TO THE EDITOR:

Luus (1972) has pointed out the sensitivity of the Arrhenius Equation

$$\ln k = \ln A - \frac{E}{RT} \qquad (1)$$

to small errors in E/R. However, his suggested substitute equation $k = a\,e^{bT}$ is undesirable because of its improper behavior on extrapolation to temperatures outside the fitted range (Aris, 1969).

A simpler solution to the difficulty is to fit the following form of Equation (1):

$$\ln k = \ln k_0 - \frac{E}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right] \qquad (2)$$

Here $\ln k_0$ and $1/T_0$ are the weighted mean values of $\ln k$ and $1/T$ for the given kinetic data.

Equation (2) is statistically preferable to Equation (1) because its constants are independently estimated. Furthermore, it does not demand such high precision of the constant E/R. Specification of E/R to 1% accuracy will suffice to represent most kinetic data, if Equation (2) is used.

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TO THE EDITOR: ON LOCAL STABILITY OF TUBULAR REACTORS

In a recent paper Clough and Ramirez (1972) reported a study of tubular reactor stability and presented stability criteria which were based on the negative definitness of matrix C. They used the method of principal minors, which is valid (necessary and sufficient conditions) for symmetric matrices only. However, their matrix C is not symmetric. The purpose of this letter is to point out specific errors and to present correct stability criteria. The following items should be noted:

1. Following Equation (A10) an assumption (rather than a fact) that PA_{bb} is symmetric has been made. Therefore, an additional restriction has to be imposed on the system equation given under the theorem on page 394, that is, PA_{bb} is symmetric (or A_{bb} is diagonal).

2. The matrix C on page 395 is not symmetric and therefore Equation (12) is incorrect. To correct this we define a new symmetric matrix $\hat{C}$ in terms of their matrix C, $\hat{C} = (C + C^T)/2$. With this symmetric matrix $\hat{C}$ we can apply the method of principal minors to insure negative definitness of C. The resulting correct expression is

$$\left(\frac{\partial P_1}{\partial x} + 2\,B_nR_1P_1\right)\left(\frac{\partial P_2}{\partial x} - 2B_yR_2P_2\right) - (B_nR_2P_1 - B_yR_1P_2)^2 > 0 \qquad (1)$$

which replaces their Inequality (12). Also the statement following Inequality (12) should be modified. For instance, we can let $P_1 = P_2 = \exp(-Kx)$. Then, it can be shown that by letting

$$K > [(B_nR_2 + B_yR_1)^2 + (B_yR_2 - B_nR_1)^2]^{1/2} - (B_yR_n - B_nR_1) \qquad (2)$$

Inequality (1) can be satisfied. Note that our Inequality (2) implies their Inequality (11) and their conclusion follows.

3. The matrix C in Appendix B is unsymmetric and the inequalities following the Matrix C are incorrect, that is, Inequalities (B13) through (B19). Using the symmetric matrix $\hat{C}$, the correct inequalities are

$$\left(r_2\frac{\partial P_1}{\partial x} + 2\,P_1B_1R_1\right)\left(r_2\frac{\partial P_2}{\partial x} - 2\,P_2B_2R_2\right) - (P_1B_1R_2 - P_2B_2R_1)^2 > 0 \qquad (3)$$

$$-2\frac{r_1}{r_2}P_1\left(r_2\frac{\partial P_1}{\partial x} + 2\,P_1B_1R_1\right)\left(r_2\frac{\partial P_2}{\partial x} - 2\,P_2B_2R_2\right) - \left(\frac{\partial P_1}{\partial x}\right)^2\left(r_2\frac{\partial P_2}{\partial x} - 2\,P_2B_2R_2\right) + 2\frac{r_1}{r_2}P_1\,(P_1B_1R_2 - P_2B_2R_1)^2 < 0 \qquad (4)$$

Note that Inequality (4) implies Inequality (3). Therefore, we look at Inequality (4). Inequality is satisfied if

$$r_2(K_1 - r_1)^2 + r_1(4\,B_1R_1 - r_1r_2) < 0 \qquad (5)$$

The least restrictive condition under which Inequality (5) holds, is when $K_1 = r_1$. When this occurs

$$\frac{B_1R_1}{r_1r_2} < 1/4 \qquad (6)$$

Also, in their Inequality (B20) replace C by $\hat{C}$, and there is a typographical error, $\partial P_2/\partial x$ instead of $\partial P_1/\partial x$ in the second term which multiplies the remaining terms. In addition, remove the first r_2 from the right-hand side of Inequality (B21). This corrected condition is then satisfied by their Inequality (B12).

4. Finally we note that the conclusion made on page 396 indicating the stability for $q = 17.6$ is incorrect, as can be seen from our Condition (6). Also, for $q \geq 24.0$ no conclusion can be made unless B_1R_1/r_1r_2 is less than 0.25.

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TO THE EDITOR: SENSITIVITY METHODS REVISITED

Hwang and Seinfeld (1972) recently presented what was claimed to be a new algorithm for the estimation of parameters arising from the analysis of systems modeled by ordinary differential equations. The algorithm which was developed is not novel, but is the classic Gauss-Newton iteration method as applied and previously presented for the estimation of parameters arising from integral data. The primary contribution of their paper is the development of this classic algorithm from an observability point of view. In addition, as a minor extension of this classic algorithm, it is suggested by conjecture

that different weighting matrices be used to insure a global minimum has been attained.

The following expression for the iterative change in the parameter vector was derived by Hwang and Seinfeld (using their notation and equation numbering directly):

$$\mathbf{p}^{(i)} = \epsilon\, \mathbf{K}^{(i)}\,(T)^{-1} \int_0^T \boldsymbol{\theta}^{(i)}\,(t)^T\, \mathbf{Q}(t)\,[\mathbf{y}(t) - \mathbf{h}(t, \mathbf{x}^{(i)})]\,dt \tag{21}$$

where

$$\mathbf{K}^{(i)}(T) = \int_0^T \boldsymbol{\theta}^{(i)}(t)^T\, \mathbf{Q}(t)\, \boldsymbol{\theta}^{(i)}\,(t)\, dt \tag{19}$$

Equations (19) and (21) constitute the Gauss-Newton method as applied to the analysis of integral data. This follows from the fact that in Equation (21) the integral term is the vector of first derivatives of the objective function with respect to the parameters, that is, the gradient vector of the objective function. Similarly Equation (19) constitutes the matrix of second derivatives of the objective function. The use of the Gauss-Newton method for the analysis of integral data was suggested in the excellent review by Bard and Lapidus (1968). This same algorithm was published and applied to ordinary differential equations by Medler and Hsu (1969).

The Gauss-Newton method is only one member of the class of parameter estimation methods known as gradient or sensitivity methods which require the simultaneous integration of the sensitivity matrix differential equations along with the state equations. Some other members of this class include: steepest descent, Gauss-Newton, Fletcher-Powell-Davidon, and Marquardt's method. The use of most of these in parameter estimation has recently been reviewed by Bekey (1970).

It was also proposed that for the case where the matrix $\mathbf{K}$ is nearly singular, use of the approximate pseudoinverse results in less computational difficulties in the resulting iterative scheme. This conclusion was based upon the work of Klinger (1968). The approximate pseudoinverse has the following form, where σ is an adjustable scalar:

$$\mathbf{K}_\sigma{}^{-1} = (\mathbf{K}^T\mathbf{K} + \sigma\mathbf{I})^{-1}\,\mathbf{K}^T$$

For $\mathbf{K}$ nearly singular it is desirable to have σ large and for $\mathbf{K}$ not singular σ should be small. Neither Hwang and Seinfeld or Klinger suggest any procedure to determine reasonable choices for σ. The use of the approximate pseudoinverse has some relation to Marquardt's (1963) procedure for nonlinear regression. The analogous relation in Marquardt's procedure to the above equation is shown by the following expression where σ is again an adjustable scalar.

$$(\mathbf{K} + \sigma\mathbf{I})^{-1}$$

Thus in both procedures when σ takes on an appropriately small value the resulting algorithm is the Gauss-Newton Method. For σ large Marquardt's procedure is the method of steepest descent. The corresponding direction for large σ using the approximate pseudoinverse form is in the direction of steepest descent but rotated by the matrix of second derivatives. It was stated but not proved that for large values of σ the magnitude of $\delta\mathbf{p}^{(i)}$ will be decreased. This conclusion is definitely true in the direction of steepest descent, but it remains to be proved that this is so in the direction found through application of expression for the approximate pseudoinverse.

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TO THE EDITOR:

Tassios' modification of the Wilson equation [*AIChE J.*, **17**, 1367 (1971)] has among others the following advantage:

Certain restraining conditions between the constants of the Wilson equation must be fulfilled if the expressions for three- and more-component systems are to be consistent with the theoretical model.

Wilson's original constants A_{ij} and A_{ji} are defined by

$$A_{ij} = (V_j/V_i)\,[\exp -(g_{ij} - g_{ii})/(RT)] \tag{1}$$

$$A_{ji} = (V_j/V_j)\,[\exp -(g_{ij} - g_{jj})/(RT)] \tag{2}$$

where V_i and V_j are liquid molar volumes of components i, j, and R gas constant, and $(g_{ij} - g_{ii})$, $(g_{ij} - g_{jj})$ denote the Wilson energy terms.

For the ternary system it can be written

$$\ln(A_{ij}/A_{ji}) - 2\ln(V_j/V_i) = (g_{ii} - g_{jj})/(RT) \tag{3}$$

$$\ln(A_{ik}/A_{ki}) - 2\ln(V_k/V_i) = (g_{ii} - g_{kk})/(RT) \tag{4}$$

$$\ln(A_{jk}/A_{kj}) - 2\ln(V_k/V_j) = (g_{jj} - g_{kk})/(RT) \tag{5}$$

It is evident from (3), (4), and (5) that Wilson constants in ternary systems are related by the equation

$$\ln(A_{jk}/A_{kj}) = \ln(A_{ik}/A_{ki}) - \ln(A_{ij}/A_{ji}) \tag{6}$$

which can be written in the form

$$(A_{jk}/A_{kj}) = (A_{ik}/A_{ki})\,(A_{ji}/A_{ij}) \tag{7}$$

The extension to four- and more-component systems is straightforward and it can be shown that $[0.5n(n-3)+1]$ restraining conditions similar to Equation (7) must be fulfilled in the n-component system.

It is evident from the preceding discussion that we cannot use constants evaluated from binary experimental data directly for the characterization of three and more component systems if we wish to be consistent with Wilson's model. The entire adjustment for the multicomponent system must be made in such a way that restraining conditions (7) are fulfilled.*

Tassios' modification of the Wilson equation fulfills the boundary condition (7) automatically as it is seen if we insert the opposite of energy of vaporization of pure component as g_{ii} (respectively g_{jj} and g_{kk}) into Equations (3), (4), and (5).

It can be concluded that the Wilson-Tassios constants evaluated from binary experimental data are free of restraining conditions and can be used directly for the characterization of three and multicomponent systems.

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* Many authors have not taken into account restraining condition (7) for the correlation of three and more component systems. [See Hudson, J.W., and M. van Winkle, *Ind. Eng. Chem. Process Design Develop.*, 466 (1970) or Prausnitz, J.M., *Molecular Thermodynamics of Fluid-Phase Equilibria*, p. 250, Prentice-Hall, Englewood Cliffs, N.J. (1969)]. Their procedure is therefore not fully consistent with Wilson's model.