



CHAPTER II

VAPOR-LIQUID EQUILIBRIUM

2.1 Phase Behavior and Physical Properties of Natural Gas

Multicomponent phase behavior or P-V-T behavior is much more difficult to describe than a pure component. Generally, the P-V-T interrelations are presented graphically and show the amount of liquid or vapor present for various combinations of temperature and pressure. Hence they are called phase diagrams. The pressure temperature diagram for a multicomponent systems depends on the molecular species present and the relative concentration of each species. For natural gas, the phase diagram (P-T Diagram) is shown in Figure 2.1.

From Figure 2.1, it is shown that the saturated vapor pressure temperature curve does not coincide with the saturated liquid pressure temperature curve; the dew point (or saturated vapor) temperature is different from (greater than) the bubble point (or saturated liquid) temperature. A saturated vapor (liquid) can exist above the critical point of a multicomponent mixture. This phenomenon infers that at least a part of the mixture can be liquefied (vaporized) at temperature above the critical temperature.

The cricondenbar of a mixture is the maximum pressure that the dew point envelope reaches. Mathematically, this maximum pressure can be derived as $(\partial P_{dp} / \partial T = 0)$. The cricondentherm is the maximum temperature that the dew point curve reaches. It can be

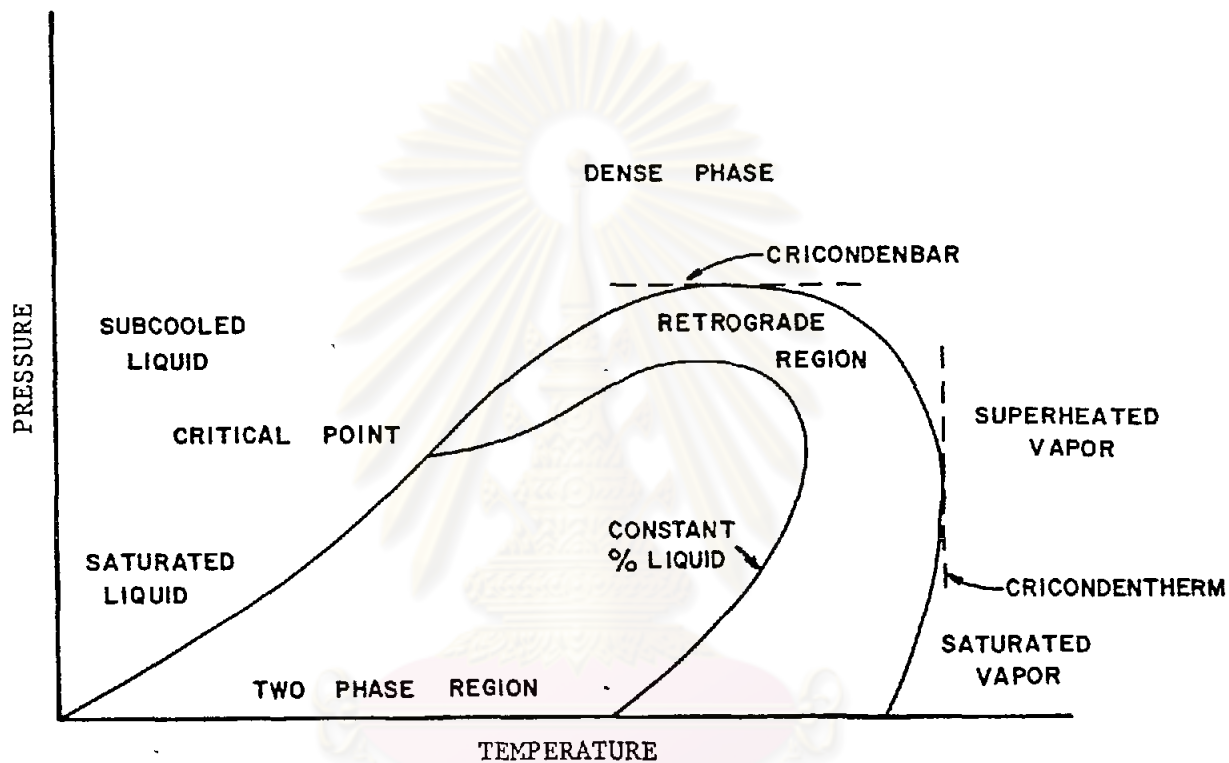


FIGURE 2.1 PHASE ENVELOPE FOR NATURAL GAS MIXTURE (19)

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defined as a $(\partial T_{dp} / \partial P = 0)$. The location and magnitude of the cricondenbar and cricondentherm are dependent on the molecular species present and the relative concentration of each species. The cricondentherm of natural gas system can range between -140°C (-230°) and about 400°C (700°F).

The critical point of mixtures is defined as that temperature-pressure combination at which the properties of the dew point vapor and bubble point liquid phase become identical, or the temperature-pressure combination above which all of the mixture cannot be liquefied. The properties considered are the optical, thermodynamic, compositional and transport properties. Experimental determination of the critical point of mixtures is difficult. However, the approximate critical point can be predicted using the thermodynamic property prediction method available today. However, knowledge of the true critical point of a mixture can be important in analysis of operational equipment and selection of design conditions. There are several situations in which process conditions curve is quite near or at the critical point of the multicomponent stream being processed. For these cases, pseudocritical conditions would have led to completely erroneous conclusions. Kay's rule(19), or the so-called combination rule, is applied to find pseudocritical values. These values are not in any way related to the true critical properties of the mixture. However, these values are valuable in that they permit convenient determination of selected thermodynamic properties from generalized correlations. Further, the true critical point, as predicted by the thermodynamic properties correlations are based on pseudocritical values predicted using Kay's rule.

A dense phase region which is shown above the critical in Figure 2.1 is a region where the mixture has the visual properties of gases but possesses physical properties somewhere between a liquid and gas. If one increases the pressure on a liquid (at constant temperature) there is no evident phase change as one begins to enter the dense phase region. The liquid just begins to lose its usual visual properties and then becomes invisible (like a gas). What one is witnessing is a molecular rearrangement. As a consequence, correlations for ordinary liquids and gases do not apply rigorously.

The location of the critical point along the pressure-temperature envelope is a function of the molecular species present and the relative concentration of the individual species. Figure 2.2 shows the potential range of critical point locations along the pressure-temperature envelopes. The theoretically possible range for the critical point locations is from Point A to Point D. The practical possible range is from Point A to Point C for naturally occurring mixture. Relatively lean natural gas reservoir systems (mol percent methane greater than about 80%) and typical natural gas process streams will have critical points located between point A and B. As the reservoir fluid becomes richer (i.e. contains more propane, butanes, pentanes and condensate or crude oil) the critical point will shift from Point A toward Point B or C. Point C probably would be representative of most crude oil reservoir fluids.

Retrograde condensation and/or retrograde vaporization is one of the most poorly understood phenomena in vapour liquid phase behavior. "Retrograde" simply means backwards, or the reverse of

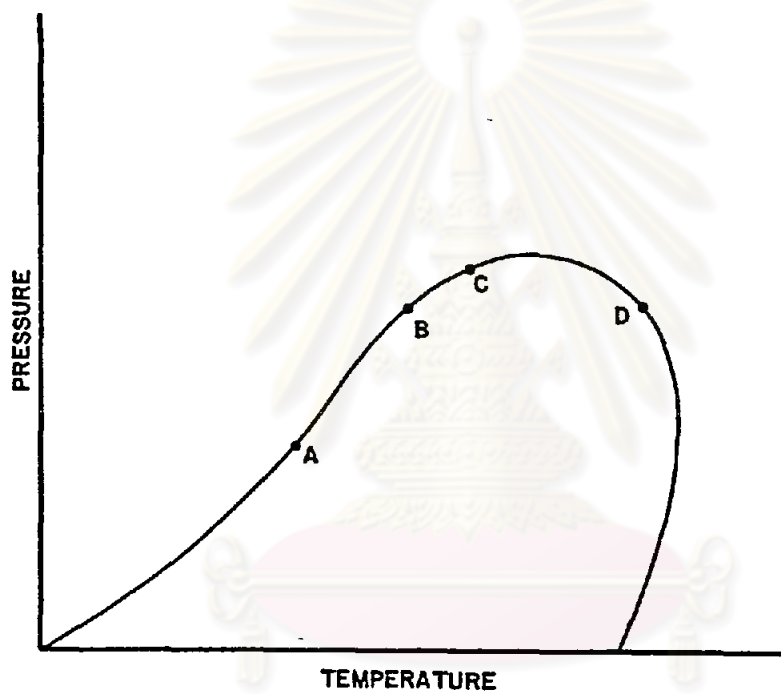


FIGURE 2.2 POSSIBLE CRITICAL POINT LOCATIONS ALONG
THE P-T ENVELOPE (19)

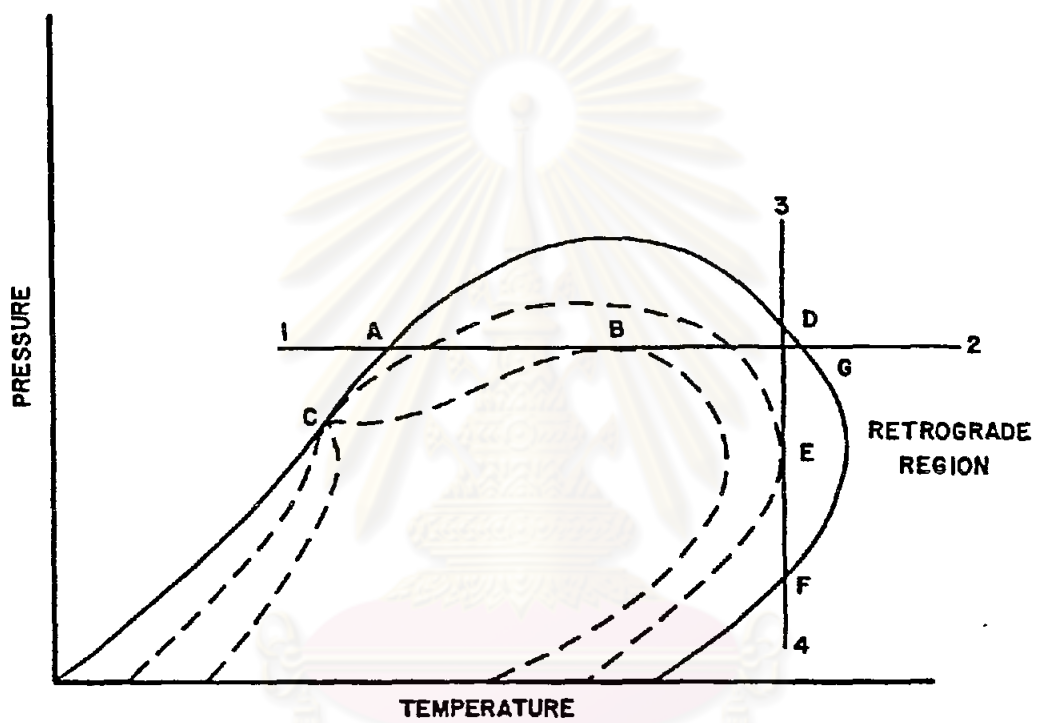


FIGURE 2.3 RETROGRADE BEHAVIOR (19)

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normal. Retrograde behavior comes about because of the location of the true critical point for the mixture and the manner in which the bubble point and dew point lines are separated from each other. In this region changes in pressure and temperature do not yield the same type behavior for pure components. Increasing the temperature at constant pressure can cause liquid to condense. Increasing the pressure at constant temperature can cause liquid to vaporize. This cannot happen for pure component. Retrograde behavior can be accurately predicted using a judicious combination of high quality experimental data for the system and any of the better thermodynamic property prediction correlations available today. It is generally accepted that thermodynamic property prediction correlations can be used with a limited amount of experimental data to predict retrograde phase envelope behavior over a wide range of temperature-pressure conditions.

2.2 Thermodynamic of Vapor Liquid Equilibrium

The equation which provides a general criterion for equilibrium with respect to mass transfer between phase is

$$\bar{\mu}_i^\alpha = \bar{\mu}_i^\beta = \dots = \bar{\mu}_i^\pi \quad (i = 1, 2, \dots, N) \quad (2.1)$$

Equation (2.1) holds for each component i of an N -component system containing π phase at equilibrium. Definition of fugacity for a component in solution is

$$d\bar{G}_i = RT d \ln f_i \quad (\text{at constant } T) \quad (2.2)$$

general integration always gives

$$G_{i,\text{final}} - G_{i,\text{initial}} = RT \ln (f_{i,\text{final}}/f_{i,\text{initial}}) \quad (2.3)$$

or

$$\Delta \bar{G} = RT \Delta \ln \bar{f}_1 \quad (2.3)$$

The relationship between the fugacity \bar{f}_1 and the chemical potential $\bar{\mu}_1$ expressed in the definition of Equation (2.2) allow us to derive an alternative criterion for phase equilibrium which is often of greater practical utility than Equation (2.1). We proceed by applying Equation (2.3) to each component 1 in each phase P;

$$\bar{\mu}_{1,\text{final}}^P - \bar{\mu}_{1,\text{initial}}^P = RT \ln (\bar{f}_{1,\text{final}}^P / \bar{f}_{1,\text{initial}}^P) \quad (2.4)$$

Since Equation (2.4) is valid both for changes in composition and for changes in physical state, we can without loss of generality let the initial state be the same for all phases, namely that of component 1 as it exists in the π th phase at equilibrium conditions. Thus, for $1 = 1, 2, \dots, N$

$$\begin{aligned} \bar{\mu}_{1,\text{initial}}^P &= \bar{\mu}_1^\pi \\ \bar{f}_{1,\text{initial}}^P &= \bar{f}_1^\pi \end{aligned}$$

and Equation (2.4) yields the following equation for 1 in each of the phases α through $\pi-1$:

$$\begin{aligned} \bar{\mu}_1^\alpha &= \bar{\mu}_1^\pi + RT \ln (\bar{f}_1^\alpha / \bar{f}_1^\pi) \\ \vdots & \\ \bar{\mu}_1^{\pi-1} &= \bar{\mu}_1^\pi + RT \ln (\bar{f}_1^{\pi-1} / \bar{f}_1^\pi) \end{aligned}$$

Substitution of these equations in Equation (2.1) and rearrangement gives

$$\ln (\bar{f}_1^\alpha / \bar{f}_1^\pi) = \ln (\bar{f}_1^\beta / \bar{f}_1^\pi) = \dots = 0$$

from which we obtain

$$\bar{f}_1^\alpha = \bar{f}_1^\beta = \dots = \bar{f}_1^\pi \quad (1 = 1, 2, \dots, N) \quad (2.5)$$

Thus the fugacity \bar{f}_1 of a component in a multicomponent,

multiphase system must be the same in all phases in which it is present at equilibrium. Equation (2.5) constitutes a major justification for the introduction of the fugacity as a thermodynamic variable.

For vapor-liquid equilibrium in a multicomponent system

$$\bar{f}_1^L = \bar{f}_1^V \quad (i = 1, 2, \dots, N) \quad (2.6)$$

Each \bar{f}_1^V is a function of temperature T , pressure P , and $N-1$ independent vapor-phase mole fraction y_1 . Similarly, each \bar{f}_1^L is a function of T , P and $N-1$ independent liquid-phase mole fraction x_1 . Thus, the $2N$ variables are related by the N equations represented by Equation (2.6). One must therefore specify variables in the formulation of a vapor-liquid equilibrium (VLE) problem in order to allow calculation of the remaining N variables by simultaneous solution of the N equilibrium relations of Equation (2.6). This conclusion also follows from the phase rule, which for this case yields $F=N$.

The Phase Rule(16) : $F = C - P + 2$

This expression applies to systems at equilibrium and relates the number of components in the system C and the number of phases P to the degrees of freedom F . The degrees of freedom are the number of intensive variables which must be fixed before the equilibrium state is properly defined and thus the system is reproducible .

It is here two-phase system ($P=2$), and N -components therefore,

$$F = N - 2 + 2 = N$$

Usually, one specifies the N variable by fixing T or P and either the liquid phase or the vapor phase composition.

One formal procedure replaces the fugacity in Equation (2.6) in favor of fugacity coefficients, defined by (35)

$$\bar{\phi}_i = \bar{f}_i / x_i P$$

Thus, letting y_i represent a vapor-phase mole fraction, we can write

$$\bar{f}_i^V = \bar{\phi}_i^V y_i P$$

Similarly, representing a liquid-phase mole fraction by x_i

$$\bar{f}_i^L = \bar{\phi}_i^L x_i P$$

With these substitution, Equation (2.6) becomes

$$x_i \bar{\phi}_i^L = y_i \bar{\phi}_i^V \quad (2.7)$$

Since $\bar{\phi}_i^L$ is a function of T,P, and the liquid-phase composition and $\bar{\phi}_i^V$ is similarly a function of T, P, and the vapor-phase composition. Equation (2.7) actually represents N highly complex expression relating T, P, the x_i , and the y_i . Solution for the N unknowns is most conveniently carried out by an iterative procedure with the aid of a computer. The fugacity coefficients are expressed as functions of T,P, and composition by means of an equation of state.

This computational procedure is usually reserved for systems at pressures high enough so that the vapor phase deviates significantly from ideal gas behavior. Moreover, it is most commonly applied to systems made up of nonpolar and non association species, such as light hydrocarbons and cryogenic gases, for which mixing rules and combination rules for equation of state parameters are firmly based on experimental data.

By the definition of the equilibrium ratio (K-values) as

$$K_i = Y_i / x_i \quad (2.8)$$

Rearrangement of Equation (2.7) becomes

$$K_1 = y_1/x_1 = \bar{\phi}_1^L/\bar{\phi}_1^V \quad (2.9)$$

Equation (2.9) indicates that there are two ways to find K-values, one is calculated from ratio between y_1 and x_1 if y_1 and x_1 are known from experiment. The other are estimated by an equation of state is used for both phases. The fugacity coefficient can be estimated for both vapor (V) and liquid (L) phase and then K-values is calculated.

2.3 Equations of state

Equations which provide P-V-T relationship are usually referred to as equation of state. Although a large number of P-V-T relations have been proposed, relatively few are suitable for practical design calculations. Equations of state have a limited capacity to predict phase equilibria.

Equations of state are broadly divided into two types which are as follows (19,23) :

1. Cubic equations of state e.g.

$$\text{Soave - Redlich - Kwong (SRK)} : Z^3 - Z^2 - (A - B - B^2)Z - AB = 0 \quad (2.10)$$

$$\text{Peng - Robinson (PR)} : Z^3 - (1 - B)Z^2 + (A - 3B - 2B^2)Z - (AB - B^2 - B^3) = 0 \quad (2.11)$$

2. Multiparametric equations of state e.g.

Benedict - Webb - Rubin - Starling (BWRS) :

$$P = \rho RT + (B_0 \rho RT - A_0 - C_0/T^2 + D_0/T^3 - E_0/T^4) \rho^2 + (bRT - a - d/T) \rho^3 + \alpha (a + d/T) \rho^6 + C_0 \rho^3/T^2 (1 + \gamma^2 \rho) \exp(-\gamma \rho^2) \quad (2.12)$$

For the cubic equations the volume is obtained directly, however, for the multiparametric equations an iterative calculation is necessary. Cubic equations of state are now frequently used for

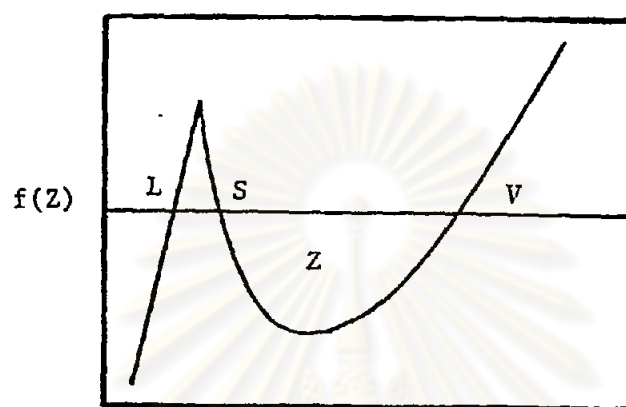
calculation of multicomponent vapor-liquid equilibria in systems involving nonpolar components.

Cubic equations of state will yield the behavior shown in Figure 2.4 (a) when the system under consideration is in the two phase region and that shown in Figure 2.4 (b) when in the single phase region.

If the system is in the single phase region. There is no possibility of determining the wrong value of the compressibility factor (or the molar volume). Solution techniques for the single phase region are relatively straight forward and not prone to error. However, when the system is in the two phase region, there are three roots that will satisfy the equation of state. The answer of which correct values depends upon whether you are dealing with a vapor phase or liquid phase system. The value of Z at the compressibility factor equal to S (in Figure 2.4 (a)) is a spurious root (solution) and is of no practical value.

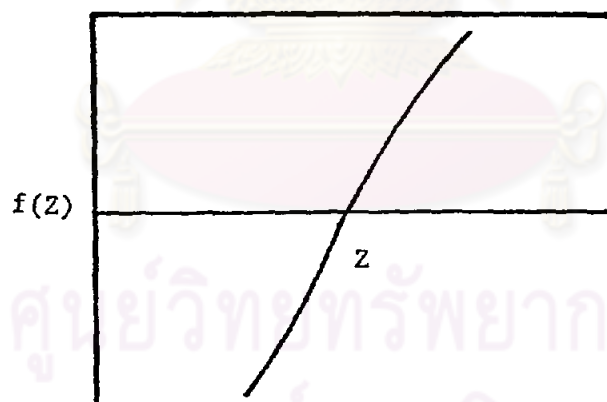
Consequently the solution procedure must be told which root is being sought and must be constrained to totally eliminate the possibility of determining either of the other roots. Direct cubic equation solution procedure offer this reliability. Trial and error methods do not unless special provisions are programmed into the solution procedure.

Selection of a method of solution for equations of state depends on many factors. For cubic equations of state, we can use either a direct procedure or a trial and error approach. The liability of the direct cubic solution is that it will occasionally



a

Two Phase Region



b

Single Phase Region

FIGURE 2.4 TYPICAL BEHAVIOR OF CUBIC EQUATION OF STATE (19)

yield bad solutions for the liquid phase compressibility factor on certain computer systems.

Consequently, a trial and error solution for a cubic equation of state is to be used in this work. In addition to being more reliable (when properly programmed) than the direct cubic solution, the trial and error solution procedure is usually about 5% faster than the direct cubic solution procedures.

The most popular equations of state (10) include the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations of state. Both can estimate with good accuracy pure component vapor pressure and mixture K values in normal systems, but they fail to provide good estimates for liquid density. The Soave-Redlich-Kwong equation has rapidly gained acceptance in the hydrocarbon processing industry because of the simplicity of the equation and because of its capability for generating reasonably accurate equilibrium ratio in VLE calculations.

Soave-Redlich-Kwong Equation of State (SRK) (10,19,32)

The SRK equation of state is

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \quad (2.13)$$

when

$$A = (ac\alpha)P/R^2T^2$$

$$B = Pb/RT$$

$$b_1 = \Omega_b RTC_1/PC_1$$

$$b = \sum x_i b_i$$

$$ac_1 = \Omega_a R^2 TC_1^2/PC_1$$

$$\alpha_1^{1/2} = 1 + m_1(1 - TR_1^{1/2})$$

$$(ac\alpha)_1 = \sum x_i ac_i^{1/2} ac_j^{1/2} \alpha_i^{1/2} \alpha_j^{1/2} (1 - k_{1j})$$

$$(ac\alpha) = \sum \sum x_i x_j ac_i^{1/2} ac_j^{1/2} \alpha_i^{1/2} \alpha_j^{1/2} (1 - k_{1j})$$

$$m_1 = 0.480 + 1.574 \omega_1 + 0.176\omega_1^2$$

$$\begin{aligned} \Omega_a &= 0.42747 \\ \Omega_b &= 0.08664 \\ k_{1j} &= \text{interaction parameter} \\ \omega_1 &= \text{acentric factor} \end{aligned}$$

The SRK procedure has been shown to be a versatile tool for estimating the phase equilibrium behavior of hydrocarbon mixtures. For hydrocarbons, the procedure is fully generalized and requires only a knowledge of the critical temperature, critical pressure, and acentric factor of each component. It is most useful for treating wide boiling mixture containing both sub- and supercritical components but should be used with caution for very close boiling systems and system which are known to form azeotropes

Except for hydrogen, the SRK equations can also be applied to light gases such as nitrogen, carbon monoxide, carbon dioxide, and hydrogen sulfide if binary interaction parameters, k_{1j} , are incorporated into the SRK equation.

The SRK equation appears to give the most reliable overall results for K values and enthalpies over wide ranges of temperature and pressure. However, as indicated, the SRK correlation still fails to predict liquid density with good accuracy. The SRK correlation appears to be particularly well suited for predicting K values and enthalpies for natural gas systems at cryogenic temperatures. (7,8,29,32)