



Evaluating Constant-Volume Depletion Data

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Abstract

This paper presents methods for evaluating constant-volume depletion (CVD) data obtained from experimental analyses of gas condensates and volatile oils. Theoretical and practical developments are supported by experimental data from a North Sea gas-condensate fluid.

The three major contributions of the work are: (1) presentation of material-balance equations to calculate fluid properties from measured CVD data, (2) a simple method for calculating black-oil formation volume factors and solution GOR's using material-balance results and a separator flash program, and (3) investigation of the Peng-Robinson (PR) equation of state (EOS) as a tool for matching measured PVT data and studying vapor/liquid phase behavior during CVD.

Introduction

CVD experiments are performed on gas condensates and volatile oils to simulate reservoir depletion performance and compositional variation. Measured data can be used in a variety of reservoir engineering calculations, among the most useful being material-balance calculations, generating black-oil PVT properties and, more recently, the tuning of empirical EOS. All these applications are addressed in this paper.

Few engineers are aware of useful fluid properties that can be derived from CVD data—e.g., liquid composition (and therefrom K -values), density, and molecular mass of the C_{7+} fraction, vapor density, and total system molecular mass. Only experimental CVD data and simple material-balance equations are used to calculate these data. A procedure outlining these calculations was first presented by Reudelhuber and Hinds.¹ Their descrip-

tion, however, is somewhat difficult to follow and not extensively known or used by petroleum engineers. The material-balance relations are presented here in equation form using current SPE nomenclature.

Based on material-balance-derived properties, a method is proposed for calculating black-oil PVT properties — i.e., FVF's and solution GOR's used in two-phase flow equations and reservoir material balances. The method was first suggested by Dodson *et al.*² in 1953 for solution-gas/crude-oil systems. Their method, however, requires expensive and time-consuming liquid sample removals and experimental flash separations. The proposed method follows the Dodson *et al.* procedure but uses experimentally determined vapor compositions and material-balance-derived liquid compositions together with a multistage separator flash program. PVT properties calculated using this method are compared with those predicted by the PR EOS.

Though more complicated, empirical equations of state are also used to evaluate CVD data. Several investigators^{3,4} have used the PR EOS to simulate PVT studies of light gas condensates and crude oils. Unfortunately most studies have emphasized K -value predictions instead of volumetric predictions, and most have avoided systems operating near the critical point. Results have varied considerably, depending on which properties are compared. Conrad and Gravier⁴ propose a method to improve liquid-density estimations by adjusting properties of the heaviest-plus fraction (boiling point and methane interaction coefficient). Firoozabadi *et al.*³ studied another lean gas condensate and found that by adjusting only the methane-heavy fraction interaction coefficient, the PR EOS highly overestimated liquid volumes.

About 30 CVD studies performed by commercial and private laboratories were analyzed using the material-balance approach. A North Sea rich gas condensate was

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chosen to be analyzed using the PR EOS. This choice was based on consistency of measured CVD data as indicated by material-balance calculations and availability of extended compositional data for the heptanes-plus fraction.

Description of CVD Process

A CVD experiment is conducted at reservoir temperature and begins at saturation pressure. Cell volume, V_{cell} , or the volume contained by the saturated fluid, is used as a reference volume.

Mercury is withdrawn from the bottom of the cell, thereby lowering the pressure as fluid expands. During this process, a second phase evolves — either retrograde liquid (for gas condensates) or solution gas (for volatile oils).

Mercury withdrawal is ceased when a predetermined pressure is reached. Some laboratories measure liquid volumes at several pressures before any vapor has been removed; these volumes, reported relative to V_{cell} , represent constant-composition depletion. They closely approximate volumes that would have been measured if the process had been CVD. (This was checked using the PR EOS simulator for lean and rich condensates; see also Ref. 5.)

Mercury is reinjected into the cell at constant pressure while simultaneously withdrawing an equivalent volume of vapor. When initial cell volume is reached, mercury injection is ceased. Withdrawn vapor is analyzed using gas chromatography to determine composition, y_j . Moles of vapor produced, n_p , are calculated using the real gas law and are reported as a cumulative percent of initial moles. Compressibility factor, Z , also is calculated by noting produced vapor surface volume and equivalent cell volume (at pressure and temperature). From measured vapor gravity and composition, heptanes-plus molecular mass is back-calculated. Liquid volume is measured visually and reported as a percent of cell volume, which is actually a type of hydrocarbon liquid saturation, S_L .

The experimental procedure is repeated several times until a low pressure is reached. The remaining liquid is removed, distilled, and analyzed using gas chromatography. Measured liquid composition should check with material-balance-derived composition. (Some major laboratories smooth and adjust measured vapor compositions until the material balance checks. This procedure is discouraged. It is good practice to ask if a laboratory reports measured or smoothed data, and to what extent material-balance-derived data are used in final CVD reports.)

Material-Balance Equations

Liquid Composition and K -Value Calculations

Perhaps the most useful application of constant-volume depletion data is for calculating liquid compositions that, together with measured vapor compositions, yield high-pressure K -values having several important reservoir- and process-engineering applications. To arrive at the final expression for liquid composition in terms of measured CVD data, we first state mole and component material balances, respectively, as

$$n_{tk} = n_{Lk} + n_{vk} \dots \dots \dots (1)$$

and

$$n_{tk} \cdot z_{jk} = n_{Lk} \cdot x_{jk} + n_{vk} \cdot y_{jk} \dots \dots \dots (2)$$

where n_L is moles of liquid with composition x_j , n_v is moles of vapor with composition y_j , and n_t is total moles in the system with composition z_j , each associated with pressure stage k . Subscript j designates components methane, ethane, etc. Eq. 1 states that total moles of the two-phase system equals the sum of liquid and vapor moles, while Eq. 2 states that total moles of component j in the two-phase system equals moles of j in the liquid plus moles of j in the vapor. The only data measured directly and appearing in either of the equations is vapor composition. The remaining unknowns can be determined from reported CVD data and modified forms of the material-balance relations.

Then we note that total moles at stage k equals initial moles minus cumulative moles of vapor produced.

We assume a basis of one mole initial fluid, $n_{t1} = 1$, yielding

$$n_{tk} = 1 - \sum_{i=2}^k \Delta n_{pi} \dots \dots \dots (3)$$

The same material balance can be applied on a component basis, resulting in

$$n_{tk} \cdot z_{jk} = z_{j1} - \sum_{i=2}^k \Delta n_{pi} \cdot y_{ji} \dots \dots \dots (4)$$

where Δn_{pi} is the incremental moles of vapor produced from the cell during stage i , and z_{j1} is the initial fluid composition at Stage 1 (saturated conditions).

Moles of vapor remaining in the cell can be calculated using a volumetric balance and the real gas law ($pV = nZRT$).

Recalling the basis of 1 mol initial fluid, cell volume can be calculated from initial fluid properties, which for gas condensates is

$$V_{cell} = \frac{Z_d \cdot R \cdot T}{p_d} \dots \dots \dots (5a)$$

and, for volatile oils (existing as a liquid at bubble-point pressure),

$$V_{cell} = M_b / \rho_b \dots \dots \dots (5b)$$

where $R = 8.3143 \text{ J/mol-K}$ for preferred SI units, and $R = 10.732 \text{ psia-cu ft/mol-}^\circ\text{R}$ for field units. M_b and ρ_b are bubble-point molecular mass and density, respectively. Z_d and p_d are dewpoint fluid compressibility factor and pressure, respectively.

At each depletion pressure, liquid volume is measured visually and reported as a fraction, S_{Lk} , of cell volume. Liquid volume, V_{Lk} , then can be calculated from

$$V_{Lk} = S_{Lk} \cdot V_{cell} \dots \dots \dots (6)$$

and, from a volume balance, vapor volume, V_{vk} , is

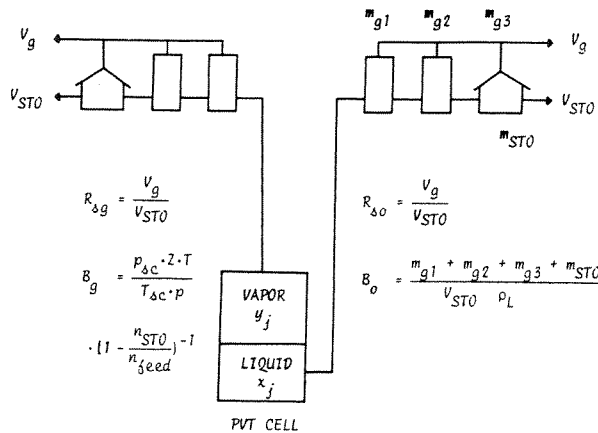


Fig. 1—Schematic of the procedure for calculating black-oil PVT properties.

$$V_{vk} = (1 - S_{Lk})V_{cell} \quad (7)$$

Using the real gas law, the corresponding moles of vapor n_{vk} are calculated from

$$n_{vk} = \frac{p_k \cdot V_{vk}}{Z_k \cdot R \cdot T} \quad (8)$$

where vapor compressibility factor, Z_k , which is measured at each stage k , corresponds to pressure p_k .

All unknowns in Eq. 1 now have been defined in terms of measured CVD data except liquid composition, which when written in terms of the other variables becomes

$$x_{jk} = \frac{n_{tk} \cdot z_{jk} - n_{vk} \cdot y_{jk}}{n_{tk} - n_{vk}} \quad (9)$$

Equilibrium constants or K -values are defined as the ratio of equilibrium vapor to liquid composition, or

$$K_{jk} = y_{jk}/x_{jk} \quad (10)$$

An effective means of correlating and checking the consistency of calculated K -values (i.e., liquid compositions) is to plot $\log Kp$ vs. the component characterization factor, F , as suggested by Hoffman *et al.*⁶

Physical Property Calculations

CVD data also can be used to calculate physical properties of equilibrium vapor and liquid. A mass balance is employed to carry out the necessary calculations:

$$m_{tk} = m_{Lk} + m_{vk} \quad (11)$$

where m_t is total mass of the system, m_L is liquid mass and m_v is vapor mass at stage k . Another way of stating the mass balance is that total mass at stage k equals initial mass minus cumulative vapor mass produced from the cell. Recalling the basis of 1 mol initial fluid, and thereby equating initial mass with initial (saturation) molecular mass, M_s , gives

$$m_{tk} = M_s - \sum_{i=2}^k \Delta n_{pi} \cdot M_{vi} \quad (12)$$

where M_{vi} is the vapor phase molecular mass at stage i . Both M_s and M_v can be calculated using Kay's mixing rule and appropriate component molecular masses.

Vapor mass can be calculated by noting that mass equals molecular mass times moles, or

$$m_{vk} = n_{vk} \cdot M_{vk} \quad (13)$$

Liquid mass then is calculated as the difference between total mass and vapor mass,

$$m_{Lk} = m_{tk} - m_{vk} \quad (14)$$

Having calculated masses and volumes of equilibrium liquid and vapor, respective densities can be calculated directly: $\rho = m/V$ (where volumes come from Eqs. 6 and 7).

An independent check of vapor density can be used to check the consistency of measured Z factors. The relation is derived directly from the real gas law and can be stated as

$$\rho_{vk} = \frac{M_{vk} \cdot p_k}{Z_k \cdot R \cdot T} \quad (15)$$

We also can calculate molecular mass of the equilibrium liquid, and specifically its heptanes-plus fraction. Rewriting the mass balance as

$$m_{tk} = M_{Lk} \cdot n_{Lk} + M_{vk} \cdot n_{vk} \quad (16)$$

we can solve for liquid molecular mass, M_{Lk} ,

$$M_{Lk} = \frac{m_{tk} - M_{vk} \cdot n_{vk}}{n_{Lk}} \quad (17)$$

Using Kay's mixing rule, the heptanes-plus molecular mass can be back-calculated to yield

$$M_{Lk7+} = \frac{M_{Lk} - \sum_{i=1}^{N-1} M_i \cdot x_{ki}}{x_{k7+}} \quad (18)$$

where M_i are molecular masses of pure components.

The average C_{7+} molecular mass of the two-phase system should be calculated using the relation

$$M_{7+} = \frac{n_{Lk} x_{k7+} + M_{Lk7+} + n_{vk} y_{k7+} + M_{vk7+}}{n_{Lk} x_{k7+} + n_{vk} y_{k7+}} \quad (19)$$

Black-Oil PVT Properties

Dodson *et al.*² suggested an experimental procedure for determining so-called black-oil PVT properties used in two-phase flow equations and solution-gas drive material-balance relations. Current laboratory procedures for estimating oil formation volume factor, B_o , and solution GOR, R_{so} , only approximate the Dodson *et al.* method without flashing the liquid phase at each stage of the differential vaporization process. For medium to low volatile crudes, this procedure appears valid for most engineering calculations. Also, vapor solution GOR, R_{sg} , is assumed to equal infinity — i.e., liquid condensation is neglected.

Highly volatile oils and gas condensates usually can-

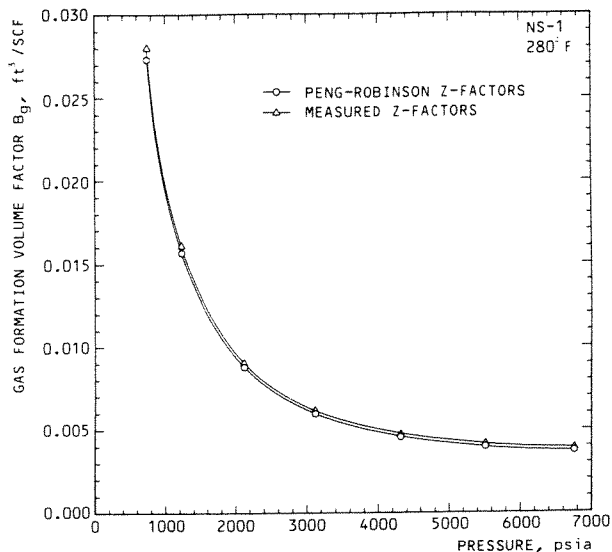


Fig. 2—Gas FVF vs. pressure for NS-1 at 280°F.

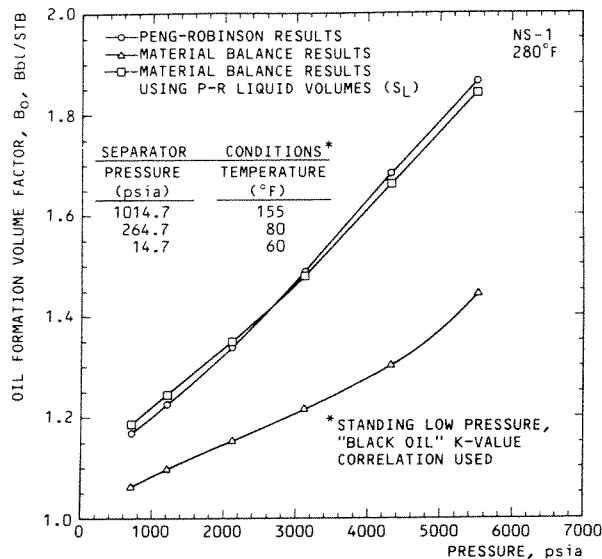


Fig. 4—Oil FVF vs. pressure for NS-1 at 280°F.

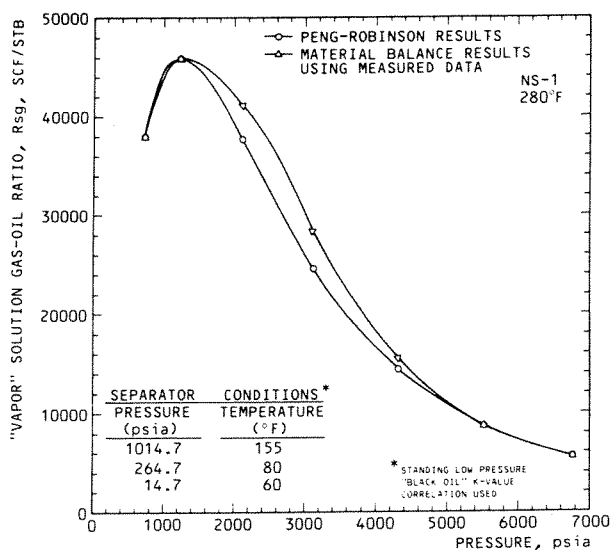


Fig. 3—Vapor solution GOR vs. pressure for NS-1 at 280°F.

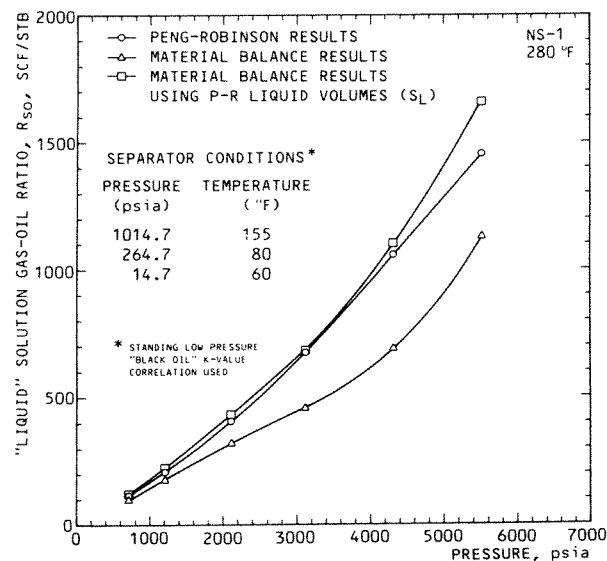


Fig. 5—Liquid solution GOR vs. pressure for NS-1 at 280°F.

not be described by the same differential process. The basic problem posed by these more volatile fluids is that during two-phase flow there exist both two phases and two components. That is, flowing oil contains solution gas that, when undergoing pressure reduction, evolves and mixes with the existing vapor phase. Likewise, flowing gas contains retrograde liquid that also evolves and mixes with the existing liquid when pressure declines. This complex thermodynamic phenomenon is, for all practical purposes, impossible to simulate in the laboratory.

An alternative method is suggested that, by making certain simplifying assumptions, approximates the true model described previously. Individual phase composi-

tions determined from CVD analysis (measured or calculated) are flashed through a multistage separator simulator representing field conditions. Fig. 1 describes the process diagrammatically.

Before beginning our discussion of the proposed method, let us define the four basic PVT properties used in two-phase flow and reservoir material-balance equations: B_o is liquid volume of x_j at reservoir conditions divided by stock-tank oil volume resulting from flash of x_j ; R_{so} is surface gas volume resulting from the flash of x_j divided by stock-tank oil volume resulting from flash of x_j ; B_g is vapor volume of y_i at reservoir conditions divided by surface gas volume resulting from the flash of y_i ; and R_{sg} is surface gas volume resulting from the

TABLE 1—MEASURED CONSTANT-VOLUME DEPLETION DATA FOR THE NS-1 FLUID AT 280°F (psia)

Component	Compositions								
	Equilibrium Vapor							Equilibrium Liquid	
	6764.7	5514.7	4314.7	3114.7	2114.7	1214.7	714.7	Experimental 714.7	Calculated 714.7
Carbon dioxide	2.37	2.40	2.45	2.50	2.53	2.57	2.60	0.59	0.535
Nitrogen	0.31	0.32	0.33	0.34	0.34	0.34	0.33	0.02	0.017
Methane	73.19	75.56	77.89	79.33	79.62	78.90	77.80	12.42	10.704
Ethane	7.80	7.83	7.87	7.92	8.04	8.40	8.70	3.36	3.220
Propane	3.55	3.47	3.40	3.41	3.53	3.74	3.91	2.92	2.896
isobutane	0.71	0.67	0.65	0.64	0.66	0.72	0.78	0.91	0.916
n-butane	1.45	1.37	1.31	1.30	1.33	1.44	1.56	2.09	2.103
isopentane	0.64	0.59	0.55	0.53	0.54	0.59	0.64	1.40	1.417
n-pentane	0.68	0.62	0.58	0.56	0.57	0.61	0.66	1.60	1.624
Hexanes	1.09	0.97	0.88	0.83	0.82	0.85	0.90	3.68	3.755
Heptanes-plus	8.21	6.20	4.09	2.64	2.02	1.84	2.12	71.01	72.815
Totals	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000
$M_{C_{7+}}$	184.0	160.0	142.0	127.0	119.0	115.0	114.0	213.0	207.8
$\gamma_{C_{7+}}$	0.816	0.799	0.783	0.770	0.762	0.758	0.757	0.833	0.843
Z	1.238	1.089	0.972	0.913	0.914	0.937	0.960		
n_p , %	0.000	9.024	21.744	38.674	55.686	72.146	81.301		
S_L , %	0.0	14.1	19.7	21.6	21.3	20.2	19.3		

flash of y_j divided by stock-tank oil volume resulting from flash of y_j , where x_j are liquid compositions determined from material-balance equations and y_j are vapor compositions measured experimentally.

First, liquid composition x_j is flashed using a set of appropriate K -values and basic vapor/liquid equilibria equations. [Glasø and Whitson⁷ have documented that Standing's⁸ low-pressure K -value equations are quite accurate for flash calculations of black oils. We have since found that they are also accurate for flash calculations of many gas condensates — e.g., systems with GOR's less than about 50,000 scf/STB (9000 std m³/stock-tank m³).] The sum of surface gas volumes divided by stock-tank oil volume is defined as the liquid GOR, R_{so} .

Oil FVF, B_o , is calculated from the relation

$$B_o = \frac{\sum_{i=1}^{\text{stages}} m_{gi} + m_{sto}}{V_{sto} \cdot \rho_L}, \dots \dots \dots (20)$$

where V_{sto} is stock-tank oil volume [e.g., 1 bbl (0.16 m³)], and m_g and m_{sto} are masses of total surface gases and stock-tank oil, respectively. Liquid density, ρ_L , can be determined either from material-balance calculations (m_L from Eq. 14 and V_L from Eq. 6) or from one of several compositional density correlations available^{9,10} using material-balance-derived liquid compositions.

At the same depletion stage k , vapor phase with composition y_j is separated through the flash simulator using identical K -values. The resulting surface gas volumes divided by stock-tank oil volume defines the vapor solution GOR, R_{sg} . Gas FVF, on the other hand, can be calculated from the CVD compressibility factor, Z , using the real gas law:

$$B_g = \frac{p_{sc} \cdot Z \cdot T}{p \cdot T_{sc}} \left(1 - \frac{n_{sto}}{n_{feed}}\right)^{-1}, \dots \dots \dots (21)$$

where n_{sto} is moles of stock-tank oil resulting from the flash of n_{feed} moles of reservoir vapor.

The major assumption implicit in the proposed method is that liquid and vapor compositions are solely dependent on pressure. That is, the composition/pressure relation is unique and not altered by physical flow.

Examples of PVT properties for a rich gas condensate (NS-1) are presented in Figs. 2 through 5. Here we have compared properties calculated using material-balance results with those calculated using PR EOS simulated data. Identical low-pressure K -values were used for both sets of data. Vapor solution GOR's are nearly the same for both methods of calculation. Liquid solution GOR's and oil FVF's are both low for material-balance-derived properties. The difference is a result of the underestimated liquid densities calculated by the PR equation.

Application of the Peng-Robinson Equation of State

Measured CVD data and material-balance-derived properties were controlled using a fluid properties package based on the PR EOS. Pure component properties (critical pressure, critical temperature, acentric factor, and molecular mass) were used for nonhydrocarbons and hydrocarbons from methane to n-pentane. Only n-hexane was considered for the C₆ fraction. Heptanes and heavier properties were estimated using the procedure and equations suggested by Whitson.¹¹

To manipulate the retrograde liquid-volume curve, the Watson characterization factor of the heaviest component was adjusted, making sure that adjusted critical properties were physically realistic.

Binary interaction coefficients were set equal to zero except¹²: N₂-N₂ = -0.02, CO₂ - hydrocarbons = 0.15, N₂ - hydrocarbons = 0.12, and C₁-C_n, n = 6,

TABLE 2—COMPOSITIONAL AND PROPERTIES DATA OF FLUID NS-1B
 SAMPLED FROM A WELL OFFSETTING NS-1 COMPARED WITH CALCULATED
 DATA GENERATED USING THE METHOD PRESENTED IN REF. 11

Single Carbon Number	Measured			Calculated*				
	Mole Percent	Molal Mass	Specific Gravity	K_{uop} Factor	Boiling Point (°R)	Mole Percent	Molal Mass	Upper Molal Mass
7	0.94	95	0.7158	12.05	641.7	0.935	95.1	99.6
8	0.84	104	0.7365	11.93	678.3	0.838	105.4	111.9
9	0.74	118	0.7557	11.90	727.3	0.739	118.9	126.8
10	0.60	132	0.7639	11.99	768.4	0.600	134.2	142.4
11	0.41	144	0.7723	12.04	804.0	0.410	148.7	155.5
12	0.34	154	0.7814	12.04	832.7	0.340	161.7	168.4
13	0.31	167	0.7939	12.03	871.2	0.310	175.0	182.2
14	0.26	180	0.8053	12.02	907.0	0.260	188.7	195.7
15	0.22	197	0.8096	12.13	947.1	0.220	202.1	209.1
16	0.19	212	0.8152	12.30	1008.1	0.190	215.4	222.4
17	0.17	226	0.8255	12.19	1019.0	0.170	228.9	236.1
18	0.15	234	0.8303	12.20	1039.4	0.150	242.8	250.1
19	0.13	250	0.8341	12.26	1069.4	0.130	256.8	264.1
20	0.11	262	0.8400	12.28	1097.6	0.110	270.6	277.8
21	0.08	277	0.8477	12.29	1130.8	0.080	283.0	289.0
22	0.07	292	0.8531	12.32	1161.0	0.070	294.1	299.9
23	0.06	308	0.8577	12.36	1191.4	0.060	304.8	310.3
24	0.06	329	0.8666	12.38	1234.9	0.070	316.7	324.0
25 +	0.51	471	0.8826	12.87	1465.6	0.508	439.1	∞
	6.19	177	0.8061	12.25 (12.02)**		6.190	177.0	

*The gamma distribution (Ref. 11) was used where an optimal alpha of 0.712 was found for eta (minimum molecular mass in the C₇₊ fraction) of 92. Upper molecular masses were found by fitting the measured compositions.

**The higher average K_{uop} value was calculated using a weight-average mixing rule, whereas the lower value was estimated using the Whitson correlation.

7...., which were estimated using a linear fit of the Katz and Firoozabadi¹² data (their Table 2),

$$\delta_{C_1-C_n} = 0.14 \cdot \gamma_n - 0.0668 \dots \dots \dots (22)$$

The interaction coefficient between methane and the heaviest component then was adjusted until a match of the measured dewpoint pressure was obtained.

Fluid Description: Rich Gas Condensate NS-1

NS-1 is a rich gas condensate first tested at a GOR of 5,500 scf/STB (980 std m³/stock-tank m³) from an initial reservoir pressure of 7,300 psia (50 MPa) and temperature of 280°F (138°C). Stock-tank oil gravity was 44°API (0.8055 g/cm³). Separator samples were taken while flowing the well at 16.3 MMscf/D (460 × 10³ std m³/d) and a flowing bottomhole pressure of 7,260 psia (50 MPa). Table 1 presents constant-volume depletion data measured on the recombined reservoir fluid.

Heptanes-Plus Characterization

Extended compositional data of the C₇₊ fraction were not available for the NS-1 fluid, only molecular mass and specific gravity. Complete true-boiling-point (TBP) data were, however, available from an offset well. These data were adapted to the NS-1 fluid using the methods presented in Ref. 11.

Molar distribution (mole fraction vs. molecular mass) of the offset well fluid was fit using the gamma distribution parameter alpha and variable upper-boundary

molecular masses. The optimal alpha was 0.712 for eta (minimum molecular mass in the C₇₊ fraction) of 92. Table 2 gives results of the match. Molar distribution of the NS-1 C₇₊ fraction then was calculated using $\alpha = 0.712$, $\eta = 92$, and $M_{C_7+} = 184$ (as compared to 177 for the NS-1b fluid). Results are presented in Table 3.

Tuning the Peng-Robinson Equation of State

Single carbon number groups were combined into five multiple carbon number (MCN) groups: C₇ through C₉, C₁₀ through C₁₃, C₁₄ through C₁₇, C₁₈ through C₂₄, and C₂₅₊, as suggested in Ref. 11. Group properties were calculated using Kay's mixing rule. Methane interaction coefficients were estimated using MCN specific gravities and Eq. 22.

Using these data, the PR EOS yielded a dewpoint pressure much lower than measured. The C₁ through C₂₅₊ interaction coefficient then was increased until dewpoint pressure was matched.

The CVD program was run using the MCN properties (Table 3). The overall match was good to excellent, except for liquid volumes, which were much too high (32% simulated maximum vs. 22% measured maximum). To check whether measured volumes were low, we compared material-balance liquid densities with Alani-Kennedy¹⁰ densities (using material-balance compositions and molecular masses). Table 4 shows results of the comparison, indicating that measured volumes are consistent except for perhaps small errors in the first two volume measurements.

On the basis of these results, we decided to lower the

TABLE 3—PHYSICAL PROPERTIES OF THE C₇₊ SINGLE AND MULTIPLE CARBON NUMBER GROUPS USED IN THE PENG-ROBINSON EQUATION OF STATE TO DESCRIBE RESERVOIR FLUID BEHAVIOR OF THE NS-1 FLUID

Single Carbon Number	Mole Percent	Molal Mass	Specific Gravity	Boiling Point (°R)	Critical			Methane Interaction Coefficient
					Temperature (°R)	Pressure (psia)	Acentric Factor	
7	1.2136	95.3	0.7177	646.8	971.6	457.5	0.2742	
8	1.1730	106.5	0.7409	690.6	1021.4	423.4	0.3056	
9	0.8600	120.7	0.7599	739.4	1073.4	383.2	0.3454	
10	0.6872	134.7	0.7682	781.4	1112.9	345.9	0.3861	
11	0.5681	148.7	0.7781	822.2	1152.1	316.8	0.4251	
12	0.4783	162.7	0.7908	863.1	1192.3	294.0	0.4622	
13	0.4074	176.7	0.8034	902.8	1231.2	274.9	0.4984	
14	0.3498	190.7	0.8153	941.2	1268.3	258.4	0.5342	
15	0.3021	204.7	0.8168	972.6	1294.2	240.4	0.5740	
16	0.2621	218.7	0.8210	1029.8	1321.5	225.7	0.6127	
17	0.2282	232.7	0.8310	1039.5	1354.0	214.6	0.6486	
18	0.1992	246.6	0.8389	1072.0	1383.6	204.3	0.6855	
19	0.1744	260.6	0.8432	1104.7	1408.7	194.0	0.7246	
20	0.1529	274.6	0.8486	1131.6	1434.4	185.1	0.7634	
21	0.1343	288.6	0.8554	1161.9	1461.0	177.4	0.8016	
22	0.1182	302.6	0.8602	1190.2	1484.9	170.0	0.8416	
23	0.1041	316.5	0.8639	1217.4	1507.0	162.9	0.8830	
24	0.0918	330.5	0.8690	1245.1	1530.2	156.8	0.9241	
25 +	0.7054	462.3	0.9292	1488.0	1734.6	91.4	1.0590	
	8.2100	184.0	0.8160					

Multiple Carbon Number Properties Used in the Final CVD Simulation

7 through 9	3.2466	106.1	0.7385	688.3	1016.5	425.5	0.3044	0.03659*
10 through 13	2.1410	152.7	0.7837	835.0	1163.6	313.1	0.4348	0.04292*
14 through 17	1.1421	209.2	0.8205	984.4	1304.5	237.4	0.5856	0.04807*
18 through 24	0.9749	281.5	0.8524	1146.9	1446.0	182.7	0.7832	0.05254*
25 +	0.7054	462.3	0.9192	1276.1**	1584.2**	168.8**	0.8819**	0.18400†
	8.2100	184.0	0.8160					

*Calculated using the Katz and Firoozabadi correlation, curve-fit to yield the relation $\delta_{C_1-C_n} = 0.14 \cdot \gamma_n - 0.0668$. Though not shown in this table, the methane/hexane interaction coefficient also was calculated using this relation.

**Adjusted values representing a K_{uop} factor of 11.80. The original values correspond to a K_{uop} factor of 12.42 and are given above (e.g., 1488.0).

†Adjusted value used to match the measured dewpoint pressure.

TABLE 4—CALCULATED LIQUID DENSITIES AS A FUNCTION OF PRESSURE FOR NS-1 FLUID

Pressure (psia)	Calculated Liquid Densities (g/cm ³)			
	Measured CVD Data		Simulated CVD Data	
	Material-Balance Density	Alani-Kennedy Density (Material-Balance Liquid Properties)*	PR Density**	Alani-Kennedy Density (PR Liquid Properties)*
5,514.7	0.670	0.608	0.541	0.570
4,314.7	0.680	0.649	0.554	0.596
3,114.7	0.688	0.670	0.580	0.632
2,114.7	0.700	0.682	0.608	0.664
1,214.7	0.711	0.700	0.636	0.692
714.7	0.722	0.711	0.653	0.707

*The Alani-Kennedy density correlation requires liquid compositions, total liquid molecular mass, heptanes-plus molecular mass, and specific gravity (as well as pressure and temperature). These data were available from either material-balance calculations or PR simulation results.

**The PR simulation used properties given in Table 3 with an adjusted $K_{uop} = 11.8$ for the C₂₅₊ fraction. Using the original K_{uop} factor of 12.42 gave even lower liquid densities than those given above, with a larger deviation from the Alani-Kennedy values.

TABLE 5—SIMULATED CONSTANT-VOLUME DEPLETION DATA FOR THE NS-1 FLUID AT 280°F USING THE PENG-ROBINSON EQUATION OF STATE (psia)

Component	Compositions							Equilibrium Liquid	
	Equilibrium Vapor							Experimental	Calculated
	6764.7	5514.7	4314.7	3114.7	2114.7	1214.7	714.7	714.7	714.7
Carbon dioxide	2.370	2.403	2.447	2.497	2.541	2.576	2.583	0.590	0.595
Nitrogen	0.310	0.323	0.336	0.344	0.343	0.334	0.321	0.020	0.029
Methane	73.190	75.549	77.644	79.135	79.712	79.242	77.772	12.420	11.939
Ethane	7.800	7.779	7.793	7.878	8.057	8.372	8.711	3.360	3.623
Propane	3.550	3.474	3.405	3.383	3.444	3.660	3.989	2.920	3.133
isobutane	0.710	0.686	0.660	0.644	0.647	0.691	0.778	0.910	0.967
n-butane	1.450	1.390	1.326	1.281	1.282	1.375	1.567	2.090	2.314
isopentane	0.640	0.604	0.564	0.530	0.516	0.548	0.638	1.400	1.509
n-pentane	0.680	0.639	0.592	0.550	0.532	0.563	0.659	1.600	1.770
Hexanes	1.090	0.996	0.889	0.789	0.727	0.744	0.877	3.680	4.223
Heptanes-plus	8.210	6.157	4.343	2.969	2.198	1.895	2.105	71.010	69.897
Totals	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000
$M_{C_{7+}}$	184.0	161.0	142.7	129.1	121.2	116.4	114.5	213.0	209.1
$\gamma_{C_{7+}}$	0.816	0.799	0.783	0.770	0.762	0.758	0.757	0.833	0.843
Z	1.203	1.037	0.937	0.890	0.886	0.911	0.936		
n_p , %	0.000	9.637	22.581	39.492	56.196	72.413	81.535		
S_L , %	0.00	19.55	26.11	26.65	25.11	23.00	21.58		

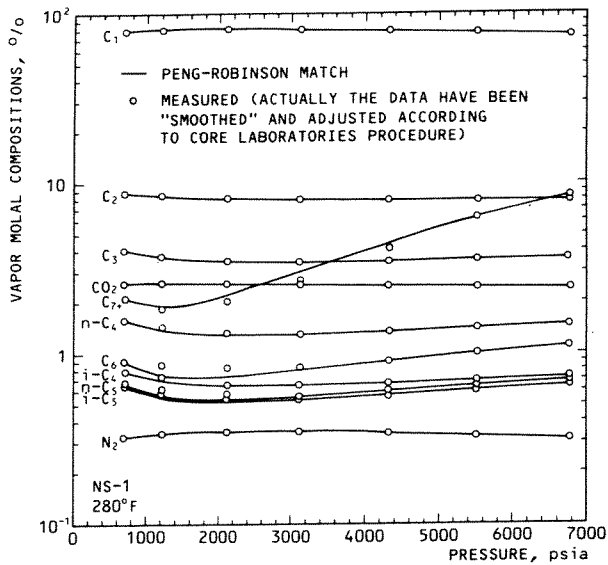


Fig. 6—Calculated and measured vapor compositions vs. pressure for NS-1 at 280°F.

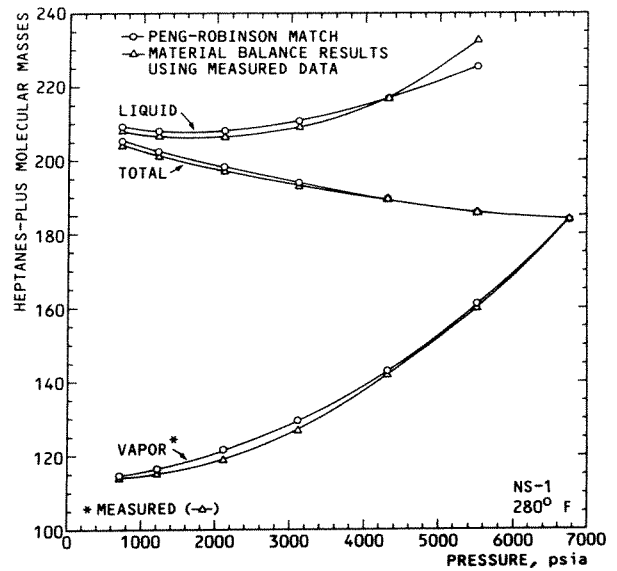


Fig. 7—Calculated heptanes-plus molecular masses vs. pressure for NS-1 at 280°F.

PR liquid volumes by adjusting the characterization factor of the C_{15+} fraction. Lowering the factor from 12.24 to 11.80 resulted in an 8% decrease of the liquid volumes for the maximum drop-out (from 32% to 26%). The adjustment had little effect on other estimated data. To have lowered the K_{uop} factor more would have created a physically unrealistic system. Adjusted physical properties for the C_{15+} fraction are found in Table 3, as is the methane interaction coefficient used to

adjust dewpoint pressure. Complete results of the CVD simulation are presented in Table 5. PR liquid densities are compared with Alani-Kennedy estimates in Table 4.

Many other adjustments of the C_{7+} characterization procedure were tried. None of these were particularly helpful, though some are worth mentioning: (1) extending the C_{7+} split to C_{40+} such that the last component was very heavy, (2) increasing the number of MCN groups used to nine, C_{25+} inclusive, (3) splitting the

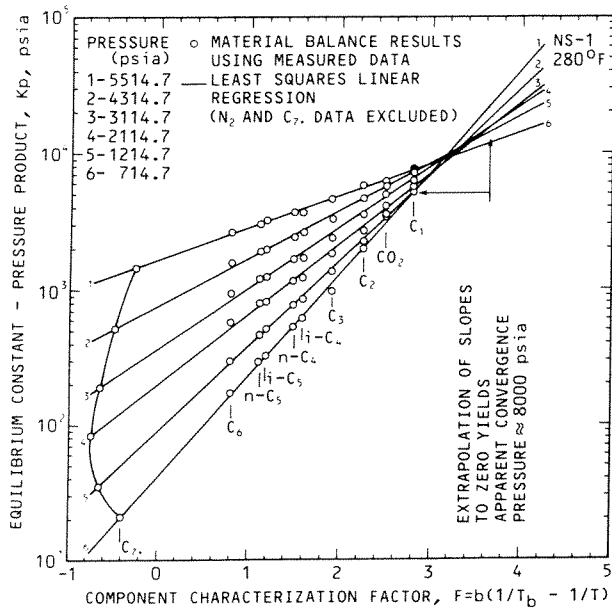


Fig. 8—NS-1 K-values at 280°F calculated using the material-balance approach.

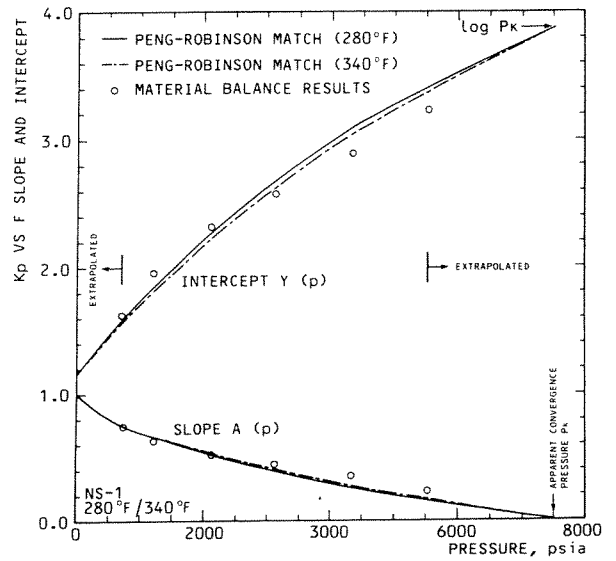


Fig. 10—Slopes and intercepts of log K_p vs. F plots vs. pressure for NS-1 at 280 and 340°F.

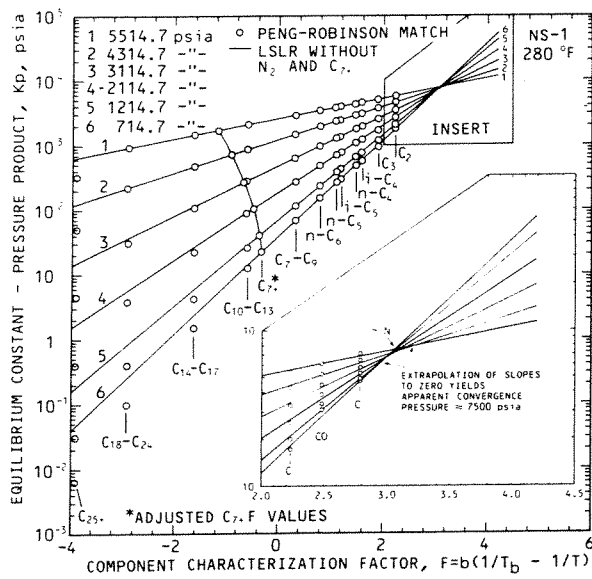


Fig. 9—NS-1 K-values at 280°F calculated using the PR EOS.

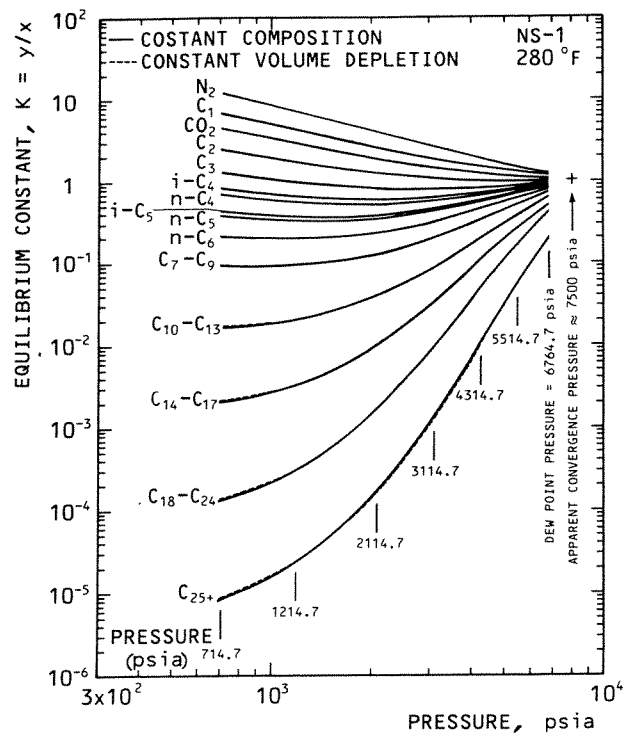


Fig. 11—PR K-values for NS-1 at 280°F representing two depletion processes.

C₇₊ fraction into eight SCN groups and a C₁₅₊ fraction, and (4) using TBP K_{uop} factors instead of those estimated from Eq. 23.

Results and Discussion

Fig. 6 compares measured (or more correctly, "smoothed") vapor compositions with those simulated using the PR EOS. The match is excellent, showing only slight deviation for the C₇₊ and C₆ components. Deviation of the hexane component is probably because of its incorrect characterization as n-hexane.

Fig. 7 presents heptanes-plus molecular masses of liquid and vapor phases and the total system. Simulated and material-balance-derived values match well. Our experience has shown that a good match of C₇₊ molecular mass using the PR EOS is usually difficult and very dependent on proper characterization of the plus fraction.

Calculated equilibrium constants were correlated using the Hoffman *et al.*⁶ method. Fig. 8 presents NS-1 K -values calculated using material-balance relations. The $\log Kp$ vs. F plots are linear and appear to approach a common point. The convergence point can give an estimate of the apparent convergence pressure. Actually, the most accurate value is obtained by extrapolating the slope vs. pressure curve to zero, as done in Fig. 10. The resulting estimate of p_K is 8,000 psia (55 MPa).

Fig. 9 presents NS-1 K -values calculated from the EOS. Once again linear plots of $\log Kp$ vs. F converge to a point. From the extrapolation of slope to zero in Fig. 10, $p_K \approx 7,500$ psia (52 MPa). Another interesting feature shown in Fig. 9 is that heavy components are better correlated using the $\log Kp$ vs. F methods at higher pressures.

Temperature effects on the $\log Kp$ vs. F plots of NS-1 were investigated by running the EOS simulator at 340°F (171.1°C), about 60°F (15.5°C) higher than reservoir temperature. Results indicate that temperature influence is (1) largest for heavy components at large pressures, (2) negligible at low pressures (as was found in Ref. 8), (3) relatively small compared to the influence of pressure, and (4) not significant in changing the apparent convergence pressure of the system.

For lighter systems, there does not always appear such a unique convergence point for $\log Kp$ vs. F plots. We thought that this perhaps resulted from a change in the total composition of the system or from alteration in the heptanes-plus properties. We investigated these possibilities by running a constant-composition simulation of NS-1. Resulting K -values were compared with CVD K -values and are presented as $\log K$ vs. $\log p$ plots in Fig. 11. This plot indicates that compositional change during constant volume depletion is not significant enough to influence K -values or convergence pressure.

Conclusions

1. Measured CVD data for a gas condensate were analyzed using simple material balances and the PR EOS.

2. A simple method was proposed for calculating black-oil PVT properties (FVF's and solution GOR's) of gas condensates and volatile oils.

3. Simulated constant-composition and CVD studies

of lean and rich gas condensates using the EOS indicate that K -values are independent of the depletion process.

4. Equations of state usually overestimate liquid volumes of petroleum reservoir fluids. The problem was improved by reducing the Watson characterization factor of the heaviest component.

Nomenclature

- A or $A(p)$ = slope of $\log Kp$ vs. F plot
 b = slope of the straight line connecting the critical point and atmospheric boiling point on a \log vapor pressure vs. $1/T$ plot, cycle-°R (cycle-K)
 B = formation volume factor, bbl/STB (m³/stock-tank m³)
 F or $F(T)$ = component characterization factor, cycle
 K = equilibrium constant (K -value)
 K_{uop} = Watson characterization factor
 m = mass, lbm (kg)
 M = molecular mass, lbm/lbm-mol (kg/kg-mol)
 n = moles, lbm-mol (kg-mol), exponent in K -value correlation
 p = pressure, psia (kPa)
 R = universal gas constant, 10.732 psia-cu ft/mol-°R (9.3143 J/mol-K)
 R_{sg} = vapor solution GOR, scf/STB (std m³/stock-tank m³)
 R_{so} = liquid solution GOR, scf/STB (std m³/stock-tank m³)
 S = saturation, fraction or %
 T = absolute temperature, °R (K)
 V = volume, cu ft (m³)
 x = liquid composition, fraction or %
 y = vapor composition, fraction or %
 Y or $Y(p)$ = intercept of $\log Kp$ vs. F plot
 z = total system composition
 Z = vapor compressibility factor
 γ = specific gravity relative to air or water (60/60)
 δ = interaction coefficient
 Δ = incremental
 ρ = density, lbm/cu ft (kg/m³)
 ω = acentric factor

Subscripts

- a = atmospheric
 b = bubble point (p_b) or boiling (T_b)
 c = critical
cell = cell, pertaining to PVT cell volume
 d = dewpoint
 g = gas
 i = index for summation
 j = component identifier
 k = depletion stage
 K = convergence

L = liquid phase
 n = carbon number
 o = oil
 p = produced
 r = reduced
 s = saturated (bubble- or dewpoint)
 sc = standard conditions
 sto = stock-tank oil
 t = total (two-phase)
 v = vapor phase

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We thank H. Norvik, H. Asheim, D. Murphy, V. Dalen, and G. Nielsen for useful comments concerning this paper. We also acknowledge computer time and facilities provided by Rogaland Dist. C., Norwegian Inst. of Technology, and Continental Shelf Inst. We thank Phillips Petroleum Co. Norway for contributing needed fluid data to the petroleum literature. Support from Frying Pan Publications Inc. is appreciated.

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SI Metric Conversion Factors

$$\begin{aligned}
 ^\circ\text{API} & 141.5/(131.5 + ^\circ\text{API}) = \text{g/cm}^3 \\
 \text{bbl} \times 1.589\ 873 & \text{E}-01 = \text{m}^3 \\
 \text{cu ft} \times 2.831\ 685 & \text{E}-02 = \text{m}^3 \\
 ^\circ\text{F} & (^{\circ}\text{F} - 32)/1.8 = ^\circ\text{C} \\
 \text{psi} \times 6.894\ 757 & \text{E}+00 = \text{kPa} \\
 \text{scf} \times 2.863\ 640 & \text{E}-02 = \text{std m}^3
 \end{aligned}$$

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