Enthalpies of Methane-Light Hydrocarbon Binary Mixtures in the Vapor Phase

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The isothermal effects of pressure and composition on the mixture and partial enthalpy differences of the methane-propane binary were derived from PVTy data. A graphical and numerical technique was used to derive the enthalpy differences from 100° to 460°F. and 200 to 2,000 lb./sq. in. abs. for the complete composition range of the binary.

The isothermal effects of pressure and composition on the mixture enthalpy data of the methane-propane binary were also calculated with the Benedict-Webb-Rubin and the Redlich-Kwong equations of state. The results of the three methods of calculation are compared. The comparison showed that the two-constant Redlich-Kwong equation of state is as good as the eight-constant Benedict equation of state in the superheated vapor region.

The data derived in this work were combined with other methane binary enthalpy data from the literature to construct a general correlation of the effect of pressure and composition on the enthalpy of methane-light hydrocarbon binaries. The correlating parameters are the pseudo reduced temperature and pressure and a mole-average acentric factor.

Process engineers now recognize the urgent need for better enthalpy values of mixtures in both the vapor and liquid phases. Industry is paying more for process plants because these engineers do not have good enough thermodynamic data for precise design.

Alternate ways of obtaining the effect of pressure and composition on the isothermal enthalpy difference ΔH for the mixture are calorimetric determination of the isothermal effect of pressure on enthalpy at a constant composition, application of thermodynamic relationships to experimental PVTy data by means of graphical and numerical methods (*5*, *19*) and application thermodynamic relationships by equations of state (*3*, *13*).

The effect of pressure and composition on the partial enthalpies of the components can be calculated from mixture enthalpy data. No mixture enthalpy data have been obtained by the first method listed above, and few data have been calculated by the second. The use of digital computers has made the third method the easiest way to calculate the effect of pressure and composition on the mixture enthalpy and the partial enthalpies of the components of the mixture. However the accuracy of enthalpy values calculated from equations of state is uncertain. Any errors in the equation of state are magnified in the calculated enthalpy value.

This paper is concerned with the calculation of the pressure and composition effects on the mixture enthalpy and the partial enthalpies of the components in the vapor phase. A numerical and graphical method was used to apply thermodynamic relationships to experimental PVTy data for the methane-propane binary system.

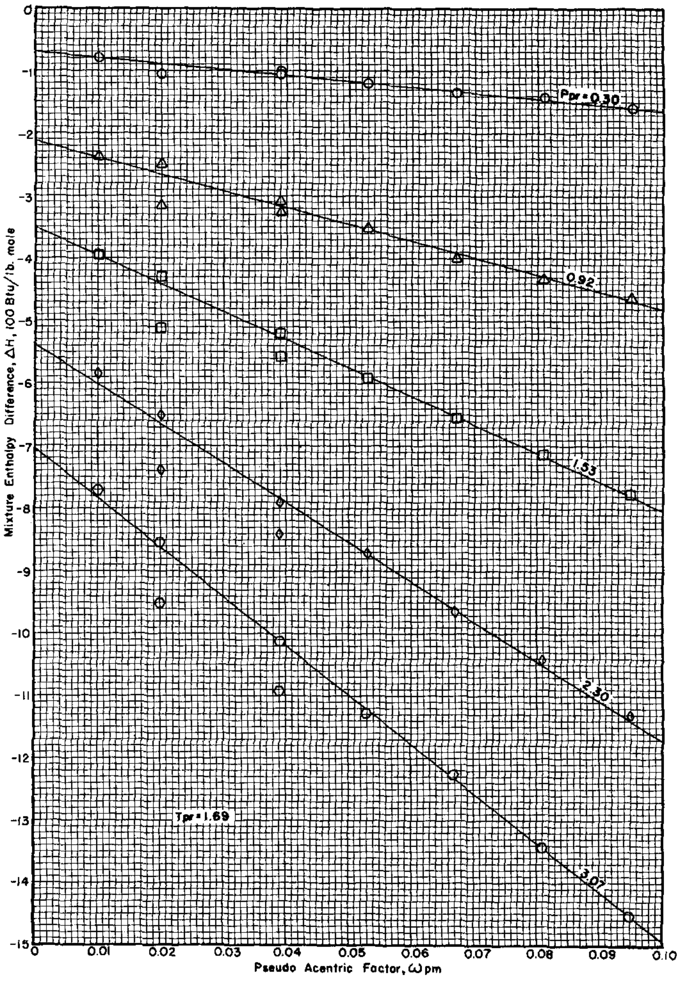

Fig. 1. Mixture enthalpy difference of methane binaries as a function of the pseudo acentric factor.

EQUATIONS AND METHODS USED

Several thermodynamic equations have been used to calculate the isothermal effect of pressure on the enthalpy for a pure component or a mixture of constant composition (7). One of these well-known equations was rearranged to give the equation used in this work (23) for deriving the isothermal effect of pressure on the mixture enthalpy from PVTy data:

$$\left(\frac{\partial H}{\partial P}\right)_{T,y} = V\left[1-\left\{\frac{\frac{RT}{P}-T\left(\frac{\partial \alpha}{\partial T}\right)_{P,y}}{V}\right\}\right] = V(1-\theta) \quad (1)$$

Equation (1) is convenient because as pressure approaches zero, θ approaches unity. Thus θ was plotted against pressure to smooth the partial derivatives $\left(\frac{\partial \alpha}{\partial P}\right)_{P,y}$, which are the main source of error in Equation (1), at low pressure. The smoothing of θ at low pressure aids the graphical integration of Equation (2)

$$\Delta H = H^P_T - H^0_T = \int_0^P V(1-\theta)\,dP \quad (2)$$

by giving a smooth curve of $V(1-\theta)$ against P to extrapolate to zero pressure.

Equations (3) and (4) (10) were used to calculate the partial enthalpy differences of the two components:

$$\Delta\overline{H}_1 = \Delta H + (1-y_1)\left(\frac{\partial \Delta H}{\partial y_1}\right)_{T,P} \quad (3)$$

$$\Delta\overline{H}_2 = \Delta H - y_1\left(\frac{\partial \Delta H}{\partial y_1}\right)_{T,P} \quad (4)$$

The partial derivative $\left(\frac{\partial \Delta H}{\partial y_1}\right)_{T,P}$ was smoothed by the following method.

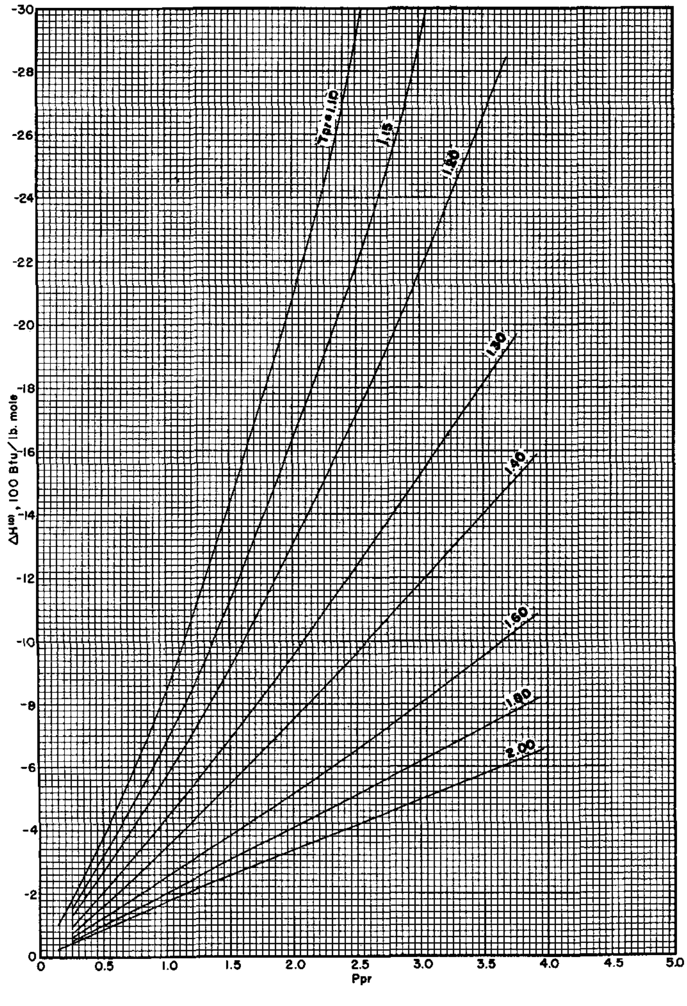

Fig. 2. $\Delta H^{(0)}$ as a function of T_{pr} and P_{pr}.

Rearranging Equations (3) and (4) one obtains

$$\frac{\Delta\overline{H}_1}{\Delta H} = 1 - \left[\frac{(y_1-1)\left(\frac{\partial \Delta H}{\partial y_1}\right)_{T,P}}{\Delta H}\right] \quad (5)$$

and

$$\frac{\Delta\overline{H}_2}{\Delta H} = 1 - \left[\frac{y_1\left(\frac{\partial \Delta H}{\partial y_1}\right)_{T,P}}{\Delta H}\right] \quad (6)$$

The right sides of Equations (5) and (6) were plotted against composition. One can see that as y_1 approaches zero, the right side of Equation (6) approaches unity. As y_1 approaches unity, the right side of Equation (5) approaches unity. Thus the right side of Equation (6) was used to smooth the partial derivative at low mole fractions of component 1. The right side of Equation (5) was used to smooth the partial derivative at high mole fractions of component 1. Then the smoothed values of the partial derivative were used to calculate the partial enthalpy differences of both components. Equation (7) (10)

$$y_1\left(\frac{\partial \Delta\overline{H}_1}{\partial y_1}\right)_{T,P} + (1-y_1)\left(\frac{\partial \Delta\overline{H}_2}{\partial y_1}\right)_{T,P} = 0 \quad (7)$$

was used to check the consistency of the partial enthalpy data.

RESULTS OF METHANE-PROPANE CALCULATIONS

PVTy data from Sage and Lacey (19) were used in calculating the mixture enthalpy difference and the partial enthalpy differences of the methane-propane binary in the superheated vapor region. Sage and Lacey tabulate smoothed values of the compressibility factor and volume for nine equally spaced mole fractions between pure methane and pure propane. The data are given at 60°F. intervals between 100° and 460°F., and the pressure range is from 200 to 10,000 lb./sq. in. abs. However the pressure range used in this work is 200 to 2,000 lb./sq. in. abs.

Sage and Lacey do not estimate the variation in the smoothed PVTy data that they present. An estimate based on variations in PVTy data that they report for other binary systems (20, 21) gives a variation in the PVTy data for the methane-propane system of 0.2 to 0.3%.

Enthalpy data for superheated methane and propane are presented by Sage and Lacey (19). These data were used to assure the binary mixture enthalpy data were consistent

TABLE 2. THE EFFECT OF PRESSURE AND COMPOSITION ON THE ENTHALPY OF THE METHANE-PROPANE BINARY BY VARIOUS CALCULATIONAL METHODS

y_1*	ΔH† PVTy	ΔH** RK	ΔH†† BWR
100°F. and 200 lb./sq. in. abs.			
0.20	-645	-496	-5,570
0.40	-419	-351	-394
0.60	-252	-239	-256
0.80	-144	-153	-153
220°F. and 200 lb./sq. in. abs.			
0.20	-353	-334	-336
0.40	-249	-242	-238
0.60	-164	-167	-159
0.80	-104	-106	-98
340°F. and 200 lb./sq. in. abs.			
0.20	-258	-246	-225
0.40	-192	-179	-162
0.60	-134	-123	-110
0.80	-83	-78	-68
460°F. and 200 lb./sq. in. abs.			
0.20	-218	-190	-164
0.40	-159	-138	-119
0.60	-107	-94	-81
0.80	-63	-59	-51
160°F. and 400 lb./sq. in. abs.			
0.20	-1,072	-910	-972
0.40	-680	-616	-642
0.60	-430	-409	-410
0.80	-254	-256	-244
280°F. and 400 lb./sq. in. abs.			
0.20	-625	-596	-570
0.40	-433	-423	-399
0.60	-300	-287	-265
0.80	-187	-181	-163
400°F. and 400 lb./sq. in. abs.			
0.20	-468	-438	-390
0.40	-342	-314	-278
0.60	-235	-214	-188
0.80	-143	-134	-117
220°F. and 800 lb./sq. in. abs.			
0.20	-1,937	-1,784	-1,804
0.40	-1,123	-1,100	-1,095
0.60	-683	-701	-680
0.80	-417	-428	-399
340°F. and 800 lb./sq. in. abs.			
0.20	-1,112	-1,074	-999
0.40	-797	-741	-684
0.60	-535	-493	-449
0.80	-324	-305	-272
460°F. and 800 lb./sq. in. abs.			
0.20	-843	-778	-685
0.40	-611	-549	-483
0.60	-415	-369	-323
0.80	-244	-227	-199
280°F. and 1,500 lb./sq. in. abs.			
0.20	-2,912	-2,697	-2,806
0.40	-1,772	-1,720	-1,708
0.60	-1,100	-1,083	-1,042
0.80	-677	-651	-605
400°F. and 1,500 lb./sq. in. abs.			
0.20	-1,780	-1,716	-1,609
0.40	-1,257	-1,170	-1,083
0.60	-847	-769	-701
0.80	-504	-469	-420
220°F. and 2,000 lb./sq. in. abs.			
0.40	-2,817	-2,715	-2,943
0.60	-1,734	-1,718	-1,766
0.80	-1,012	-1,012	-983
340°F. and 2,000 lb./sq. in. abs.			
0.20	-2,773	-2,626	-2,668
0.40	-1,903	-1,787	-1,754
0.60	-1,227	-1,159	-1,105
0.80	-730	-703	-649
460°F. and 2,000 lb./sq. in. abs.			
0.20	-2,007	-1,848	-1,730
0.40	-1,453	-1,284	-1,184
0.60	-967	-848	-772
0.80	-563	-516	-462

* Component 1 is methane.
† Values derived from PVTy data.
** Calculated by Redlich-Kwong equation.
†† Calculated by Benedict-Webb-Rubin equation.

with pure component data by drawing the end points of a ΔH against composition plot to the pure component methane and propane data.

With the method described above the mixture enthalpy difference and the partial enthalpy differences for the components were calculated for the methane-propane binary system. The calculated values are tabulated in Table 1.*

The accuracy of the mixture enthalpy difference is limited by the errors in the original data, errors introduced in calculating the partial derivatives, errors in smoothing, and errors in graphical integration. The errors in smoothing and graphical integration were assumed to be negligible. The partial derivatives were calculated by numerical differentiation equations (22), and the error introduced by using the equations was calculated by the error functions of the equations. By means of this approach the overall average error in the calculated mixture enthalpy difference is about 2%.

The accuracy of the partial enthalpy differences is less than that of the mixture enthalpy difference. The partial enthalpy difference of methane is the difference between two numbers. It is positive for low concentrations of methane and negative for high concentrations of methane.

Thus in the middle concentration range the partial enthalpy difference of methane is a small difference between two relatively large numbers, and a percentage deviation would have little meaning. However the average deviation of the partial enthalpy difference of methane probably does not exceed 25 B.t.u./lb. mole except near the two-phase region or at low mole fractions of methane (0.10 or 0.20).

The partial enthalpy difference of propane is the sum of two quantities. The average error in the partial enthalpy difference of propane should be the sum of the overall average errors of the mixture enthalpy difference and the partial derivative $(\partial \Delta H/\partial y_1)_{T,P}$. This error was calculated to be about 5%.

Equation (7) was applied to twenty-four points at $y_1 = y_2 = 0.50$. At this point the ratio of the partial derivatives in Equation (7) should equal -1. Of the twenty-four points checked the ratio $(\partial \Delta \overline{H}_1/\partial y_1)_{T,P}/(\partial \Delta \overline{H}_2/\partial y_1)_{T,P}$ was greater than -1 at seven of the points, less than -1 at fifteen of the points, and -1 twice. The average of the seven points greater than -1 was -0.94, and the average of the fifteen points less than -1 was -1.08. The overall average value of the ratio was -1.03. Thus consistent partial enthalpy values were obtained by the calculation method used.

COMPARISON OF CALCULATED ENTHALPIES WITH EQUATIONS OF STATE AND LITERATURE DATA

It is possible to apply thermodynamic relationships to an equation of state to derive an expression for the isothermal effect of pressure on the mixture enthalpy. The two equations of state used herein have been programmed for the IBM-650 digital

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* Tabular material has been deposited as document 7417 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

computer, the Redlich-Kwong equation (7), and the Benedict-Webb-Rubin equation (*1*).

The Redlich-Kwong equation of state is an empirical, two-constant equation of the form

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)} \qquad (8)$$

This equation is completely generalized, since the two constants *a* and *b* are functions of the critical properties of the component used. The Redlich-Kwong equation of state used in this work was programmed for the IBM-650 by Erbar and Thompson (9). This equation of state is recommended for conditions above the critical temperature of the gas.

The Benedict-Webb-Rubin equation of state is an empirical, eight-constant equation which is applicable to both gas and liquid phases. The Benedict-Webb-Rubin equation is of the form

$$P = RT/V + (B_oRT - A_o - C_o/T^2)/V^2 + (bRT - a)/V^3 + a\alpha'/V^6 + (c/T^2V^3)(1 + \gamma/V^2)e^{-\gamma/V^2} \qquad (9)$$

All eight constants must be evaluated for each component from experimental data. The Benedict-Webb-Rubin equation of state that was used in this work was programmed for the IBM-650 by Edwards, et al. (*8*). This program takes pure component coefficients and uses the combination rules given by Benedict, et al. (*2*). The pure component coefficients used in this work were taken from Opfell, et al. (*12*).

A comparison of the effect of pressure and composition on the enthalpy of the methane-propane binary is shown in Table 2. The enthalpy effect calculated by the Redlich-Kwong and Benedict-Webb-Rubin equations is compared with that calculated from the experimental PVTy data. Some of the conditions shown in Table 2 (temperatures and pressures) lay outside the range of data for which the pure component Benedict-Webb-Rubin equation coefficients had been obtained. For these conditions the Benedict-Webb-Rubin equation was extrapolated, and the calculated enthalpy values deviated as much as 30% from the enthalpy values calculated from the PVTy data. The overall absolute average deviation from the values calculated from the PVTy data was 12.9% for the Benedict-Webb-Rubin equation and 6.6% for the Redlich-Kwong equation. However for the conditions where the coefficients for both methane and propane had been determined from pure component data, the overall absolute average deviation for the Benedict-Webb-Rubin equation was 6.6%.

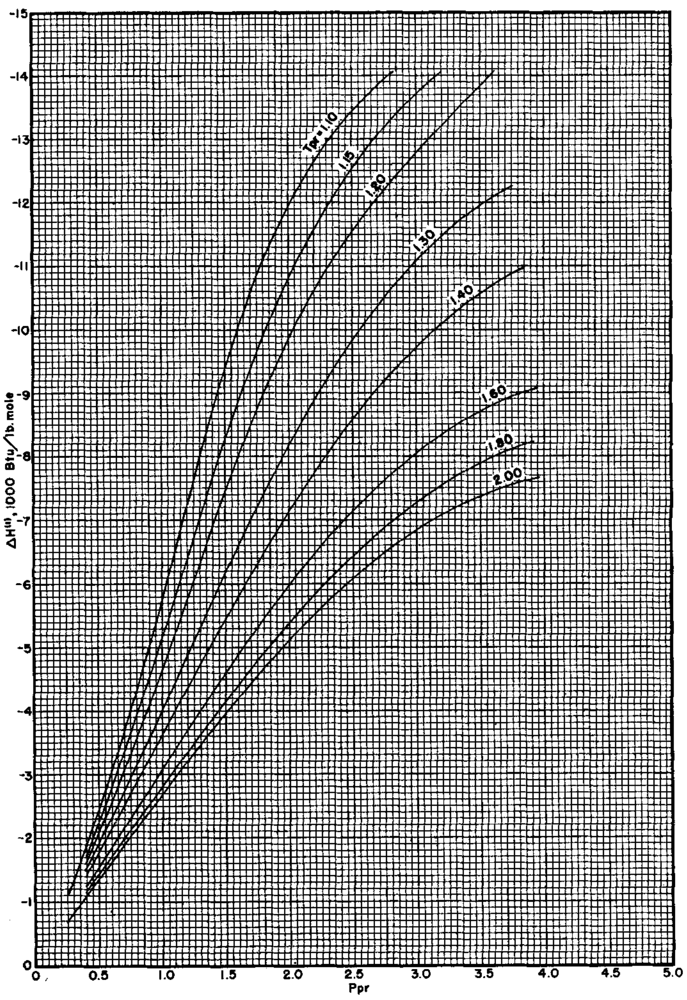

Fig. 3. $\Delta H^{(1)}$ as a function of T_{pr} and P_{pr}.

TABLE 3. COMPARISON OF METHANE-PROPANE BINARY ENTHALPY DIFFERENCES

	100°F.		160°F.		220°F.		280°F.	
P, lb./sq. in. abs.	ΔH* PVTy	ΔH† Ref. *4*	ΔH PVTy	ΔH Ref. *4*	ΔH PVTy	ΔH Ref. *4*	ΔH PVTy	ΔH Ref. *4*
			0.647 Mole fraction methane					
200	—227	—223	—189	—186	—148	—151	—133	—125
400	—484	—468	—381	—384	—297	—311	—264	—245
600			—591	—591	—463	—476	—396	—386
800			—792	—799	—614	—645	—539	—521
1,000			—968	—1,008	—771	—812	—671	—654
1,250					—977	—1,013	—843	—822
1,500					—1,189	—1,196	—992	—986
			0.805 Mole fraction methane					
200	—142	—150	—125	—123	—100	—103	—92	—89
400	—308	—312	—253	—254	—206	—213	—182	—179
600	—473	—486	—383	—389	—315	—324	—271	—271
800	—642	—667	—530	—529	—413	—436	—365	—361
1,000	—838	—858	—648	—668	—518	—546	—454	—452
1,250			—830	—841	—659	—679	—564	—562
1,500			—1,001	—1,006	—779	—802	—662	—665
			0.917 Mole fraction methane					
200	—102	—110	—88	—91	—76	—76	—67	—65
400	—205	—227	—181	—184	—156	—154	—133	—131
600	—322	—350	—279	—283	—228	—235	—199	—198
800	—441	—479	—374	—381	—307	—316	—264	—266
1,000	—552	—613	—471	—481	—374	—394	—327	—330
1,250	—712	—788	—591	—607	—459	—489	—405	—410
1,500	—874	—972	—703	—730	—562	—582	—473	—486

* Values derived from PVTy data.
† Values from Budenholzer, et al. (*4*).

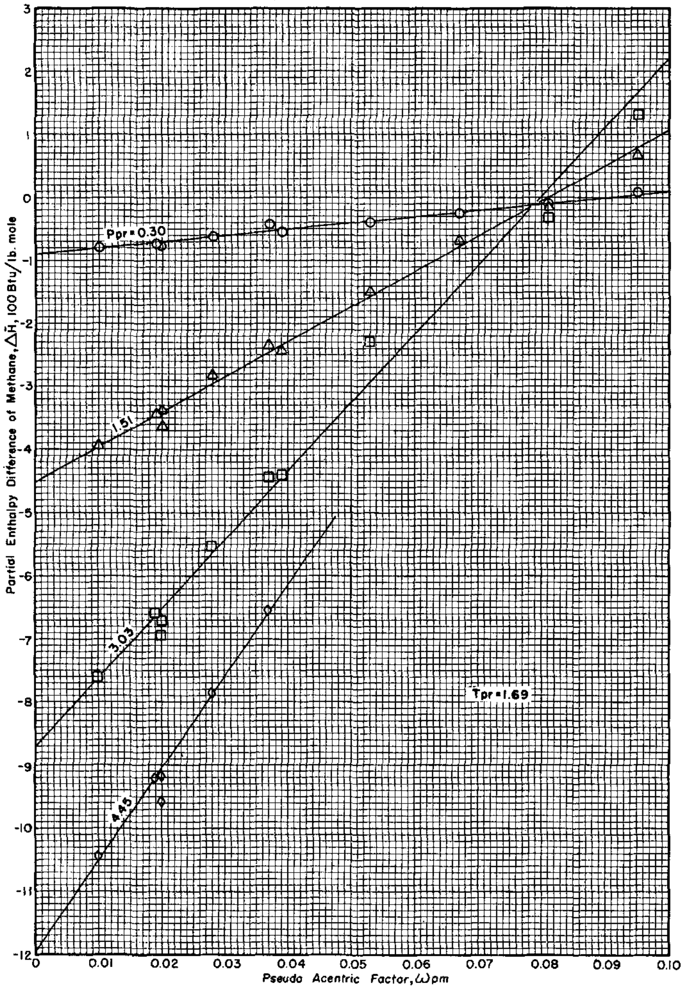

Fig. 4. Partial enthalpy difference of methane as a function of the pseudo acentric factor.

Budenholzer, et al. (*4*) give some partial enthalpy values for both components in the methane-propane binary system. The data of Budenholzer, et al. were obtained from measured Joule-Thomson coefficients and calculated heat capacities.

The mixture enthalpy difference values derived in this work were plotted against composition at constant temperature and pressure in order to interpolate to the composition of the mixtures given by Budenholzer, et al. A comparison of the two sets of mixture enthalpy difference data is given in Table 3. The absolute average deviation of the two sets of data is 3.1%. However it is worth noting that there are discrepancies between the methane enthalpy differences reported by Sage

TABLE 4. PURE COMPONENT ACENTRIC FACTORS

Component	Acentric factor
Methane	0.010
Ethane	0.099
Propane	0.152
n-Butane	0.201
n-Pentane	0.252

TABLE 5. COMPARISON OF METHANE BINARY ENTHALPY DIFFERENCE CORRELATION WITH DERIVED VALUES

T, °F.	*P*, lb./sq. in. abs.	y_1*	ΔH** PVTy	ΔH† Y and E
C_1-C_3 Binary				
160	200	0.60	—211	—190
220	600	0.40	—808	—819
220	600	0.80	—311	—316
220	1,500	0.50	—1,706	—1,695
280	400	0.20	—625	—641
280	400	0.60	—300	—290
280	1,000	0.40	—1,173	—1,156
280	1,000	0.80	—462	— 471
340	800	0.20	—1,112	—1,152
340	800	0.60	—535	—526
340	2,000	0.40	—1,903	—1,896
340	2,000	0.80	—730	—773
400	1,000	0.20	—1,188	—1,210
400	1,000	0.60	—579	—596
C_1-C_2 Binary				
100	1,000	0.60	—878	—916
160	600	0.60	—395	—402
160	2,000	0.50	—1,675	—1,693
220	200	0.50	—139	—134
220	1,500	0.60	—841	—859

* Component 1 is methane.
** Values derived from PVTy data.
† Yarborough and Edmister correlation.

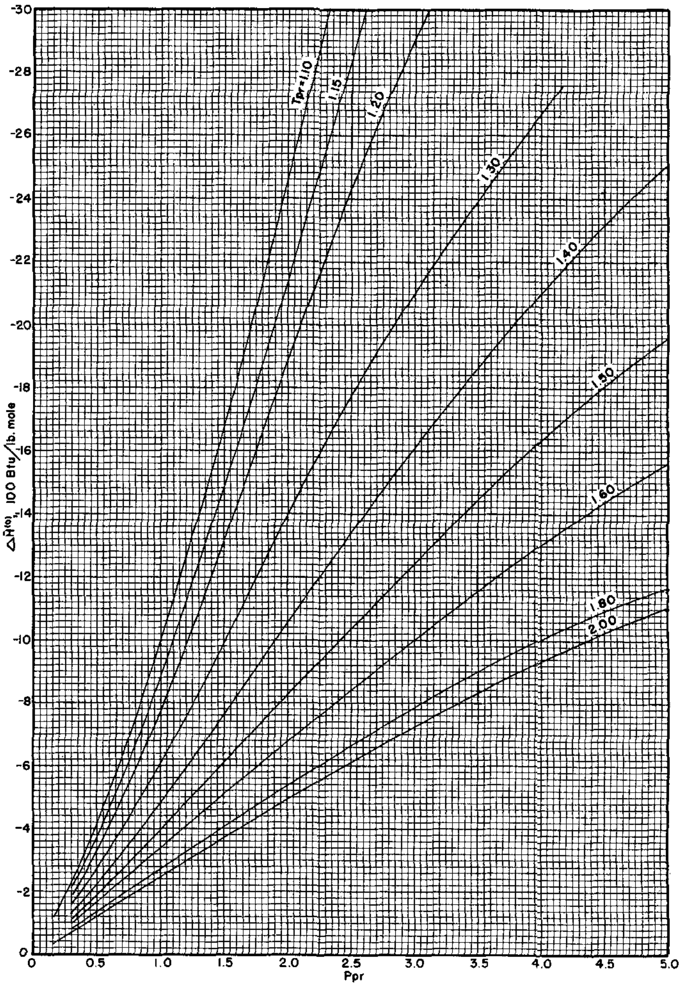

Fig. 5. $\Delta \overline{H}^{(0)}$ as a function of T_{pr} and P_{pr}.

and Lacey (*19*) and by Budenholzer, et al. (*4*). The absolute average deviation between the two sets of data for pure methane is 6.5%.

CORRELATION OF METHANE BINARY ENTHALPY DATA

Sage and Lacey (*19*) tabulate limited partial enthalpy values for both components of the methane-ethane, methane-*n*-butane, and methane-*n*-pentane binary systems. Sage and Lacey also tabulate pure component data for methane, ethane, propane, and *n*-butane. The pure component data were included with the data derived in this work and the Sage and Lacey mixture data to assure that the mixture data and the pure component data were consistent.

The above enthalpy data were correlated by extending Pitzer's modified principle of corresponding states to mixtures. Pitzer, et al. (*14*) introduced a third parameter, the acentric factor ω, to the principle of corresponding states. The acentric factor of a pure component is defined as

$$\omega = -\,[\log (P^{\circ}/P_c) + 1.000] \quad \text{at } T_r = 0.70 \qquad (10)$$

For a pure fluid the acentric factor measures the deviation of the intermolecular potential function from that of the spherical molecules of the simple fluids, argon, krypton, and xenon.

Several properties of pure fluids have been correlated by the use of the reduced temperatures T/T_c, reduced pressures P/P_c, and the acentric factors of the pure components (*6*) (compressibility factor, pressure correction to the ideal gas state entropy, and enthalpy). The method for correlating the pressure correction to the ideal gas state mixture enthalpies of methane binaries is an extension of this method. A pseudo reduced temperature T/T_{pc}, a pseudo reduced pressure P/P_{pc}, and a pseudo acentric factor were used in the correlation. The pseudo critical temperature and pressure (T_{pc} and P_{pc}) were calculated by Kay's Rule (*11*). The pseudo acentric factor was calculated for the binary by a mole fraction average of the pure component acentric factors after Prausnitz and Gunn (*16*) and Pitzer and Hultgren (*15*):

$$\omega_{pm} = y_1\omega_1 + y_2\omega_2 \qquad (11)$$

The pure component acentric factors used in this work were calculated from the data of Rossini (*18*). The values are shown in Table 4.

The mixture enthalpy difference from an ideal gas was correlated by the equation

$$\Delta H = \Delta H^{(0)} + \omega_{pm}\,\Delta H^{(1)} \qquad (12)$$

With this correlation method the mixture enthalpy difference was plotted against ω_{pm} as shown in Figure 1. Straight lines were drawn through the data points which included both mixture and pure component data. The intercepts and slopes of the lines give $\Delta H^{(0)}$ and $\Delta H^{(1)}$ respectively. The final correlations of $\Delta H^{(0)}$ and $\Delta H^{(1)}$ are shown in Figures 2 and 3.

An attempt was made to correlate the mixture enthalpy difference by means of a dimensionless equation of the form

$$\frac{\Delta H}{RT_{pc}} = \left(\frac{\Delta H}{RT_{pc}}\right)^{(0)} + \omega_{pm}\left(\frac{\Delta H}{RT_{pc}}\right)^{(1)}$$

However the initial plots of $\Delta H/RT_{pc}$ against ω_{pm} gave a greater scatter of data than did the plots of ΔH against ω_{pm}.

The partial enthalpy difference of methane was correlated in the same manner as the mixture enthalpy difference. The equation used to correlate the partial enthalpy difference was

$$\Delta \overline{H} = \Delta \overline{H}^{(0)} + \omega_{pm}\,\Delta \overline{H}^{(1)} \qquad (14)$$

The partial enthalpy difference of methane and the pure component methane data were plotted against ω_{pm} and straight lines were drawn through the data as shown in Figure 4. The final correlations of $\Delta \overline{H}^{(0)}$ and $\Delta \overline{H}^{(1)}$ are shown in Figures 5 and 6.

It must be noted that these correlations have been based on a very small range of ω_{pm}. No enthalpy data higher than $\omega_{pm} = 0.15$ were used in the mixture enthalpy difference correlation, and these data were at a very low pseudo reduced temperature. The partial enthalpy difference of methane correlation is not recommended for mixtures that have an ω_{pm} above 0.10.

The general correlation of methane binary mixture enthalpy differences presented here was compared with experimental data. The comparison is shown in Table 4. The methane-ethane derived enthalpy differences were taken from Sage and Lacey (*19*). The absolute average deviation of the general correlation presented in this article is 2.74%.

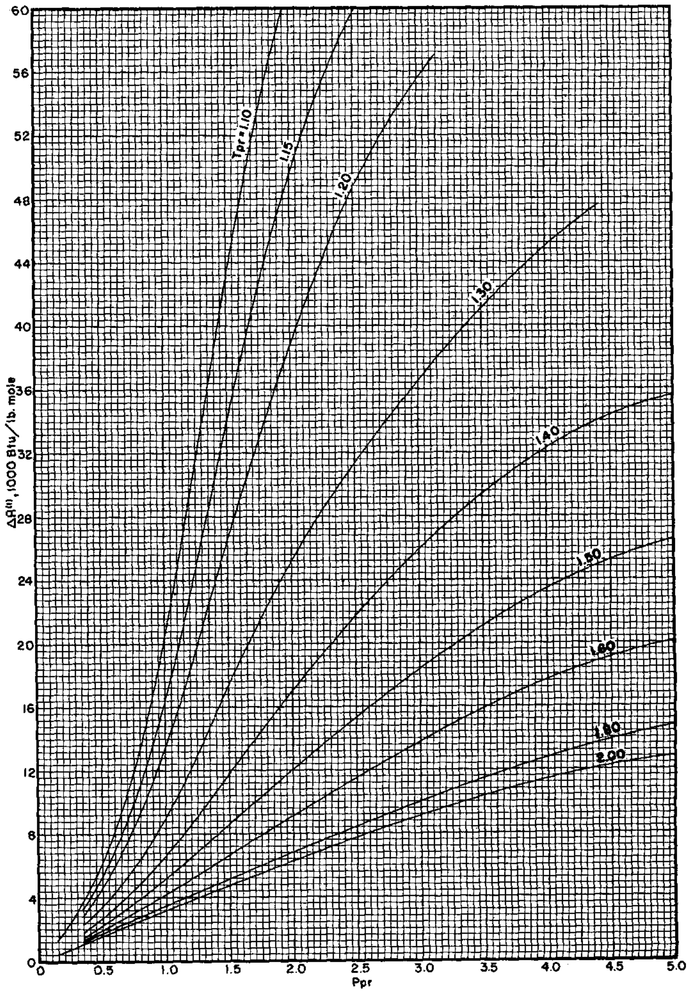

Fig. 6. $\Delta \overline{H}^{(1)}$ as a function of T_{pr} and P_{pr}.

The general correlation of the methane partial enthalpy differences presented was compared with twelve derived methane partial enthalpy values from the methane-ethane and methane-propane binaries. The absolute average difference was 22 B.t.u./lb.-mole.

CONCLUSIONS

The comparison of mixture enthalpy differences calculated by two equations of state with those calculated from PVTy data shows the equations of state to give fairly inaccurate values. This comparison also points out that the Benedict-Webb-Rubin equation of state should not be extrapolated into a region where coefficients for the equation have not been determined. The mixture enthalpy differences calculated from PVTy data compare reasonably well with the data of Budenholzer, et al. (*4*).

A general correlation for the mixture enthalpy difference of methane-light hydrocarbon binaries is presented. The correlation predicts enthalpy differences of methane binaries much better than either the Redlich-Kwong or Benedict-Webb-Rubin equations of state.

NOTATION

$a,b,c,A,B,$ = parameters for the Redlich-Kwong equation of state and/or

A_o,B_o,C_o = the Benedict-Webb-Rubin Equation of state

H = enthalpy, B.t.u./lb.-mole, $(H^P{}_T - H^o{}_T)_y + (H^o{}_T - H^o{}_o)_y$

$\overline{H}$ = partial enthalpy of a component, B.t.u./lb.-mole, $(\overline{H}^P{}_T - H^o{}_T)_{y,i} + (H^o{}_T - H^o{}_o)_i$

ΔH = mixture enthalpy difference from an ideal gas or the effect of pressure on the mixture enthalpy, B.t.u./lb.-mole, $(H^P{}_T - H^o{}_T)_y$

$\Delta\overline{H}$ = partial enthalpy difference of a component from an ideal gas or the effect of pressure on the partial enthalpy of a component, B.t.u./lb.-mole, $(\overline{H}^P{}_T - H^o{}_T)_{y,i}$

$H^P{}_T$ = enthalpy at temperature T and pressure P

$H^o{}_T$ = enthalpy at temperature T and the ideal gas state

$H^o{}_o$ = enthalpy at 0 temperature and the ideal gas state

$\overline{H}^P{}_T$ = partial enthalpy at temperature T and pressure P

P = absolute pressure, lb./sq. in. abs.

P° = vapor pressure, lb./sq. in. abs.

R = universal gas constant

T = absolute temperature, °R.

V = volume/mole

y = mole fraction of a component in the vapor

α = residual volume, volume/mole, $\dfrac{RT}{P} - V$

α',γ = constants for the Benedict-Webb-Rubin equation of state

ω = acentric factor

Superscripts

P = value at the system pressure

O = value in the ideal gas state

(0) = universal function of reduced temperature and pressure at $\omega = 0$.

(1) = universal function of reduced temperature and pressure that is dependent on the acentric factor

Subscripts

0 = zero absolute temperature

1,2 = methane (component 1) and the heavy component (component 2) of a binary system

c = critical values

i = value of component i

pc = pseudo critical values

pm = pseudo mixture values

pr = pseudo reduced values

r = reduced values

T, P, y = values held constant during an operation

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ERRATA

Equation (10) of "The Heat of Solution of Gases at High Pressure," by A. E. Sherwood and J. M. Prausnitz, which appeared in the *A.I.Ch.E. Journal*, **8**, No. 4, p. 519 (September, 1962), should read

$$\ln \phi_i = -\ln z + \frac{2}{v^g} \sum_j y_j B_{ij}$$

Equation (7) of "Solubility of Chlorofluoromethanes in Nonvolatile Polar Organic Solvents," by Lyle F. Albright, Paul T. Shannon, Francois Terrier, and Ping Lin Chueh, which appeared in the *A.I.Ch.E. Journal*, **8**, No. 5, p. 670 (November, 1962), should read

$$a_R = \frac{f^\circ{}_{RG}}{f^\circ{}_R} = \gamma_R x_R$$