of the MBWR equation will be required because some of the chlorinated and fluorinated hydrocarbons in addition to ammonia and water have appreciable dipole moments, whereas the MBWR equation was developed using essentially nonpolar hydrocarbon data (mainly normal paraffin hydrocarbon data). However, some preliminary work has given us confidence in the MBWR equation or a modification for describing the more polar fluids.

Phase II - Correlation of Mixture Thermodynamic Properties (Second year)

(1) Literature survey and data collection. Binary and multicomponent thermodynamic property and vapor-liquid equilibrium data will be collected, recorded on IBM cards and put on magnetic tape or disk for use in mixture equation of state evaluation studies.

(2) Using the tentative pure fluid equation of state parameters determined in Phase I, tests of mixture prediction methods will be made. The type of parameter mixing rule method used successfully in the past for the MBWR equation will be tested, but we also may test the use of conformal solution theory and perhaps other methods. The objective will be to predict mixture properties and vapor-liquid equilibrium from knowledge of the pure component parameters and only a few binary interaction parameters.

(3) Tentative values of the binary interaction parameters will be determined for each binary system for which vapor-liquid equilibrium data are available using sensitivity analysis or regression analysis.

(4) The equation of state parameters for the pure fluids and even the equation of state itself will be modified as necessary to obtain accurate predictions of both pure fluid and mixture behavior. It may be necessary to simultaneously use pure fluid and mixture data in multiproperty analysis to achieve this goal for individual systems. Further, it may be necessary to develop the equation as a generalized equation to insure consistent changes in parameters from fluid to fluid and system to system.

(5) Generalized expressions for the binary interaction parameters will then be developed. This step is necessary because the experimental binary system thermodynamic property data from which the binary interaction parameters are determined are lacking. The success of this effort to develop generalized binary interaction expressions obviously will be dependent upon the extent and self consistency of available binary data.

(6) The resultant equation of state correlation will be tested for multicomponent system thermodynamic properties predictions and modified further if necessary to obtain accuracies acceptable for geothermal energy conversion process design.

Phase III - Finalization of Correlation and Development of User Oriented Documentation(Third year)

(1) The correlation developed in Phases I and II will be finalized with respect to any parameter values or other aspects of the correlation which need fine tuning before reporting in final documentation.

(2) Thermodynamic properties tables will be developed for each pure fluid studied up to a maximum of twenty fluids and excluding fluids for which we have developed tabulations previously. Tables of properties for both saturated conditions and for the single phase regions(compressed liquid, superheated gas and supercritical fluid). Properties included are temperature, pressure, specific volume, enthalpy and entropy. Existing computer programs for properties calculation and table construction will be utilized or modified as necessary.

(3) A thermodynamic properties diagram(pressure-enthalpy) also will be produced for selected fluids studied, up to a maximum of ten diagrams(additional diagrams would require additional funding). An existing computer program will be utilized or modified as necessary for generating thermodynamic properties along (a)isotherms, (b)isochores and (c)isentrops. This information is then fed into a computer plotting program which plots isotherms, isochores and isentrops. In our earlier work on the hydrocarbons, a draftsman had to trace the isotherms, isochores and isentrops and the saturation curve onto a single diagram because the resolution of the available plotter was not adequate for direct production of the diagram. The draftsman also did all of the lettering for each diagram. In the proposed work we plan to automate diagram production to a much greater extent; however, the production of high quality diagrams will continue to require considerable effort. The production of thermodynamic properties diagrams for mixtures would require even greater effort than production of pure fluid diagrams. Mixture diagrams are not planned as part of this project, although mixture diagrams could be produced with additional funding.

(4) A user oriented thermodynamic properties computer program will be developed. This program will be capable of predicting the thermodynamic properties and phase behavior of each pure fluid and mixture studied in this research. These

properties include density, enthalpy, entropy, heat capacity for both pure fluids and mixtures and mixture vapor-liquid equilibrium ratios or K-values. The program will perform flash calculations, dew point temperature and pressure calculations and bubble point temperature and pressure calculations. The program also will be capable of performing certain important process calculations, including calculations for isentropic expansions and compressions, isenthalpic expansions and compressions and heat exchanger exit temperatures.

(5) The thermodynamic properties tables, diagrams and computer program, along with the correlation basis and documentation for the computer program will be presented in a final report on the project. The user oriented documentation developed in this project could be presented in the form of a monograph, although the preparation of such a monograph is not part of the proposed project.

APPENDIX B

MODIFIED BWR EQUATION OF STATE PARAMETERS FOR TWENTY-SEVEN COMPOUNDS

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ABSTRACT

Parameters for a modified Benedict-Webb-Rubin equation of state are presented for twenty-seven fluids of industrial interest. The fluids included are twelve hydrocarbons, ten halocarbons, nitrogen, carbon dioxide, hydrogen sulfide, ammonia and water. The hydrocarbons are the eight normal paraffins methane through normal octane, isobutane, isopentane, ethylene and propylene. The halocarbons are (with the refrigerant number in parentheses) trichlorofluoromethane (R-11), dichlorodifluoromethane (R-12), chlorotrifluoromethane (R-13), carbon tetraflouride (R-14), chlorodifluoromethane (R-22), fluoroform (R-23), trichlorotrifluoromethane (R-113), dichlorotetrafluoromethane (R-114), chlorodifluoroethane (R-142b) and ethylene difluoride (R-152a). The presentation provides the most extensive single compilation of MBWR (Modified Benedict-Webb-Rubin) equation parameters available. The ranges of applicability of the MBWR equation are presented for each fluid, along with estimates of the uncertainty in predicted thermodynamic properties. The pertinent equation of state relations for thermodynamic properties also are presented.

Introduction

The MBWR (Modified Benedict-Webb-Rubin) equation of state[1] discussed herein has found extensive use in recent years in the hydrocarbon production, transmission and processing industries and in the emerging energy conversion industries utilizing low temperature resources. The MBWR equation has been particularly valuable for predictions of thermodynamic properties in the compressed liquid region, especially at low reduced temperatures, where most previous equations of state were not reliable. The fact that vapor pressure and enthalpy information were utilized along with density values to determine MBWR parameters for each fluid enhanced the accuracy of predicted properties such as the entropy and provided reasonable predictions of properties in the compressed liquid region even when there were very few or no data in the region. Although MBWR equation parameters for individual fluids and groups of fluids have been reported previously, the most extensive compilation of MBWR parameters to date is presented herein. Besides presentation of the MBWR parameters, the pertinent thermodynamic property relations, methods for calculation and expected uncertainties in predicted properties are discussed.

MBWR Equation of State

The MBWR equation of state expression for the absolute pressure, P, is the following function of absolute temperature, T, and molar density, ρ:

$$P = \rho RT + \left(B_o RT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4}\right)\rho^2 + \left(bRT - a - \frac{d}{T}\right)\rho^3 + \alpha\left(a + \frac{d}{T}\right)\rho^6 + \frac{c\rho^3}{T^2}\left(1 + \gamma\rho^2\right)\exp\left(-\gamma\rho^2\right) \quad (1)$$

In this equation, R is the universal gas constant and B_o, A_o, C_o, D_o, E_o, b, a, d, α, c and γ are the eleven MBWR parameters.

Because the MBWR equation for the pressure is a high order function of density, prediction of the density at a given temperature-pressure condition requires use of an iterative method for solution of Equation (1). High speed density solution methods such as the false position method [1], the Newton-Raphson method, or the method of Plöcker and Knapp [2] are preferred when large numbers of density calculations are to be performed. It should be noted that Equation (1) can possess three or more density roots at all temperatures below the critical temperature. Only the smallest and largest roots have physical significance, corresponding to vapor and liquid densities, respectively.

Enthalpy

The enthalpy, H, of a compound at a given temperature-pressure condition can be calculated using the relation:

$$H = (H - H^o) + (H^o - H^o_o) + (H^o_o - H_R) + H_R \quad (2)$$

In Equation (2) H_R is the enthalpy in the reference state chosen

for the compound, $(H^{o}_{o} - H_R)$ is the difference in the enthalpy, H^{o}_{o}, of the fluid in the ideal gas state at the temperature T_o, and the enthalpy, H_R, in the reference state, $(H^{o} - H^{o}_{o})$ is the difference in the enthalpy, H^{o}, of the fluid in the ideal gas state at the temperature, of interest, T, and the enthalpy H^{o}_{o} and $(H - H^{o})$ is the enthalpy departure, the difference in the enthalpy, H, of the fluid at the temperature-pressure condition of interest, (T,P), and the enthalpy, H^{o}, of the fluid in the ideal gas state at the same temperature. A number of reference states for the enthalpy are in common use. If the reference state is chosen to be the elements in the ideal gas state at absolute zero temperature, then $H_R = 0$ and, if T_o is chosen to be absolute zero temperature, then $(H^{o}_{o} - H_R)$ becomes the enthalpy of formation of the compound from the elements in the ideal state at absolute zero temperature. This reference state was utilized in tabulations and pressure-enthalpy diagrams presented previously [1] for fifteen of the fluids considered herein. If the reference state is chosen to be the compound in the ideal gas state at absolute zero temperature and T_o is chosen to be absolute zero temperature, then both $H_R = 0$ and $(H^{o}_{o} - H_R) = 0$. This reference state was utilized for the properties prediction computer program presented previously.[1] If the reference state is chosen to be some other specific state, such as the saturated liquid at a specified temperature, then $H_R = 0$ in this reference state condition and T_o must be chosen to be a temperature for which $(H^{o}_{o} - H_R)$ is known. The ASHRAE (American Society of Heating, Refrigeration and Air Conditioning Engineers) tabulations [3]

utilize the saturated liquid at $-40^{o}F$ as the reference state for a number of fluids. An exception among the halocarbons considered herein is trifluoromethane (Refrigerant 23) for which the ASHRAE reference state is the ideal gas at $-200^{o}F$.

The enthalpy difference in the ideal gas state, $(H^{o} - H^{o}_{o})$ can be calculated using the ideal gas heat capacity, C_p^{o},

$$\left(H^{o} - H^{o}_{o}\right) = \int_{T_o}^{T} C_p^{o} dT \tag{3}$$

Numerous relations for C_p^{o} as functions of absolute temperature have been presented in the literature. Coefficients for the following relation, obtained from the work of Passut and Danner[4], Downing[5] and Thinh, et al.[6] are presented in Table 1 for the twenty-seven fluids considered herein,

$$C_p^{o} = A_1 + A_2T + A_3T^2 + A_4T^3 + A_5T^4 + \frac{A_6}{T^2} \tag{4}$$

Values of T_o and $(H^{o}_{o} - H_R)$ which give agreement with the referenced computer program[1] or ASHRAE tabulations[3] for enthalpy are given in Table 2.

The enthalpy departure is related to the equation of state by the following equation[1]:

$$(H - H^{o}) = P/\rho - RT + \int_0^{\rho} \left[P - T\left(\frac{\partial P}{\partial T}\right)_{\rho}\right] \frac{d\rho}{\rho^2} \tag{5}$$

When the MBWR equation of state given in Equation (1) is used in Equation (5), the equation of state expression for the enthalpy

TABLE 1. Coefficients for the Ideal Gas Heat Capacity Relation

$$C^{o}_{p} = A_1 + A_2T + A_3T^2 + A_4T^3 + A_5T^4 + \frac{A_6}{T^2} \quad (^{Btu}/_{lb\ ^{o}R})$$

Compound	A_1	$A_2 \times 10^3$	$A_3 \times 10^6$	$A_4 \times 10^{10}$	$A_5 \times 10^{14}$	A_6	Reference
Methane	0.564834	-0.565946	1.252197	-6.102304	9.794285	0.0	4
Ethane	0.273088	-0.085012	0.938445	-5.55956	10.035115	0.0	4
Propane	0.179733	0.132116	0.752994	-4.989844	9.467545	0.0	4
I-Butane	-0.036626	0.957759	-0.2963136	0.359653	0.0	0.0	6
N-Butane	0.002040	0.869758	-0.24543	0.289396	-0.0728	0.0	4
I-Pentane	-0.031531	0.931471	-0.278860	0.3248241	0.0	0.0	6
N-Pentane	-0.002795	0.880146	-0.258864	0.327056	-0.098575	0.0	4
N-Hexane	-0.023096	0.922666	-0.292206	0.413472	-0.153215	0.0	4
N-Heptane	-0.023143	0.921962	-0.294222	0.419008	-0.15670	0.0	4
N-Octane	-0.022402	0.919424	-0.294186	0.419016	-0.156775	0.0	4
Ethylene	0.020724	0.770862	-0.248163	0.369272	-0.14642	0.0	4
Propylene	0.044867	0.648526	-0.091812	-0.334928	0.944885	0.0	4
Carbon Dioxide	0.114433	0.202264	-0.079482	0.138824	-0.06570	0.0	4
Hydrogen Sulfide	0.238575	-0.048914	0.123201	-0.520504	0.72426	0.0	4
Nitrogen	0.253664	-0.029098	0.037632	-0.068424	-0.041195	0.0	4
R-11	0.038278	0.279882	-0.212373	0.599901	0.0	-336.807	5
R-12	0.024525	0.332662	-0.241389	0.672363	0.0	0.0	5
R-13	0.035039	0.282299	-0.115899	0.0	0.0	0.0	5
R-14	0.052632	0.237043	-0.028566	-0.295339	0.0	0.0	5
R-22	0.051105	0.225541	-0.065096	0.0	0.0	257.341	5
R-23	0.104666	-0.007562	0.390657	-2.454904	0.0	0.0	5
R-113	0.090233	0.115900	0.0	0.0	0.0	0.0	5
R-114	0.029124	0.34900	-0.16700	0.0	0.0	0.0	5
R-142B	0.059740	0.363984	-0.146128	0.216111	0.0	0.0	6
R-152A	0.0399061	0.561228	-0.209702	0.292165	0.0	0.0	6
Water	0.457392	-0.105024	0.193782	-0.811036	1.18155	0.0	4
Ammonia	0.476211	-0.141364	0.455949	-2.192904	3.4735	0.0	4

TABLE 2. Enthalpy Reference States

Compound	Reference State* T_R (°R)	P_R (Psia)	H_R ($\frac{Btu}{lb}$)	T_o (°R)	$(H_o^o - H_R)$ ($\frac{Btu}{lb}$)	Reference
Methane	0.0	0.0	0.0	0.0	-5.58114	1
Ethane	0.0	0.0	0.0	0.0	-0.76005	1
Propane	0.0	0.0	0.0	0.0	-1.22301	1
I-Butane	0.0	0.0	0.0	0.0	13.28660	1
N-Butane	0.0	0.0	0.0	0.0	29.11502	1
I-Pentane	0.0	0.0	0.0	0.0	27.62342	1
N-Pentane	0.0	0.0	0.0	0.0	27.17183	1
N-Hexane	0.0	0.0	0.0	0.0	32.03560	1
N-Heptane	0.0	0.0	0.0	0.0	30.70117	1
N-octane	0.0	0.0	0.0	0.0	29.50114	1
Ethylene	0.0	0.0	0.0	0.0	51.78893	1
Propylene	0.0	0.0	0.0	0.0	26.17773	1
Carbon Dioxide	0.0	0.0	0.0	0.0	4.77805	1
Hydrogen Sulfide	0.0	0.0	0.0	0.0	-0.61782	1
Nitrogen	0.0	0.0	0.0	0.0	-0.68925	1
R-11	419.69	0.0	0.0	459.69	92.209	3
R-12	419.60	0.0	0.0	307.69	60.628	3
R-13	419.69	0.0	0.0	259.69	38.545	3
R-14	419.69	0.0	0.0	209.69	102.199	3
R-22	419.69	0.0	0.0	304.69	86.945	3
R-23	259.69	0.0	0.0	259.69	-0.02951	3
R-113	419.69	0.0	0.0	429.60	74.65	3
R-114	419.69	0.0	0.0	334.69	52.54	3
R-142B	419.69	0.0	0.0	379.69	89.061	3
R-152A	419.69	0.0	0.0	309.69	117.92	3
Water	0.0	0.0	0.0	0.0	-2.46342	1
Ammonia	0.0	0.0	0.0	0.0	-0.79603	1

*Reference state is pure fluid

departure has the form:

$$(H - H^o) = \left(B_o RT - 2A_o - \frac{4C_o}{T^2} + \frac{5D_o}{T^3} - \frac{6E_o}{T^4}\right)\rho$$

$$+ \frac{1}{2}\left(2bRT - 3a - \frac{4d}{T}\right)\rho^2 + \frac{1}{5}\alpha\left(6a + \frac{7d}{T}\right)\rho \qquad (6)$$

$$+ \frac{c}{\gamma T^2}\left[3 - \left(3 + \frac{1}{2}\gamma\rho^2 - \gamma^2\rho^4\right)\exp\left(-\gamma\rho^2\right)\right]$$

For self-consistency, the density value used in Equation (6) for calculation of the enthalpy departure must be determined by the solution of Equation (1) for the temperature-pressure condition of interest.

Entropy

The entropy, S, of a compound at a given temperature-pressure condition can be calculated using the relation:

$$S = (S - S^o) + (S^o - S^o_o) + (S^o_o - S_R) + S_R \qquad (7)$$

In Equation (7), S_R is the entropy in the reference state chosen for the compound, $(S^o_o - S_R)$ is the difference in the entropy, S^o_o, of the fluid in the ideal gas state at the temperature, T_o, and pressure, P_o, and the entropy, S_R, in the reference state, $(S^o - S^o_o)$ is the difference in the entropy, S^o, of the fluid in the ideal gas state at the temperature, T, of interest, and

the entropy S^o_o, and $(S - S^o)$ is the entropy departure, the difference in the entropy, S, of the fluid at the temperature-pressure condition of interest (T,P) and the entropy, S^o, of the fluid in the ideal gas state at the same temperature, T, and the pressure P_o. If the reference state is chosen to be the elements at absolute zero temperature, T_o is chosen to be absolute zero temperature and P_o is chosen to be unit pressure, then $S_R = 0$ and $S^o_o = 0$ and Equation (7) becomes $S = (S - S^o) + S^o$. This reference state was utilized in tabulations and pressure-enthalpy diagrams presented previously[1]. If the reference state is chosen to be the compound in the ideal gas state at 1^oR ($T_o = 1^oR$) and unit pressure (P_o = 1 psia), then $S_R = 0$ and $(S^o_o - S_R) = 0$ and Equation (7) becomes $S = (S - S^o) + (S^o - S^o_o)$. This is the reference state chosen by Passut and Danner [4], which was utilized in the properties prediction computer program presented previously[1]. If the reference state is chosen to be some other specific state, such as the saturated liquid at a specified temperature, then $S_R = 0$ and T_o and P_o must be chosen to be a temperature-pressure condition for which $(S^o_o - S_R)$ is known.

The entropy difference in the ideal gas state at constant pressure, $(S^o - S^o_o)$, can be calculated using the relation:

$$S^o - S^o_o = \int_{T_o}^{T} \frac{C_p^o}{T}\, dT \qquad (8)$$

Values of T_o, P_o and $(S^o_o - S_R)$ which give agreement with the referenced computer program[1] or ASHRAE tabulations[3] for entropy are given in Table 3.

The entropy departure is related to the equation of state by the following equation[1] when P_o is unit pressure,

$$(S - S^o) = -R \ln (\rho RT) - \int_o^\rho \left[\rho R - \left(\frac{\partial P}{\partial T}\right)_\rho\right] \frac{d\rho}{\rho^2} \qquad (9)$$

When the MBWR equation of state given in Equation (1) is used in Equation (9), the equation of state expression for the entropy departure has the form:

$$(S - S^o) = -R \ln (\rho RT) - \left(B_o R + \frac{2C_o}{T^3} - \frac{3D_o}{T^4} + \frac{4E_o}{T^5}\right) \rho$$

$$- \frac{1}{2}\left(bR + \frac{d}{T^2}\right)\rho^2 + \frac{\alpha d \rho^5}{5T^2} \qquad (10)$$

$$+ \frac{2c}{\gamma T^3}\left[1 - \left(1 + \frac{1}{2}\gamma\rho^2\right) \exp\left(-\gamma\rho^2\right)\right]$$

The density value used in Equation (10) should be determined by solution of Equation (1).

Fugacity

The fugacity, f, may be expressed in terms of the enthalpy departure and entropy departure by the thermodynamic relation:

$$RT \ln f = (H - H^o) - T(S - S^o) \qquad (11)$$

TABLE 3. Entropy Reference States

Compound	T_R (°R)	P_R (Psia)	S_R ($\frac{Btu}{lb°R}$)	T_o (°R)	P_o (Psia)	$(S_o^o - S_R)$ ($\frac{Btu}{lb°R}$)	Reference
Methane	0.0	1.0	0.0	1.0	1.0	-0.290200	1
Ethane	0.0	1.0	0.0	1.0	1.0	0.223450	1
Propane	0.0	1.0	0.0	1.0	1.0	0.299680	1
I-Butane	0.0	1.0	0.0	1.0	1.0	0.701924	1
N-Butane	0.0	1.0	0.0	1.0	1.0	0.921860	1
I-Pentane	0.0	1.0	0.0	1.0	1.0	0.946856	1
N-Pentane	0.0	1.0	0.0	1.0	1.0	0.811049	1
N-Hexane	0.0	1.0	0.0	1.0	1.0	0.830676	1
N-Heptane	0.0	1.0	0.0	1.0	1.0	0.765946	1
N-Octane	0.0	1.0	0.0	1.0	1.0	0.712296	1
Ethylene	0.0	1.0	0.0	1.0	1.0	1.550895	1
Propylene	0.0	1.0	0.0	1.0	1.0	1.028821	1
Carbon Dioxide	0.0	1.0	0.0	1.0	1.0	0.464918	1
Hydrogen Sulfide	0.0	1.0	0.0	1.0	1.0	0.111072	1
Nitrogen	0.0	1.0	0.0	1.0	1.0	0.240729	1
R-11	419.69	1.0	0.0	459.69	1.0	0.21483	3
R-12	419.69	1.0	0.0	307.69	1.0	0.17564	3
R-13	419.69	1.0	0.0	259.69	1.0	0.16473	3
R-14	419.69	1.0	0.0	209.69	1.0	0.6444	3
R-22	419.69	1.0	0.0	304.69	1.0	0.26318	3
R-23	259.69	1.0	0.0	259.69	1.0	0.98115	3
R-113	419.69	1.0	0.0	429.60	1.0	0.16098	3
R-114	419.69	1.0	0.0	334.69	1.0	0.12931	3
R-142B	419.69	1.0	0.0	379.69	1.0	0.23733	3
R-152A	419.69	1.0	0.0	309.69	1.0	0.339180	3
Water	0.0	1.0	0.0	1.0	1.0	-0.043279	1
Ammonia	0.0	1.0	0.0	1.0	1.0	0.045824	1

*Reference State is pure fluid

Using Equations (6) and (10) in Equation (11), the MBWR equation of state expression for the fugacity is:

$$RT \ln f = RT \ln (\rho RT) + 2\left(B_o RT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4}\right)\rho$$

$$+ \frac{3}{2}\left(bRT - a - \frac{d}{T}\right)\rho^2 + \frac{6\alpha}{5}\left(a + \frac{d}{T}\right)\rho^5 \qquad (12)$$

$$+ \frac{c}{\gamma T^2}\left[1 - \left(1 - \frac{1}{2}\gamma\rho^2 - \gamma^2\rho^4\right)\exp\left(-\gamma\rho^2\right)\right]$$

As was also noted for enthalpy and entropy, the density value used in Equation (12) for computing the fugacity should be determined by solving Equation (1).

Vapor Pressure

Determination of the vapor pressure P_s at a given temperature requires the simultaneous solution of the following condition equations for vapor-liquid equilibrium.[1]

$$P^L = P^V = P_s \qquad (13)$$

$$f^L = f^V \qquad (14)$$

where L and V refer to liquid and vapor, respectively. Iterative methods, such as the Newton-Raphson method in two variables, must be used to solve for vapor pressure. The following procedure can be carried out easily by computer and is rapidly convergent. To start the procedure, an initial estimate of the vapor pressure P_s is made (eg., using a generalized vapor pressure equation). Then

P^L and P^V are set equal to P_s to satisfy Equation (13). Liquid and vapor densities (ρ^L and ρ^V) are then calculated by solving for the largest and smallest roots satisfying Equation (1), with $P = P_s$. These liquid and vapor densities are then used to calculate the liquid and vapor fugacities f^L and f^V. A new estimate of the vapor pressure is then obtained by multiplying the initial estimate of P_s by the ratio f^L/f^V. This procedure is continued iteratively until Equation (14) is satisfied within a specified tolerance or $|1 - f^L/f^V|$ approaches a specified small value (e.g., 0.000001). The final pressure is the calculated vapor pressure.

Saturated Properties

Saturated vapor and liquid enthalpies and entropies are calculated by using in Equations (6) and (10) the saturated vapor and liquid densities determined in calculating the vapor pressure. Enthalpies and entropies of vaporization are then calculated as the difference in the computed saturated vapor and liquid property values.

MBWR Equation Parameters and Accuracy

Presented in Table 4 are the ranges of data (or reported values) of density, vapor pressure and enthalpy values utilized in multiproperty analysis for determination of MBWR parameters for the twenty-seven fluids considered. It should be noted that for ammonia and water, the MBWR equation should be used only in the restricted ranges of conditions indicated in Table 4. The average absolute deviations of predicted properties from experi-

mental data (or reported values) also are given in Table 4. These uncertainties are small enough for virtually any present-day engineering calculations. The MBWR equation of state parameters for the twenty-seven compounds are presented in Table 5.

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TABLE 4. Average Absolute Deviations (A.A.D.) of Predicted Properties from Reported Values and Temperature and Pressure Ranges of Data Used for Determination of MBWR Parameters

	Density				Vapor Pressure				Enthalpy Departure			
Compound	No. Pts.	Temp., °F	Press., psia	A.A.D., %	No. Pts.	Temp., °F	Press., psia	A.A.D., %	No. Pts.	Temp., °F	Press., psia	A.A.D., Btu/lb
Methane	41	-253 ∿662	129 ∿2325	0.32	29	-259 ∿-116	14.7 ∿669	0.44	39	-250 ∿50	450 ∿2000	0.68
Ethane	41	-250 ∿350	14.7 ∿8000	0.80	30	-220 ∿90	0.3 ∿700	0.70	39	-250 ∿310	500 ∿2000	1.41*
Propane	41	-250 ∿527	14.7 ∿3910	1.20	39	-220 ∿206	0.3 ∿617	0.46	39	-250 ∿250	500 ∿2000	0.61
I-Butane	353	-253 ∿592	0.01 ∿5000	0.59	82	-125 ∿274	0.3 ∿527	0.49	24	100 ∿480	250 ∿3000	1.68
N-Butane	41	-220 ∿430	14.7 ∿7000	1.29	39	-110 ∿305	0.18 ∿550	0.38	39	100 ∿430	200 ∿5000	1.00
I-Pentane	74	-60 ∿527	14.7 ∿3107	1.49	31	-122 ∿370	0.014 ∿494	1.14	0			
N-Pentane	41	-200 ∿460	14.7 ∿10000	1.91	33	-129 ∿385	0.004 ∿489	0.89	39	100 ∿460	200 ∿10000	0.66*
N-Hexane	41	-140 ∿340	14.7 ∿4000	2.12	40	-45 ∿440	0.22 ∿386	1.08	0			
N-Heptane	78	-90 ∿460	14.7 ∿3082	0.82	35	-80 ∿497	0.032 ∿350	0.80	17	512 ∿706	79 ∿2363	1.88*
N-Octane	55	-70 ∿527	14.7 ∿4400	2.63	31	32 ∿565	0.06 ∿362	1.03	30	75 ∿600	100 ∿1400	2.75*
Ethylene	73	-250 ∿260	14.7 ∿2000	0.99	32	-269 ∿49	0.019 ∿742	0.82	39	-120 ∿260	100 ∿2000	1.15*
Propylene	69	-240 ∿460	14.7 ∿5000	1.45	31	-233 ∿197	.002 ∿670	1.03	33	200 ∿400	400 ∿3000	0.84*
Carbon Dioxide	41	-22 ∿284	220 ∿5580	1.02	33	-70 ∿88	75 ∿1070	0.63	39	-22 ∿284	441 ∿7350	1.27
Hydrogen Sulfide	41	40 ∿340	100 ∿2000	0.66	24	-76 ∿212	14.7 ∿1306	0.63	0			
Nitrogen	41	-320 ∿240	14.7 ∿8936	0.45	19	-309 ∿232	29 ∿492	0.83	39	-300 ∿0	500 ∿2500	0.52
R-11	138	-85 ∿470	0.12 ∿640	0.19	25	-85 ∿170	0.12 ∿640	0.11	57	-85 ∿470	0.12 ∿640	0.22
R-12	128	-153 ∿459	0.14 ∿524	0.27	39	-160 ∿260	0.2 ∿430	0.34	113	-160 ∿460	0.14 ∿524	0.19
R-13	128	-200 ∿460	0.5 ∿535	0.27	33	-200 ∿260	0.5 ∿535	0.73	102	-200 ∿460	0.5 ∿535	0.17
R-14	111	-230 ∿250	3.5 ∿540	0.99	32	-216 ∿-66	9.0 ∿423	0.37	111	-230 ∿250	3.5 ∿540	0.31
R-22	143	-151 ∿399	0.27 ∿554	0.26	36	-101 ∿149	2.4 ∿396	0.27	139	-151 ∿399	0.27 ∿554	0.28
R-23	132	-191 ∿439	0.62 ∿543	0.87	23	-171 ∿49	1.7 ∿471	0.26	122	-191 ∿439	0.62 ∿543	0.23
R-113	124	-31 ∿489	0.3 ∿400	0.40	22	-31 ∿249	0.3 ∿101	0.85	112	-31 ∿489	0.3 ∿400	0.30
R-114	159	-136 ∿529	0.03 ∿304	0.34	32	-106 ∿229	0.16 ∿247	0.28	156	-136 ∿529	0.03 ∿304	0.18
R-142B	141	-81 ∿459	1.1 ∿502	0.73	28	-61 ∿219	2.0 ∿336	0.79	134	-81 ∿459	1.1 ∿502	0.96
R-152A	142	-151 ∿419	0.1 ∿448	0.56	31	-141 ∿159	0.2 ∿282	0.60	136	-151 ∿419	0.1 ∿448	1.54
Water	260	31 ∿2291	0.09 ∿2500	0.57	64	31 ∿675	0.09 ∿2616	0.67	260	31 ∿2291	0.09 ∿2616	1.39
Ammonia	146	62 ∿571	2.0 ∿980	0.52	41	49 ∿218	89 ∿980	0.47	97	-59 ∿556	1.0 ∿980	1.6
Average:				0.88				0.63				0.73 1.45*

*These average absolute deviations in enthalpy departure are in percent.

TABLE 5. Modified BWR Equation of State Parameters for Twenty-Seven Pure Components
(Pressure in psia, Temperature in ^{o}R, Density in $lb\text{-}mole/_{ft}3$)

	B_o	A_o	$C_o X10^{-8}$	γ	b	a	α	c $X10^{-8}$	$D_o X10^{-10}$	d $X10^{-4}$	$E_o X10^{-10}$
Methane	0.723251	7520.29	2.71092	1.48640	0.925404	2574.89	0.468828	4.37222	1.07737	4.74891	3.01122
Ethane	0.826059	13439.3	29.5195	2.99656	3.11206	22404.5	0.909681	68.1826	25.7477	70.2189	1468.19
Propane	0.964762	18634.7	79.6178	4.56182	5.46248	40066.4	2.01402	274.461	45.3708	1505.20	2560.53
I-Butane	2.02615	38980.2	106.581	9.21378	6.70763	38864.4	6.87727	328.220	147.046	618.303	8981.52
N-Butane	1.56588	32544.7	137.436	7.54122	9.14066	71181.8	4.00985	700.044	33.3159	3642.38	230.902
I-Pentane	1.27752	35742.0	228.430	11.7384	19.8384	204344.	6.16154	1290.83	142.115	3492.20	2413.26
N-Pentane	2.44417	51108.2	223.931	11.8593	16.6070	162185.	7.06702	1352.86	101.769	3885.21	3908.60
N-Hexane	2.66233	45333.1	526.067	14.8720	29.4983	434517.	9.70230	3184.12	552.158	3274.60	62643.3
N-Heptane	3.60493	77826.9	615.662	24.7604	27.4415	359087.	21.8782	3748.76	777.123	835.115	636.251
N-Octane	4.86965	81690.6	996.546	21.9888	10.5907	131646.	34.5124	6420.53	790.575	18590.6	3464.19
Ethylene	0.747945	12133.9	16.3203	2.27971	2.62914	15988.1	0.589158	40.9725	5.17563	90.3550	1.61706
Propylene	0.114457	6051.36	97.4762	4.07919	7.64114	81880.4	1.36532	294.141	70.5921	541.935	3412.50
Carbon Dioxide	0.394117	6592.03	29.5902	1.64916	0.971443	5632.85	0.395525	27.4668	40.9151	5.99297	1.02898
Hydrogen Sulfide	0.297508	10586.3	21.1496	1.20447	2.53315	20511.0	0.165961	43.6132	4.86518	1.99731	3.93226
Nitrogen	0.677022	4185.05	1.37936	1.10011	0.833470	1404.59	0.302696	0.844317	1.95183	3.11894	121.648
R-11	2.075010	40744.70	175.5198	7.483052	8.898936	92892.19	3.874479	736.7655	141.2435	1386.647	7275.933
R-12	1.598333	28858.68	81.95445	5.975451	7.112878	55769.99	2.635286	318.5777	52.66135	921.3462	2769.722
R-13	1.218645	17443.34	31.98527	3.815694	5.437993	36049.57	1.359589	104.2572	11.27538	372.3436	284.3204
R-14	0.5944908	11740.10	7.041541	3.419115	3.492386	7863.879	0.7608927	14.19856	5.307972	131.9613	67.75317
R-22	1.217710	20137.78	61.69690	3.311584	4.363955	36450.57	1.095192	174.2752	31.90431	370.1302	0.0
R-23	0.3793391	12621.08	24.01073	2.656389	3.647122	16273.04	0.5314757	47.69722	23.83591	169.9933	929.0587
R-113	2.504935	72597.88	160.1631	34.20486	18.81586	64737.47	8.910174	390.5316	741.6812	1451.649	126549.6
R-114	2.332235	47189.66	129.6248	12.33499	12.35784	84157.50	7.658150	516.620	152.9365	785.8706	5601.881
R-142B	2.364154	30185.41	139.2919	5.034503	6.364923	75356.19	2.557422	530.2078	57.40686	1347.710	161.2859
R-152A	2.231568	30219.47	91.15738	3.834157	4.401977	42785.45	1.521588	270.5770	79.04121	221.5356	3806.589
Water	0.4552756	12432.87	122.7536	0.2215509	0.2088909	514.5405	0.03580983	94.10372	68.22462	394.753	2258.151
Ammonia	0.7172304	10063.212	47.78621	0.5369631	0.542222	7368.62	0.0910937	65.226392	0.2420266	99.273209	0.0012865

NOMENCLATURE

H = enthalpy, Btu/lb.

$(H - H^o)$ = enthalpy for the fluid less the enthalpy for the ideal gas at the same temperature, Btu/lb.

$(H^o - H^o_o)$ = enthalpy for the ideal gas state at temperature T, less the enthalpy for the ideal gas at temperature T_o, Btu/lb.

$(H^o_o - H_R)$ = ideal gas enthalpy at temperature T_o less the reference state enthalpy, Btu/lb.

H_R = enthalpy in reference state, Btu/lb.

P = absolute pressure, psia

P_o = ideal gas standard state pressure

S = entropy, Btu/lb. ^oR

$(S - S^o)$ = entropy for the fluid less the entropy for the ideal gas at pressure P_o at the same temperature, Btu/lb. ^oR.

$(S^o - S^o_o)$ = entropy for ideal gas state at temperature T, and pressure P_o, less entropy for ideal gas at temperature T_o and pressure P_o, Btu/lb. ^oR.

$(S^o_o - S_R)$ = ideal gas entropy at T_o, P_o less the reference state entropy, Btu/lb. ^oR.

S_R = entropy in reference state, Btu/lb. ^oR.

T = temperature, ^oR.

T_o = ideal gas standard state temperature.

V = specific volume, cu. ft./lb.

f = fugacity

R = gas constant

ρ = molar density, lb-moles/cu.ft.

B_o, A_o, C_o, D_o, E_o, b, a, c, d, α, γ = equation of state parameters.

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APPENDIX C

CORRELATION OF THE THERMODYNAMIC PROPERTIES OF TEN HALOCARBONS USING A MODIFIED BWR EQUATION OF STATE

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ABSTRACT

The thermodynamic properties of ten halocarbons (halogenated hydrocarbons) in both the vapor and liquid regions have been correlated using a modified BWR (Benedict-Webb-Rubin) equation of state. The ten halocarbons, which are potentially good working fluids for low temperature difference energy conversion cycles, are trichlorofluoromethane, dichlorodifluoromethane, chlorotrifluoromethane, carbontetra fluoride, chlorodifluoromethane, fluoroform, trichlorotrifluoroethane, dichlorotetrafluoroethane, chorodifluoroethane, and ethylene difluoride. The eleven parameters in the modified BWR equation have been determined for each fluid using multiproperty analysis of reported density, enthalpy departure, and vapor pressure values. The average absolute deviations of predicted properties from reported values is 0.49% for densities, 0.46% for vapor pressures, and 1.02 joules/gram (0.44 Btu/lb) for enthalpy departures. The fact that compressed liquid properties can be predicted using the modified BWR equation is of particular value for energy conversion cycle calculations, since previously available calculations were cumbersome or unreliable in this region.

INTRODUCTION

A modified BWR (Benedict-Webb-Rubin), equation of state (1) developed originally for hydrocarbon thermodynamic properties predictions was utilized in this study for correlation of halocarbon (halogenated hydrocarbon) thermodynamic properties. Ten halocarbons which are potential working fluids for low temperature difference energy conversion systems were studied. These fluids are trichlorofluoromethane, dichlorodifluoromethane, chlorotrifluoromethane, carbon tetrafluoride, chlorodifluromethane, fluoroform, trichlorotrifluoroethane, dichlorotetrafluoroethane, chlorodifluoroethane and ethylene difluoride.

The thermodynamic properties of these halocarbons have been compiled (2) by ASHRAE (American Society of Heating Refrigeration and Airconditioning Engineers). However, the ASHRAE compilation generally excludes the compressed liquid region. This exclusion of the compressed liquid properties makes energy conversion cycle pumping power and preheater design calculations difficult. Although the Martin-Hou equation has been used for halogenated hydrocarbons (3), difficulties in its use also have been encountered (4,5), probably because the Martin-Hou equation was not originally intended for use in the compressed liquid region at low reduced temperatures. On the other hand, the modified BWR equation of state utilized herein was developed primarily to extend the original BWR equation for calculations in the compressed liquid region at low reduced temperatures. The MBWR equation

presently is being used in geothermal (4) ocean thermal (6), solar and waste heat energy conversion cycle design calculations using hydrocarbons as working fluids.

The MBWR Equation

The MBWR (Modified Benedict-Webb-Rubin) equation of state, the related thermodynamic functions and methodology for computations are well documented (1) and therefore, only a summary discussion of the MBWR equation is presented here. The MBWR equation for the absolute pressure, P, is the following function of absolute temperature, T, and molar density, ρ,

$$P = \rho RT + (B_o RT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4})\ \rho^2$$

$$+ (bRT - a - \frac{d}{T})\rho^3 + \alpha(a + \frac{d}{T})\rho^6 \qquad (1)$$

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

where R is the universal gas constant and B_o,A_o, etc., are the eleven MBWR equation of state parameters. It is convenient to express the MBWR in dimensionless form. The MBWR equation for the compressibility factor, $Z = P/\rho RT$ can be expressed as the following function of the reduced temperature, $T_r = T/T_c$, and reduced density, $\rho_r = \rho/\rho_c$, where T_c is the critical temperature and ρ_c is the critical density,

$$Z = 1 + \left(A_1 - \frac{A_2}{T_r} - \frac{A_3}{T_r^3} + \frac{A_9}{T_r^4} - \frac{A_{11}}{T_r^5} \right) \rho_r$$

$$+ \left(A_5 - \frac{A_6}{T_r} - \frac{A_{10}}{T_r^2} \right) \rho_r^2 + A_7 \left(\frac{A_6}{T_r} + \frac{A_{10}}{T_r^2} \right) \rho_r^5 \qquad (2)$$

$$+ \frac{A_8 \rho_r^2}{T_r^3} \left(1 + A_4 \rho_r^2\right) \exp\left(-A_4 \rho_r^2\right)$$

In Equation (2), the equation of state parameters $A_1, A_2, \ldots A_{11}$ are dimensionless and therefore can be used with any desired system of units. The dimensionless parameters are related to the dimensional parameters by the following relations,

$$A_1 = \rho_c B_o \qquad (3)$$

$$A_2 = \frac{\rho_c A_o}{R T_c} \qquad (4)$$

$$A_3 = \frac{\rho_c C_o}{R T_c^3} \qquad (5)$$

$$A_4 = \rho_c^2 \gamma \qquad (6)$$

$$A_5 = \rho_c^2 b \qquad (7)$$

$$A_6 = \frac{\rho_c^2 a}{R T_c} \qquad (8)$$

$$A_7 = \rho_c^3 \alpha \tag{9}$$

$$A_8 = \frac{\rho_c^2 c}{RT_c^3} \tag{10}$$

$$A_9 = \frac{\rho_c D_o}{RT_c^4} \tag{11}$$

$$A_{10} = \frac{\rho_c^2 d}{RT_c^2} \tag{12}$$

$$A_{11} = \frac{\rho_c E_o}{RT_c^5} \tag{13}$$

Predictions of the thermodynamic properties of a given substance using the MBWR equation require specification of the dimensionless equation of state parameters, along with the critical temperature, T_c and the critical density, ρ_c, in the desired units.

Characterization Parameters for Halocarbons Studied

The chemical formulas, molecular weights and critical constants of the ten halogenated hydrocarbons considered in this study are given in Table 1. All property values used in this work were taken from ASHRAE tabulations (2). The property values used include the vapor pressure, saturated liquid and saturated vapor densities and enthalpies and superheated gas densities and enthalpies. The temperature and pressure ranges of the property values and number of points utilized are summarized in Table 2.

Table 1. Characterization Parameters for Halocarbons Studied

Compound Name	Chemical Formula	ASHRAE Refrigerant No.	Molecular Weight	Critical Temperature °K	Critical Press., Bar	Critical Density, Kg mole/m^3
Trichlorofluoromethane	CCl_3F	R-11	137.38	471.16	44.092	4.03460
Dichlorodifluormethane	CCl_2F_2	R-12	120.93	385.16	41.162	4.61535
Chlorotrifluoromethane	$CClF_3$	R-13	104.47	301.99	38.680	5.53540
Carbon Tetrafluoride	CF_4	R-14	88.01	227.50	37.439	7.10966
Chlorodifluoromethane	$CHClF_2$	R-22	86.48	369.16	49.773	6.07303
Fluoroform	CHF_3	R-23	70.0	298.77	48.360	7.35595
Trichlorotrifluoroethane	$C_2Cl_3F_3$	R-113	187.39	487.27	34.398	3.07488
Dichlorotetrafluorethane	$C_2Cl_2F_4$	R-114	170.94	418.88	32.612	3.40757
Chlorodifluoroethane	$C_2H_3ClF_2$	R-142b	100.5	410.27	41.231	4.32883
Ethylene difluoride	$C_2H_4F_2$	R-152a	66.05	386.66	44.954	5.52438

Table 2. Temperature and Pressure Ranges of Data Used for Determination of MBWR Parameters

	Density			Vapor Pressure			Enthalpy Departure		
Compound	No. Pts.	Temp., °K	Press. Bar	No. Pts.	Temp., °K	Press.,Bar	No. Pts.	Temp., °K	Press.,Bar
R-11	138	208 - 516	0.-44.1	25	208 - 350	0. - 44.1	57	208 - 516	0. - 44.1
R-12	185	170 - 510	0.-36.1	36	174 - 366	0. - 29.6	186	174 - 366	0. - 36.1
R-13	128	144 - 511	0.-36.9	33	144 - 400	0. - 36.9	102	144 - 511	0. - 36.9
R-14	111	127 - 394	0.2-37.2	32	135 - 218	0.6- 29.1	111	127 - 394	.2- 37.2
R-22	143	171 - 477	0.-38.2	36	199 - 338	0.1- 28.3	139	171 - 477	0. - 38.2
R-23	132	149 - 499	0.-37.4	23	160 - 282	0.1- 37.5	122	149 - 499	0. - 37.4
R-113	124	238 - 527	0.-27.6	22	238 - 393	0. - 7.0	112	238 - 527	0. - 27.6
R-114	159	180 - 549	0.-21.0	32	196 - 382	0. - 17.0	156	180 - 549	0. - 21.0
R-142B	141	210 - 510	0.-34.6	28	221 - 377	0.1- 23.2	134	210 - 510	0. - 34.6
R-152A	142	171 - 488	0.-30.9	31	177 - 343	0. - 19.4	136	171 - 488	0. - 30.9

The enthalpy departure, ΔH, was calculated by choosing a low pressure reference condition, thereby fixing the reference temperature and reference enthalpy and calculating enthalpy departure as follows:

$$\Delta H = [H(T,P) - H^\circ(T)] \tag{14}$$

where

$$H^\circ(T) = H^\circ_{ref} + \int_{T_{ref}}^{T} c_p^\circ \, dT \tag{15}$$

where c_p° is the ideal gas heat capacity at constant pressure, which is expressed as a polynominal in absolute temperature. Coefficients for the c_p° polynominals used are given in Table 3.

Multiproperty Analysis

For many of the halocarbons of interest as working fluids in energy conversion cycles, thermodynamic data in the compressed liquid region are lacking. Liquid phase properties in the ASHRAE tabulations generally are for the saturated liquid only. Thus, in order to assure reasonable accuracy for the prediction of compressed liquid properties, it is important to use a correlation technique which will take maximum advantage of available property information. Multiproperty analysis[9] was developed for this purpose.

Table 3. Heat Capacity Polynominal Coefficients for Halocarbons Studied

$$c_p^\circ = a + bT + cT^2 + dT^3 + f/T^2 + R \quad \text{(BTU/lb mole °R)}$$

Compound	Ref	a	b x 10^2	c x 10^5	d x 10^9	f x 10^{-4}
R-11	7	3.271705	3.845023	-2.917586	8.241451	-4.627055
R-12	7	0.978868	4.022882	-2.919124	9.130886	0.0
R-13	7	1.673609	2.949188	-1.210807	0.0	0.0
R-14	7	2.645222	2.0862186	-0.2514094	-2.599277	0.0
R-22	7	2.43254	1.950477	-0.5629508	0.0	2.225485
R-23	7	5.3396609	-0.05293263	2.73460	-17.18433	0.0
R-113	7	14.921866	2.17185	0.0	0.0	0.0
R-114	7	2.99145	5.965806	-2.854698	0.0	0.0
R-142B	8	4.01685	3.6580388	-1.4685895	2.171935	0.0
R-152A	8	0.648798	3.7058111	-1.3850802	1.9291496	0.0

*Coefficients are consistent with the use of absolute temperature in °R.

The method of multiproperty analysis, as utilized in this study, simultaneously uses density, vapor pressure and enthalpy departure values in regression to determine equation of state parameters. The computational procedure is to minimize the objective function Q in the following expression,

$$Q = \sum_i \left[1 - \frac{\rho c_i}{\rho E_i}\right]^2 + W_{P_\sigma} \sum_j \left[1 - \frac{P_\sigma C_j}{P_\sigma E_j}\right]^2 + W_H \sum_k \left[1 - \frac{(HC-H°)_k}{(HE-H°)_k}\right]^2 \quad (16)$$

In this relation, ρE_i and ρc_i are reported and calculated densities at the ith state point, $P_\sigma E_j$ and $P_\sigma C_j$ are reported and calculated vapor pressures at the jth temperature, and $(HE-H°)_k$ and $(HC-H°)_k$ are the reported and calculated enthalpy departures at the kth state point. W_P and W_H are weighting factors for the subscripted property relative to a density weighting factor of unity. In the present study, these weighting factors were varied to obtain density and vapor pressure average absolute percentage deivations of the same magnitudes. Experience has indicated that when the density and vapor pressure are accurately correlated, reasonable values for other properties also are obtained.

Regression Results

The results of the multiproperty regression calculations for the ten halocarbons studied are summarized in Tables 4 and 5.

Table 4. Dimensionless MBWR Equation of State Parameters for Halocarbons

Compound	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	A_{11}
R-11	.522637	1.127610	.675384	.474721	.564544	.647511	.0619089	.714059	.06408572	.113973	$.38926 \times 10^{-2}$
R-12	.463218	1.10194	.660030	.489854	.580108	.625439	.0626798	.732987	.0564055	.140764	$.336055 \times 10^{-2}$
R-13	.421120	1.03330	.641215	.455649	.649375	.737947	.0561039	.722251	.0415828	.140216	$.192894 \times 10^{-2}$
R-14	.263860	1.185760	.424137	.673551	.687985	.352525	.06652862	.379587	.07807708	.144463	$.243378 \times 10^{-2}$
R-22	.461667	1.07065	.742887	.475998	.627263	.734725	.0596822	.795572	.0578123	.112276	$.7189209 \times 10^{-9}$
R-23	.174199	1.00425	.660579	.56018	.769106	.594609	.051468	.602602	.121938	.1155	$.8837659 \times 10^{-2}$
R-113	.480845	1.480720	.424729	1.26039	.693332	.253462	.0630248	.198799	.224268	.0648065	.0436326
R-114	.496132	1.240640	.599454	.558198	.559232	.470670	.07372212	.508234	.09380227	.058292	$.455690 \times 10^{-2}$
R-142B	.6388890	1.02930	.870927	.367668	.464828	.694406	.0504721	.895883	.0486043	.168169	$.184911 \times 10^{-3}$
R-152A	.769614	1.395360	.868931	.456032	.523568	.6813310	.0624145	.889502	.108254	.0506877	$.7490721 \times 10^{-2}$

Table 5. Summary of Deviations from Reported Values of Properties Predicted Using the MBWR Equation.

Average Absolute Deviation				
Compound	Density (%)	Vapor Pressure (%)	Enthalpy Departure Joules/g	Enthalpy Departure Btu/lb
R-11	0.19	0.11	0.51	0.22
R-12	0.27	0.34	0.44	0.19
R-13	0.27	0.73	0.39	0.17
R-14	0.99	0.37	0.72	0.31
R-22	0.26	0.27	0.65	0.28
R-23	0.87	0.26	0.53	0.23
R-113	0.40	0.85	0.69	0.30
R-114	0.34	0.28	0.42	0.18
R-142B	0.73	0.79	2.23	0.96
R-152A	0.56	0.60	3.57	1.54
Overall Average	0.49	0.46	1.02	0.44

Table 4 presents the eleven dimensionless MBWR parameters for each halocarbon. It can be noted that each dimensionless MBWR parameter generally is of the same order of magnitude for each fluid. The notable exception is A_{11}, which has only a small influence on property values at all but the lowest temperatures. Table 5 presents a summary of the average absolute deviation of predicted property values from reported values. The overall average absolute deviations for the ten halocarbons are 0.49% for density, 0.46% for vapor pressure and 1.02 joules/gm or 0.44 Btu/lb for enthalpy departure. These levels of uncertainty in predicted properties are adequate for most industrial calculations.

Conclusions

The thermodynamic properties of ten halocarbons have been correlated with reasonable accuracy using a modified BWR equation of state. Because the resultant correlations of the thermodynamic behavior of these halocarbons allows for reasonable predictions of thermodynamic properties in the compressed liquid region, these results should be of particular value for low temperature difference energy conversion cycle calculations.

Acknowledgement

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APPENDIX D

THERMODYNAMIC PROPERTIES OF ISOBUTANE USING A MODIFIED BWR EQUATION OF STATE

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ABSTRACT

The thermodynamic behavior of isobutane (2-methyl propane) has been accurately described using a MBWR (Modified Benedict-Webb-Rubin) equation of state which has been applied successfully to describe the fluid thermodynamic behavior of light petroleum systems and halocarbons. Our previous correlation of isobutane thermodynamic properties using the MBWR equation of state was based in part on smoothed property values and because of the bias thereby introduced lacked the superior prediction capabilities reported in this research. In addition, recently reported low temperature data have been utilized in the present study. A major contribution of this study is a single equation of state (MBWR) which can be used to accurately predict the thermodynamic behavior of isobutane over wide ranges of temperature and pressure. The MBWR equation of state predicts the density and vapor pressure of isobutane with average absolute deviations of 0.59% and 0.49%, respectively. The enthalpy of vaporization at the boiling point has a deviation of 0.26% and the average absolute deviation of the constant pressure heat capacity is 2.2%, so that predicted enthalpies should be within one calorie per gram of the true values.

INTRODUCTION

In recent years isobutane has become a primary candidate working fluid for waste heat and geothermal binary cycle power conversion systems using medium temperature thermal sources [27]. An equation of state which provides an accurate description of the thermodynamic properties of isobutane and also describes the behavior of mixtures involving isobutane is desirable in design calculations for these and other industrial processes.

Our previous work in correlation of the thermodynamic properties of isobutane using the MBWR equation of state [24] was based in part on biased reported property values, and hence lacked the superior prediction capabilities of the present set of parameters for the equation of state. In the present study, raw experimental data were used to the maximum extent possible. Due to the availability of new data, the ranges of temperature and pressure are wider than our previous study. Due to inconsistencies in reported experimental data reported in the literature [2,3,4,6, 7,8,9,12,14,16,17,18,19,20,21,23,25,26] the purity of the isobutane sample used in the experimental studies was used as a major criterion in the selection and weighting of data used in the correlation effort. The resultant equation has an accuracy which hitherto could be obtained only with the use of different equation parameters in different regions of state conditions [11].

EXPERIMENTAL DATA UTILIZED

Experimental density and vapor pressure data for isobutane have been reported by several investigators. The vapor pressures for isobutane reported by Seibert and Burrell [22], Gilliland and Scheeline [12], are quite high when compared to other reported values. The density data of Coffin and Maass [7] are also quite high when compared to the data of other investigators. Dana's [9] density measurements are high due to the purity of the isobutane sample he used (97% isobutane), however his vapor pressure data (99.5% isobutane) are in fair agreement with reported values in the literature.

The vapor pressure data reported by Aston [2], Beattie [4], Connolly [8], Dana [9], Sage and Lacey [20], Wackher [26], and Zwolinski [28], were used in the present correlation.

The density data of Beattie [3,4], Haynes and Hiza [14], Kahre [16], McClune [17], and Sliwinski [23] were weighted heavily and used with density values reported by Morris [18], Sage and Lacey [20,21], API [1] and Canjar and Manning [5].

The enthalpy values reported by Canjar and Manning [5], which were determined from density data, were used for comparison with enthalpy departure values predicted by the MBWR equation of state, but were not used for equation parameter determination due to probable bias. The experimental data in the critical region reported by Beattie [3] were used to compare the pressures predicted by the equation of state in this region.

THERMODYNAMIC RELATIONS

The MBWR equation of state is the following expression:

$$P = \rho RT + \left(B_o RT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4}\right)\rho^2 + \left(bRT - a - \frac{d}{T}\right)\rho^3 + \alpha\left(a + \frac{d}{T}\right)\rho^6 + \frac{c\rho^3}{T^2}\left(1 + \gamma\rho^2\right)\exp\left(-\gamma\rho^2\right) \qquad [1]$$

where P, ρ, T, R are the pressure, molar density, absolute temperature and universal gas constant respectively.

The enthalpy departure is related to equation [1] by the following expression [24]:

$$\phi\ (H-H^o) = \left(B_o RT - 2A_o - \frac{4C_o}{T^2} + \frac{5D_o}{T^3} - \frac{6E_o}{T^4}\right)\rho + \frac{1}{2}\left(2bRT - 3a - \frac{4d}{T}\right)\rho^2 + \frac{1}{5}\alpha\left(6a + \frac{7d}{T}\right)\rho^5 + \frac{c}{\gamma T^2}\left[3 - \left(3 + \frac{1}{2}\gamma\rho^2 - \gamma^2\rho^4\right)\exp\left(-\gamma\rho^2\right)\right] \qquad [2]$$

The fugacity in terms of equation [1] is given by

$$RT \ln f = RT\,(\ln(\rho RT)) + 2\left(B_o RT - A_o - \frac{C_o}{T^2} + \frac{D_o}{T^3} - \frac{E_o}{T^4}\right)\rho$$

$$+ \frac{3}{2}\left(bRt - a - \frac{d}{T}\right)\rho^2 + \frac{6\alpha}{5}\left(a + \frac{d}{T}\right)\rho^5$$

$$+ \frac{c}{\gamma T^2}\left[1 - \left(1 - \frac{1}{2}\gamma\rho^2 - \gamma^2\rho^4\right)\exp\left(-\gamma\rho^2\right)\right] \qquad [3]$$

Other derived property expressions in terms of the MBWR equation of state are given by Starling [24].

PREDICTION OF PROPERTIES

The eleven parameters for the MBWR equation for isobutane are given in Table 1, while the deviations of predicted properties from experimental values are given in Table 2, along with a comparison with the results of our previous study [24]. The units for these parameters correspond to pressure in psia, temperature in ^{o}R and molar density in lb-mole/cu.ft with a value of R = 10.7315 in the British engineering system units and pressure in KPA, temperature in ^{o}K and molar density in kg-mole/M^3 with a value of R = 8.3144 in the SI units. These parameter values were determined using 58.12 for the molecular weight of isobutane. The prediction of individual properties is discussed below.

Density. The MBWR equation of state predicts the density of isobutane with an average absolute deviation of 0.59% for 353 data points in a temperature range of 115 to 573^{o}K (207^{o}R to 1032^{o}R) and a pressure range of 0.6×10^{-4} to 34450 KPA (0.1×10^{-4} to 5000 psia). The low temperature as well as high temperature density behavior of isobutane thus is predicted accurately by a single equation of state. Figure 1 shows deviations of predicted saturated and compressed liquid densities from experimental data, while Figure 2 shows deviations in the gas and liquid phases for selected isotherms.

Table 1. MBWR Equation Parameters for Isobutane

PARAMETERS TO BE USED IN MBWR EQN.	PARAMETER VALUE	
	BRITISH ENG. SYSTEM OF UNITS	SI UNITS
B_o	2.026152731	0.126488576
A_o	38980.20150	1047.426346
$C_o \times 10^{-8}$	106.58145088	0.883935651
γ	9.213784536	0.0359084208
b	6.707625908	0.02614129432
a	38864.3892	65.1948326771
α	6.877265605	0.0016732205
$c \times 10^{-8}$	328.2196701	0.16993496773
$D_o \times 10^{-10}$	147.0459327	0.67751956746
$d \times 10^{-4}$	618.3034445	0.576222232
$E_o \times 10^{-10}$	8981.524117	22.99051347

Table 2. Summary of Deviations of Predicted Isobutane Thermodynamic Properties from Experimental Data and Comparison with Previous Results.

PARAMETER SET FOR MBWR EQN.	PROPERTY	NUMBER OF DATA POINTS	PRESSURE RANGE	TEMPERATURE RANGE	AVERAGE ABSOLUTE DEVIATION
Original Set (1972)	Density	73	100 ~ 20600 KPA 14.7 ~3000 psia	195 ~ 522 ^{o}K 350 ~ 940 ^{o}R	1.12%
	Vapor Pressure	28	0.6 ~ 3650 KPA 0.09 ~ 529.1 psia	179 ~ 407.7 ^{o}K 323 ~ 734 ^{o}R	1.04%
	Enthalpy Departure	24	1720 ~ 20750 KPA 250 ~ 3000 psia	310 ~ 522 ^{o}K 560 ~ 940 ^{o}R	5.183 KJ/KG 2.23 Btu/lb
This Work	Density	353	0.6×10^{-4} ~ 34450 KPA 0.1×10^{-4} ~ 5000 psia	115 ~ 573 ^{o}K 207 ~ 1032 ^{o}R	0.59%
	Vapor Pressure	82	0.1 ~ 3630 KPA 0.18 ~ 527 psia	186 ~ 407.7 ^{o}K 335 ~ 734 ^{o}R	0.49%
	Pressure*	172		407.75 ~ 408.3 ^{o}K 733.95 ~ 734.94 ^{o}R	1.12%
	C_p Departure	21	50 ~ 780 KPA 7 ~ 113 psia	295 ~ 343 ^{o}K 530 ~ 635 ^{o}R	0.0414 KJ/KG ^{o}K 0.0099 Btu/lb ^{o}R
	Enthalpy Departure	24	1720 ~ 20750 KPA 250 ~ 3000 psia	310 ~ 522 ^{o}K 560 ~ 940 ^{o}R	3.905 KJ/KG 1.68 Btu/lb

*Density Range 3.10758 ~ 4.645354 Kg mole/M^3
0.194 ~ 0.290 lb mole/ft^3

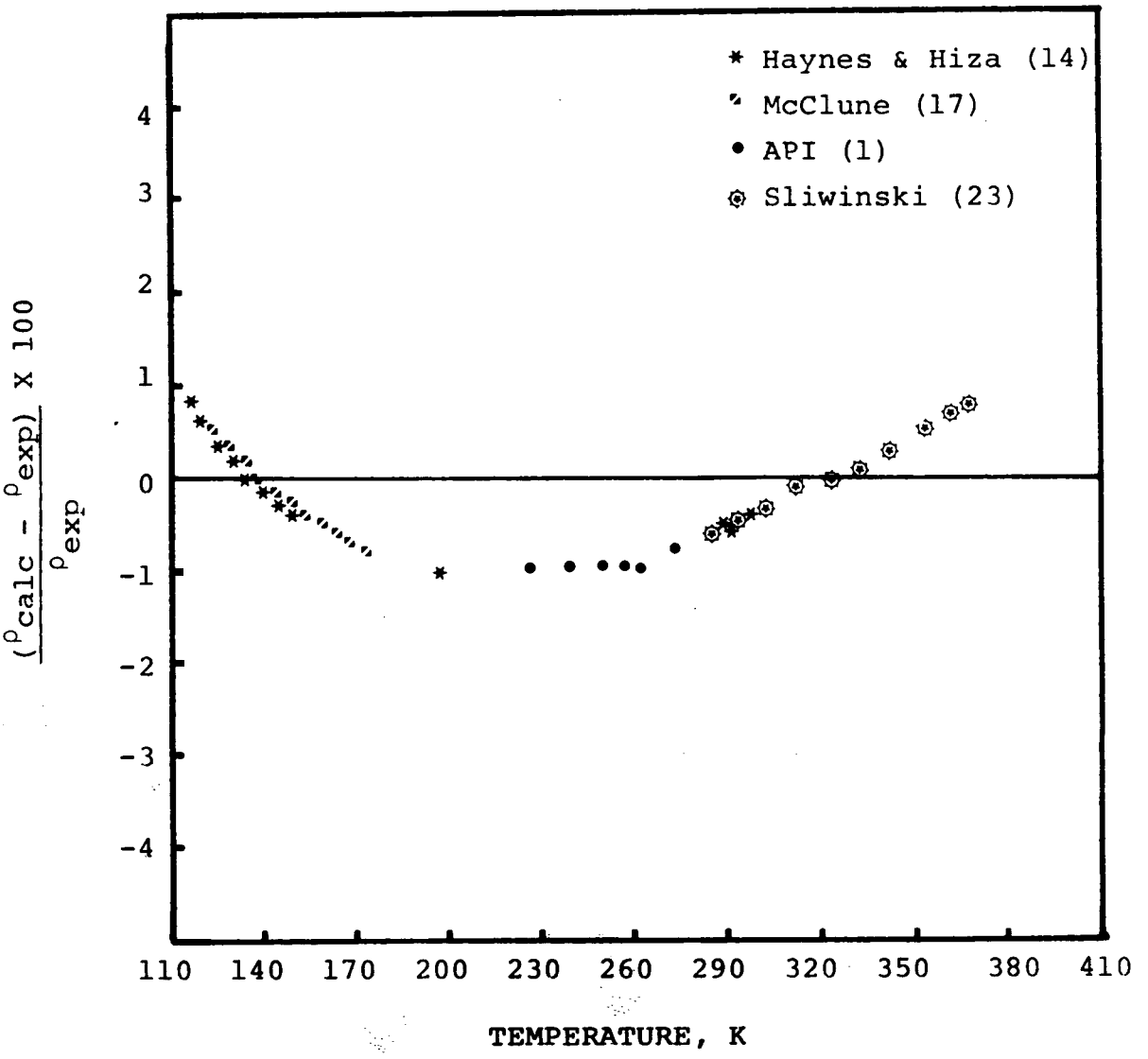

Figure 1. Percent Deviations of Calculated Liquid Densities from Experimental Data for Isobutane

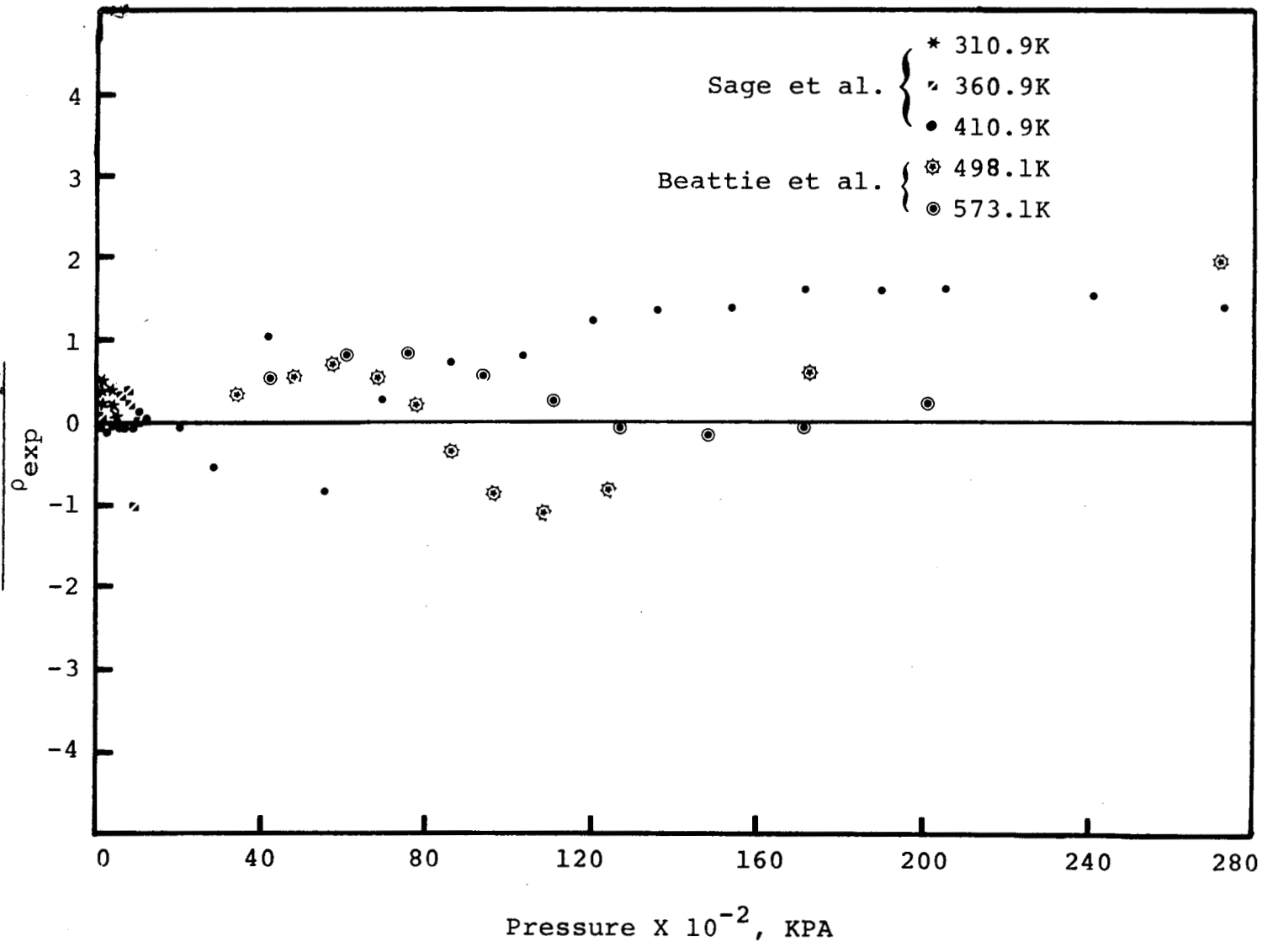

Figure 2. Percent Deviations of Calculated Gas Phase Densities from Experimental Data for Selected Isotherms for Isobutane

Vapor Pressure. Equation [1] describes the vapor pressure of isobutane with an average absolute deviation of 0.49% for 82 data points from 335°R to the critical point. Relative to other investigators' vapor pressure data, the experimental vapor pressure values of Dana et.al. [9] are relatively high, while the experimental vapor pressure values of Sage and Lacey [20] are relatively low. Nevertheless, these data were included with other data [2,8,21,26,28] to develop the correlation because otherwise there would have been a paucity of data in the range from 270°K to 340°K. Figure 3 shows the deviations of predicted vapor pressures from experimental data.

Pressure. Although the accuracies of predicted densities within 3°K and 100 KPA of the critical point are significantly reduced compared to the overall accuracy, the calculated pressures in this region when compared to the experimental data of Beattie et.al, (172 data points) [4] have an average absolute deviation of 1.12%. Thus, it can be concluded that the critical behavior of the MBWR equation for isobutane is reasonable.

Enthalpy of Vaporization. The predicted enthalpy of vaporization at the normal boiling point agrees closely with the experimental value reported by Aston et.al. [2]. The uncertainty is 0.26% or less than 1.00 KJ/KG(0.5 Btu/lb). The predicted value is 367.287 KJ/KG as compared to the experimental value of 366.395 KJ/KG of Aston et.al. [2].

Heat Capacity Departure. The MBWR equation of state predicts the constant pressure heat capacity departure with an average absolute deviation of 0.0414 KJ/KG°K(0.01 Btu/lb °R). The reported values of Ernst and Busser [10] were used for comparison in the temperature range 295°K to 353°K and the pressure range 50 to 780 KPA. The uncertainty in the constant pressure heat capacity is about 2.2% in this range.

Enthalpy Departure. Enthalpy departure values predicted by the MBWR equation of state were compared with the tabulated values determined from PVT data by Canjar and Manning [5]. The enthalpy departures in the temperature range 310°K to 522°K (560°R to 940°R) and the pressure range 1720 to 20750 KPA (250 psia) to 3000 psia) have an average absolute deviation of 3.905 KJ/KG (1.68 Btu/lb).

Second Virial Coefficients. Calculated values of second virial coefficients generally are in good agreement with values reported in the literature and are given in Table 3, where

$$B = B_o - \frac{A_o}{RT} - \frac{C_o}{RT^3} + \frac{D_o}{RT^4} - \frac{E_o}{RT^5}$$

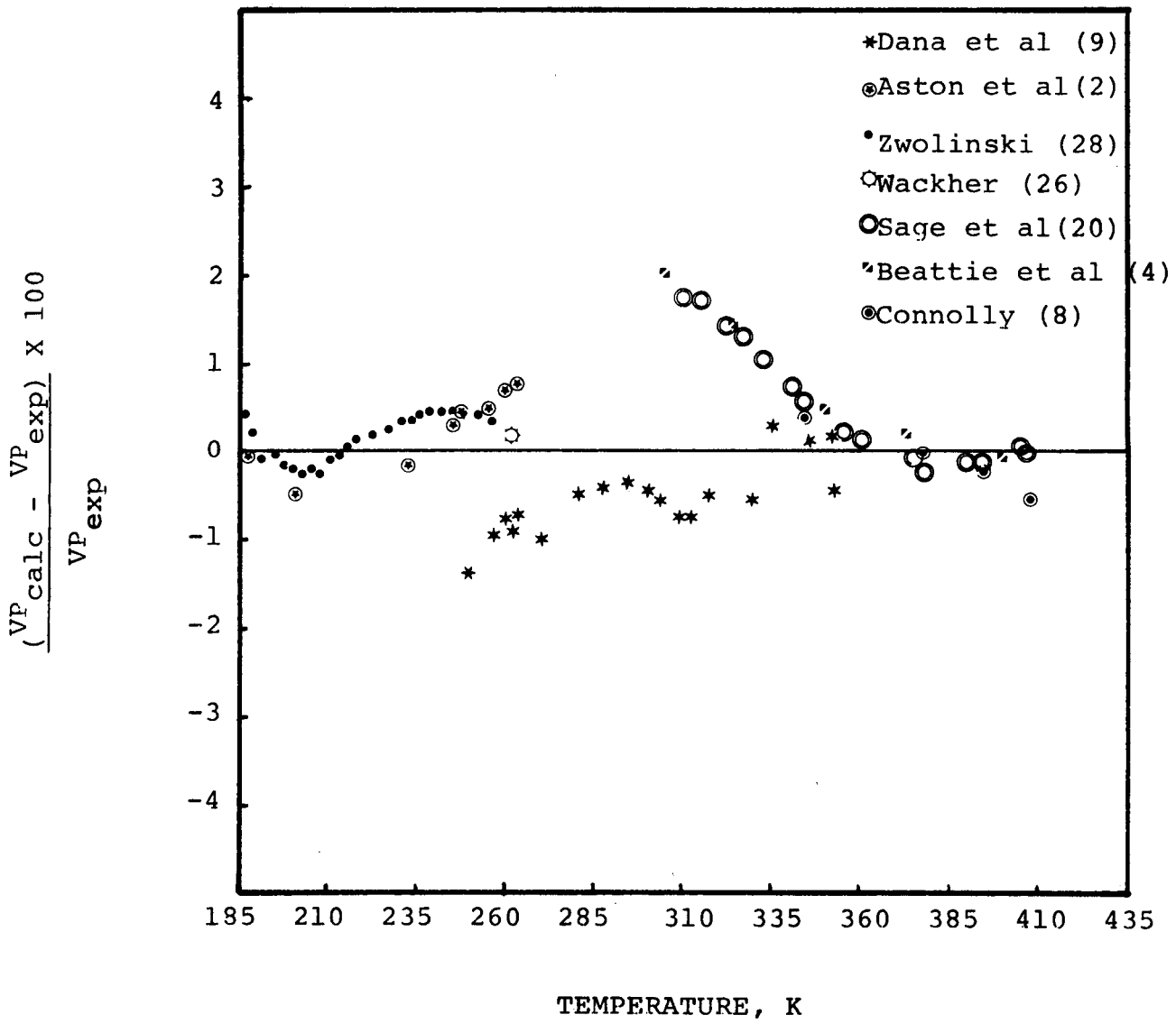

Figure 3. Percent Deviations of Calculated Vapor Pressures from Experimental Values for Isobutane

Table 3. Isobutane Second Virial Coefficients

T °K	-B, $cm^3\ mol^{-1}$		
	LITERATURE VALUES	API	MBWR
273.16	889[a]	786.0	728.0
303.16	699[a]	608.2	584.9
344.26	457.2[b]	449.8	447.7
360.93	412.7[b]	402.6	405.1
377.59	374.0[b]	362.2	368.1
394.26	341.1[b]	327.1	335.6
406.87	318.3[b]	303.6	313.7
410.93	311.5[b]	296.5	307.0
444.26	259.6[b]	245.7	259.0
477.6	230.2[c]	205.2	220.3
510.9	191.6[c]	172.2	188.6

[a] Jesson and Lightfoot [15]

[b] Connolly [8]

[c] Gunn [13]

CONCLUSIONS

The correlation of the thermodynamic properties of isobutane presented herein probably approaches the combined limits of the MBWR equation and the available experimental data. It is possible to obtain some improvement in the description of isobutane thermodynamic properties using a more complicated equation of state. However, the inconsistencies in some of the available experimental data are too great to allow development of a highly accurate correlation for the complete range of isobutane fluid conditions.

The inconsistency in available vapor pressure data has been discussed herein and is shown dramatically in Figure 3. In the few regions where direct comparisons can be made, deviations in the density data of different investigators approach the average absolute deviation of the correlation presented here.

These inconsistencies and the virtual lack of calorimetric data indicate a need for new, highly accurate and self consistent experimental data for isobutane thermodynamic properties over the wide range of potential industrial process conditions.

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NOMENCLATURE

$(H-H^{O})$ enthalpy of the real gas less the enthalpy of the ideal gas at the same temperature, KJ/KG or Btu/lb

P absolute pressure, KPA or psia

T temperature, ^{O}K or ^{O}R

ϕ conversion factor, from KJ/KG to KPA M^3/Kg mole or from Btu/lb to psia cu.ft/lb-mole

f fugacity

R gas constant

ρ molar density, kg-mole/M^3 or lb-mole/cu.ft.

$B_o, A_o, C_o, D_o, E_o, b, a, c, d, \alpha, \gamma$ = equation of state parameters

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