A Critical Review of Correlations for the Critical Properties of Defined Mixtures

An extensive critical evaluation of available correlations for predicting critical properties of binary defined hydrocarbon as well as some multicomponent hydrocarbon and hydrocarbon-nonhydrocarbon mixtures is presented using all available literature data. The Li method is recommended for critical temperature prediction based upon its accuracy and simplicity, although the Chueh-Prausnitz method is equivalent in accuracy. The Kreglewski method is most accurate for critical pressure prediction. All methods evaluated yielded high errors for the critical properties of methane-containing mixtures. Current correlations on critical volume are discussed, and correlational work on prediction using an excess volume approach is described.

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SCOPE

A knowledge of the critical behavior of mixtures is important in order to determine the existing phase conditions or permissible operating ranges in reactors and mass transfer equipment. Because of the difficulty of measuring the critical properties of mixtures experimentally, it is desirable to have reliable methods for correlating and predicting these properties.

A survey of the literature indicates that a large number of correlations have been advanced for predicting the critical state of hydrocarbon mixtures. These methods have been evaluated. Methods are recommended for estimation of the critical properties of binary and multicomponent mixtures. Areas where additional work is required are also discussed.

CONCLUSIONS AND SIGNIFICANCE

An extensive evaluation of available correlations for the critical properties of defined mixtures has been made. The Li (1971) and the Chueh-Prausnitz (1967b) equations are equivalent in accuracy for calculation of the critical temperature of defined binary and multicomponent systems as well as hydrocarbon-nonhydrocarbon systems. Critical pressure of binary hydrocarbon systems not containing methane is best predicted by the Kreglewski (1969) method using the Li equation to estimate critical temperature. No accurate method currently exists for estimating critical pressure of binary, methane-containing systems.

Additional experimental data and correlational work on critical volumes are required before any prediction method can be recommended. An indirect approach to critical pressure determination using an equation of state can be used after an accurate method of predicting critical volume is developed. An approach using excess volume criteria appears to be promising.

Many correlations have been developed for predicting true critical properties of mixtures. One of three approaches is generally followed in developing these correlations.

The empirical approach involves calculations of the form

$$G_c = \sum_{i=1}^{n} x_i G_{ci} + G_{\text{corr}}$$

where G_c is the critical property desired and G_{corr} is a correction term which is often called the *excess* property of the mixture. Excess properties are normally estimated from empirical relations.

The second approach is based on the rigorous thermodynamic conditions for the critical state, that is, the second and third partial derivatives of the molar Gibbs free energy G with respect to composition at constant temperature and pressure must be equal to zero. Determination of T_c, V_c, and P_c for the mixtures involves a simultaneous solution of an extended form of the derivatives and an equation of state such as reported by Spear et al. (1971).

The third approach is the theory of conformal solutions which states that all thermodynamic properties of a mixture can be evaluated from those of the pure compounds if the components conform to certain simple postulates of statistical mechanics. A conformal solution is one whose pair potential as a function of intermolecular distance $u_{ij}(r)$ is related to that of a reference species $u_{00}(r)$ by

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the equation

$$u_{ij}(r) = f_{ij}\, u_{00}\,(g_{ij}, r)$$

where f_{ij} and g_{ij} are constants for a given mixture depending only on the chemical nature of the components. f_{ij} is usually called the energy parameter while g_{ij} is related to the intermolecular distance r^* at the minimum point of the potential energy curve $u(r)$.

Correlations derived by the empirical and conformal solution approaches have been evaluated in this study. The classical thermodynamic approach was not considered because generalization to multicomponent mixtures is not practicable.

DATA SOURCES

An extensive literature search was made to locate critical property data for binary hydrocarbon-hydrocarbon, hydrocarbon-nonhydrocarbon, and multicomponent mixtures. In the compilation of this data set, only experimental values were considered, that is, properties calculated or obtained by extrapolation from a nomograph were eliminated. The final data set is composed of the following:

	Number of data sets	Number of points
Binary Hydrocarbon-Hydrocarbon		
Critical temperature	135	1241
Critical pressure	122	1171
Critical volume	28	161
Binary Hydrocarbon-Nonhydrocarbon		
Critical temperature	74	430
Critical pressure	57	352
Critical volume	8	36
Multicomponent		
Critical temperature	35	233
Critical pressure	38	245

The data for the binary hydrocarbon-hydrocarbon mixtures are summarized in greater detail in Table 1. The paucity of critical volume data results from the fact that it is the most difficult of the critical properties to measure and little experimental work has been initiated.

CRITICAL TEMPERATURE

The critical temperature of the defined mixture was predicted by eight methods, all empirical in nature except for the method of Kreglewski (1969) which was developed from the theory of conformal solutions.

The methods and parameters required for use of each are listed in Table 2. The simplified Chueh-Prausnitz and Barner-Quinlan methods were originally developed to generate pseudocritical properties but were evaluated in this work for possible extension to true critical prediction. Direct computer evaluation was made for the methods of Li (1971), simplified Chueh-Prausnitz (1967a), Kreglewski (1969), and Ekiner-Thodos (1965, 1967). Since the other methods were either partially or totally graphical in nature, major auxiliary calculations were necessary before a computer evaluation could be made. The values of the parameters characterizing the 1-2 interactions needed for the techniques of Grieves-Thodos (1962), Barner-Quinlan (1969), and Chueh-Prausnitz (1967b) were determined as a function of their correlating parameters using a least squares regression technique. Modifications of the Chueh-Prausnitz interaction parameters as presented by Schick and Prausnitz (1968) were utilized. For the Smith-Watson (1937) charts a table-lookup (two-dimensional array) was used. In this case the value of T_c is determined by a double search of the array, first to locate the respective specific gravity and then in the opposite direction to find the corresponding average normal boiling point.

The results of testing the hydrocarbon-hydrocarbon binary data set for these eight correlations are summarized in Table 2. With the exception of the Kreglewski and Grieves-Thodos methods, where required parameters were unavailable or out of range, all of the approaches were able to handle the entire data set. The method of Li, the least complicated of the eight correlations, gave the most accurate predictions with the method of Prausnitz also giving satisfactory results. All methods yield poor results for systems containing methane.

Only the Li and Chueh-Prausnitz correlations were tested for prediction of the critical temperature of hydrocarbon-nonhydrocarbon (polar) and multicomponent systems. When dealing with nonhydrocarbon systems separate equations for τ_{12} (Chueh-Prausnitz interaction parameter) are given for mixtures containing carbon dioxide, hydrogen sulfide, and carbon monoxide. Li reports a high

TABLE 1. TYPES OF BINARY MIXTURES IN HYDROCARBON-HYDROCARBON CRITICAL TEMPERATURE DATA SET

Binary system	Number in data set
Paraffin	
Paraffin	66*
Olefin	7
Acetylene	1
Naphthene	17°
Aromatic	14
Olefin	
Olefin	2
Acetylene	3
Aromatic	1
Naphthene	
Naphthene	6
Aromatic	9
Aromatic	
Aromatic	9
Total	135

* 12 include methane as a component.
° 2 include methane as a component.

TABLE 2. OVERALL RESULTS FOR THE EVALUATION OF METHODS FOR PREDICTING THE TRUE CRITICAL TEMPERATURE OF DEFINED MIXTURES

Correlation	Parameters required	Avg. deviation, K
Li (1971)	$T_{c1}, T_{c2}, x_1, V_{c1}, V_{c2}$	3.44
Chueh-Prausnitz (1967b)	$T_{c1}, T_{c2}, x_1, V_{c1}, V_{c2}, \tau_{12}$	3.92
Simplified Chueh-Prausnitz (1967a)	$T_{c1}, T_{c2}, x_1, V_{c1}, V_{c2}$	4.28
Smith-Watson (1937)	MABP, MAG	6.22
Grieves-Thodos (1962)	$T_{c1}, T_{c2}, x_1, T_{b1}, T_{b2}, A_{12}, A_{21}$	7.17
Kreglewski (1969)	$T_{cp}, \Delta_1, \Delta_2, V_\phi^*, V_1^*, V_2^*$	7.35
Ekiner-Thodos (1965, 1967)	$T_{cp}, x_1, A, B, M_1, M_2$	7.50
Barner-Quinlan (1969)	$T_{c1}, T_{c2}, x_1, V_{c1}, V_{c2}, k_{12}$	10.72

error for mixtures of hydrocarbons containing CO and CO_2 but does not correct for it.

Both equations were tested with the hydrocarbon-nonhydrocarbon data sets described earlier with summarized results given in Table 3. As expected the Chueh-Prausnitz approach is more accurate for mixtures containing carbon dioxide, carbon monoxide, and hydrogen sulfide. Both methods predict the critical temperature of the highly nonideal helium-*n*-butane system rather well; however, the Chueh-Prausnitz approach appears to be superior for hydrogen systems. The overall error reported for the Chueh-Prausnitz correlation is biased by the results for ethyne-ammonia and *n*-decane-hydrogen sulfide while the error for the Li correlation is biased by the *n*-hexane-hydrogen system. In general, both correlations did an adequate job of predicting the critical temperature of nonhydrocarbon mixtures. The overall errors are low when the large differences in the polarities of the components are considered.

Prausnitz's method can be generalized for mixtures containing any number of components. The generalized equation is

$$T_{cm} = \sum_{i}^{n} \theta_i T_{ci} + \sum_{i}^{n} \sum_{j}^{n} \theta_i \theta_j \tau_{ij} \qquad (1)$$

where

$$\theta_i = \frac{x_i V_{ci}^{2/3}}{\sum x_i V_{ci}^{2/3}}$$

and τ_{ij} for each interacting pair of molecules is determined from the relationships derived earlier for the binary mixture. Prausnitz tested Equation (1) with a limited data set of six ternary systems, two quaternary systems, and two quinary systems. He reports an overall deviation of 0.4%.

Li did not formulate equations for multicomponent systems although his equation can easily be extended to higher-order systems. For any mixture, Li's equation has the following form:

$$T_{cm} = \sum_{i} \phi_i T_{ci} \qquad (2)$$

where

$$\phi_i = \frac{x_i V_{ci}}{\sum_{i} x_i V_{ci}}$$

The data set described earlier and containing systems with three to nine components, was used to evaluate both equations. The results of the evaluation are summarized in Table 4 and indicate that both equations are of equivalent accuracy although the method of Chueh-Prausnitz requires an additional $n(n-1)/2$ terms. The overall absolute error of 10.7°K is reasonable for the majority of engineering purposes. The predicted values agree for mixtures containing naphthenes or aromatics and higher-order systems without methane. The error is much higher for systems containing methane and increases as the number of components increases.

Detailed results of testing for each of the data sets are available from the authors.

CRITICAL PRESSURE

Sutton (1965) has noted that the dependence of the critical pressure on composition is more nonlinear than that of the critical temperature and critical volume. In many systems a plot of critical pressure versus mole fraction shows a sharp maximum and a point of inflection, suggesting that prediction of critical pressure may be best approached indirectly through a correlation with the critical temperature and critical volume.

Table 3. Summary of the Results of the Evaluation of the Li and Chueh-Prausnitz Correlations for Estimating the True Critical Temperature of Hydrocarbon-Nonhydrocarbon Mixtures

System type	Data points	Avg. deviation, K: Chueh-Prausnitz	Avg. deviation, K: Li
Hydrocarbon-carbon monoxide	9	0.37	13.49
Hydrocarbon-carbon dioxide	47	6.46	17.00
Hydrocarbon-hydrogen sulfide	35	5.69	8.01
Hydrocarbon-nitrogen, oxygen, argon, or helium	32	5.01	12.08
Hydrocarbon-2-propanone	52	8.37	9.59
Hydrocarbon-ammonia	9	45.91	18.56
Oxygen-argon-nitrogen-carbon monoxide	24	0.16	0.57
Hydrocarbon-fluorinated compound	161	4.42	6.07
Hydrocarbon-alcohol	33	10.03	10.36
Miscellaneous	28	—	—
Overall	430	7.93	10.17

An indirect approach utilizes an equation of state to derive the critical pressure of the mixture. The critical temperature and critical volume must be known or predicted. Direct approaches are similar to those for critical temperature and calculate the critical pressure of the mixture from the critical pressure of the components and an interaction parameter.

The method of Chueh and Prausnitz (1967b) utilizes such an indirect approach to determine the critical pressure of defined binary mixtures. The critical pressure is derived from the Redlich-Kwong (1949) equation of state with a number of minor modifications for the constants *a* and *b*. The critical temperature and critical volume for use in this equation are determined from correlations presented by Chueh and Prausnitz. This approach was evaluated with the hydrocarbon-hydrocarbon portion of the data set described earlier with an overall error of 5.6%. The results indicate that the correlation was particularly inaccurate for systems containing methane, acetylene, and cis-decalin. In general, the error was magnified as the ratio of the molecular weights of the components becomes two or greater.

Mixtures Containing Methane. Thodos and Akijama (1970) used an excess property approach in deriving an expression for critical pressure. This method required the pseudocritical pressure, the mixture composition, and four binary methane interaction coefficients which are generalized as functions of a critical pressure-molecular weight ratio.

Grieves and Thodos (1962) developed a correlation which is basically graphical although a certain amount of trial and error is also involved. The ratio of the actual critical pressure to the pseudo-critical pressure is obtained graphically as a function of the mole fraction of methane and also a boiling point parameter T_b'/T_b chosen to represent the differences in the properties of the components. T_b' is the molar average of the normal boiling points of two components and T_b is the boiling point of the mixture at atmospheric pressure. The atmospheric boiling point is calculated, assuming Raoult's law is valid, by a trial-

and-error method.

Each of these correlations was evaluated with the methane portion of the critical pressure hydrocarbon-hydrocarbon data set as summarized in Table 5. In the Grieves-Thodos evaluation the Frost-Kalkwarf (1953) equation was used to determine the vapor pressure of the pure compounds. The overall values given for these correlations correspond to an average error of approximately 10% with correlations developed by Thodos et al. showing some improvement over the method of Prausnitz. None of the correlations appear accurate enough to recommend for general use, although the Thodos correlations give better predictions.

Methane Free Mixtures. In the original evaluation, the Chueh-Prausnitz correlation was more accurate for methane-free mixtures. However, since the errors were high for some binary systems, methods proposed by Ekiner and Thodos (1966) and Kreglewski and Kay (1969) as well as the Smith and Watson (1937) chart were evaluated.

Ekiner and Thodos (1966) obtained an expression for the critical pressure of methane-free binary hydrocarbon mixtures which was dependent on the pseudocritical pressure, the composition of the mixture, and three binary interaction parameters which have been generalized as functions of a critical pressure parameter. They report an average deviation of 3.25% for 23 hydrocarbon mixtures.

Kreglewski and Kay (1969), using the conformal solution approach, have correlated the critical pressure as follows:

$$P_{cm} = P_{cp} + P_{cp}\,[5.808 + 4.93\,(\omega_1 x_1 + \omega_2 x_2)]\,\frac{T_{cm} - T_{cp}}{T_{cp}} \quad (3)$$

When obtaining the true critical pressure from the Smith-Watson charts, the true critical and pseudocritical temperatures and the pseudocritical pressure must first be determined by other methods. Thus, errors in the derived true critical pressure can be compounded by errors in the estimation of the other three properties. In the case of defined mixtures, the pseudocritical properties are derived using a molar average value. The true critical temperature is determined from the Smith-Watson chart described earlier.

Each of the correlations was evaluated with the methane-free portion of the hydrocarbon-hydrocarbon critical pressure data set. The Kreglewski correlation was tested in two different ways. In one case, the experimental value of T_{cm} for each respective P_{cm} and mole fraction was used. In the other case, the value of T_{cm} was calculated from the Li equation, since in most cases the experimental value of T_{cm} is not available in practice. The summary of the results of the evaluation is given in Table 6.

The method of Ekiner-Thodos derived only from paraffin data is by far the poorest of the three methods evaluated and was eliminated from further consideration. The method of Chueh and Prausnitz, which is more accurate for ethane, propane, and naphthenic mixtures, gives slightly improved results when compared to the Smith-Watson charts. The Smith-Watson approach is more accurate for paraffin-paraffin mixtures when the lightest component has a carbon number of five or greater. Both methods are equivalent in accuracy for systems containing aromatics.

Both variations of the Kreglewski approach predict the experimental points more accurately than the other methods with an overall average deviation of 3.2%. The Kreglewski correlation using a predicted critical temperature shows a marked improvement for ethane, ethene, and acetylene mixtures. Thus, for this data set the use of a predicted critical temperature appears at least as accurate as the use of the actual experimental critical temperature. Thus, the Kreglewski method is recommended using the Li correlation for predicting critical temperature. A detailed analysis of the Chueh-Prausnitz correlation and the

TABLE 4. SUMMARY OF THE RESULTS OF THE EVALUATION OF THE LI AND CHUEH-PRAUSNITZ CORRELATIONS FOR ESTIMATING THE TRUE CRITICAL TEMPERATURE OF MULTICOMPONENT HYDROCARBON MIXTURES

System type	Data points	Avg. deviation, K: Li	Avg. deviation, K: Chueh-Prausnitz
Methane ternaries	88	18.41	17.33
Ethane ternaries	46	3.44	4.54
Other hydrocarbon ternaries	72	0.84	1.11
4-Component mixtures	2	0.81	0.64
5-Component mixtures	3	2.63	4.52
6-Component mixtures	1	10.90	14.23
7-Component mixtures	11	36.11	37.77
9-Component mixtures	10	24.54	24.00
	233	10.70	10.69

TABLE 5. SUMMARY OF RESULTS FOR THE EVALUATION OF METHODS FOR PREDICTING THE TRUE CRITICAL PRESSURE OF DEFINED METHANE MIXTURES

System	Number of data points	Average actual deviations, MN/m²: Grieves-Thodos	Thodos-Akiyama	Chueh-Prausnitz
Methane				
Ethane	8	0.306	0.358	0.203
Propane	5	0.530	0.187	0.479
Propane	6	0.799	0.827	1.177
Propane	7	0.451	0.152	0.486
Propane	7	0.253	0.333	0.728
n-Butane	12	1.168	0.537	0.761
2-Methylpropane	3	1.865	2.298	0.592
n-Pentane	5	1.943	1.843	1.795
2-Methylbutane	2		0.109	0.362
n-Heptane	16	1.891	0.559	0.593
n-Nonane	4	5.366	1.765	12.032
n-Decane	7	6.742	2.161	17.536
Cyclohexane	13	3.853	6.242	8.927
Methylcyclohexane	6	6.393	9.482	16.284
Ethene	3	0.831	1.183	1.033
Overall	104	2.082	1.997	4.206

TABLE 6. SUMMARY OF RESULTS FOR THE EVALUATION OF CRITICAL PRESSURE CORRELATIONS WITH THE HYDROCARBON-HYDROCARBON DATA SET

	Number of data points	Average actual deviation, MN/m²
Kreglewski and Kay*	967	0.134
Kreglewski and Kay	967	0.153
Chueh-Prausnitz	967	0.197
Smith-Watson	967	0.222
Ekiner-Thodos	967	0.416

* *Li* equation used for critical temperature.

two versions of Kreglewski is available.

The Kreglewski equation has been tested with both hydrocarbon-nonhydrocarbon and multicomponent hydrocarbon critical pressure data. Based on these evaluations the *method* is not recommended for the hydrocarbon-nonhydrocarbon systems and only for multicomponent hydrocarbon systems containing less than 15% methane. For nonmethane multicomponent systems the method is accurate within 1%.

CRITICAL VOLUME

Few correlations appear in the literature for critical volume prediction due to the lack of verifiable experimental data. As critical volume is the most difficult to measure of all of the critical properties, little experimental work has been initiated.

Chueh and Prausnitz (1967b) have developed an equation for critical volume which is a function of the critical volumes of the pure components, θ_1 and θ and a binary interaction parameter presented graphically as a function of the critical volumes of each component. A unique curve exists for each type of mixture such as paraffin-paraffin, paraffin-nonhydrocarbon, etc. Schick and Prausnitz (1968) modified this approach with a number of additional rules for the binary interaction parameter which have been included in the current work.

Grieves and Thodos (1963) developed a graphical critical volume correlation which includes their method for critical temperature. Since this critical temperature method was eliminated in the earlier work, the critical volume method was not considered.

The Chueh and Prausnitz correlation was evaluated using the critical volume data set described earlier. The results which are available from the authors show an average deviation from the experimental data of 10.5% which is higher than desired for many engineering calculations. The equation is particularly poor for ethane-cyclohexane, ethene-propene, and a number of the systems containing nonhydrocarbons. For this evaluation the value of ν_{12} was determined from a least squares regression of the graphical data.

Improvement is needed in the field of critical volume prediction. This may involve optimization of the interaction parameters in the Prausnitz equation or utilizing the excess volume approach.

Partington et al. (1960), Kay et al. (1969), and others have used the excess property approach for correlating critical property data. In this work critical volume is defined as

$$V_{cm} = V_c^e + x_1 V_{c1} + x_2 V_{c2}$$

where V_c^e is the excess critical volume of the binary mixture. For correlational work two types of equations for V_c^e can be used. The interaction type is given as

$$V_c^e = x_1 x_2 (A_{12} + B_{12} x_1 + C_{12} x_1^2 + \ldots)$$

where A_{12}, B_{12} and C_{12} are specific for each mixture. The free energy form of the excess volume equation is stated as

$$V_c^e = x_1 x_2 (A_{12} + B_{12} (x_1 - x_2) + C_{12} (x_1 - x_2)^2)$$

This equation is so named because it has been used in work involving the Gibbs free energy of a mixture. Actually both equations reduce to the same form if the term $(1 - x_1)$ is substituted for x_2, the multiplications performed, and the equations simplified.

Values of the interaction parameters were determined for the experimental data set with a maximum error for any one system of 1.66%. However, these equations are not of real value unless the coefficients can be generalized. Specific coefficients for each mixture serve only as a means of reporting rather than correlating data.

Attempts at generalizing these coefficients are currently being undertaken. Since excess volume is positive for some mixtures and negative for others, each specific group of critical volume data (paraffin-paraffin, paraffin-olefin, etc.) contains different trends even within itself.

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NOTATION

A, B = Ekiner-Thodos interaction parameters
A_{12}, A_{21} = Grieves-Thodos interaction parameters
G = Gibbs free energy
MABP = mean average boiling point
MAG = mean average specific gravity
M_i = molecular weight, component i
n = number of components
P_{cm} = critical pressure of mixture
P_{cp} = molar average pseudocritical pressure of mixture
T_b = normal boiling point temperature
T_{ci} = critical temperature, component i
T_{cm} = critical temperature of mixture
T_{cp} = molar average pseudocritical temperature of mixture
u = potential energy
V_c^e = excess critical volume
V_{ci} = critical volume, component i
V_{cm} = critical volume of mixture
V_i^* = the liquid molar volumes of the pure components at $T/T_{ci} = 0.6$
V_ϕ^* = the molar pseudo-volume of a mixture of rigid spheres at the reduced temperature $T/T_{ci} = 0.6$
x_i = mole fraction, component i
Δ_i = Kreglewski surface fraction, component i
θ_i = Chueh-Prausnitz surface fraction, component i (as defined in paper)
τ_{ij} = Prausnitz critical temperature interaction parameter
ϕ_i = Li surface fraction, component i
ω_i = acentric factor, component i

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Calculation of Temperature Distribution in the Human Body

An improved procedure is presented for the calculation of detailed steady-state temperature distributions throughout the human body. The efficacy of the proposed computation procedure is demonstrated by comparison of calculated and experimental results for seven studies conducted on four subjects. Core temperatures were predicted within ±0.2°C and deviations for individual skin temperatures generally were within ±0.5°C.

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SCOPE

The ability to calculate temperature distributions throughout the human body at resting conditions in a neutral thermal environment is a prerequisite for studying quantitatively the manner in which the body responds to various types of heat and exercise stresses. Proposed control mechanisms for human thermoregulation can be evaluated only by means of an acceptable model of the controlled body system.

This information can be of value to both engineering and medical practitioners. Computer simulation of the human thermal system would greatly facilitate the specification of optimum work-rest cycles for production workers who must perform their tasks in hostile thermal environments as compared with schedules based solely on traditional, subjective trial and error observations. Likewise, this approach can be a boon to clinicians under both acute and long-term care situations. On the one hand, there is a chance that computer analysis will lead to improved management of fevers, and on the other it could perhaps lead to the more effective use of heating as a physical therapeutic modality in the rehabilitation medicine field.

In addition, the techniques developed in this study demonstrate generally applicable methods for treating distributed parameter systems having both internal heat generation and partial internal regulation of heat dissipation. In view of the fact that the operation of large packed-bed reactors bears many analogies to such a system, the the techniques developed for the physiologic system may well be used to advantage in the analysis of such corresponding technological situations.

Most of the previous work in this field was conducted by physiologists who were concerned primarily with making experimental measurements of body heat balance under