Chapter 5
Heptanes-Plus Characterization

5.1 Introduction

Some phase-behavior applications require the use of an equation of state (EOS) to predict properties of petroleum reservoir fluids. The critical properties,acentric factor, molecular weight, and binary-interaction parameters (BIP's) of components in a mixture are required for EOS calculations. With existing chemical-separation techniques, we usually cannot identify the many hundreds and thousands of components found in reservoir fluids. Even if accurate separation were possible, the critical properties and other EOS parameters of compounds heavier than approximately C20 would not be known accurately. Practically speaking, we resolve this problem by making an approximate characterization of the heavier compounds with experimental and mathematical methods. The characterization of heptanes-plus (C7+) fractions can be grouped into three main tasks:

1. Dividing the C7+ fraction into a number of fractions with known molar compositions.
2. Defining the molecular weight, specific gravity, and boiling point of each C7+ fraction.
3. Estimating the critical properties and acentric factor of each C7+ fraction and the key BIP's for the specific EOS being used.

This chapter presents methods for performing these tasks and gives guidelines on when each method can be used. A unique characterization does not exist for a given reservoir fluid. For example, different component properties are required for different EOS's; therefore, the engineer must determine the quality of a given characterization by testing the predictions of reservoir-fluid behavior against measured pressure/volume/temperature (PVT) data.

The amount of C7+ typically found in reservoir fluids varies from >50 mol% for heavy oils to <1 mol% for light reservoir fluids. Average C7+ properties also vary widely. For example, C7+ molecular weight can vary from 110 to >300 and specific gravity from 0.7 to 1.0. Because the C7+ fraction is a mixture of many hundreds of paraffinic, naphthenic, aromatic, and other organic compounds, the C7+ fraction cannot be resolved into its individual components with any precision. We must therefore resort to approximate descriptions of the C7+ fraction.

Sec. 5.2 discusses experimental methods available for quantifying C7+ into discrete fractions. True-boiling-point (TBP) distillation provides the necessary data for complete C7+ characterization, including mass and molar quantities, and the key inspection data for each fraction (specific gravity, molecular weight, and boiling point). Gas chromatography (GC) is a less-expensive, time-saving alternative to TBP distillation. However, GC analysis quantifies only the mass of C7+ fractions; such properties as specific gravity and boiling point are not provided by GC analysis.

Typically, the practicing engineer is faced with how to characterize a C7+ fraction when only yC7+, the mole fraction; MwC7+, and specific gravity, γC7+, are known. Sec. 5.3 reviews methods for splitting C7+ into an arbitrary number of sub-fractions. Most methods assume that mole fraction decreases exponentially as a function of molecular weight or carbon number. A more general model based on the gamma distribution has been successfully applied to many oil and gas-condensate systems. Other splitting schemes can also be found in the literature; we summarize the available methods.

Sec. 5.4 discusses how to estimate inspection properties γ and Tg for C7+ fractions determined by GC analysis or calculated from a mathematical split. Katz and Firoozabadi's generalized single carbon number (SCN) properties are widely used. Other methods for estimating specific gravities of C7+ subfractions are based on forcing the calculated γC7+ to match the measured value.

Many empirical correlations are available for estimating critical properties of pure compounds and C7+ fractions. Critical properties can also be estimated by forcing the EOS to match the boiling point and specific gravity of each C7+ fraction separately. In Sec. 5.5, we review the most commonly used methods for estimating critical properties.

Finally, Sec. 5.6 discusses methods for reducing the number of components describing a reservoir mixture and, in particular, the C7+ fraction. Splitting the C7+ into pseudocomponents is particularly important for EOS-based compositional reservoir simulation. A large part of the computing time during a compositional reservoir simulation is used to solve the flash calculations; accordingly, minimizing the number of components without jeopardizing the quality of the fluid characterization is necessary.

5.2 Experimental Analyses

The most reliable basis for C7+ characterization is experimental data obtained from high-temperature distillation or GC. Many experimental procedures are available for performing these analyses; in the following discussion, we review the most commonly used methods. TBP distillation provides the key data for C7+ characterization, including mass and molar quantities, specific gravity, molecular weight, and boiling point of each distillation cut. Other such inspection data as kinematic viscosity and refractive index also may be measured on distillation cuts. Simulated distillation by GC requires smaller samples and less time than TBP distillation. However, GC analysis measures only the mass of carbon-number fractions. Simulated distillation results can be calibrated against TBP data, thus providing physical properties for the individual fractions. For many oils, simulated distillation...
provides the necessary information for C7+ characterization in far less the time and at far less cost than that required for a complete TBP analysis. We recommend, however, that at least one complete TBP analysis be measured for (1) oil reservoirs that may be candidates for gas injection and (2) most gas-condensate reservoirs.

5.2.1 TBP Distillation. In TBP distillation, a stock-tank liquid (oil or condensate) is separated into fractions or “cuts” by boiling-point range. TBP distillation differs from the Hempel and American Soc. for Testing Materials (ASTM) D-158 distillations10 because TBP analysis requires a high degree of separation, which is usually controlled by the number of theoretical trays in the apparatus and the reflux ratio. TBP fractions are often treated as components having unique boiling points, critical temperatures, critical pressures, and other properties identified for pure compounds. This treatment is obviously more valid for a cut with a narrow boiling-point range.

The ASTM D-289211 procedure is a useful standard for TBP analysis of stock-tank liquids. ASTM D-2892 specifies the general procedure for TBP distillation, including equipment specifications (see Fig. 5.1), reflux ratio, sample size, and calculations necessary to arrive at a plot of cumulative volume percent vs. normal boiling point. Normal boiling point implies that boiling point is measured at normal or atmospheric pressure. In practice, to avoid thermal decomposition (cracking), distillation starts at atmospheric pressure and is changed to subatmospheric distillation after reaching a limiting temperature. Subatmospheric boiling-point temperatures are converted to normal boiling-point temperatures by use of a vapor-pressure correlation that corrects for the amount of vacuum and the fraction’s chemical composition. The boiling-point range for fractions from TBP analyses. Also, the ASTM D-289211 procedure gives details on experimental equipment and the procedure for conducting TBP analysis at atmospheric and subatmospheric conditions. Table 5.3 gives an example TBP analysis from a commercial laboratory.
Boiling points are not reported because normal-paraffin boiling-point intervals are used as a standard; accordingly, the average boiling points suggested by Katz and Firoozabadi (Table 5.2) can be used.

5.2.2 Chromatography. GC and, to a lesser extent, liquid chromatography are used to quantify the relative amount of compounds found in oil and gas systems. The most important application of chromatography to C7 is its use in the characterization of a paraffinic sample; the GC response for carbon number C7 factor was used to match the two distillation curves.

As an alternative to correcting the internal standard, Maddox and Erbar suggested that the reported chromatographic boiling points be adjusted by a correction factor that depends on the reported boiling point and the “paraffinity” of the composite sample. This correction factor varies from 1 to 1.15 and is slightly larger for aromatic than paraffinic samples.

Several laboratories have calibrated GC analysis to provide simulated-distillation results up to C20. However, checking the accuracy of simulated distillation for SCN fractions greater than approximately C25 is difficult because C25 is usually the upper limit for reliable TBP distillation. The main disadvantage of simulated distillation is that inspection data are not determined directly for each fraction and must therefore either be correlated from TBP data or estimated from correlations (see Sec. 5.4).

Sophisticated analytical methods, such as mass spectrometry, may provide detailed information on the compounds separated by GC. For example, mass spectrometry GC can establish the relative amounts of paraffins, naphthenes, and aromatics (PNA's) for carbon number fractions distilled by TBP analysis. Detailed PNA information should provide more accurate estimation of the critical properties of petroleum fractions, but the analysis is relatively costly and time-consuming from a practical point of view. Recent work has shown that PNA analysis may improve C7 characterization for modeling phase behavior with EOS's. Our experience, however, is that PNA data have limited usefulness for improving EOS fluid characterizations.

5.3 Molar Distribution

Molar distribution is usually thought of as the relation between mole fraction and molecular weight. In fact, this concept is misleading because a unique relation does not exist between molecular weight and mole fraction unless the fractions are separated in a consistent manner. Consider for example a C7 sample distilled with constant 10-vol% cuts, the two sets of data will not
<table>
<thead>
<tr>
<th>Fraction Number</th>
<th>Lower $T_b$ (°F)</th>
<th>Upper $T_b$ (°F)</th>
<th>Average $T_b$ (°F)</th>
<th>$\gamma^*$</th>
<th>Defined $T_b$ (°F)</th>
<th>$R_i$ (psia)</th>
<th>$\omega$</th>
<th>$V_i$ (bbl/lbm mol)</th>
<th>$Z_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>147.0</td>
<td>156.7</td>
<td>151.3</td>
<td>0.690</td>
<td>84.01</td>
<td>12.27</td>
<td>914.0</td>
<td>476.0</td>
<td>0.273</td>
</tr>
<tr>
<td>7</td>
<td>197.4</td>
<td>204.0</td>
<td>200.7</td>
<td>0.727</td>
<td>96.01</td>
<td>11.96</td>
<td>976.0</td>
<td>457.0</td>
<td>0.310</td>
</tr>
<tr>
<td>8</td>
<td>242.1</td>
<td>250.0</td>
<td>246.0</td>
<td>0.749</td>
<td>107.01</td>
<td>11.86</td>
<td>1,027.0</td>
<td>428.0</td>
<td>0.349</td>
</tr>
<tr>
<td>9</td>
<td>288.0</td>
<td>295.0</td>
<td>291.5</td>
<td>0.768</td>
<td>121.01</td>
<td>11.82</td>
<td>1,077.0</td>
<td>397.0</td>
<td>0.392</td>
</tr>
<tr>
<td>10</td>
<td>330.4</td>
<td>338.0</td>
<td>334.2</td>
<td>0.782</td>
<td>134.01</td>
<td>11.82</td>
<td>1,120.0</td>
<td>367.0</td>
<td>0.437</td>
</tr>
<tr>
<td>11</td>
<td>369.0</td>
<td>376.0</td>
<td>372.5</td>
<td>0.793</td>
<td>147.01</td>
<td>11.84</td>
<td>1,158.0</td>
<td>341.0</td>
<td>0.479</td>
</tr>
<tr>
<td>12</td>
<td>406.9</td>
<td>414.0</td>
<td>410.4</td>
<td>0.804</td>
<td>161.01</td>
<td>11.86</td>
<td>1,192.0</td>
<td>315.0</td>
<td>0.523</td>
</tr>
<tr>
<td>13</td>
<td>441.0</td>
<td>448.0</td>
<td>444.5</td>
<td>0.808</td>
<td>175.01</td>
<td>11.85</td>
<td>1,229.0</td>
<td>291.0</td>
<td>0.561</td>
</tr>
<tr>
<td>14</td>
<td>476.1</td>
<td>484.0</td>
<td>480.0</td>
<td>0.812</td>
<td>189.01</td>
<td>11.84</td>
<td>1,265.0</td>
<td>268.0</td>
<td>0.601</td>
</tr>
<tr>
<td>15</td>
<td>510.8</td>
<td>518.0</td>
<td>514.4</td>
<td>0.816</td>
<td>206.01</td>
<td>11.84</td>
<td>1,301.0</td>
<td>246.0</td>
<td>0.644</td>
</tr>
<tr>
<td>16</td>
<td>545.4</td>
<td>552.0</td>
<td>548.7</td>
<td>0.819</td>
<td>222.01</td>
<td>11.83</td>
<td>1,337.0</td>
<td>224.0</td>
<td>0.684</td>
</tr>
<tr>
<td>17</td>
<td>579.2</td>
<td>586.0</td>
<td>582.6</td>
<td>0.823</td>
<td>237.01</td>
<td>11.83</td>
<td>1,373.0</td>
<td>204.0</td>
<td>0.724</td>
</tr>
<tr>
<td>18</td>
<td>613.8</td>
<td>621.0</td>
<td>617.4</td>
<td>0.826</td>
<td>251.01</td>
<td>11.83</td>
<td>1,409.0</td>
<td>186.0</td>
<td>0.764</td>
</tr>
<tr>
<td>19</td>
<td>648.4</td>
<td>655.0</td>
<td>651.7</td>
<td>0.829</td>
<td>265.01</td>
<td>11.83</td>
<td>1,445.0</td>
<td>169.0</td>
<td>0.804</td>
</tr>
<tr>
<td>20</td>
<td>683.0</td>
<td>689.0</td>
<td>685.5</td>
<td>0.832</td>
<td>279.01</td>
<td>11.83</td>
<td>1,481.0</td>
<td>153.0</td>
<td>0.844</td>
</tr>
<tr>
<td>21</td>
<td>717.6</td>
<td>723.0</td>
<td>719.8</td>
<td>0.835</td>
<td>293.01</td>
<td>11.83</td>
<td>1,517.0</td>
<td>138.0</td>
<td>0.885</td>
</tr>
<tr>
<td>22</td>
<td>752.2</td>
<td>757.0</td>
<td>754.6</td>
<td>0.838</td>
<td>307.01</td>
<td>11.83</td>
<td>1,553.0</td>
<td>124.0</td>
<td>0.925</td>
</tr>
<tr>
<td>23</td>
<td>786.8</td>
<td>792.0</td>
<td>789.4</td>
<td>0.841</td>
<td>321.01</td>
<td>11.83</td>
<td>1,589.0</td>
<td>111.0</td>
<td>0.965</td>
</tr>
<tr>
<td>24</td>
<td>821.4</td>
<td>826.0</td>
<td>823.7</td>
<td>0.844</td>
<td>335.01</td>
<td>11.83</td>
<td>1,625.0</td>
<td>99.0</td>
<td>1.006</td>
</tr>
<tr>
<td>25</td>
<td>856.0</td>
<td>860.0</td>
<td>858.5</td>
<td>0.847</td>
<td>349.01</td>
<td>11.83</td>
<td>1,661.0</td>
<td>88.0</td>
<td>1.046</td>
</tr>
<tr>
<td>26</td>
<td>890.6</td>
<td>895.0</td>
<td>892.8</td>
<td>0.850</td>
<td>363.01</td>
<td>11.83</td>
<td>1,697.0</td>
<td>78.0</td>
<td>1.087</td>
</tr>
<tr>
<td>27</td>
<td>925.2</td>
<td>929.0</td>
<td>927.3</td>
<td>0.853</td>
<td>377.01</td>
<td>11.83</td>
<td>1,733.0</td>
<td>69.0</td>
<td>1.127</td>
</tr>
<tr>
<td>28</td>
<td>960.0</td>
<td>964.0</td>
<td>962.0</td>
<td>0.856</td>
<td>391.01</td>
<td>11.83</td>
<td>1,769.0</td>
<td>60.0</td>
<td>1.167</td>
</tr>
<tr>
<td>29</td>
<td>994.8</td>
<td>999.0</td>
<td>996.4</td>
<td>0.859</td>
<td>405.01</td>
<td>11.83</td>
<td>1,805.0</td>
<td>51.0</td>
<td>1.207</td>
</tr>
<tr>
<td>30</td>
<td>1,029.6</td>
<td>1,033.0</td>
<td>1,031.3</td>
<td>0.862</td>
<td>419.01</td>
<td>11.83</td>
<td>1,841.0</td>
<td>42.0</td>
<td>1.247</td>
</tr>
<tr>
<td>31</td>
<td>1,064.4</td>
<td>1,068.0</td>
<td>1,066.1</td>
<td>0.865</td>
<td>433.01</td>
<td>11.83</td>
<td>1,877.0</td>
<td>34.0</td>
<td>1.287</td>
</tr>
<tr>
<td>32</td>
<td>1,109.2</td>
<td>1,113.0</td>
<td>1,109.8</td>
<td>0.868</td>
<td>447.01</td>
<td>11.83</td>
<td>1,913.0</td>
<td>26.0</td>
<td>1.327</td>
</tr>
<tr>
<td>33</td>
<td>1,144.0</td>
<td>1,148.0</td>
<td>1,146.4</td>
<td>0.871</td>
<td>461.01</td>
<td>11.83</td>
<td>1,949.0</td>
<td>18.0</td>
<td>1.367</td>
</tr>
<tr>
<td>34</td>
<td>1,178.8</td>
<td>1,183.0</td>
<td>1,180.4</td>
<td>0.874</td>
<td>475.01</td>
<td>11.83</td>
<td>1,985.0</td>
<td>10.0</td>
<td>1.407</td>
</tr>
<tr>
<td>35</td>
<td>1,213.6</td>
<td>1,218.0</td>
<td>1,215.3</td>
<td>0.877</td>
<td>489.01</td>
<td>11.83</td>
<td>2,021.0</td>
<td>10.0</td>
<td>1.447</td>
</tr>
</tbody>
</table>

*At 1 atmosphere.
**Water.
should produce a single curve. Strictly speaking, therefore, molar
distribution is the relation between cumulative molar quantity and
some expression for cumulative molecular weight.

In this section, we review methods commonly used to describe
molar distribution. Some methods use a consistent separation of
fractions (e.g., by SCN) so the molar distribution can be expressed
directly as a relationship between mole fraction and molecular
weight of individual cuts. Most methods in this category assume that
C7+ mole fractions decrease exponentially. A more general ap-
proach uses the continuous three-parameter gamma probability
function to describe molar distribution.

5.3.1 Exponential Distributions. The Lohrenz-Bray-Clark24
(LBC) viscosity correlation is one of the earliest attempts to use an
exponential-type distribution for splitting C7

where

and are determined by trial and error so that

A constant indicating the slope on a plot of ln

and the assumption that the distribution

is infinite, constants Cz

and A can be determined explicitly. With the general expression

where

are used in

A Newton-Raphson algorithm can be used to solve Eqs. 5.5 and 5.6. Note that the LBC model cannot be used when

and

The LBC form of the exponential distribution

has not found widespread application.

More commonly, a linear form of the exponential distribution is
used to split the C7+ fraction. Writing the exponential distribution
in a general form for any Cn+ fraction, constants

and

are given by

and

so that

and (c) for a crude oil with internal standard (after MacAllister
and DeRuiter).
and

\[ \sum_{i=1}^{n} z_i M_i = M_{C_7} \quad \text{................. (5.12)} \]

are satisfied.

Eqs. 5.9 and 5.10 imply that once a molecular weight relation is chosen (i.e., \( h \) is fixed), the distillation is uniquely defined by \( C_7 \), molecular weight. Realistically, on the other hand, reservoir fluids having a given \( C_7 \) molecular weight will not have the same molar distribution, which is one reason why more complicated models have been proposed.

### 5.3.2 Gamma-Distribution Model

The three-parameter gamma distribution is a more general model for describing molar distribution. Whitson and Whitson discuss the gamma distribution and its application to molar distillation. They give results for 44 oil and condensate \( C_7 \) samples that were fit by the gamma distribution with data from complete TBP analyses. The absolute average deviation in estimated cut molecular weight was 2.5 amu distribution with data from complete TBP analyses. The absolute average deviation in estimated cut molecular weight will not have the same molar distribution, which is one reason why more complicated models have been proposed.

The three parameters in the gamma distribution are \( \alpha \), \( \beta \), and \( M_{C_7} \). The key parameter \( \alpha \) defines the form of the distribution, and its value usually ranges from 0.5 to 2.5 for reservoir fluids; \( \alpha = 1 \) gives an exponential distribution. Application of the gamma distribution to heavy oils, bitumen, and petroleum residues indicates that the upper limit for \( \alpha \) is 25 to 30, which statistically is approaching a log-normal distribution (see Fig. 5.628).

The parameter \( \beta \) can be physically interpreted as the minimum molecular weight found in the \( C_7 \) fraction. An approximate relation between \( \alpha \) and \( \beta \) is

\[ \beta = \frac{M_{C_7}}{\alpha - \eta} \quad \text{................. (5.14)} \]

The continuous distribution \( p(M) \) is defined as

\[ p(M) = \frac{(M - \eta)^{\alpha - 1} \exp[-(M - \eta)/\beta]}{\beta^\alpha \Gamma(\alpha)} \quad \text{................. (5.13)} \]

where \( \Gamma = \text{gamma function} \) and \( \beta \) is given by

\[ \beta = \frac{M_{C_7} - \eta}{\alpha} \quad \text{................. (5.14)} \]

The parameter \( \eta \) can be thought of as the minimum molecular weight for which the \( C_7 \) fraction is also thought of as the minimum molecular weight. Practically, \( \eta \) should be considered as a mathematical constant more than as a physical property, either calculated from Eq. 5.15 or determined by fitting measured TBP data.

### Fig. 5.5—Comparison of TBP and GC-simulated distillation for a North Sea gas-condensate sample (after Austad et al.7).

![Graph showing comparison of TBP and GC-simulated distillation](image)

### Fig. 5.6—Gamma distributions for petroleum residue (after Brulé et al.28).

![Gamma distributions for petroleum residue](image)

for reservoir-fluid \( C_7 \) fractions. Practically, \( \eta \) should be considered as a mathematical constant more than as a physical property, either calculated from Eq. 5.15 or determined by fitting measured TBP data.
The gamma distribution can be fit to experimental molar-distribution data by use of a nonlinear least-squares algorithm to determine $\alpha$, $\eta$, and $\beta$. Experimental TBP data are required, including weight fraction and molecular weight for at least five $C_{27}$ fractions (use of more than 10 fractions is recommended to ensure a unique fit of model parameters). The sum-of-squares function can be defined as

$$F(\alpha, \eta, \beta) = \sum_{i=1}^{n} (\Delta M)^2,$$  \hspace{1cm} (5.24)

where $\Delta M = (M_i)_{\exp} - (M_i)_{\text{mod}}$ \hspace{1cm} (5.25)

Subscripts $\text{mod}$ and $\exp$ model and experimental, respectively. This sum-of-squares function weights the lower molecular weights more than higher molecular weights, in accordance with the expected accuracy for measurement of molecular weight. Also, the sum-of-squares function does not include the last molecular weight because this molecular weight may be inaccurate or backcalculated to match the measured average $C_{27}$ molecular weight. If the last fraction is not included, the model average molecular weight, $(M_{c27})_{\text{mod}} = \eta + \alpha \beta$, can be compared with the experimental value as an independent check of the fit.

A simple graphical procedure can be used to fit parameters $\alpha$ and $\eta$ if experimental $M_{c27}$ is fixed and used to define $\beta$. Fig. 5.10 shows a plot of cumulative weight fraction,

$$Q_{\alpha} = \sum_{i=1}^{n} q_i,$$  \hspace{1cm} (5.26)

vs. the cumulative dimensionless molecular-weight variable,

$$Q_{\eta} = \frac{Q_{\alpha}}{M_{c27}}.$$

Table 5.5 and the following outline describe the procedure for determining model parameters with Fig. 5.10 and TBP data.

1. Tabulate measured mole fractions $q_i$ and molecular weights $M_i$ for each fraction.
2. Calculate experimental weight fractions, $w_i = (q_i M_i) / \sum q_i$, and choose the curve that fits one of the model curves best. Read the value of $\alpha$ from Fig. 5.10.
3. Normalize weight fractions and calculate cumulative normalized weight fraction $Q_{\alpha}$.
4. Calculate cumulative molecular weight $Q_{\alpha}$, from Eq. 5.3.
5. Assume several values of $\eta$ (e.g., from 75 to 100) and calculate $Q_{\eta}$ for each value of the estimated $\eta$.
6. For each estimate of $\eta$, plot $Q_{\eta}$ vs. $Q_{\alpha}$ on a copy of Fig. 5.10 and choose the curve that fits one of the model curves best. Read the value of $\eta$ from Fig. 5.10.
7. Calculate molecular weights and mole fractions of Fractions $i$ using the best-fit curve in Fig. 5.10. Enter the curve at measured values of $Q_{\eta}$, read $Q_{\alpha}$, and calculate $M_i$ from

$$M_i = \eta + (M_{c27} - \eta) \left( \frac{Q_{\alpha} - Q_{\alpha-1}}{(Q_{\alpha}/Q_{\eta}) - (Q_{\alpha-1}/Q_{\eta-1})} \right).$$

Fig. 5.7—Gamma density function for the Hoffman et al.\textsuperscript{20} oil (dashed line) and a North Sea volatile oil (solid line). After Whitson et al.\textsuperscript{27}

where $Q = e^{-x^2} \Gamma(\alpha)$,  \hspace{1cm} (5.20)

$$S = \sum_{j=0}^{\infty} x^j \left( \int_{0}^{1} (\alpha + k) \right)^{-1},$$  \hspace{1cm} (5.21)

and $y = \frac{M}{\eta}$.  \hspace{1cm} (5.22)

Note that $P_0(M_0 = \eta) = P_1(M_0 = \eta) = 0$.

The summation in Eq. 5.21 should be performed until the last term is $< 1 \times 10^{-8}$. The gamma function can be estimated by\textsuperscript{30}

$$\Gamma(x + 1) = 1 + \sum_{i=1}^{n} A_i x^i,$$  \hspace{1cm} (5.23)

where $A_1 = -0.577191652$, $A_2 = 0.988205891$, $A_3 = -0.897056937$, $A_4 = 0.418208657$, $A_5 = -0.756704078$, $A_6 = 0.482199394$, $A_7 = -0.103527818$, and $A_8 = 0.035868343$ for $0.5 < x < 1$. The recurrence formula, $\Gamma(x + 1) = \Gamma(x)$, is used for $x > 1$ and $x < 1$; furthermore, $\Gamma(1) = 1$.

The equations for calculating $z_i$ and $M_i$ are summarized in a short FORTRAN program GAMSPL found in Appendix A. In this simple program, the boundary molecular weights are chosen arbitrarily at increments of 14 for the first 19 fractions, starting with $\eta$ as the first lower boundary. The last fraction is calculated by setting the upper molecular weight boundary equal to 10,000. Table 5.4 gives three sample outputs from GAMSPL, for $\alpha = 0.5$, 1, and 2 with $\eta = 90$ and $M_{c27} = 200$ held constant. Fig. 5.9 plots the results as log $z_i$ vs. $M_i$.

The amount and molecular weight of the C\textsubscript{26+} fraction varies for each value of $\alpha$.  

The gamma distribution can be fit to experimental molar-distribution data by use of a nonlinear least-squares algorithm to determine $\alpha$, $\eta$, and $\beta$. Experimental TBP data are required, including weight fraction and molecular weight for at least five $C_{27}$ fractions (use of more than 10 fractions is recommended to ensure a unique fit of model parameters). The sum-of-squares function can be defined as

$$F(\alpha, \eta, \beta) = \sum_{i=1}^{n} (\Delta M)^2,$$  \hspace{1cm} (5.24)

where $\Delta M = (M_i)_{\exp} - (M_i)_{\text{mod}}$ \hspace{1cm} (5.25)

Subscripts $\text{mod}$ and $\exp$ model and experimental, respectively. This sum-of-squares function weights the lower molecular weights more than higher molecular weights, in accordance with the expected accuracy for measurement of molecular weight. Also, the sum-of-squares function does not include the last molecular weight because this molecular weight may be inaccurate or backcalculated to match the measured average $C_{27}$ molecular weight. If the last fraction is not included, the model average molecular weight, $(M_{c27})_{\text{mod}} = \eta + \alpha \beta$, can be compared with the experimental value as an independent check of the fit.

A simple graphical procedure can be used to fit parameters $\alpha$ and $\eta$ if experimental $M_{c27}$ is fixed and used to define $\beta$. Fig. 5.10 shows a plot of cumulative weight fraction,

$$Q_{\alpha} = \sum_{i=1}^{n} w_i,$$  \hspace{1cm} (5.26)

vs. the cumulative dimensionless molecular-weight variable,

$$Q_{\eta} = \frac{Q_{\alpha}}{M_{c27}}.$$

Table 5.5 and the following outline describe the procedure for determining model parameters with Fig. 5.10 and TBP data.

1. Tabulate measured mole fractions $q_i$ and molecular weights $M_i$ for each fraction.
2. Calculate experimental weight fractions, $w_i = (q_i M_i) / \sum q_i$, and choose the curve that fits one of the model curves best. Read the value of $\alpha$ from Fig. 5.10.
3. Normalize weight fractions and calculate cumulative normalized weight fraction $Q_{\alpha}$.
4. Calculate cumulative molecular weight $Q_{\alpha}$, from Eq. 5.3.
5. Assume several values of $\eta$ (e.g., from 75 to 100) and calculate $Q_{\eta}$ for each value of the estimated $\eta$.
6. For each estimate of $\eta$, plot $Q_{\eta}$ vs. $Q_{\alpha}$ on a copy of Fig. 5.10 and choose the curve that fits one of the model curves best. Read the value of $\eta$ from Fig. 5.10.
7. Calculate molecular weights and mole fractions of Fractions $i$ using the best-fit curve in Fig. 5.10. Enter the curve at measured values of $Q_{\eta}$, read $Q_{\alpha}$, and calculate $M_i$ from

$$M_i = \eta + (M_{c27} - \eta) \left( \frac{Q_{\alpha} - Q_{\alpha-1}}{(Q_{\alpha}/Q_{\eta}) - (Q_{\alpha-1}/Q_{\eta-1})} \right).$$

Fig. 5.7—Gamma density function for the Hoffman et al.\textsuperscript{20} oil (dashed line) and a North Sea volatile oil (solid line). After Whitson et al.\textsuperscript{27}
TABLE 5.4—RESULTS OF GAMSPL PROGRAM FOR THREE DATA SETS WITH DIFFERENT GAMMA-DISTRIBUTION PARAMETER $\alpha$

<table>
<thead>
<tr>
<th>Fraction Number</th>
<th>$\alpha = 0.5$</th>
<th></th>
<th>$\alpha = 1.0$</th>
<th></th>
<th>$\alpha = 2.0$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mole Fraction</td>
<td>Molecular Weight</td>
<td>Mole Fraction</td>
<td>Molecular Weight</td>
<td>Mole Fraction</td>
<td>Molecular Weight</td>
</tr>
<tr>
<td>1</td>
<td>0.2787233</td>
<td>94.588</td>
<td>0.1195065</td>
<td>96.852</td>
<td>0.0273900</td>
<td>99.132</td>
</tr>
<tr>
<td>2</td>
<td>0.1073842</td>
<td>110.525</td>
<td>0.0726497</td>
<td>124.852</td>
<td>0.0852269</td>
<td>125.172</td>
</tr>
<tr>
<td>3</td>
<td>0.0610991</td>
<td>138.758</td>
<td>0.0815774</td>
<td>138.852</td>
<td>0.0927229</td>
<td>139.038</td>
</tr>
<tr>
<td>4</td>
<td>0.0505020</td>
<td>152.796</td>
<td>0.0718284</td>
<td>152.852</td>
<td>0.0925552</td>
<td>152.963</td>
</tr>
<tr>
<td>5</td>
<td>0.0428377</td>
<td>166.819</td>
<td>0.0632444</td>
<td>166.852</td>
<td>0.0925552</td>
<td>152.963</td>
</tr>
<tr>
<td>6</td>
<td>0.0369607</td>
<td>180.836</td>
<td>0.0556863</td>
<td>180.852</td>
<td>0.0840707</td>
<td>180.888</td>
</tr>
<tr>
<td>7</td>
<td>0.0322804</td>
<td>194.848</td>
<td>0.0490314</td>
<td>194.852</td>
<td>0.0720157</td>
<td>194.859</td>
</tr>
<tr>
<td>8</td>
<td>0.0284480</td>
<td>208.857</td>
<td>0.0431719</td>
<td>208.852</td>
<td>0.0632969</td>
<td>208.841</td>
</tr>
<tr>
<td>9</td>
<td>0.0252470</td>
<td>222.864</td>
<td>0.0380125</td>
<td>222.852</td>
<td>0.0548597</td>
<td>222.826</td>
</tr>
<tr>
<td>10</td>
<td>0.0225321</td>
<td>236.870</td>
<td>0.0334698</td>
<td>236.852</td>
<td>0.0470180</td>
<td>236.814</td>
</tr>
<tr>
<td>11</td>
<td>0.0202013</td>
<td>250.875</td>
<td>0.0294699</td>
<td>250.852</td>
<td>0.0399302</td>
<td>250.805</td>
</tr>
<tr>
<td>12</td>
<td>0.0181808</td>
<td>264.879</td>
<td>0.0259481</td>
<td>264.852</td>
<td>0.0336535</td>
<td>264.797</td>
</tr>
<tr>
<td>13</td>
<td>0.0164152</td>
<td>278.883</td>
<td>0.0228471</td>
<td>278.852</td>
<td>0.0281813</td>
<td>278.790</td>
</tr>
<tr>
<td>14</td>
<td>0.0148619</td>
<td>292.886</td>
<td>0.0201167</td>
<td>292.852</td>
<td>0.0234690</td>
<td>292.784</td>
</tr>
<tr>
<td>15</td>
<td>0.0134879</td>
<td>306.888</td>
<td>0.0177127</td>
<td>306.852</td>
<td>0.0194514</td>
<td>306.778</td>
</tr>
<tr>
<td>16</td>
<td>0.0122665</td>
<td>320.890</td>
<td>0.0155959</td>
<td>320.852</td>
<td>0.0160543</td>
<td>320.774</td>
</tr>
<tr>
<td>17</td>
<td>0.0111762</td>
<td>334.894</td>
<td>0.0137321</td>
<td>334.852</td>
<td>0.0120170</td>
<td>334.770</td>
</tr>
<tr>
<td>18</td>
<td>0.0101996</td>
<td>348.892</td>
<td>0.0120910</td>
<td>348.852</td>
<td>0.0088166</td>
<td>348.752</td>
</tr>
<tr>
<td>19</td>
<td>0.0091934</td>
<td>362.890</td>
<td>0.0108204</td>
<td>362.841</td>
<td>0.0063296</td>
<td>362.841</td>
</tr>
<tr>
<td>20</td>
<td>0.0081996</td>
<td>376.890</td>
<td>0.0093017</td>
<td>376.805</td>
<td>0.0040707</td>
<td>376.805</td>
</tr>
</tbody>
</table>

For all three cases $\eta = 90$ and $M_{C7} = 200$.

Mole fractions $z_i$ are given by

$$z_i = z_{C7} \frac{Q_{w_i}}{Q_{w_i} - Q_{w_{i-1}}}$$

(5.29)

For computer applications, $Q_{w_i}$ and $Q_{w_i}^*$ can be calculated exactly from Eqs. 5.16 through 5.23 with little extra effort.

Fig. 5.9—Three example molar distributions for an oil sample with $M_{C7} = 200$ and $\eta = 90$, calculated with the GAMSPL program (Table A-4) in Table 5.4.

Fig. 5.10—Cumulative-distribution type curve for fitting experimental TBP data to the gamma-distribution model. Parameters $\alpha$ and $\eta$ are determined with $M_{C7}$ held constant.

Fig. 5.11 shows a $Q_{w_i}^* - Q_{w_i}$ match for the Hoffman et al. oil with $p = 70, 72.5, 75,$ and 80 and indicates that a best fit is achieved for $\eta = 72.5$ and $\alpha = 2.5$ (see Fig. 5.12).

Although the gamma-distribution model has the flexibility of treating reservoir fluids from light condensates to bitumen, most reservoir fluids can be characterized with an exponential molar distribution ($\alpha = 1$) without adversely affecting the quality of EOS pre-
dictionaries. Whitson et al.\textsuperscript{27} proposed perhaps the most useful application of the gamma-distribution model. With Gaussian quadrature, their method allows multiple reservoir-fluid samples from a common reservoir to be treated simultaneously with a single fluid characterization. Each fluid sample can have different $C_7^+$ properties when the split is made so that each split fraction has the same molecular weight (and other properties, such as $\gamma$, $T_0$, $T_c$, $p_c$, and $\omega$), while the mole fractions are different for each fluid sample. Example applications include the characterization of a gas cap and underlying reservoir oil and a reservoir with compositional gradient.

The following outlines the procedure for applying Gaussian quadrature to the gamma-distribution function.

1. Determine the number of $C_7^+$ fractions, $N$, and obtain the quadrature values $x_i$ and $W_i$ from Table 5.6 (values are given for $N = 3$ and $N = 5$).

2. Specify $\gamma$ and $\alpha$. When TBP data are not available to determine these parameters, recommended values are $\gamma = 90$ and $\alpha = 1$.

3. Specify the heaviest molecular weight of fraction $N$ (recommended value is $M_N = 2.5M_{C_7^+}$). Calculate a modified $\beta^*$ term, $\beta^* = (M_N - \bar{M})/\bar{M}$.

**Table 5.5—Calculation of Cumulative Weight Fraction and Cumulative Molecular Weight Variable for Hoffman et al.\textsuperscript{29} Oil**

<table>
<thead>
<tr>
<th>Component</th>
<th>$\alpha$</th>
<th>$\Sigma x_i$</th>
<th>$M_i$</th>
<th>$\Sigma M_i$</th>
<th>$\bar{M}$</th>
<th>$\Sigma x_i M_i$</th>
<th>$\bar{M}_c$</th>
<th>$Q_{0M}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0263</td>
<td>0.0263</td>
<td>99</td>
<td>2.604</td>
<td>2.604</td>
<td>0.036</td>
<td>99.0</td>
<td>0.225</td>
</tr>
<tr>
<td>2</td>
<td>0.0334</td>
<td>0.0497</td>
<td>110</td>
<td>2.574</td>
<td>5.178</td>
<td>0.071</td>
<td>104.2</td>
<td>0.266</td>
</tr>
<tr>
<td>3</td>
<td>0.0235</td>
<td>0.0732</td>
<td>121</td>
<td>2.844</td>
<td>8.021</td>
<td>0.110</td>
<td>109.6</td>
<td>0.308</td>
</tr>
<tr>
<td>4</td>
<td>0.0224</td>
<td>0.0956</td>
<td>132</td>
<td>2.957</td>
<td>10.978</td>
<td>0.150</td>
<td>114.8</td>
<td>0.348</td>
</tr>
<tr>
<td>5</td>
<td>0.0241</td>
<td>0.1197</td>
<td>145</td>
<td>3.497</td>
<td>14.475</td>
<td>0.198</td>
<td>120.9</td>
<td>0.396</td>
</tr>
<tr>
<td>6</td>
<td>0.0246</td>
<td>0.1443</td>
<td>158</td>
<td>3.882</td>
<td>18.357</td>
<td>0.251</td>
<td>127.2</td>
<td>0.445</td>
</tr>
<tr>
<td>7</td>
<td>0.0266</td>
<td>0.1709</td>
<td>172</td>
<td>4.570</td>
<td>22.928</td>
<td>0.313</td>
<td>134.2</td>
<td>0.499</td>
</tr>
<tr>
<td>8</td>
<td>0.0326</td>
<td>0.2035</td>
<td>196</td>
<td>6.067</td>
<td>28.995</td>
<td>0.396</td>
<td>142.5</td>
<td>0.563</td>
</tr>
<tr>
<td>9</td>
<td>0.0363</td>
<td>0.2398</td>
<td>203</td>
<td>7.371</td>
<td>36.366</td>
<td>0.497</td>
<td>151.7</td>
<td>0.634</td>
</tr>
<tr>
<td>10</td>
<td>0.0229</td>
<td>0.2627</td>
<td>222</td>
<td>5.093</td>
<td>41.458</td>
<td>0.566</td>
<td>157.8</td>
<td>0.682</td>
</tr>
<tr>
<td>11</td>
<td>0.0171</td>
<td>0.2799</td>
<td>238</td>
<td>4.079</td>
<td>45.538</td>
<td>0.622</td>
<td>162.7</td>
<td>0.720</td>
</tr>
<tr>
<td>12</td>
<td>0.0143</td>
<td>0.2941</td>
<td>252</td>
<td>3.596</td>
<td>49.134</td>
<td>0.671</td>
<td>167.0</td>
<td>0.754</td>
</tr>
<tr>
<td>13</td>
<td>0.0130</td>
<td>0.3072</td>
<td>266</td>
<td>3.466</td>
<td>52.600</td>
<td>0.719</td>
<td>171.2</td>
<td>0.787</td>
</tr>
<tr>
<td>14</td>
<td>0.0108</td>
<td>0.3180</td>
<td>279</td>
<td>3.008</td>
<td>55.607</td>
<td>0.760</td>
<td>174.9</td>
<td>0.815</td>
</tr>
<tr>
<td>15</td>
<td>0.0087</td>
<td>0.3267</td>
<td>290</td>
<td>2.526</td>
<td>58.133</td>
<td>0.794</td>
<td>178.0</td>
<td>0.839</td>
</tr>
<tr>
<td>16</td>
<td>0.0072</td>
<td>0.3338</td>
<td>301</td>
<td>2.152</td>
<td>60.285</td>
<td>0.824</td>
<td>180.6</td>
<td>0.859</td>
</tr>
<tr>
<td>17</td>
<td>0.0058</td>
<td>0.3536</td>
<td>315</td>
<td>1.811</td>
<td>62.097</td>
<td>0.848</td>
<td>182.9</td>
<td>0.877</td>
</tr>
<tr>
<td>18</td>
<td>0.0048</td>
<td>0.3444</td>
<td>329</td>
<td>1.582</td>
<td>63.679</td>
<td>0.870</td>
<td>184.9</td>
<td>0.893</td>
</tr>
<tr>
<td>19</td>
<td>0.0039</td>
<td>0.3483</td>
<td>343</td>
<td>1.351</td>
<td>65.031</td>
<td>0.888</td>
<td>186.7</td>
<td>0.907</td>
</tr>
<tr>
<td>20</td>
<td>0.0034</td>
<td>0.3517</td>
<td>357</td>
<td>1.196</td>
<td>66.227</td>
<td>0.905</td>
<td>188.3</td>
<td>0.919</td>
</tr>
<tr>
<td>21</td>
<td>0.0028</td>
<td>0.3545</td>
<td>371</td>
<td>1.039</td>
<td>67.265</td>
<td>0.919</td>
<td>189.8</td>
<td>0.931</td>
</tr>
<tr>
<td>22</td>
<td>0.0025</td>
<td>0.3570</td>
<td>385</td>
<td>0.963</td>
<td>68.228</td>
<td>0.932</td>
<td>191.1</td>
<td>0.941</td>
</tr>
<tr>
<td>23</td>
<td>0.0023</td>
<td>0.3593</td>
<td>399</td>
<td>0.926</td>
<td>69.154</td>
<td>0.945</td>
<td>192.5</td>
<td>0.952</td>
</tr>
<tr>
<td>24</td>
<td>0.00091</td>
<td>0.3684</td>
<td>444</td>
<td>0.409</td>
<td>73.203</td>
<td>1.000</td>
<td>198.7</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Total 0.3684

198.7 73.203

Fig. 5.11—Graphical fit of the Hoffman et al.\textsuperscript{29} oil molar distribution by use of the cumulative-distribution type curve. Best-fit model parameters are $\alpha = 2.5$ and $\gamma = 72.5$.

Fig. 5.12—Calculated normalized mole fraction vs. molecular weight of fractions for the Hoffman et al.\textsuperscript{29} oil based on the best fit in Fig. 5.11 with $\alpha = 2.5$ and $\gamma = 72.5$. HEPTANES-PLUS CHARACTERIZATION

9
4. Calculate the parameter $\delta$.

$$
\delta = \exp \left( \frac{a \beta^2}{M_{C7+} - \eta} - 1 \right) \quad (5.30)
$$

5. Calculate the $C_7+$ mole fraction $z_i$ and $M_i$ for each fraction.

$$
z_i = \frac{w_i}{M_i} \left( \frac{f(x)}{x} \right) \quad (5.31)
$$

and $f(x) = \frac{(\lambda x - 1) (1 + \ln \lambda)^{\lambda}}{\lambda} \quad (5.31)$

6. Check whether the calculated $M_{C7+}$ from Eq. 5.12 equals the measured value used in Step 4 to define $\delta$. Because Gaussian quadrature is only approximate, the calculated $M_{C7+}$ may be slightly in error. This can be corrected by (slightly) modifying the value of $\delta$, and repeating Steps 5 and 6 until a satisfactory match is achieved.

When characterizing multiple samples simultaneously, the values of $M_{C7+}$ or $M_{C7+}$ should be the same for all samples. Individual sample values of $M_{C7+}$ and $\eta$ can, however, be different. The result of this characterization is one set of molecular weights for the $C_7+$ fractions, while each sample has different mole fractions $z_i$ (so that their average molecular weights $M_{C7+}$ are honored).

Specific gravities for the $C_7+$ fractions can be calculated with one of the correlations given in Sec. 5.4 (e.g., Eq. 5.44), where the characterization factor ($e$, $F_e$) must be the same for all mixtures. The specific gravities, $\gamma_{C7+}$, of each sample will not be exactly reproduced with this procedure (calculated with Eq. 5.37), but the average characterization factor can be chosen so that the differences are very small ($\gamma \leq 0.0005$). Having defined $M_i$ and $\gamma_i$ for the $C_7+$ fractions, a complete fluid characterization can be determined with correlations in Sec. 5.5.

### 5.4 Inspection-Properties Estimation

#### 5.4.1 Generalized Properties

The molecular weight, specific gravity, and boiling point of $C_7+$ fractions must be estimated in the absence of experimental TBP data. This situation arises when simulated distillation is used or when no experimental analysis of $C_7+$ is available and a synthetic split must be made by use of a molar distribution model. For either situation, inspection data from TBP analysis of a sample from the same field would be the most reliable source of $M_i$, $\gamma_i$, and $T_b$ for each $C_7+$ fraction. The next-best source would be measured TBP data from a field producing similar oil or condensate from the same geological formation. Generalized properties from a producing region, such as the North Sea, have been proposed.\(^{31}\)

Kate and Firoozabadi\(^{6}\) suggest a generalized set of SCN properties for petroleum fractions $C_6$ through $C_{45}$. Table 5.2 gives an extended version of the Katz-Firoozabadi property table. Molecular weights can be used to convert weight fractions, $w_i$, from simulated distillation to mole fractions, $z_i = \frac{w_i}{M_i} \quad (5.32)$

$$
\sum_{i=1}^{N} w_i/M_i = 1 \quad (5.32)
$$

However, the molecular weight of the heaviest fraction, $C_{30}$, is not known. From a mass balance, $M_{C30}$ is given by

$$
M_{C30} = \frac{w_{C30}}{M_{C30}} = \frac{w_i}{M_i} / \sum_{i=1}^{N} w_i/M_i \quad (5.33)
$$

where $M_i$ for $i = 1, \ldots, N - 1$ are taken from Table 5.2. Unfortunately, the calculated molecular weight $M_{C30}$ is often unrealistic because of measurement errors in $M_{C_{30}}$, or in the chromatographic analysis and because generalized molecular weights are only approximate. Both $w_{C30}$ and $M_{C30}$ can be adjusted to give a “reasonable” $M_{C30}$, but caution is required to avoid nonphysical adjustments. The same problem is inherent with backcalculating $M_i$ with any set of generalized molecular weights used for SCN Fractions 7 to $N - 1$ (e.g., paraffin values).

During the remainder of this section, molecular weights and mole fractions are assumed to be known for $C_7+$ fractions, either from chromatographic analysis or from a synthetic split. The generalized properties for specific gravity and boiling point can be assigned to SCN fractions, but the heaviest specific gravity must be backcalculated to match the measured $C_{30}$ specific gravity. The calculated $\gamma_{C30}$ also may be unrealistic, requiring some adjustment to generalized specific gravities. Finally, the boiling point of the heaviest fraction must be estimated. $T_b$ can be estimated from a correlation relating boiling point to specific gravity and molecular weight.

### 5.4.2 Characterization Factors

Inspection properties $M_i$, $\gamma_i$, and $T_b$ reflect the chemical makeup of petroleum fractions. Some methods for estimating specific gravity and boiling point assume that a particular characterization factor is constant for all $C_7+$ fractions. These methods are only approximate but are widely used.

- Watson or Universal Oil Products (UOP) Characterization Factor $K_w$ is based on boiling point, $T_b$, in °R and specific gravity, $\gamma$.\(^{32,33}\)

$$
K_w = \frac{x^{2/3}}{1 - x} \quad (5.34)
$$

$K_w$ varies roughly from 8.5 to 13.5. For paraffinic compounds, $K_w = 12.5$ to 13.5; for naphthenic compounds, $K_w = 10.0$ to 12.5; and for aromatic compounds, $K_w = 8.5$ to 11.0. Some overlap in $K_w$ exists among these three families of hydrocarbons, and a combination of paraffins and aromatics will obviously “appear” naphthenic.

However, the utility of this and other characterization factors is that they give a qualitative measure of the composition of a petroleum fraction. The Watson characterization factor has been found to be useful for approximate characterization and is widely used as a parameter for correlating petroleum-fraction properties, such as molecular weight, viscosity, vapor pressure, and critical properties. An approximate relation\(^{7}\) for the Watson factor, based on molecular weight and specific gravity, is

$$
K_w = 4.5579 \frac{M_{C7+}^{0.1178} \gamma_{C7+}^{-0.4571}}{1 - \gamma_{C7+}} \quad (5.35)
$$

This relation is derived from the Rizzi-Daubert\(^{14}\) correlation for molecular weight and is generally valid for petroleum fractions with normal boiling points ranging from 560 to 1,310°F ($C_7$ through $C_{30}$). Experience has shown, however, that Eq. 5.35 is not very accurate for fractions heavier than $C_{30}$.

$K_w$ calculated with $M_{C7+}$ and $\gamma_{C7+}$ in Eq. 5.35 is often constant for a given field. Figs. 5.13A and 5.13B\(^{34}\) plot molecular weight vs. specific gravity for $C_7+$ fractions from two North Sea fields. Data for the gas condensate in Fig. 5.13A indicate an average $K_{C7+} = 11.99 \pm 0.01$ for a range of molecular weights from 135 to 150. The volatile oil shown in Fig. 5.13B has an average $K_{C7+} = 11.90 \pm 0.01$ for a range of molecular weights from 220 to
The high degree of correlation for these two fields suggests accurate molecular-weight measurements by the laboratory. In general, the spread in $K_{c7}$ values will exceed $\pm 0.01$ when measurements are performed by a commercial laboratory.

When the characterization factor for a field can be determined, Eq. 5.35 is useful for checking the consistency of $C_7$ molecular-weight and specific-gravity measurements. Significant deviation in $K_{c7}$, such as $\pm 0.03$ for the North Sea fields above, indicates possible error in the measured data. Because molecular weight is more prone to error than determination of specific gravity, an anomalous $K_{c7}$ usually indicates an erroneous molecular-weight measurement. For the gas condensate in Fig. 5.13A, a $C_7$ sample with specific gravity of 0.775 would be expected to have a molecular weight of $141$ (for $K_{c7} = 11.99$). If the measured value was 135, the Watson characterization factor would be 11.90, which is significantly lower than the field average of 11.99. In this case, the $C_7$ molecular weight should be redetermined.

Eq. 5.35 can also be used to calculate specific gravity of $C_7$ fractions determined by simulated distillation or a synthetic split (i.e., when only mole fractions and molecular weights are known). Assuming a constant $K_w$ for each fraction, specific gravity, $\gamma_{c7}$, can be calculated from

$$\gamma_{c7} = 6.0108 M_i^{0.1747} K_{w1.1324}. \quad (5.36)$$

Boiling points, $T_{bi}$, can be estimated from Eq. 5.36.

$$T_{bi} = (K_w \gamma_{c7})^{0.5}. \quad (5.40)$$

Unfortunately, Eqs. 5.36 through 5.40 overpredict $\gamma$ and $T_b$ at molecular weights greater than $\approx 250$ (an original limitation of the Riazi-Daubert molecular-weight correlation).

Jacoby Aromaticity Factor. The Jacoby aromaticity factor, $J_a$, is an alternative characterization factor for describing the relative composition of petroleum fractions. Fig. 5.14 shows the original Jacoby relation between specific gravity and molecular weight for several values of $J_a$. The behavior of specific gravity as a function of molecular weight is similar for the Jacoby factor and the relation for a constant $K_w$. However, specific gravity calculated with the Jacoby method increases more rapidly at low molecular weights, flattening at high molecular weights (a more physically consistent behavior). A relation for the Jacoby factor is

$$J_a = \left[ \frac{0.16637 \gamma_{c7} A_b}{\gamma_{c7} M_i^{1.6208}} \right]^{-0.04877}. \quad (5.37)$$

where $A_b = \sum_{i=1}^{N} \gamma_{c7} M_i^{1.8208}. \quad (5.38)$

HEPTANES-PLUS CHARACTERIZATION
changing character of fractions up to C13 better and by representing

The first two terms in Eq. 5.42 (i.e., when $c_i = 0$) express the relation

between specific gravity and molecular weight for normal paraffins.

The Jacoby factor can also be used to estimate fraction specific gravities when mole fractions and molecular weights are available from simulated distillation or a synthetic split. The Jacoby factor satisfying measured $C_7$ specific gravity (Eq. 5.37) must be calculated by trial and error. We have found that this relation is particularly

accurate for gas-condensate systems.27

**Yarborough Aromaticity Factor.** Yarborough1 modified the
Jacoby aromaticity factor specifically for estimating specific gravities when mole fractions and molecular weights are known. Yarborough tried to improve the original Jacoby relation by reflecting the changing character of fractions up to C13 better and by representing the larger naphthenic content of heavier fractions better. Fig. 5.15 shows how the Yarborough aromaticity factor, $Y_a$, is related to specific gravity and carbon number. A simple relation representing $Y_a$ is not available; however, Whitson26 has fit the seven aromaticity curves originally presented by Yarborough using the equation

$\gamma = \exp(1.07722 + 0.2456 - 1.77 \times 10^{-3} M_a)$. (5.42)

where $i = $ carbon number. Table 5.7 gives the constants for Eq. 5.43. The aromaticity factor required to satisfy measured $C_7$ specific gravity (Eq. 5.37) is determined by trial and error. Linear interpolation of specific gravity should be used to calculate specific gravity for a $Y_a$ value falling between two values of $Y_a$ in Table 5.7.

**Søreide** Correlations. Søreide developed an accurate specific-gravity correlation based on the analysis of 843 TBP fractions from 68 reservoir $C_7$ samples. $\gamma = 0.2855 + C_7(M_a - 66)^{0.11}$. (5.44)

$C_7$ typically has a value between 0.27 and 0.31 and is determined for a specific $C_7$ sample by satisfying Eq. 5.37.

**Boiling-Point Estimation.** Boiling point can be estimated from molecular weight and specific gravity with one of several correlations. Søreide also developed a boiling-point correlation based on 843 TBP fractions from 68 reservoir $C_7$ samples, $T_b = 1922.8 - (1.695 \times 10^3) M_a^{0.03522} \gamma^{1.206}$

$\times \exp\left[-(4.922 \times 10^{-3}) M_a - 4.7685 \gamma\right] + (3.462 \times 10^{-3}) M_a^{0.13}$. (5.44)

with $T_b$ in °R.

Table 5.8 gives estimated specific gravities determined with the methods just described for a $C_7$ sample with the exponential split given in Table 5.4 ($\sigma = 1$, $\eta = 90$, $M_c = 200$) and $Y_a = 0.832$.

The following equations also relate molecular weight to boiling point and specific gravity; any of these correlations can be solved for boiling point in terms of $M$ and $\gamma$. We recommend, however, the Søreide correlation for estimating $T_b$ from $M$ and $\gamma$.

**Kesler and Lee.** $M = -12, 272.6 + 9, 486.4\gamma + (4.6523 - 3.3287) (T_b)$

$\times \exp\left[-0.77084\gamma - 0.02058\gamma^2\right] + (1.3437 - 720.79 T_b^{0.01})^{10^{1.77}} + (1.0164 - 720.79 T_b^{0.01})^{10^{1.77}}$. (5.46)

**Riazzi and Daubert.** $M = (4.5673 \times 10^{-5}) T_b^{1.0186} \gamma^{0.0004}$. (5.47)

**American Petroleum Inst. (API).** $M = (2.0438 \times 10^{-5}) T_b^{0.1148} \gamma^{0.0004} \exp(0.00218 T_b - 3.07\gamma)$. (5.48)

**Rao and Bardon.** $\ln M = (1.27 + 0.071 K_a) \ln\left(\frac{1.87 T_b^{0.031} + 1.68 K_a}{22.3} \right)$. (5.49)

**Riazzi and Daubert.** $M = 581.96 T_b^{0.02476} \gamma^{0.5275} \exp(5.43076 \times 10^{-1} T_b^{0.03})$

$\times [(1.1056 - 10^{-3}) T_b^{0.03}]$. (5.50)

<table>
<thead>
<tr>
<th>$Y_a$</th>
<th>$A_0$</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$A_3$</th>
<th>$A_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-7.43855 $\times 10^{-2}$</td>
<td>-1.72341</td>
<td>1.38058 $\times 10^{-3}$</td>
<td>-3.34169 $\times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>-4.25800 $\times 10^{-1}$</td>
<td>-7.00017 $\times 10^{-2}$</td>
<td>-3.30947 $\times 10^{-5}$</td>
<td>8.65465 $\times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>-4.47553 $\times 10^{-1}$</td>
<td>-7.65111 $\times 10^{-1}$</td>
<td>1.77982 $\times 10^{-4}$</td>
<td>1.07746 $\times 10^{-1}$</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>-4.39105 $\times 10^{-1}$</td>
<td>-9.44068 $\times 10^{-1}$</td>
<td>4.93708 $\times 10^{-4}$</td>
<td>1.19267 $\times 10^{-1}$</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>-2.73719 $\times 10^{-1}$</td>
<td>-1.39960</td>
<td>3.80564 $\times 10^{-3}$</td>
<td>5.92005 $\times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>-7.39412 $\times 10^{-3}$</td>
<td>-1.97063</td>
<td>5.87273 $\times 10^{-3}$</td>
<td>-1.67141 $\times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>-3.17618 $\times 10^{-1}$</td>
<td>-7.78432 $\times 10^{-1}$</td>
<td>2.58616 $\times 10^{-3}$</td>
<td>1.08382 $\times 10^{-2}$</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 5.8—COMPARISON OF SPECIFIC GRAVITIES WITH CORRELATIONS BY USE OF DIFFERENT CHARACTERIZATION FACTORS

<table>
<thead>
<tr>
<th>Fraction</th>
<th>( z_i )</th>
<th>( \gamma_i )</th>
<th>( K_p = 12.080 )</th>
<th>( J_p = 0.2395 )</th>
<th>( Y_p = 0.2794 )</th>
<th>( C_p = 0.2864 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1195</td>
<td>96.8</td>
<td>0.7177</td>
<td>0.7472</td>
<td>0.7051</td>
<td>0.7327</td>
</tr>
<tr>
<td>2</td>
<td>0.1052</td>
<td>110.8</td>
<td>0.7353</td>
<td>0.7684</td>
<td>0.7286</td>
<td>0.7550</td>
</tr>
<tr>
<td>3</td>
<td>0.0926</td>
<td>124.8</td>
<td>0.7511</td>
<td>0.7849</td>
<td>0.7486</td>
<td>0.7719</td>
</tr>
<tr>
<td>4</td>
<td>0.0816</td>
<td>138.8</td>
<td>0.7656</td>
<td>0.7981</td>
<td>0.7660</td>
<td>0.7856</td>
</tr>
<tr>
<td>5</td>
<td>0.0718</td>
<td>152.8</td>
<td>0.7789</td>
<td>0.8088</td>
<td>0.7813</td>
<td>0.7972</td>
</tr>
<tr>
<td>6</td>
<td>0.0632</td>
<td>166.8</td>
<td>0.7913</td>
<td>0.8178</td>
<td>0.7951</td>
<td>0.8072</td>
</tr>
<tr>
<td>7</td>
<td>0.0557</td>
<td>180.8</td>
<td>0.8028</td>
<td>0.8253</td>
<td>0.8075</td>
<td>0.8161</td>
</tr>
<tr>
<td>8</td>
<td>0.0490</td>
<td>194.8</td>
<td>0.8136</td>
<td>0.8318</td>
<td>0.8169</td>
<td>0.8241</td>
</tr>
<tr>
<td>9</td>
<td>0.0432</td>
<td>208.8</td>
<td>0.8238</td>
<td>0.8374</td>
<td>0.8294</td>
<td>0.8314</td>
</tr>
<tr>
<td>10</td>
<td>0.0380</td>
<td>222.8</td>
<td>0.8335</td>
<td>0.8423</td>
<td>0.8391</td>
<td>0.8380</td>
</tr>
<tr>
<td>11</td>
<td>0.0335</td>
<td>236.8</td>
<td>0.8426</td>
<td>0.8466</td>
<td>0.8482</td>
<td>0.8442</td>
</tr>
<tr>
<td>12</td>
<td>0.0295</td>
<td>250.8</td>
<td>0.8514</td>
<td>0.8505</td>
<td>0.8567</td>
<td>0.8500</td>
</tr>
<tr>
<td>13</td>
<td>0.0259</td>
<td>264.8</td>
<td>0.8597</td>
<td>0.8539</td>
<td>0.8646</td>
<td>0.8554</td>
</tr>
<tr>
<td>14</td>
<td>0.0228</td>
<td>278.8</td>
<td>0.8677</td>
<td>0.8750</td>
<td>0.8722</td>
<td>0.8604</td>
</tr>
<tr>
<td>15</td>
<td>0.0201</td>
<td>292.8</td>
<td>0.8753</td>
<td>0.8598</td>
<td>0.8793</td>
<td>0.8652</td>
</tr>
<tr>
<td>16</td>
<td>0.0177</td>
<td>306.8</td>
<td>0.8827</td>
<td>0.8623</td>
<td>0.8861</td>
<td>0.8697</td>
</tr>
<tr>
<td>17</td>
<td>0.0156</td>
<td>320.8</td>
<td>0.8898</td>
<td>0.8646</td>
<td>0.8926</td>
<td>0.8740</td>
</tr>
<tr>
<td>18</td>
<td>0.0137</td>
<td>334.8</td>
<td>0.8966</td>
<td>0.8668</td>
<td>0.8988</td>
<td>0.8782</td>
</tr>
<tr>
<td>19</td>
<td>0.0121</td>
<td>348.8</td>
<td>0.9033</td>
<td>0.8687</td>
<td>0.9048</td>
<td>0.8821</td>
</tr>
<tr>
<td>20</td>
<td>0.0091</td>
<td>362.0</td>
<td>0.9141</td>
<td>0.8805</td>
<td>0.9468</td>
<td>0.9096</td>
</tr>
<tr>
<td>Total</td>
<td>1.0000</td>
<td>200.0</td>
<td>0.8320</td>
<td>0.8320</td>
<td>0.8320</td>
<td>0.8320</td>
</tr>
</tbody>
</table>

5.5 Critical-Properties Estimation

Thus far, we have discussed how to split the \( C_7 + \) fraction into pseudocomponents described by mole fraction, molecular weight, specific gravity, and boiling point. Now we must consider the problem of assigning critical properties to each pseudocomponent. Critical temperature, \( T_c \); critical pressure, \( P_c \); andacentric factor, \( \omega \), of each component in a mixture are required by most cubic EOS’s. Critical volume, \( v_c \), is used instead of critical pressure in the Benedict-Webb-Rubin \( 18 \) (BWR) EOS, and critical molar volume is used with the LBC viscosity correlation. \( 24 \) Critical compressibility factor has been introduced as a parameter in three- and four-constant cubic EOS’s.

Critical-property estimation of petroleum fractions has a long history beginning as early as the 1930’s; several reviews \( 22,25,26,39,40 \) are available. We present the most commonly used correlations and a graphical comparison (Figs. 5.16 through 5.18) that is intended to highlight differences between the correlations. Finally, correlations based on perturbation expansion (a concept borrowed from statistical mechanics) are discussed separately.

The units for the remaining equations in this section are \( T_b \) in \( \text{°F}, T_{bf} \) in \( \text{°F} = T_b - 459.67, T_c \) in \( \text{°R}, P_c \) in psia, and \( v_c \) in \( \text{ft}^3/\text{lbm} \). Oil gravity is denoted \( \gamma_{API} \) and is related to specific gravity by

\[
\gamma_{API} = 141.5\gamma - 131.5
\]

5.5.1 Critical Temperature, \( T_c \). \( T_c \) is perhaps the most reliably correlated critical property for petroleum fractions. The following critical-temperature correlations can be used for petroleum fractions.

**Roess.** \( 41 \) (modified by API \( 36 \)),

\[
T_c = \frac{645.83 + 1.6667\left[\frac{1}{P_{bf}} + 100\right]}{1 - 0.7127 \times 10^{-3}\left[\frac{1}{P_{bf}} + 100\right]^2}
\]

**Kesler-Lee.** \( 12 \)

\[
T_c = \frac{341.7 + 811y + (0.4244 + 0.1174y)T_b}{(0.4669 - 3.2623y) \times 10^{3}T_b^{-1}}
\]

**Cavett.** \( 42 \)

\[
T_c = \frac{768.07121 + 1.7133693T_{bf}}{1 - 0.10834003 \times 10^{-2}T_{bf}^{-1} - 0.89212579 \times 10^{-7}T_{bf}^{-1} + 0.38890584 \times 10^{-10}T_{bf}^{-1} + 0.5309492 \times 10^{-3}T_{bf}^{-1} + 0.327116 \times 10^{-7}T_{bf}^{-1}}
\]

**Riazi-Daoubert.** \( 14 \)

\[
T_c = \frac{24.27871 + 0.38860584}{0.1174}
\]

**Nokay.** \( 43 \)

\[
T_c = \frac{19.078}{0.832}
\]

5.5.2 Critical Pressure, \( P_c \). Correlations are less reliable than \( T_c \) correlations. The following are \( P_c \) correlations that can be used for petroleum fractions.

**Kesler-Lee.** \( 12 \)

\[
\ln P_c = 8.3634 - 0.0566 \gamma
\]

\[
\left[0.24244 + 2.2898 y + 0.11857 y^2\right] \times 10^{-3}
\]
where pure hydrocarbons and should not be used for C₇ fractions. The three correlations follow.

\[
\begin{align*}
\text{Kesler-Lee:} & \quad p_c = 2.8290406 + (0.94120109 \times 10^{-3})T_{br}^2 \\
& - (0.2087611 \times 10^{-3})T_{br}^2T_c + (0.15184103 \times 10^{-3})T_{br}^2T_c^2 \\
& + (0.11047899 \times 10^{-3})T_{br}^2T_c^2 - (0.48271599 \times 10^{-3})T_{br}^2T_c^2 + (0.13949619 \times 10^{-3})T_{br}^2T_c^2. \quad \text{(5.56)}
\end{align*}
\]

\[
\begin{align*}
\text{Riaz-Daubert:} & \quad p_c = 3.12281 \times 10^3T_b^{1.3129}T_c^{2.3201}. \quad \text{(5.57)}
\end{align*}
\]

5.5.3 Acentric Factor. Pitzen et al.\textsuperscript{14} defined acentric factor as

\[
\omega = -\log \left(\frac{p^*}{p_i}\right) - 1. \quad \text{(5.59)}
\]

where \(p^*\) = vapor pressure at temperature \(T = 0.7T_b\) (\(T_b = 0.7\)). Practically, acentric factor gives a measure of the steepness of the vapor-pressure curve from \(T_b = 0.7\) to \(T_b = 1\), where \(p^*/p_i = 0.01\) for \(\omega = 0\) and \(p^*/p_i = 0.01\) for \(\omega = 1\). Numerically, \(\omega = 0.01\) for methane, \(\omega = 0.25\) for C₅, and \(\omega = 0.5\) for C₆ (see Table A.1 for literature values of acentric factor for pure compounds). \(\omega\) increases to \(\geq 1.0\) for petroleum fractions heavier than approximately C₃₂ (see Table 5.2).

The Kesler-Lee\textsuperscript{12} acentric factor correlation (for \(T_b/T_c < 0.8\)) is developed specifically for petroleum fractions, whereas the correlation for \(T_b/T_c > 0.8\) is based on an accurate vapor-pressure correlation for pure compounds. The Edmister\textsuperscript{45} correlation is limited to pure hydrocarbons and should not be used for C₇ + fractions. The three correlations follow.
5.5.4 Critical Volume. The Hall-Yarborough\textsuperscript{46} critical-volume correlation is given in terms of molecular weight and specific gravity, whereas the Riazi-Daubert\textsuperscript{14} correlation uses normal boiling point and specific gravity.

Hall-Yarborough,\textsuperscript{46} \[ v_c = 0.025M^{0.153} - 0.7955 \] \hspace{1cm} (5.63)

Riazi-Daubert,\textsuperscript{14} \[ \nu_c = (7.0434 \times 10^{-7})T_c^{0.3625} \rho^{0.1081} \] \hspace{1cm} (5.64)

Critical compressibility factor, \( Z_c \), is defined as \[ Z_c = \frac{Rv}{\nu_c T_c^2} \] \hspace{1cm} (5.65)

where \( R \) is universal gas constant. Thus, \( Z_c \) can be calculated directly from critical pressure, critical volume, and critical temperature. Reid et al.\textsuperscript{48} and Pitzer et al.\textsuperscript{44} give an approximate relation for \( Z_c \).

\[ Z_c = 0.291 - 0.08\alpha \] \hspace{1cm} (5.66)

Eq. 5.66 is not particularly accurate (grossly overestimating \( Z_c \) for heavier compounds) and is used only for approximate calculations.

5.5.5 Correlations Based on Perturbation Expansions. Correlations for critical temperature, critical pressure, critical volume, and molecular weight have been developed for a perturbation-expansion model with normal paraffins as the reference system. To calculate critical pressure, for example, critical temperature, critical volume, and specific gravity of a paraffin with the same boiling point as the petroleum fraction must be calculated first. Kesler et al.\textsuperscript{47} first used the perturbation expansion (with \( n \)-alkanes as the reference fluid) to develop a suite of critical-property andacentric-factor correlations.

Two\textsuperscript{48} uses the same approach to develop a suite of critical-property correlations. We give his normal-paraffin correlations first, then the correlations for petroleum fractions.

**Normal Paraffins (Alkanes).**

\[ T_{cr} = T_b \left[ 0.533272 + (0.191017 \times 10^{-3})T_b \right] \]

\[ + 0.779681 \times 10^{-7}T_b^4 - \left( 0.284376 \times 10^{-10} \right)T_b^6 \]

\[ + 0.959468 \times 10^{-9} \] \hspace{1cm} (5.67)

\[ P_{cr} = (3.83354 + 1.19620x^{0.7} + 0.0012342 \] \hspace{1cm} (5.68)

\[ + 0.0175691 \] \hspace{1cm} (5.69)

\[ \nu_{cr} = \left[ 1 - \left( 0.419869 - 0.505839 \alpha - 0.128624 \alpha^2 - 3.36159 \alpha^3 - 1374.5x^{12} \right) \right] \] \hspace{1cm} (5.70)

and \( T_b = \exp(5.71419 + 2.715790 - 0.28659 \alpha^2 - 39.8544 \alpha^{-1} - 0.122488 \alpha^{-2}) \]

\[ - 24.75220 + 35.31552 \] \hspace{1cm} (5.71)

where \( \alpha = 1 - \frac{T_b}{T_{cr}} \) \hspace{1cm} (5.72)

and \( \theta = \ln \frac{v_c}{\nu_{cr}} \) \hspace{1cm} (5.73)

Paraffin molecular weight, \( M_p \), is not explicitly a function of \( T_b \), and Eqs. 5.67 through 5.73 must be solved iteratively; an initial guess is given by

\[ M_p = \frac{T_{cr}}{0.44 - 0.0052T_b} \] \hspace{1cm} (5.74)

Two\textsuperscript{48} claims that the normal-paraffin correlations are valid for \( C_1 \) through \( C_{100} \) although the properties at higher carbon numbers are only approximate because experimental data for paraffins heavier than approximately \( C_{20} \) do not exist. The following relations are used to calculate petroleum-fraction properties.

**Critical Temperature.**

\[ T_c = T_{cr} \left( \frac{1 + 2\nu}{1 - 2\nu} \right)^2 \]

\[ f_T = \Delta T_c = \left[ 0.362456 - \left( 0.0398285 - 0.948125 \right) \right] \Delta T_c \] \hspace{1cm} (5.75)

and \( \Delta T_c = \exp\{5(\nu - \gamma)\} - 1 \). \hspace{1cm} (5.76)

**Critical Pressure.**

\[ P_c = P_{cr} \left( \frac{T_{cr}}{T_b} \right)^{\frac{1 + 2\nu}{1 - 2\nu}} \]

\[ f_P = \Delta P_c = \left[ 2.53262 - \left( 46.1955 - 0.00127888T_b \right) \right] \Delta P_c \] \hspace{1cm} (5.77)

and \( \Delta P_c = \exp\{5(\nu - \gamma)\} - 1 \). \hspace{1cm} (5.78)

**Molecular Weight.**

\[ \ln M = \ln M_p \left( \frac{1 + 2\nu}{1 - 2\nu} \right)^2 \]

\[ f_M = \Delta M = \left[ 1 + \left( -0.0175691 + 0.193168 \right) \right] \Delta M \]

\[ x = 0.012342 - 0.328086 \] \hspace{1cm} (5.79)

and \( \Delta M = \exp\{5(\nu - \gamma)\} - 1 \). \hspace{1cm} (5.78)

Figs. 5.16 through 5.18 compare the various critical-property correlations for a range of boiling points from 600 to 1,500°F.

**5.5.6 Methods Based on an EOS.** Fig. 5.19\textsuperscript{16} illustrates the important influence that critical properties have on EOS-calculated properties of pure components. Vapor pressure is particularly sensitive to critical temperature. For example, the Riazi-Daubert\textsuperscript{16} critical-temperature correlation for toluene overpredicts the experimental value.
by only 1.7%. Even with this slight error in \( T_c \), the average error in vapor pressures predicted by the Peng-Robinson (PR) EOS is 16%. The effect of critical properties and acentric factor on EOS calculations for reservoir-fluid mixtures is summarized by Whitson.\(^5\)\(^6\)

In principle, the EOS used for mixtures should also predict the behavior of individual components found in the mixture. For pure compounds, the vapor pressure is accurately predicted because all EOS’s force fit vapor-pressure data. Some EOS’s are also fit to saturation type (bubblepoint or dewpoint), and both retrograde behavior just below the dewpoint).

When measured TBP data are not available, a mathematical split characterization procedure out-lined previously for the PR EOS and SRK EOS are probably the best currently available (other EOS characterizations, such as the Redlich-Kwong EOS modified by Zuckevitch and Joffe,\(^5\)\(^6\) and some three-constant characterizations should provide similar accuracy but are not significantly better). Practically, the two characterization procedures give the same results for almost all PVT properties (usually within 1 to 2%). With these EOS-characterization procedures, we can expect reasonable predictions of densities and Z factors (±1 to 5%), saturation pressures (±5 to 15%), gas/oil ratios and formation volume factors (±2 to 5%), and condensate-liquid dropout (±5 to 10% for maximum dropout, with poorer prediction of tail-like behavior just below the dewpoint).

The recommended EOS methods are less reliable for prediction of minimum miscibility conditions, near-critical saturation pressure and saturation type (bubblepoint or dewpoint), and both retrograde and near-critical liquid volumes. Improved predictions can be obtained only by tuning EOS parameters to accurate PVT data covering a relatively wide range of pressures, temperatures, and compositions (see Sec. 4.7 and Appendix C).

5.7 Grouping and Averaging Properties

The cost and computer resources required for compositional reservoir simulation increase substantially with the number of compo-
ents used to describe the reservoir fluid. A compromise between accuracy and the number of components must be made according to the process being simulated (i.e., according to the expected effect that phase behavior will have on simulated results). For example, a detailed fluid description with 12 to 15 components may be needed to simulate developed miscibility in a slim-tube experiment. With current computer technology, however, a full-field simulation with fluids exhibiting near-critical phase behavior is not feasible for a 15-component mixture. The following are the main questions regarding component grouping:

1. How many components should be used?
2. How should the components be chosen from the original fluid description?
3. How should the properties of pseudocomponents be calculated?

5.7.1 How Many and Which Components To Group. The number of components used to describe a reservoir fluid depends mainly on the process being simulated. However, the following rule of thumb reduces the number of components for most systems: group N2 with methane, CO2 with ethane, iso-butane with n-butane, and iso-pentane with n-pentane. Nonhydrocarbon content should be less than a few percent in both the reservoir fluid and the injection gas if a nonhydrocarbon is to be grouped with a hydrocarbon.

Five- to eight-component fluid characterizations should be sufficient to simulate practically any reservoir process, including (1) reservoir depletion of volatile-oil and gas-condensate reservoirs, (2) gas cycling above and below the dewpoint of a gas-condensate reservoir, (3) retrograde condensation near the wellbore of a producing well, and (4) immiscible and miscible gas-injection. Coats57 discusses a method for combining a modified black-oil model with a simplified EOS representation of separator oil and gas streams. The “oil” and “gas” pseudocomponents in this model contain all the original fluid components in contrast to the typical method of grouping where each pseudocomponent is made up of only selected original components. Lee et al.58 suggest that C7+ fractions can be grouped into two pseudocomponents according to a characterization factor determined by averaging the tangents of fraction properties M, γ, and J0 plotted vs. boiling point. Whitson2 suggests that the C7+ fraction can be grouped into N1 pseudocomponents given by

\[ N_1 = 1 + 3.3 \log(N - 7) \]  

(5.81)  

where N = carbon number of the heaviest fraction in the original fluid description. The groups are separated by molecular weights Mj given by

\[ M_j = M_{C_7} \left( \frac{M_j}{M_{C_7}} \right)^{11/9} \]  

(5.82)  

where \( I = 1, \ldots, N_1 \). Molecular weights, Mj, from the original fluid description (i = 7, ..., N) falling within boundaries \( M_{j-1} \) to \( M_{j} \) are included in Group J. This method should only be used when C7+ fractions are originally separated on a carbon-number basis and for N greater than \( \approx 20 \).

Li et al.75 suggest a method for grouping components of an original fluid description that uses K values from a flash at reservoir temperature and the “average” operating pressure. The original mixture is divided arbitrarily into “light” components (H2S, N2, CO2, and C1 butane) and “heavy” components (C7+). Different criteria are used to determine the number of light and heavy pseudocomponents. Li et al. also suggest use of phase diagrams and compositional simulation to verify the grouped fluid description (a practice that we highly recommend).

Still other pseudization methods have been proposed60,61. Schlüper61 method also treats the problem of retrieving detailed compositional information from pseudized (grouped) components. Behrens and Sandifer25 suggest a grouping method for C2+ fractions based on application of the Gaussian-quadrature method to continuous thermodynamics. Although a simple exponential distribution is used with only two quadrature points (i.e., the C7+ fractions are grouped into two pseudocomponents), Whitson et al.23 show that the method is general and can be applied to any molar-distribution model and for any number of C7+ groups.

In general, most authors have found that broader grouping of C7+ as C2 through C6, C7 through C15, C16 through C20, and C21+ is substantially better than splitting only the first few carbon-number fractions (e.g., C7, C8, C9, and C10). Gaussian quadrature is recommended for choosing the pseudocomponents in a C7+ fraction; equal-mass fractions or the Li et al.59 approach are valid alternatives.

5.7.2 Mixing Rules. Several methods have been proposed for calculating critical properties of pseudocomponents. The simplest and most common mixing rule is

\[ \theta_j = \frac{\sum_{i=1}^{j} z_i \theta_i}{\sum_{i=1}^{N} z_i}, \]  

(5.83)  

where \( \theta \) = any property (T, pc, M, or M) and \( z_i \) = original mole fraction for components \( (i = 1, \ldots, N) \) making up Pseudocomponent J. Average specific gravity should always be calculated with the assumption of ideal solution mixing.

Pedersen et al.23 and others suggest use of weight fraction instead of mole fraction. Wu and Batycky60 empirical mixing-rule approach uses both the molar- and weight-average mixing rules and a proportioning factor, F, to calculate \( \rho_m, T_F, \) and \( \omega_m \).

\[ \theta_j = \frac{\sum_{i=1}^{j} \rho_i \phi_j \theta_i}{\sum_{i=1}^{N} \rho_i \phi_j}, \]  

(5.85)  

where \( \theta_j \) represents \( \rho_m, \) \( T_F, \) and \( \omega \) and \( \phi_j = \) average of the molar and weight fractions,

\[ \phi_j = F \phi_j z_j + (1 - F) \theta_j w_j, \]  

where \( w_j = \sum_{j=1}^{N} z_j \) with \( 0 \leq F \leq 1 \).

A generalized mixing rule for BIP’s can be written

\[ \frac{k_{ij}}{\sum_{i=1}^{N} k_{ij} k_{ji} \phi_j \phi_i} \]  

(5.87)  

where \( k_{ij} \) is also given by Eq. 5.86.

On the basis of Chueh and Prausnitz’s54 arguments, Lee-Kesler13 proposed the mixing rules in Eqs. 5.88 through 5.92.

\[ v_{ij} = \frac{1}{8} \sum_{i=1}^{N} \sum_{j=1}^{N} \left( \frac{1}{r_{13}^2} + \frac{1}{r_{13}^2} \right) \left( \frac{1}{r_{13}^2} + \frac{1}{r_{13}^2} \right) \]  

(5.88)  

\[ T_{ij} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left( \frac{1}{r_{13}^2} + \frac{1}{r_{13}^2} \right) \]  

(5.89)  

\[ \omega_{ij} = \frac{1}{8} \sum_{i=1}^{N} \sum_{j=1}^{N} \left( \frac{1}{r_{13}^2} + \frac{1}{r_{13}^2} \right) \]  

(5.90)  

\[ Z_{ij} = 0.2905 - 0.085 \omega_{ij} \]  

(5.91)  

and \( \phi_{ij} = \frac{Z_{ij} R T_{ij}}{v_{ij}} \)
Lee et al.58 and Whitson2 consider an alternative method for calculating C7 + critical properties based on the specific gravities and boiling points of grouped pseudocomponents.

Coats57 presents a method of pseudoization that basically eliminates the effect of mixing rules on pseudocomponent properties. The approach is simple and accurate. Coats requires the pseudoized pseudocomponent properties, together with Eq. 5.87 for LBC24 viscosity correlation. Coats’ approach is preferred to all the other proposed methods. It ensures accurate volumetric calculations that are consistent with the original EOS characterization, and the method is easy to implement.

5.7.3 Stepwise Regression. A reduced-component characterization should strive to reproduce the original complete characterization that has been used to match measured PVT data. One approach to achieve this goal is stepwise regression, summarized in the following procedure.

1. Complete a comprehensive match of all existing PVT data with a characterization containing light and intermediate pure components and at least three to five C7 + fractions.

2. Simulate a suite of depletion and multicontact gas-injection PVT experiments that cover the expected range of compositions in the particular application.

3. Use the simulated PVT data as “real” data for pseudoization based on regression.

4. Create two new pseudocomponents from the existing set of components. Use the pseudoization procedure of Coats to obtain new regression parameters. The method is easy to implement. Further, any grouping of a complete EOS characterization deteriorates beyond an acceptable fluid description.

5. Use regression to fine tune the parameters. The method is easy to implement. Further, any grouping of a complete EOS characterization deteriorates beyond an acceptable fluid description.

6. Repeat Steps 4 and 5 until the quality of the characterization deteriorates beyond an acceptable fluid description. Table 5.9 shows an example five-step pseudoization procedure.

### Table 5.9—Example Stepwise-Regression Procedure for Pseudoization to Fewer Components for a Gas Condensate Fluid Undergoing Depletion

<table>
<thead>
<tr>
<th>Original Component Number</th>
<th>Original Component</th>
<th>Step 1</th>
<th>Step 2</th>
<th>Step 3</th>
<th>Step 4</th>
<th>Step 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N2</td>
<td>N2 + C4 (x^*)</td>
<td>N2 + C1</td>
<td>N2 + C1</td>
<td>N2 + C1 + CO2 + C2 + (n)</td>
<td>N2 + C1 + CO2 + C2 + (n)</td>
</tr>
<tr>
<td>2</td>
<td>CO2</td>
<td>CO2 + C2 (x^*)</td>
<td>CO2 + C2</td>
<td>CO2 + C2</td>
<td>CO2 + C2 + C4 + (n)</td>
<td>CO2 + C2 + C4 + (n)</td>
</tr>
<tr>
<td>3</td>
<td>C1</td>
<td>C3</td>
<td>C3</td>
<td>C3 + C4 + (n)</td>
<td>C3 + C4 + (n)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>C2</td>
<td>C4 + C4 + (n)</td>
<td>C4 + C4 + (n)</td>
<td>C4 + (n)</td>
<td>C4 + (n)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>C3</td>
<td>C6</td>
<td>C6</td>
<td>C6</td>
<td>C6</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>(\alpha)</td>
<td>(\beta)</td>
<td>(\gamma)</td>
<td>(\delta)</td>
<td>(\epsilon)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>(\eta)</td>
<td>(\kappa)</td>
<td>(\lambda)</td>
<td>(\mu)</td>
<td>(\nu)</td>
<td></td>
</tr>
</tbody>
</table>

Regression Parameters

<table>
<thead>
<tr>
<th>(k_i)</th>
<th>1, 9, 10, and 11</th>
<th>1, 7, 8, and 9</th>
<th>1, 5, 6, and 7</th>
<th>1, 3, 4, and 5</th>
<th>1, 3, and 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Omega_1)</td>
<td>1</td>
<td>4</td>
<td>3</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>(\Omega_2)</td>
<td>1</td>
<td>4</td>
<td>3</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>(\Omega_3)</td>
<td>2</td>
<td>5</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>(\Omega_4)</td>
<td>2</td>
<td>5</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>

*(Indicates the grouped pseudocomponents being regressed in a particular step.)

In summary, any grouping of a complete EOS characterization into a limited number of pseudocomponents should be checked to ensure that predicted phase behavior (e.g., multicontact gas injection data, saturation pressures, and densities) are reasonably close to the predictions for the original (complete) characterization. Stepwise regression is the best approach to determine the number and
HEPTANES-PLUS CHARACTERIZATION

properties of pseudocomponents that can accurately describe a reservoir fluid behavior. Stepwise regression is not possible, standard grouping of the light and intermediates (N2 + C1, CO2 + C2, i-C4 + n-C4 and i-C5 + n-C5) and Gaussian quadratic for Cx (or equal-mass fractions) is recommended; a validated alternative is the Li et al.\textsuperscript{25} method. The Coats\textsuperscript{3} method (Eqs. 5.93 and 5.94) is always recommended for calculating pseudocomponent properties.


### SI Metric Conversion Factors

<table>
<thead>
<tr>
<th>Unit</th>
<th>Conversion Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>°F</td>
<td>°C = (°F − 32) × 5/9</td>
</tr>
<tr>
<td>°F</td>
<td>°K = (°F + 459.67) × 5/9</td>
</tr>
<tr>
<td>psi</td>
<td>kPa = psi × 6.894 757</td>
</tr>
<tr>
<td>psi</td>
<td>°F = °C × 9/5 + 32</td>
</tr>
</tbody>
</table>

20 • PHASE BEHAVIOR