

ford and Phillips, as was done by Herzog in his original article. Constants were also derived for these equations using experimental parachors but no significant improvement in correlation was observed. Hence, it was decided to use the calculated parachors throughout since calculated parachors are normally more convenient to use.

Equations with the re-evaluated constants are shown in Tables I, II, and III, together with their per cent "reliabilities." Reliabilities of the estimated T_c values were calculated using the equation shown below. This equation gives the maximum deviation to be expected in 95% of the cases.

The same approach was used in determining the p_c and V_c equation reliabilities.

$$d = 200 \sqrt{\frac{1}{n-1} \sum \left(\frac{T_c(\text{exptl.}) - T_c(\text{calcd.})}{T_c(\text{exptl.})} \right)^2}$$

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Prediction of Compressibility of Natural Gas Mixtures by Use of the Benedict-Webb-Rubin Equation of State

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A knowledge of the pressure-volume-temperature properties of natural gas is of great importance in the transportation, storage, and use of the gas as a fuel and as a source of raw materials for chemical syntheses. Because of the variable composition of natural gas and the time and skill required to determine the P - V - T properties in the laboratory, it has long been the goal of research engineers within the industry to find an accurate method for their calculation. Heretofore, the methods proposed have been of limited application. The tentative standards as set forth by the Natural Gasoline Association of America (15) and the California Natural Gasoline Association (9, 10) are either not of sufficient accuracy or are limited to relatively low pressures. Following the pseudo-critical concept of Kay (13), and assuming the law of corresponding state valid for any natural gas mixture, Dunkle (12) proposed a method using pure methane as the basis for evaluating the compressibility of natural gas mixtures. Dunkle's approach was later used by Zimmerman and Beitler (16, 17). Their

method is simple and accurate for most natural gases, and has been adopted by the American Gas Association as a new standard for the natural gas industry (1). However when the ethane and/or nitrogen and carbon dioxide contents are high, this method is not so accurate as is generally desired.

The present study was undertaken to test the application of the Benedict-Webb-Rubin equation of state (4, 5) to the prediction of the compressibility of natural gas mixtures and particularly to mixtures of high ethane and/or nitrogen and carbon dioxide content. The study was confined to the gaseous phase in the pressure and temperature ranges usually encountered in its transportation and storage. The data on natural gas mixtures compiled by Zimmerman and Beitler (16, 17) were used for purposes of comparison in the study.

CONSTANTS FOR BENEDICT-WEBB-RUBIN EQUATION OF STATE

Benedict, Webb, and Rubin (5) have proposed the following empirical equation for the representation of the P - V - T relations of a pure gas:

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Table I. Values of Constants in Benedict-Webb-Rubin Equation of State for Compounds Constituting Natural Gas Mixtures

	Methane, (4)	Ethane, (4) Adjusted	Propane, (4)	Isobutane, (4)	n-Butane, (4)	Isopentane, (4)
B_0	0.682401	1.00554	1.55884	2.20329	1.99211	2.56386
A_0	6,995.25	15,525.3	25,915.4	38,587.4	38,029.6	48,253.6
$C_0 \times 10^{-6}$	275.763	2,194.27	6,209.93	10,384.7	12,130.5	21,336.7
b	0.867325	2.85393	5.77355	10.8890	10.2636	17.1441
a	2,984.12	20,850.2	57,248.0	117,047	113,705	226,902
$c \times 10^{-6}$	498.106	6,279.39	25,247.8	55,977.7	61,925.6	136,025
α	0.511172	1.00044	2.49577	4.41496	4.52693	6.98777
γ	1.53961	3.02790	5.64524	8.72447	8.72447	11.8807
	n-Pentane, (4)	n-Hexane, (4)	n-Heptane, (4)	Carbon Dioxide, Proposed	Nitrogen, (8)	
B_0	2.51096	2.84835	3.18782	0.558255	0.652648	
A_0	45,928.8	54,443.4	66,070.6	8,192.54	3,973.31	
$C_0 \times 10^{-6}$	25,917.2	40,556.2	57,984.0	1,864.48	98.4657	
b	17.1441	28.0032	38.9917	1.36384	0.597292	
a	246,148	429,901	626,106	10,554.4	1,516.34	
$c \times 10^{-6}$	161,306	296,077	483,427	2,959.67	142.564	
α	7.43992	11.5539	17.9056	0.193192	0.522851	
γ	12.1886	17.1115	23.0942	1.07773	1.35999	

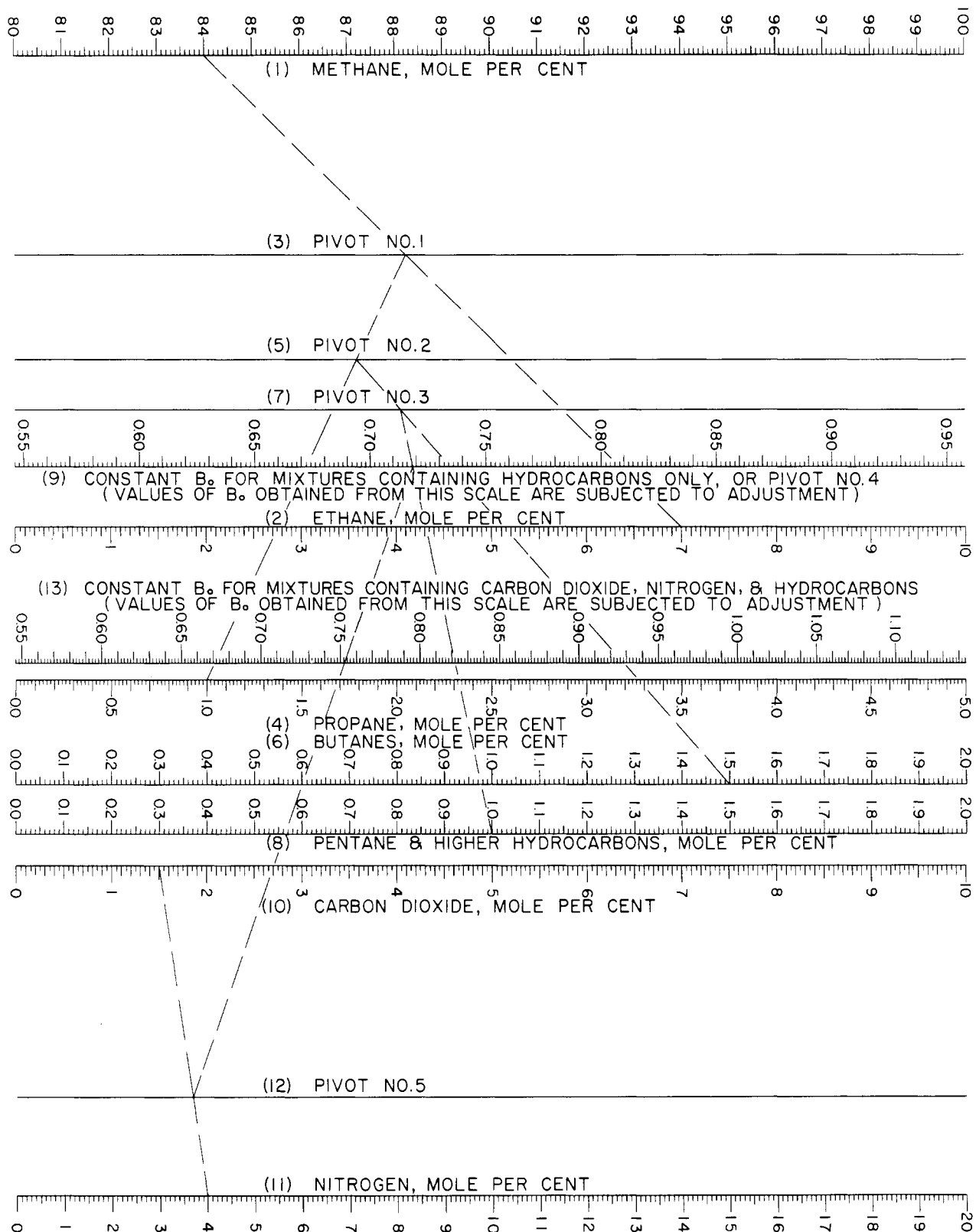


Figure 1. Alignment chart for constant B_0 .

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

where P is absolute pressure, T is absolute temperature, d is molal density, R is the universal gas constant, and

B_0 , A_0 , C_0 , b , a , c , α , and γ are constants characteristic of the individual gases and the dimensional units employed.

The eleven chemical compounds most commonly appearing in natural gas mixtures and the corresponding values of the eight characteristic constants required in Equation 1 are listed in Table I.

The values of the constants for the hydrocarbons are principally those given by Benedict, Webb, and Rubin (4),

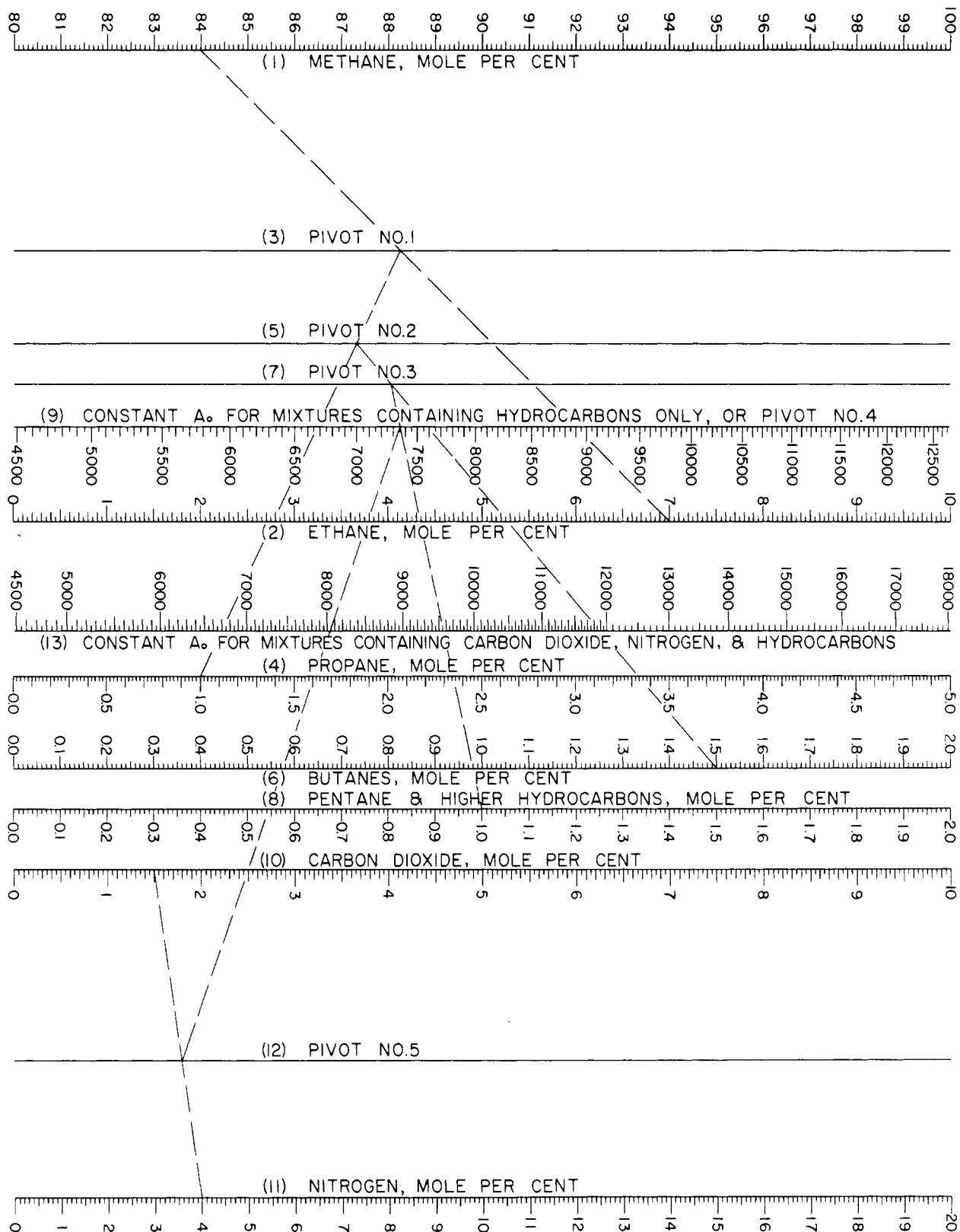


Figure 2. Alignment chart for constant A_0 .

while those for nitrogen were evaluated by Bloomer and Rao (8). Constants A_0 and c for ethane were adjusted so that the calculated P - V - T relationships of gaseous ethane agree more closely with the experimental data in the temperature range 0° to 150° C. Table II shows a comparison of average per cent deviations of pressure calculated by the equation of state using the original and the adjusted constants of gaseous ethane from the experimental data of

Beattie, Haddock, and Poffenberger (2) and Beattie, Su, and Simard (3).

The constants of the equation of state for carbon dioxide given in Table I were evaluated according to the stepwise procedure described by Benedict, Webb, and Rubin (5), using the data on carbon dioxide of Michels and Michels (14). Table III shows the agreement between the experimental pressure and the pressure calculated by the equa-

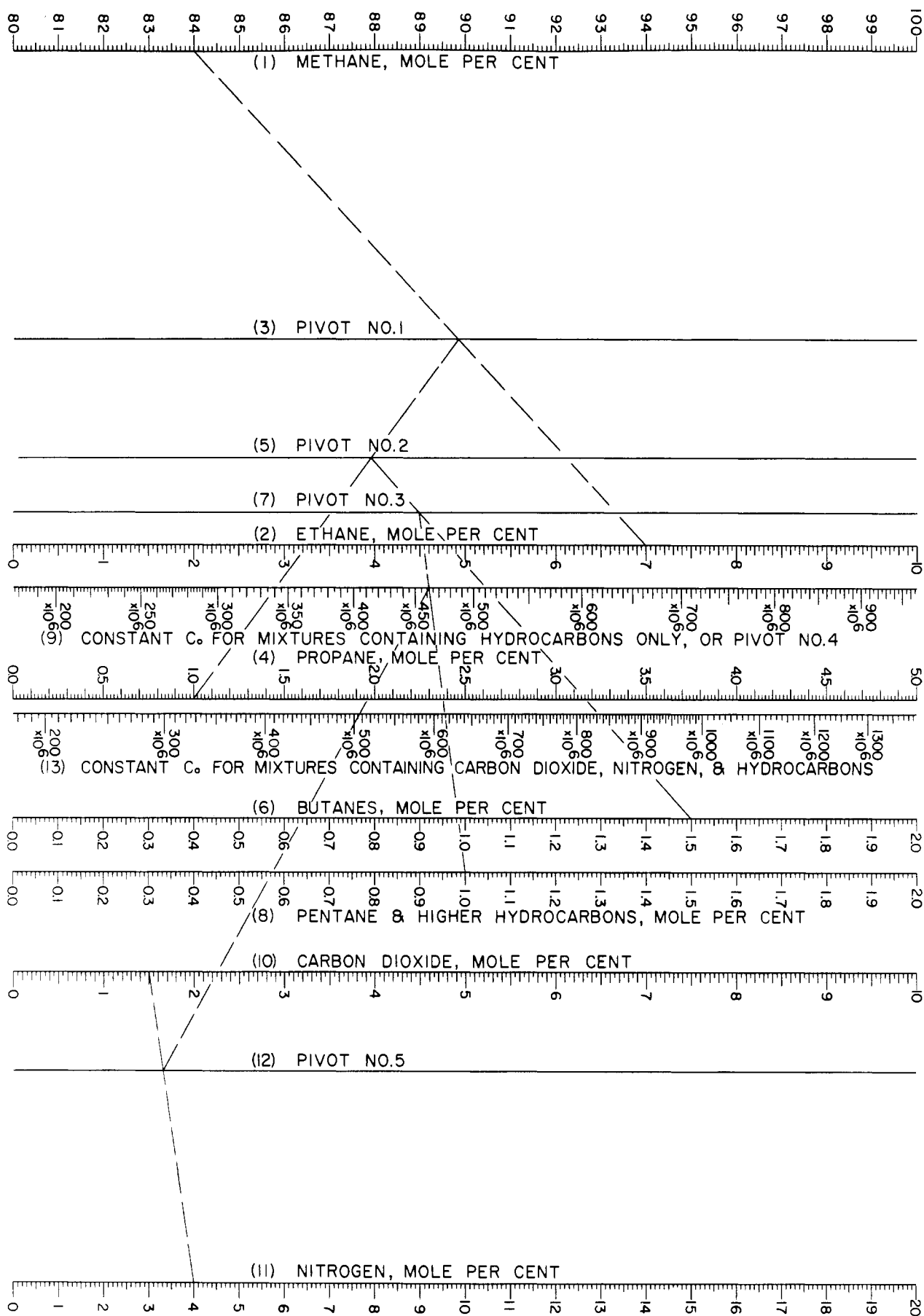


Figure 3. Alignment chart for constant C_0

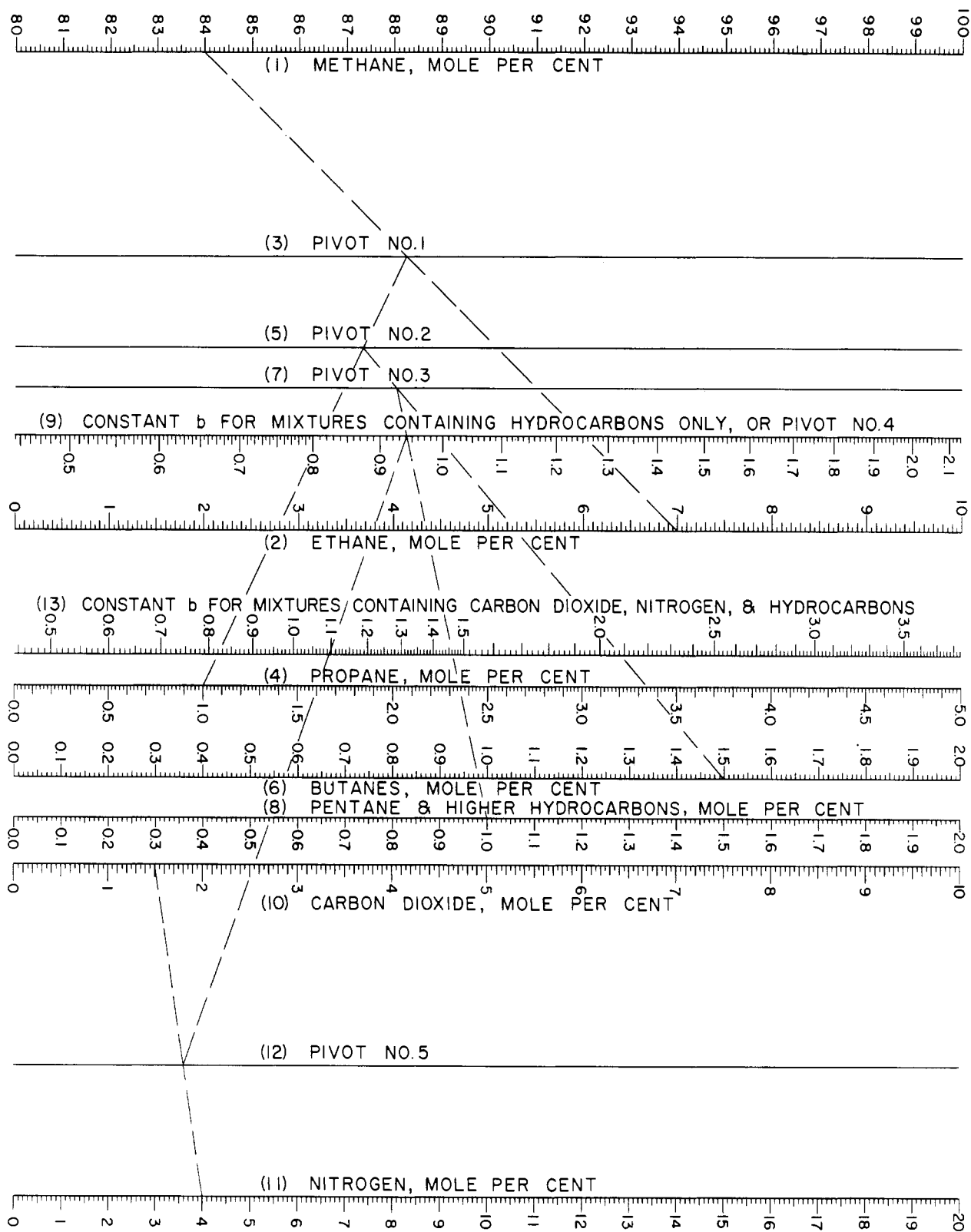


Figure 4. Alignment chart for constant b

tion of state. The carbon dioxide constants developed by Cullen and Kobe (11) were not available at the time of this study. A comparison of the predicted compressibility factor of carbon dioxide using these constants and the constants presented in Table I yields agreement to less than 0.1% for pressures under 2000 p.s.i.a. and within 0.2% for pressures up to 3000 p.s.i.a.

COMBINATION OF CONSTANTS IN EQUATION OF STATE FOR MIXTURES

In the application of the Benedict-Webb-Rubin equation of state to mixtures, the following equations were used for combining the constants of individual gases to obtain the constants for the mixture:

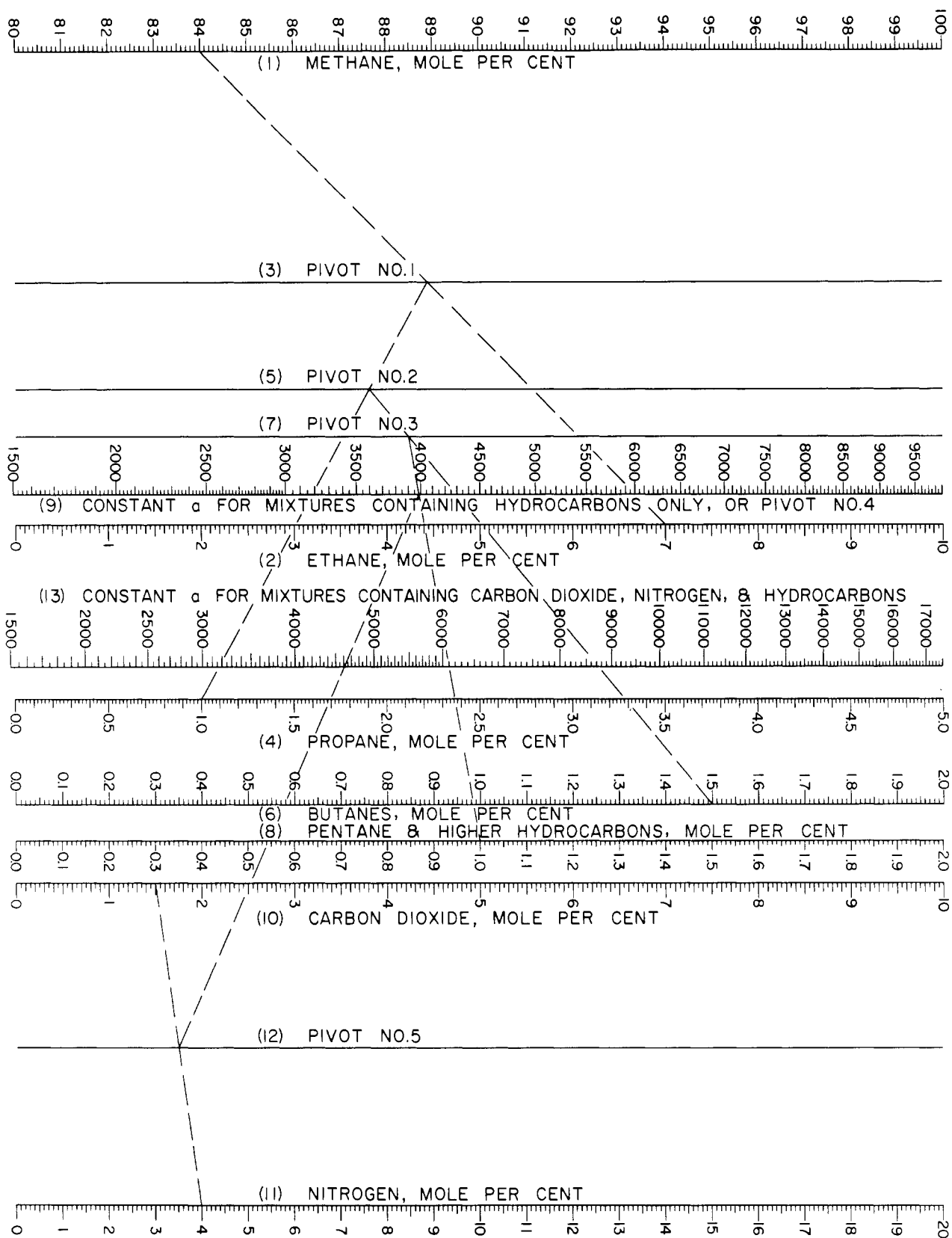


Figure 5. Alignment chart for constant a

$$B_0 = (\sum x_i B_{0i}) - 16.0188 x_M (0.007 x_E - 0.0055 x_N) \quad (2)$$

$$A_0 = (\sum x_i A_{0i}^{1/2})^2 \quad (3)$$

$$C_0 = (\sum x_i C_{0i}^{1/2})^2 \quad (4)$$

$$b = (\sum x_i b_i^{1/3})^3 \quad (5)$$

$$a = (\sum x_i a_i^{1/3})^3 \quad (6)$$

$$c = (\sum x_i c_i^{1/3})^3 \quad (7)$$

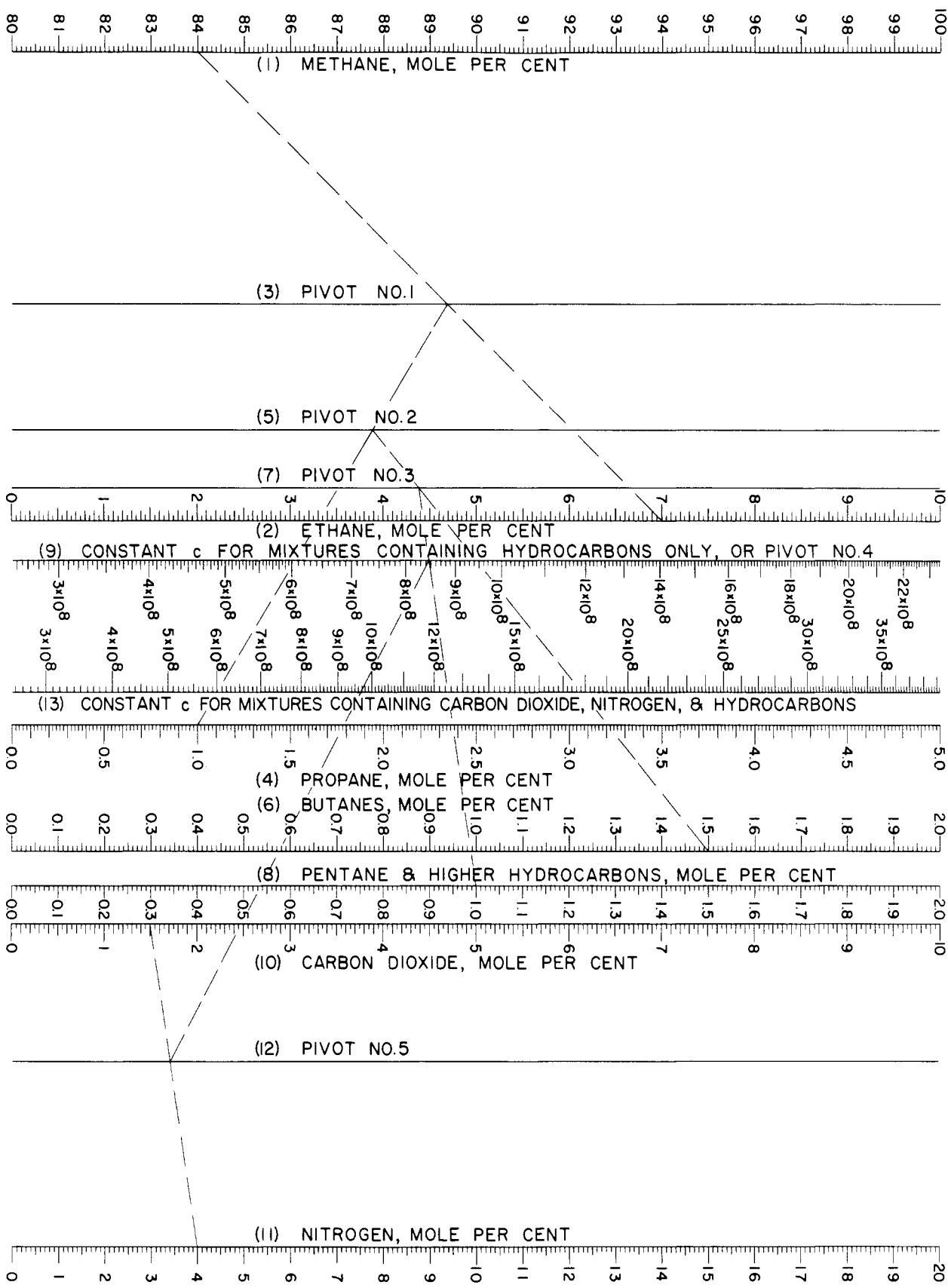


Figure 6. Alignment chart for constant c

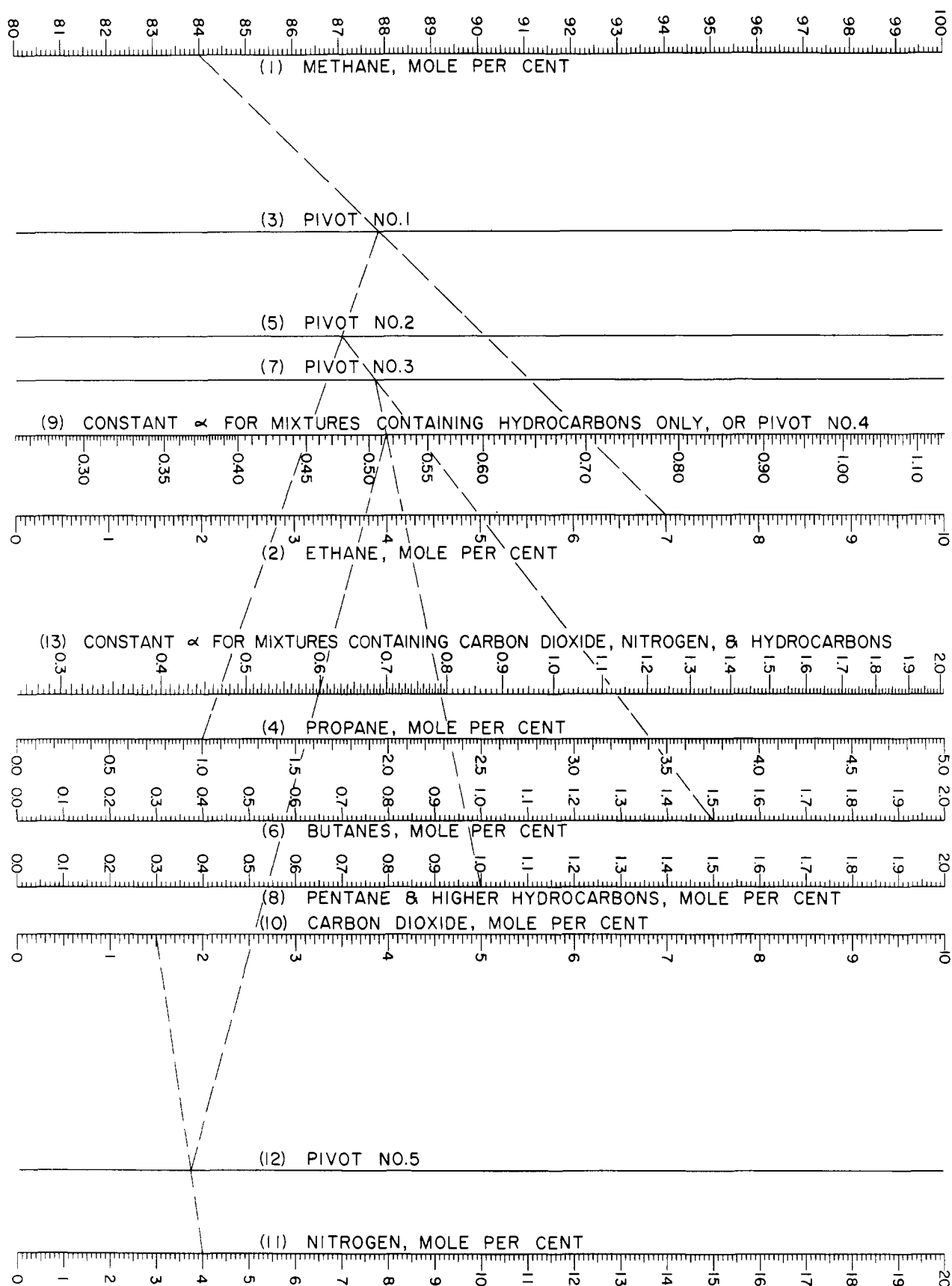


Figure 7. Alignment chart for constant α .

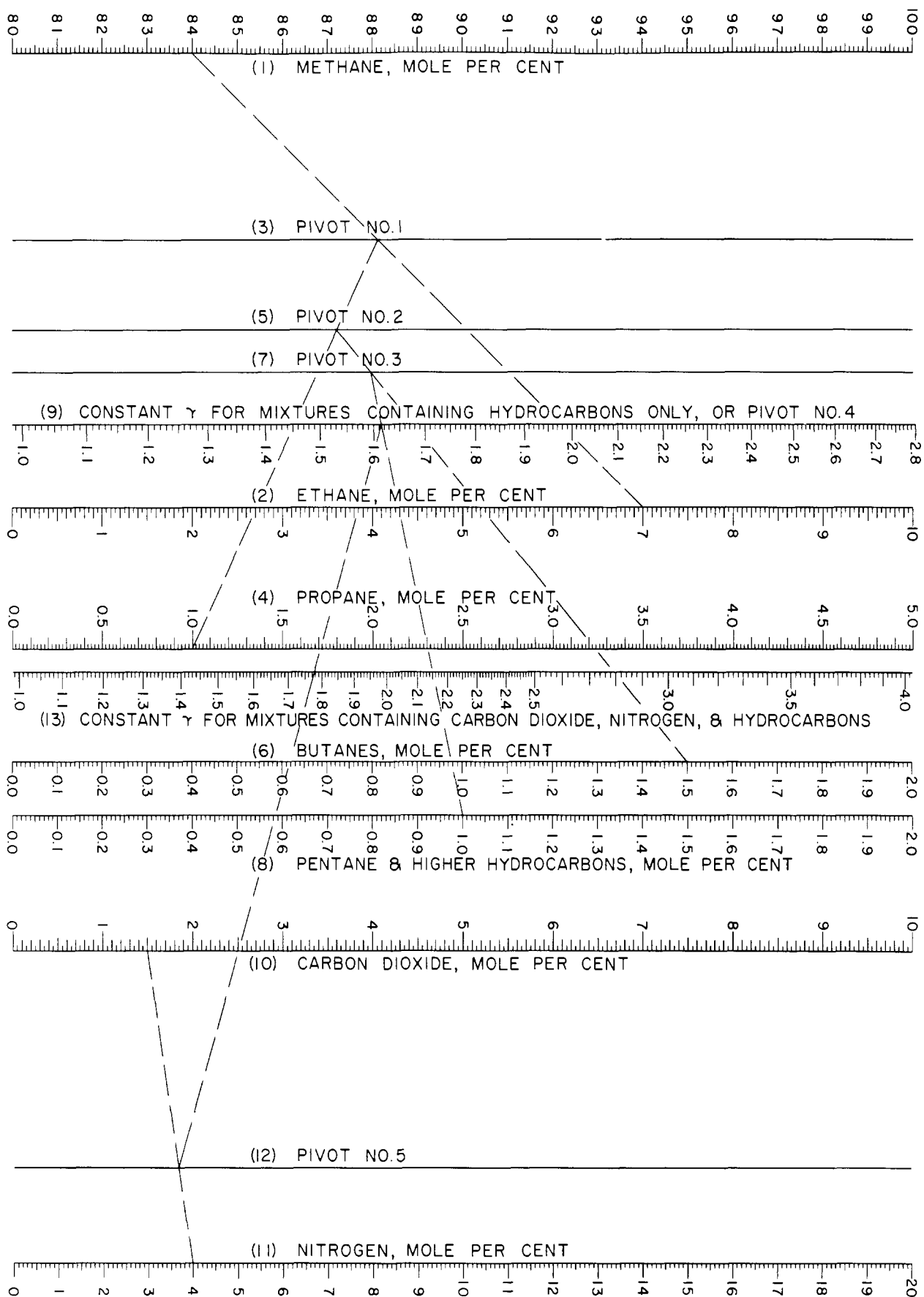


Figure 8. Alignment chart for constant γ

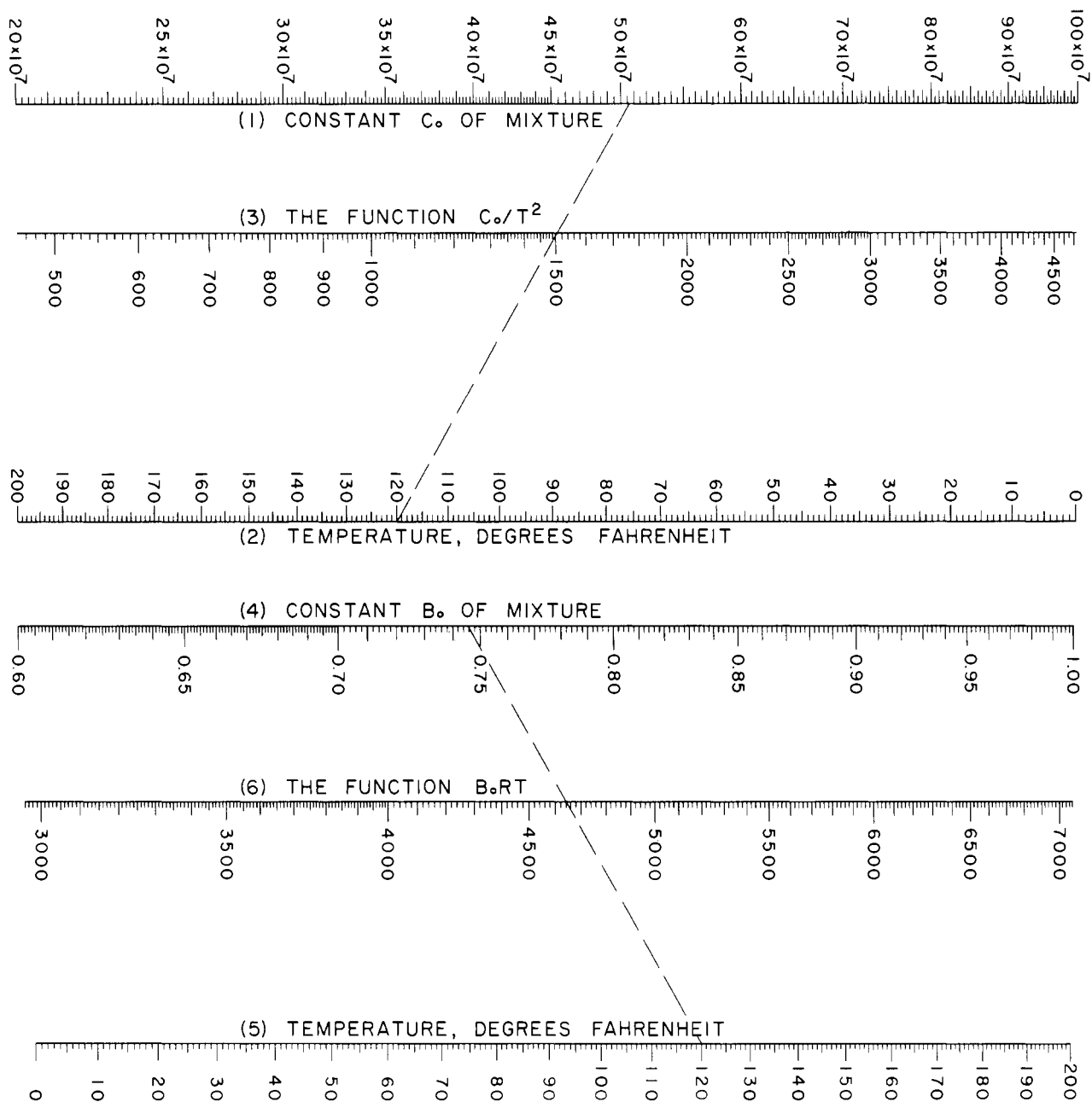


Figure 9. Alignment chart for $\frac{C_o}{T^2}$ and $B_o RT$ in function $F(t) = A_o + \frac{C_o}{T^2} - B_o RT$

$$\alpha = (\sum x_i \alpha_i^{1/3})^3 \quad (8)$$

$$\gamma = (\sum x_i \gamma_i^{1/2})^2 \quad (9)$$

These equations with the exception of Equation 2 are given by Benedict, Webb, and Rubin (4), whose original

Table II. Comparison of Absolute Average Per Cent Deviations of Calculated Pressures from Experimental Data of Gaseous Ethane for Density Range 0.5 to 10 Gram-Moles per Liter (2, 3)

Temp. °C.	25	50	75	100	125	150	Over-all Average
By original constants	0.19	0.45	0.38	0.36	0.33	0.23	0.34
By adjusted constants	0.18	0.21	0.22	0.19	0.14	0.19	0.19

equation for combining the constant B_o is $B_o = \sum x_i B_{oi}$. The modification of Equation 2 was found desirable on the basis of a comparison of calculated P - V - T data with the

Table III. Absolute Average Per Cent Deviations of Calculated Pressures from Experimental Data of Gaseous Carbon Dioxide for Temperature Range 0° to 150° C. (14)

Density, gram-moles/liter	1.05385	1.90565	3.10633	4.09273	5.03908
Abs. av. % deviation	0.05	0.04	0.08	0.14	0.21
Density, gram-moles/liter	5.99555	6.90826	7.65599	8.46911	9.27348
Abs. av. % deviation	0.27	0.23	0.16	0.11	0.30
Over-all average % deviation	0.15				

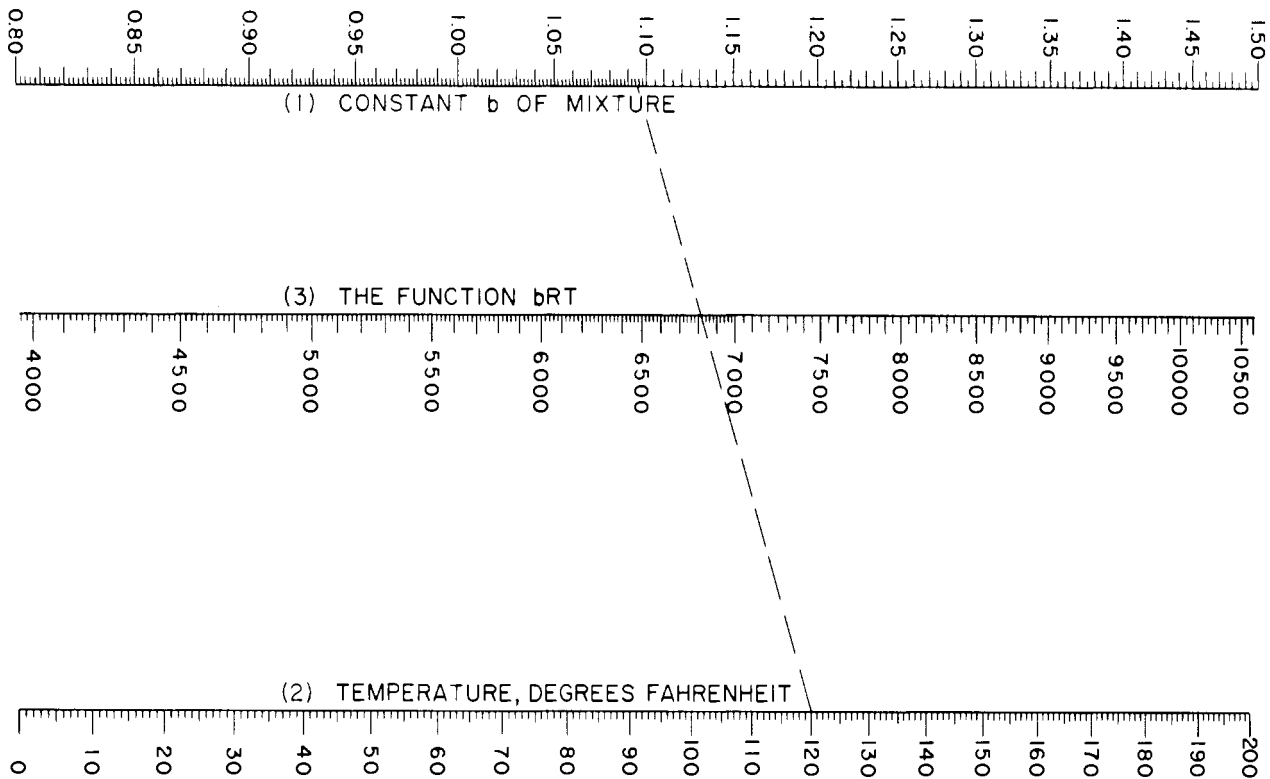


Figure 10. Alignment chart for bRT in function $G(t) = bRT - a$

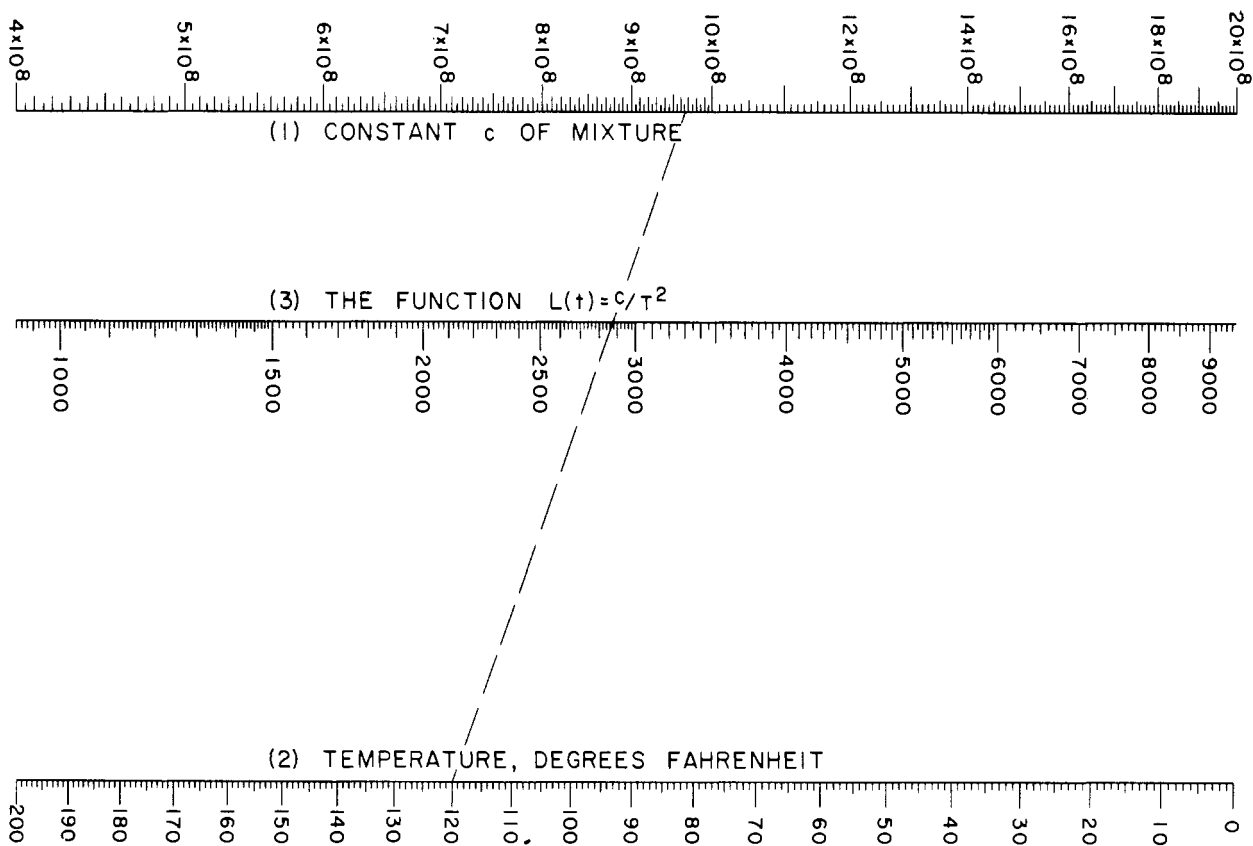


Figure 11. Alignment chart for function $L(t) = \frac{c}{T^2}$

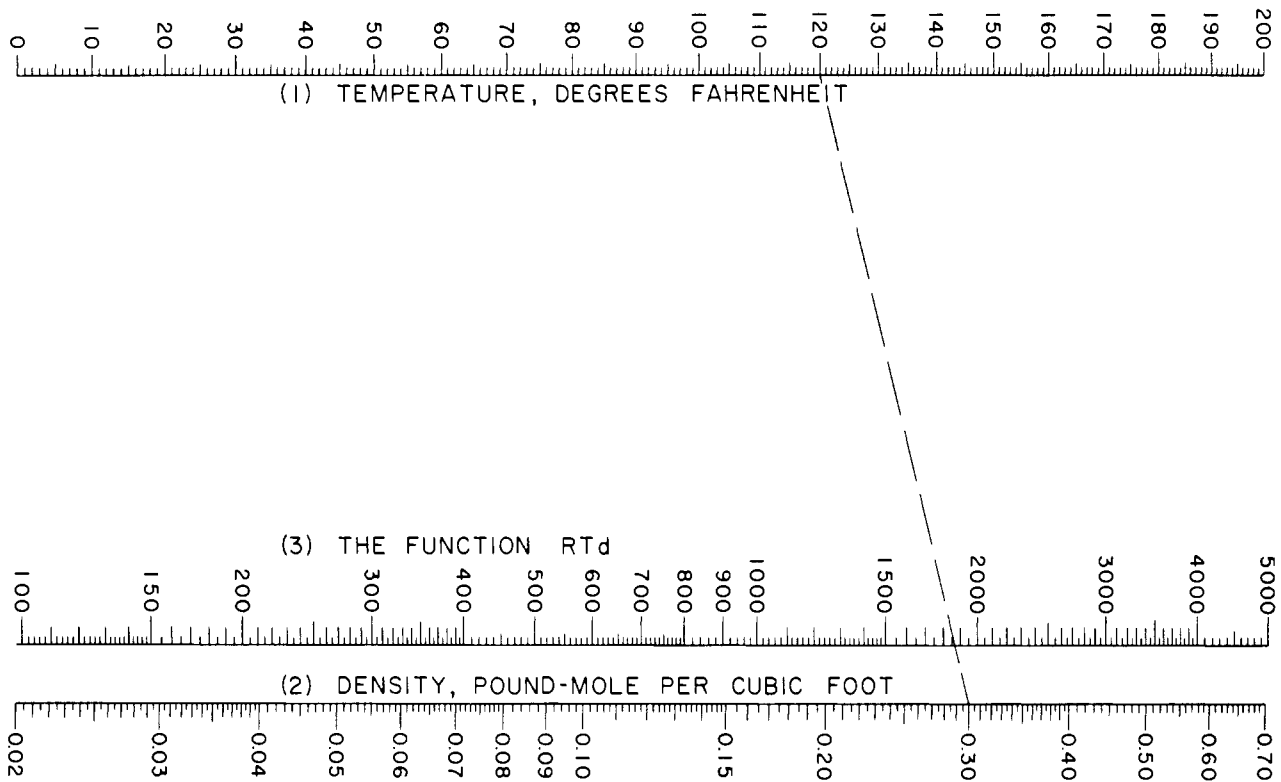


Figure 12. Alignment chart for function RTd

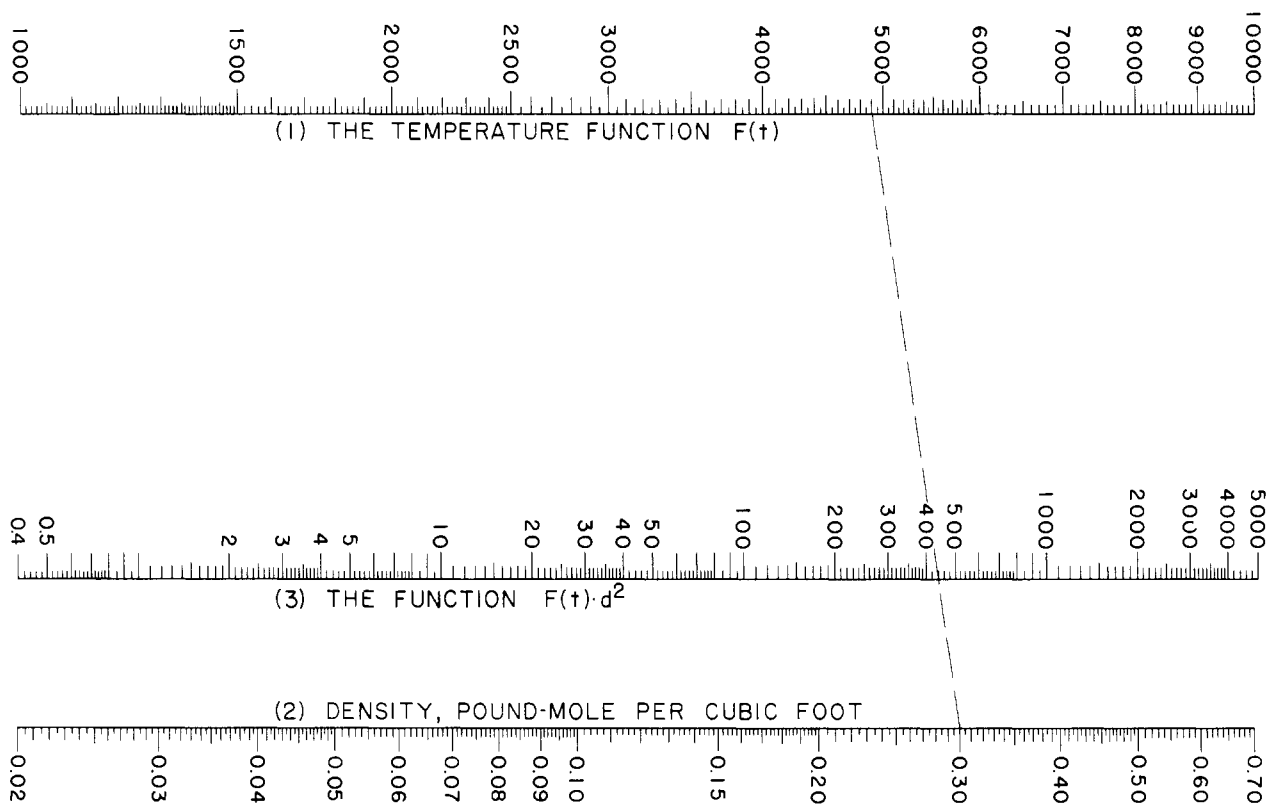


Figure 13. Alignment chart for function $F(t) d^2$

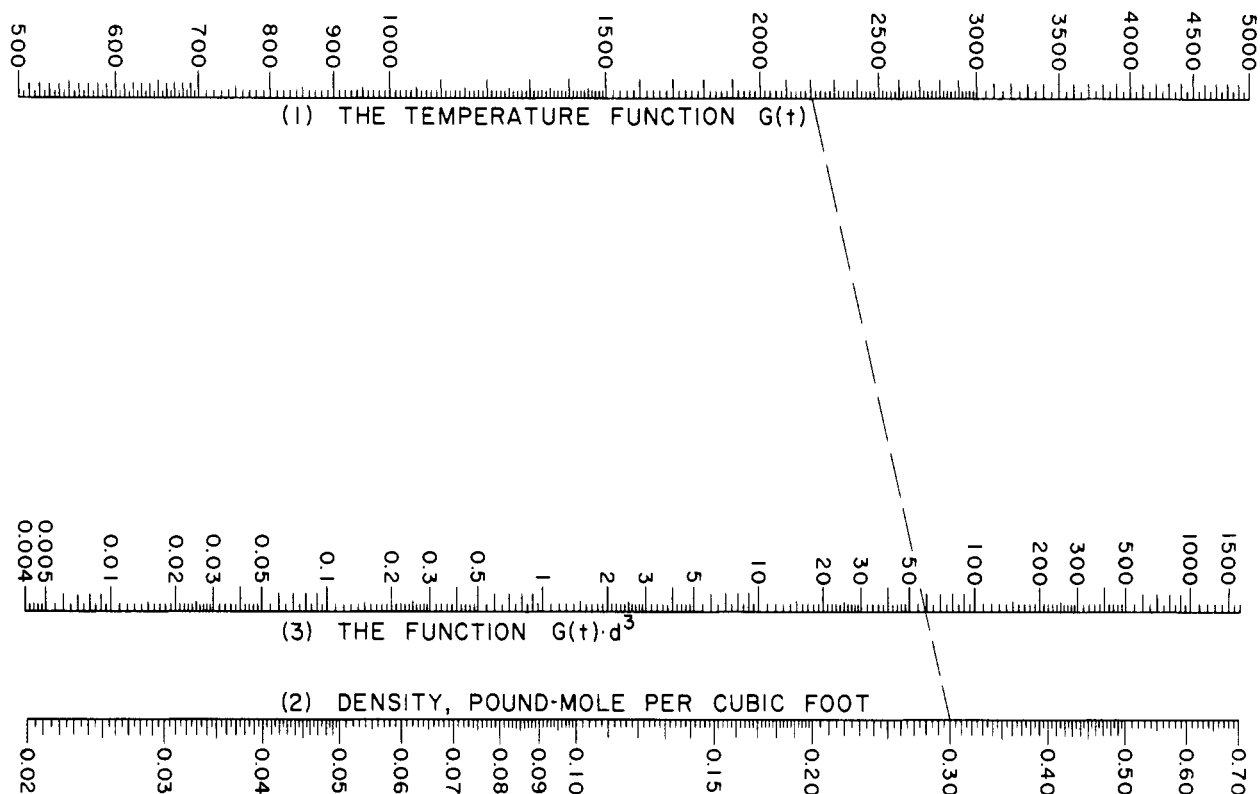


Figure 14. Alignment chart for function $G(t) d^3$

experimental data on the methane-ethane and methane-nitrogen systems. If either the ethane or nitrogen content is under 5 mole %, the modification made in Equation 2 for that component is small and may be neglected. If both ethane and nitrogen contents are under 5 mole %, Equation 2 reduces to the original form.

Natural gas is essentially a mixture of methane and ethane, commonly, with only minor quantities of the higher hydrocarbons, carbon dioxide and nitrogen. Accurate representation of the P - V - T relations of methane-ethane mixtures is essential to the prediction of compressibility of

natural gas. However, the equations given by Benedict, Webb, and Rubin for combining constants lead to results which give only a fair representation of the experimental data of methane-ethane mixtures. Use of Equation 2 greatly reduces the average error of the calculated pressures. The average deviations of the calculated pressures from the experimental data of Bloomer, Gami, and Parent (7) for a mixture containing 85.06 mole % of methane and 14.94 mole % of ethane are 1.03 and 0.18% by the use of the equations of Benedict, Webb, and Rubin for combining constants and by Equations 2 through 9, respectively. As most natural gases contain considerably less than 15% of ethane, the present modification is considered satisfactory for natural gas mixtures having a high ethane content.

The expanding and ever-increasing use of natural gas, as a fuel and in many industrial applications, forecasts the necessity of using gas reserves of increasingly high nitrogen content. Again, in this case, the equations of Benedict, Webb, and Rubin for combining constants lead to results which give only fair representation of actual data. The error in the calculated pressure is greatly reduced by the use of Equation 2. The average deviations of calculated pressures from the experimental data of Bloomer (6) for two methane-nitrogen mixtures, one containing 30 mole % and the other 50.06 mole % of nitrogen, are 0.84 and 1.04% respectively, by the use of the equations of Benedict, Webb, and Rubin for combining constants and 0.16 and 0.20% respectively, by the use of Equations 2 through 9.

Table IV shows a sample of the average and maximum per cent deviations in pressure and in compressibility factor, PV/RT , as predicted by three methods. Mixture A has an ethane content which is higher than the average, and its propane and carbon dioxide contents are about the maximum amounts which appeared in all available samples. Mixture B is the only sample available with a high nitrogen content, but, unfortunately, data at high pressures were not obtained. For all natural gas mixtures studied in this work, the Zimmerman-Beitler method (16, 17) gave a total over-all absolute average deviation of 0.32% in the com-

Table IV. Per Cent Deviations for Two Natural Gas Samples

Sample	Maximum Pressure, P.S.I.	Temp. Range, F.	% Deviation in Pressure			
			Benedict original rules (4)		Present modified rules, (Equations 2 through 9)	
			Average	Maximum	Average	Maximum
A	3000	70 to 150	0.25	1.04	0.18	0.64
B	800	40 to 80	0.19	0.51	0.15	0.40
Sample	% Deviation in Compressibility Factor					
	Present modified rules, (Equations 2 through 9)		Zimmerman-Beitler correlation (16, 17)			
	Average	Maximum	Average	Maximum		
A	0.19	0.57	0.77	1.41		
B	0.16	0.46	0.23	0.40		

Note. Fractional analysis, mole per cent

Sample A. 85.36 methane, 6.14 ethane, 3.72 propane, 0.50 isobutane, 0.79 *n*-butane, 0.20 isopentane, 0.07 *n*-pentane, 0.08 hexane, 0.04 heptanes, 3.10 carbon dioxide, 0.00 nitrogen

Sample B. 71.25 methane, 5.69 ethane, 3.37 propane, 0.34 isobutane, 0.64 *n*-butane, 0.08 isopentane, 0.06 *n*-pentane, 0.13 hexane, 0.07 heptane, 0.10 carbon dioxide, 18.27 nitrogen

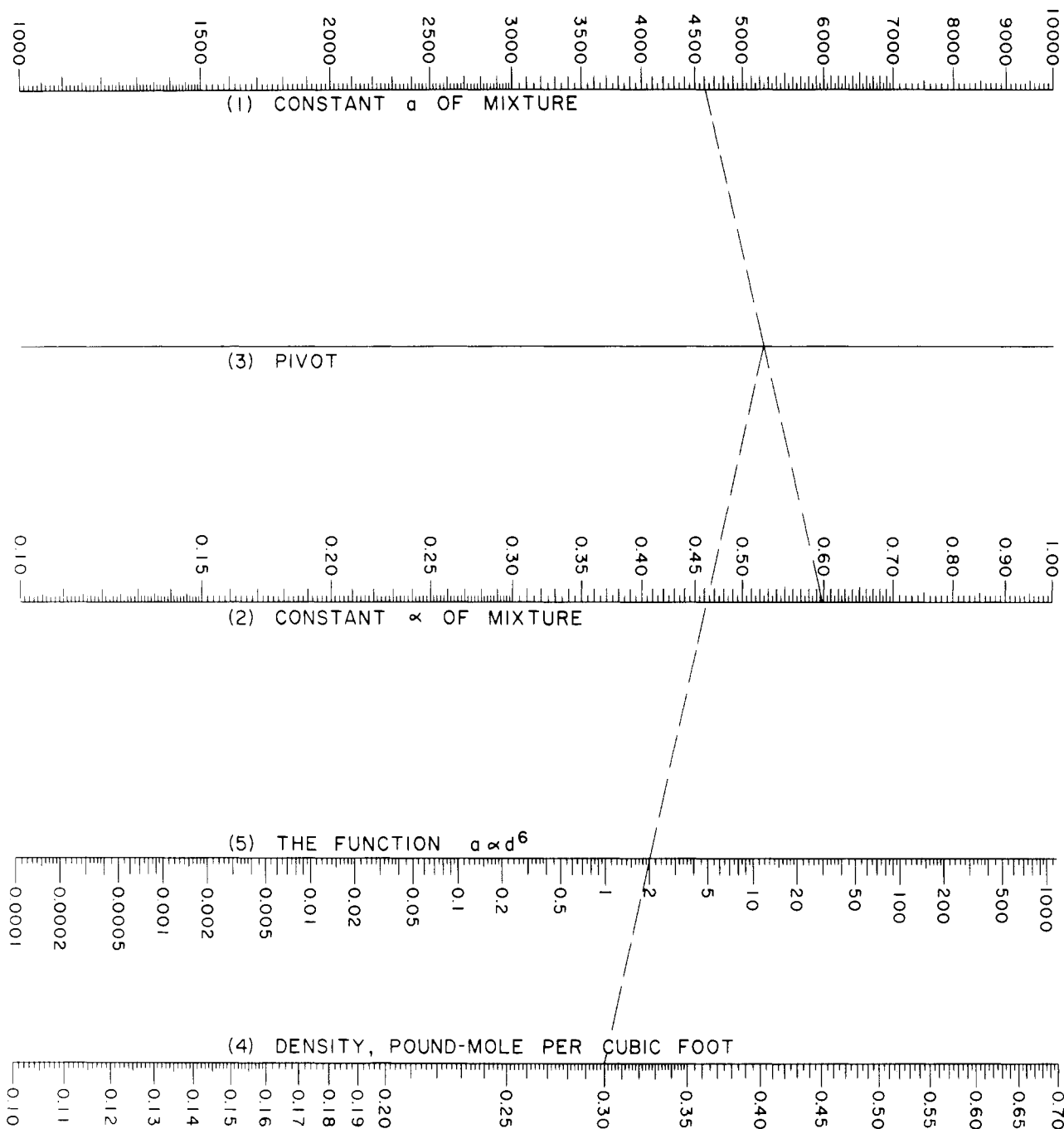


Figure 15. Alignment chart for function $a \propto d^6$

compressibility factor, PV/RT , as compared to a deviation of 0.18% by the method presented here.

GRAPHICAL SOLUTION OF EQUATION OF STATE

Although the use of Equation 1 with Equations 2 through 9 to predict the compressibility of natural gas is accurate and useful, the use of these equations by direct mathematical computations is very time-consuming. In order to reduce the time required to handle these equations, a system of graphical solutions has been established. First, an alignment chart for each of the Equations 2 through 9 was constructed (Figures 1 through 3). The values of the constants read from Figures 2 through 8 are final ones, ready for use in the equation of state, Equation 1, while the value of B_0 read from Figure 1 is for the term $\sum x_i B_{0i}$ in Equation 2 and is subjected to adjustment according to Equation 2.

The equation of state, 1, contains the following three temperature functions:

$$F(t) = A_0 + \frac{C_0}{T^2} - B_0 RT \quad (10)$$

$$G(t) = bRT - a \quad (11)$$

$$L(t) = \frac{c}{T^2} \quad (12)$$

Alignment charts for these three temperature functions were constructed and are shown in Figures 9, 10, and 11.

After the evaluation of the three temperature functions, the equation of state, 1, reduces to the form:

$$P = RTd - F(t)d^2 + G(t)d^3 + a\alpha d^6 + L(t)d^3(1 + \gamma d^2)e^{-\gamma d^2} \quad (13)$$

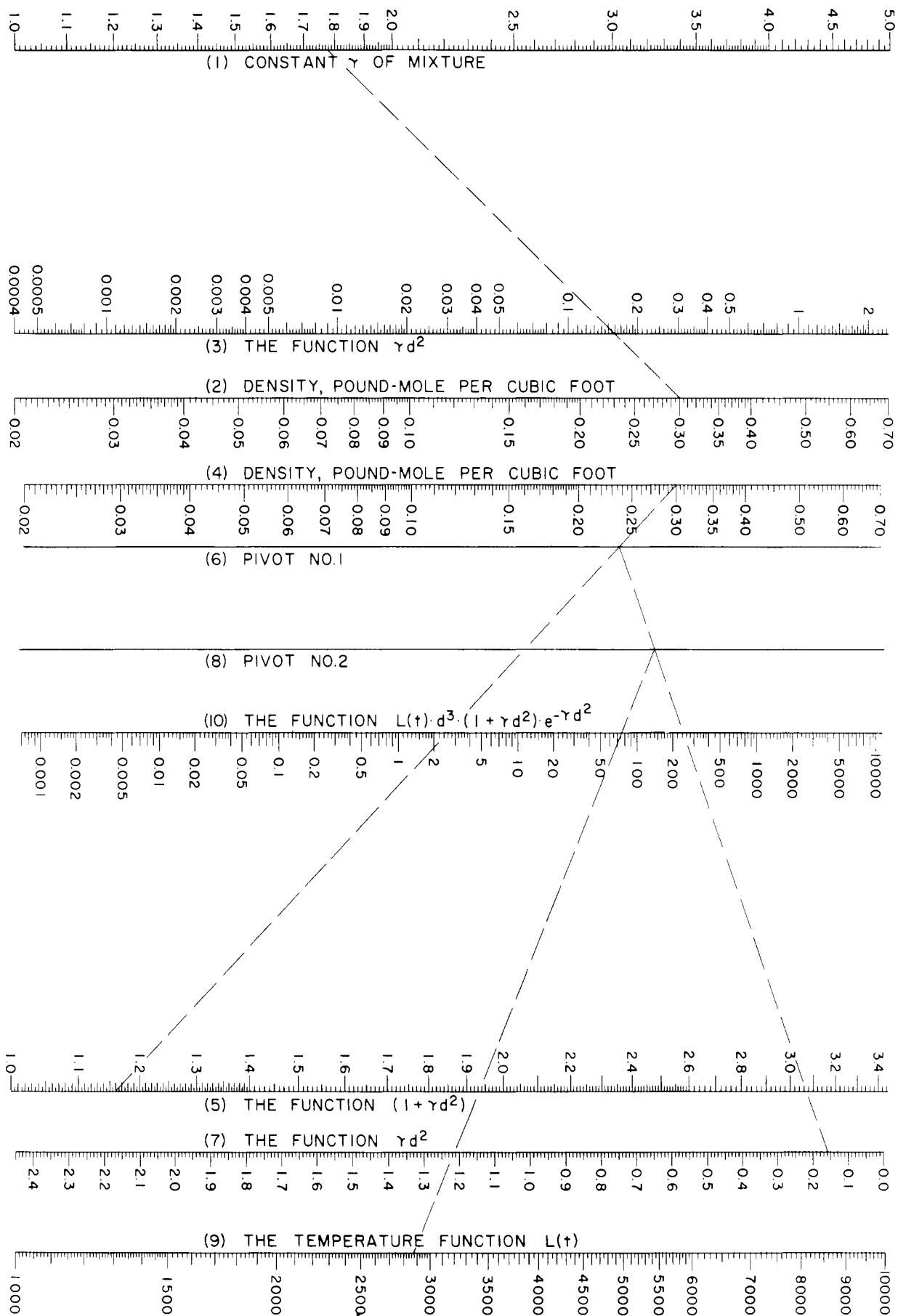


Figure 16. Alignment chart for function $L(t) d^3 (1 + \gamma d^2) e^{-\gamma d^2}$

Five alignment charts for the evaluation of the five individual terms in the right-hand side of Equation 13 have been constructed (Figures 12 through 16).

The procedures which should be followed in using the charts are illustrated by the following example.

The mole fractional analysis for a natural gas mixture consists of 84.0% of methane, 7.0% of ethane, 1.0% of propane, 1.5% of butanes, 1.0% of pentane and higher hydrocarbons, 1.5% of carbon dioxide, and 4.0% of nitrogen. Find the pressure of the mixture at a temperature of 120°F. and a density of 0.3 pound-mole per cubic foot.

In solving this problem, Figures 1 through 8 are used to evaluate the eight constants for the mixture.

In each of Figures 1 through 8, connect 84.0% of methane on No. 1 scale and 7.0% of ethane on No. 2 scale by means of an index line. Connect the intersection of the first index line on No. 3 scale and 1.0% of propane on No. 4 scale by means of a second index line. Connect the intersection of the second index line on No. 5 scale and 1.5% of butanes on No. 6 scale by means of a third index line. Connect the intersection of the third index line on No. 7 scale and 1.0% of pentane and higher hydrocarbons on No. 8 scale by means of a fourth index line. In the case of pure hydrocarbon mixtures, read the value of the constant on No. 9 scale at its intersection with the fourth index line. Since the mixture in this example contains carbon dioxide and nitrogen, connect the points defined by 1.5% of carbon dioxide on No. 10 scale and 4.0% of nitrogen on No. 11 scale by means of a fifth index line. Connect the intersection of the fourth index line on No. 9 scale and the intersection of the fifth index line on No. 12 scale by means of a sixth index line. Read the value of the constant on No. 13 scale at its intersection with the sixth index line. Values of the constants for the mixture as read from Figures 1 through 8 are as follows:

$$\begin{array}{lll} B_0 = 0.7525 & A_0 = 8040 & C_0 = 506.5 \times 10^7 \\ b = 1.095 & a = 4610 & c = 9.66 \times 10^8 \\ \alpha = 0.5980 & \gamma = 1.777 & \end{array}$$

Because the mixture contains more than 5% of ethane, the above value for B_0 should be modified to read, according to Equation 2

$$B_0 = 0.7525 - 16.0188 \times 0.007 \times 0.84 \times 0.07 = 0.7459$$

In Figure 9, connect $C_0 = 506.5 \times 10^7$ on No. 1 scale and $t = 120^\circ\text{F.}$ on No. 2 scale by means of an index line to obtain $C_0/T^2 = 1505$ at its intersection on No. 3 scale. Connect $B_0 = 0.7459$ on No. 4 scale and $t = 120^\circ\text{F.}$ on No. 5 scale by means of a second index line to get $B_0 RT = 4640$ at its intersection on No. 6 scale. Then $F(t) = 8040 + 1505 - 4640 = 4905$.

In Figure 10, connect $b = 1.095$ on No. 1 scale and $t = 120^\circ\text{F.}$ on No. 2 scale by means of an index line to get $bRT = 6815$ at its intersection on No. 3 scale. Then $G(t) = 6815 - 4610 = 2205$.

In Figure 11, connect $c = 9.66 \times 10^8$ on No. 1 scale and $t = 120^\circ\text{F.}$ on No. 2 scale by means of an index line to read $L(t) = 2875$ at its intersection on No. 3 scale.

In Figure 12, connect $t = 120^\circ\text{F.}$ on No. 1 scale and $d = 0.30$ pound-mole per cubic foot on No. 2 scale by means of an index line to read $RTd = 1870$ at its intersection on No. 3 scale.

In Figure 13, connect $F(t) = 4905$ on No. 1 scale and $d = 0.30$ pound-mole per cubic foot on No. 2 scale by means of an index line to read $F(t)d^2 = 440$ at its intersection on No. 3 scale.

In Figure 14, connect $G(t) = 2205$ on No. 1 scale and $d = 0.30$ pound-mole per cubic foot on No. 2 scale by means of an index line to read $G(t)d^3 = 59.5$ at its intersection on No. 3 scale.

In Figure 15, connect $a = 4610$ on No. 1 scale and $\alpha = 0.5980$ on No. 2 scale by means of an index line. Connect the intersection of the first index line on No. 3 scale and $d = 0.30$ pound-mole per cubic foot on No. 4 scale by means of a second index line. Read $a\alpha d^6 = 2.01$ on No. 5 scale at its intersection with the second index line.

In Figure 16, connect $\gamma = 1.777$ on No. 1 scale and $d = 0.30$ pound-mole per cubic foot on No. 2 scale by means of an index line to obtain $\gamma d^2 = 0.159$ at its intersection on No. 3 scale. Connect $d = 0.30$ pound-mole per cubic foot on No. 4 scale and $(1 + \gamma d^2) = 1.159$ on No. 5 scale by means of a second index line. Connect the intersection of the second index line on No. 6 scale and $\gamma d^2 = 0.159$ on No. 7 scale by means of a third index line. Connect the intersection of the third index line on No. 8 scale and $L(t) = 2875$ on No. 9 scale by means of a fourth index line. Read $L(t)d^3(1 + \gamma d^2)e^{-\gamma d^2} = 76$ on No. 10 scale at its intersection with the fourth index line.

Finally, by calculation, $P = 1870 - 440 + 59.5 + 2.0 + 76 = 1567.5$ pounds per square inch absolute.

The compressibility factor may be evaluated from P/RTd . In this example, $RTd = 1870$ and $P = 1567.5$. Hence, the compressibility factor is 0.8382.

The Benedict-Webb-Rubin equation of state gives the pressure explicitly. Solving the equation for density for given values of pressure and temperature involves a trial-and-error process. In the graphical solution only Figures 12 through 16 need be repeatedly used in the trial process.

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NOMENCLATURE

$A_0, B_0, C_0, a, b, c, \alpha, \gamma$ = constants in equation of state in English units as defined in Table I
 $F(t), G(t), L(t)$ = temperature functions as defined by Equations 10, 11, and 12, respectively
 P = absolute pressure, pounds per square inch
 $R = 10.7335$ (pounds) (cubic foot)/(square inch) (pound-mole) (degree Rankine)
 T = absolute temperature, degrees Rankine
 V = molal volume, cubic feet per pound-mole
 d = molal density, pound-moles per cubic foot
 e = base of natural logarithms
 x = mole fraction of component

Subscripts

E = ethane
 M = methane
 N = nitrogen
 i = i th component

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