Partial Enthalpies of Components in Gas Mixtures via Redlich-Kwong Equation of State

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Enthalpies of components in ideal gas mixtures can be computed from existing data. However the isothermal effects of pressure and composition on partial enthalpies of mixture components have not been completely characterized. An investigation of the application of the Redlich-Kwong equation of state to the calculation of partial enthalpies is reported here. Methods are developed for convenient hand calculations and for computations on the IBM-650.

Calculated partial enthalpies are compared with values derived from experimental P-V-T-C data for binary hydrocarbon mixtures. The calculated values agree fairly well with the derived data for pressures up to 2,500 lb./sq. in. abs. Best agreement is generally obtained when the mixture is well above the critical temperature of the more abundant component. No consistent bias was indicated however.

Partial enthalpies of mixture components cannot be measured directly. Some calculations are always required, whether one starts from calorimetric data, pressure-volume-temperature-composition (P-V-T-C) data, or when one uses an equation of state. These calculations are usually made graphically or analytically (that is on the digital computer).

In calculating enthalpies of mixtures three effects must be evaluated: effect of temperature, effect of pressure, and effect of composition. Also a datum or reference state of zero enthalpy must be selected. The effect of temperature on the enthalpy is most conveniently evaluated at the ideal gas state for any system, that is pure component or mixture, and enthalpy values are referred to zero absolute temperature, at which temperature the enthalpy of the ideal gas is arbitrarily taken as zero.

For hydrocarbons and many other gases the ideal gas state enthalpy values have been evaluated and tabulated in reference *6*. These compilations have been widely accepted as standard and are used in calculating enthalpies of pure components and of mixtures and also partial enthalpies of mixture components. This part of the enthalpy calculation problem has already been solved, leaving the effects of pressure and composition on mixture enthalpies undeveloped. Heats of vaporization and condensation of mixtures are other enthalpy values about which very little is known.

Effects of pressure and composition on the enthalpy of mixtures in the gas phase was the concern of the work reported in this paper. More specifically the objectives were to develop a general and rapid program for computing the partial enthalpies of gas mixture components on an IBM-650, and convenient generalized charts and procedure for making these same partial enthalpy calculations manually.

The versatile and convenient Redlich-Kwong equation of state served as the basis for the development of an IBM-650 computer program and a set of charts for estimating the partial enthalpy differences for components of gas mixtures. The effect of pressure on the enthalpy of the entire mixture is also found in these calculations.

REDLICH-KWONG EQUATION

The Redlich-Kwong equation of state (5) is an empirical two-constant equation of the form

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)} \tag{1}$$

where

$$a = 0.4278\,R^2T_c^{2.5}/P_c$$
$$b = 0.0867\,R\,T_c/P_c$$

The equation was originally developed for gases, as opposed to vapors, the arbitrary distinction being that gases exist above the critical temperature and vapors below the critical temperature. Any inadequacies in the Redlich-Kwong equation will be reflected and even magnified in the derived thermodynamic properties.

Equation (1) was rearranged to the following form for use in deriving thermodynamic properties:

$$Z = \frac{1}{1-h} - \left(\frac{A^2}{B}\right)\left(\frac{h}{1+h}\right) \tag{2}$$

where

$$A^2 = a/R^2T^{2.5}$$
$$B = b/RT$$
$$h = BP/Z$$

Equation (2) may be applied to multicomponent mixtures by the use of the following combination rules (5):

$$A = \sum_{i=1}^{n} y_i A_i$$
$$B = \sum_{i=1}^{n} y_i B_i$$

Inspection of Equations (1) and (2) shows that solving for *V* or *Z* (given *T* and *P*) involves trial-and-error calculations. Equation (2) has the advantage that Z is expressed as a function of only two parameters, A^2/B and BP. The latter are calculated easily for a given problem. Thus a plot of Z as a function of BP with lines of constant A^2/B allows rapid hand calculations. Either of Equations (1) and (2) may be programmed for digital computer solution.

FUGACITY COEFFICIENTS

Redlich and Kwong (5) used Equation (2) to derive an expression for gas-phase fugacity coefficients:

$$\ln \varphi_i = (Z-1)\frac{B_i}{B} - \ln(Z-BP) - \frac{A^2}{B}\left(\frac{2\,A_i}{A} - \frac{B_i}{B}\right)\ln\left(1 + \frac{BP}{Z}\right) \tag{3}$$

Equation (3) can also be programmed easily for the digital computer. However for hand calculations it is more convenient to rearrange Equation (3) in the following way (4):

$$\log \varphi_i = \log \bar{\varphi} - U\left(\frac{A_i}{A} - 1\right) + W\left(\frac{B_i}{B} - 1\right) \tag{4}$$

where

$$\log \overline{\varphi} = 0.4343\,(Z-1) - \log\,(Z-BP) - \frac{A^2}{B}\log\left(1+\frac{BP}{Z}\right)$$

$$U = \left(\frac{2A^2}{B}\right)\log\left(1+\frac{BP}{Z}\right)$$

$$W = 0.4343\,(Z-1) + \frac{A^2}{B}\log\left(1+\frac{BP}{Z}\right)$$

The parameters $\log \overline{\varphi}$, U, and W can be plotted as functions of A^2/B and BP. Data for plotting these diagrams are presented by Comings (*2*).

ENTHALPIES

The effect of pressure on enthalpy is given by

$$\left(\frac{\partial \ln \varphi_i}{\partial T}\right)_{P,y} = \frac{(H^\circ_i - \overline{H}^P_i)_T}{RT^2} = -\frac{\Delta \overline{H}_i}{RT^2} \quad (5)$$

Equation (3) may be differentiated to obtain an analytical expression for partial enthalpies (*1*). Application of Equation (5) to Equation (3) gives

$$-\frac{\Delta \overline{H}_i}{RT^2} = \frac{B_i}{B}\left(\frac{\partial Z}{\partial T}\right)_{P,y} - \frac{1}{(Z-BP)}\left[\left(\frac{\partial Z}{\partial T}\right)_{P,y} - P\left(\frac{\partial B}{\partial T}\right)_{P,y}\right] - \left[2\frac{A_i}{A}-\frac{B_i}{B}\right]\left[\ln\left(1+\frac{BP}{Z}\right)\right]\left[\frac{\partial (A^2/B)}{\partial T}\right]_{P,y} - \frac{A^2}{B}\left(2\frac{A_i}{A}-\frac{B_i}{B}\right)\left[\frac{\frac{P}{Z}\left(\frac{\partial B}{\partial T}\right)_{P,y} - \frac{BP}{Z^2}\left(\frac{\partial Z}{\partial T}\right)_{P,y}}{1+\frac{BP}{Z}}\right] \quad (6)$$

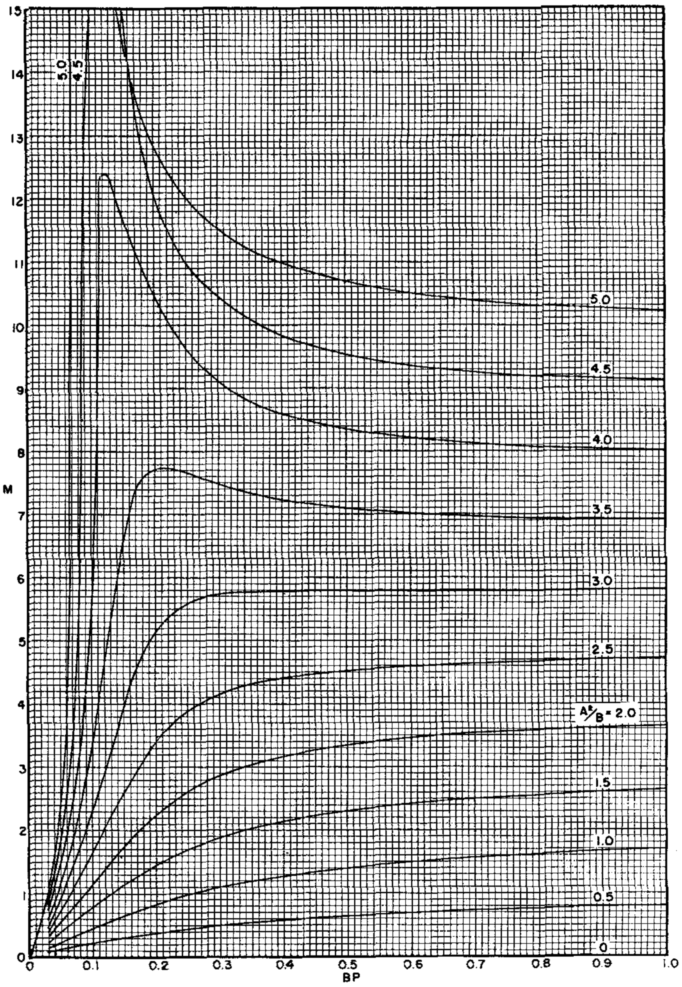

Fig. 2. *M* as a function of A^2/B and BP.

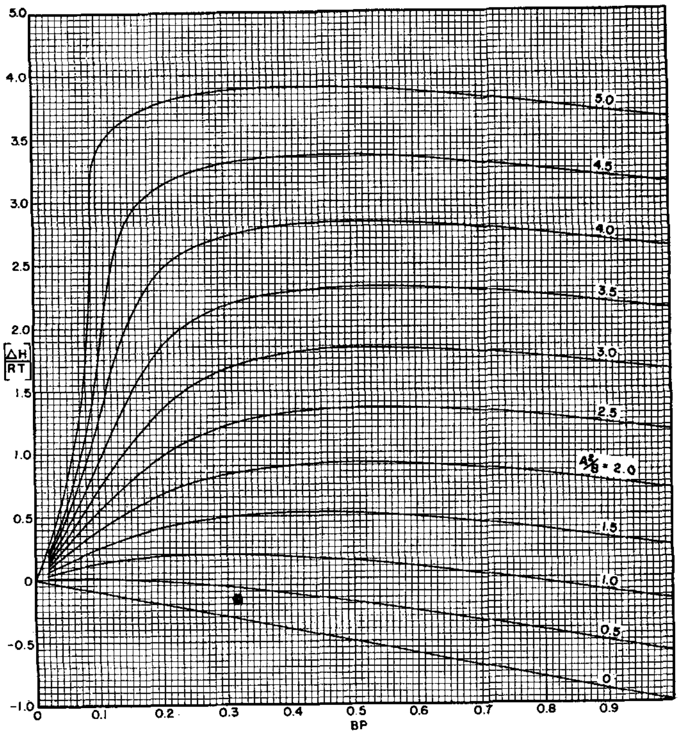

Fig. 1. $[\Delta H/RT]$ as function of A^2/B and BP.

The ratios A_i/A and B_i/B are independent of temperature. The definitions of A and B lead to

$$\left(\frac{\partial B}{\partial T}\right)_{P,y} = -B/T \quad (7)$$

$$\left[\frac{\partial (A^2/B)}{\partial T}\right]_{P,y} = -\frac{1.5\,A^2}{BT} \quad (8)$$

The only remaining term needed is $(\partial Z/\partial T)_{P,y}$, which is evaluated from

$$\left(\frac{\partial Z}{\partial T}\right)_{P,y} = \left(\frac{\partial Z}{\partial T}\right)_{V,y} + \left(\frac{\partial Z}{\partial V}\right)_{T,y}\left(\frac{\partial V}{\partial T}\right)_{P,y}$$

The term $(\partial V/\partial T)_{P,y}$ cannot be obtained directly from Equation (1) or (2). But

$$\left(\frac{\partial V}{\partial T}\right)_{P,y} = -\frac{\left(\frac{\partial P}{\partial T}\right)_{V,y}}{\left(\frac{\partial P}{\partial T}\right)_{T,y}}$$

Therefore

$$\left(\frac{\partial Z}{\partial T}\right)_{P,y} = \left(\frac{\partial Z}{\partial T}\right)_{V,y} - \left(\frac{\partial Z}{\partial V}\right)_{T,y} \frac{\left(\frac{\partial P}{\partial T}\right)_{V,y}}{\left(\frac{\partial P}{\partial V}\right)_{T,y}} \qquad (9)$$

Equations (1) and (2) may now be used to obtain the required derivatives:

$$\left(\frac{\partial Z}{\partial T}\right)_{V,y} = \frac{1.5\,a}{RT^{2.5}(V+b)} \qquad (10)$$

$$\left(\frac{\partial Z}{\partial V}\right)_{T,y} = -\frac{b}{(V-b)^2} + \frac{a}{RT^{1.5}(V+b)^2} \qquad (11)$$

$$\left(\frac{\partial P}{\partial T}\right)_{V,y} = \frac{R}{V-b} + \frac{0.5\,a}{T^{1.5}V(V+b)} \qquad (12)$$

$$\left(\frac{\partial P}{\partial V}\right)_{T,y} = -\frac{RT}{(V-b)^2} + \frac{a}{T^{0.5}V^2(V+b)} + \frac{a}{T^{0.5}V(V+b)^2} \qquad (13)$$

Equation (6) can be evaluated by the use of Equations (7) to (13).

COMPUTER PROGRAM

All equation-of-state calculations for this work were done on an IBM-650 computer (3). The input data to the computer program included mixture composition, temperature, pressure, and component critical data. Output data included component fugacity coefficients, partial enthalpy differences, and the mixture volume and enthalpy difference.

Any trial-and-error computation on the digital computer requires a convergence routine, that is a method whereby the machine may seek the correct answer. In this program Newton's method (8) was used. Equation (13) is written in difference form:

$$V_{n+1} = V_n - \frac{(P_n - P)}{(\partial P/\partial V)_{T,y}} \qquad (14)$$

A value V_n is assumed and P_n calculated by Equation (1). Equation (13) is used with V_n to obtain $(\partial P/\partial V)_{T,y}$. The next value, V_{n+1}, is calculated by Equation (14), and the process is repeated until $(P_n - P)$ is arbitrarily small. In the event that this method of convergence fails, a simple step-by-step procedure is used. The initial assumption is $V_n = RT/P$.

CHART METHOD

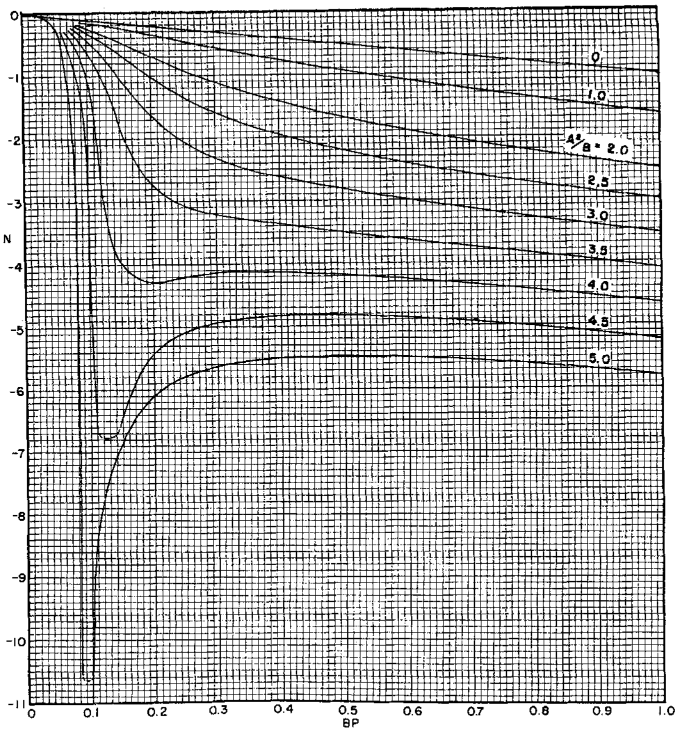

Fig. 3. *N* as a function of A^2/B and *BP*.

Equations (6) to (13), while sufficient for machine computation, involve laborious hand calculations. Yarborough (9) developed a form for partial enthalpy differences that is analogous to that used by Redlich for component fugacities.

$$\left(\frac{\partial Z}{\partial T}\right)_{P,y} = \frac{1}{T}\left\{\frac{1.5\,k}{(j+1)} + \frac{j[j(j+1)^3 + 0.5k(j+1)^2(j-1) - kj(j+1)(j-1)^2 - 0.5k^2(j-1)^3]}{(j-1)(j+1)[-j^2(j+1)^2 + k(j-1)^2(j+1) + kj(j-1)^2]}\right\} \qquad (15)$$

First change all the parameters into terms in A^2/B and BP. This can be done since $a = A^2R^2T^{2.5}$ and $b = BRT$:

$$\left(\frac{\partial Z}{\partial T}\right)_{V,y} = \frac{A^2}{B}\frac{1}{T}\frac{1.5}{(Z/BP+1)} \qquad (10a)$$

$$\left(\frac{\partial Z}{\partial V}\right)_{T,y} = -\frac{1}{BRT(Z/BP-1)^2} + \frac{A^2}{B}\frac{1}{BRT(Z/BP+1)^2} \qquad (11a)$$

$$\left(\frac{\partial P}{\partial T}\right)_{V,y} = \frac{R}{BRT(Z/BP-1)} + \frac{A^2}{B}\frac{0.5\,R}{BRT(Z/BP)(Z/BP+1)} \qquad (12a)$$

$$\left(\frac{\partial P}{\partial V}\right)_{T,y} = -\frac{RT}{(BRT)^2(Z/BP-1)^2} + \frac{A^2}{B}\frac{RT}{(BRT)^2(Z/BP)^2(Z/BP+1)} + \frac{A^2}{B}\frac{RT}{(BRT)^2(Z/BP)(Z/BP+1)^2} \qquad (13a)$$

Let $Z/BP = j = 1/h$ and $A^2/B = k$. Substitute j and k into Equations (10a) to (13a), and then substitute the latter into Equation (9):

or

$$\left(\frac{\partial Z}{\partial T}\right)_{P,y} = \frac{1}{T}\left[\frac{1.5\,k}{j+1} + L\right] \qquad (15a)$$

where Equation (15) defines L.

Equation (6) can be rearranged to the following form:

$$-\frac{\Delta\overline{H}_i}{RT^2} = \left[\left(\frac{B_i}{B}-1\right)+1\right]\left(\frac{\partial Z}{\partial T}\right)_{P,y} - \frac{1}{(Z-BP)}\left[\left(\frac{\partial Z}{\partial T}\right)_{P,y} - P\left(\frac{\partial B}{\partial T}\right)_{P,y}\right] - \left[2\left(\frac{A_i}{A}-1\right) - \left(\frac{B_i}{B}-1\right)+1\right]\left[\ln\left(1+\frac{BP}{Z}\right)\right]\left[\frac{\partial(A^2/B)}{\partial T}\right]_{P,y} - \frac{A^2}{B}\left[2\left(\frac{A_i}{A}-1\right)-\left(\frac{B_i}{B}-1\right)+1\right]\left[\frac{\frac{P}{Z}\left(\frac{\partial B}{\partial T}\right)_{P,y} - \frac{BP}{Z^2}\left(\frac{\partial Z}{\partial T}\right)_{P,y}}{1+\frac{BP}{Z}}\right] \qquad (6a)$$

Collect terms multiplied by $(A_i/A - 1)$ and $(B_i/B - 1)$ and substitute

Equations (7), (8), and (15*a*) into Equation (6*a*):

$$-\frac{\Delta\overline{H}_i}{RT^2}=\frac{1}{T}\left[L-\frac{1}{(Z-BP)}(L+BP)+1.5\,k\ln(1+h)+kh\left(\frac{1+L/Z}{1+h}\right)\right]+\frac{1}{T}\left(\frac{A_i}{A}-1\right)\left[3\,k\ln(1+h)+2\,kh\left(\frac{1+L/Z}{1+h}\right)\right]$$

$$+\frac{1}{T}\left(\frac{B_i}{B}-1\right)\left[L-1.5\,k\ln(1+\mathrm{h})-kh\left(\frac{1+L/Z}{1+h}\right)\right]\quad(16)$$

or

$$-\frac{\Delta\overline{H}_i}{RT}=\left[\frac{\Delta H}{RT}\right]+\left(\frac{A_i}{A}-1\right)M+\left(\frac{B_i}{B}-1\right)N\quad(16a)$$

where equation (16) defines $[\Delta H/RT]$, M and N, which are all functions of A^2/B and BP only. Note that $[\Delta H/RT]$ gives the mixture enthalpy difference directly.

Equation (16*a*) was programmed for the IBM-650 computer (9). The values of $[\Delta H/RT]$, M, and N were computed as functions of A^2/B and BP. Figures 1, 2, and 3 are diagrams of these data.

SAMPLE CALCULATION

A sample calculation is shown for the system methane-ethane at 0°F. and 950 lb./sq. in. abs. The composition of the mixture is 0.742 mole fraction methane (component 1) and 0.258 mole fraction ethane (component 2). A_i and B_i for each component are calculated from the relations shown in Equations (1) and (2), that is from the critical temperature and critical pressure of the component and the system temperature.

Component	A_i^2	A_i	B_i
Methane	0.000306	0.0175	0.0000961
Ethane	0.000945	0.0308	0.0001461

The A and B for the mixture were calculated with $A = \sum_i y_iA_i$ and $B = \sum_i y_iB_i$; $A = 0.0210$; $A^2 = 0.000441$, $B = 0.0001090$, $A^2/B = 4.02$, $BP = 0.1036$.

From Figures 1, 2 ,and 3

$$\left[\frac{\Delta H}{RT}\right]=1.29,\quad M=6.30,\quad N=-1.30$$

$$-\frac{\Delta\overline{H}_1}{RT}=1.29+\left(\frac{0.0175}{0.0210}-1\right)6.3+\left(\frac{0.0000961}{0.0001090}-1\right)(-1.30)$$

$$=1.29-1.05+0.15=0.39$$

$$\Delta\overline{H}_1=(-0.39)(460)(1.987)=-356\ \text{B.t.u./lb. mole}$$

$$-\frac{\Delta\overline{H}_2}{RT}=1.29+\left(\frac{0.0308}{0.0210}-1\right)6.3+\left(\frac{0.0001461}{0.0001090}-1\right)(-1.30)$$

$$=1.29+2.94-0.44=3.79$$

$$\Delta\overline{H}_2=(-3.79)(460)(1.987)=-3{,}460\ \text{B.t.u./lb. mole}$$

$$\Delta H=(0.742)(-356)+(0.258)(-3{,}460)=-1{,}178\ \text{B.t.u./lb. mole Mix.}$$

or

$$\Delta H=-\mathrm{RT}[\Delta H/RT]=-(1.987)(460)(1.29)=-1{,}178\ \text{B.t.u./lb. mole Mix.}$$

The computer solution gives $\Delta\overline{H}_1 = -383$ B.t.u./lb. mole, $\Delta\overline{H}_2 = -3443$ B.t.u./lb. mole, and $\Delta H = -1{,}173$ B.t.u./lb. mole.

EVALUATION OF REDLICH-KWONG ENTHALPIES

Gas-phase partial enthalpy differences ($\Delta\overline{H}$) calculated by the Redlich-Kwong equation of state were compared with partial enthalpy differences calculated from P-V-T-C data. $\Delta\overline{H}$ values calculated from P-V-T-C data were available for four binary mixtures: the methane-propane binary (9), the methane-ethane binary (7), the methane-*n*-butane binary (7), and the methane-*n*-pentane binary (7). The conditions (temperature, pressure, and composition) covered in the comparison are shown in Table 1. A discussion of the results of the comparison follows.

The $\Delta\overline{H}$ values for methane calculated by the Redlich-Kwong equation of state agrees better with the $\Delta\overline{H}$ values derived from P-V-T-C data at high concentrations of methane than at low concentrations of methane. This trend was evident in the methane-ethane, methane-propane, and methane-*n*-butane comparisons. The overall trend of the comparisons may be seen in the statistical comparison shown in Table 2. The only other noticeable trend in the methane $\Delta\overline{H}$ values was in the methane-propane binary, which was the only set of P-V-T-C based $\Delta\overline{H}$ values that covered the complete composition range of the binary. This trend showed that at low methane concentrations the Redlich-Kwong $\Delta\overline{H}$ values for methane were lower than the P-V-T-C $\Delta\overline{H}$ values at low temperatures, while they were higher at high temperatures.

The $\Delta\overline{H}$ values for the heavy components calculated by the Redlich-Kwong equation agreed better with the P-V-T-C based $\Delta\overline{H}$ values at high concentrations of the heavy component than at low concentrations of the heavy component. This trend can be seen in Table 2. The comparison also showed that at a given mole fraction of the heavy component the deviation between the Redlich-Kwong $\Delta\overline{H}$ values and the P-V-T-C $\Delta\overline{H}$ values increased as the molecular weight of the component increased.

A point worth mentioning is that no definite trend with respect to temperature or pressure was noted other than the one pointed out above. In other words the equation of state $\Delta\overline{H}$ values compared with the P-V-T-C $\Delta\overline{H}$ values as well at low temperature as at high temperature, and compared as well at high pressure as at low pressure, provided saturated vapor was not approached. In the few cases where the conditions (temperature, pressure, composition) approached those of saturated vapor the equation of state $\Delta\overline{H}$ values became very unreliable.

TABLE 1. CONDITIONS COVERED IN COMPARISON OF $\Delta\overline{H}$ VALUES

Binary	Temperature, °F.	Pressure, lb./sq. in. abs.	Composition, mole % methane
Methane-ethane	100, 160, 220	200, 600, 1,000, 2,000	60, 80 for methane 20, 40, 60 for ethane
Methane-propane	100, 160, 220 340, 400, 460	200, 400, 800 1,500, 2,000	20, 40, 60, 80
Methane-*n*-butane	100, 160, 220	200, 600, 1,000 1,500, 2,000, 2,500	85, 90, 95
Methane-*n*-pentane	100, 160, 220	200, 600, 1,000 1,500, 2,000, 2,500, 3,000	96

TABLE 2. SUMMARY OF COMPARISON OF $\Delta\overline{H}$ VALUES

Methane: absolute average difference* $= |\Delta\overline{H}_{PVTC} - \Delta\overline{H}_{RK}|$

Comparison for $y \geqq 60$ mole % methane
number of points = 102
absolute average difference = 26 B.t.u./lb.-mole

All comparisons ($y \geqq 20$ mole % methane)
number of points = 131
absolute average difference = 50 B.t.u./lb.-mole

Heavy components (ethane, propane, *n*-butane, *n*-pentane):

$$\text{absolute average \% deviation} = \frac{|\Delta\overline{H}_{PVTC} - \Delta\overline{H}_{RK}|}{|\Delta H_{PVTC}|} 100$$

Comparison for $y \leqq 80$ mole % methane
number of points = 95
absolute average % deviation = 8.0%

Comparison for $y \leqq 90$ mole % methane
number of points = 109
absolute average % deviation = 8.6%

All comparisons ($y \leqq 96$ mole % methane)
number of points = 143
absolute average % deviation = 10.9%

* Did not show % deviation because methane $\Delta\overline{H}$ is positive at low *concentrations and is negative at high concentrations of methane* (at one composition methane $\Delta\overline{H} = 0$).

Most of the trends noticed in the Redlich-Kwong $\Delta\overline{H}$ values were to be expected. The equation of state should describe the partial quantities (volume, enthalpy, etc.) of the more abundant component more accurately than the partial quantities of the less abundant component. The Redlich-Kwong equation for mixtures requires arbitrary combination of the constants of the pure components. The most exacting test for such an equation of state would be for it to accurately describe the partial quantities of a component that is present in very small concentrations in a mixture. Another point is that the Redlich-Kwong equation of state was developed for gaseous substances. The heaviest components used in the original development of the equation of state were *n*-butane and iso-butane. Thus one would expect the equation of state to describe the behavior of light components better than heavy components.

In spite of some relatively large discrepancies between the Redlich-Kwong $\Delta\overline{H}$ values and the P-V-T-C $\Delta\overline{H}$ values the mixture enthalpy differences ($\Delta\overline{H}$) compare rather well. In several cases the pressure correction to the methane partial enthalpy calculated by the Redlich-Kwong equation was too large. However this was partly compensated for by the fact that the pressure correction to the partial enthalpy of the heavier component calculated by the Redlich-Kwong equation is usually smaller that that calculated from P-V-T-C data. Also the greatest discrepancies in the $\Delta\overline{H}$ values for any component occurred when the component was present in low concentration as noted in Table 2. Hence the error in the ΔH ($= y_1\Delta\overline{H}_1 + y_2\Delta\overline{H}_2$) value was reduced by multiplying the inaccurate $\Delta\overline{H}$ value by its small mole fraction; that is the greatest contribution to the ΔH was made by the more accurate $\Delta\overline{H}$ value.

The absolute average deviations between the ΔH calculated by the Redlich-Kwong equation and by the use of P-V-T-C data are as follows for the four binary systems considered:

1. Methane-ethane binary—4.6%
2. Methane-propane binary—6.6%
3. Methane-*n*-butane binary—5.1%
4. Methane-*n*-pentane binary—10.2%

CONCLUSIONS

Component and mixture enthalpies computed by the Redlich-Kwong equation of state agree fairly well with those calculated from experimental P-V-T-C data for binary hydrocarbon gas mixtures. Thus the Redlich-Kwong equation would appear to be useful for process enthalpy balance calculations.

NOTATION

A,a,B,b = constants in Redlich-Kwong equation of state
C = general composition parameter
$\Delta\overline{H}_i$ = isothermal effect of pressure on the partial enthalpy or the partial enthalpy difference of component i, $(\overline{H}^P{}_i - H^\circ{}_i)_T$
ΔH = isothermal effect of pressure on the mixture enthalpy or the mixture enthalpy difference, $(H^P - H^\circ)_T$
$H^\circ{}_{i,T}$ = ideal gas enthalpy of component i at temperature T
$\overline{H}^P{}_{i,T}$ = partial enthalpy of component i at temperature T and pressure P
$H^\circ{}_T$ = ideal gas enthalpy of the mixture at temperature T
$H^P{}_T$ = enthalpy of the mixture at temperature T and pressure P
h,j,k,L = parameters in the Redlich-Kwong equation of state
$\left[\frac{\Delta H}{RT}\right],M,N$ = functions of A^2/B and BP in the Redlich-Kwong general enthalpy equation
P = absolute pressure
R = universal gas constant
T = absolute temperature
V = specific volume
U,W = functions of A^2/B and BP in the Redlich-Kwong general fugacity equation
y = mole fraction of a component in the gas phase
Z = compressiblity factor
$\log\varphi$ = function of A^2/B and BP in the Redlich-Kwong general fugacity equation
φ_i = fugacity coefficient of component i, $\overline{f}_i/Py_i$

Superscripts

$^\circ$ = value in the ideal gas state

Subscripts

c = critical values
i = value for component i
n = value of nth trial
T,P,V,y = values held constant during an operation

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