

Norske Sivilingeniørers Forening

NORTH SEA FLOW METERING
WORKSHOP

Stavanger

30 Aug. - 1 Sept. 1983

Calculation of Liquid Densities
and Their Mixtures

D. K. Petree
G. H. Thomson
R. W. Hankinson
Phillips Petroleum Company

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THE CALCULATION OF LIQUID
DENSITIES AND THEIR MIXTURES

Donald K. Petree*

George H. Thomson**

Risdon W. Hankinson*

Phillips Petroleum Company
Bartlesville, OK 74004

*Corporate Engineering - Process Division

**Information Services - Technical Systems Division

1.0 METHODOLOGY

There are three physical phenomena that must be taken into account by any valid model of the density behavior of pure liquids and their mixtures. The intentional and, hopefully, well-informed neglect of any of these phenomena places well defined limitations on the potential application of the resulting model. The intentional omission of the so called "dilation effect" from the list of phenomena considered, automatically limits the scope of this paper to liquids well-removed from their critical region.

TEMPERATURE EFFECT

The expansion and contraction of the volume of a fixed mass of constant composition liquid is the most significant departure term that must be quantitatively described. The change in specific volume with a change in temperature is defined by the thermodynamically fundamental term known as the coefficient of thermal expansion.

$$\alpha = \frac{1}{V} \frac{dv}{dt} \quad (1)$$

The final form of any model relating alpha to easily obtainable measurements depends upon the integration of this basic definition. The integration, in turn, depends upon the assumptions made and the sequence in the derivation at which the assumptions are invoked.

Typical temperature corrections for hydrocarbon oils in the neighborhood of 0.62 specific gravity are about 0.09% per °F (0.2% per °C). Data that have been developed on butanes and lighter show much higher corrections, 0.2% per °F (0.4% per °C).

PRESSURE EFFECT

Compressibility is a physical property causing an isothermal reduction in volume occupied by a constant composition fluid as pressure increases. The degree of compressibility of liquids is defined by the instantaneous compressibility.

$$\beta = \left(-\frac{1}{V} \right) \frac{dv}{dp} \quad (2)$$

This equation states that the compressibility is the slope of the P-V

curve at a given pressure and temperature divided by the total volume at that pressure. For industrial applications the pressure effect is normally expressed by compressibility factors.

$$F = \frac{1}{\Delta P} \left(1 - \frac{V}{V_s} \right) \quad (3)$$

which can be written

$$F = \left(\frac{V_s - V}{P - P_s} \right) \left(\frac{1}{V_s} \right) \quad (4)$$

In this equation $\Delta V/\Delta P$ represents the mean volume change from saturation pressure to system pressure.

For heavy hydrocarbons at pressures and temperatures well below their critical condition, the adjustment for pressure is small. It is on the order of 0.00005% per psi (0.0003% per kPa). For light hydrocarbons at 100°F, the correction is in the magnitude of 0.004% per psi (0.024% per kPa).

MIXING EFFECT

The volume of hydrocarbon mixtures will be less than the combined volume of the components existing at the same conditions. The magnitude of this "volume shrinkage" is dependent on the composition and type of hydrocarbons being blended as well as the temperature and pressure of the resulting mixture.

This chemical/physical phenomenon is caused primarily by three basic factors.

- When combining components whose molecules differ considerably in size, the smaller molecules pack into voids between the larger molecules.
- When the operating conditions approach the critical conditions of one of the components, there is more free space between the molecules of the near critical component. In addition, the increased kinetic energy causes the molecules of the near critical component to become malleable. This permits the more stable molecules of the heavier, and larger, components to force their way between the lighter molecules. This effect is typical in NGL streams where ethane is a near critical material. The excess volume in this case can exceed -5% and increases with decreasing pressure and increasing ethane mole fraction (18).

- When the components exhibit a high degree of hydrogen bonding, the pseudochemical effect produces more compact volumes than can be attributed to the purely physical mixing phenomenon previously described. The chemical shrinkage upon mixing is accompanied by discernable heat release.

The modeling effort usually attempts to account for the temperature and pressure effects by various integrations of Equations (1) and (2). Hence it is convenient to define two states of liquids, one of which is pressure independent.

SATURATED LIQUIDS

A saturated liquid is a pure liquid in equilibrium at its own vapor pressure, or a liquid mixture at its bubble point, either being at a specified temperature. The bubble point pressure is that pressure at which the first bubble of vapor forms. Densities of such liquids are sometimes called "orthobaric" or "bubble point" densities. It is easily shown by the Phase Rule that in either case pressure is not an independent variable.

COMPRESSED LIQUIDS

A compressed liquid is defined as one for which the pressure at the prevailing temperature is greater than the vapor pressure for a pure compound or greater than the bubble point pressure for a multicomponent liquid mixture. The densities of many compressed liquids at nominal pressures are not much different from the saturated densities. In fact, for many process applications this difference is considered to be insignificant. Thus, in these cases, the saturated liquid densities often adequately represent compressed liquid densities for up to several atmospheres of excess pressure. On the other hand, at very high pressures, or even at moderate pressures for liquid metering operations, changes in liquid density may be of considerable importance. This is especially true of liquid determinations for the purpose of custody transfer of such liquids as LNG/LPG mixtures and NGL products. In these cases, the pressure effect is significant and a high degree of accuracy of quantity measurement is required.

The comparative temperature and pressure effect on compressibility factor with increasing molecular weight of the liquid is shown in Figures 1 and 2.

The models used to represent these effects may be classified as Factor Models or Compositional Models.

FACTOR MODELS

Factor models express the temperature and pressure dependence as differences in density from a known or base density. For example, the

FIGURE 1

COMPRESSIBILITY OF LIQU

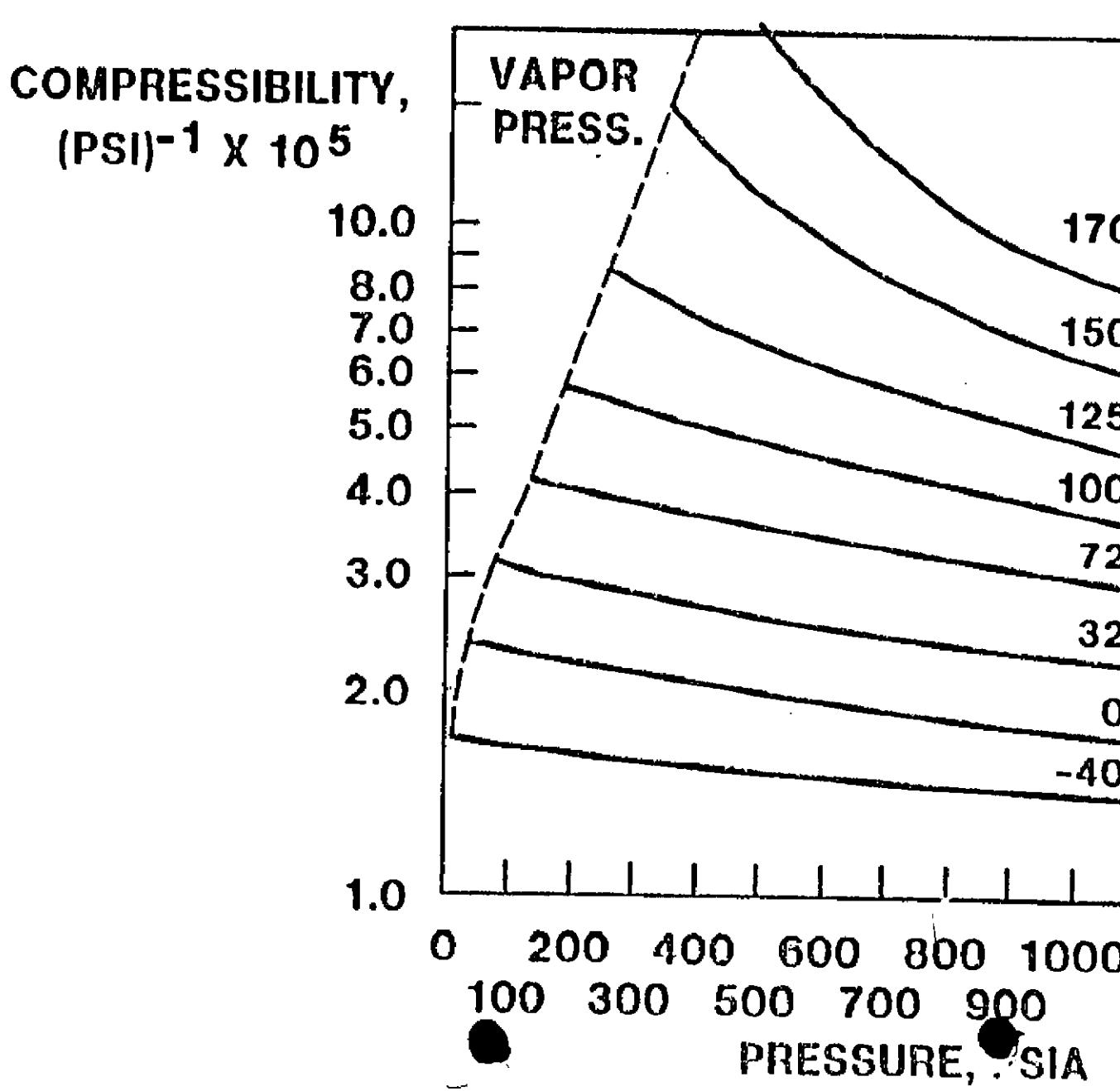
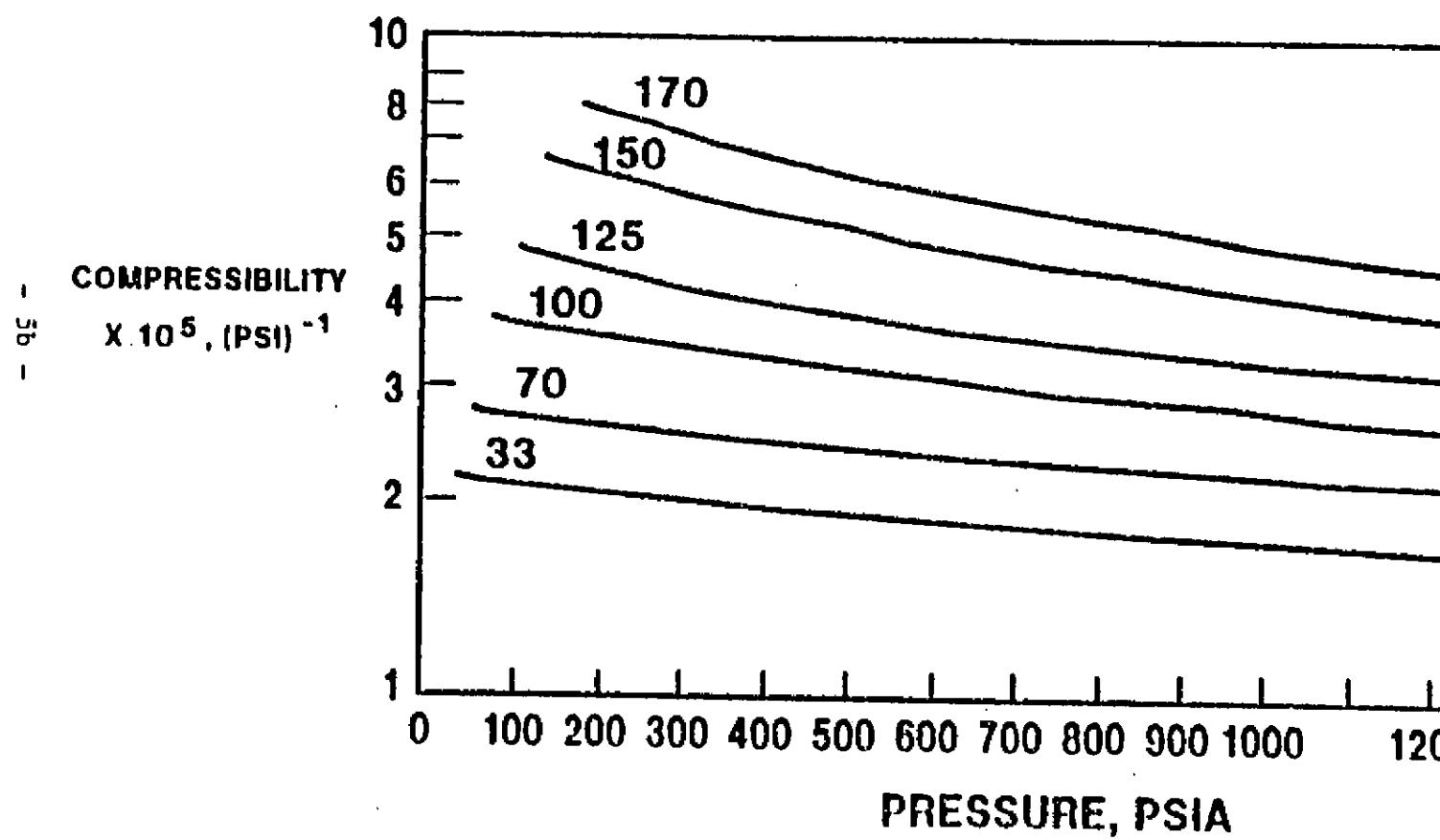


FIGURE 2

COMPRESSIBILITY OF LIQUID ISOBO



oil industry expresses the temperature dependence in terms of a volume correction factor defined by

$$VCF = \rho / \rho_t \quad (5)$$

Where VCF is a function of temperature and base density, ρ_t . The base density may be at 60°F, 15°C or 20°C depending on the particular national standard being used (10).

The factor approach is based on the requirement that the base density is known. This known value is usually measured but may be computed from a compositional model in some cases.

The factor approach has the built in assumption that mixing effects are not functions of temperature or pressure. Hence the measurement of a 60°F density of a mixture of specified composition takes the mixing effect into account. The factor model approach then corrects this single measurement for temperature and pressure variation.

The approach is highly accurate when used for oils and petroleum fractions with densities greater than 620 kg/m³ at 60°F (10, 11).

The compositional effects on light ends are, however, dependent on both temperature and pressure. Hence, the attempt to factor density from a base value for the light ends results in a significant loss of absolute accuracy.

COMPOSITIONAL MODELS

The compositional model depends on both the existence of a sufficient analysis of the compositions of the molecular species involved and on a set of mixing rules capable of blending model parameters using these compositions.

The simplest compositional model is the "Law of Additive Volumes".

$$V_{MIX} = \sum_i x_i V_i \quad (6)$$

This common model is useful for process calculations involving mixtures comprised of components of similar molecular size and structure. Expected errors are, when the equation applies, on the order of 3 to 5%.

The challenge of the accurate compositional model is the adequate representation of the mixing effect. Hence, the typical set of mixing rules are far more complicated than shown in Equation (6).

2.0 SATURATED LIQUID DENSITIES

2.1 FACTOR MODEL FOR SATURATED LIQUID DENSITIES

The most common Factor Model in worldwide use is embodied in the Petroleum Measurement Tables (1980). These are represented by API Standard 2540, IP Standard 200, ASTM Standard D1250 in addition to the standards of other national bodies and the International Standards Organization, ISO/R91 (10, 11).

The approach was developed in 1916 by Beurce and Peffer (2). Their data base consisted of but 18 crude oils and 60 products. All samples were of American origin. These original tables, with few additions over the years, were the basis for oil and hydrocarbon product measurement until 1980.

In 1972, citing studies by Downer and Inkley, The Institute of Petroleum showed that thermal expansion coefficient data for crude oils of current economic importance had thermal expansion coefficients averaging 5% greater than those represented in the 1940's edition of Table 6 in API Standard 2540 (3).

In 1974, the American Petroleum Institute (API) and the National Bureau of Standards (NBS) initiated a cooperative venture, funded by the API, to create a data base of density measurements on both crude oils and refined petroleum products. The joint venture by API and NBS provided the scientific data base for the development of the more accurate measurement tables (5).

The completion of this five year, \$500,000 project in March, 1979 provided the necessary data to modernize the tables of API Standard 2540. Using the NBS density data and related publications of outstanding technical authorities, the members of the Physical Properties Working Group of the API/ASTM Joint Committee on Static Petroleum Measurement (COSM) produced the modernized tables for Volume Correction Factors presently available from American Petroleum Institute.

The new tables were developed from the NBS data by screening the data by the use of linear equations and computer generated plots. During the screening process it was determined that there were five major identifiable groups of materials that had significantly different

relationships between the coefficient of thermal expansion and density. The five groups are shown in Figure 3. The coefficient of thermal expansion of crude and the four classes of products (gasolines, jet fuels, fuel oils and lube oils) follow separate curves as a function of inverse density squared, or corresponding °API Gravity ranges. Figure 4 shows a more detailed breakdown of the product classification with respect to the °API Gravity ranges and groups. Thus the strict factor model was modified to incorporate the compositional effect by grouping materials into classes.

A study of Figure 3 shows that it was not possible to represent the different classes of fluids with a single equation or table. Hence, separate tables were developed to represent crude oils and products. The products table consists of segments representing each of the major products classes as shown in Figure 5. The dashed region, called the transition zone, was filled in to eliminate any discontinuities in the tables.

In addition to the crude and products tables, a third type of table was developed for special applications. This third table provides a mechanism for incorporating those materials that do not have thermal expansion properties similar to those fluids tested by the NBS. It is highly probable that most materials of this class are not naturally occurring petroleum oils or products obtained from such oils. It is anticipated that this third table will find maximum utilizations in the custody transfer of alternate energy fluids. Such applications include liquids from coal, tar sands, shale oils and blends of petroleum with the biomass fluids or alcohol from other sources. This, of course, does not prevent the special application tables from being used for crudes and products under the conditions described below.

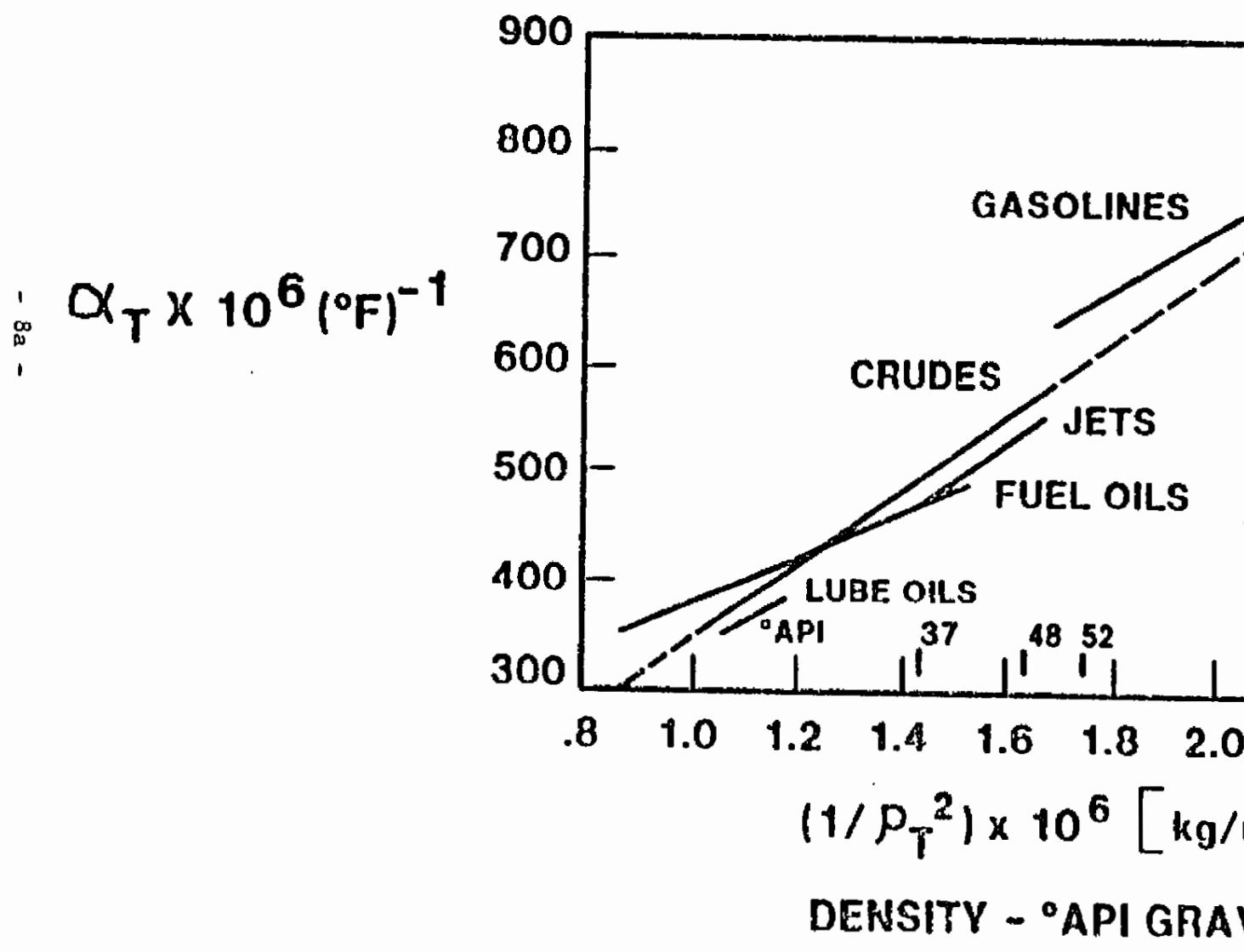
The new tables retained the format of the old Table 6, with Volume Correction Factors or densities tabulated as functions of temperature. The Products Table was computed in the segments shown in Figure 5 and tabulated below:

Products	°API Gravity
Fuel Oils	0 to 37
Jet Fuel Type A & Al	37 to 50
Gasolines	50 to 85

Crude oil covers a range from 0 to 100° API Gravity.

Table 6C, the Special Application Table, represents tabular entries of volume correction factor against thermal expansion coefficient and temperature. It is suggested that Table C be used when:

FIGURE 3
**COEFFICIENTS OF EXPANSION
FOR FIVE STATISTICALLY HOMOGENEOUS**



CLASSIFICATION OF PROD INTO GROUPS

- GASOLINE**

$50 \leq {}^{\circ}\text{API} < 80$

- JET FUELS**

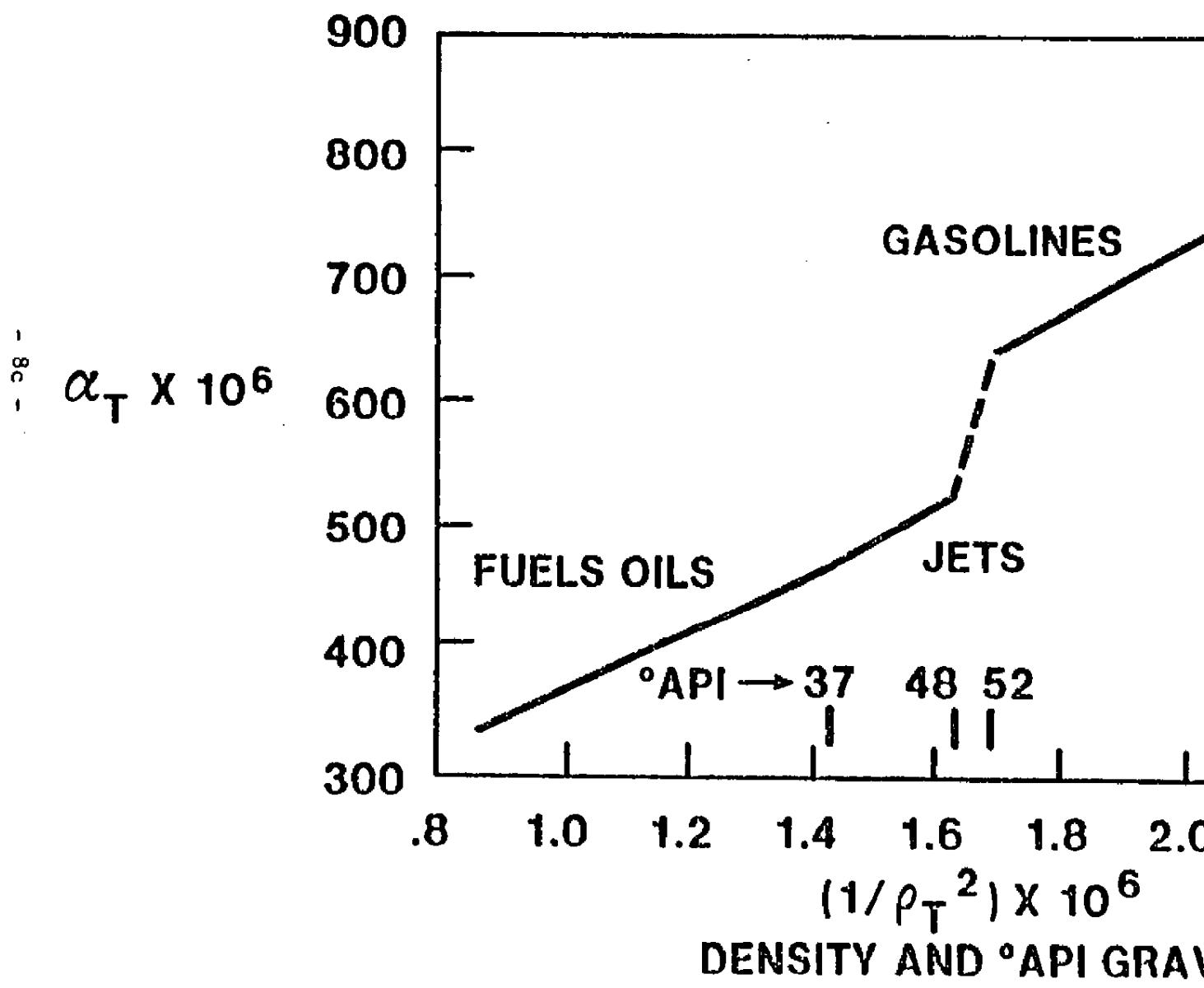
$37 \leq {}^{\circ}\text{API} < 50$

- FUEL OILS**

$0 \leq {}^{\circ}\text{API} < 37$

- LUBRICATING OILS**

FIGURE 5
COEFFICIENTS OF EXPANSION
PRODUCT TABLES, TAB



1. Tables A & B do not adequately represent the thermal expansion properties of the fluids of interest and;
2. Precise thermal expansion coefficients may be obtained directly or indirectly by experiments, and;
3. If buyers and sellers of petroleum products or crude agree that for their use, a greater degree of equity can be obtained.

CORRELATION DEVELOPMENT

The 2,278 point NBS/API data base was reduced to a predictive correlation using an integrated form of Equation (1). Equation (7) was premised

$$\alpha = \alpha_T + \beta \Delta t \quad (7)$$

where: $\alpha_T = \alpha$ at the base temperature.

β = a function of α and is independent of temperature. Hence, from Equations (1) and (7):

$$\frac{1}{V} \frac{dV}{dt} = \alpha_T + \beta \Delta t \quad (8)$$

$$\Delta t = t - T$$

which can be rearranged and integrated between t and T to give:

$$\ln \frac{V}{V_T} = \alpha_T \Delta t + \frac{\beta}{2} \Delta t^2 \quad (9)$$

A study of the NBS data demonstrated that:

$$\beta = K \alpha^2 T \quad (10)$$

where k is a temperature-independent constant.

These equations were statistically validated by computer studies of the NBS data base. The precise value of k was selected from a consideration of: (a) the computer studies, (b) the theoretical curvature of density with temperature, and (c) high temperature literature data on crudes, petroleum fractions, and C₆ through C₃₂ alkanes.

These literature data were obtained from the work of Jessup and Orwell and Flory. The value of k best expressing these criteria is 1.6 (10).

Thus, Equation (9) becomes:

$$VCF = \frac{V_T}{V} = \frac{\rho}{\rho_T} = EXP \left[-\alpha_T \Delta t (1 + 0.8 \alpha_T \Delta t) \right] \quad (11)$$

where: t = any temperature

T = base temperature

Equation (11) is valid for a particular fluid of known alpha.

It was determined that the coefficients of thermal expansion at the base temperature for each group are related to the densities at the base temperature by

$$\alpha_T = \frac{K_0 + K_1 \rho_T}{\rho_T^2} \quad (12)$$

The values of K_0 and K_1 were established for each major group from a

simultaneous nonlinear regression of all data points within that group.

The results and accuracy indicators are presented in Tables 5 and 6. Percent standard deviation given in the table is defined by:

$$\sigma = \left[\sum_{i=1}^{NO} \left(\frac{\rho_i - \rho_c}{\rho_i} \right)^2 / (NP-1) \right]^{1/2} \times 100$$

NP = number of points

NO = total number of observations in a group

A complete set of results including the percent standard deviation, the maximum percent error, the density at 60°F and the coefficient of thermal expansion is presented in API documents for each sample. This information comprises a portion of the printed documentation in the final edition of the Tables. (1)

TABLE 1

Constants to relate thermal expansion coefficient at base temperature to base density.

Group	K ₀	K ₁
Crude oils	341.0957	0.0
Gasolines	192.4571	0.2438
Jet fuels	330.3010	0.0
Fuel oils	103.8720	0.2701
Lubricating oils	144.0427	0.1896

Constants for English units (per °F). Obtained from global regression of NBS data.

TABLE 2

Results of global regression of NBS data to final equations.

	No. of points	Percent standard deviation
Crude oils	690	0.0253
Gasolines	436	0.0266
Jet fuels	351	0.0174
Fuel oils	617	0.0180
Lubricating oils	107	0.0197

Because of the economic impact of the new table, two major independent tests were commissioned. The first, a study of Prudhoe Bay crude oil, supplied by SOHIO, was performed in the laboratories of Phillips Petroleum Company. A detailed description of these results is given in Volume X of the new table (1). These data both confirmed the accuracy of the new table and showed errors of up to 0.3 percent in the old tables. The results are shown graphically in Figure 6.

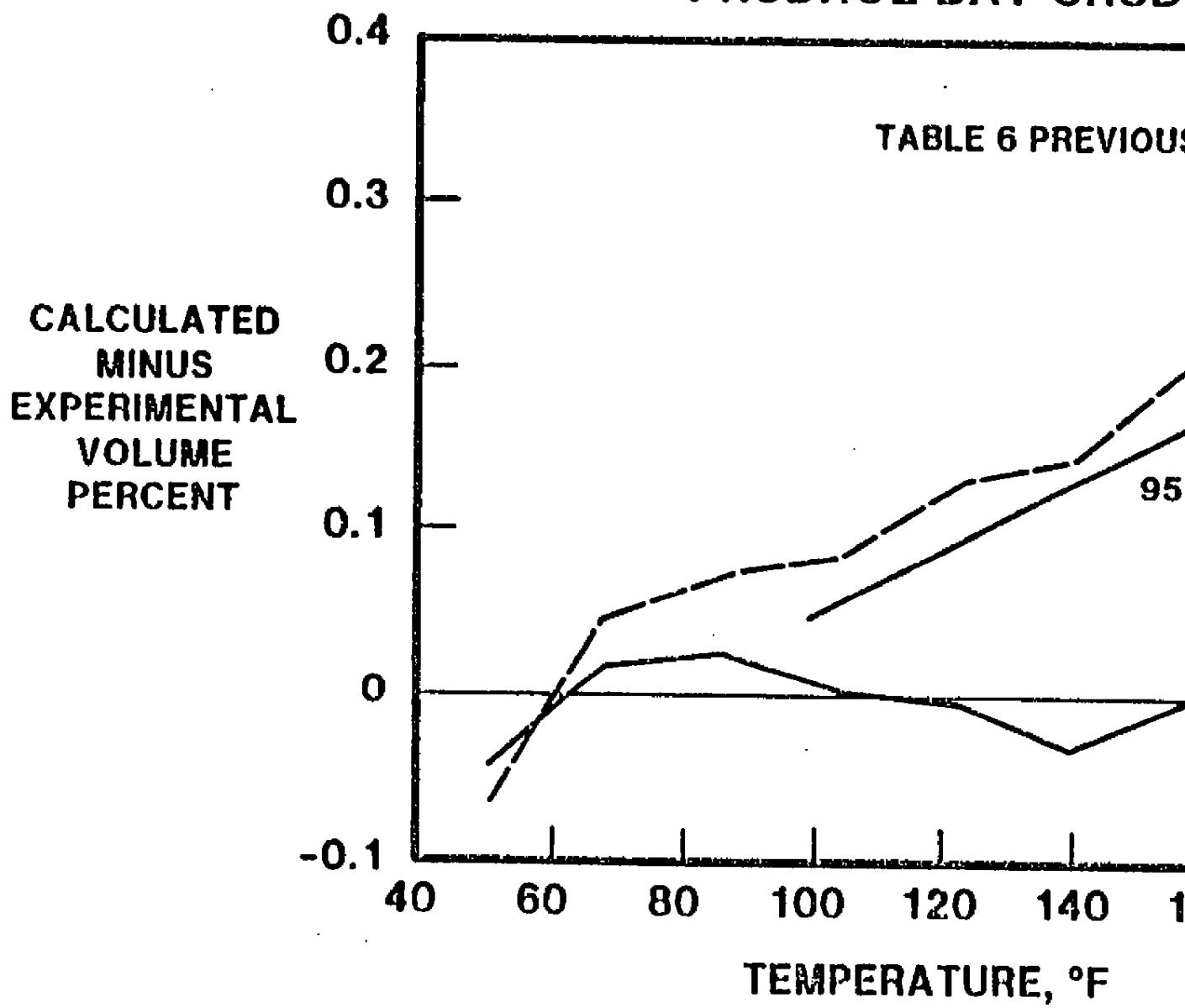
The second set of tests were performed on twenty of the original samples at temperatures up to 300°F and down to -50°F. The results of these tests, which were performed under API contract at the University of Missouri-Rolla, have not yet been publically released. The evaluation definitely shows a confirmation of the new tables to 300°F and to low temperatures of -50°F. (16)

Expansions to the Factor Model have been developed for lubricating oils (12) and gasohol (13). The lubricating oils publication became the source document for the fourth in the series of standard tables and was given the designation "D" series.

In summary, the new tables are based on the largest and most representative set of density data on oils and fractions ever collected. The data were measured by the most modern techniques in one of the most highly respected laboratories in the world; that of the U.S. National Bureau of Standards.

The crude oils in the data base were obtained from over 40% of the world's crude production in 1974. The refined products were representative of the major classes of fluids transported in bulk. When compared to the limited amount of data on primarily domestic stock collected in 1915 and the late 1920's, which formed the basis of

FIGURE 6
PRUDHOE BAY CRUD



the old measurement tables, the new data base must be considered orders of magnitude more representative of modern crudes and products.

These new measurement tables will significantly improve the pipeline industry's ability to measure petroleum more accurately in custody transfer transactions and improve operating overages and shortages caused by these transactions. (4)

2.2 COMPOSITIONAL MODELS FOR SATURATED LIQUID DENSITIES

Liquid density correlations may be divided into classes in another way. They may be empirical, theoretical, or semitheoretical in origin. Most of the published correlations have been empirical; that is, they are not based on any particular physical model. The developer of the correlation has found some mathematical expression describing the relationship between one or more independent variables, usually temperature, pressure, and composition, and the dependent variable, density. Theoretical correlations are derived from the behavior of well-defined models. Two examples are the hard sphere model in which the atoms or molecules of the liquid are assumed to behave as rigid spheres, and the cell model in which each atom or molecule of the liquid is assumed to be contained in a cell or cage made up of the other liquid particles.

There are also some theoretical models describing the behavior of mixtures. Some of these models are based on the assumption of random mixing while others treat non-random mixing. Corresponding states correlations may be considered to be semitheoretical in that they adhere to the Principle of Corresponding States but the analytical forms are of empirical origin.

The principal of corresponding states was developed from the observation of experimental data. It was discovered that many properties of pure compounds change by about the same percent when compared on a common basis. The classical common basis is the same reduced temperature and pressure. The reducing parameters are the critical temperature and the critical pressure. Enhancements to the principal have been common during the past twenty-five years. The most successful enhancement is the addition of a "third parameter" by Curl and Pitzer. They called their third parameter the acentric factor.

The use of the principal of corresponding states for mixtures presents a significant problem. A suitable set of reducing parameters must be selected to represent mixture behavior as a function of composition. The reducing parameters for mixtures are called pseudocritical properties and are defined by a variety of mixing rules.

Equations of state, relationships between pressure, temperature, and composition, are sometimes used to calculate both liquid as well as vapor densities. They have one advantage over most liquid density correlations: the calculated properties change smoothly as the critical region is crossed. This is not generally true of liquid density correlations. However, equations of state such as the Soave-Redlich-Kwong and the Peng-Robinson equations are generally not suitable for accurate calculation of liquid densities. Errors in liquid densities calculated using equations of state are seldom smaller than five percent and are often as large as ten to fifteen percent.

In the discussion below, the application of saturated liquid density correlations to LNG's will be emphasized.

KLOSEK-MCKINLEY CORRELATION (15)

This correlation has been called a "totally empirical recipe for calculating the density of an LNG-like mixture." (2)

The calculated density is a function of temperature and composition, but not of pressure. The specific volume of the mixture is calculated from the equation

$$V_m = \sum_i x_i V_i - k x_{CH_4} \quad (14)$$

where the x_i and the V_i are the mole fractions and the specific volumes of the components, x_{CH_4} is the mole fraction of methane, and k is a constant which depends on both temperature and the molecular weight of the mixture. The V_i vary with temperature also, of course.

MCCARTY-KLOSEK-MCKINLEY

Fitting very accurate density data for "LNG-like mixtures" measured recently at the U.S. National Bureau of Standards laboratories in Boulder, Colorado, McCarty (17) reported that the values of Klosek and McKinley's k fell on one of two curves. The curve depended on whether the mixture contained no nitrogen or about 4.5% nitrogen. He then developed the equation:

$$V_m = \sum_i x_i V_i - \left[\frac{k_1 + (k_2 - k_1)x_{N_2}}{0.0425} \right] x_{CH_4} \quad (15)$$

in which all terms have the same meaning as those in Equation (14) except that k_1 and k_2 have different numerical values and x_{N2} is the mole fraction of nitrogen. Of the forty densities calculated for the "LNG-like" mixtures in the NBS data base, thirty-one were within 0.1% of the measured values and eight of the other nine were within 0.2%.

The advantages of McCarty's modification of the Klosek-McKinley method are its accuracy and its simplicity. The disadvantages are its severely limited composition and temperature ranges. It is valid only for LNG-like mixtures containing at least 60% methane, less than 4% nitrogen, less than 4% each of iso and normal butane, and less than 2% total of normal and isopentane, at temperatures between 105 and 115 K.

RACKETT EQUATION

The Rackett equation is an empirical correlation which is said to reproduce the densities of pure, saturated liquids from their triple points to their critical points. The equation as originally written by Rackett (19) is

$$\log \left(\frac{V_f}{V_c} \right) = (1-T_R)^{2\gamma} \log Z_c \quad (16)$$

where V_f is the saturated liquid specific volume. The term V_f/V_c is the reduced volume. The Rackett equation is, then, an equation relating reduced volume to reduced temperature, which makes it a corresponding states type of equation. The equation is empirical in the sense that, as Rackett wrote, "There is no known theoretical basis for (the equation) or for the specific value selected for this exponent." Rackett also points out that several liquid density correlations have used one or more terms containing the quantity $(1-T_R)$ for their temperature functions. In summarizing his comparisons, Rackett wrote "...the equation here proposed is more precise than any of the others." It is interesting to note, however, that his equation gave the smallest standard errors for only five out of twenty-nine data sets for sixteen compounds, while each of the other correlations gave the lowest errors in eight cases. Rackett also pointed out that several polar liquids did not "conform" to his equation. That is, their density-temperature curves did not have the correct shape.

Rackett devised rather complex mixing rules for his equation (20) and made rather limited comparisons of their reliability. He compared the results calculated using his method to experimental values and to the values calculated using four other methods for only six different methane-pentane mixtures at 100°F. In addition, he compared his own results with experimental measurements on twenty-two other mixtures.

SPENCER-DANNER-RACKETT EQUATION

Spencer and Danner made two major modifications in Rackett's method: They treated his Z_c as an adjustable parameter which they called Z_{RA} , and they simplified the mixing rules (22). They also tested the modified correlation and developed Z_{RA} parameters for a large number of compounds.

In testing the Rackett equation and its closest competitor, the Francis equations, Spencer and Danner (22) found that the former reproduced densities for hydrocarbons considerably better, but that the latter was better for "organics" (non-hydrocarbons) and inorganics. Although they conclude that "...the modified Rackett equation is by far the best for the hydrocarbons and quite good for the other organic and inorganic materials," a rough adjustment for the number of data points in each class (1948 for hydrocarbons, 652 for "organics", and 148 for inorganics) shows that the Francis equations are significantly better.

In their modification of the Rackett equation for mixtures (6) Spencer and Danner give these mixing rules (23):

$$Z_{\text{cm}} = \sum_i x_i Z_{ci} \quad (17)$$

$$V_{\text{cm}} = \sum_i x_i V_{ci} \quad (18)$$

$$T_{\text{cm}} = \sum_i \sum_j \phi_i \phi_j T_{cij}$$

$$\phi_i = \frac{x_i V_{ci}}{\sum_i x_i V_{ci}} \quad (20)$$

$$T_{cij} = (T_{ci} T_{cj})^{1/2} / (1 - k_{ij}) \quad (21)$$

$$k_{ij} = 1 - \left[\frac{(V_{ci}^{-1/3} V_{cj}^{-1/3})^{1/2}}{1/2 (V_{ci}^{-1/3} + V_{cj}^{-1/3})} \right]$$

Spencer and Danner found "... there is no apparent criterion for recommending Harmsen's method or the modified Rackett" (23).

The advantages of Spencer and Danner's modification of the Rackett equation are its applicability to a large number of compounds and mixtures over a wide range of temperatures, its accuracy, and the simplicity of the pure-liquid equation. The drawbacks are its lower accuracy for polar compounds and the relatively small number of compounds for which values of Z_{RA} are available. The Spencer-Danner-Rackett equation has not, to our knowledge, been evaluated explicitly for LNG's.

COSTALD

The COSTALD density correlation (6, 8) was based on the Gunn-Yamada correlation. COSTALD is a corresponding states correlation of the form

$$\frac{V_s}{V^*} = V_R^{(o)} \left(1 - w_{SRK} V_R^{(\delta)} \right) \quad (23)$$

where V^* is a characteristic volume analogous to the critical volume, $V_R^{(o)}$ is the spherical molecule function, $V_R^{(\delta)}$ is a function which, when multiplied by $V_R^{(o)}$ gives the deviation function, and w_{SRK} is the Phillips acentric factor based on the Soave-Redlich-Kwong equation of state which is used instead of the Pitzer acentric factor (9). $V_R^{(o)}$ and $V_R^{(\delta)}$ are both functions of reduced temperature only:

$$V_R^{(o)} = 1 + a(1-T_R)^{1/3} + b(1-T_R)^{2/3} + c(1-T_R) + d(1-T_R)^{4/3} \quad (24)$$

$$V_R^{(\delta)} = (e + fT_R + gT_R^2 + hT_R^3)/(T_R - 1.00001) \quad (25)$$

V^* is usually regressed by fitting these equations to experimental density data, using known values of T_c and w_{SRK} , but it can be calculated from a single density point or estimated from a generalized correlation of the form

$$V^* = \frac{RT_c}{k_1 + k_2 w_{SRK} + k_3 w_{SRK}^2}$$

Extensive comparisons showed that COSTALD is significantly better than the Yen-Woods correlation (25) and somewhat better than the Spencer and Danner modification of the Rackett equation (22) in reproducing densities of a variety of types of saturated liquids. Values of ω_{SRK} and V^* for 200 compounds were given in the original paper (6), and values for almost 200 more have been obtained more recently.

Hankinson and Thomson tested several different sets of mixing rules and recommended the following (6, 8):

$$V^*_{ij} T_{ci} = (V^*_{ii} T_c V^*_{jj} T_c)^{1/2} \quad (27)$$

$$T_m = \frac{\sum_i \sum_j x_i x_j V^*_{ij} T_{ci}}{V^*_{\infty}} \quad (28)$$

$$V^* = \frac{1}{4} \left[\sum_i x_i V^*_{ii} + 3(\sum_i x_i V_i^{-2/3})(\sum_i x_i V_i^{-1/3}) \right] \quad (29)$$

$$W_{SRKm} = \sum_i x_i W_{SRKi} \quad (30)$$

Comparisons of COSTALD with the Yen-Woods correlation and the Spencer-Danner-Rackett method over a fairly large quantity of mixture density data showed that COSTALD gave significantly lower errors.

Interaction parameters have been developed for some of the light paraffins, carbon dioxide, and nitrogen to permit the use of COSTALD for custody transfer of LNG's. In comparing COSTALD with McCarty's version of the Klosek-McKinley equation, Hankinson, Coker, and Thomson (7) found that after inserting interaction parameters, COSTALD gave an average absolute error of 0.078% for the densities of forty "LNG-like" mixtures (less than the estimated experimental accuracy), and gave an average absolute error for the densities of the whole 285 points of National Bureau of Standards mixture data of 0.199% compared with 0.227% for McCarty's Equation.

Advantages of the COSTALD correlation are its high accuracy for many types of liquids and their mixtures over wide temperature ranges, its overall accuracy, and the availability of the required parameters for many liquids. The COSTALD correlation has several unique features. One of these is its accuracy in the prediction of LNG densities. It has also been shown that COSTALD fits densities of crude oils and petroleum fractions quite well (9), and it has been suggested that it can fit densities of aqueous solutions well. Finally, Hankinson and Thomson showed that, given good values of T_c and ω_{SRK} , COSTALD can be

used to give good estimates of the critical volumes of nonpolar compounds.

There are a few disadvantages. The COSTALD equations are not as simple as one might like, although this presents no problem on a digital computer. Its predictions close to the critical point are less accurate than we would like, and it does not predict densities of polar liquids as well as would be desired. COSTALD is still being applied to new systems, however, and we may see some interesting new results soon.

3.0 COMPRESSED LIQUID DENSITIES

3.1 FACTOR MODELS FOR SATURATED LIQUID DENSITIES

The existing factor model as contained in the present API 1101 is generally accepted as being inadequate. The tables 1101 were constructed graphically and a basic mathematical model to represent the values does not exist. In 1979 Hankinson and Phillips regressed these tables to a complex function (14). This model was given to the API and is in general domestic use.

In 1979 Donner of British Petroleum presented an alternative model to the ISO/TC 28/SC3. This model is given by:

$$\ln C = 1.38315 + 0.003438 T - 3.02909 \ln e$$

$$- 0.0161654 T \ln e \quad (31)$$

$$\text{and } \bar{\beta} = C \times 10^5 \text{ bar}^{-1}$$

where T : °C

ρ : 15°C density, kg/litre

He claims a calculational error of 0.05% in volume for temperatures up to 76°C and pressures of 34 bar. The American Petroleum Institute has a project under the technical direction of Dr. Mark Plummer (Marathon Oil) to incorporate new data into the existing base and develop a replacement for API 1101. This work is complete and is presently in COPM ballot. Equations and results cannot be released until the ballot procedure is completed.

3.2 COMPOSITIONAL MODEL FOR COMPRESSED LIQUID DENSITIES

Previous Work

Thomson, Brobst, and Hankinson (24) and Hankinson and Thomson (6, 8) have carefully examined the previously available compressed liquid density correlations. Each of these correlations was found to be deficient for general use in one respect or another. The most common problem was a lack of mixing rules. Other problems included narrow ranges of temperature, pressure, and composition; restricted component list; and difficulty in translating the method to computer applications. Table 3 summarizes the main deficiencies of some of the more prominent density correlations for compressed liquids.

Desirable Correlation Features

The rationale behind the development of COSTALD was to combine as many desirable features as possible into a single unified, accurate liquid density correlation. The following attributes were considered to be important in the formulation of a new compressed liquid density correlation:

1. Applicable to many types of liquids including nonpolar, slightly polar, polar, and quantum.
2. Contain generalized mixing rules which are consistent for all types of liquid mixtures.
3. Contain only generalized parameters of readily available, or easily determined, pure component data.
4. High degree of accuracy, particularly for refrigerated liquid mixtures such as NGL products and LNG/LPG mixtures.
5. Predictive, so that compressed densities can be calculated for those liquids for which no experimental density data exist.
6. Readily adaptable to efficient computer and on-line microprocessor programming for use in process design and simulation calculations, and for liquid metering in custody transfer operations.
7. Relatively simple equations.
8. Continuous, single-valued functions over the whole range of interest.

9. Compressed density function that smoothly approaches the saturated density and whose lower limit exactly reduces to the saturated density.

10. Give accurate calculated densities near the critical point.

COSTALD Correlation

This section outlines the extension of the generalized COSTALD method for saturated liquid densities of pure compounds and their bubble point mixtures, shown above in Section 2.2, to the calculation of compressed liquids of pure compounds and mixtures. The resultant COSTALD correlation is applicable for pressures from saturation up to 68,950 kPa (10,000 psia) and temperatures up to just below the critical temperature. With the partial exception of items 7 and 10, all of the desired features listed above have been incorporated into the COSTALD compressed liquid density correlation. The double sums and the product of sums, which appear in the mixing rules, are quite tedious to calculate by hand for mixtures of more than two or three components. However, these terms pose no difficulty for programmed computer calculations.

Equations for the COSTALD Compressed Liquid Model

The basis of the COSTALD compressed liquid density correlation is the extension and generalization of the Tait equation using corresponding states principles. This equation for the molar volume of the compressed liquid at the system temperature and pressure is given by:

$$V = V_s \left[1 - C \ln \left(\frac{B + P}{B + P_s} \right) \right] \quad (33)$$

where the B and C terms have been correlated by

$$B = P_c \left[-1.0 + a_1(1-T_B)^{1.3} + b_1(1-T_B)^{2.3} + d_1(1-T_B) + e_1(1-T_B)^{4.3} \right] \quad (34)$$

$$P_1 = \text{EXP}(f + g_1 W_{SRK} + h_1 W_{SRK}^2) \quad (35)$$

$$C = j_1 + k_1 W_{SRK} \quad (36)$$

Values of the numerical correlating constants a_1 through k_1 are given in Table 4.

Note that in Equation (33) as P approaches P_s , the natural logarithm of $(B+P)/(B+P_s)$ approaches zero and, consequently, the molar volume V approaches the saturated molar volume V_s . This is an essential feature of the correlation. The corresponding states principle was used to correlate B , which has units of pressure, as a function of reduced temperature. Other criteria, the step-by-step procedures, and the experimental data sets used both for determining the final forms of the parameters B , e_1 , and C and for evaluation of the numerical constants are discussed in greater detail in reference (24).

In order to use Equation (33), a knowledge of both the saturated molar volume V_s and the saturation pressure P_s at the system temperature is required. V_s is determined by the procedures given above. The saturation pressure P_s , or P_{sm} for bubble point mixtures*, may be calculated from the following generalized Riedel vapor pressure equation developed by Hankinson, Estes, and Coker (9):

$$\log(P_{xs}) = P_B^{(0)} + W_{SRK} P_B^{(1)} \quad (37)$$

$$P_B^{(0)} = 5.8031817 \log(T_B) + 0.07608141 F \quad (38)$$

$$P_B^{(1)} = 4.86601 G \quad (39)$$

$$F = 35.0 - 36.0/T_B - 96.376 \log(T_B) + T_B^6 \quad (40)$$

$$G = \log(T_B) + 0.03721754 F \quad (41)$$

$$P_s = (P_{xs} P_c) \quad (42)$$

Alternatively, any other suitable vapor pressure equation such as

$$\ln P_s = C_1 + C_2/T + C_3T + C_4\ln T \quad (43)$$

for pure compounds, where C_1 , C_2 , C_3 , and C_4 are constants specific to each compound, or a bubble point calculation to yield P_{sm} for mixtures, may be used.

* Note: The subscript m is added to denote a mixture property when the equations in this section are applied to mixtures, e.g. T_{cm} , T_{Rm} , P_{cm} , P_{Rm} , V_{sm} , V_m , etc.

In addition to the mixing rules, a knowledge of the mixture pseudocritical pressure P_{cm} is needed when Equations (37) through (42) and Equation (34) for parameter B are being applied to compressed liquid mixtures. Thomson, et al (24) recommended the following equations:

$$P_{cm} = \frac{Z_{cm} R T_{cm}}{V_m} \quad (44)$$

$$Z_{cm} = 0.291 - 0.080 W_{SRKm} \quad (45)$$

The accuracy of determining the density of mixtures, such as LNG, depends upon accurate compositional analyses, since the mole fractions of all components, x_i , are needed both in the COSTALD mixing rules and to calculate the mixture molecular weight M_m :

$$\rho_m = \frac{M_m}{V_m}$$

$$M_m = \sum_i x_i M_i \quad (47)$$

The composition of liquid mixtures can be determined from chromatographic analysis which yields accurate values of component weight fractions. Weight fractions are easily converted to mole fractions for insertion into Equation (47).

COSTALD Accuracy

Thomson, Brobst, and Hankinson (24) tested the COSTALD compressed liquid density correlation against a total of 7690 data points of pure liquid compounds and 6926 data points of liquid mixtures. The results are given in Table 5 along with the corresponding results obtained from the Yen-Woods correlation. The COSTALD correlation gives significantly less error than the Yen-Woods correlation in all cases. These data covered temperatures from 50 to 600 K and pressures from saturation to 68,950 kPa (10,000 psia). Of particular interest are the 319 data points for LNG/LPG mixtures for which COSTALD densities averaged 0.369 percent absolute error, while the Yen-Woods (25) errors averaged nearly four times that or 1.46 percent.

TABLE 3

Deficiencies of Previous Compressed Liquid Density Correlations

Correlation (Date)	Deficiencies
Tait (1888)	No mixing rules.
Hudleston (1937)	No mixing rules. Inaccurate close to saturation.
Lyckman, et al (1965, 1969)	No mixing rules.
Yen-Woods (1966)	Requires two specific parameters per compound.
Generalized Lu equation extended by Ewbank & Harden (1967)	No mixing rules.
McCarty-Klosek-McKinley (1980)	Restricted component list. Narrow composition and temperature ranges. Difficult to program for computer.

TABLE 4

Numerical Constants for Equations 34, 35, and 36.

$a_1 = -9.070217$
 $b_1 = 62.45326$
 $d_1 = -135.1102$
 $f_1 = 4.79594$

$g_1 = 0.250047$
 $h_1 = 1.14188$
 $j_1 = 0.0861488$
 $k_1 = 0.0344483$

TABLE 5

Average Absolute Percent Error and Bias Between Calculated and Experimental Density of Compressed Liquids

<u>Compressed Liquid</u>	<u>No. of Data Points</u>	<u>COSTALD Correlation</u>		<u>Yen-Woods Correlation</u>	
		<u>% Error</u>	<u>Bias</u>	<u>% Error</u>	<u>Bias</u>
Pure Compounds					
Nonpolar	6338	0.446	-0.269	1.49	-5.72
Polar and Quantum	1352	2.57	-9.75	3.48	-0.770
Mixtures					
All mixtures	6926	1.61	9.50	2.51	-12.5
LNG/LPG mixtures	319	0.369	1.26	1.46	-6.82

4.0 ACKNOWLEDGEMENTS

The authors express their thanks to Phillips Petroleum Company for the opportunity to perform and publish this work and to the American Petroleum Institute Committee on Petroleum Measurement for their patient support over the years.

Dr. Hankinson wishes to pay a special tribute to Mr. T. L. Hillburn, Phillips Petroleum Company, for the introduction to the application of, and need for, liquid density methods and to Dr. J. K. Walters, API, for the continued encouragement during the Table 6 project.

5.0 NOMENCLATURE

α	coefficient of thermal expansion	
β	liquid compressibility	
$a_1, b_1, d_1, f_1, g_1, h_1, j_1, k_1$	constants in Equations (34, 35, 36)	
B	parameter in Equation (33) defined by Equation (34)	kPa
C	parameter in Equation (33) defined by Equation (36)	L/mol
e_1	constant in Equation (34) defined by Equation (35)	
F	parameter in Equations (38) and (41) defined by Equation (40); also parameter in Equation (3) for Liquid Compressibility Factor	psia
G	parameter in Equation (39) defined by Equation (41)	
M	molecular weight	g/mol
N	number of components in the mixture	
P	pressure	kPa
$P_R^{(0)}$	parameter in Equation (37) defined by Equation (38)	
$P_R^{(1)}$	parameter in Equation (37) defined by Equation (39)	
R	gas constant	L·kPa/(mol·K)
t	temperature	°C
T	absolute temperature	K
V	molar volume of liquid	L/mol
V_s	saturated molar volume	L/mol

V*	COSTALD characteristic volume	L/mol
VCF	volume correction factor Equation (5)	
x	mole fraction	
z	compressibility factor	
ρ	density	kg/m ³
w	acentric factor	

Subscripts

c	critical state
i,j	component i and component j
m	mixture
R	reduced property, for example, $T_R = T/T_c$
s	saturation or saturated
SRK	obtained using Soave-Redlich-Kwong equation of state

Mathematical Symbols

ln	logarithm to the base "e", or natural logarithm
log	logarithm to the base "10", or common logarithm
Σ_i	summation of terms over index i, often written with the limits of i specified

6.0 LITERATURE CITED

1. API, Manual of Petroleum Measurement Standards, Chapter 11.1, Volume X Background, Development, and Program Documentation, pp X-73, 1980.
2. Beurce, H. W. and Peffer, E. L., "Technology Papers of the National Bureau of Standards - Density and Thermal Expansion of American Petroleum Oils". Washington, D.C. 1916, GPO (pp. 125-154)
3. Downer, L. and Inkley, F. A., Oil and Gas Journal, pp. 52-55, June (1972).
4. Fulton, W. D., and Hankinson, R. W., "Modern Tables for Volumetric Correction of Liquid Petroleum Products", 9th International Pipeline Technology Conference, Houston, TX, Feb. 24-26, 1981.
5. Hall, A. H. Simpson, J. A. Whetstone, J. R., "Investigation of Densities and Thermal Expansion Coefficients Applicable to Petroleum Measurement". SP77. 1975 Petroleum Congress, Tokyo.
6. Hankinson, R. and Thomson, G., "A New Correlation for Saturated Densities of Liquids and Their Mixtures", AIChE Journal 25 (4), 653 (1979).
7. Hankinson, R., Coker, T., and Thomson, G., "Get Accurate LNG Densities with COSTALD", Hydrocarbon Processing, April, 1982, page 207.
8. Hankinson, R. W. and Thomson, G. H., "Calculate Liquid Densities Accurately", Hydrocarbon Processing, pp. 277-283 (September, 1979).
9. Hankinson, R. W., Estes, R. C., and Coker, T. A., "Physical Properties From a Modified Soave-Redlich-Kwong Equation of State in a Process System Environment," presented at the 68th Annual AIChE Meeting, Los Angeles, November 1975.
10. Hankinson, R. W., Segers, R. G., Buck, T. K., Gielzacki, F. P., Oil and Gas Journal, pp. 66-70, December 24, 1979.
11. Hankinson, R. W., et al., Proceedings of the 59th Annual Gas Processors Associations Convention, Houston, Texas, March 1980.
12. Hankinson, R. W., West, K. I., Segers, R. G., Gielzecki, F. P., Plummer, M. A., Oil and Gas Journal, pp. 297-308, Sept. 28, 1981.
13. Hankinson, R. W., West, K. I., Coker, T. A., Krisher, D. L., Manley, D. S., Oil and Gas Journal, pp. 74-75, July 20, 1981.

14. Hankinson, R. W. and Phillips, K. A., "Equations for API 1101 Compressibility Factors", American Petroleum Institute, COPM, Phoenix, 1979.
15. Klosek, J. and McKinley, C., "Densities of Liquefied Natural Gas and of Low Molecular Weight Hydrocarbons", Proc. First Int. Conf. on LNG, Institute for Gas Technology, Chicago (1968).
16. Manley, David, University of Missouri-Rolla, Progress Reports to the COSM Tables Advisory Committee, Fall 1980.
17. McCarty, R. D., "Four Mathematical Models for the Prediction of LNG Densities", NBS Technical Note 1030, National Bureau of Standards, Boulder, CO, 1980.
18. Parrish, W. R., Pollin, A. G., and Schmidt, T. W., "Properties of Ethane-Propane Mixes, Water Solubility and Liquid Densities," GPA, 61st Annual Convention, March 1982.
19. Rackett, H. G., "Equation of State for Saturated Liquids", J. Chem. Eng. Data 15 (4), 514 (1970).
20. "Calculation of the Bubble-Point Volumes of Hydrocarbon Mixtures", ibid. 15 (3), 308 (1971)
21. Robinson, E., "Calculate Density of Spiked Crudes", Hydrocarbon Processing, May, 1983, page 115.
22. Spencer, C. and Danner, R., "Improved Equation for Prediction of Saturated Liquid Density", ibid 17 (2), 236 (1972)
23. "Prediction of Bubble-Point Density of Mixtures", ibid. 18 (2), 230 (1973)
24. Thomson, G. H., Brobst, K. R., and Hankinson, R. W., "An Improved Correlation for Densities of Compressed Liquids and Liquid Mixtures," AIChE J., 28, No. 4, pp. 671-676 (July, 1982).
25. Yen, L. C. and Woods, S. S., "A Generalized Equation for Computer Calculation of Liquid Densities," AIChE J., 12, p. 95 (1966).

RWH:CE-550