LITERATURE CITED

Acrivos, A., and P. L. Chambre, "Laminar Boundary Layer Flows with Surface Reactions," *Ind. Eng. Chem.*, 49, 1025 (1957).

Bird, R. B., W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena,* Wiley, New York (1960).

Caro, C. G., "Transport of ^{14}C-4-cholesterol between Perfusing Serum and Dog Common Carotid Artery: A Shear Dependent Process," *Cardiovasc. Res.*, **8,** 194 (1974).

Carslaw, H. S., and J. C. Jaeger, *Conduction of Heat in Solids,* 2 ed., Clarendon Press, Oxford, England (1959).

Chambre, P. L., and A. Acrivos, "On Chemical Surface Reactions in Laminar Boundary Layer Flows," *J. Appl. Phys.*, **27,** 1322 (1956).

Ehrlich, L. W., and M. H. Friedman, "Steady Convective Diffusion in a Bifurcation," *IEEE Trans. Biomed. Eng.*, to be published (1976).

Friedman, M. H., "Self-Consistent Analysis of Arterial Uptake of Cholesterol from Perfusing Serum," *Circ. Res.*, to be published (1976).

———, and L. W. Ehrlich, "The Effect of Spatial Variations in Shear on Diffusion at the Wall of an Arterial Branch," *ibid.*, 37, 446 (1975).

Lighthill, M. J., "Contribution to the Theory of Heat Transfer through a Laminar Boundary Layer," *Proc. Roy. Soc.*, **A202,** 359 (1950).

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A Comparison of Enthalpy Prediction Methods

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A reliable method for estimating the liquid and vapor phase enthalpies of hydrocarbon mixtures is of critical importance in many calculations encountered in the petroleum and chemical industries. In the past 5 or 6 yr., a number of promising generalized correlations have appeared in the literature, several in the *Journal*. An extensive study, over a period of 5 yr., to evaluate the relative merits of these methods has now been completed. This work was carried out primarily to provide the basis for selecting the methods to be recommended in the Third Edition of the API Technical Data Book, Petroleum Refining (1976). A concise summary of this work is presented here.

The enthalpy prediction methods chosen for detailed evaluation were:

1. The Curl-Pitzer Tables (1958) using the molar average of the pure component critical points for the pseudocritical temperatures and pressures as suggested by Kay (1936).
2. The Curl-Pitzer Tables using the pseudocritical rules defined by Stewart, Burkhart, and Voo (1959). (These pseudocritical equations are hereafter referred to as the SBV rules.)
3. The equation of state given by Lee, Erbar, and Edmister (1973).
4. The Soave modification (1972) of the Redlich-Kwong equation of state.
5. Starling's (1971) modification of the BWR equation.
6. The Lee and Kesler (1975) three parameter corresponding states correlation.

Other correlations that were included in preliminary evaluations but which are not discussed in this paper were the Redlich-Kwong-Wilson equation (1966), the Hirschfelder et al. equation (1958), the Powers generalized correlation (Furtado et al., 1970), the Fisher-Leland corresponding states correlation (1970), and the Johnson-Colver two fluid method (1970). The six methods included in the final detailed evaluation were chosen on the basis of their generality or superior accuracy, based on the preliminary testing.

THE DATA

These six methods were tested against a data set consisting of 5 632 experimentally determined values. This set comprised sixteen single components, fifty-six binary mixtures, and six ternary mixtures. Except for pure nitrogen and the nitrogen-methane system, all data were for hydrocarbon systems. Only data derived from direct calorimetric determinations were used in the evaluations. More than 85% of the data were taken from the projects sponsored by the American Petroleum Institute and carried out by Lenoir and co-workers. References for these data are given in the supplement to this paper.*

The data set was classified into two categories. The first category consisted of those systems for which the actual experimental values were available. This set was comprised entirely of the data of Lenoir and co-workers. The second category consisted of those systems for which only smoothed values were reported by the authors. One would expect higher average deviations with the first category of data, since the random experimental errors have not been averaged out. The smoothing of the data, however, provides possibilities for biasing of the data. Table 1 gives a listing of the systems in the two categories.

In all cases, the data were represented in the form of enthalpy departures from the ideal gas values. Only single phase experimental points were used, since inclusion of two phase points would necessitate knowledge of the composition of each phase, data which were generally not available. All the data were plotted to confirm their assignments to the liquid or vapor phase. It was thus assured that the data set formed a consistent basis for comparison of the different methods. The critical properties and acentric factors needed for the evaluation were taken from the Second Edition of the API Technical Data Book, Petroleum Refining.

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* Supplementary material has been deposited as Document No. 02734 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016 and may be obtained for $3.00 for microfiche or $5.00 for photocopies.

TABLE 1. SYSTEMS IN EACH DATA CATEGORY

Unsmoothed data

System	Number of compositions	Number of points
n-pentane	—	148
n-heptane	—	24
n-octane	—	109
Cyclohexane	—	140
cis-2-pentene	—	144
Benzene	—	73
n-hexadecane	—	33
Tetralin	—	69
cis-decalin	—	48
trans-decalin	—	128
Propane—2-methylbutane	1	50
n-pentane—*n*-octane	4	270
n-pentane—cyclohexane	4	455
n-pentane—cyclohexane—benzene	3	328
n-pentane—*cis*-2-pentene	1	70
n-pentane—benzene	4	405
n-octane—benzene	6	723
Cyclohexane—benzene	4	478
n-pentane—*n*-hexadecane	4	93
n-pentane—tetralin	5	360
n-pentane—*trans*-decalin	4	314
n-octane—benzene—tetralin	2	100
n-hexadecane—benzene	5	363

Smoothed data

System	Number of compositions	Number of points
Nitrogen	—	55
Methane	—	39
Ethane	—	69
Propane	—	61
n-pentane	—	48
Benzene	—	47
Nitrogen—methane	1	31
Methane—ethane—propane	1	31
Methane—propane	7	218
Ethane—propane	3	77
Propane—benzene	3	31

RESULTS OF THE EVALUATION

Table 2 summarizes the results of the evaluations with the unsmoothed data taken by Lenoir and co-workers. Table 3 is a similar summary for the smoothed data from other sources. Besides the overall errors for each method, the errors in the vapor, liquid, and critical regions have also been given. The critical region was defined as having a reduced temperature between 0.95 and 1.10 and a reduced pressure between 0.90 and 2.50. The reduced temperatures and reduced pressures were determined according to the pseudocritical rules applicable to each method. As a result, some points which may be classified as being in the critical region by one method may fall in the liquid or the vapor region by another method. For the Starling correlation, which does not use a pseudocritical approach, the classification for the critical region was based on a molar average of the pure components' critical values.

Tables analogous to Tables 2 and 3 giving system by system results for each of the methods are included in the supplement to this article.

DISCUSSION OF RESULTS

On an overall basis, the six different methods are almost equivalent when compared against the unsmoothed data. When compared against the smoothed data set, which consists mostly of light hydrocarbons and their mixtures, the methods of Soave, Starling, and Lee and Kesler are found to be definitely superior to the other three.

In the vapor region, all six methods give equivalent results for the unsmoothed data set; the last three methods are again better for the smoothed data set. In the liquid and critical regions, the Lee-Kesler equations are definitely superior to the rest. The Curl-Pitzer, Lee-Erbar-Edmister, and the Soave equations often give large errors in the critical region, especially for mixtures of light hydrocarbons.

While the methods of Starling and Lee-Kesler appear to give more or less the same accuracy overall, the Lee-Kesler method is again ,significantly better in the liquid and critical regions. This latter method also shows considerably better accuracy for mixtures containing components of widely different molecular shape and size.

The errors for the Lee-Kesler method cited in the tables were obtained from computer calculations with the analytical equations given by Lee and Kesler. These authors have also provided a tabular form of their cor-

TABLE 2. DEVIATIONS* FROM UNSMOOTHED EXPERIMENTAL VALUES

Method	Overall			Vapor region			Liquid region			Critical region		
	No. pts.	Avg.	Bias	No. pts.	Avg.	Bias	No. pts.	Avg.	Bias	No. pts.	Avg.	Bias
Curl-Pitzer (Kay)	4 444	9.4	4.0	1 457	9.5	5.3	1 705	8.4	3.5	1 282	10.8	3.1
Curl-Pitzer (SBV)	4 450	9.4	4.3	1 450	9.1	4.8	1 685	8.4	4.2	1 315	10.9	3.9
Lee-Erbar-Edmister	4 925	10.6	5.8	1 875	9.4	5.9	1 769	9.1	6.0	1 282	14.4	5.3
Soave†	4 925	9.9	7.3	1 874	10.1	7.5	1 768	8.3	5.7	1 283	11.9	9.0
Starling	4 925	10.0	5.6	1 875	9.7	6.2	1 768	9.7	5.4	1 282	10.8	4.8
Lee-Kesler	4 925	8.0	0.9	1 853	9.0	4.4	1 769	6.3	2.2	1 303	8.7	−6.0

* All deviations are in kiloJoules per kilogram.

$$\text{Avg.} = \frac{\Sigma|\text{calculated-experimental}|}{\text{number of points}}$$

$$\text{Bias} = \frac{\Sigma(\text{calculated-experimental})}{\text{number of points}}$$

† The expression for the enthalpy departure, which has not been given in Soave's paper, can be shown, by using Soave's notation, to be

$$\frac{H - H^\circ}{RT} = Z - 1 - \ln\left[1 + \frac{B}{Z}\right]\left[\frac{A}{B} + \frac{\sqrt{a}}{RTb}\sum_i x_i m_i \sqrt{a_{c_i} T_{r_i}}\right]$$

TABLE 3. DEVIATIONS* FROM SMOOTHED EXPERIMENTAL VALUES

Method	Overall No. pts.	Overall Avg.	Overall Bias	Vapor region No. pts.	Vapor region Avg.	Vapor region Bias	Liquid region No. pts.	Liquid region Avg.	Liquid region Bias	Critical region No. pts.	Critical region Avg.	Critical region Bias
Curl-Pitzer (Kay)	702	10.3	9.7	330	5.0	4.1	319	14.8	14.4	53	16.6	16.3
Curl-Pitzer (SBV)	702	7.8	7.1	330	4.0	3.0	318	10.5	10.2	54	14.3	14.0
Lee-Erbar-Edmister	707	9.3	7.6	329	5.4	5.2	325	10.4	7.5	53	26.5	23.7
Soave	707	4.5	2.4	329	2.7	0.9	325	5.1	2.4	53	12.2	12.2
Starling	707	4.8	1.9	330	2.4	1.1	324	6.7	2.0	53	7.6	6.0
Lee-Kesler	707	3.6	1.6	327	2.3	0.1	324	4.7	3.1	56	4.4	1.6

* All deviations in kiloJoules per kilogram.

relations from which rapid desk calculations can be made. With these tables one would most likely use a linear interpolation and simplified pseudocritical rules, resulting in some loss in accuracy. The results will, however, still be quite good.

CONCLUSIONS

All the six methods evaluated in this study can be expected to give fairly reliable estimates of enthalpies of hydrocarbon mixtures. The methods of Starling and Lee-Kesler, however, have been found to be significantly superior to the others. The Lee-Kesler method is the most reliable of the six methods for the prediction of enthalpies for a wide range of hydrocarbons.

LITERATURE CITED

American Petroleum Institute, Technical Data Book, *Petroleum Refining*, 3 ed., American Petroleum Institute, Washington, D. C. (to be published, 1976).

Curl, R. F., and K. S. Pitzer, "Volumetric and Thermodynamic Properties of Fluids—Enthalpy, Free Energy and Entropy," *Ind. Eng. Chem.*, **50**, 265 (1958).

Fisher, G. D., and T. W. Leland, "Corresponding States Principle Using Shape Factors," *Ind. Eng. Chem. Fundamentals*, **9**, 537 (1970).

Furtado, A. W., D. L. Katz, and J. E. Powers, "Progress at the Thermal Properties of Fluids Laboratory of the University of Michigan: March 1969-March 1970," 49th Ann. Conv. NGPA, 1 (1970).

Hirschfelder, J. O., R. J. Buehler, H. A. McGee, Jr., and J. R. Sutton, "Generalized Equation of State for Gases and Liquids," *Ind. Eng. Chem.*, **50**, 375 (1958). [Corrections: *Ind. Eng. Chem. Fundamentals*, **1**, 224 (1962).]

Johnson, D. W., and C. P. Colver, "A Method for Predicting Enthalpy Departures," 49th Ann. Conv. NGPA, 19 (1970).

Kay, W. B., "Density of Hydrocarbon Gases and Vapors at High Temperature and Pressure," *Ind. Eng. Chem.*, **28**, 1014 (1936).

Lee, B. I., J. H. Erbar, and W. C. Edmister, "Prediction of Thermodynamic Properties for Low Temperature Hydrocarbon Process Calculations," *AIChE J.*, **19**, 349 (1973).

Lee, B. I., and M. G. Kesler, "A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States," *ibid.*, **21**, 510 (1975).

Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Sci.*, **27**, 1197 (1972).

Starling, K. E., "Thermo Data Refined for LPG," *Hydrocarbon Processing*, No. 3, 101 (1971).

Stewart, W. E., S. F. Burkhart, and D. Voo, "Prediction of Pseudocritical Constants for Mixtures," paper presented at the AIChE Meeting, Kansas City, Mo. (May 18, 1959).

Wilson, G. M., "Calculation of Enthalpy Data from a Modified Redlich-Kwong Equation of State," *Advan. Cryogenic Eng.*, **2**, 392 (1966).

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BOOKS

Handbook of Enzyme Biotechnology, Alan Wiseman, editor. Ellis Horwood, Publisher. Chichester, Great Britain (Distributed by Wiley). 275 pages. $45.00.

The intentions of the editor are much more restricted than might be indicated by the title. The book's objective is to describe the industrial practice of large-scale enzyme production and utilization and to develop those aspects of theory directly coupled with present enzyme technology. The potential industrial use of immobilized enzymes and their preparation are discussed.

To achieve this objective the book adopts a novel approach to organization. The book is divided into two parts; the first is concerned with establishing principles while the second part provides the data for the industrial application of these principles. The author (or authors) of a chapter in part 1 write the corresponding chapter in part 2. The book achieves a cohesiveness by utilizing such a follow-up structure.

This integration of material, unfortunately, does not overcome several weaknesses in topics discussed. These problems result from an apparent attempt to appeal to a very diverse audience. A minimal knowledge of biochemistry and engineering is assumed. Most topics in part 1 are not treated in depth while several others are virtually ignored. Specifically, quantitative relationships, except for oxygen transfer, have been completely neglected, and design engineering aspects are inadequately treated. Sufficient (but not exhaustive) references are presented, however, for the enterprising reader to initiate a literature search or to enhance materials sparsely introduced. Part 2 should have included examples of actual fermentation data, as well as more information on enzyme recovery and purification operations.

The book's strongest points occur in