Prediction of Thermodynamic Properties for Low Temperature Hydrocarbon Process Calculations

Analytical expressions for calculating vapor-liquid compositions, enthalpies, and entropies have been developed for hydrocarbon mixtures containing none or some of the nonhydrocarbon gases and evaluated against experimental measurements of vapor-liquid equilibria and enthalpies. The evaluation results show that the proposed equations can be applied over wide range of conditions with good accuracy. These equations are extensions and improvements of equations presented previously by Lee and Edmister (1971c) mainly for low temperature thermodynamic property calculations.

BYUNG-IK LEE
JOHN H. ERBAR and
WAYNE C. EDMISTER

Oklahoma State University
Stillwater, Oklahoma 74074

SCOPE

The objective of this work was to develop an improved method for predicting equilibrium vapor and liquid compositions as well as the enthalpies and entropies for mixtures of hydrocarbons and associated gases. A computer program, for use in process design calculations, is to be the ultimate form of this prediction method. Previous methods by Chao-Seader (1961) and Lee-Edmister (1971c) are of this same format but are not accurate enough at low temperatures, a deficiency to be corrected in this work.

CONCLUSIONS AND SIGNIFICANCE

An improved generalized method for predicting thermodynamic properties of hydrocarbon mixtures has been developed. This prediction method is based upon three equations: (1) an equation of state for all vapor phase calculations, (2) a fugacity coefficient expression for the pure liquid reference state, and (3) an activity coefficient expression describing the departure from ideal solution behavior.

This new method for predicting the thermodynamic properties of hydrocarbon mixtures agrees with experimental vapor-liquid equilibrium data appreciably better than does the NGPA (1967) version of the Chao-Seader (1961) method and is simpler than the Lee-Edmister (1971c) method, both being generalized methods. In particular, the *K*-values of heavy components are predicted with notably high accuracy. This success is due to the correct prediction of vapor phase fugacity coefficient, which has a strong effect on the *K*-values of heavy components. This method is recommended for the ranges of temperature from 115°K to 535°K and pressure up to 0.9 of the convergence pressure for the mixture. These are broader than are the ranges of applicability for other generalized methods. The method is not recommended for the systems containing 50% or more nonhydrocarbon gases in the liquid phases and for infinitely diluted components. Although data on petroleum fractions were not included in their development, the equations can be extended to petroleum fractions. This extension might require new constants for the activity coefficient equation.

The prediction method of isothermal enthalpy differences is consistent with the *K*-value prediction method and as accurate as the best of other available methods. The isothermal entropy difference equations are also found to be accurate and reliable.

DEVELOPMENT

The increased use of cryogenic conditions in hydrocarbon separation operations was an incentive to develop better tools for making the required thermodynamic calculations for the various low temperature processes. Accurate predictions of *K*-value, enthalpy, and/or entropy are essential for the design of such processes.

An important consideration in the development of this proposed method was to retain generality and consistency among the equations for the prediction of different properties. In previous work, Lee and Edmister (1971c) proposed a generalized method for predicting vapor-liquid equilibrium distribution ratios for hydrocarbon systems. This previous correlation had three drawbacks: (1) it was complicated, (2) it did not give accurate predictions for mixtures having very high solute concentrations in the vapor phase, and (3) the temperature limitation, via pure component reduced temperatures, was not very practical.

Correspondence concerning this paper should be addressed to W. C. Edmister, 75 Summit Avenue, San Rafael, California 94901. B. I. Lee is with Mobil Research & Development, Princeton, New Jersey.

The objectives of this work were to simplify the previous equations and extend them down to lower temperatures, using some additional cryogenic data that had not been available in the previous work.

As in the previous work, the *K*-value for component "*i*" of a mixture is formulated as the following function of fugacities and activity coefficient.

$$K_i = \gamma_i \nu_i / \phi_i \tag{1}$$

ϕ_i values are calculated via an equation of state while γ_i and ν_i values are calculated via empirical equations. For maximum flexibility and utility, it is important that these three expressions be generalized, partially or completely, using component properties such as the critical conditions, solubility parameter, molal volume, etc. as correlating parameters.

Complete generalization with acceptable accuracy was not possible. Partial generalization, with reduced constants and coefficients for similar groups of components, turned out to be a satisfactory compromise between the extremes of complete generalization and individual fits to specific systems. The constants for the equations were empirically determined by fitting experimental data on density, enthalpy, and vapor-liquid compositions to the proposed equations, keeping maximum possible generalization, minimum deviations, and consistency in mind.

EQUATION OF STATE

In the Lee-Edmister (1971c) generalized correlation, a three-parameter equation of state that required seven separate mixing rules was used. The following modification was made in the equation of state to employ a simpler mixing rule for the parameter *c*. A new "*c*," with the dimensions of "*a*," was introduced to give

$$P = \frac{RT}{V-b} - \frac{a}{V(V-b)} + \frac{bc}{V(V-b)(V+b)} \tag{2}$$

The three parameters *a*, *b*, and *c* are for the system, which may be a pure substance or a mixture. Values of *a*, *b*, and *c* may be determined for each substance by fitting Equation (2) to experimental pressure-volume-temperature data on that substance. This can be done for all substances of interest, and then the individual constants can be combined to get the values of the parameters for mixtures. For more flexibility, the procedure followed in this work was to derive generalized expressions for the constants. The parameters for component "*i*", a_i, b_i, and c_i were determined as functions of critical temperature, critical pressure, acentric factor, and reduced temperature using *P-V-T* and enthalpy data for the substances of interest, as follows:

$$b_i = \frac{RT_{ci}}{P_{ci}} (0.086313 + 0.002\omega_i) \tag{3}$$

$$a_i = \frac{R^2 T^2_{ci}}{P_{ci}} [(0.246105 + 0.02869\omega_i) - (0.037472 + 0.149687\omega_i) T_{ri} + (0.16406 + 0.023727\omega_i) T_{ri}^{-1} + (0.04937 + 0.132433\omega_i) T_{ri}^{-2}] \tag{4}$$

$$c_i = \frac{R^2 T^2_{ci}}{P_{ci}} [(0.451169 + 0.00948\omega_i) T_{ri}^{-1/2} + (0.387082 + 0.078842\omega_i) T_{ri}^{-2}] \tag{5}$$

VAPOR-PHASE FUGACITY COEFFICIENT

From Equation (2) the following expression was derived for the fugacity coefficient of vapor-phase components:

$$\ln \phi_i = \frac{1}{bRT} \left[(2A_i' - aB_i' - bRT) \ln \left(1 - \frac{b}{V}\right) + \left(\frac{cB_i'}{2} - C_i'\right) \ln \left(1 - \frac{b^2}{V^2}\right) \right] + B_i'(Z-1) - \ln Z \tag{6}$$

where

$$b = \sum_{i=1}^{n} y_i b_i \tag{7}$$

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} y_i y_j \alpha_{ij} (a_i a_j)^{1/2} \tag{8}$$

$$c = \sum_{i=1}^{n} \sum_{j=1}^{n} y_i y_j \beta_{ij} (c_i c_j)^{1/2} \tag{9}$$

$$B_i' = b_i / b \tag{10}$$

$$A_i' = a_i^{1/2} \sum_{j=1}^{n} y_j \alpha_{ij} \, a_j^{1/2} \tag{11}$$

$$C_i' = c_i^{1/2} \sum_{j=1}^{n} y_j \beta_{ij} \, c_j^{1/2} \tag{12}$$

The interaction coefficients α_{ij} and β_{ij} are related to the geometric and arithmetic means of the critical temperatures of components "*i*" and "*j*" as follows:

$$\beta_{ij} = \left[\frac{2(T_{c_i} T_{c_j})^{1/2}}{T_{c_i} + T_{c_j}} \right]^{m_1} \tag{13}$$

$$\alpha_{ij} = \beta_{ij}^{m_2} \tag{14}$$

The values of exponents m_1 and m_2 are given below in the order of preference from left to right. For example, for H_2-CO_2 pair, the values under the heading of H_2 should be used, likewise, for CO_2-CH_4 pair, the values under CO_2 should be used.

	H_2	CO_2	CH_4 & N_2	Other Hydrocarbons & H_2S
m_1	0.3	−2.0	−2.0	0
m_2	1.1	−0.8	0	0

In most cases, the values of α_{ij} and β_{ij} are unity, which leads to the usual square root mixing rule for *a* and *c*. The interaction coefficients that differ from unity have significant effects on the fugacity coefficients and the partial properties of minor components in the vapor phase, but the nonunity interaction coefficients have very little effects on the properties of bulk mixture. Thus calculations of *Z*, *H*, and *S* can be made using the ordinary square root mixing rule for *a* and *c*.

VAPOR PHASE ENTHALPY AND ENTROPY

Expressions for the isothermal enthalpy difference and entropy difference in the vapor phase were also derived from Equation (2):

TABLE 1. CONSTANTS IN EQUATIONS (19) AND (20)

	All hydrocarbons		Methane	Nitrogen		CO_2	H_2S	H_2
Constant	(N_2 included) $T_r \leq 1.0$	(CH_4 excluded) $T_r > 1.0$	$T_r > 0.93$	$1.0 < T_r \leq 2.2$	$T_r < 2.2$	For all temp.	For all temp.	For all temp.
A_1	6.2741	9.52326	9.55412	9.26614	6.82287	28.9284	13.94	0.43571
A_2	−7.3401	−9.88046	−8.31211	−10.538	−8.9725	−20.01	−1.75213	5.34346
A_3	−4.2751	−6.00351	−3.23962	−7.98618	−9.78514	−10.3989	14.0164	−0.46
A_4	−0.22647	−0.41660	−2.26419	0.76209	2.67084	−12.5	−12.5	−0.1043
A_5	0.93842	0.18150	0.46272	0.21677	0.0	3.52631	−0.00024	0.04794
A_6	−0.23825	0.0	0.0	0.0	0.0	0.0	0.0	0.0
A_7	0.03798	−0.02010	−0.09953	−0.05624	0.90970	−12.7	2.84127	0.35304
A_8	−0.00344	0.10390	0.2516	0.18917	−1.01342	12.9708	−4.94796	−0.68039
A_9	−0.21974	−0.06538	0.2727	0.12474	−0.40848	15.4946	−8.0	−0.10673
A_{10}	0.10862	0.08916	0.01198	−0.00023	0.0	−0.94143	1.5889	−0.00023
A_{11}	0.0298	0.0	0.0	0.0	0.0	0.0	0.0	0.0
A_{12}	−0.00188	−0.00188	−0.00188	0.0	0.0	−0.22382	0.48453	0.0
A_{13}	10.2920	−1.027	0.0	0.0	0.0	0.0	0.0	0.0
A_{14}	−11.6780	−0.59264	0.0	0.0	0.0	0.0	0.0	0.0
A_{15}	−1.6470	0.0	0.0	0.0	0.0	0.0	0.0	0.0
A_{16}	−0.03885	−0.03885	0.0	0.0	0.0	0.0	0.0	0.0
A_{17}	−0.00101	−0.00101	−0.00101	−0.05652	−0.05652	2.32463	−0.00101	0.0

$$\frac{H^V - H^0}{RT} = Z - 1 + \frac{1}{bRT}\left[(a + a') \ln\left(1 - \frac{b}{V}\right) - \frac{c + c'}{2} \ln\left(1 - \frac{b^2}{V^2}\right)\right] \quad (15)$$

$$\frac{S^V - S^0}{R} + \ln \frac{P}{P^0} = \left(1 + \frac{a'}{bRT}\right) \ln\left(1 - \frac{b}{V}\right) - \left(\frac{c'}{2bRT}\right) \ln\left(1 - \frac{b^2}{V^2}\right) + \ln Z \quad (16)$$

where

$$a' = \sum_{i=1}^{n} \sum_{j=1}^{n} y_i y_j \alpha_{ij} \frac{R^2 T^2_{cj}}{P_{cj}} \left(\frac{a_i}{a_j}\right)^{1/2} [(0.037472 + 0.149687\omega_j) T_{r_j} + (0.16406 + 0.023727\omega_j) T_{r_j}^{-1} + (0.09874 + 0.264866\omega_j) T_{r_j}^{-2}] \quad (17)$$

$$c' = \sum_{i=1}^{n} \sum_{j=1}^{n} y_i y_j \beta_{ij} \frac{R^2 T^2_{cj}}{P_{cj}} \left(\frac{c_i}{c_j}\right)^{1/2} [(0.225585 + 0.00474\omega_j) T_{r_j}^{-1/2} + (0.774174 + 0.157684\omega_j) T_{r_j}^{-2}] \quad (18)$$

Equation (15) was also used with experimental values of ΔH in the determination of the constants for Equation (2).

LIQUID PHASE FUGACITY COEFFICIENT

The pure liquid fugacity at the system temperature and pressure is the reference fugacity for the activity coefficient in Equation (1). This will be in the real liquid state at temperatures below the critical and at pressures equal to or above the vapor pressure. It will be in a hypothetical liquid state at temperatures above the critical and at pressures below the vapor pressure.

Lee and Edmister (1971b) developed an empirical equation for $\ln\nu_i$ using vapor pressure and volumetric data for real liquids. For the hypothetical liquid state, Lee and Edmister (1971c) derived the $\ln\nu_i$ equation from experimental composition data and the other parts of the *K*-value correlation, that is, values of γ_i and ϕ_i.

In the present work, a single equation was formulated using 17 constants to cover both real and hypothetical liquid states. In determining the values of these constants, the first and second temperature derivatives were carefully analyzed to be assured of obtaining accurate enthalpy differences and to avoid inflection points within the temperature limits of interest.

In addition to the data used in the previous liquid fugacity calculations and correlation, new low temperature data of Carruth (1970) were used in the present $\ln\nu_i$ equation development. These new data permitted calculating values of $\ln\nu_i$ at reduced temperatures down to 0.32. The resulting expression is as follows:

$$\ln\nu_i = A_{1_i} + A_{2_i} T_{r_i}^{-1} + A_{3_i} \ln T_{r_i} + A_{4_i} T_{r_i} + A_{5_i} T_{r_i}^2 + A_{6_i} T_{r_i}^7 + (A_{7_i} + A_{8_i} T_{r_i}^{-1} + A_{9_i} \ln T_{r_i} + A_{10_i} T_{r_i}^2 + A_{11_i} T_{r_i}^7) P_{r_i} + A_{12_i} T_{r_i}^3 P_{r_i}^2 + [(1 - T_{r_i})(A_{13_i} + A_{14_i} T_{r_i}^{-1} + A_{15_i} T_{r_i}) + A_{16_i} P_{r_i} T_{r_i}^{-1} + A_{17_i} T_{r_i} P_{r_i}^2]\omega_i - \ln P_{r_i} \quad (19)$$

Values of the constants in Equation (19) are given in Table 1 for eight different cases. These include one set of constants for the real liquid and seven sets for the hypothetical liquids.

LIQUID ENTHALPY AND ENTROPY DIFFERENCES

The isobaric temperature derivative of Equation (19) gives the isothermal enthalpy difference for a pure liquid, as follows:

$$\frac{H^L - H^0}{RT} = \frac{A_{2_i}}{T_{r_i}} - A_{3_i} - A_{4_i} T_{r_i} - 2A_{5_i} T_{r_i}^2 - 7A_{6_i} T_{r_i}^7 + \left(\frac{A_{8_i}}{T_{r_i}} - A_{9_i} - 2A_{10_i} T_{r_i}^2 - 7A_{11_i} T_{r_i}^7\right) P_{r_i} - 3A_{12_i} T_{r_i}^3 P_{r_i}^2 + [A_{13_i} T_{r_i} + A_{14_i} T_{r_i}^{-1} + A_{15_i}(2T_{r_i}^2 - T_{r_i}) + A_{16_i} T_{r_i}^{-1} P_{r_i} - A_{17_i} T_{r_i} P_{r_i}^2]\omega_i \quad (20)$$

For the systems of interest in this work, the excess enthalpy, which is obtainable from the isobaric temperature derivative of $\ln\gamma_i$, is considered small and neglected in the calculation of mixture liquid enthalpy.

TABLE 2. CONSTANTS FOR EQUATION (24)

"i"	Component "j"	Temp., °K	q_1	q_2	q_3	q_4	q_5
PHC	PHC	All T	0.50246	2.30808	0.00241	0.0	0.39722
CH_4	PHC	$T \leqq 300$	−0.32242	181.329	−0.71383	0.0	0.30196
CH_4	PHC	$T > 300$	−4.70151	183.348	−0.67426	−5.91575	0.92738
N_2	PHC, CH_4	$T \leqq 300$	0.81316	−19.1879	0.12695	0.0	0.04708
N_2	PHC, CH_4	$300 \leqq T < 420$	−4.1398	−0.76224	0.06388	−3.40467	0.26579
NHC	PHC, CH_4, N_2	All T	−0.59575	4.16426	−0.00401	0.0	1.40086
AHC	PHC, CH_4, N_2, NHC	All T	0.82764	1.94477	−0.00454	0.0	−0.38419
CO_2	All Hydrocarbons, N_2	All T	2.51107	73.5411	−0.18812	0.0	0.18174
H_2S	LHC	All T	20.085	−17.666	0.05936	0.0	−3.3107
H_2S	HHC, N_2, CO_2	All T	−1.04519	45.116	−0.10872	0.0	−0.4247
H_2	CH_4	All T	−6.846	−0.79664	0.32524	−3.3626	0.73463
H_2	PHC, NHC ,AHC, N_2, CO_2, H_2S	$T \leqq 350$	−2.3982	0.8191	0.1960	−2.0831	0.35379

PHC—Paraffinic hydrocarbons except methane; NHC—Naphthenic hydrocarbons; AHC—Aromatic hydrocarbons; LHC—Light hydrocarbons (CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8); and HHC—All hydrocarbons except LHC.

Having the other liquid phase properties, it is a simple matter to compute the isothermal entropy difference from its thermodynamic relationship with enthalpy and fugacity.

ACTIVITY COEFFICIENT IN LIQUID SOLUTIONS

The following model of Scatchard-Hildebrand (1950) was used in correlating liquid activity coefficients:

$$\ln\gamma_i = \frac{V_i^L}{RT}\left[\sum_{j=1}^{n} B_{ij}\Phi_j - \frac{1}{2}\sum_{j=1}^{n}\sum_{m=1}^{n} B_{jm}\Phi_j\Phi_m\right] \tag{21}$$

where

$$B_{ij} = (\delta_i - \delta_j)^2 + 2\,l_{ij}\,\delta_i\,\delta_j \tag{22}$$

The binary interaction coefficient l_{ij} which was defined by Eckert and Prausnitz (1965) was generalized by using critical temperatures as well as solubility parameters and liquid molal volumes that are inherent to the Scatchard-Hildebrand (1931, 1934, 1950) equation, as follows:

$$l_{ij} = 2\left\{\left[\frac{\delta_i + \delta_j}{2(\delta_i\,\delta_j)^{1/2}}\right]^2 - 1\right\}\left\{q_1 - 1 + q_2(T_{ri}\,T_{rj})^{1/2} + q_3\,T\left[\frac{T_{ri} + T_{rj}}{2(T_{ri}\,T_{rj})^{1/2}}\right]^{-2} + q_4\,T_{ri}\,T_{rj}\right\} - q_5\left[\frac{V_i^L + V_j^L}{2(V_i^L\,V_j^L)^{1/2}} - 1\right] \tag{23}$$

Equation (23) expresses the liquid phase interaction coefficient as a combination of energy differences and molecule size differences. Energy difference is represented by the ratio of arithmetic to geometric means of the solubility parameter while the size difference is represented by the ratio of arithmetic to geometric means of the liquid molar volumes, both put in a form of departure from unity.

The following combination of Equations (22) and (23) to give an expression for B_{ij} has been found to be convenient for applications of Equation (21):

$$B_{ij} = (\delta_i - \delta_j)^2\left\{q_1 + q_2(T_{ri}\,T_{rj})^{1/2} + q_3\,T\left[\frac{2(T_{ri}\,T_{rj})^{1/2}}{T_{ri} + T_{rj}}\right]^2 + q_4 T_{ri}\,T_{rj}\right\} - q_5\,\delta_i\,\delta_j\left[(V_j^L/V_i^L)^{1/2} + (V_i^L/V_j^L)^{1/2} - 2\right] \tag{24}$$

TABLE 3. SOLUBILITY PARAMETER AND LIQUID MOLAL VOLUME

Compounds	Solubility parameter δ (cal./ml.)$^{1/2}$	Liquid molal volume V^L ml./g-mole
Methane	5.64	64.0
Ethene	6.02	72.0
Ethane	6.04	73.0
Propene	6.43	84.0
Propane	6.41	86.0
Hydrogen	3.5	40.0
Nitrogen	3.7	44.0
H_2S	6.6	74.0
CO_2	6.2	57.0

TABLE 4. COMPARISON OF CALCULATED WITH EXPERIMENTAL VAPOR PRESSURES

Hydrocarbon	No. of points	Lowest temp., °K	Avg. Abs. Deviation % Chao-Seader (1961)	This work
Methane	42	77	29.10	2.37
Ethane	43	91	22.50	3.76
Propane	31	94	31.04	3.98
i-Butane	56	187	22.90	4.18
n-Butane	40	135	26.91	4.21
i-Pentane	49	214	23.25	4.09
n-Pentane	41	143	28.68	3.99
n-Hexane	39	177	31.08	3.84
n-Heptane	47	186	32.26	3.83
n-Octane	38	216	33.05	3.74
n-Nonane	31	224	34.59	3.84
n-Decane	16	244	36.07	3.89
Overall	453		31.00	3.99

Values of the interaction coefficient constants q_1 through q_5 were determined from binary vapor-liquid equilibria data and the equations of the proposed prediction method. Values of these five constants are given in Table 2 for a variety of systems. In determining the constants, care was taken to fit both light and heavy component activity coefficients equally. It is our belief that the constants for nonhydrocarbon gases should be redetermined as soon as more accurate and consistent data become available. Existing data on these gases are fairly scattered. As the solubility parameters and liquid molal volumes of light hydrocarbons and nonhydrocarbon gases are hypothetical at 298°K, the values were readjusted and the new values are given in Table 3.

EVALUATIONS

Evaluations of the equations derived in this work were made by computing pure component vapor pressures, dew points, bubble points, *K*-values, and enthalpies, and then comparing the results with experimental data and the results of other methods. Pure component vapor pressures are found by applying Equations (6) and (19) simultaneously to find the pressure at which the vapor fugacity is equal to the liquid fugacity. Such vapor pressure predictions were made for 453 points on twelve hydrocarbons. Average absolute deviations of these calculated vapor pressures from the values of Carruth (1970) are given in Table 4. Also included are the results of similar predictions by the Chao-Seader (1961) equations. As can be seen by the comparison of deviations in Table 4, the present equations are far superior to the Chao-Seader equations in the prediction of vapor pressures. This evaluation is believed to be a good method to test the interconsistency of vapor and liquid fugacity equations.

Vapor-liquid *K*-values were computed for 2,298 selected points for 13 hydrocarbons and four nonhydrocarbon gases at the conditions and compositions of the experimental measurements. The experimental composition data were taken from a supplemented version of a deck obtained from Chevron (1961), which covers from binary to five component mixtures. Such *K*-value computations were also made by NGPA (1967) Chao-Seader (1961) prediction method, and were compared with the experimental *K*-values. In this computation the data having either x_i or y_i less than 0.01 were excluded, because the uncertainty in such small experimental values is relatively large to make the percentage deviation less meaningful. The comparisons are shown in Table 5. Ranges of conditions covered are indicated by the minimum temperature and maximum pressure for each substance. The extreme conditions did not occur at the same point or the same system. It should be noted that a portion of experimental data used is outside the recommended range of Chao-Seader (1961) correlation, which accounts for some of the poor results.

A more rigorous evaluation was also made on a limited amount of data by calculating single flash, dew points, bubble points, and equilibrium temperature or pressure with a specified vapor-liquid split. The results are shown in Table 6. This was done by a computer program, of which an excerpt is included in Appendix A.* This excerpt is only for the calculations of flash and enthalpies, that is, the parts for entropy, dew points, bubble points, and others were dropped out to reduce the volume of the appendix.

Isothermal enthalpy differences were calculated using Equations (16) and (20) for 1471 data points on 21 mixtures studied and compiled by Starling et al. (1971). In addition to the result of our proposed method, similar results of six other correlations are given in Table 7. The overall average deviation for the proposed method is 4.4 k joule/kg, compared to 4.0 for the best of the other methods which indicates that the proposed method is as good as the best of the other methods for predicting isothermal enthalpy differences.

Table 5. Comparison of K-Value Prediction Methods with Experimental Data

Hydrocarbon	No. of points	Min. temp., °K	Max. press. kN/m²	Avg. Abs. Deviation % Chao-Seader (1961) NGPA (1967)	Avg. Abs. Deviation % This work
Methane	446	144	27,580	16.2	6.2
Ethane	214	144	12,563	7.2	5.4
Propane	336	144	11,970	6.1	3.7
i-Butane	17	244	8,964	11.6	11.5
n-Butane	170	222	27,580	8.5	5.9
i-Pentane	41	273	6,895	3.4	5.2
n-Pentane	119	244	12,563	7.6	5.8
n-Hexane	94	311	12,563	10.7	7.5
n-Heptane	91	278	18,961	5.7	2.9
n-Nonane	4	325	9,805	17.4	15.3
n-Decane	61	311	27,580	26.2	7.3
Ethene	43	243	8,274	8.5	4.6
Propene	121	243	4,978	6.3	4.7
Hydrogen	103	103	34,475	15.6	10.7
Nitrogen	197	89	34,475	34.1	7.6
H_2S	127	189	10,343	6.6	6.3
CO_2	126	200	12,066	18.8	6.8
Overall	2,298			12.7	5.9

PHYSICAL PROPERTY DATA TO BE USED

It is recommended to use the critical temperatures and pressures in *Technical Data Book—Petroleum Refining of American Petroleum Institute,* and the acentric factors given in Edmister (1961). The solubility parameters and the liquid molal volumes for activity coefficient equation should be taken from Lee-Edmister (1971c) or Chao-Seader (1961) except those values listed in Table 3

NOTATION

A_1 to A_{17} = empirical constants for Equations (19) and (20)
A_i' = combined parameter defined by Equation (11)
a = equation of state parameter defined by Equation (8)
a' = combined parameter defined by Equation (17)
B_{ij} = binary pair coefficient defined by Equations (22) and (24)
B_i' = combined parameter defined by Equation (10)
b = equation of state parameter defined by Equation (7)
C_i' = combined parameter defined by Equation (12)
c = equation of state parameter defined by Equation (9)
c' = combined parameter defined by Equation (18)
H = enthalpy, joule/kg
$K_i = y_i/x_i$ = vapor-liquid equilibrium distribution ratio of component "i"
l_{ij} = binary interaction coefficient given by Equations (22) and (23)
m_1, m_2 = empirical exponents for Equations (13) and (14)
n = number of components
P = pressure, k N/m²
q_1 to q_5 = empirical constants for Equation (23)
R = gas constant, 8.3147 m³ kN/kg-mole °K

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S = entropy, joule/kg °K

T = temperature, °K

V = molal volume, m^3/kg-mole

x_i = mole fraction of component "i" in liquid phase

y_i = mole fraction of component "i" in vapor phase

$Z = PV/RT$ = compressibility factor

Greek Letters

α_{ij}, β_{ij} = binary interaction coefficients for vapor phase

TABLE 6. COMPARISON OF EQUILIBRIUM PREDICTIONS

System	Temp., K		Press, $k\ N/m^2$		K of Comp. 1		K of Comp. 2		Liq. Fract.	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
Single flash at given temperature and pressure										
Hydrogen-methane	117.0	—	10,273.0	—	9.964	10.203	0.059	0.060	0.70	0.70
Nitrogen-methane	89.0	—	101.0	—	5.301	5.700	0.100	0.097	0.70	0.69
Methane-H_2S	211.0	—	2,758.0	—	15.081	17.250	0.069	0.066	0.70	0.69
CO_2-n-decane	478.0	—	6,895.0	—	3.133	3.089	0.089	0.092	0.70	0.70
Methane-ethane	144.0	—	296.0	—	3.034	2.898	0.025	0.023	0.70	0.72
Methane-n-heptane	233.0	—	1,379.0	—	8.603	9.724	0.000	0.000	0.70	0.69
Ethane-propane	200.0	—	138.0	—	1.474	1.517	0.169	0.155	0.70	0.67
n-butane-n-decane	511.0	—	4,137.0	—	1.394	1.409	0.420	0.398	0.70	0.71
Bubble point temperature at given pressure										
Hydrogen-methane	117.0	120.0	10,273.0	—	9.964	9.838	0.059	0.072	1.00	—
Nitrogen-propane	123.0	133.0	12,411.0	—	7.011	7.091	0.013	0.000	1.00	—
H_2S-n-butane	367.0	364.0	3,702.0	—	1.679	1.640	0.538	0.565	1.00	—
Methane-ethane	144.0	145.0	296.0	—	3.034	3.033	0.025	0.025	1.00	—
Methane-n-pentane	344.0	332.0	10,377.0	—	2.079	2.096	0.225	0.213	1.00	—
Ethane-propane	228.0	227.0	517.0	—	1.183	1.183	0.199	0.198	1.00	—
Ethane-n-decane	378.0	377.0	3,447.0	—	2.600	2.595	0.011	0.013	1.00	—
Propene-propane	261.0	262.0	361.0	—	1.142	1.117	0.905	0.922	1.00	—
Bubble point pressure at given temperature										
Hydrogen-methane	117.0	—	10,273.0	10,468.0	9.964	9.946	0.059	0.061	1.00	—
N_2-n-heptane	353.0	—	20,836.0	19,088.0	3.996	3.985	0.017	0.021	1.00	—
H_2S-n-butane	367.0	—	3,702.0	3,849.0	1.679	1.616	0.538	0.581	1.00	—
Methane-ethane	144.0	—	296.0	284.0	3.034	3.036	0.025	0.024	1.00	—
Ethane-n-decane	378.0	—	3,447.0	3,469.0	2.600	2.595	0.011	0.014	1.00	—
Propene-propane	261.0	—	361.0	348.0	1.142	1.118	0.905	0.922	1.00	—
n-butane-n-hexane	425.0	—	2,534.0	2,512.0	1.196	1.198	0.543	0.539	1.00	—
Dew point temperature at given pressure										
Methane-CO_2	224.0	225.0	4,040.0	—	3.969	2.754	0.283	0.328	0.0	—
H_2S-n-decane	411.0	411.0	1,379.0	—	5.837	5.815	0.037	0.036	0.0	—
Methane-propane	158.0	158.0	689.0	—	2.846	2.765	0.002	0.002	0.0	—
Methane-n-decane	378.0	382.0	6,895.0	—	4.228	4.553	0.007	0.007	0.0	—
Ethane-n-pentane	311.0	310.0	3,447.0	—	1.296	1.260	0.129	0.098	0.0	—
Propene-propane	261.0	273.0	361.0	—	1.142	1.487	0.905	1.245	0.0	—
Dew point pressure at given temperature										
Nitrogen-methane	89.0	—	101.0	85.0	5.301	4.165	0.100	0.106	0.0	—
H_2S-n-decane	411.0	—	1,379.0	1,412.0	5.837	5.672	0.037	0.037	0.0	—
CO_2-propane	344.0	—	4,137.0	4,092.0	2.073	2.036	0.830	0.832	0.0	—
Methane-H_2S	211.0	—	2,758.0	2,591.0	15.081	18.339	0.069	0.068	0.0	—
Methane-propane	158.0	—	689.0	718.0	2.846	2.477	0.002	0.002	0.0	—
Ethane-n-pentane	311.0	—	3,447.0	3,142.0	1.296	1.328	0.129	0.120	0.0	—
Propene-propane	261.0	—	361.0	320.0	1.142	1.123	0.905	0.916	0.0	—
n-butane-n-hexane	425.0	—	2,534.0	2,504.0	1.196	1.200	0.543	0.539	0.0	—
Equilibrium temperature at given L/F and pressure										
Hydrogen-propene	228.0	226.0	27,579.0	—	7.647	7.731	0.023	0.021	0.70	—
H_2S-n-butane	367.0	363.0	3,702.0	—	1.679	1.633	0.538	0.561	0.70	—
CO_2-n-decane	478.0	480.0	6,895.0	—	3.133	3.097	0.089	0.096	0.70	—
Methane-n-heptane	233.0	224.0	1,379.0	—	8.603	8.614	0.000	0.000	0.70	—
Ethane-propane	200.0	199.0	138.0	—	1.474	1.490	0.169	0.152	0.70	—
Ethane-n-decane	378.0	377.0	3,447.0	—	2.600	2.591	0.011	0.013	0.70	—
Propane-n-decane	511.0	503.0	5,516.0	—	1.568	1.607	0.392	0.364	0.70	—
Equilibrium pressure at given L/F and temperature										
Hydrogen-propane	311.0	—	34,474.0	32,555.0	2.428	2.549	0.245	0.211	0.70	—
Nitrogen-methane	89.0	—	101.0	106.0	5.301	5.411	0.100	0.093	0.70	—
Methane-H_2S	211.0	—	2,758.0	3,013.0	15.081	15.824	0.069	0.063	0.70	—
CO_2-propane	344.0	—	4,137.0	4,074.0	2.073	2.047	0.830	0.833	0.70	—
Methane-ethane	144.0	—	296.0	284.0	3.034	3.038	0.025	0.024	0.70	—
Ethane-propane	228.0	—	517.0	530.0	1.183	1.182	0.199	0.200	0.70	—
n-butane-n-decane	511.0	—	4,137.0	4,100.0	1.394	1.418	0.420	0.395	0.70	—
Nitrogen-n-decane	311.0	—	27,579.0	24,247.0	3.285	3.291	0.002	0.001	0.70	—

$\gamma_i = f_i^L / f_i^0 x_i$ = activity coefficient of component "i" in liquid phase
δ_i = solubility parameter, (cal/ml.)$^{1/2}$
$\nu_i = f_i^0 / P$ = fugacity coefficient of component "i" as pure liquid
$\phi_i = f_i^V / P y_i$ = fugacity coefficient of component "i" in vapor phase
Φ_i = liquid volume fraction of component "i" in Equation (21)
ω_i = acentric factor of component "i"

Subscripts and Superscripts

c = critical condition
i, j, m = component identity
r = reduced condition
L = liquid phase
V = vapor phase
0 = ideal gas state

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Table 7. Results of Enthalpy Correlation Evaluations

System	No. of points	K&H	CPY	MBWR	RKW	PGC	FR3	This work
		(Avg. abs. deviations) × 10^{-3}, joule/kg						
N_2 (100%)	49	3.5	1.4	1.2	4.0	0.9	0.7	1.6
N_2-CH_4 (43.4:56.6)	54	8.6	2.1	1.4	7.4	0.7	2.8	2.3
CH_4 (100%)	35	45.8	4.2	1.4	7.4	0.9	1.9	3.3
CH_4-C_3H_8 (94.8:5.2)	47	38.6	3.3	1.6	7.4	2.1	1.6	2.8
CH_4-C_3H_8 (88.3:11.7)	47	40.9	6.8	1.6	8.6	1.4	2.6	3.0
CH_4-C_3H_8 (72.0:28.0)	45	46.8	12.1	2.1	13.3	1.6	2.3	3.7
CH_4-C_3H_8 (49.4:50.6)	45	48.1	17.2	3.0	23.0	2.6	2.8	5.4
CH_4-C_3H_8 (23.4:76.6)	45	47.2	14.2	2.1	29.8	1.6	3.3	4.0
C_3H_8 (100%)	43	43.3	14.0	2.3	36.5	1.2	2.6	3.5
CH_4-C_2H_6-C_3H_8 (36.6:31.1:32.3)	31	48.8	15.8	9.3	27.0	2.3	1.6	4.7
C_5H_{12} (100%)	160	10.9	4.2	3.5	5.8	3.7	4.4	3.7
C_5H_{12}-C_6H_{12} (79.3:20.7)	115	9.1	4.0	2.8	4.7	3.5	3.5	3.3
C_5H_{12}-C_6H_{12} (61.2:38.8)	118	7.7	5.1	3.3	5.1	4.2	4.0	4.2
C_5H_{12}-C_6H_{12} (38.5:61.5)	112	6.5	2.8	3.5	4.4	3.7	4.0	2.8
C_5H_{12}-C_6H_{12} (19.7:80.3)	103	9.8	6.1	5.1	5.4	6.8	6.3	5.1
C_6H_{12} (100%)	113	10.2	6.3	3.5	5.1	4.0	3.0	4.7
C_5H_{12}-C_8H_{18} (80.9:19.1)	66	22.1	10.5	7.2	10.2	6.8	6.3	7.2
C_5H_{12}-C_8H_{18} (59.7:40.3)	66	30.0	11.2	6.5	11.2	7.4	5.4	7.2
C_5H_{12}-C_8H_{18} (39.2:60.8)	47	38.6	13.0	7.2	15.1	8.6	7.2	8.6
C_5H_{12}-C_8H_{18} (21.8:78.2)	60	36.3	8.6	7.0	13.3	5.8	5.8	6.5
C_8H_{18} (100%)	70	28.8	6.5	6.5	14.4	6.5	6.3	5.8
Overall average	1471	21.6	7.0	4.0	10.0	4.0	4.0	4.4

K&H refers to NGPA K&H package, Edmister, Persyn and Erbar (1963, 1964, 1967); CPY, extension of Curl-Pitzer (1958) correlation by Yarborough for NGPA Data Book (1966); MBWR, modified Benedict-Webb-Rubin Equation, Starling (1970); RKW, modified Redlich-Kwong Equation, Wilson (1966); PGC, Furtado et al (1970); and FR3, 1970 Rice Properties III, Anonymous (1971).

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Kinetics of Crystallite Sintering During Heat Treatment of Supported Metal Catalysts

Models are developed to describe sintering of metal crystallites during heat treatment. The growth rate of such crystallites is assumed to depend upon particle migration over the surface of the support as well as on the rate the colliding particles merge (sinter) into a single unit. The theory predicts that the rate of decay of exposed metal surface area S is given as in Equation (1a). The exponent n is related to the assumed size dependence of the diffusion coefficients or of the rate constant of the merging process. It varies from 4 to 8 for diffusion controlled decay and it is less than 3 for sintering controlled decay, that is, when the rate controlling step is the merging of two colliding particles. Diffusion control is associated with strong interactions between the metal and the support, but in sintering control there is a weaker metal-support interaction.

E. RUCKENSTEIN and
B. PULVERMACHER

Department of Chemical Engineering
University of Delaware
Newark, Delaware 19711

SCOPE

The degree of dispersion of a metal on a support affects the activity and selectivity of the supported metal catalyst. In freshly prepared catalyst, the metal is generally highly dispersed so that a large number of the metal atoms are accessible to reactants. Deactivation observed after excessive heating is associated with aggregation and sintering of the small crystallites (Adler and Keavney, 1960; Mills et al., 1960; Maat and Moscou, 1965).

The goals of the present paper are:

1. to develop a model as those used in chemical kinetics to describe the sintering process caused by heat treatment,
2. to obtain an equation for the rate of decrease of the exposed metal surface area during heat treatment,
3. to explain the effect of temperature and of the chemical atmosphere upon the decay of the exposed surface area of metal.

In the model one assumes migration of the metal crystallites upon the surface of the support and sintering of the colliding particles.