General Correlations of Vapor-Liquid Equilibria

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The vapor-liquid equilibria ratio $K_i = y_i/x_i$ for the components of coexisting equilibrium vapor and liquid mixtures is a complex function of the conditions and compositions of the coexisting phases. Many investigators have attempted to develop a generalized method for predicting vapor-liquid equilibrium. However, most of these methods in their present form include some parameter (or parameters) which depends on the mixtures. In other words, most of these methods do not satisfy the need for generality. Chao and Seader (1961) developed a general correlation of vapor-liquid equilibria in hydrocarbon mixtures. Their method is quite popularly used by industry today. Lee and Edmister (1971) developed a new generalized method for predicting vapor-liquid equilibrium to compare with Chao-Seader's correlation.

When a reader applies Lee-Edmister's correlation to evaluate vapor-liquid equilibrium, he may find that the calculated result does not give a good comparison with the experimental result. This is because of an error in their correlation of activity coefficient in liquid solution γ_i. Lee and Edmister derived the activity coefficient γ_i from an expression of the excess Gibbs free energy of a mixture, which was proposed by them. A reader may not be able to follow their derivation to obtain the present form

$$\begin{aligned}\ln \gamma_i = V_i^L & \left[\sum_j^n \Phi_j B_{ij}^* - 1/2 \sum_j^n \sum_k^n \Phi_j \Phi_k B_{jk}^* \right] \\ & + \left[\sum_j^n x_j C_{ij}^* - 1/2 \sum_j^n \sum_k^n x_j x_k C_{jk}^* \right] \\ & + \left[\frac{\Phi_i}{x_i} \sum_j^n \Phi_j D_{ij}^* - \left(\frac{\Phi_i}{x_i} - 1/2 \right) \right. \\ & \left. \sum_j^n \sum_k^n \Phi_j \Phi_k D_{jk}^* \right] \qquad (1)\end{aligned}$$

It is not necessary that a correlation have any physical meaning. It is only necessary that it has a good formulation. Assuming Equation (1) is correct, Lee and Edmister defined the binary-pair parameter B_{ij}^* as

$$B_{ij}^* = \frac{1}{RT} [(\delta_i - \delta_j)^2 + 2\, l_{ij}\, \delta_i \delta_j] \qquad (2)$$

The extra "2" before l_{ij} should be removed in order to arrive at the same result claimed by Lee and Edmister. The correct form of B_{ij}^* is

$$B_{ij}^* = \frac{1}{RT} [(\delta_i - \delta_j)^2 + l_{ij}\, \delta_i \delta_j] \qquad (3)$$

l_{ij} was proposed by Lee and Edmister as follows:

$$l_{ij} = [q_1 + q_2 (T_{ri} T_{rj})^{1/2}] \left[\frac{(\delta_i^{1/2} - \delta_j^{1/2})^2}{(\delta_i \delta_j)^{1/2}} \right] \qquad (4)$$

The interaction constants C_{ij}^* and D_{ij}^* in Equation (1) and all the notations are the same as those given by Lee and Edmister.

As we can see, Lee-Edmister's correlation is very complicated. It is not surprising that we obtain more accurate results by using a more sophisticated correlation. Those readers who would like to use Lee-Edmister's correlation should make sure the application conditions are in the ranges of data given by the authors in their appendix. This correlation may give erroneous results even around the boundary of the given ranges for some systems, for example, a system containing methane or a nonhydrocarbon compound. The comparison of predicted K-values with observed data for methane—n-heptane system (Reamer et al., 1956) is shown in Table 1.

For a binary system calculation, a user may not realize how much more computing time Lee-Edmister's correlation will take to calculate a vapor-liquid equilibrium ratio K_i. However, the ratio of the computing time required by Lee-Edmister's correlation to that required by Chao-

Table 1. Comparison of Predicted K-Values with Observed Data for Methane—n-Heptane System (Reamer et al., 1956)

				Developed from observed K-value (%)			
				Methane		n-Heptane	
Temperature, °F	Pressure, lb/sq in. abs	K_1 (observed)	K_7 (observed)	Lee-Edmister	After correction	Lee-Edmister	After correction
100	200	15.416	0.0143	87.83	15.29	−20.76	−20.83
100	600	5.476	0.0111	68.89	9.77	−28.98	−29.63
100	1,000	3.487	0.0126	52.04	4.33	−23.51	−25.45
100	2,000	1.980	0.0398	18.65	−8.03	−10.15	−19.21
220	200	18.101	0.1113	79.56	6.53	0.38	0.32
220	600	6.333	0.0648	66.49	3.91	−8.32	−8.90
220	1,000	3.966	0.0582	54.05	1.04	−3.45	−5.22
220	2,000	2.126	0.0949	27.23	−5.75	3.77	−4.60
340	200	16.721	0.5107	86.36	7.44	0.18	0.15
340	600	5.882	0.2591	71.69	4.33	−2.28	−2.77
340	1,000	3.688	0.2242	54.17	−1.39	−0.94	−2.53
340	2,000	1.814	0.3519	20.02	−12.20	1.75	−6.62
460	400	5.443	0.7735	139.37	37.31	3.83	3.77

Seader's correlation can be expressed as follows:

$$\frac{\text{CPU time for Lee-Edmister's correlation}}{\text{CPU time for Chao-Seader's correlation}} = NC^m$$

CPU means central processor unit, NC is number of components in the system. The power m ranges from 1.43 for a three-component system to 1.56 for a ten-component system. The larger the NC, the larger the m. However, m is not expected to be larger than 2. For practical application, these correlations may be employed for a calculation of a distillation tower. In most of cases, iteration is required. Therefore, computing time consumed by Lee-Edmister's correlation becomes very critical.

In short, Lee-Edmister's correlation may be better for certain ranges given as ranges of data in their appendix. However, computing time required is serious, especially for a multicomponent system with iteration. For most hydrocarbon systems, Chao-Seader's correlation may be adequate for a design purpose.

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Trajectory Optimization Techniques in Chemical Reaction Engineering. II. Comparison of the Methods

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Although the theory and practice of methods for solving two-point boundary-value problems in chemical reaction engineering is quite well developed (*1* to *9*, *11*, *13*), a critical appraisal of these methods along the lines of that in the aerospace context (*10*) is lacking.

For obvious reasons only control vector iteration, boundary value iteration, and quasilinearization (which is really a subset of the first) will be considered here. Most other methods are variations of these three types. Observations, comments, and criticisms of the methods will be largely based on direct experience with them, although some conclusions may also be drawn from the literature.

Following Tapley and Lewallen (*10*) comparison will now be made on the basis of the following criteria:

1. Simplicity of formulation and ease of programming
2. Computer storage requirements
3. Convergence sensitivity
4. Stability
5. Convergence time

RECAPITULATION IN BRIEF

A short review of the methods of Boundary Condition and Control Vector Iteration and Quasilinearization will serve to pinpoint the basic differences in concept between these methods.

In Boundary Condition Iteration (BCI) (*9*) one guesses the missing boundary conditions—for example, the initial values of the adjoint variables—and integrates to the other boundary condition (say, the final adjoint variables) and the actual boundary conditions together with the transversality condition to calculate a new guess of the missing boundary condition.

Control Vector Iteration (CVI) uses the known boundary conditions to integrate from both ends of the interval, and this then constitutes one iteration which permits calculation of $\partial H/\partial u$ (which, according to the necessary condition of Pontryagin's Maximum Principle must be zero at the optimum) to step towards the optimum. In first-variation methods, the control function is corrected by an amount proportional to $\partial H/\partial u$, generally $\epsilon\,\partial H/\partial u$. Second-variation methods use a second-order expansion of H around the optimum and integration of additional (Riccati) costate equations (classical second-variation method) or without these Riccati equations (direct second-variation method) to achieve second-order convergence.

Quasilinearization (*4*) is effectively a subset of CVI in that stipulated boundary conditions are used, and successive approximations to the optimal control function are obtained by linearizing state and adjoint equations and solving, using a Newton-Raphson-Kantorovich method in function space. The quasilinearization method used here is that of Lee (*13*).

It is apparent that the foregoing observations are dependent to some extent on the numerical method of integration used. This is especially true of convergence time and stability of integration. The technique used throughout, except where noted, is the predictor-corrector method of Crane and Klopfenstein (*12*), with the Runge-Kutta-Gill method for starting. The problem used as a basis for comparison of the various algorithms is the well-known consecutive reaction system

$$A \rightarrow B \rightarrow C \tag{1}$$

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