LETTERS TO THE EDITOR

To the Editor:

A recent paper by Price and Danner (1987) claims that they developed "a new method of predicting adsorption equilibria which combines the thermodynamic and kinetic treatments of liquid adsorption." For adsorption from binary liquid mixtures, the thermodynamic method (Minka and Myers, 1973) is to equate the chemical potential in the adsorbed and liquid phases for each component:

$$a_1 = a_1' \exp\left[\frac{-(\phi - \phi_1^0)}{m_1 RT}\right] \quad (1)$$

$$a_2 = a_2' \exp\left[\frac{-(\phi - \phi_2^0)}{m_2 RT}\right] \quad (2)$$

where a_i is the activity of ith component in the liquid phase and a_i' is its activity in the adsorbed phase. ϕ is the free energy of immersion of the adsorbent in the liquid mixture in J/kg and ϕ_i^o refers to the free energy of immersion in the pure ith liquid. m_i is the saturaton capacity of the ith component in mol/kg.

The kinetic method attributed to Dabrowski (1983) is an extension of the phase-exchange reaction concept developed extensively by Everett (1964) to the case of molecules of unequal size. The "reaction" is:

$$rC_1(\text{ads.}) + C_2(\text{liq.}) = rC_1(\text{liq.}) + C_2(\text{ads.}) \quad (3)$$

where C_i is the ith component and r is the size ratio m_1/m_2. The chemical equilibrium constant associated with Eq. 3 is:

$$K = \frac{(a_1)^r a_2'}{(a_1')^r a_2} \quad (4)$$

Price and Danner (1987) proposed a "hybrid approach" that would combine these two methods. In fact, they are exactly equivalent because Eq. 4 may be derived from Eqs. 1 and 2 by simple algebra, without any kinetic arguments. The link between the phase equilibrium expressed by Eqs. 1 and 2 and the chemical equilibrium of Eqs. 3 and 4 is:

$$K = \exp\left[\frac{-(\phi_2^0 - \phi_1^0)}{m_2 RT}\right] \quad (5)$$

Price and Danner carried out extensive calculations to obtain an optimized value of K for Eq. 4. They could have obtained the value of K directly from Eq. 5. In fact, they compared their calculations with Eq. 5 and concluded that the values of K are in "excellent agreement." This is not surprising.

Finally, Price and Danner (1987) proposed to derive values of constants using Eq. 4 by optimizing its fit of experiment data for surface excess. This approach is impractical because there are too many unknowns: K, m_1, m_2 and the activity coefficient parameters. The set of experimental data examined by Price and Danner was unusual in that values of m_1, m_2, ϕ_1^0 and ϕ_2^0 were available from independent vapor-phase adsorption experiments. Usually these constants are unknown and a brute-force optimization cannot provide unique values for all of them.

Literature Cited

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2. Everett, D. H., "Thermodynamics of Adsorption from Solution," *Trans. Faraday Soc.*, **60**, 1803 (1964).
3. Minka, C., and A. L. Myers, "Adsorption from Ternary Liquid Mixtures on Solids," *AIChE J.*, **19**, 453 (1973).
4. Price, Jr., P. E., and R. P. Danner, "Prediction of Multicomponent Liquid Adsorption Equilibria," *AIChE J.*, **33**, 551 (1987).

Alan L. Myers
Dept. of Chemical Engineering
University of Pennsylvania
Philadelphia, PA 19104

Reply:

As Professor Myers states, ϕ_1^0 and ϕ_2^0 are not often available. For such cases, Eq. 5 will be difficult to use, and it would seem logical to regress a value of K_{ij} from available data. As described in our paper, K_{ij} is a function of composition except when the molecular sizes are identical or the bulk and surface phase compositions are the same. Hence, it is not obvious that the regressed values and those calculated by Eq. 5 will be "in excellent agreement."

We did not suggest that the adsorbent capacities m_1 and m_2 be regressed along with K_{ij} and the activity coefficient parameters. Clearly one cannot expect to regress unique values for so many parameters. We did find, however, that we could regress K_{ij} and the activity coefficient parameters and obtain values that were similar to those obtained independently. In any case, the simplicity of the calculations in comparison to the thermodynamic method is an important advantage of the hybrid model.

Peter E. Price, Jr.
and
Ronald P. Danner
Dept. of Chemical Engineering
The Pennsylvania State University
University Park, PA 16802

To the Editor:

This letter discusses the equivalence between two chain rule algorithms in simultaneous-modular flowsheeting (Chen and Stadtherr, 1985; Chan and Prince, 1986).

Let p and q denote respectively the connecting streams and the set of tear and design variables. Let the connecting streams be given by:

$$f(p, q) = 0 \quad (1a)$$

and the torn stream (and retention variable) equations by:

$$g(p, q) = 0 \quad (1b)$$

Then Eq. 1a can be used to eliminate p, giving the torn stream (and retention variable) equations explicitly in terms of q.

$$\bar{g}(p(q), q) = 0 \quad (2)$$

The derivatives of $\bar{g}$ with respect to q can

then be obtained by the chain rule, giving:

$$\frac{\partial \bar{g}}{\partial q^T} = \frac{\partial g}{\partial q^T} - \frac{\partial g}{\partial p^T}\left[\frac{\partial f}{\partial p^T}\right]^{-1}\frac{\partial f}{\partial q^T} \quad (3)$$

Equations 1 to 3 summarize the chain rule algorithm of Chen and Stadtherr.

Since the flowsheet has been torn, the matrix $\partial f/\partial p^T$ is lower triangular. Connecting stream p_j does not depend on any connecting stream p_k downstream. Furthermore, the unit output p_j is a function of the unit inputs, giving:

$$f(p, q) = f_j(p_j, p_i, q) = p_j - \bar{f}_j(p_i, q) = 0 \quad (4)$$

where p_i are the connecting streams upstream of p_j. From Eq. 4, it is clear $\partial f/\partial p^T$ is lower triangular with 1s down the diagonal. Consequently, its inverse can be obtained by forward substitution. This forward substitution and the matrix multiplications in Eq. 3 are performed automatically from one unit to the next as they are executed according to the calculation order in the algorithm of Chan and Prince. Consequently, chaining in the algorithm of Chen and Stadtherr is simultaneous while that in the algorithm of Chan and Prince is sequential. The correspondence between the above notation of Chen and Stadtherr, and that of Chan and Prince is:

- p are the Type 1 outputs (also Type 1 inputs)
- q are the Type 2 inputs
- f are the equations for the Type 1 outputs
- g are the equations for the Type 2 outputs, where p, q, f and g were used by Chen and Stadtherr

The matrices $\partial g/\partial q^T$ are the local derivatives of Type 2 outputs with respect to the Type 2 inputs; $\partial g/\partial p^T$, the local derivatives of Type 2 outputs with respect to the Type 1 inputs; and $\partial f/\partial q^T$, the local derivatives of Type 1 outputs with respect to the Type 2 inputs, where by the term "local derivatives," the inputs and outputs referred to belong to the same unit.

Finally, the matrix $[\partial f/\partial p^T]^{-1}$ contains the chains of local derivatives required for chaining between the units producing the Type 2 outputs and those receiving the Type 2 inputs.

An example used by Chan and Prince is given below to demonstrate this equivalence between the two algorithms. The flowsheet in Figure 1 of Chan and Prince is reproduced (without the design and retention variables) in Figure 1 here. For simplicity, only the tear variables and calculated values of the torn streams are considered. Therefore,

$$p^T = [b, d, f, g, q],$$

$$f(p, q) = \begin{bmatrix} b - b(a, c) \\ d - d(b) \\ f - f(b) \\ g - g(d) \\ q - q(g, p) \end{bmatrix} = 0,$$

$$q^T = [a, c, p],$$

$$g(p, q) = \begin{bmatrix} a - h(d) \\ c - e(b) \\ p - t(q, f) \end{bmatrix} = 0,$$

The matrices required for chain ruling using the algorithm of Chen and Stadtherr are:

$$\begin{bmatrix} \frac{\partial f}{\partial p^T} & \frac{\partial f}{\partial q^T} \\ \frac{\partial g}{\partial p^T} & \frac{\partial g}{\partial q^T} \end{bmatrix} = \begin{bmatrix} \underline{I} & \underline{0} & \underline{0} & \underline{0} & \underline{0} & \frac{-\partial b}{\partial a^T} & \frac{-\partial b}{\partial c^T} & \underline{0} \\ \frac{-\partial d}{\partial b^T} & \underline{I} & \underline{0} & \underline{0} & \underline{0} & \underline{0} & \underline{0} & \underline{0} \\ \frac{-\partial f}{\partial b^T} & \underline{0} & \underline{I} & \underline{0} & \underline{0} & \underline{0} & \underline{0} & \underline{0} \\ \underline{0} & \frac{-\partial g}{\partial d^T} & \underline{0} & \underline{I} & \underline{0} & \underline{0} & \underline{0} & \underline{0} \\ \underline{0} & \underline{0} & \underline{0} & \frac{-\partial q}{\partial g^T} & \underline{I} & \underline{0} & \underline{0} & \frac{-\partial q}{\partial p^T} \\ \underline{0} & \frac{-\partial h}{\partial d^T} & \underline{0} & \underline{0} & \underline{0} & \underline{I} & \underline{0} & \underline{0} \\ \frac{-\partial e}{\partial b^T} & \underline{0} & \underline{0} & \underline{0} & \underline{0} & \underline{0} & \underline{I} & \underline{0} \\ \underline{0} & \underline{0} & \frac{-\partial t}{\partial f^T} & \underline{0} & \frac{-\partial t}{\partial q^T} & \underline{0} & \underline{0} & \underline{I} \end{bmatrix}$$

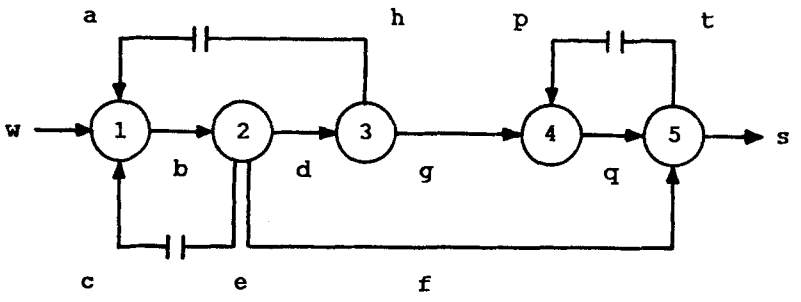

Figure 1.

and

$$\left[\frac{\partial f}{\partial p^T}\right]^{-1} = \begin{bmatrix} \underline{I} & \underline{0} & \underline{0} & \underline{0} & \underline{0} \\ \frac{\partial d}{\partial b^T} & \underline{I} & \underline{0} & \underline{0} & \underline{0} \\ \frac{\partial f}{\partial b^T} & \underline{0} & \underline{I} & \underline{0} & \underline{0} \\ \frac{\partial g}{\partial d^T}\frac{\partial d}{\partial b^T} & \frac{\partial g}{\partial d^T} & \underline{0} & \underline{I} & \underline{0} \\ \frac{\partial q}{\partial g^T}\frac{\partial g}{\partial d^T}\frac{\partial d}{\partial b^T} & \frac{\partial q}{\partial g^T}\frac{\partial g}{\partial d^T} & \underline{0} & \frac{\partial q}{\partial g^T} & \underline{I} \end{bmatrix}$$

It is a simple matter then to show:

$$\frac{\partial g}{\partial p^T}\left[\frac{\partial f}{\partial p^T}\right]^{-1}\frac{\partial f}{\partial q^T} = \begin{bmatrix} \frac{\partial h}{\partial a^T} & \frac{\partial h}{\partial c^T} & \frac{\partial h}{\partial p^T} \\ \frac{\partial e}{\partial a^T} & \frac{\partial e}{\partial c^T} & \frac{\partial e}{\partial p^T} \\ \frac{\partial t}{\partial a^T} & \frac{\partial t}{\partial c^T} & \frac{\partial t}{\partial p^T} \end{bmatrix}$$

$$= \begin{bmatrix} \frac{\partial h}{\partial d^T}\frac{\partial d}{\partial b^T}\frac{\partial b}{\partial a^T} & \frac{\partial h}{\partial d^T}\frac{\partial d}{\partial b^T}\frac{\partial b}{\partial c^T} & \underline{0} \\ \frac{\partial e}{\partial b^T}\frac{\partial b}{\partial a^T} & \frac{\partial e}{\partial b^T}\frac{\partial b}{\partial c^T} & \underline{0} \\ \frac{\partial t}{\partial q^T}\frac{\partial q}{\partial g^T}\frac{\partial g}{\partial d^T}\frac{\partial d}{\partial b^T}\frac{\partial b}{\partial a^T} + \frac{\partial t}{\partial f^T}\frac{\partial f}{\partial b^T}\frac{\partial b}{\partial a^T} & \frac{\partial t}{\partial q^T}\frac{\partial q}{\partial g^T}\frac{\partial g}{\partial d^T}\frac{\partial d}{\partial b^T}\frac{\partial b}{\partial c^T} + \frac{\partial t}{\partial f^T}\frac{\partial f}{\partial b^T}\frac{\partial b}{\partial c^T} & \frac{\partial t}{\partial q^T}\frac{\partial q}{\partial p^T} \end{bmatrix}$$

The results on the r.h.s. are identical to those obtained with the algorithm of Chan and Prince, as shown in Table 2 of that reference.

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W. K. Chan and R. G. H. Prince
Dept. of Chemical Engineering
University of Sydney
N.S.W., 2006, Australia