PHASE BEHAVIOR IN RESERVOIR SIMULATION

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INTRODUCTION

The importance of phase behavior to reservoir simulation is most obvious when we consider the burden that most companies have inflicted upon themselves to develop or purchase equation-of-state (EOS) simulators that run one or two orders of magnitude slower than traditional black-oil models. For truly large simulations, most companies have had no choice but to modify the black-oil PVT formulation in a way that allows for consideration of mass transfer by vaporization and condensation. The variety and complexity of modified black-oil formulations is simply mind-boggling. I've many times said that given the choice of explaining an EOS or a modified black-oil formulation to an engineer, I'd choose the EOS because it would be faster and more readily understood. Either way, EOS-based compositional or modified black-oil simulation, the resulting model is slower and more difficult for engineers to understand. So, to begin our look at the role that phase behavior plays in reservoir simulation, let's ask the simple question: *why do we need a more complicated PVT formulation than offered by the black-oil approach?*

Petroleum engineers have dealt with production from reservoirs with compositionally sensitive behavior since the 1940s (and probably even earlier). Two reservoir types that were identified as requiring special PVT treatment were gas condensate fields, and reservoirs that showed significant compositional variation. The latter was described in publications by Burtchaell (1949), Espach and Fry (1951), Cook et al. (1951), and others. Already in the 1930s several researchers had postulated the possible occurrence of vertical compositional variation based on equilibrium calculations that included both gravitational and chemical potentials [Muskat (1930) and Sage and Lacey (1939)]. These calculations were based on the original theory developed by Gibbs in the late 1800s. The behavior of gas condensate reservoirs and the phenomenon of retrograde condensation were also described in the 1930s and 1940s, with comprehensive research programs initiated (1) at the U.S. Bureau of Mines under the direction of C. Kenneth Eilerts, from 1934 to the late 1950s [Eilerts et al. (1957)], (2) by Katz and coworkers at the University of Michigan

[Katz et al. (1959)], and (3) at the California Inst. of Technology by Sage, Olds, and Lacey [e.g. Sage and Olds (1947)].

In the late 1940s and 1950s gas injection in oil reservoirs, and gas cycling in gas condensate reservoirs created additional need for methods to describe complex phase behavior. Initially the emphasis was how to estimate the rate and degree of vaporization of reservoir oil or retrograde condensate, with most gas injection projects being conducted at pressures lower than necessary to develop miscibility. It was found that accurate prediction of K-values for light and heavy components was the key to modelling the vaporization process. Work by Cook et al. (1969), for example, provided extensive K-values for C_{7+} fractions, specifically for simulating the vaporization process.

In 1965, Kniazeff and Naville proposed a modification of the black-oil PVT formulation by including a term to account for liquids that would condense or vaporize into reservoir gases. So-called partial densities were used as the basic PVT properties. The idea was eventually implemented in terms of the more familiar black-oil formulation [Spivak and Dixon (1973)], where solution oil-gas ratio was introduced. With these modified black-oil formulations it was possible to simulate depletion of gas condensate and volatile oil reservoirs. Cook et al. (1974) proposed a further improvement of the modified black-oil approach by introducing a gas-injection parameter to account for changing PVT properties that resulted from multiple contacts with non-equilibrium gas.

Much of the work in miscible gas displacement in the 1950s used enriched gas in a process that was assumed to be first-contact miscible. In the 1960s and 1970s *multicontact* miscibility was given more attention, including the vaporizing-gas drive mechanism which results from injection of lean gas, flue gas or nitrogen at high pressures, and the condensing-gas drive mechanism which develops from the injection of enriched gas. In the domestic U.S., CO_2 injection into low-temperature reservoirs has dominated gas-injection enhanced oil recovery (EOR) in the 1980s, and probably will continue to do so in the 1990s. Both immiscible and miscible CO_2 projects have

proven economic, and now large quantities of relatively inexpensive CO_2 are available from a large network of CO_2 pipelines serving the Rocky Mountain, Mid Continent, and Gulf Coast areas.

Multicontact miscible processes have been the main impetus in the development of improved methods for calculating phase behavior in the near-critical region. As opposed to near-critical calculations of gas condensate and volatile oil fluids, the compositions existing in the near-critical region of a gas-injection process are far removed from the insitu reservoir fluid compositions for which laboratory data may be available. Existing compositional models based on tabulated K-values proved not to be adequate for treating such complex systems, and even K-value models based on convergence pressure methods could not properly account for the complex VLE encountered in multicontact miscible processes. In the 1970s and early 1980s compositional models based on cubic equations of state were developed. Some companies had already gained experience with cubic equations, where Amoco's pioneer work on the modified Redlich-Kwong EOS was perhaps the most impressive. Most petroleum engineers, however, were (and still are) unfamiliar with these relatively complex thermodynamic models. Also, there were two unsolved problems with the practical application of EOSs to petroleum reservoir fluids:

1. Cubic equations of state could not accurately *predict* the phase and volumetric behavior of petroleum reservoir fluids, thereby requiring extensive tuning of the fluid characterization to match experimental PVT data.

2. Existing algorithms for the two-phase flash calculation were (a) time consuming, (b) numerically unstable near phase boundaries and in the critical region, and (c) could not detect whether a mixture would split into two phases when the flash calculation was performed.

These problems have been solved for the most part in the 1980s. Significant contributions to improved EOS fluid characterization were made by Amoco engineers [e.g. Yarborough (1979) and Turek (1984)], Katz and Firoozabadi (1978) and

Whitson (1983) in C_{7+} characterization, Coats and Smart (1986) in multiparameter regression, and Peneloux et al (1982) with the method of volume translation. In the early 1980s, Michelsen presented several papers that solved practically all of the calculational problems listed in the second point above, including algorithms for the two-phase flash (1982), phase stability test based on Gibbs tangent plane criterion (1982), and saturation pressure (1985). More recently, Michelsen (1988) has also developed an algorithm for calculating a mixture critical point that is faster than a two-phase flash calculation.

The task of developing a truly *fast* EOS-based compositional model seemed unthinkable. Young (1987), however, used Michelsen's phase stability test in the development of a very fast compositional simulator. The ability to test whether a composition was single or two-phase led Young to construct a system of fluid types that allowed the model to vectorize over the number of grid blocks, instead of over the number of components, as was usually done. This gave a much better utilization of vector processors than was typically being achieved. Another important aspect of Young's model was the efficient use of a volume (mole) balance to couple flow and equilibrium equations, together with selective updating of the Jacobian matrix. More recently, Young has suggested that an extension to Michelsen's Newton-Raphson flash algorithm is ideally suited for improving the efficiency and storage in compositional simulators.

Although Young shows that it is now feasible to run full-field compositional simulations with as many as 100,000 grid blocks and 10 components, this approach is not valid for the special situations when a fully implicit model is required. Coats (1989) and da Silva (1989), for example, discuss the application of a fully-implicit, full-field EOS model to simulate a giant North Sea naturally fractured reservoir. The main drawback with the fully-implicit formulation is that the number of components is limited to about four, as a larger number will push the limits of existing linear solvers. Coats (1989) and others have indicated that as few as three to four components is adequate in an EOS formulation describing complicated vaporizing and condensing gas-drive processes. An adaptive implicit formulation in compositional

simulation also offers a solution to treating highly non-linear problems locally without slowing down calculations in regions of the reservoir where implicit pressure/composition calculations are not necessary.

SIMPLIFIED PVT FORMULATIONS

TRADITIONAL BLACK-OIL

QUICK AND DIRTY

The traditional black-oil PVT formulation assumes that reservoir oil consists of two pseudocomponents, *stock-tank oil* and *surface gas*, and that reservoir gas contains no condensable liquids and remains entirely as a gas phase at surface conditions. The properties of the stock-tank oil and surface gas are assumed constant throughout the life of a reservoir, and surface gas from the reservoir oil has identical properties with the surface gas from the reservoir gas. Interestingly, this simplified PVT formulation is still the standard for most petroleum engineering applications, including inflow (backpressure) performance, multiphase pipe flow, reservoir material balance, and reservoir simulation.

The basic quantities used in the traditional black-oil formulation are solution gas-oil ratio R_s, formation volume factors B_o and B_g, and surface gravities γ_o and γ_g. These properties can be estimated from correlations [e.g. Standing (1977)] or they can be determined from differential liberation and multistage separator test data. Solution GOR expresses the ratio of total surface gas to stock-tank oil when a reservoir oil is brought to surface conditions; oil volume factor represents the volume of reservoir oil required to produce one volume of stock-tank oil; and gas volume factor expresses the volume of reservoir gas to yield one volume of surface gas, with the assumption that all of the reservoir gas remains as a gas at surface conditions.

The validity of the traditional black-oil PVT formulation depends primarily on the reservoir oil's volatility, where low-volatile oils described with the traditional black-oil formulation usually have the following characteristics: $R_s < 750$ scf/STB, $B_o < 1.4$ bbl/STB, $\gamma_{API} < 30$. Perhaps the best way to determine the validity of traditional black-oil treatment is to compare depletion performance using a material balance

based on black-oil PVT properties with material balance calculations based on a compositional formulation (e.g. with tabulated K-values or an EOS). If producing GOR and average reservoir pressure versus cumulative oil production vary significantly for the two methods of material balance calculation, then the traditional black-oil approach should be used with caution.

MODIFIED BLACK-OIL

BLACK IS NOT REALLY BLACK

Oil is (presently) a $15-$20 commodity produced from underground reservoirs in liquid form. Oil may vary in color from pink to straw to light brown to dark brown to black. The color doesn't really matter to anyone, only how much that gets produced. And when the practice of calling oil "black" gets in the way of figuring out how much oil gets produced, that's when we stop using the description "black" for something that is really brown, red, or pink.

Already in the 1950s several publications indicated that the stock-tank oil produced from a volatile oil reservoir came from two sources — (1) stock-tank oil from the flowing reservoir oil and (2) condensate from the flowing reservoir gas [Jacoby and Berry (1957)]. Fig. 1 shows the actual depletion characteristics of a volatile oil reservoir, where reservoir pressure decreases from 5000 to 1800 psia, total surface oil gravity varies from 44 to 62 °API, and producing GOR increases from 3800 to 22,000 scf/STB. It can be shown from material balance calculations that towards the later stages of depletion more than half of the produced "oil" in a volatile oil reservoir comes from the flowing reservoir gas.

The most common modification of the black-oil PVT formulation includes (1) solution oil-gas ratio r_s as an additional PVT parameter and (2) a more precise definition of the gas formation volume factor B_g. Fig. 2 shows schematically the

relation between reservoir phases and surface "components" in the modified black-oil formulation. Definitions of the four PVT parameters are:

$$B_o = \frac{V_o}{V_{oo}} = \text{oil formation volume factor}$$

$$R_s = \frac{V_{go}}{V_{oo}} = \text{solution gas-oil ratio}$$

$$B_{gd} = \frac{V_g}{V_{gg}} = \text{dry gas formation volume factor}$$

$$r_s = \frac{V_{og}}{V_{gg}} = \text{solution oil-gas ratio}$$

where V_o is the reservoir oil volume, V_{oo} is the volume of surface oil produced from reservoir oil, V_{go} is the volume of surface gas from reservoir oil, V_{og} is the volume of surface oil from reservoir gas, and V_{gg} is the volume of surface gas from reservoir gas.

Methods for generating modified black-oil properties are given by Whitson and Torp (1983), Coats (1985), Spivak and Dixon (1973), and Drohm and Goldthorpe (1987). It is always a good idea to check the reservoir densities calculated by the model using the pressure-dependent black-oil properties and surface gravities:

$$\rho_o = \frac{62.4\gamma_{oo}+0.0136\gamma_{go}R_s}{B_o} \tag{1}$$

$$\rho_g = \frac{0.0764\gamma_{gg}+350r_s\gamma_{og}}{B_{gd}} \tag{2}$$

with R_s in scf/STB, r_s in STB/scf, B_o in bbl/STB, B_{gd} in ft^3/scf, and ρ in lb/ft^3. Most reservoir simulators assume that $\gamma_{oo}=\gamma_{og}$ and $\gamma_{gg}=\gamma_{go}$, though Fig. 3 shows that the assumption is not really valid for volatile reservoir fluids.

Extension of the modified black-oil formulation for vaporizing gas-injection processes is given by Cook et al. (1974), where a gas-injection parameter G_i is defined as the cumulative volume of injection gas entering a grid cell, divided by the grid cell volume. PVT properties B_o, R_s, B_{gd}, and r_s are then correlated in tabular form versus G_i. Other extensions to the modified black-oil formulation are proposed by Lo and Youngren (1985), Whitson et al. (1988), and others; the complexity of some of these extensions is unbelievable, mainly because so many nonphysical quantities are used.

K-VALUE METHODS

BETTER BUT NOT GOOD ENOUGH

A more rigorous approach to treating the phase behavior of reservoir fluids uses K-values and a multicomponent flash calculation. The K-values are usually expressed as a function of pressure, temperature, and convergence pressure p_K. Convergence pressure is a parameter that characterizes the composition dependence of K-values. Rowe (1967) and others have presented definitions of convergence pressure and shown how it can be used to correlate K-values. Numerous forms of the functional relation $K_i(p,T,p_K)$ can be found in the literature.

If gas is *not* injected in a reservoir, the convergence pressure of reservoir fluids will remain more-or-less constant, greatly simplifying the correlation of K-values in compositional simulators. Reservoir processes that can be accurately modelled with this approach include pressure depletion, water flooding, and well testing.

On the other hand, gas-injection processes usually cause strong composition dependence of K-values, thus requiring use of the convergence-pressure approach. Several researchers [Fussel and Yarborough (1972), Henry (1976), and Coats (1982)] have confirmed the composition dependence of K-values for methane and C_{7+} fractions during gas cycling. Unfortunately, convergence pressure methods are burdened with several problems. First, the composition dependence of convergence pressure is based on empirical correlations for critical temperature and critical

pressure of reservoir mixtures. As these correlations are not generally accurate, the extrapolation of K-values (in composition) is highly uncertain. Also, the calculation of convergence pressure may be an expensive iterative calculation, even compared with EOS calculations.

In summary, the K-value method has become a method of the past, being left behind by relatively fast and thermodynamically-consistent EOS alternatives. There are, however, two main applications where the K-value method may be the preferred alternative: (a) fully implicit problems, and particularly where more than four components are required, and (b) non-gas-injection studies requiring detailed compositional information for process design. Whitson and Michelsen (1989) show that the concept of convergence pressure has a rigorous thermodynamic interpretation that can be readily calculated with an EOS. This observation can help in the development of more consistent K-values in a K-value-based compositional simulator (e.g. at pressures above the initial saturation pressure).

EQUATIONS OF STATE

REVIEW OF CUBIC EQUATIONS OF STATE

MIRROR, MIRROR ON THE WALL ...

> *It is fair to say that no cubic equation of state -- no matter how complicated -- can accurately predict the volumetric and phase behavior of reservoir mixtures over a large range of pressure, temperature, and composition.*

Professor J.J. Martin (1979) from the University of Michigan summarizes the problem resulting from an overabundence of cubic equations of state by quoting from none other than Snow White: "Mirror, mirror on the wall, who's the fairest of them all?" Despite Martin's claim to have developed the *fairest* cubic equation, it is probably safe to say that all equations have inherent limitations and that no single equation performs better than all others.

van der Waals (vdW) proposed the first cubic EOS in 1873,

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \tag{3}$$

where a is the "attraction" parameter and b is the "repulsive" parameter (or effective molecular volume). van der Waals also stated the critical criteria which are typically used to define the two constants a and b — namely, that the first and second derivatives of pressure with respect to volume equal zero at the critical point of a pure component:

$$\left(\frac{\partial p}{\partial v}\right)_{p_c, T_c, v_c} = \left(\frac{\partial^2 p}{\partial v^2}\right)_{p_c, T_c, v_c} = 0 \tag{4}$$

As shown by Martin and Hou (1955), this constraint is equivalent to the condition $(Z-Z_c)^3 = 0$ at the critical point.

Since the introduction of the vdW EOS, evolution of cubic equations has resulted in many new forms such as those proposed by Redlich and Kwong (RK) (1949), Peng and Robinson (PR) (1976), and Martin (1979), only to name a few. The RK equation has certainly been the most popular basis for developing improved equations of state. Another trend [Martin (1979), Abbott (1979), Schmidt and Wenzel (1980), Coats (1982), Reid et al. (1987) and others] has been to generalize the cubic EOS such that it can be conveniently simplified to the PR, RK, and other familiar forms. Kumar and Starling (1982) use the most general five-constant cubic EOS to fit volumetric and phase behavior of nonpolar compounds, though they fail to show the utility of their equation for mixtures.

Most petroleum engineering applications rely on the Peng-Robinson EOS, or a modification of the RK EOS. Numerous variants of the RK equation have found acceptance, where Soave's modification (SRK or, more politely, RKS) is the simplest and most widely used. Unfortunately it yields poor liquid densities. Zudkevich and Joffe (ZJRK) propose a method where EOS constants A and B are both corrected by temperature functions, resulting in improved volumetric predictions. Yarborough with Amoco (1977) and Gray with Exxon (1977) propose similar forms of the ZJRK EOS for petroleum reservoir mixtures.

The PR EOS is comparable to the SRK equation in simplicity and form. Peng and Robinson report that their equation predicts liquid densities better than the SRK EOS (though PR densities are usually inferior to those calculated by the ZJRK EOS). A distinct advantage of the PR and SRK equations is reproducibility, where a simple temperature-dependent expression is used to express the correction to EOS constant A. The ZJRK equations rely on tables or complex best-fit functions to represent the highly nonlinear correction terms for EOS constants A and B.

A new concept to cubic equations of state — *volume translation* — was proposed by Martin in 1979. The application given by Martin was essentially to ease the comparison of his generalized EOS with previously published equations. It also shows similarities and differences in simple volumetric predictions by the various

equations of state. In an independent study, Peneloux et al. (1982) uses the idea of volume translation to improve volumetric capabilities of the EOS. Peneloux et al.'s key contribution, however, was to show that the volume shift does not affect equilibrium calculations, thereby unaltering the original VLE capabilities of the SRK EOS. Peneloux et al. show that the component volume shift parameters cancel when the ratio of fugacity coefficients are calculated. Volume translation works equally well with any two-constant EOS, as shown by Jhaveri and Youngren (1984) for the Peng-Robinson equation.

Applications requiring direct use of the fugacity coefficient (e.g. compositional gradient calculations and semi-solid phase equilibrium) must include the volume translation coefficient in the fugacity expression and other thermodynamic properties. Several recent papers have incorrectly used volume translation by making the volume shift parameter pressure-dependent or non-linear in composition (Bjorlykke and Firoozabadi, 1990).

A three-constant EOS was proposed by Schmidt and Wenzel (1980), and although this equation has received considerable attention, it is still not (and probably won't become) available in commercial reservoir simulators. The temperature-dependent correction term α is a hodge-podge of correction functions, with discontinuities at acentric factors of 0.4, 0.3671, and 0.55, and at $T_r = 1$. It is doubtful that this three-constant equation is any better than other three-constant equations [Usdin and McAuliffe (1976), Fuller (1976), etc.], and finally, with volume translation, both the SRK and PR equations predict vapor and liquid densities as accurately as three-constant equations such as the Schmidt-Wenzel equation.

Redlich-Kwong

The Redlich-Kwong equation of state, including expressions for fugacity coefficents, is

$$p = \frac{RT}{v-b} - \frac{a}{v(v+b)} \tag{5}$$

or in terms of the Z-factor ($Z = pv/RT$),

$$Z^3 - Z^2 + (A-B-B^2)Z - AB = 0$$

$$Z_c \equiv 1/3$$

(6)

with EOS constants defined as

$$a = \Omega_a^o \frac{R^2 T_c^2}{p_c} \alpha(T_r) \quad ; \quad \Omega_a^o = 0.42748...$$

$$b = \Omega_b^o \frac{RT_c}{p_c} \quad ; \quad \Omega_b^o = 0.08664...$$

$$A = a \frac{p}{R^2 T^2}$$

(7)

$$B = b \frac{p}{RT}$$

$$\alpha(T_r) = T_r^{-0.5}$$

Fugacity expressions for pure components and mixtures, respectively, are

$$\ln \frac{f}{p} = \ln \phi = Z - 1 - \ln(Z-B) - \frac{A}{B} \ln \left[1 + \frac{B}{Z} \right]$$

$$\ln \frac{f_i}{y_i p} = \ln \phi_i = \frac{B_i}{B}(Z-1) - \ln(Z-B) + \frac{A}{B} \left[\frac{B_i}{B} - \frac{2}{A} \sum_{j=1}^{N} y_j A_{ij} \right] \ln \left[1 + \frac{B}{Z} \right]$$

(8)

for the traditional mixing rules:

$$A = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j \sqrt{A_i A_j} \, (1 - k_{ij})$$

$$B = \sum_{i=1}^{N} y_i B_i$$

(9)

k_{ij} are binary interaction parameters (BIPs), where $k_{ii}=0$ and $k_{ij}=k_{ji}$. Usually, $k_{ij}=0$ for most hydrocarbon-hydrocarbon (HC-HC) pairs (except perhaps C_1-C_{7+} pairs). Nonhydrocarbon-HC k_{ij} are usually nonzero, where $k_{ij} \approx 0.1$-0.15 for N_2-HC and CO_2-HC pairs.

A newcomer who studies the RK EOS may be intrigued by its simplicity, accuracy, and the mathematical pleasure which results from deriving its thermodynamic properties. This has lead to innumerable attempts to better, extend, an in some cases, bastardize the original equation. There are certainly hundreds if not thousands of technical papers and theses written about the RK equation. With the advent of digital computers, this craze developed into what Abbott coined the Redlich-Kwong decade (1967-1977). Abbott claims that the remarkable success of the RK EOS results from its excellent prediction of the second virial coefficient (securing good performance at low densities) and reliable predictions at high densities in the supercritical region. This latter observation results from the compromise fit of densities in the near-critical region; all pure compounds are required by the RK EOS to have a critical compressibility factor $Z_c=1/3$, where in fact Z_c ranges from 0.29 for methane to less than 0.2 for heavy C_{7+} fractions. The RK value of 1/3 is reasonable for lighter hydrocarbons but is less satisfactory for heavier components.

Soave-Redlich-Kwong

Several attempts have been made to improve VLE predictions of the RK EOS by introducing a component-dependent correction term α for EOS constant A. Soave (1972) used vapor pressures to determine the functional relation for the correction factor,

$$\alpha = \left[1+m(1-T_r^{0.5})\right]^2$$

$$m = 0.480+1.574\,\omega-0.176\,\omega^2$$

(10)

The SRK EOS appears to be the most accepted modification proposed to date. Still it grossly overestimates liquid volumes of petroleum mixtures. The present use of the SRK EOS results from historical and practical reasons. It offers an excellent predictive tool for systems requiring accurate predictions of VLE and vapor properties. It should be used with caution, however, when liquid densities are important to the engineering application, in which case volume translation is a must.

Zudkevich-Joffe-Redlich-Kwong

Zudkevich and Joffe (1970) propose a novel procedure for improving the volumetric predictions of the RK EOS without sacrificing VLE capabilities of the original equation. Their method suggests that the EOS constants A and B be corrected as functions of temperature to match saturated liquid densities and liquid fugacities. They show that errors in vapor fugacities and fugacity ratios (K-values) are practically unaffected. Also, their procedure does not greatly affect vapor densities.

Only six months after the original ZJRK modification appeared, Joffe, Schroeder, and Zudkevich (1970) proposed an alternative method (similar to one previously used for a modified BWR EOS) whereby liquid fugacity was dropped and vapor pressure used directly. That is, constants A and B were determined by matching the RK EOS to saturated liquid densities and vapor pressures at subcritical temperatures. The procedure is trial and error, but readily solved. The Joffe-Schroeder-Zudkevich procedure, which is little more than a twist on the original Zudkevich-Joffe procedure (though it makes much more sense) retains the identification of ZJRK, and to my knowledge no one uses the original procedure.

The ZJRK approach has been used to determine correction terms α and β for EOS constants A and B for pure paraffins [Haman et al. (1977)] and for C_{7+} fractions [Yarborough (1979) and Gray (1979)].

$$a = \Omega_a^o \frac{R^2 T_c^2}{p_c} T_r^{-0.5} \alpha(T_r,\omega)$$

$$b = \Omega_b^o \frac{R T_c}{p_c} \beta(T_r,\omega)$$

(11)

Unfortunately the temperature dependent functions are complex, being represented by higher-order polynomials or cubic splines (see Fig. 4). The behavior of these functions is highly nonlinear near $T_r = 1$, and a discontinuity is introduced by setting the correction factors to one for $T_r > 1$. There is not a single set of A and B correlations used in the industry, thereby making it difficult to reproduce results from one version to another. Preferably a table of A and B correction factors should be provided when reporting a fluid characterization based on a ZJRK-type EOS.

In review, two Redlich-Kwong modifications — SRK and ZJRK — have found most application to petroleum reservoir fluids. The Soave equation is preferred because of its simplicity and overall accuracy (particularly when used with volume translation). The ZJRK EOS is surprisingly accurate for both liquid and vapor properties estimation, where its main disadvantage is the complexity of functions used to represent temperature-dependent corrections for the EOS constants A and B.

Peng-Robinson

In 1975 Peng and Robinson proposed a two-constant equation which created great expectations for improved liquid density predictions,

$$p = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)}$$

(12)

or in terms of the Z-factor,

$$Z^3 - (1-B)Z^2 + (A-3B^2-2B)Z - (AB-B^2-B^3) = 0$$

$$Z_c \equiv 0.3074...$$

(13)

where EOS constants are given by,

$$a = \Omega_a^o \frac{R^2 T_c^2}{p_c} \alpha \quad ; \quad \Omega_a^o = 0.45724$$

$$b = \Omega_b^o \frac{R T_c}{p_c} \quad ; \quad \Omega_b^o = 0.07780 \tag{14}$$

$$\alpha = \left[1 + m(1 - \sqrt{T_r}) \right]^2$$

$$m = 0.37464 + 1.54226\,\omega - 0.26992\,\omega^2$$

and fugacity expressions for pure components and mixtures are given by

$$\ln \frac{f}{p} = \ln \phi = Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}\,B} \ln \left[\frac{Z + (2 + \sqrt{2})B}{Z - (2 - \sqrt{2})B} \right] \tag{15}$$

$$\ln \frac{f_i}{y_i p} = \ln \phi_i = \frac{B_i}{B}(Z - 1) - \ln(Z - B) + \frac{A}{2\sqrt{2}\,B} \left[\frac{B_i}{B} - \frac{2}{A} \sum_{j=1}^{N} y_j A_{ij} \right] \ln \left[\frac{Z + (2 + \sqrt{2})B}{Z - (2 - \sqrt{2})B} \right]$$

where the mixing rules in Eq. (14) are used.

The PR equation does not calculate inferior VLE compared with the RK equations, and the temperature-dependent correction term for EOS constant A is nearly identical to the Soave correction. The largest improvement offered by the PR equation is a universal critical compressibility factor of 0.307 — somewhat lower than the RK value of 1/3 and closer to experimental values of heavier hydrocarbons. The difference between PR and SRK liquid volumetric predictions can be substantial, though in many cases the errors in oil densities are unacceptable from both equations. There is evidence that the PR equation slightly underpredicts saturation pressure of reservoir fluids, requiring larger binary interaction parameters than the SRK equation.

Availability and considerable "PR" have given the Peng-Robinson equation an obvious advantage in recent years. Peng and Robinson have certainly make their

equation well known by documenting how it can be applied to petroleum and nonhydrocarbon systems. They also have presented numerical solutions to problems near the critical region, and methods for predicting multiphase and semi-solid phase behavior. In addition to their own efforts, the PR EOS has almost become *chic* to use in research applications, and by virtue of the interest which industry has bestowed upon Peng and Robinson's efforts, it almost seems obligatory to choose the PR over the SRK equation.

In review, the PR EOS is a popular, simple, and relatively accurate alternative to RK equations. But it is just that — an alternative — and not really a replacement. Finally, volume translation should always be used with the PR EOS when liquid densities are important to the engineering application.

Volume Translation

I've said many times that had the concept of volume translation been introduced shortly after Soave's modification of the Redlich-Kwong equation that the Peng-Robinson and many other cubic equations of state would never have appeared in the literature. Volume translation solves the only major deficiency of the RK EOS — poor liquid volumetric prediction. Peneloux et al (1982) suggest the following simple correction term to the EOS-calculated molar volume,

$$v = v^{EOS} - c \tag{16}$$

where v is the corrected volume, v^{EOS} is volume calculated by the unmodified EOS, and c is a component-specific constant with a mole-fraction average used for mixtures. The shift in volume is actually equivalent to adding a third constant to the EOS, but it is special in that the equilibrium conditions are unaltered. This is readily seen for a pure component where the van der Waals "loop" defines vapor pressure by equalling areas above and below the $p = p_v$ line on a p-v plot. Shifting the p-v plot to the left or right doesn't change the equal area (fugacity) balance, and it is readily seen that vapor pressure predictions are unaltered by introducing the volume shift term c.

Peneloux et al. also show that multicomponent VLE are unaltered by introducing the correction term as a mole-fraction average,

$$v_L = v_L^{EOS} - \sum_{i=1}^{N} x_i c_i$$

$$v_V = v_V^{EOS} - \sum_{i=1}^{N} y_i c_i$$

(17)

which results in a modification of the fugacity expression that cancels when fugacity ratios are calculated,

$$\frac{f_{Vi}^{modified}}{y_i p} = \frac{f_{Vi}^{original}}{y_i p} \exp(c_i \frac{p}{RT}) = \frac{f_{Li}^{modified}}{x_i p} = \frac{f_{Li}^{original}}{x_i p} \exp(c_i \frac{p}{RT})$$

(18)

or

$$\frac{f_{Vi}^{modified}}{f_{Li}^{modified}} = \frac{f_{Vi}^{original}}{f_{Li}^{original}}$$

(19)

Peneloux et al. propose that the c_i term be determined to match exactly saturated liquid density at $T_r = 0.7$. In fact, c_i can be used to force the EOS to fit a single density value at any temperature, or to match densities as a function of temperature [Soreide (1989].

Jhaveri and Youngren (1984) express c_i as a ratio $s_i = c_i / b_i$ for the PR EOS, suggesting the following equation form (for C_{7+} fractions),

$$s_i = 1 - D M_i^{-E}$$

(20)

where average D and E values for the PR EOS are D=2.5 and E=0.2. The table below gives values of s_i for selected pure components at $T_r = 0.7$ [Soreide (1989)].

Component	PR EOS	SRK EOS
N_2	-0.1927	-0.0079
CO_2	-0.0817	0.0833
H_2S	-0.1288	0.0466
C_1	-0.1595	0.0234
C_2	-0.1134	0.0605
C_3	-0.0863	0.0825
iC_4	-0.0844	0.0830
nC_4	-0.0675	0.0975
iC_5	-0.0608	0.1022
nC_5	-0.0390	0.1209
nC_6	-0.0080	0.1467
nC_7	0.0033	0.1554
nC_8	0.0314	0.1794
nC_9	0.0408	0.1868
nC_{10}	0.0655	0.2080

Soreide also gives a correlation for s_i in terms of acentric factor and reduced temperature at subcritical temperatures determined by matching saturated liquid densities, as well as a correlation in terms of T_r at supercritical temperatures for nonhydrocarbons and light hydrocarbons C_1-C_3 determined by matching densities in the pressure range 15 to 6000 psia.

RESERVOIR FLUID CHARACTERIZATION

CHOP, SCREW, AND SQUISH

The recipe for a good reservoir fluid characterization consists of three main ingredients:

1. Splitting and characterizing the heptanes-plus (C_{7+}) into a reasonable number of fractions (3-20), the number being dependent on the process being simulated, the characterization procedure, and how fast your computer runs;

2. Modifying the properties of C_{7+} critical properties (p_c, T_c, ω, Ω_a, Ω_b) and binary interaction parameters (BIPs) to match experimental PVT data, where pure component properties for methane and non-hydrocarbons may also be modified;

3. Reducing the total number of components to a minimum while still maintaining an accurate description of the phase behavior.

The following discussion considers each of these three aspects in some detail.

Heptanes-Plus Characterization

Petroleum reservoir fluids are made up of pure components (N_2, CO_2, H_2S, C_1, C_2, C_3, iC_4, nC_4, iC_5, nC_5, C_{6s}) and many hundreds of petroleum fractions making up the *heptanes-plus*. Properties of pure components are well defined, whereas the description of C_{7+} is perhaps the most difficult problem associated with characterizing reservoir fluids. First of all, it is physically impossible to isolate, quantify, and characterize the individual components making up C_{7+}. True boiling point (TBP) analysis and simulated distillation by gas chromotography (GC) are the methods available for approximating the distribution and properties of C_{7+} fractions. In my opinion, TBP analysis is superior to simulated distillation because it provides measured properties — molecular weight (M), specific gravity (γ), and normal boiling point (T_b) — of the individual fractions, albeit each fraction consisting of many isomers and overlapping carbon number species. Gas chromatography measures weight fractions which must be converted to mole fractions using assumed molecular weights; γ and T_b also must be estimated.

Compounding the situation, it is a simple fact that most PVT studies do not include TBP *or* simulated distillation information. Only M_{7+} and γ_{7+} are reported! Saddled with the problem of coming up with a magical split and characterization of C_{7+}, there is no way you can ignore this troublesome non-componenent. Several methods have been proposed for characterizing the C_{7+} fraction, and all of them consist of three basic elements: (a) splitting the C_{7+} into a discrete number of fractions described by mole fraction and molecular weight (sometimes referred to as *molar distribution*), (b) defining the "inspection" properties γ and T_b, and (c) estimating "critical" properties T_c, p_c, and ω (and v_c for viscosity calculations).

Exponential Molar Distribution

An exponential distribution is the simplest method for splitting the C_{7+} fraction,

$$z_i = z_7 \exp[m(i-7)]$$
$$M_i = 14i+h \tag{21}$$

where m is the slope of a log z_i versus carbon number plot. h gives the average number of hydrogen atoms according to the formula C_nH_{2n+h}, where h=2 for paraffins, h=0 for napthenes, and h=-6 for aromatics. By imposing the two criteria

$$\sum_{i=7}^{\infty} z_i = 1$$
$$\sum_{i=7}^{\infty} z_iM_i = M_{7+} \tag{22}$$

m and z_7 are given by

$$z_7 = \frac{14}{M_{7+}-84-h}$$
$$m = \ln(1-z_7) \tag{23}$$

Setting h=0 is usually adequate, though Pedersen et al. (1985) recommend h=-4.

Gamma Distribution Model

Other molar distribution models have been proposed, with the three-parameter gamma distribution model being the most commonly used,

$$p(M) = \frac{(M-\eta)^{\alpha-1}\exp\left[-\frac{M-\eta}{\beta}\right]}{\beta^{\alpha}\Gamma(\alpha)} \tag{24}$$

$p(M)$ is a probability density function with parameters α, β, and η. α describes the distribution form, with $\alpha=1$ giving an exponential distribution which is recommended when measured data are not available. η represents the minimum molecular weight expected to be found in the C_{7+} mixture, and $\beta=(M_{7+}-\eta)/\alpha$. Whitson and coworkers describe this molar distribution model in several publications, including

1. Definition of the molar distribution model [Whitson (1983)].

2. How the model can be fit to experimental TBP data [Whitson et al. (1986)].

3. How the model can be modified to determine a split for *related* reservoir fluids that have different C_{7+} properties (M_{7+}, γ_{7+}, and α); the molecular weights (and other properties) of split fractions are the same for each fluid, where only the mole fractions of fractions vary from fluid to fluid [Whitson et al. (1989)].

4. How the Gaussian quadrature method can be used to accurately reduce the number of C_{7+} fractions [Whitson et al. (1989)].

The gamma distribution model has also found widespread use in continuous thermodynamics [e.g., Cotterman and Prausnitz (1985)].

Estimating Specific Gravities and Boiling Points

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 TBP data are not available. Paraffin molecular weights are usually assumed when converting simulated distillation results to a mole-fraction basis. A molar distribution yields z_i and M_i directly. The best estimates of T_{bi} and γ_i come from a TBP analysis of a sample from the same field, and the next-

best source is TBP data from a field producing from the same geological formation. Generalized properties from a producing region such as the North Sea also can provide reasonable estimates of inspection properties [Haaland (1981)]. Katz and Firoozabadi (1978) suggest a generalized set of SCN (single carbon number) properties for petroleum fractions C_6 to C_{45}.

An alternative approach to estimate the specific gravities and boiling points of C_{7+} fractions involves choosing an empirical relation between specific gravity, molecular weight, and a characterization factor (e.g. the Watson UOPK factor, $K_w \equiv T_b^{1/3}/\gamma$). Whitson gives the relation

$$K_w = 4.5579 M^{0.15178} \gamma^{-0.84573} \tag{25}$$

which is fairly accurate for $M < 250$. Given a molar distribution with mole fractions z_i and molecular weights M_i, Eq. (25) can be solved for K_w such that the measured γ_{7+} is honored according to ideal mixing,

$$\gamma_{7+}^{measured} = \frac{z_{7+}M_{7+}}{\sum\limits_{i=1}^{N} \left[\dfrac{z_i M_i}{\gamma_i} \right]} \tag{26}$$

Given the specific gravities and Watson characterization factor (which is assumed to be the same for all C_{7+} fractions), normal boiling points can be calculated from the definition of K_w,

$$T_{bi} = (K_w \gamma_i)^3 \tag{27}$$

Because Eq. (25) is only accurate for $M < 250$, T_b values calculated using Whitson's approach will be overestimated at higher molecular weights, this being reflected in heavier component critical properties.

Other characterization factors can be used to estimate specific gravities [Jacoby (1964), Yarborough (1979), etc.], in which case the normal boiling point must be estimated from a correlation of the form $T_b = f(M, \gamma)$ [Hariu and Sage (1969), Riazi

and Daubert (1980, 1987), Kesler and Lee (1976), Rao and Bardon (1985)]. A simple yet accurate specific gravity correlation that gives reasonable extrapolation at high molecular weights is

$$\gamma_i = 0.2855 + C_f (M_i - 66)^{0.13} \tag{28}$$

where C_f typically has a value between 0.27 and 0.31, and it is determined such that Eq. (26) is satisfied. The numerical constants in Eq. (28) were determined by Soreide using TBP data for 68 crude oil and condensate samples. Soreide also gives the following boiling point relation based on 843 petroleum fractions (from the 68 crude oil and condensate samples),

$$T_b = T_b^\infty - D_1 \cdot \exp(D_2 M + D_3 \gamma + D_4 M\gamma) M^{D_5} \gamma^{D_6} \tag{29}$$

$$
\begin{aligned}
T_b^\infty &= 1928.3 \\
D_1 &= 1.695(10^5) \\
D_2 &= -4.922(10^{-3}) \\
D_3 &= -4.7685 \\
D_4 &= 3.462(10^{-3}) \\
D_5 &= -3.522(10^{-2}) \\
D_6 &= 3.266
\end{aligned}
$$

with T_b in °R.

Critical Properties Estimation

Critical temperature, critical pressure, and acentric factor of each component in a mixture are required by most cubic equations of state. Critical volume is used instead of critical pressure in the BWR EOS, and critical volume is also used with the Lohrenz-Bray-Clark (1964) viscosity correlation. Finally, critical compressibility factor has been introduced as a parameter in some three- and four-constant cubic equations of state.

Critical-properties estimation of petroleum fractions has a long history, beginning already in the 1930s. The Lee-Kesler (1975) and Kesler-Lee (1977) correlations for T_c, p_c, and ω are given below, as they have reasonable behavior when extrapolated

to high molecular weights. The v_c correlation is given by Hall and Yarborough (1971).

$$T_c = 341.7 + 811\gamma + (0.4244 + 0.1174\gamma)T_b$$
$$+ (0.4669 - 3.2623\gamma)10^5 T_b^{-1} \tag{30}$$

$$\ln p_c = 8.3634 - \frac{0.0566}{\gamma}$$
$$- \left[0.24244 + \frac{2.2898}{\gamma} + \frac{0.11857}{\gamma^2} \right] (10^{-3})T_b$$
$$+ \left[1.4685 + \frac{3.648}{\gamma} + \frac{0.47227}{\gamma^2} \right] (10^{-7})T_b^2 \tag{31}$$
$$- \left[0.42019 + \frac{1.6977}{\gamma^2} \right] (10^{-10})T_b^3$$

$$\omega = \frac{-\ln(\frac{p_c}{14.7}) + D_1 + D_2 T_{br}^{-1} + D_3 \ln T_{br} + D_4 T_{br}^6}{D_5 + D_6 T_{br}^{-1} + D_7 \ln T_{br} + D_8 T_{br}^6} \quad ; \quad T_{br} = \frac{T_b}{T_c} < 0.8 \tag{32}$$

$$D_1 = -5.92714 \qquad D_5 = 15.2518$$
$$D_2 = 6.09648 \qquad D_6 = -15.6875$$
$$D_3 = 1.28862 \qquad D_7 = -13.4721$$
$$D_4 = -0.169347 \qquad D_8 = 0.43577$$

$$\omega = -7.904 + 0.1352 K_w - 0.007465 K_w^2$$

$$+ 8.359 T_{br} + (1.408 - 0.01063 K_w) T_{br}^{-1} \quad ; \tag{33}$$

$$K_w = \frac{T_b^{1/3}}{\gamma} \quad and \quad T_{br} \geq 0.8$$

$$v_c = 0.025 M^{1.15} \gamma^{-0.7935} \tag{34}$$

Correlations for T_c, p_c, v_c, and M have also been developed for petroleum fractions using a perturbation-expansion model with normal paraffins as the reference system. To calculate p_c, for example, T_c, v_c, and γ of a normal paraffin with the same boiling point as the petroleum fraction must first be calculated. Kesler et al. (1979) first employed the perturbation expansion (with n-alkanes as the reference fluid) to develop a suite of critical property and acentric factor correlations. Twu (1984) also used this approach to develop critical property correlations.

In principle, the equation of state used for mixtures should also predict the behavior of individual components found in the mixture. For pure compounds the vapor pressure should be accurately predicted because most EOSs force-fit vapor pressure using a temperature-dependent correction term. Some EOSs also are tuned to give accurate estimates of saturated liquid densities. Along the same line of thinking, the measured properties of petroleum fractions T_b and γ can be compared with the values predicted by the EOS using critical properties estimated from the correlations above. If the EOS does not calculate reasonable estimates of measured boiling point and specific gravity for individual petroleum fractions, one might consider adjusting the critical properties and/or acentric factor of each fraction to match the measured T_b and γ. In fact, for each petroleum fraction separately, two of the EOS parameters (T_c, p_c, ω, s, or Ω_a and Ω_b) can be chosen such that the EOS

exactly reproduces experimental boiling point and specific gravity. This approach has been suggested in different forms by several authors [e.g. Whitson (1983)]. We have found that determining ω and s to match T_b and γ gives the best results, with T_c and p_c estimated from correlations based on T_b and γ.

Regression-Based Fluid Characterization

The number of proponants contending to have developed a truly predictive EOS fluid characterization has diminished to only a few. Yarborough (1979) indicated that the Amoco version of ZJRK EOS could be used as a predictive tool, but the work by Turek and coworkers (1984) subsequently showed that modification to this EOS was necessary to predict CO_2 phase and volumetric behavior. Other authors have implied that the Schmidt-Wenzel EOS is predictive for reservoir fluids, though no one has really documented this. In fact, the C_{7+} characterization will always wag the tail of any EOS, thereby making fluid characterization an EOS-dependent problem.

Pedersen et al. (1985) comment on the application of nonlinear regression to EOS characterization in "On the Dangers of 'Tuning' Equation of State Parameters" (1985), concluding that:

> ... *Equation of state parameters "tuned" to one specific property are found to yield unreliable predictions of other thermodynamic properties. If the analytical data are inaccurate "tuning" will merely serve as to make up for these deficiencies. "Tuning" to properties reported at erroneous compositions will lead to highly uncertain predictions.*
>
> *The authors have no principal arguments against "tuning," if the "tuning" procedure is carried out and applied cautiously. This means that a proper parameter sensitivity analysis must be performed relating the sensitivity of the data to which the EOS is "tuned" to the sensitivity of the desired properties.*

In 1989 Pedersen et al. presented a supposedly predictive characterization procedure for petroleum reservoir fluids using the SRK EOS. Their procedure is based on methods presented in earlier publications (1984, 1985a, and 1985b), and a colossal regression of 17 reservoir fluids (7 gas condensates, 2 near-critical fluids, and 8 oil mixtures) to determine "generalized" C_{7+} property correlations for T_c, p_c, and ω.

Interestingly, they don't present a parameter sensitivity analysis, and they don't seem to be bothered by the prediction of a decreasing acentric factor at high molecular weights:

The T_c, P_c, and ω correlations presented ... are, however, not to be regarded as generally applicable correlations for the mentioned pure component properties. They are to be considered as correlations which used with the SRK-equation of state and the C_{7+}-characterization procedure described in this work permit an accurate representation of the phase behavior of a wide variety of petroleum reservoir fluids.

The Pedersen et al. procedure (as implemented in the commercial program PVTsim) is summarized below:

1. Split the plus fraction C_{n+} (preferably $n > 10$) into SCN fractions up to C_{80} using Eq. (21) and $h = -4$.

2. Calculate SCN densities ρ_i $(\gamma_i = \rho_i/0.9991)$ using the equation $\rho_i = D_0 + D_1 \ln(i)$, where D_0 and D_1 are determined by satisfying the experimental plus density ρ_{n+} and measured (or assumed) density ρ_{n-1} $(\rho_6 = 0.690$ can be used for $C_{7+})$.

3. Calculate critical properties of all C_{7+} fractions (distillation cuts from C_7 to C_{n-1}, and split SCN fractions from C_n to C_{80}) using the correlations,

$$T_c = 163.12\rho + 86.052 \ln M + 0.43475 M - \frac{1877.4}{M}$$

$$\ln p_c = -0.13408 + 2.5019\rho + \frac{208.46}{M} - \frac{3987.2}{M^2}$$

$$m_{SRK} = 0.48 + 1.574\omega - 0.176\omega^2$$

$$= 0.7431 + 0.0048122 M + 0.0096707\rho - \frac{3.7184(10^{-6})}{M^2}$$

(35)

4. Group C_{7+} into 11 fractions using equal weight fractions in each group; use weight average mixing rules.

5. Calculate volume translation parameters for C_{7+} fractions by matching specific gravities; pure component c values are taken from Peneloux et al (1982).

6. HC-HC BIPs are set to zero. Reid et al. (1987) values are used for nonhydrocarbon-HC pairs.

Supposedly with this procedure you will never need to regress individual fluid characterizations again. *Believe it or not* (...rumors are that the new release of PVTsim includes multiparameter, non-linear regression, so I guess the last claim to "predictive" fame has finally died...).

Coats and Smart (1986), in a pioneering work on regression methods for EOS reservoir fluid characterization, shows that a cookbook approach to regression can be applied to individual reservoir fluids in an efficient way. Basically they define five regression parameters: $\Omega_a(C_1)$, $\Omega_b(C_1)$, $\Omega_a(C_+)$, $\Omega_b(C_+)$, and $k_{ij}(C_1-C_+)$ which are modified to minimize a weighted sum of absolute average deviations using a linear programming technique. C_+ indicates the heaviest C_{7+} fraction, where the Whitson (1983) characterization procedure is used. Ranges of the regression variables are summarized below for the PR EOS:

	$\Omega_a(C_1)$	$\Omega_b(C_1)$	$\Omega_a(C_+)$	$\Omega_b(C_+)$	k_{ij}
EOS VALUE	0.4572	0.0778	0.4572	0.0778	-
MINIMUM	0.1000	0.0200	0.1000	0.0200	-1.000
SMALLEST REPORTED (fraction of EOS value)	0.3130 (0.68)	0.0500 (0.64)	0.2640 (0.58)	0.0440 (0.57)	-0.202
LARGEST REPORTED (fraction of EOS value)	0.7080 (1.55)	0.1080 (1.39)	0.7970 (1.74)	0.0970 (1.25)	0.408
MAXIMUM	1.3000	0.2500	1.3000	0.2500	0.900

Despite the fact that results presented by Coats and Smart are convincing, and that a better published alternative does not really exist (unless you believe Pedersen et al.) I still tend to think of this method as the *Sledge Hammer* solution. What Coats and Smart have really done is to identify the Achilles tendon(s) of the EOS — i.e. which parameters affect calculated PVT properties most. And why isn't this a good engineering approach? It is; but if the application is developed miscibility, where calculations involve near-critical calculations and extrapolation into a region of composition space where measured data are not available, my comment is simply — *beware!* The basic problem with this approach is that there are too many

deficiencies of the EOS *and* the fluid characterization, all of which must be compensated for by large adjustments to sensitive EOS parameters. It's like building a race car. You *can* take a Corvette, modify the engine [$\Omega_a(C_1)$ and $\Omega_b(C_1)$], change the tires [$(\Omega_a(C_+)$], put on headers [$\Omega_b(C_+)$], and add a spoiler [$k_{ij}(C_1\text{-}C_+)$]. With this hotrod you'll be fast enough to beat most of the kids dragging main street on Saturday night. Then again, you'd never consider entering such a car at the Indy 500.

What is the alternative? First, we should clearly identify the deficiencies of EOS fluid characterization. The main problem with two-constant EOSs is poor liquid density prediction, where the best (and most fundamentally sound) solution is volume translation. A second deficiency is the estimation of critical properties for the C_{7+} fractions, and BIPs between nonhydrocarbon-HC pairs and $C_1\text{-}C_{7+}$ fractions; these are the best candidates for regression parameters. Beware, though, because the sensitivity and intercorrelation between the various properties (T_c, p_c, and ω) is difficult to identify and may reek havoc on some regression algorithms.

Let us consider the effect of volume translation on EOS predictions, and in particular what effect including volume translation would have on the sledge-hammer regression approach. I conducted a PVT simulation as follows. An oil sample is characterized with three C_{7+} fractions. The PR EOS is used with volume translation parameters from Jhaveri and Youngren, and the resulting PVT predictions are quite accurate compared with experimental data. Only a slight adjustment to $k_{ij}(C_1\text{-}C_+)$ is necessary to match the bubblepoint pressure of 3650 psia at 258°F. The PR EOS *with volume translation* is used to simulate a differential liberation experiment (DLE), and the results are treated as "data" for a sledge-hammer regression *without* volume translation. The result is as follows: $\Omega_a(C_1)$ and $\Omega_b(C_1)$ remain almost unchanged, whereas $\Omega_a(C_+)$ and $\Omega_b(C_+)$ both approach the imposed lower limits of 0.274 and 0.047 (0.6 times the EOS value). The $k_{ij}(C_1\text{-}C_+)$ changes from 0.113 to -0.113. As one might expect, the fit of the DLE "data" is very accurate. Both EOS characterizations were then used to predict a swelling test with a relatively lean HC

injection gas. Results of the p-x diagram are shown in Fig. 5, and the table below shows calculated equilibrium compositions near the critical point at 3 moles injected.

Component	Total Vapor Composition (mol-%)	Sledge-Hammer Regression		EOS with Volume Translation		
		Liquid Composition (mol-%)	K-value	Liquid Composition (mol-%)	K-value	Inj. Gas Composition (mol-%)
CO2	2.548	2.488	1.024	2.498	1.020	3.00
N2	1.628	1.457	1.117	1.440	1.130	2.00
C1	71.303	67.663	1.054	65.512	1.088	80.00
C2	7.773	7.818	0.994	7.904	0.983	8.00
C3	5.653	5.891	0.960	5.997	0.943	6.00
IC4	1.173	1.248	0.940	1.276	0.919	1.00
C4	0.703	0.758	0.927	0.777	0.904	0.00
IC5	0.388	0.428	0.906	0.440	0.880	0.00
C5	0.503	0.559	0.899	0.576	0.872	0.00
C6	1.105	1.263	0.875	1.310	0.843	0.00
C7+ (1)	3.682	4.592	0.802	4.915	0.749	0.00
C7+ (2)	3.009	4.681	0.643	5.486	0.549	0.00
C7+ (3)	0.536	1.155	0.465	1.869	0.287	0.00
C7+ Total	7.227	10.427	0.693	12.269	0.589	0.00

Coats and Smart also claim that regression is a time saver:

The man-hours (sic) spent in studying the 12 samples, including data preperation, ranged from about six for Gas 3 to about 20 for Oil 1 and Gas 4. Obviously, required man-hours depend upon the engineer's experience and familiarity with the PVT program used, the amount of available data and difficulties which arise in the matching effort. However, the rather low man-hours quoted primarily reflect the fact that the regression feature allows rapid evaluation of EOS parameter sets and values.

None of us can claim to be as experienced or familiar with available PVT programs as Coats and Smart, and depending on the *inexperience factor* you apply, we are probably talking about 24 to 72 engineering hours to complete a reliable EOS fluid characterization. This translates into 1 to 3 weeks real time. And let's not forget that many petroleum engineers don't know what an equation of state is, let alone the idiosyncracies of nonlinear regression! My point is that an EOS fluid characterization, when done properly, may require several weeks or more to develop. And particularly if the characterization is for processes like multicontact miscible gas displacement. A classic example is the fluid characterization reported by Zick (1986)

which apparently took many months of fine tuning to match standard and custom-designed multicontact PVT experiments.

Soreide (1989) gives a comprehensive study of EOS fluid characterization and regression techniques, including successful application of his proposed methods to *many* reservoir fluids. Our work the past five years has lead to the following recipe for reliable regression-based fluid characterization:

1. Start with a good C_{7+} characterization, preferably with experimental TBP data. Several characterization procedures can be used, including those by Whitson and coworkers (1983-1989), Pedersen et al. (1985-1989), and Yarborough (1977).

2. Use *all* reliable PVT data in the matching process. Multicontact PVT data are a *must* when the characterization is intended for simulation of a gas injection process. Weight factors should be specified on a data-by-data basis or by data type, with a tabular or graphical indication of each data's influence on the SSQ (sum-of-squares) function.

3. Make sure the VLE algorithms are truly robust — i.e. they must converge 99.99% of the time even for near-critical problems. Michelsen's algorithms for the phase stability test, two-phase flash, and saturation pressure are highly recommended. The GDEM (General Dominant Eigenvalue Method) can be implemented so that it is fast and more reliable than a Newton method even near critical points. Very tight convergence tolerances must be used.

4. Make sure to use the *best* nonlinear regression algorithm — which in my opinion is the Law and Farris method of *Rotational Discrimination* (1972) that allows each parameter to change independent of the other parameters (in an orthoganl coordinate system). In a given iteration, the best-defined parameters progress with a full Newton step while lesser-defined parameters change more slowly by weighted steepest descent. Null-effect variables automatically fall out of the problem on an iteration-by-iteration basis. A good bounding routine is also necessary.

5. Graphical comparison of calculated and experimental results is very helpful in redefining weight factors to get a best "eyeball" match.

"Pseudoization" — Grouping Components

The cost and computer resources required for compositional reservoir simulation increase substantially with the number of components 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 fifteen components may be needed to simulate developed miscibility in a slim-tube experiment. On the other hand, full-field simulation of naturally fractured reservoirs [Coats (1989) and da Silva (1989)] is limited to a maximum of about four components with the current technology for linear solvers. The main questions regarding component grouping are:

- How many components should be used?
- How should the components be chosen from the original fluid description?
- How should the properties of pseudocomponents be determined?

The number of components used to describe a reservoir fluid is mainly dependent on the process being simulated. However, the following rule of thumb will reduce the number of components for most systems: group N_2+C_1, CO_2+C_2, iC_4+nC_4, and iC_5+nC_5. Nonhydrocarbon content should be less than a few percent in both the reservoir fluid *and* the injection gas if a nonhydrocarbon is grouped with a hydrocarbon.

Four-component fluid characterizations should be sufficient to simulate (1) reservoir depletion of volatile-oil and gas-condensate reservoirs, (2) gas cycling above the dew point of a gas-condensate reservoir, and (3) retrograde condensation near the wellbore of a producing well [Coats (1985)]. Coats discusses a method for combining a modified black-oil formulation with a simplified EOS representation of separator oil and gas streams. Interestingly, the "oil" and "gas" pseudocomponents in this model contain all of the original fluid components, in contrast to the typical method of grouping in which each pseudocomponent is made up of only selected original components.

Whitson (1983) suggests the C_{7+} fraction can be grouped into N_H pseudocomponents given by $N_H = 1 + 3.3 \log(N-7)$, where N is the carbon number of

the heaviest fraction in the original fluid description. The groups are separated by molecular weights given by $M_I = M_7(M_N/M_7)^{1/NH}$. Molecular weights, M_i, from the original fluid description (i=7,...,N) falling within boundaries M_{I-1} to M_I are included in group I. This method should only be used when C_{7+} fractions are separated on a carbon-number basis, and for N greater than about 20.

Li et al. (1984) suggest a method for grouping components of an original fluid description using K-values from a flash at reservoir temperature and the "average" operating pressure. The original mixture is divided arbitrarily into "light" components (H_2S, N_2, CO_2, and C_1-C_6) and "heavy" components (C_{7+}). The light components are grouped into N_L pseudocomponents according to $N_L=3$ $\log(K_{max}/K_6)$, where K_{max} is the largest K-value, and K_6 is the K-value for C_6. Grouping is made according to the logarithm of K-values. Using the notation $A = \log(K_{max})$, the groups are specified as follows:

Group 1:	A-1/3 < log K < A
Group 2:	A-2/3 < log K < A-1/3
Group 3:	A-1 < log K < A-2/3
...	
Group N_L:	A-(N_L-1)/3 < log K < log K_6

Heptanes-plus fractions are grouped into N_H pseudocomponents, where $N_H = 1.5\log(K_7/K_H)+1$. Component "H" is chosen so that the sum of mole fractions from C_7 to C_H is approximately 95% of the total C_{7+} mole fraction. Using the notation $B = \log(K_7$, the C_{7+} groups are specified as follows:

Group 1:   B-2/3 < log K < B

Group 2:   B-4/3 < log K < B-2/3

Group 3:   B-6/3 < log K < B-4/3

...

Group N_{H-1}: B-2(N_H-2)/3 < log K < log K_H

Group N_H :   log K_H < log K

Li et al. (1984) suggest that phase diagrams and, if possible, compositional simulation be used to verify the grouped fluid description.

Behrens and Sandler (1986) suggest a grouping method for C_{7+} fractions based on application of Gaussian quadrature (often used in continuous thermodynamics). Although they use a simple exponential distribution with only two quadrature points (i.e., the C_{7+} fractions are grouped into two pseudocomponents), the method is general and can be applied to any molar distribution model and for any number of C_{7+} groups [Whitson et al (1989)]. The proposed method gives surprisingly good results compared with earlier studies where "optimal" grouping is determined by trial-and-error or statistical testing. In general, most authors have found that grouping of the type C_{7-10}, C_{11-15}, C_{16-20}, and C_{21+} is substantially better than C_7, C_8, C_9, and C_{10+}.

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

$$\Theta_I = \frac{\sum_{i \in I} z_i \Theta_i}{\sum_{i \in I} z_i} \tag{36}$$

where Θ_i is any property (T_c, p_c, ω, M) and z_i is the mole fraction for components i making up pseudocomponent I. Specific gravity should be calculated using ideal volume mixing,

$$\gamma_I = \frac{\sum\limits_{i=1}^{I} z_i M_i}{\sum\limits_{i=1}^{I} \dfrac{z_i M_i}{\gamma_i}} \tag{37}$$

Pedersen, et al (1985) suggest using weight fraction instead of mole fraction for critical properties. An empirical mixing-rule approach suggested by Batycky and Wu (1986) uses both mole and weight fractions and a proportioning factor λ, with $0 < \lambda < 1$. Batycky and Wu suggest that the value of λ (which is assumed to be equal for p_{cI}, T_{cI}, and ω_I) be determined by matching calculated multicontact vaporization results from the complete fluid characterization.

A generalized mixing rule for BIPs can be written as

$$k_{IJ} = \sum_{i=1}^{I} \sum_{j=1}^{I} z_i z_j k_{ij} \tag{38}$$

Based on the original arguments presented by Chueh and Prausnitz (1967), the Lee-Kesler (1975) mixing rules have also been widely used. Lee et al. (1981) and Whitson (1983) consider an alternative method for calculating C_{7+} critical properties, based on the specific gravities and boiling points of pseudocomponents. This method does not appear to be superior to the mixing rules given above. Others have considered the pseudoization problem, including Schlijper (1986), Benmekki and Mansoori (1989), Carrier et al. (1989), and Newley and Merrill (1989).

Coats (1982) presents a method of pseudoization that basically eliminates the effect of mixing rules on pseudocomponent properties. The approach is simple and accurate. *It's the best!* Basically, Coats requires that the pseudoized characterization reproduces exactly the volumetric behavior of the original reservoir fluid at undersaturated conditions. This is achieved by ensuring that the mixture EOS constants A and B are identical for the original and the pseudoized characterizations.

First, pseudocritical properties (p_{cI}, T_{cI}, and ω_I) are estimated using any mixing rule. Then Ω_{aI} and Ω_{bI} are determined to satisfy the following equations:

$$\Omega_{aI} = \frac{\displaystyle\sum_{i \in I} \sum_{j \in I} z_i z_j a_i a_j (1 - k_{ij})}{\dfrac{R^2 T_{cI}^2}{p_{cI}} \alpha_I(T_{rI}, \omega_I)}$$

$$\Omega_{bI} = \frac{\displaystyle\sum_{i \in I} z_i b_i}{\dfrac{R T_{cI}}{p_{cI}} \beta_I(T_{rI}, \omega_I)}$$

(39)

where

$$a_i = \Omega_{ai} \frac{R^2 T_{ci}^2}{p_{ci}} \alpha_i(T_{ri}, \omega_i)$$

$$b_i = \Omega_{bi} \frac{R T_{ci}}{p_{ci}} \beta_i(T_{ri}, \omega_i)$$

Ω_{ai} and Ω_{bi} may include previously-determined corrections to the numerical constants Ω_a^o and Ω_b^o. This approach to determining pseudocomponent properties, together with Eq. (38) for k_{IJ}, is surprisingly accurate even for VLE calculations. Coats also gives an analogous procedure for determining pseudocomponent v_{cI} for the Lohrenz-Bray-Clark (1964) viscosity correlation.

Stepwise Regression

A reduced-component characterization should strive to reproduce the original complete characterization that has been used to match measured PVT data. An approach to achieve this goal is what I refer to as *stepwise regression*, which is 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 C_{7+} 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.   Consider the simulated PVT data as "real" data.

4.   Group two pairs of components using the pseudoization procedure of Coats to obtain Ω_{aI} and Ω_{bI} values, and Eq. (38) for k_{IJ}.

5.   Use regression to fine tune the Ω_{aI} and Ω_{bI} values estimated in Step 4; also include key BIPs such as (N_2+C_1)-C_{7+}, (CO_2+C_2)-C_{7+}, and other nonzero BIPs involving pseudocomponents from Step 4.

6.   Repeat Steps 4 and 5 for various pseudocomponent groupings until the quality of the reduced-component characterization deteriorates beyond an acceptable fluid description. The following table suggests a 4-step pseudoization procedure.

ORIGINAL	STEP 1	STEP 2	STEP 3	STEP 4
1 - N_2 2 - CO_2 3 - C_1 4 - C_2 5 - C_3 6 - iC_4 7 - nC_4 8 - iC_5 9 - nC_5 10 - C_6 11 - F_1 12 - F_2 13 - F_3	1 * (N_2+C_1) 2 * (CO_2+C_2) 3 - C_3 4 - iC_4 5 - nC_4 6 - iC_5 7 - nC_5 8 - C_6 9 - F_1 10 - F_2 11 - F_3	1 - (N_2+C_1) 2 - (CO_2+C_2) 3 - C_3 4 * (iC_4+nC_4) 5 * (iC_5+nC_5) 6 - C_6 7 - F_1 8 - F_2 9 - F_3	1 - (N_2+C_1) 2 - (CO_2+C_2) 3 - C_3 4 - (iC_4+nC_4) 5 - (iC_5+nC_5) 6 * (C_6+F_1) 7 * (F_2+F_3)	1 - (N_2+C_1) 2 - (CO_2+C_2) 3 * $(C_3+(iC_4+nC_4))$ 4 - (iC_5+nC_5) 5 * $((C_6+F_1)+(F_2+F_3))$
REGRESSION PARAMETERS:	$k_{ij}(N_2+C_1$-$F_{1-3})$ $\Omega_a(N_2+C_1)$ $\Omega_b(N_2+C_1)$ $\Omega_a(CO_2+C_2)$ $\Omega_b(CO_2+C_2)$	$k_{ij}(N_2+C_1$-$F_{1-3})$ $\Omega_a(iC_4+nC_4)$ $\Omega_b(iC_4+nC_4)$ $\Omega_a(iC_5+nC_5)$ $\Omega_b(iC_5+nC_5)$	$k_{ij}(N_2+C_1$-$C_{6+})$ $\Omega_a(C_6+F_1)$ $\Omega_b(C_6+F_1)$ $\Omega_a(F_2+F_3)$ $\Omega_b(F_2+F_3)$	$k_{ij}(N_2+C_1$-$C_{6+})$ $\Omega_a(C_3+(iC_4+nC_4))$ $\Omega_b(C_3+(iC_4+nC_4))$ $\Omega_a((C_6+F_1)+(F_2+F_3))$ $\Omega_b((C_6+F_1)+(F_2+F_3))$

* Indicates the grouped pseudocomponents being regressed in a particular Step.

In summary, any grouping of a complete, extended 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 complete characterization. Stepwise regression is the best approach to determine the number and properties of pseudocomponents that can accurately describe a reservoir fluid's phase behavior. If stepwise regression is not possible, the Li et al. method is recommended for choosing the number of pseudocomponents; standard grouping of the light and intermediates (N_2+C_1, CO_2+C_2, iC_4+nC_4, and iC_5+nC_5) and Gaussian quadrature

for C_{7+} should be equally valid. The Coats method is always recommended for calculating pseudocomponent properties.

CONCLUDING REMARKS

1. PVT properties of petroleum reservoir fluids should always be given *special* consideration in two situations: (a) volatile oil and gas condensate reservoirs producing by depletion below the initial saturation pressure and (b) gas injection projects that are immiscible or multicontact miscible.

2. In order of increasing computational effort, the following PVT formulations can be used as an alternative to the standard black-oil formulation: (a) modified black-oil properties that account for solubility of liquid hydrocarbon in the reservoir gas phase, and the variation in PVT properties with the amount of gas injected, (b) K-value methods that use convergence pressure to account for changing reservoir compositions, (c) highly pseudoized 4- and 5-component EOS characterizations, and (d) complete 9-15 component EOS characterizations.

3. The recommended EOS formulation is either the Peng-Robinson or Soave-Redlich-Kwong equation with *volume translation* [alternatively a ZJRK equation], using at least 3 C_{7+} fractions characterized by (a) mole fraction and molecular weight, (b) normal boiling point and specific gravity, and (c) acentric factor, critical pressure, critical temperature, and critical volume; and finally, non-zero binary interaction parameters for nonhydrocarbon-hydrocarbon and C_1-C_{7+} pairs.

4. An EOS characterization should always be compared with laboratory PVT data from depletion and multicontact gas experiments, where in most cases the characterization must be modified by nonlinear regression (or "smart" manual adjustment). In general, however, the better the starting characterization, the less one should have to *jimmy* with the EOS parameters to get a match.

NOMENCLATURE

a,b; A,B	=	EOS constants
B_o	=	oil formation volume factor, bbl/STB
B_{gd}	=	dry gas formation volume factor, ft^3/scf
c	=	volume shift parameter
C_f	=	specific gravity correlating parameter
f	=	fugacity coefficient, psia
h	=	number of hydrogen atoms (C_nH_{2n+h})
k_{ij}	=	binary interaction parameter
K_w	=	Watson (UOPK) characterization factor
N_H	=	number of "heavy" pseudocomponents (C_{7+} fractions)
N_L	=	number of "light" pseudocomponents
p	=	pressure, psia
p_c	=	critical pressure, psia
R_s	=	solution gas-oil ratio, scf/STB
r_s	=	solution oil-gas ratio, STB/scf
s	=	normalized volume shift parameter
T	=	temperature, °R
T_c	=	critical temperature, °R
T_b	=	normal boiling point, °R
T_r	=	reduced temperature
T_{br}	=	reduced normal boiling point temperature
w	=	weight fraction
x	=	liquid mole fraction
y	=	vapor mole fraction
z	=	feed (overall) mole fraction
α,β,η	=	gamma distribution parameters
α,β	=	correction terms to EOS constants A and B
γ_o	=	surface oil gravity, water=1
γ_{oo}	=	surface oil gravity from reservoir oil, water=1
γ_{og}	=	surface oil gravity from reservoir gas, water=1
γ_g	=	surface gas gravity, air=1
γ_{gg}	=	surface gas gravity from reservoir gas, air=1
γ_{go}	=	surface gas gravity from reservoir oil, air=1
λ	=	mixing rule averaging constant
ϕ	=	fugacity coefficient
ϕ	=	mixing rule weighting fraction
ρ_o, ρ_g	=	oil and gas density, lb/ft^3
ω	=	Pitzer acentric factor
Θ	=	any property
Ω_a, Ω_b	=	EOS numerical constants

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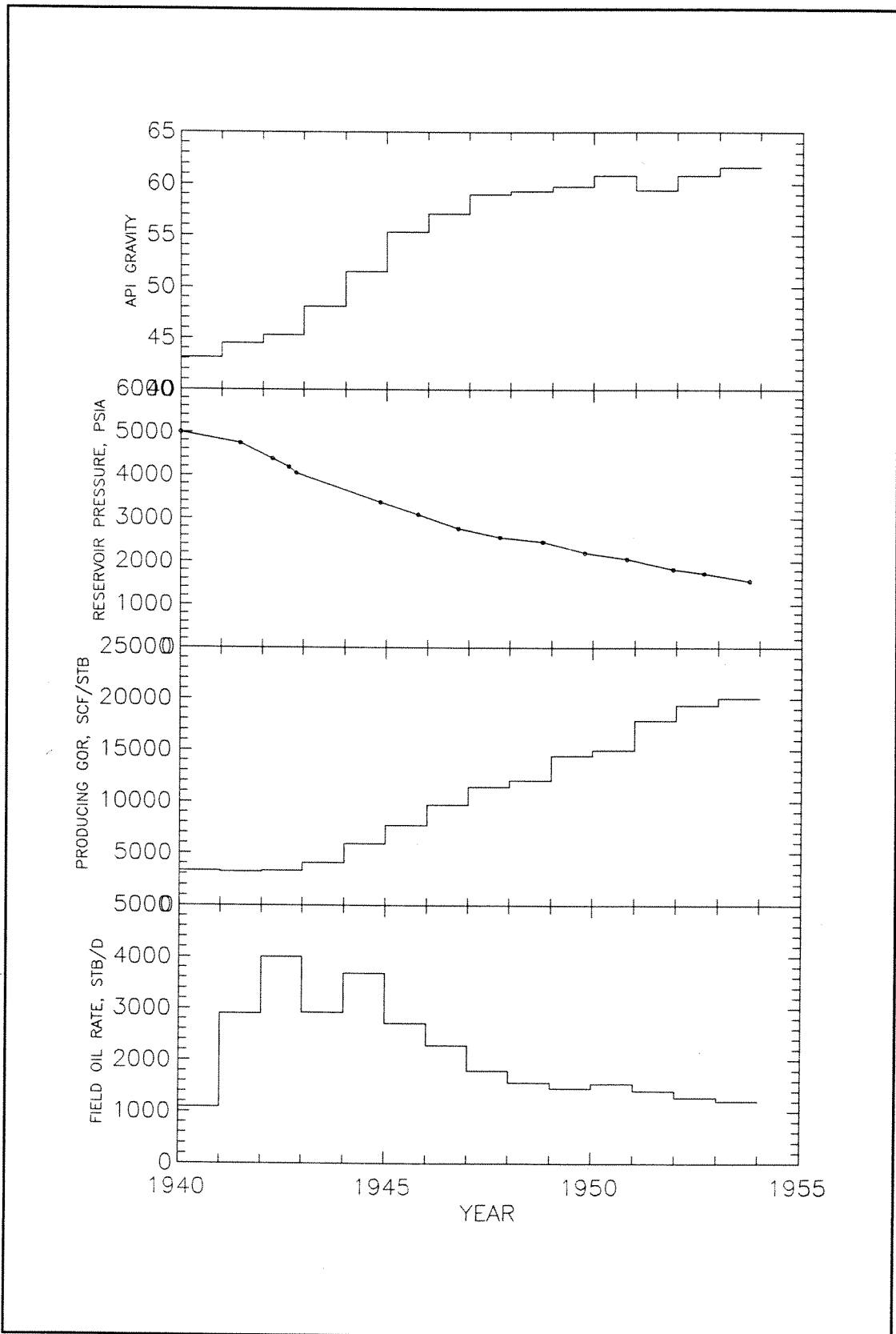Zudkevich, D. and Joffe, J.: "Correlation and Prediction of Vapor-Liquid Equilibrium with the Redlich-Kwong Equation of State," *AIChE J.* (Jan. 1970), 112-119.

Fig. 1 Producing characteristics of a volatile oil reservoir [after Woods (1955)].

MODIFIED BLACK-OIL FORMULATION

FROM RESERVOIR GAS:

SURFACE GAS

SURFACE OIL

FROM RESERVOIR OIL:

SURFACE GAS

SURFACE OIL

RESERVOIR GAS
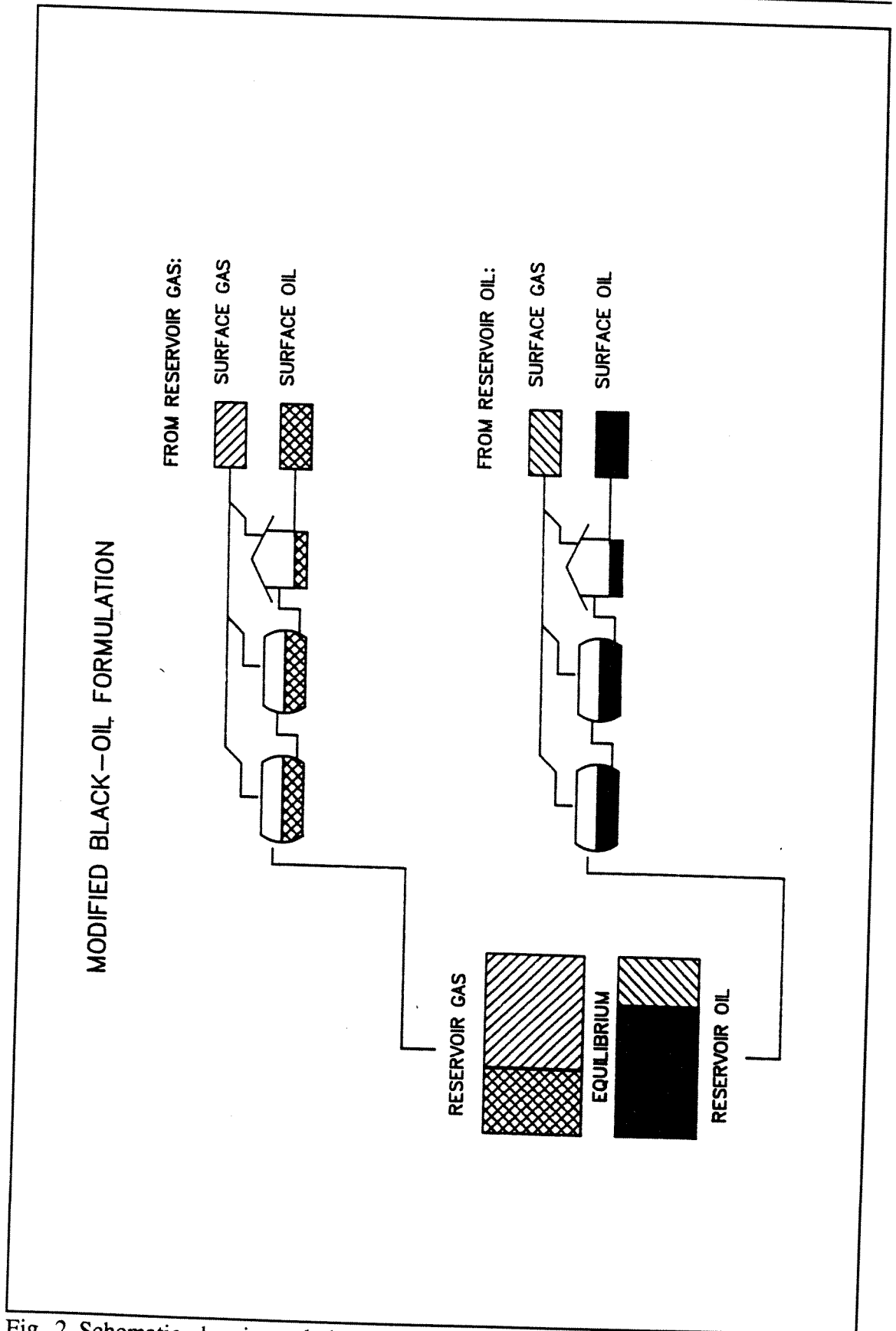
EQUILIBRIUM

RESERVOIR OIL

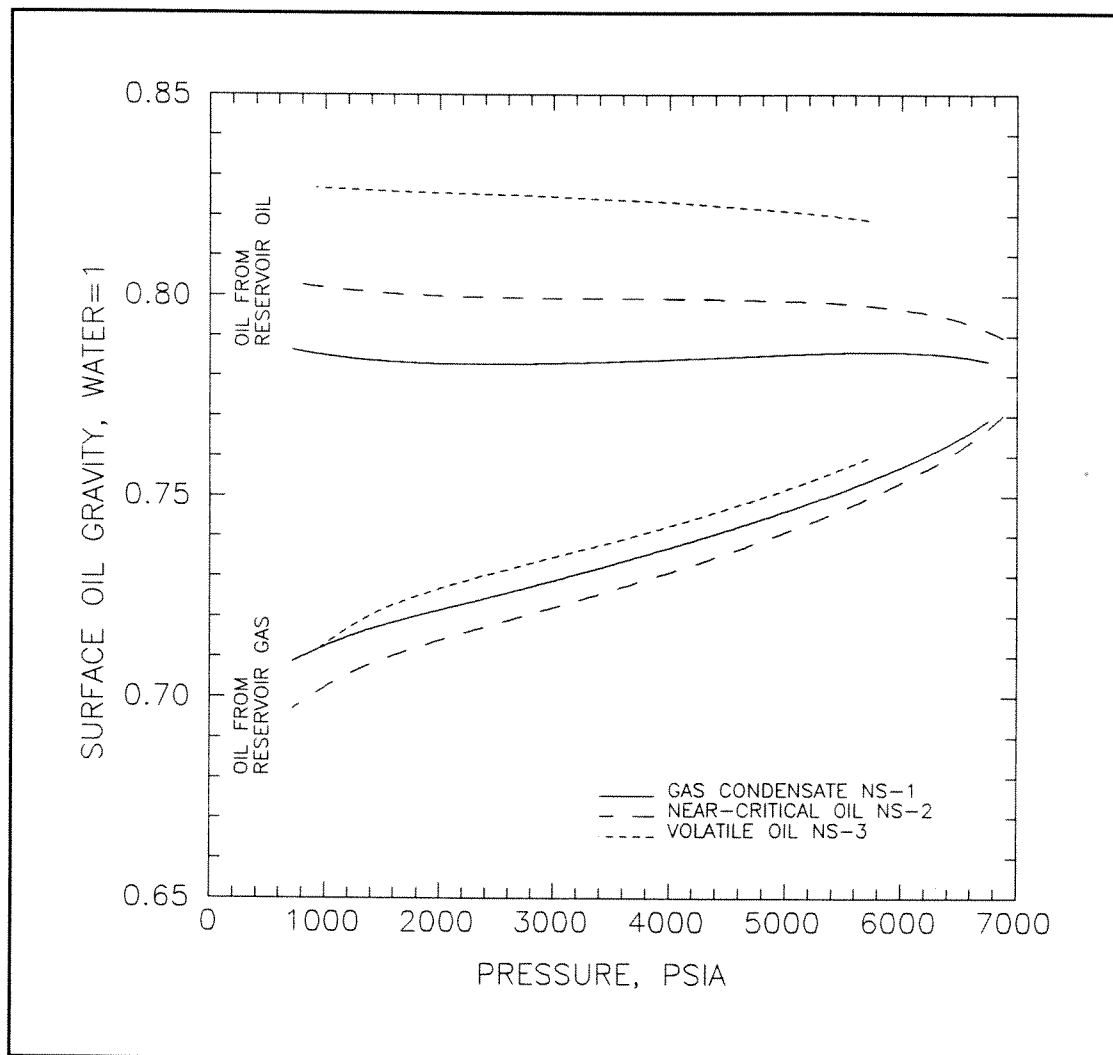Fig. 2 Schematic showing relation of modified black-oil properties to surface and reservoir volumes.

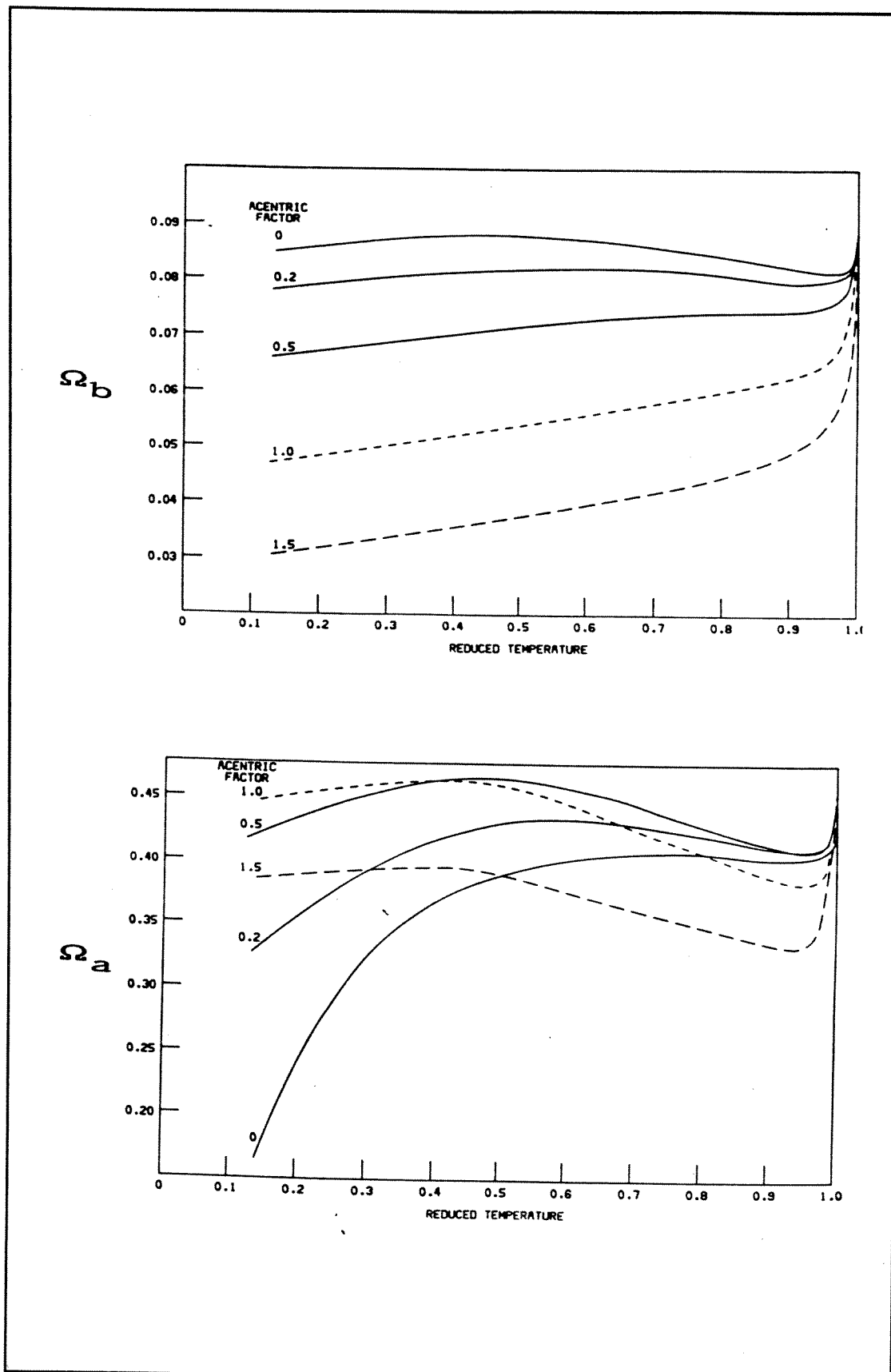Fig. 3 Variation in surface oil gravities during depletion of volatile oil and gas condensate reservoirs.

Fig. 4 Behavior of Ω_a and Ω_b versus reduced temperature and acentric factor for the Amoco version of the ZJRK EOS [Yarborough (1979)].
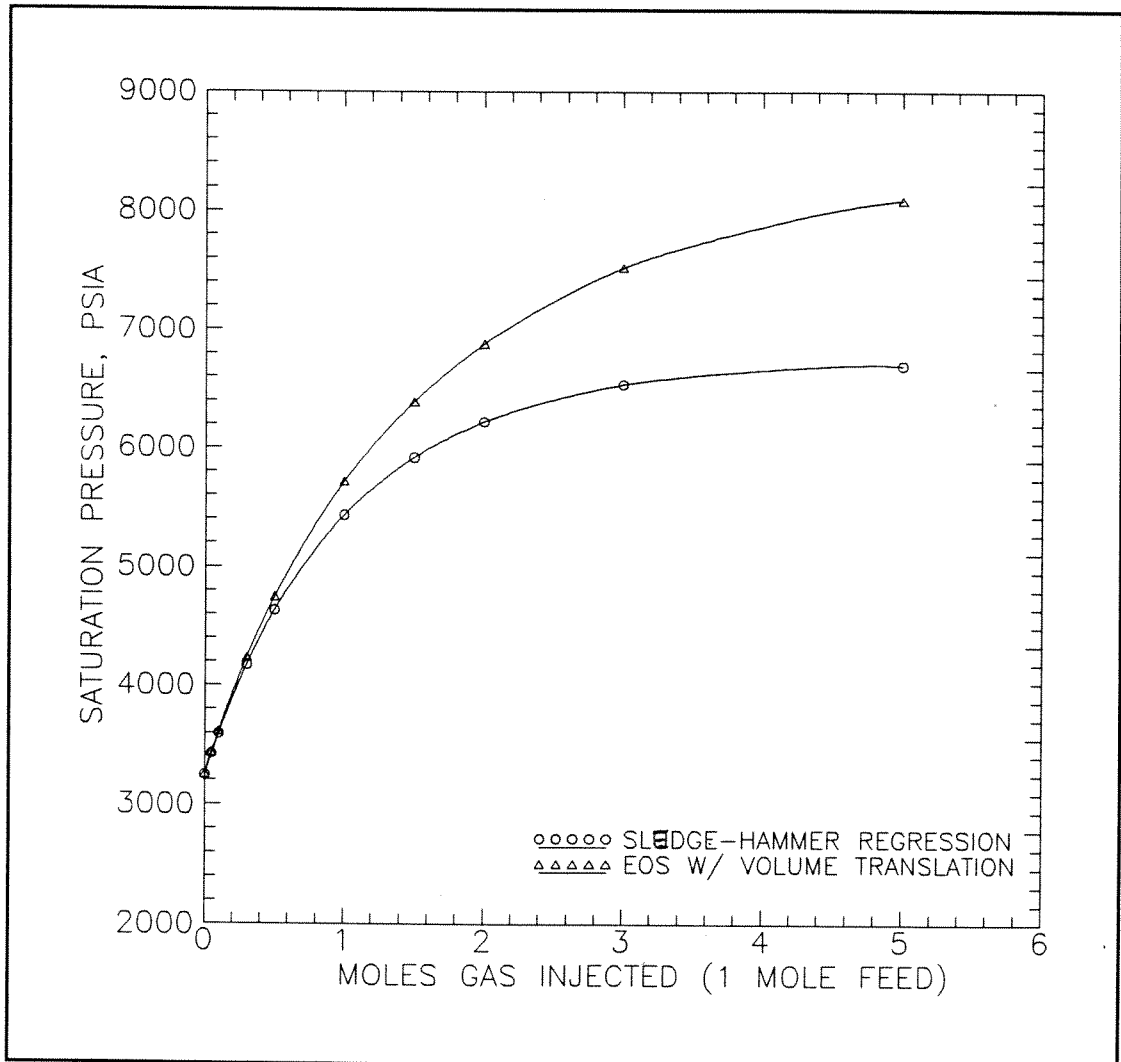
Fig. 5 Swelling test predictions for the sludge-hammer regression vs. the volume-translation prediction.