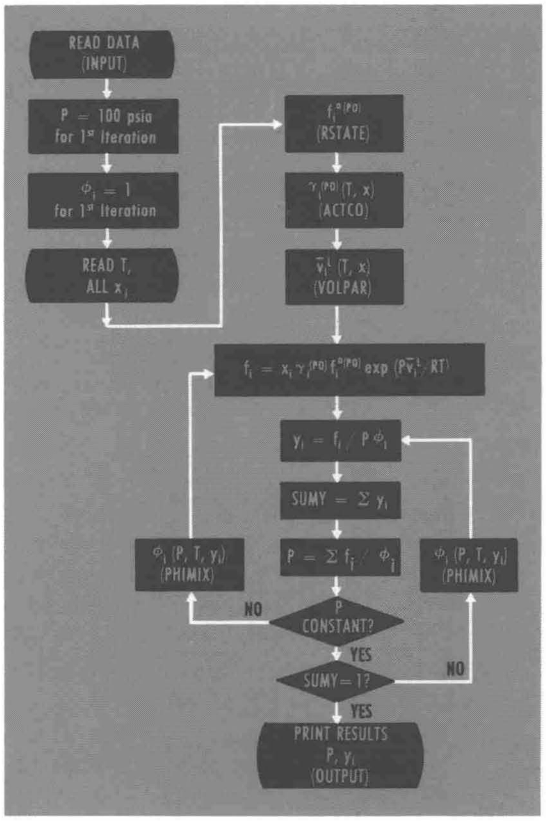

Figure 9. Schematic diagram of bubble-pressure program

value, due to its "condensing" effect. As a result, pressure has exactly opposite effects on the activity coefficients of the lighter component and the heavier component, as indicated by Equation 72. The simple approximation of using partial molar volumes at infinite dilution leads to large error near the critical region.

Also shown in Figure 8 are the partial molar volumes calculated with the universal values $\Omega_a = 0.4278$ and $\Omega_b = 0.0867$. The results are much less satisfactory, indicating the need for evaluating Ω_a and Ω_b for each pure saturated liquid.

All of the above equations for the calculation of partial molar volumes in saturated liquid mixtures are applicable to multicomponent systems without any further assumptions.

With partial molar volumes, the effect of pressure on liquid-phase activity coefficients can be taken into account. By separating the effect of pressure from that of composition, experimental liquid-phase activity coefficients can be subjected to rigorous thermodynamic analysis. Such analysis permits meaningful intepretation and correlation of binary, high-pressure, vapor-liquid equilibrium data and facilitates prediction of multicomponent-phase behavior.

D. Prediction of Mulicomponent-Phase Equilibria

For vapor-liquid equilibria of an N-component system, the variables of interest are the temperature, total pressure, $N - 1$ independent liquid-phase mole fractions and $N - 1$ independent vapor-phase mole fractions. Since there are 2 N variables but only N variables may be independently specified, the other N variables must be determined by solving the N simultaneous equations. They are the N equations of equilibrium:

$$f_i^V = f_i^L \qquad \text{for } i = 1, 2, \ldots, N \tag{76}$$

In the N equations of equilibrium expressed in Equation 76, the vapor-phase fugacities are given by:

$$f_i^V = \varphi_i y_i P \tag{77}$$

and the liquid-phase fugacities are given by:

$$f_i^L = \gamma_i^{(P^r)} x_i f_i^{o(P^r)} \exp \frac{(P - P^r)\bar{v}_i^L}{RT} \tag{78}$$

The solution of the N equations of equilibrium must satisfy the two stoichiometric relations

$$\sum_{i=1}^{N} x_i = 1 \tag{79}$$

and

$$\sum_{i=1}^{N} y_i = 1 \tag{80}$$

The phase-equilibrium calculations most often encountered in the design of separation processes are bubble-point and dew-point calculations. In the first case, pressure (or temperature) and all of the liquid-phase mole fractions are given; the temperature (or pressure) and the vapor-phase mole fractions are to be calculated. In the second case, pressure (or temperature) and all of the vapor-phase mole fractions are given, and the temperature (or pressure) and the liquid-phase mole fractions are desired. The calculations involve the simultaneous solution of the N equations given by Equation 76 which satisfies Equations 79 and 80. These calculations are most conveniently performed by iteration schemes.

The solution of each of these four problems involves the same thermodynamic quantities and relationships; only the order of calculation and the convergence technique are different. It is, therefore, convenient to calculate those thermodynamic quantities in separate subroutines which can then be used with all of the main programs. The fugacity coefficients are calculated in subroutine PHIMIX, the activity coefficients $\gamma_i^{(PO)}$ in subroutine ACTCO, the reference fugacities in the subroutine RSTATE, and the partial molar volumes, $\bar{v}_i^L$, are calculated in subroutine VOLPAR. Details of the computer programs are given elsewhere (*26*).

BUBL P program. The main program, BUBL P, performs a bubble pressure calculation. The temperature and the liquid-phase mole fractions are given. The program finds the equilibrium pressure and vapor-phase mole fractions.

Figure 9 shows a schematic diagram of the method of solution used in the BUBL P program. The itera-

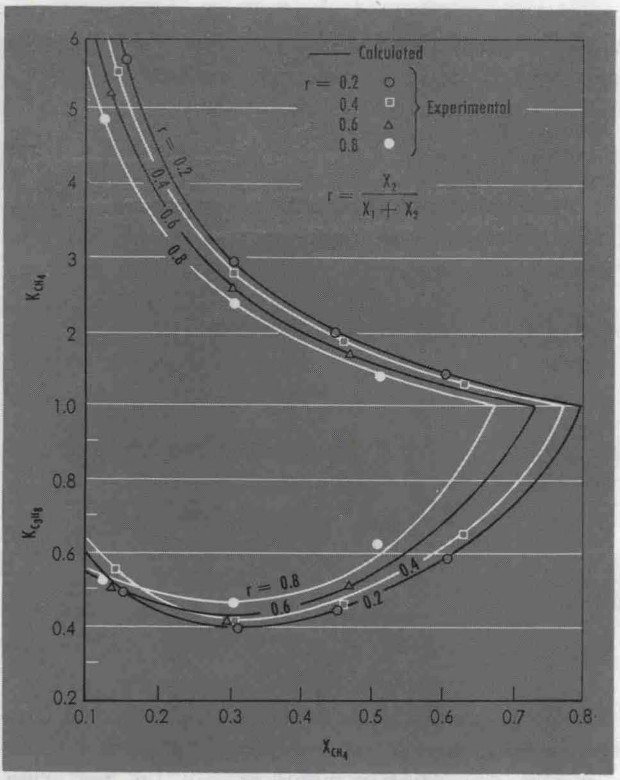

Figure 10. Vapor-liquid equilibrium constants for the n-pentane(1)–propane(2)–methane(3) system at 100° F.

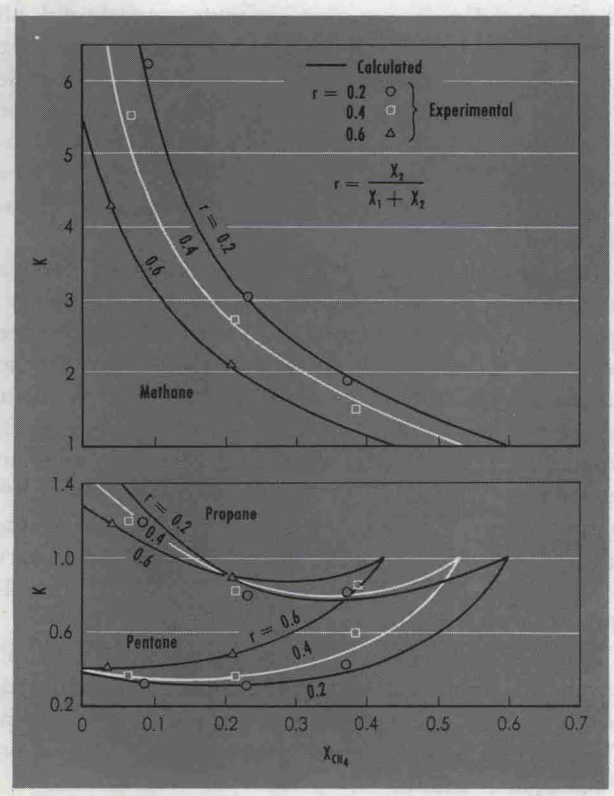

Figure 11. Vapor-liquid equilibrium constants for the n-pentane(1)–propane(2)–methane(3) system at 220° F.

tion scheme used is essentially the same as that discussed elsewhere (27). Data are read in by subroutine INPUT. Initial guesses for pressure and fugacity coefficients are then made for the first iteration. It is important that the solution be always approached from the ideal-gas side—i.e., a sufficiently low pressure and $\varphi_i = 1$. Use of an unreasonably high pressure as the first guess may cause divergence due to the large effect of a large Poynting correction. For this reason, each bubble-pressure calculation must always start from a low-pressure first guess; it is important not to use the result from a previous, unrelated bubble-pressure calculation which may have converged to a very high equilibrium pressure. We arbitrarily set the first guess of pressure at 100 psia. The speed of convergence is essentially independent of this value; however, neither a value of zero nor a very high value should be used.

Next, the main program reads in the known variable T and all x_i's. Subroutines RSTATE, ACTCO, and VOLPAR and then called to calculate those thermodynamic quantities which depend only on the known temperature and liquid-phase compositions.

Calculation of the liquid-phase fugacities begins the loop of iteration. The vapor-phase compositions are calculated, for the first time, by

$$y_i = f_i / P\varphi_i \tag{81}$$

and pressure is calculated by

$$P = \sum_{i=1}^{N} f_i / \varphi_i \tag{82}$$

The new pressure is then compared to the former value and, if it has changed, the vapor-phase fugacity coefficients (subroutine PHIMIX) are recalculated using the new pressure and vapor-phase compositions (after normalizing by SUMY). The loop is then re-entered by the recalculation of liquid-phase fugacity using Equation 78.

When an unchanging value of the pressure is achieved (within some small tolerance) the stoichiometry $\Sigma y_i = 1$ is tested. Usually this is satisfied when the pressure has attained an unchanging value. If $\sum y_i$ is not satisfied, the vapor-phase fugacity coefficients are recalculated and the loop is re-entered at the calculation of vapor-phase compositions. When the two conditions of unchanging pressure and $\sum y_i$ are met, the equations are all satisfied and the equilibrium results are printed out. Usually, convergence is attained after several iterations, taking a total time of about half a second on an IBM 7094 computer (for a ternary system).

Figures 10 to 13 and Tables IV to IX give examples of predicted bubble pressures and vapor compositions for some multicomponent systems uging binary data only. In the calculation for the ternary system acetylene–