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2. The method eliminates any guesswork when determining how many proving runs are needed.

3. The method ensures the desired accuracy of the calculated meter factor.

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Shiaw Y. Su
Sun Co. Inc.
Dallas

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A Set of Equations for Computing Equilibrium Ratios of a Crude Oil/Natural Gas System at Pressures Below 1,000 psia

Use of equilibrium ratios (*K* values) to compute the quantity and composition of gas and liquid phases in equilibrium at given temperatures and pressures is documented extensively in the petroleum literature. While *K* values usually come from laboratory experiments, the values available to petroleum engineers are presented most often in the form of charts. The Gas Processors Suppliers Assn. (GPSA) charts[1] of *K* data are well known in the industry.

It long has been recognized that equilibrium ratios are system-compositional, temperature, and pressure dependent. Composition dependency usually is indicated by the apparent convergence pressure value (for example, 5,000 psia, 10,000 psia). However, at pressures below about 1,000 psia, the effect of the system composition is small and often may be neglected.

A computer program package for evaluating GPSA ratios is available from the association. However, use of the GPSA programs requires a large computer. The equations presented here are simple enough to be handled by small programmable calculators, such as the HP-67, TI-52, and TI-59 machines. It is my opinion that *K* values developed from these equations are more appropriate than GPSA *K* values for calculating flash vaporizations at conditions usually found in oilfield gas/oil separation processes.

The basic *K* data involved here are those developed by Katz and Hachmuth[2] on recombined samples of gas and oil from the Wilcox sand of the Oklahoma City Field. Crude gravity was 38.4°API. Based on the reported viscosity of the crude oil, 43.5 Saybolt Seconds Universal (SSU) at 100°F, the Universal Oil Products Characterization Factor (UOP *K*) of this crude is judged to be about 12.2. While 22 sets of experimental data were determined at three temperatures (up to 3,422 psia), the *K* values used here were smoothed values read from 11- × 17½-in. charts prepared by Katz and Hachmuth. The *K* values corresponded to pressures of 14, 200, 400, 600, 800, and 1,000 psia, at temperatures of 40°, 120°, and 200°F.

The basic equation used to correlate the Katz and Hachmuth data was that proposed by Hoffman *et al.*:[3]

$$\log Kp = f[b(1/T_B - 1/T)], \qquad (1)$$

where:

K = equilibrium ratio, y/x, of the compound
p = pressure, psia (MPa)
T = temperature, °R (K)
b = slope of the straight line connecting the critical point and the atmospheric boiling point on a log vapor pressure vs $1/T$ plot

$$= \frac{\log (p_c/14.7)}{(1/T_B - 1/T_c)}$$

T_B = boiling point of the compound at 14.7 psia, °R (K)
T_c = critical temperature of the compound, °R (K)
p_c = critical pressure of the compound, psia (MPa)

The function inside brackets is the component characterization factor, designated by the symbol *F*.

Several authors[4-6] have shown that plots of log *Kp* vs *F*, at a given pressure, often form essentially straight lines. Also, the effect of increasing pressure has been shown to raise the position of the line on the plot and to yield a line of lesser slope. Actually, there are no

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theoretical reasons for the isobar lines to be straight or for them to converge at a common point, as indicated by Brinkman and Sicking[4] (see their Fig. 2). However, when straight lines are indicated by the data, simpler equations for K result.

Correlation of Katz and Hachmuth K Data

Since the Katz and Hachmuth charts gave K values for lumped butanes, pentanes, and hexanes, it was necessary to use "lumped" F values in the correlative work. The butanes fraction was treated as being composed of 25% iso-butane and 75% n-butane; the pentanes fraction as 35% isopentane and 65% n-pentane; and the hexanes as 25% 2-methylpentane, 25% 3-methylpentane, and 50% normal hexane. These butanes and pentanes splits were indicated by the authors; the hexanes split is my assumption. The resulting b and T_B values for the lumped fractions were: butanes, $b = 2124$, $T_B = 486°R$; pentanes, $b = 2441$, $T_B = 552°R$; hexanes, $b = 2738$, $T_B = 610°R$.

Early in the research, values of b and T_B listed by Hoffman *et al.*[3] for methane and ethane were found to give undesirable results. Fig. 1 is a plot of log Kp vs component characterization factors, F, at 800 psia. While the propane and heavier compounds form an adequate straight line, the methane values, and to a lesser degree, the ethane values, do not align with the general trend. Behavior similar to that shown in Fig. 1 was found at other pressures. This behavior was rectified by determining values of b and T_B that caused the methane and ethane points to align with and fall on the line formed by the heavier compounds. The overall best "adjusted" values for methane were found to be $b = 300$, $T_B = 94°R$; for ethane the values were $b = 1145$, $T_B = 303°R$. Note that using these adjusted values rather than values proposed by Hoffman *et al.* reduced the average difference between methane equation K values and chart K values from 16.2 to 2.3%. Use of adjusted b and T_B values for ethane reduced the average difference from 8.5 to 2.1%.

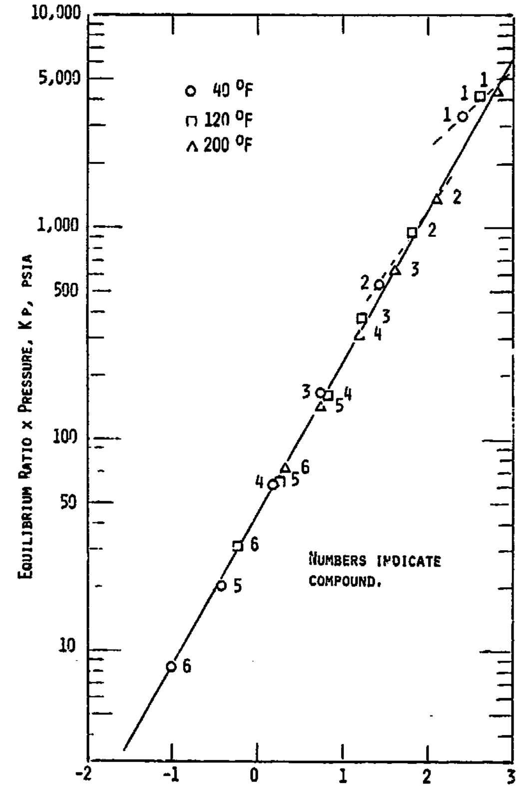

Fig. 1—Log kp vs F, relationship of Katz and Hachnuth 800-psia data at temperatures of 40, 120, and 200°F.

It is not surprising that this spurious behavior was found for methane and ethane. Values of b and T_B listed by Hoffman *et al.* originate from vapor pressure values of pure compounds. It long has been known[7,8] that equilibrium ratios of methane and ethane depend on the character of the heavy components (UOP K, for example) in the mixture, as well as on temperature, pressure, and total composition. Thus, the adjusted values of b and T_B above should be considered specific to the Oklahoma City crude oil systems. However, they also probably represent other crude oil systems of comparable paraffinicity very well.

Six isobar plots of log Kp vs F were made for the 18 sets of chart K values using b and T_B values from Table 1. The best straight-line fit to the points was made by inspection, and the slope and intercept value at $F = 0$ was determined. The slope and intercept values then were plotted vs pressure, and the best fit by a quadratic equation was determined. Results of this study are summarized by the following four equations.

$$K = 1/p \; 10^{(a+cF)} \quad \text{(2)}$$

$$F = b(1/T_B - 1/T) \quad \text{(3)}$$

$$a \text{ (intercept)} = 1.2 + 4.5(10^{-4})\,p + 15(10^{-8})\,p^2 \quad \text{(4)}$$

$$c \text{ (slope)} = 0.890 - 1.7(10^{-4})\,p - 3.5(10^{-8})\,p^2 \quad \text{(5)}$$

Use of these equations to compute Katz and Hachmuth K values should be restricted to pressures below 1,000 psia and temperatures between 40 and 200°F. One also must use the b and T_B values listed in Table 1. Within these restraints, one may expect a standard deviation of

TABLE 1—VALUES OF b and T_B FOR USE IN COMPUTING KATZ AND HACHMUTH EQUILIBRIUM RATIOS BELOW 1,000 psia

Compound	b (cycle °R)	T_B (°R)
Nitrogen	470	109
Carbon dioxide	652	194
Hydrogen sulfide	1136	331
Methane	300	94
Ethane	1145	303
Propane	1799	416
iso-Butane	2037	471
n-Butane	2153	491
iso-Pentane	2368	542
n-Pentane	2480	557
iso-Hexanes	2696	603
n-Hexane	2780	616
n-Heptane	3068	669
n-Octane	3335	718
n-Nonane	3590	763
n-Decane	3828	805
Hexanes (lumped)	2738	610
Heptanes and heavier		

$n = 7.3 + 0.0075\,T(°F) + 0.0016\,p$ (psia)
$b = 1013 + 324\,n - 4.256\,n^2$
$T_B = 301 + 59.85\,n - 0.971\,n^2$

about 3.5% between equation-generated K values and the original Katz and Hachmuth chart K values.

K's for Heptanes-and-Heavier Fraction

When making flash calculations, the question of the K value to use for the lumped "plus" fraction always arises. One rule of thumb proposed by Katz and Hachmuth[2] is that the K value for C_7^+ can be taken as 15% of the K of C_7.

The correlation method that involves a semilog plot of K_p vs F offers an answer to this question, at least for the Oklahoma City crude oil/natural gas systems Katz and Hachmuth studied. In this portion of the work, plots of log K_p vs F were made from the hexanes and lighter component *experimental* data and the best straight line fit of the data determined by least-squares method. Knowing the experimental value of the C_7^+ K, it was then easy to compute the corresponding C_7^+ F value, and from this to specify the pure normal parraffin hydrocarbon that would have the K value of the C_7^+ fraction.

Results of this analysis were somewhat ragged, but definitely indicated that the effective K of the C_7^+ fraction varied with temperature and pressure. If the symbol n is used to designate the number of carbon atoms of the normal paraffin hydrocarbon that has the K value of the C_7^+ fraction, the relationship of n, temperature, and pressure is:

$$n(C_7^+) \cong 7.3 + 0.0075\,T(°\mathrm{F}) + 0.0016\,p(\mathrm{psia}). \qquad (6)$$

Thus, in the temperature and pressure ranges studied, the C_7^+ K can be characterized as equivalent to K's of normal paraffin compounds ranging from $C_{7.3}H_{16.6}$ to $C_{10.4}H_{22.8}$.

To use this information to calculate K values for C_7^+ fractions requires relationships between b and n, and T_B and n. For n values between 7 (normal heptane) and 20 (normal eicosane), the b and T_B values listed by Hoffman *et al.* are fit very closely by the equations:

$$b(n) = 1013 + 324\,n - 4.256\,n^2. \qquad (7)$$

$$T_B\,(n) = 301 + 59.85\,n - 0.971\,n^2. \qquad (8)$$

Thus, b and T_B values for the C_7^+ fraction in the Oklahoma City crude oil/natural gas system can be evaluated by substituting the value of n from Eq. 6 into Eqs. 7 and 8.

K's for Nonhydrocarbon Compounds

Many naturally occurring systems contain various amounts of N_2, CO_2, and H_2S, as well as the usual hydrocarbons. For maximum utility, some provision should be made for computing K's for these nonhydrocarbon compounds.

Equilibrium ratios of N_2, CO_2, and H_2S in mixtures of natural gas and absorber oil and mixtures of natural gas and crude oil have been reported by Jacoby and Rzasa.[9] Poettmann[10] also has reported K values for CO_2 in mixtures of natural gas and crude oil. API gravities of the Oklahoma City crude oil and those used in Poettmann's studies were essentially the same (±38°API), while the crude oil Jacoby and Rzasa used was lower (±27°API). Poettmann's systems contained 6 and 11% CO_2, while Jacoby and Rzasa's systems contained 5% N_2, 5% CO_2, and 5% H_2S. Katz and Hachmuth's systems had none of these compounds.

The general procedure used to develop b and T_B values for the nonhydrocarbon gases was: (1) it was first assumed that at a given temperature and pressure, the relative volatility of the nonhydrocarbon and methane (ratio of their K's) measure in the Jacoby/Rzasa and in the Poettmann systems could be applied directly to the Katz and Hachmuth systems, (2) using the measured relative volatilities and the methane K values indicated by the Katz and Hachmuth data, equivalent K's were computed for the nonhydrocarbon in the Katz and Hachmuth systems, (3) having computed the equivalent nonhydrocarbon K's, the appropriate log K_p vs F chart was entered from the K_p axis, and a corresponding F value determined for the nonhydrocarbon, and (4) from the F values at various temperatures, the corresponding values of b and T_B were computed.

Results of conducting this procedure at 100, 150, and 200°F and at 200, 400, 600, 800, and 1,000 psia were N_2 values of $b = 470$, $T_B = 109°\mathrm{R}$; CO_2 values of $b = 652$, $T_B = 194°\mathrm{R}$, and H_2S values of $b = 1{,}136$, $T_B = 331°\mathrm{R}$. These should be properly labled as "adjusted" values because they originated from multicomponent system behavior, not vapor pressure measurements, and have been adjusted to fit equations for Katz and Hachmuth's hydrocarbons equilibrium ratios.

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SI Metric Conversion Factors

°API		141.5/131.5	+ °API	= kg/m³
°F		(°F-32)/1.8		= °C
psia	×	6.894 757	E−03	= MPa
°R		°R/1.8		= K

M. B. Standing, SPE-AIME
Stanford U.
Stanford, CA

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