

## ACKNOWLEDGMENT

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## NOMENCLATURE

$\ln$  = natural logarithm  
 $n_1$  = mole fraction methane  
 $P$  = pressure, lb./sq. inch  
 $\rho$  = probability of a bubble being formed  
 $P_b$  = bubble point pressure, lb./sq. inch  
 $P_s$  = supersaturation pressure ( $P_b - P$ ), lb./sq. inch  
 $\theta$  = time, sec.  
 $\theta_b$  = time of strain to first bubble, sec.  
 $\theta_m$  = mean time corresponding to a given value of supersaturation pressure, sec.

## SUPERSCRIPT

\* = time average of quantity during run

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# *P-V-T* and Related Properties for Methane and Ethane

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The American Petroleum Institute Research Project 44 (19) began to work in 1952 on the collection and critical analysis and correlation of the existing data on the *P-V-T* and related properties for the simple hydrocarbons, with the aim of providing tables of selected values of these properties. The work has now reached the stage where the first tables of the series, on methane and ethane, are appearing. The first report (7) described the general plan of the work, the properties for which values are tabulated, the general procedure for analysis, correlation, and calculation of the data, and the tables produced and contemplated.

This second report describes in detail the treatment of the experimental data on *P-V-T* properties and the calculation of the related thermodynamic properties, and to give the results for methane and ethane. The work on the other compounds in the program, propane, *n*-butane, isobutane, *n*-pentane, etc., is similarly planned and will be reported in later papers.

## PROPERTIES TABULATED

The properties for which values for *P-V-T* and related properties are given in the tables of the API Research Project 44 are listed in detail in Table I, including the name, symbol, and units for the property, the units of temperature and pressure, and the letter identifying the given table.

The definitions of the thermodynamic symbols and standard states are given by Lewis and Randall (13), and Rossini (18), and in the earlier report (7).

In connection with the standard state for tables in which pressure is given in pounds per square inch, it should be noted that the standard state is the hypothetical state where the fugacity is 1 in the given units, in this case where the fugacity is 1 p.s.i.

## METHOD OF CALCULATION AND EQUATIONS INVOLVED

In the present report, only the region of "superheated" vapor is treated, with the discussion of the liquid and two-phase region being reserved for a later time.

The several investigators generally use different forms and values of the variable in making the measurements and reporting the results. For proper comparison of such heterogeneous data, a convenient and powerful method is to use an appropriate equation of state as a reference frame and to calculate the difference between the observed values and the corresponding ones given by the reference frame.

The equation of state used as the reference frame need not be one which reproduces the data accurately. Indeed, this might be an impossible requirement, since no known equation of state reproduces the most accurate data within the limits of uncertainty. The most useful property to use in evaluating that difference between the observed experimental value and the value calculated from the reference equation of state is that of volume, either molal or specific.

For the present work, the Benedict-Webb-Rubin (BWR) equation of state was selected to provide the reference frame because it reproduces the general character of *P-V-T* relationships better over a wider range of temperature and pressure than any of the other equations of state of similar complexity:

$$P = RTd + (B_0 RT - A_0 - C_0/T^2)d^2 + (bRT - a)d^3 + a\alpha d^6 + (cd^3/T^2)(1 + \gamma d^2)e - \gamma d^2 \quad (1)$$

In Equation 1,  $R$ ,  $P$ ,  $T$ , and  $d$  are the gas constant, pressure, temperature, and density, respectively, and  $a$ ,  $b$ ,  $c$ ,  $A_0$ ,  $B_0$ ,  $C_0$ ,  $\alpha$ , and  $\gamma$  are constants.

For the present work, it is necessary only that the selected set of constants to be used for the BWR equa-

tion for methane represent the data reasonably well. Accurate fit with any one lot of data is not necessary.

Letting  $V$  be the observed experimental volume, and  $V_{\text{BWR}}$  be the volume calculated from the BWR equation of state, we define a residual volume as

$$r_v = V - V_{\text{BWR}} \quad (2)$$

For each experimental volume at a given pressure and temperature, for each investigation, a value of  $r_v$  is determined. Suitable plots of the resulting values of  $r_v$  permit critical evaluation of the data and the fixing of a set of selected best values of  $r_v$  as a function of pressure at various temperatures. Suitable treatment then permits one to obtain at various desired pressures and temperatures the corresponding selected best values of the temperature coefficient of  $r_v$  at constant pressure,  $(\delta r_v / \delta T)_P$ .

The  $P$ - $V$ - $T$  data of all of the investigators of a given compound are reduced in this way to very small quantities which retain all the significant figures of the original data and which can also be easily compared because of their smallness.

Figures 1, 2, 3, and 4 represent graphically the residual volumes for methane and ethane, and illustrate the characteristics of the residual. Once a selection has been made, the selected values for the residual volume are smoothed and interpolated. The resulting appropriately interpolated values are added to the values of  $V_{\text{BWR}}$  which have already been calculated for evenly spaced values of temperature and pressure.

The final values of the compressibility factor are given as

$$Z = PV/RT = (P/RT)V = (P/RT)(V_{\text{BWR}} + r_v) \quad (3)$$

The related thermodynamic properties are obtained by use of the following equations.

Let

$$\alpha = RT/P - V \quad (4)$$

Combination of Equations 2 and 4 gives

$$\alpha = (RT/P - V_{\text{BWR}}) - r_v \quad (5)$$

Letting

$$\alpha_{\text{BWR}} = RT/P - V_{\text{BWR}} \quad (6)$$

Equation 5 becomes

$$\alpha = \alpha_{\text{BWR}} - r_v \quad (7)$$

Then

$$F - F_{\text{ideal}} = - \int_0^P \alpha dP \quad (8)$$

and

$$F - F_{\text{ideal}} = - \int_0^P \alpha_{\text{BWR}} dP + \int_0^P r_v dP \quad (9)$$

Denoting

$$(F - F_{\text{ideal}})_{\text{BWR}} = - \int_0^P \alpha_{\text{BWR}} dP \quad (10)$$

we can write

$$F - F_{\text{ideal}} = (F - F_{\text{ideal}})_{\text{BWR}} + \int_0^P r_v dP \quad (11)$$

Table I. Symbols, Name, and Units of Properties Tabulated

Symbol	Property Name	Units	Unit of Temperature	Unit of Pressure	Table Letter
$z$	Compressibility factor for real gas	None	$^{\circ}\text{K}$ .	Atm.	ja
$\gamma$	Activity coefficient for real gas	None	$^{\circ}\text{R}$ . $^{\circ}\text{K}$ .	P. s. i. Atm.	ja-E jb
$H - H^{\circ}$	Heat content (enthalpy) for real gas less heat content (enthalpy) of gas in standard state at same temperature	Cal./mole	$^{\circ}\text{R}$ . $^{\circ}\text{K}$ .	P. s. i. Atm.	jb-E jc
$(H - H^{\circ})/T$	Foregoing property divided by absolute temperature	B.t.u./lb. Cal./deg. mole	$^{\circ}\text{R}$ . $^{\circ}\text{K}$ .	P. s. i. Atm.	jc-E jd
$S - S_{\text{ideal}}$	Entropy for real gas less entropy for gas in ideal state at same pressure and same temperature	Cal./deg. mole	$^{\circ}\text{K}$ .	Atm.	je
$S - S^{\circ}$	Entropy for real gas less entropy for gas in standard state at same temperature	Cal./deg. mole	$^{\circ}\text{K}$ .	Atm.	jf
$F - F_{\text{ideal}}$	Free energy for real gas less free energy for gas in ideal state at same pressure and same temperature	B.t.u./lb. deg. R Cal./mole	$^{\circ}\text{R}$ . $^{\circ}\text{K}$ .	P. s. i. Atm.	jf-E jg
$F - F^{\circ}$	Free energy for real gas less free energy for gas in standard state at same temperature	Cal./mole	$^{\circ}\text{K}$ .	Atm.	jh
$(F - F^{\circ})/T$	Foregoing property divided by absolute temperature	Cal./deg. mole	$^{\circ}\text{K}$ .	Atm.	ji

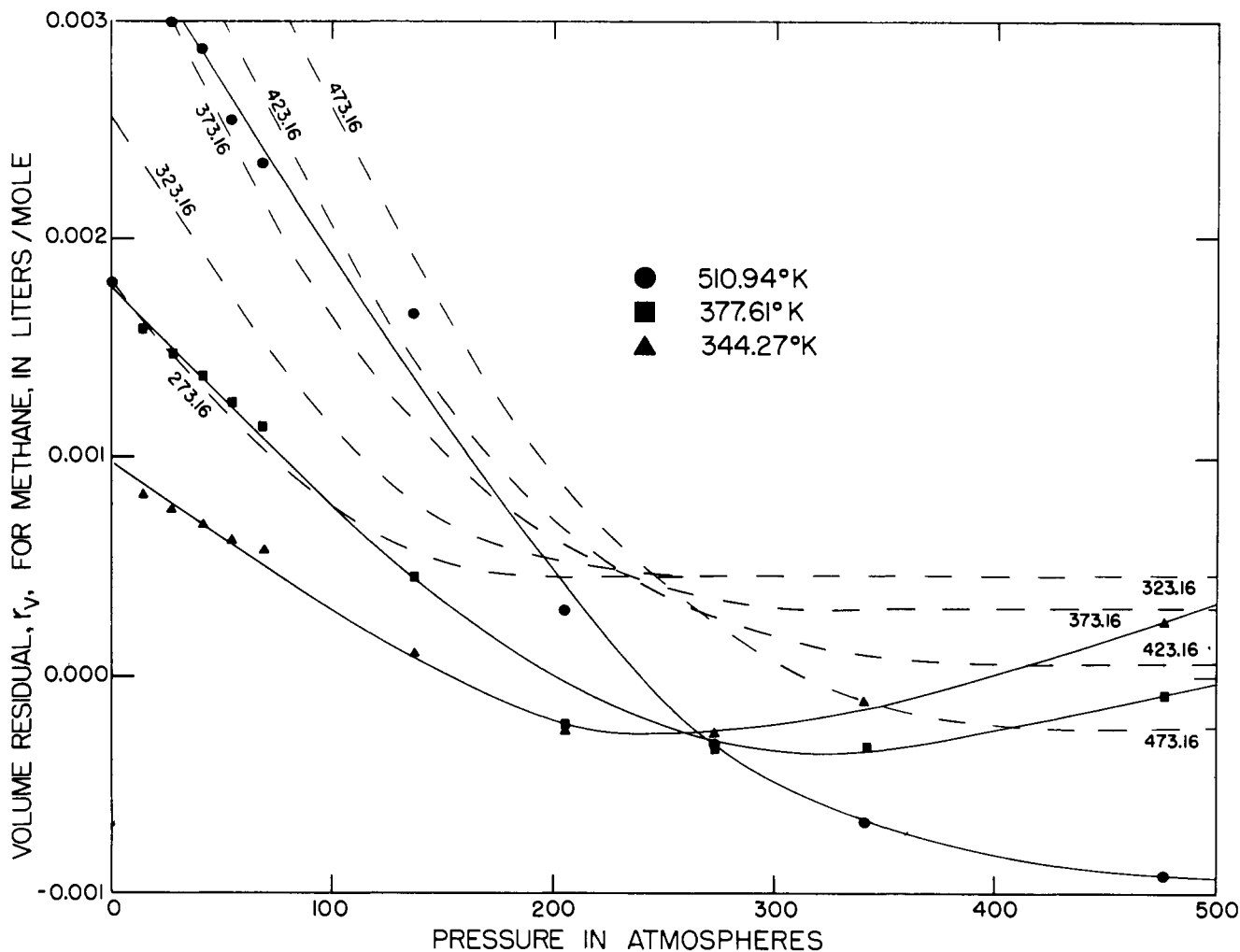


Figure 1. Comparison of smoothed volume residuals for methane. Dashed lines represent smoothed residuals  
 a. Michels and Nederbragt (14, 15)  
 b. Keyes and Burks (10)  
 c. Kvalnes and Gaddy (11)  
 d. Olds, Reamer, Sage, and Lacey (17)

In a similar way, we may write the corresponding equations for activity coefficient, entropy, and heat content:

$$\ln \gamma = (\ln \gamma)_{\text{BWR}} + (1/RT) \int_0^P r_v dP \quad (12)$$

$$S - S_{\text{ideal}} = (S - S_{\text{ideal}})_{\text{BWR}} - \int_0^P (\delta r_v / \delta T)_P dP \quad (13)$$

$$H - H_{\text{ideal}} = (H - H_{\text{ideal}})_{\text{BWR}} + \int_0^P r_v dP - T \int_0^P (\delta r_v / \delta T)_P dP \quad (14)$$

$$H - H_{\text{ideal}} = (F - F_{\text{ideal}}) + T(S - S_{\text{ideal}}) \quad (15)$$

In connection with the foregoing, the following relations are summarized, to bring in the standard state:

$$H = H_{\text{real}}; H_{\text{ideal}} = H^\circ \quad (16)$$

$$H - H^\circ = (H - H_{\text{ideal}}) \quad (17)$$

$$S = S_{\text{real}}; S_{\text{ideal}} = S^\circ - R \ln P \quad (18)$$

$$S - S^\circ = (S - S_{\text{ideal}}) - R \ln P \quad (19)$$

$$F = F_{\text{real}}; F_{\text{ideal}} = F^\circ + R \ln P \quad (20)$$

$$F - F^\circ = (F - F_{\text{ideal}}) + RT \ln P \quad (21)$$

$$(F - F_{\text{ideal}}) = (H - H_{\text{ideal}}) - T(S - S_{\text{ideal}}) \quad (22)$$

$$(F - F^\circ) = (H - H^\circ) - T(S - S^\circ) \quad (23)$$

$$(S - S^\circ) = (H - H^\circ)/T - (F - F^\circ)/T \quad (24)$$

$S_{\text{ideal}}$  at unit pressure is identical with  $S^\circ$ , and, similarly,  $F_{\text{ideal}}$  at unit pressure is identical with  $F^\circ$ .

In the foregoing equations, the quantities labeled with the subscript BWR, as

$$V_{\text{BWR}}, \alpha_{\text{BWR}}, (F - F_{\text{ideal}})_{\text{BWR}}, (\ln \gamma)_{\text{BWR}}, (S - S_{\text{ideal}})_{\text{BWR}}, \text{ and } (H - H_{\text{ideal}})_{\text{BWR}}$$

are computed from the appropriate thermodynamic relations from the BWR equation of state using an IBM 650 electronic computer.

The equations for calculating the values of  $(F - F_{\text{ideal}})_{\text{BWR}}$  from the BWR equation of state are:

$$(F - F_{\text{ideal}})_{\text{BWR}} = RT \ln dRT/P + 2d(BoRT - Ao - Co/T^2) + 3d^2/2 (bRT - a) + 6a\alpha d^3/5 + cd^2/T^2 [(1 - e^{-\gamma d^2})/\gamma d^2 + e^{-\gamma d^2}/2 + d^2 e^{-\gamma d^2}] \quad (25)$$

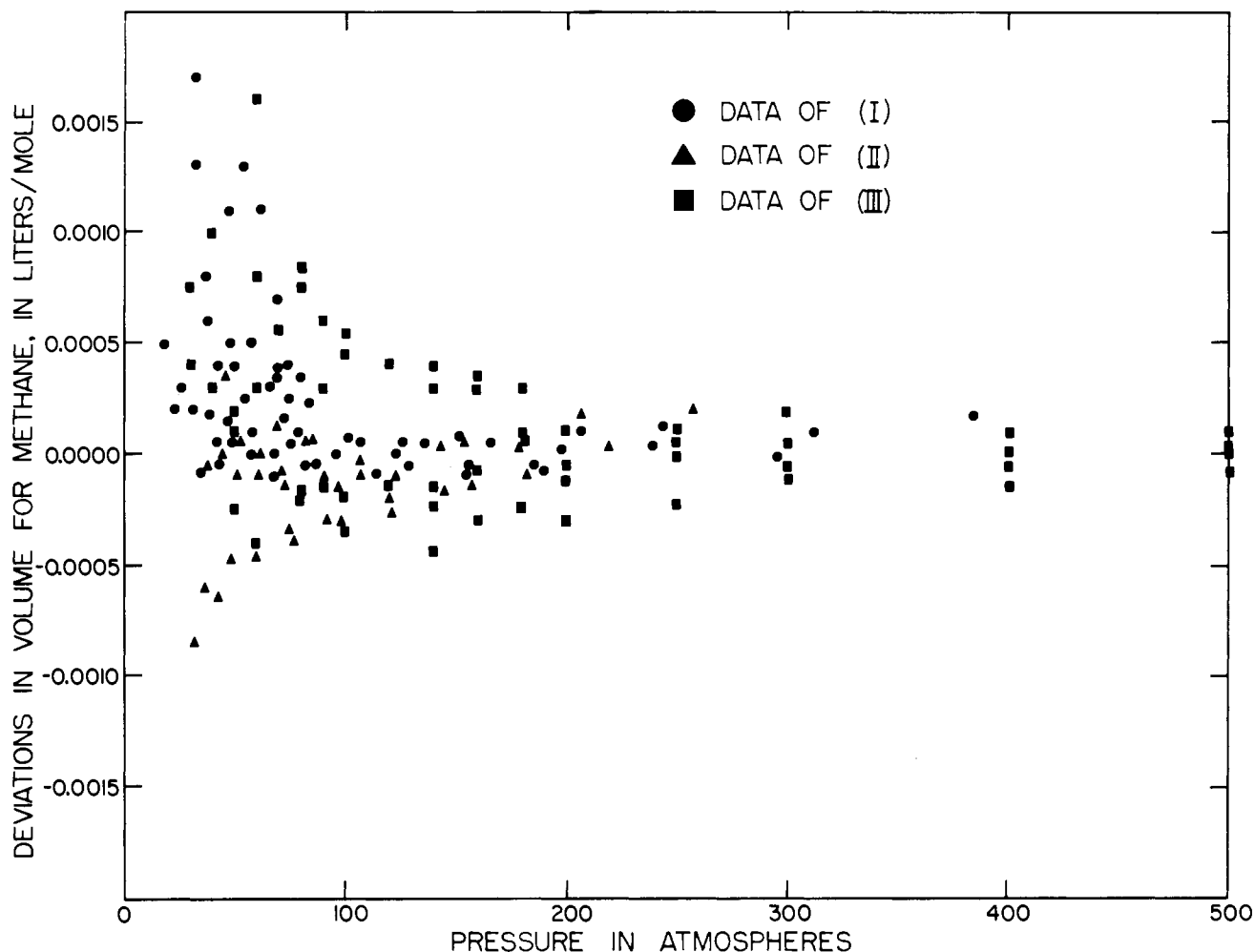


Figure 2. Differences between selected values of volume for methane and experimental data  
 I. Michels and Nederbragt (14, 15)  
 II. Keyes and Burks (10)  
 III. Kvalnes and Gaddy (11)

$$(S - S_{ideal})_{BWR} = -R \ln dRT/P - (BoRT + 2Co/T^2)d - bRd^2 + 2cd^2/T^3 [(1 - e^{-\gamma d^2})/\gamma d^2 - e^{-\gamma d^2}/2] \quad (26)$$

The great bulk of the calculations required for the many temperatures and pressures at which the final properties are to be tabulated involve the BWR equation of state and equations derived from it. Because this part of the program is essentially routine and is the same for all the compounds to be studied, an electronic computer, the IBM 650, is used to great advantage. A computing program has been devised and will produce in a matter of minutes all the calculated properties for any given compound once the BWR constants and prescribed levels of temperature and pressure have been determined.

Figure 5 is a schematic representation of the over-all computational program.

A second advantage in the use of the residuals can now be seen. From time to time  $P$ - $V$ - $T$  properties of the different compounds are remeasured and it becomes necessary to revise earlier selections of the "best" values. It is not necessary to repeat the entire program, but merely to re-examine the new residuals and change the tabulated values by the amount of change in the residuals only. In actual practice, this entails adding the newly revised residuals to the set of properties previously calculated by the computer using the BWR equation.

A close fit of the BWR equation to any particular set of data is not necessary, as the results of the IBM computa-

tion actually never appear in the final tabulation. They are subtracted from the original data to give the residuals and are then added back into the smoothed residuals to give smoothed experimental data.

#### REGIONS FOR WHICH EXPERIMENTAL DATA ARE NOT AVAILABLE

The equation of state has importance of its own, only in the matter of extrapolation of the  $P$ - $V$ - $T$  data to high temperatures and low pressures. It has been well established that isometrics—i.e., curves of pressure vs. temperature plotted at constant volume—are straight lines at high temperatures.

The form of the BWR equation of state exhibits this same characteristic

$$P = A + BT + C/T^2 \quad (27)$$

Thus the BWR equation which represents the experimental data at lower temperatures can be used for extrapolation to high temperatures. This use of the BWR equation is valid only for the very light hydrocarbons. The extrapolation will probably require careful study for the heavier compounds. Also, for the lighter hydrocarbons, experimentally determined saturated vapor volumes are either unavailable or unreliable. Because the BWR equation can be made to fit vapor pressure data fairly well, it can be used, when

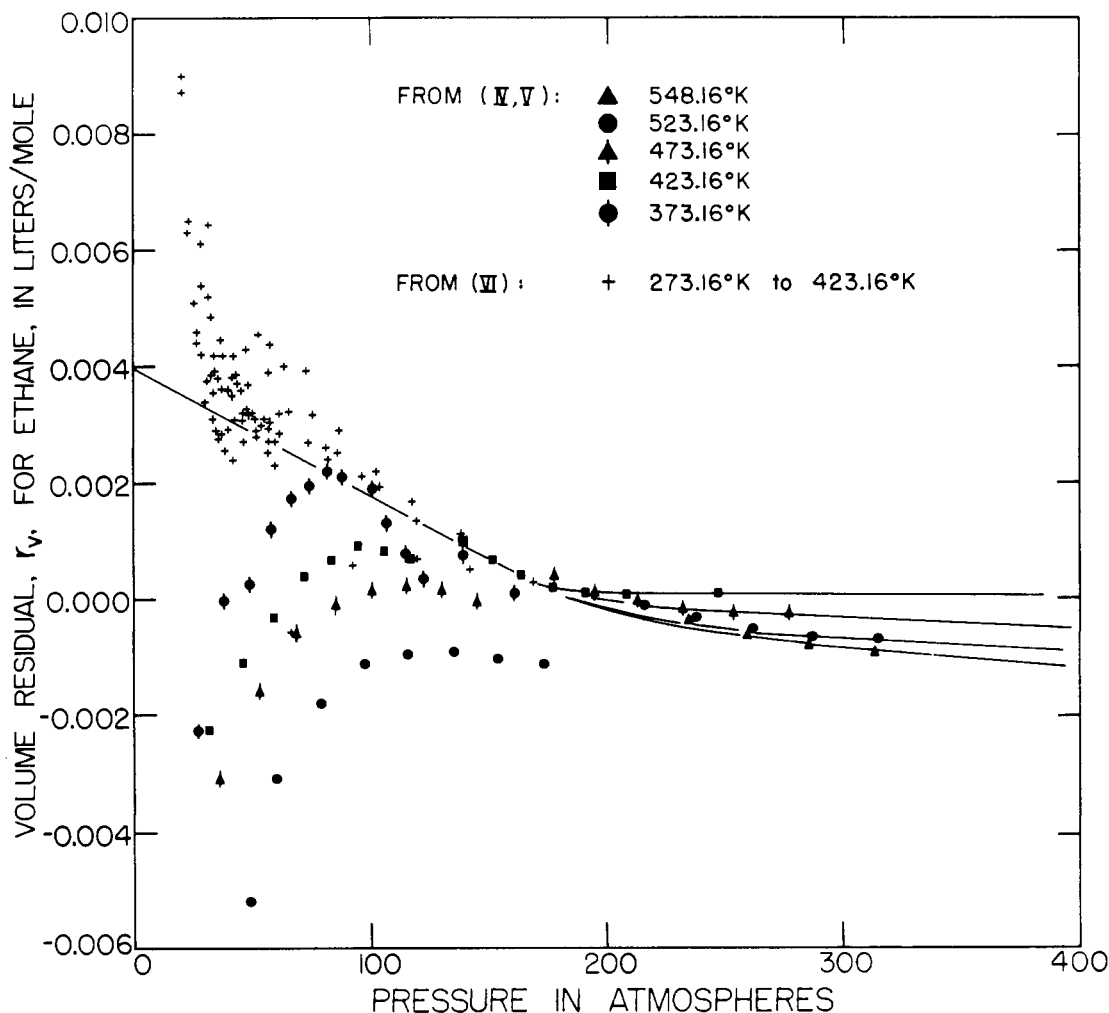


Figure 3. Comparison of selected volume residuals for ethane with experimental data

IV. Beattie, Hadlock, and Poffenberger (2)  
 V. Beattie, Su, and Simard (3, 4)  
 VI. Michels, Van Straaten, and Dawson (16)

necessary, for low pressure, low temperature extrapolation to the two-phase region.

#### VAPOR PRESSURES AND CRITICAL PROPERTIES

Reliable vapor pressures, critical properties, and  $P$ - $V$ - $T$  properties cannot be selected independently of one another, because they are all part of the same  $P$ - $V$ - $T$  surface. A critical analysis of vapor pressure and critical properties is therefore made simultaneously with the  $P$ - $V$ - $T$  study. The details of this phase of the work will be discussed at another time.

#### PROGRAM FOR COMPUTATIONS WITH IBM-650 ELECTRONIC COMPUTER

A detailed report describing the IBM 650 program for computing  $P$ - $V$ - $T$  and related thermodynamic properties using the Benedict-Webb-Rubin equation of state was prepared by Cohen (9).

Briefly, this program uses the BWR equation to compute in fixed decimal, the density roots, entropies, enthalpies, and other quantities for light hydrocarbons at preselected temperatures and pressures given in either English or c.g.s. units. Having once entered the main program into the 650, only a few input cards need be loaded to process successive compounds. Once the input data have been loaded, the program will be in complete control punching

two output cards for every temperature-pressure combination. Output cards will be in sort ready for listing all pressures for a fixed temperature.

#### PLAN AND DESCRIPTION OF TABLES

In the solution of a problem involving real states at some high pressure at a given temperature, the best procedure is to calculate the results for the thermodynamic standard reference states (or standard states, for short) at the given temperature, and then to compute, at that constant temperature, the change in the values of the properties in going from the standard states to the given real states at the high pressure. This means that a complete evaluation of the thermodynamic properties of a substance can be provided by means of a tabulation giving values of the several thermodynamic properties for the standard state at various temperatures, and a tabulation giving, for the same temperatures, values of the difference in the thermodynamic properties between the real states at various high pressures and the standard state.

The existing tables of the API Research Project 44 (1), which are labeled  $r$ ,  $s$ ,  $t$ ,  $u$ ,  $v$ ,  $w$ ,  $x$ , and  $y$  [see Rossini and Lyman (19) for description], contain an essentially complete framework of values for all the important thermodynamic properties for the standard state at various temperatures, generally from  $0^\circ$  to  $1500^\circ\text{K}$ .

The present work on  $P$ - $V$ - $T$  and related properties was

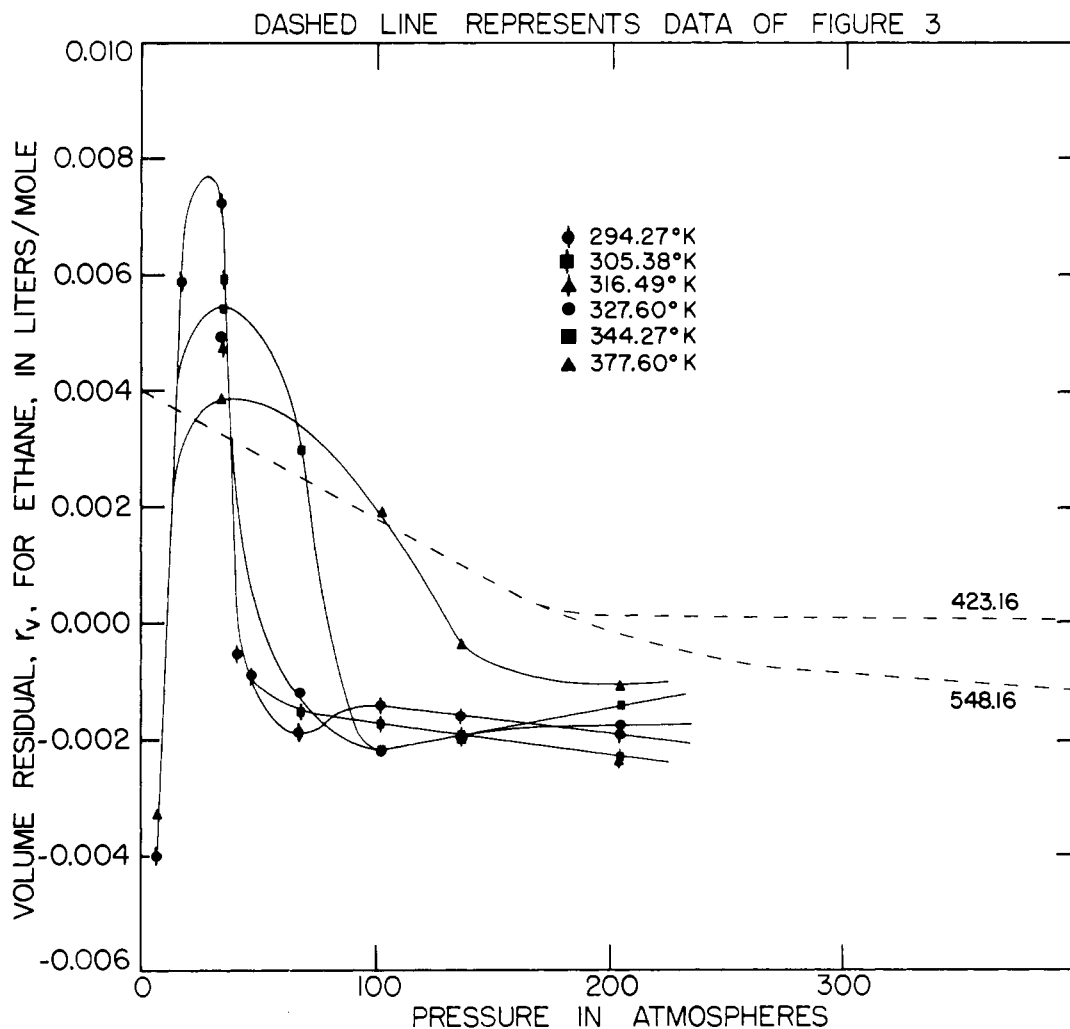


Figure 4. Comparison of selected volume residuals for ethane with data of Sage, Webster, and Lacey (20)

arranged so as to take full advantage of the existence of the tables of the API Research Project 44 containing values for all the regular thermodynamic properties for gaseous hydrocarbons in the standard state at temperatures from  $0^{\circ}$  to  $1500^{\circ}\text{K}$ . With these values available, one needs only to evaluate, for a given temperature, the property for the real gas less that for the standard state at the same temperature. By adding this latter difference to the value for the standard state, one obtains the value of the given high pressure at the given temperature.

For the tables of properties to have maximum utility it is necessary to space the independent variables, temperature

and pressure, so that simple interpolation is possible. Although it is desirable to have the tables arranged for linear interpolation, this would entail a prohibitively large number of tabulated values for each compound. As a compromise between facility of interpolation and number of tables, quadratic interpolation is the criterion used in determining the spacing of the independent variables.

If the three-point Lagrangian interpolation coefficients are used for interpolation, the maximum error incurred is less than 0.065 times the second difference of the tabulated function. In selecting the actual pressures and temperatures at which the properties are tabulated, the spacing is such that the second difference of the property is less than the uncertainty of the property divided by 0.065. Along the critical isotherm, a singular point appears at the critical pressure for most of the properties. Interpolation across the critical point is impossible. However, sufficient pressures are reported on either side of the critical region so that interpolation is possible on one side or the other.

Values for the properties of the superheated vapor are given at those pressures and temperatures at which only the liquid phase can exist as a stable state. This has been done to facilitate interpolation in the vicinity of the curve for the saturated vapor. It is also desirable in some engineering calculations to have values for these unstable states in order to estimate properties of mixtures. These values are marked by superscript *A* when they appear in the tables.

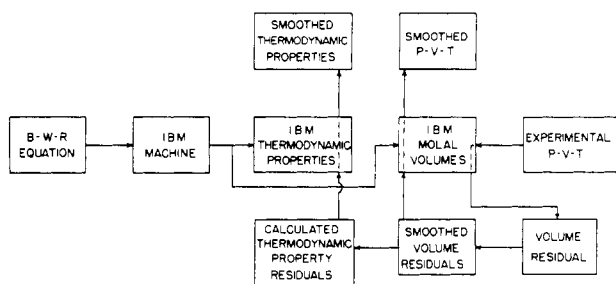


Figure 5. Schematic representation of plan of calculation of *P-V-T* and related thermodynamic properties of light hydrocarbons

## TREATMENT OF EXPERIMENTAL DATA

Before the most reliable data can be selected, it is necessary to plot all of the available data in the form of volume residuals so that agreement or disagreement between various investigators can be detected. After selection is made, the "best" curve is drawn through the data and in this way the residuals are smoothed. However, because three variables are involved this can only be accomplished isotherm by isotherm. Finally a cross plot of isotherms at constant pressure is developed to assure smoothness along isobars. This process is vitally important, not only to assure smoothness of the final tabulations in both temperature and pressure, but also to determine the temperature coefficient of the volume residual, which is required in the integrand of Equation 13. This cross plot smoothing process requires an adjustment of the original best curves drawn through isothermal data. In addition, it is imperative that the smoothed residuals extrapolate in a reasonable manner to zero pressure and high temperatures. This entire process is largely trial and error requiring considerable judgment and tedious checking. It is this process which cannot be generalized for all compounds and reduced to electronic machine instructions. The following section describes the results of this type of study for the compounds methane and ethane.

### P-V-T DATA FOR METHANE

The *P-V-T* properties of methane were measured by Michels and Nederbragt (14, 15), Kvalnes and Gaddy (11), and Keyes and Burks (10), along the same isotherms. Olds, Reamer, Sage, and Lacey (17) have measured additional data at other temperatures along with Burrell and Jones (6), who did extensive work at only one temperature. Cardoso (8) measured saturated vapor volumes.

Because Kvalnes and Gaddy (11) were the only investigators reporting data below the ice point, and extending to very high pressure, their data were used as a basis for comparison with Michels and Nederbragt (14, 15) and Keyes and Burks (10). The dashed lines of Figure 1 represent the final smoothed volume residuals based on these three investigations. Figure 2 is a representation of how closely the experimental data agree with the four isotherms of Figure 1. It can be seen in Figure 2 that for some isotherms the deviations of the data of Kvalnes and Gaddy (11) from the smoothed curve are high and for others they are low. The curves fit the data of Keyes and Burks (10) and Michels and Nederbragt (14, 15) more closely except at low pressures, where the deviations of the data of Michels and Nederbragt's tended to be high and those of Keyes and Burks (10) tended to be low. The upward sweep of the data of both Michels and Nederbragt (14, 15) and Kvalnes and Gaddy (11) could have been eliminated by forcing the isotherm at 423.16°K. of Figure 1 to sweep more sharply upward at low pressure. However, the compressibility factors, computed by using volume residuals extrapolated to zero pressure in this way, did not extrapolate in a reasonable manner to zero pressure—i.e., they assumed values of unity at about 5 atm. The residual isotherms could have been drawn downward or even horizontal at lower pressures to correct for this behavior in the compressibility factor. However, the uncertainty in the residuals as demonstrated in Figure 2 did not warrant drawing the isotherms in this manner.

Because Olds, Reamer, Sage, and Lacey (17) did not measure the same isotherms as those of the other investigators direct comparison is not possible. Figure 1 presents selected isotherms taken from their work. Their data lie somewhat below the data of the other three investigators.

Figure 2 indicates that the uncertainty in the residual volume is largest at low pressures. However, the molal volume at 30 atm. is of the order of magnitude of unity and

therefore an uncertainty of 0.001 is equivalent to 1 part in 1000. At 500 atm. the molal volume is roughly 0.1 and therefore an uncertainty of 0.0001 is still 1 part in 1000, although the absolute uncertainty is much smaller. It is obvious from such an analysis that the comparing of volume residuals is a very stringent test of *P-V-T* data.

In extrapolating the residual volumes to low temperatures, it is necessary to have at least saturated vapor volume to establish the boundary of the two-phase region. The work of Cardoso (8), which is the only experimental determination of the saturated vapor volume for methane, appears to be unreliable. This can be established by computing the volume residuals,  $\alpha$ , defined by Equation 4. Normally  $\alpha$  should decrease with increasing pressure or temperature along the saturated vapor curve. The  $\alpha$  computed from the data of Cardoso is nearly constant. One value for the saturated vapor volume can be estimated from vapor pressure data and the heat of vaporization at the boiling point by means of the Clapeyron equation. Cardoso's measurements disagree with this estimated saturated vapor volume by 3%.

In the absence of reliable experimental data, the BWR equation must be used for extrapolation to low temperatures. The use of the equation of state is justified only if the equation has been made to fit vapor pressure data. The particular set of constants used for methane were adjusted by Benedict, Webb, and Rubin (5) to give the proper values for vapor pressure. When  $\alpha$  is computed using BWR saturated vapor volumes, it behaves in the normal manner and the vapor volume at the boiling point agrees with that calculated from the Clapeyron equation to within 0.5%.

Extrapolation to higher temperatures was accomplished by assuming a constant value for the volume residual and zero slope for the isobars.

### P-V-T DATA FOR ETHANE

The *P-V-T* properties of ethane have been measured by Beattie, Hadlock, and Poffenberger (2), Beattie, Su, and Simard (3, 4), Michels, Van Straaten, and Dawson (16), Sage, Webster, and Lacey (20), Burrell and Jones (6), and Leduc (12). The most reliable data were selected from the measurements of Beattie, Su, and Simard (3, 4), and Michels, Van Straaten, and Dawson (16), which are presented in Figure 3. Beattie and his coworkers (2, 4) measured ethane at two different times. The first measurements in the low pressure region exhibited a large temperature coefficient for the volume residual. Later measurements in the high pressure region exhibited a convergence of the volume residual isotherm as the pressure decreased. Beattie (3) expressed greater reliance on the high pressure data than on the earlier measurements which manifested the greatest discrepancy at high temperatures. It was suspected by Beattie that a chemical change had occurred during the earlier measurements and this would be evidenced by a larger discrepancy at the higher temperatures. Recently Michels, Van Straaten, and Dawson (16) confirmed this when they measured volumes which exhibited a temperature coefficient of zero for the volume residual and which appeared to be a continuation of Beattie's high pressure data. Michels ethane data seem to have the same characteristic as his methane data, in that the volume residual tends to extrapolate high at low pressure. Once again, as in the case of methane, such an extrapolation appeared to be incorrect when compressibility factors were computed.

The data of Sage, Webster, and Lacey (20) are compared with the "selected" volume residuals in Figure 4. Their volume residuals fall below those of Figure 3.

No experimental determinations of the saturated vapor volumes have been made. Therefore, the BWR equation combined with the selected residuals of Figure 3 was used

for extrapolation to lower temperatures. For extrapolation to high temperatures the value of the volume residual was assumed to be constant and the slopes of the isobars were taken as zero.

The uncertainty in the volume residuals for ethane appears to be somewhat larger than those for methane at low pressures, but are probably less than 2 parts in 1000. At higher pressures, data of equally reliable investigators are not available for comparison and an estimate of uncertainty cannot be made. However, from studies of Beattie's measurements on other compounds, it is safe to assume an uncertainty of less than 1 part in 1000 for the volume residuals at higher pressures.

#### UNCERTAINTIES IN FINAL VALUES TABULATED

The uncertainty in the value for free energy,  $F - F_{\text{ideal}}$  and  $F - F^\circ$ , is equal to the integral of the uncertainty in the volume residual with respect to pressure. For methane and ethane the upper limit of this uncertainty in the regions where experimental  $P$ - $V$ - $T$  data are available is of the order of magnitude of 1.0 cal. per gram-mole at 50 atm., 2.0 cal. per gram-mole at 100 atm., 5.5 cal. per gram-mole at 500 atm., and 8.0 cal. per gram-mole at 1000 atm. These uncertainties are somewhat larger in the extrapolated regions of low and high temperatures.

It is impossible to estimate the uncertainty in the value of entropy, because the temperature coefficient of an uncertainty is involved. Considering methane alone for the time being, it can be seen in Figure 1 that while the volume residuals of selected data differ markedly from those of Olds, Reamer, Sage, and Lacey, the slopes of the volume residual isobars are in fair agreement. There is a strong temptation to estimate a very small uncertainty in the temperature coefficient of the volume residual and a correspondingly small uncertainty in the entropy functions. On the other hand, if the curves of Figure 4 were selected as the most reliable data, a very slight change in the steep slope of the low temperature isotherms could result in a considerable change in the slope of the isobars. As no estimate of uncertainty of the entropy residual can be made by an analysis of the volume residuals, it will suffice to place an upper limit on the possible magnitude of the uncertainty.

A rough estimate of the upper bound of the uncertainty in the isobaric slope can be taken as twice the uncertainty of the volume residual divided by the temperature interval over which the isobar is monotonic. For methane and ethane the upper bound on the possible uncertainty in the entropy functions,  $S - S_{\text{ideal}}$  and  $S - S^\circ$  is approximately 0.01 the uncertainty in the free energy functions.

The heat content or enthalpy may be considered as combinations of the free energy and entropy according to Equations 15 and 23. Therefore the upper limit on the uncertainty in the enthalpy may be taken as the uncertainty in the free energy function plus the uncertainty in the entropy multiplied by the absolute temperature.

By suitable mathematics it can be shown that the uncertainty in the activity coefficient is less than 0.5 the uncertainty in the free energy function divided by the absolute temperature.

For compounds other than methane and ethane, the

estimates of uncertainty will not be the same as those given here. Each compound must be analyzed separately. However, the method of analysis will be similar to that used for methane and ethane.

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#### CORRECTION

##### Vapor Pressure and Viscosity of Solutions in the Calcium Oxide-Phosphoric Oxide-Water System at 25° C.

In the article "Vapor Pressure and Viscosity of Solutions in the Calcium Oxide-Phosphoric Oxide-Water System at 25° C." [E. O. Huffman, J. D. Fleming, A. J. Smith, *Ind. Eng. Chem., Chem. Eng. Data Series* **3**, No. 1, 17 (1958)] on page 18 in the second paragraph under Results, the figure for uncertainty in the density should be 0.0004 gram per ml.