

# CALCULATION OF VAPOR-LIQUID EQUILIBRIUM\*

## A Simplified Method

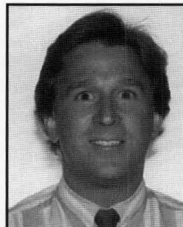
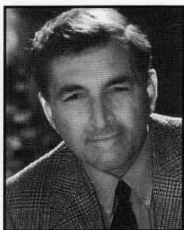
JACK WINNICK, DENNIS E. SENOL  
Georgia Institute of Technology • Atlanta, GA 30332-0100

Vapor-liquid equilibrium is calculated by equating the fugacities in each phase for each component in a mixture:

$$f_i^v = f_i^l \quad (1)$$

The reproduction of a vapor-liquid phase diagram, or even finding the composition of the equilibrium phases at one point, requires that these fugacities be known functions of temperature (T), pressure (P), and composition (x in the liquid, y in the vapor). There are two general methods for representing these equilibria: 1) at low pressures, say below 10 bar or so, the liquid phase fugacities are described using activity coefficients and the vapor using fugacity coefficients, and 2) at higher pressures, both phases are described with fugacity coefficients derived from a single equation of state.

**Jack Winnick** is Professor of Chemical Engineering at Georgia Tech, where he has been since 1979. Prior to 1979 he was on the faculty at the University of Missouri. He has worked for short stints in the private sector, in the petroleum and aircraft industries, and for NASA, in life support. He currently consults on electrochemical engineering and environmental topics.



**Dennis Senol** is Computing coordinator for the School of Chemical Engineering at Georgia Tech. He earned his undergraduate degree in chemical engineering, has Masters degrees in chemical engineering and electrical engineering, and is now working on a doctorate in chemical engineering. He is currently working with real time embedded systems in the automotive and aviation industries.

Situations involving the need for reproduction of vapor-liquid equilibria, say in distillation, are of five general types:

1. **Bubble-Pressure** • liquid phase composition and temperature known; vapor composition and pressure unknown
2. **Bubble-Temperature** • liquid phase composition and pressure known; vapor composition and temperature unknown
3. **Dew-Pressure** • vapor phase composition and temperature known; liquid composition and pressure unknown
4. **Dew-Temperature** • vapor phase composition and pressure known; liquid composition and temperature unknown
5. **Flash** • temperature and pressure known; both phase compositions unknown

The problem inherent in these calculations, even when all necessary parameters are known, is that the equilibrium equation, in almost all cases, is implicit in one or more of the variables. We here show a new scheme, one that circumvents many of the difficulties encountered in the standard computing strategies, through use of a widely available commercial math library routine. Because the basic equations for the two pressure regimes are different, we will describe the strategies separately.

### LOW PRESSURE

At low pressure, activity coefficients,  $\gamma_i$ , are used to describe the nonideality of the liquid and fugacity coefficients,  $\phi_i$ , for the vapor:

\* This is an abridged version of a chapter in the textbook Engineering Thermodynamics, by Jack Winnick, soon to be published by John Wiley and Sons.

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$$f_i^l = x_i \gamma_i P_i^o \phi_i^o \quad (2a)$$

$$f_i^v = y_i \phi_i P \quad (2b)$$

where the fugacity coefficient of the pure component,  $\phi_i^o$ , at its vapor pressure,  $P_i^o$ , corrects for the nonideality of the pure component. (The "Poynting" factor, which further corrects for the difference between  $P_i^o$  and  $P$ , the total pressure, is neglected here.) Equations for activity coefficients are available in several forms—the Wilson, the Margules, van Laar and UNIFAC are a few. All are complex functions of  $x$  and  $T$

$$\gamma = \gamma(x, T) \quad (3)$$

For example, the Wilson equation for a binary system is expressed by the equations

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right) \quad (4a)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left( \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right) \quad (4b)$$

where the parameters  $\Lambda_{ij}$  are evaluated from

$$\Lambda_{ij} = \frac{v_j}{v_i} e^{-\frac{a_{ij}}{RT}} \quad (5)$$

with the constant  $a_{ij}$  independent of  $T$ . The molar volumes of the pure liquid components,  $v_i$ , are evaluated at  $T$ , but are mild enough functions of temperature to be taken as constant.

A separate equation exists for the fugacity coefficients in the vapor:

$$\phi = \phi(y, T, P) \quad (6)$$

where the component fugacity coefficients,  $\phi_i$ , are found from the exact expression

$$RT \ln \left( \frac{f_i}{y_i P} \right) \equiv RT \ln \phi_i = \int_{\infty}^V \left( \frac{RT}{V} - \left( \frac{\partial P}{\partial n_i} \right)_{T, V, n_j} \right) dV - RT \ln(z) \quad (7)$$

which requires an equation of state for evaluation of the RHS. For example, at low pressure, a form derived from the virial equation is

$$\ln(\phi_i) = \frac{2}{v} \sum_j y_j B_{ij} - \ln(z) \quad (8)$$

where

$$z = 1 + \frac{BP}{RT}; \quad B = \sum_i \sum_j y_i y_j B_{ij}; \quad v = \frac{zRT}{P}$$

and the component parameters are evaluated from

$$B_{ii} = \left( B^{(0)} + \omega B^{(1)} \right) \frac{RT_c}{P_c} \quad (8a)$$

$$B^{(0)} \equiv 0.083 - \frac{0.422}{T_r^{1.6}} \quad (8b)$$

$$B^{(1)} \equiv 0.139 - \frac{0.172}{T_r^{4.2}} \quad (8c)$$

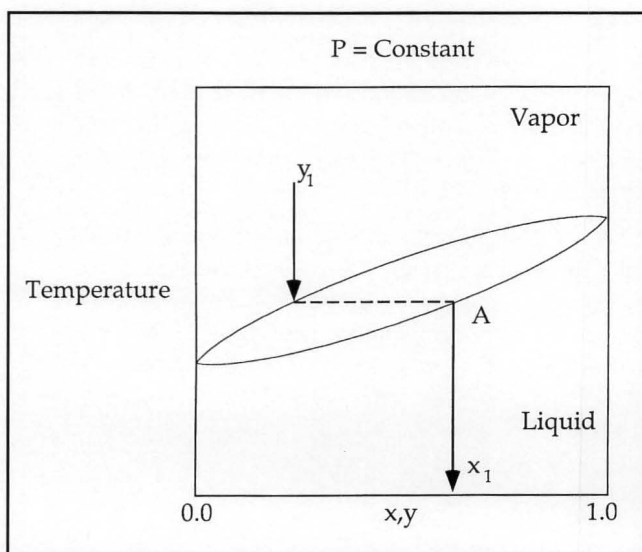
In order to find  $T_{r_{ij}}$  ( $i \neq j$ ), a value for  $T_{c_{ij}}$  is needed ( $T_r \equiv T/T_c$ ); at these pressures the simple approximation

$$T_{c_{ij}} = \sqrt{T_{c_i} T_{c_j}} \quad (9)$$

is often used.

Equation (1) is now

$$y_i \phi_i P = x_i \gamma_i P_i^o \phi_i^o \quad (10)$$



**Figure 1.** VLE diagram for a binary mixture at constant pressure.

which is implicit in  $T$ ,  $P$ , and mole fraction in view of Eqs. (4) and (7). Therefore, solution of Eq. (1), for example, for  $x$  and  $T$  at any  $y$  and  $P$  (a dew temperature calculation) becomes a matter of iterating on  $x$  and  $T$ .

Consider, for example, a “dew-temperature” calculation; for the relatively simple case of a binary, we can show it on Figure 1. We are looking for point A, the first drop of condensate on bringing vapor composition  $y_1$  down in temperature until it meets the phase envelope.

The difficulty for the student or practicing engineer in calculating VLE lies not in finding the form of equation to use or in evaluating the parameters—that is an entirely separate problem. We assume here that it has already been done, as it has for very many systems. The compilations by Gmehling, *et al.*<sup>[1]</sup> for low pressure, and Knapp<sup>[2]</sup> for high pressure, are excellent sources. The problem lies in the implicit nature of the equations. For example, in Eq. (8), the fugacity coefficient is a function of  $y$ ,  $T$ , and  $P$ , and the activity coefficient (Eq. 4) is a function of  $x$  and  $T$ . So, if we want to calculate, say, the liquid phase mole fraction and temperature for a binary mixture where the vapor composition and pressure are known, direct solution is not possible.

Most thermodynamics textbooks describe complex computer programs to handle this calculation, ones that involve nested loops to iterate on the variables. These programs are necessarily specific to the particular equations used, the temperature range, etc. A typical flow chart for this calculation scheme is shown in Figure 2.

Mathematics programs are now available, however, that solve these kinds of implicit equations and make these calculations extremely simple. With them, all that is required is to express these implicit equations in forms that equal zero; one equation for each variable.

The best way to illustrate is through an example. Take the binary system: 2-Propanol-Water at 0.508 bar pressure. At a given vapor composition, we wish to find the dew temperature and composition. We write

$$x_1 + x_2 - 1.0 = 0 \quad (11)$$

$$y_1 \phi_1 P - x_1 \gamma_1 P_1^o \phi_1^o = 0 \quad (12)$$

$$y_2 \phi_2 P - x_2 \gamma_2 P_2^o \phi_2^o = 0 \quad (13)$$

These three equations must all go to zero (actually, some preset limit like 0.0001 is sufficient) for the

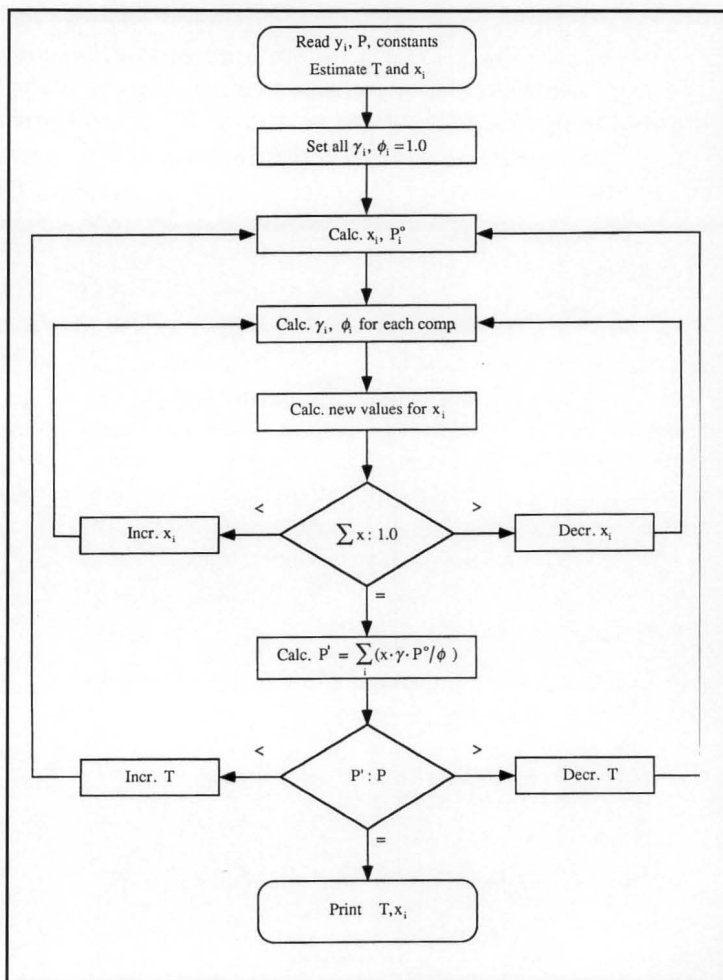


Figure 2. Typical flow chart for dew temperature calculation at low pressure.

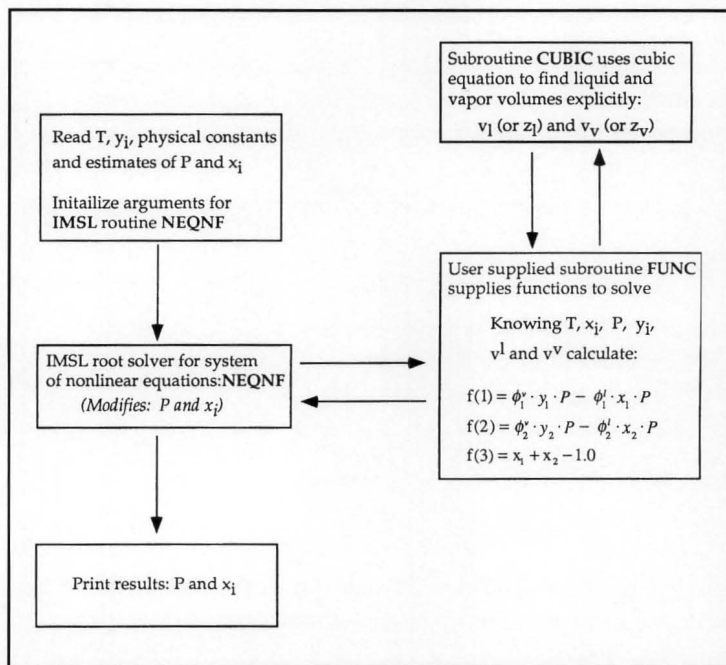


Figure 3. Low pressure dew temperature calculation.

solution. Employing the virial, Wilson, and Antoine (pure component vapor pressure) equations, we provide expressions for  $\phi$ ,  $\gamma$ , and  $P_i^0$ , respectively. Pure component parameters are available from texts such as Prausnitz, *et al.*<sup>[3]</sup> The binary parameters required for the system demonstrated were obtained from Gmehling, *et al.*<sup>[4]</sup> The expressions for  $\phi$ ,  $\gamma$ , and  $P_i^0$  are generated in a subroutine with a main program providing initial guesses for the three unknowns:  $T$ ,  $x_1$ ,

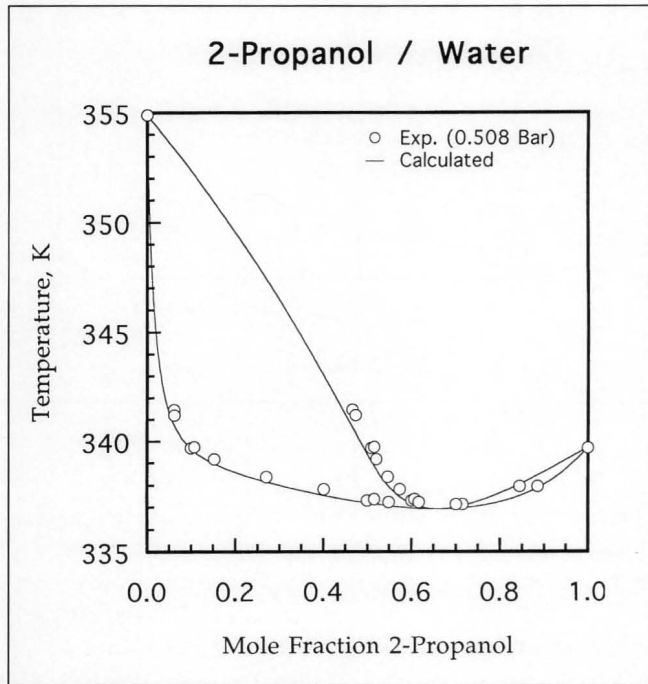


Figure 4. Constant pressure VLE results.

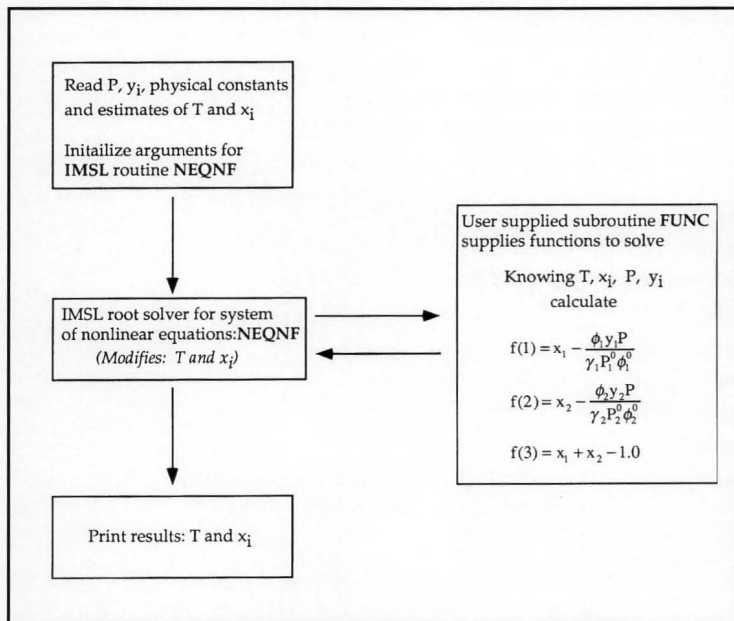


Figure 5. High pressure dew-pressure calculation.

and  $x_2$ . The main routine then calls the IMSL\* routine NEQNF<sup>[5]</sup> that changes temperature and liquid composition until Eqs. (11-13) are all near zero. The technique is shown schematically in Figure 3.

The routine is insensitive to the initial guesses for numerous binary systems in a range of temperatures; the example below was compiled with

$$x_1^0 = x_2^0 = 0.5 \quad \text{and} \quad T^0 = 373 \text{ K}$$

As shown in Figure 4, for the system of 2-Propanol-Water, the phase diagram is reproduced in its entirety, as shown in the literature.<sup>[6]</sup>

While we have illustrated a series of dew temperature calculations, the same procedure is used for bubble pressure or temperature or flash calculations. Multicomponent mixtures also offer no complication; for each additional component, there is one more equation and one more unknown.

### HIGH PRESSURE

At higher pressures, say above 10 bar or so, an equation of state (EOS) is used, one that represents both phases, so that

$$\phi_i^v y_i P = \phi_i^l x_i P \quad (14)$$

is the basic equation of equilibrium. The fugacity coefficients are once again found from the exact expression

$$RT \ln \left( \frac{f_i}{y_i P} \right) \equiv RT \ln \phi_i = \int_{\infty}^V \left( \frac{RT}{V} - \left( \frac{\partial P}{\partial n_i} \right)_{T, V, n_j} \right) dV - RT \ln(z) \quad (7)$$

but here we need an equation of state valid for both phases.

There are several in the literature; the form used does not alter the calculation procedure. For our purposes we use the Soave form of the Redlich-Kwong EOS (SRK), available in most thermodynamics texts

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \quad (15)$$

Since the phases are at the same  $T$  and  $P$ , this means the EOS must be solved for the specific volumes of each of the two phases. Unfortunately, these EOS's have three real (in the math sense) roots in the two-phase region, so some care must be taken to assure that the central, physically unreal root is not one of those used. The proper roots for the specific volume of liquid and vapor phases are easily handled by selecting the largest root for the vapor phase and the smallest root for the liquid phase. For example, when a cubic EOS is used, the cubic equation can be used as part of the minimization routine so that the proper roots could be explicitly obtained. For other types of EOS's, the liquid and vapor specific volumes are frequently dependent on initial guesses. In this case, a systematic "surface" search is made to allow roots to be obtained from different starting points.

\* IMSL is a copyrighted trademark of Visual Numerics Inc.



The standard method for solving say, a dew-pressure problem at high pressure, is similar in concept to that for the dew-temperature at low pressure, described earlier, (Figure 2). That is, an initial estimate is made for liquid composition and pressure, based on an ideal solution of the vapor composition given at the specified temperature. The EOS is solved for the vapor and liquid roots and the fugacity coefficients found for each component in each phase. Now, new liquid compositions are found from the equilibrium relationship, Eq. (1), and nested DO loops are used to vary  $x$  and  $P$  so as to simultaneously satisfy the material balance and equilibrium.

Alternatively, we can use the same strategy of simultaneous-equation solution as we did at low pressure. The scheme is shown in Figure 5. A dew point pressure calculation with an EOS for a binary involves five equations with five unknowns:  $x_1$ ,  $x_2$ ,  $P$ ,  $v^l$ , and  $v^v$ . For example, with the SRK

$$P - \frac{RT}{v^v - b^v} + \frac{a^v(T)}{v^v(v^v + b^v)} = 0 \quad (16)$$

$$P - \frac{RT}{v^l - b^l} + \frac{a^l(T)}{v^l(v^l + b^l)} = 0 \quad (17)$$

$$\phi_i^v y_i P - \phi_i^l x_i P = 0 \quad \text{with } i=1 \text{ and } 2 \quad (18)$$

and

$$x_1 + x_2 - 1.0 = 0 \quad (19)$$

and, from the SRK, the form for the fugacity coefficients derived using Eq. (7) is

$$\ln \phi_k = \frac{b_k}{b} (z-1) - \ln(z-B) - \frac{A}{B} \left( 2 \frac{\sqrt{a_k}}{\sqrt{a}} - \frac{b_k}{b} \right) \ln \left( 1 + \frac{B}{z} \right) \quad (20)$$

where  $A$  and  $B$  are defined as

$$A \equiv aP/(RT)^2$$

$$B \equiv bP/(RT)$$

We have not gone into the details of the evaluation of the parameters in these equations; they are available in standard sources such as Prausnitz, *et al.*,<sup>[7]</sup> and are directly calculated from individual critical properties. The only required input for the calculation are  $T_c$ ,  $P_c$ ,  $\omega$  and  $k_{12}$ . An example of an isothermal phase diagram calculated by this method is shown in Figure 6. As shown, the diagram is reproduced using the SRK EOS; in this case, it agreed very well with experimental results.<sup>[8]</sup>

The procedure is somewhat sensitive to the initial values used for mole fraction and  $P$  (or  $T$ ). If a single point is required, say a specific dew or bubble point, a spurious result is sometimes converged upon, one in which the "vapor" and "liquid" volume roots are equal. In this case, slight changes in the initial guesses arrive at the correct

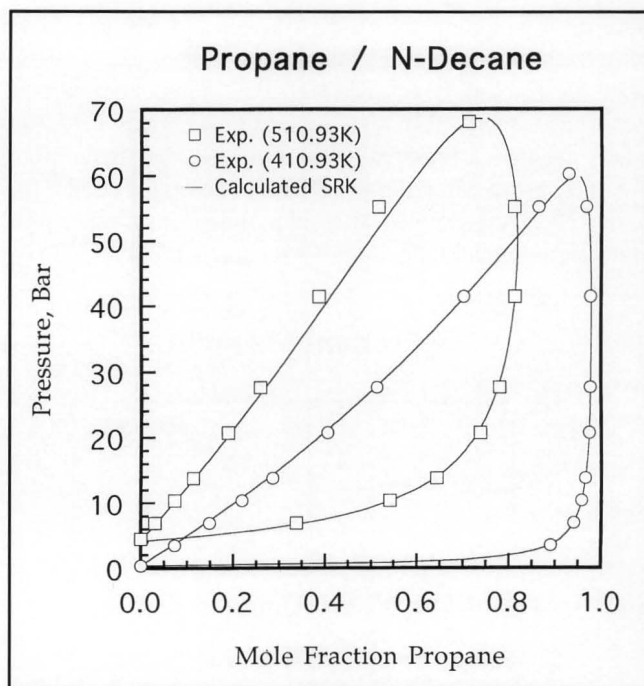


Figure 6. VLE results obtained from SRK.

solution. But when constructing the entire phase diagram, we start at one pure component and march across, say at increments of 0.05 mole fraction. Here the last values of  $x$ ,  $y$ ,  $T$ , and  $P$  provide convergent starting points for each subsequent iteration.

## CONCLUSIONS

A simplified method can be used to reproduce vapor-liquid equilibrium. Instead of individualized iterative routines to solve the implicit equations, a math library program is used along with the correlating equations. The user-written subroutines are clearly evident to even the beginning thermodynamics student so that the focus of any exercise can be the comparison among the correlating equations and experimental data.

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