Calculation of Enthalpy of Gaseous Mixtures

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ECONOMIC DESIGN of gas separation plants, especially those including cryogenic processes, depends upon the accuracy of enthalpy data. The usual process design requires calculations of enthalpies of mixtures because almost no direct experimental data are available. Simple generalized procedures may be used or enthalpies may be calculated from equations of state for mixtures based on empirical equations of state for pure components. Unfortunately, the safety factors which are added because of uncertainties in the calculations lead to increased costs.

Two new methods for calculating the enthalpies of gaseous mixtures are proposed. The first method utilizes pseudoacentric factors, pseudocritical constants, and generalized enthalpy functions which have been developed for pure fluids. The second method uses virial equations of state of mixtures and recent correlations for cross-coefficients. The results of calculations for the methane-nitrogen systems at 24 conditions, covering a pressure range from 100 to 1500 p.s.i.a., at temperatures of 80° and −100° F., and at compositions of 90% and 70% methane, have been compared with published enthalpies based on experimental P-V-T data for the mixtures. The average deviation for $(H^* - H)$, the enthalpy correction for real gases, was 4.5% for the relatively rapid pseudocritical method and 2.8% for the more tedious virial method.

PSEUDOCRITICAL METHOD

This method for calculating the enthalpies of gaseous mixtures is an extension of the method developed by Curl and Pitzer (2) for determining the enthalpies of pure fluids. Pitzer and others (7) defined an acentric factor by

$$\omega = -\log P_r - 1.000 \tag{1}$$

calculated from the value of the reduced vapor pressure at the reduced temperature of 0.7. For simple fluids they found that the compressibility factor could be represented by an equation, linear in the acentric factor ω,

$$Z = Z^{(o)}(P_r, T_r) + \omega Z^{(1)}(P_r, T_r) \tag{2}$$

where $Z^{(o)}$ and $Z^{(1)}$ are universal functions of the reduced temperature and pressure.

The compressibility functions were presented in tabular form. The correlation was tested successfully using volumetric data covering a range of reduced pressures from 0 to 9 and of reduced temperatures from 0.8 to 4.0.

Using the tabulated values of the compressibility functions $Z^{(o)}$ and $Z^{(1)}$ Curl and Pitzer (2) determined the enthalpy function of pure fluids by

$$\left(\frac{H^* - H}{RT_c}\right) = \left(\frac{H^* - H}{RT_c}\right)^{(o)} + \omega \left(\frac{H^* - H}{RT_c}\right)^{(1)} \tag{3}$$

where

$$\left(\frac{H^* - H}{RT_c}\right)^{(o)} \text{ and } \left(\frac{H^* - H}{RT_c}\right)^{(1)}$$

were calculated from the appropriate form of

$$\left(\frac{H^* - H}{RT_c}\right) = T_r^2 \int_0^{P_r} \left(\frac{1}{P_r}\right) \left(\frac{\partial Z}{\partial T_r}\right)_p dP_r \tag{4}$$

They prepared tabulated values of the enthalpy functions

$$\left(\frac{H^* - H}{RT_c}\right)^{(o)} \text{ and } \left(\frac{H^* - H}{RT_c}\right)^{(1)}$$

at selected values of T_r and P_r (2).

It is now proposed to extend the above enthalpy functions for pure fluids to mixtures of gases, by selecting appropriate values for a pseudoacentric factor ω_m, a pseudocritical temperature T_{cm} and a pseudocritical pressure P_{cm}.

The pseudoacentric factor ω_m may be calculated by

$$\omega_m = \sum X_i \omega_i \tag{5}$$

as recommended by Prausnitz and Gunn (9) and the pseudocritical temperature and pressure may be calculated by one of the two procedures they recommended for use in calculating compressibility factors for mixtures. For a mixture of gases Equation 3 becomes

$$\left(\frac{H^* - H}{RT_{cm}}\right) = \left(\frac{H^* - H}{RT_{cm}}\right)^{(o)} + \omega_m \left(\frac{H^* - H}{RT_{cm}}\right)^{(1)} \tag{6}$$

The results of enthalpy calculations for the methane-nitrogen system at 24 conditions have been compared with published enthalpies (1) based on experimental P-V-T data for the system. The published data had been fitted with a modified Benedict-Webb-Rubin equation of state. The calculations were made at compositions of 90% methane–10% nitrogen and 70% methane–30% nitrogen, at temperatures of 80° and −100° F., and over a pressure range from 100 to 1500 p.s.i.a.

Using the mixing rules of Prausnitz and Gunn (9), the values of the pseudofactors for the 90% methane–10% nitrogen system were calculated to be $\omega_m = 0.0157$, $T_{cm} = 182.8°$ K., and $P_{cm} = 44.7$ atm. For the 70% methane–30% nitrogen system, the values were calculated to be $\omega_m = 0.0211$, $T_{cm} = 172.9°$ K., and $P_{cm} = 43.7$ atm.

The results of the calculations are summarized in Table I in which the computed and the experimental values of $(H^* - H)$, the enthalpy correction for real gases, are compared. The deviations appear to be about equally divided between positive and negative values, and the average deviation was found to be 4.5% for the pseudocritical method. The per cent departure in the enthalpy correction is shown graphically in Figure 1.

VIRIAL METHOD

This method for calculating the enthalpies of gaseous mixtures is based on a virial equation of state. A virial equation of state using only the second and third virial coefficients is satisfactory, if the reduced density is not too high. The equation for a mixture may be written as

$$Z = \frac{PV}{RT} = 1 + \frac{B_m}{V} + \frac{C_m}{V^2} \tag{7}$$

where

$$B_m = \sum_i^n \sum_j^n X_i X_j B_{ij} \tag{8}$$

$$C_m = \sum_i^n \sum_j^n \sum_k^n X_i X_j X_k C_{ijk} \tag{9}$$

For binary mixtures, Equations 8 and 9 reduce to

$$B_m = X_1^2 B_{11} + 2 X_1 X_2 B_{12} + X_2^2 B_{22} \tag{10}$$

$$C_m = X_1^3 C_{111} + 3 X_1^2 X_2 C_{112} + 3 X_2^2 X_1 C_{122} + X_2^3 C_{222} \tag{11}$$

The enthalpy correction for real gases $(H^* - H)$ is conveniently calculated (4) from the following equation in which it is expressed in terms of the second and third virial coefficients and their temperature derivatives:

$$(H^* - H) = -RT \left[\frac{1}{V} \left(B_m - T \frac{dB_m}{dT} \right) \right.$$

$$\left. + \frac{1}{V^2} \left(C_m - \frac{1}{2} T \frac{dC_m}{dT} \right) + \ldots \right] \tag{12}$$

The following discussion outlines the steps which were followed for calculating the enthalpies of mixtures, using the virial method. The second virial coefficient B_m was calculated from Equation 10 using the correlation of Prausnitz (8) to obtain B_{11}, B_{22}, and B_{12}. (The calculated values of the second virial coefficients for the pure components were compared with experimental data and good agreement was found.) The third virial coefficient C_m was estimated from Equation 11 using another correlation of Prausnitz (8) for the cross-coefficients. The temperature derivative of the second virial coefficient dB_m/dT was calculated by differentiation of Equation 10 giving

$$\frac{dB_m}{dT} = X_1^2 \frac{dB_{11}}{dT} + 2 X_1 X_2 \frac{dB_{12}}{dT} + X_2^2 \frac{dB_{22}}{dT} \tag{13}$$

The temperature derivatives of the second virial coefficients

for the pure components dB_{11}/dT and dB_{22}/dT were determined from an empirical equation for B developed by Pitzer and Curl (6).

$$\frac{BP_c}{RT_c} = (0.1445 + .073\omega) - \frac{(0.330 - 0.46\omega)}{T_r} - \frac{(0.1385 + 0.50\omega)}{T_r^2}$$

$$- \frac{(0.0121 + 0.097\omega)}{T_r^3} - \frac{0.0073\omega}{T_r^8} \tag{14}$$

Differentiation of Equation 14 yields

$$\frac{dB}{dT} = \left(\frac{R}{P_c} \right) \left[\frac{(0.330 - 0.46\omega)}{T_r^2} + \frac{2(0.1385 + 0.50\omega)}{T_r^3} \right.$$

$$\left. + \frac{3(0.0121 + 0.097\omega)}{T_r^4} + \frac{8(0.0073\omega)}{T_r^9} \right] \tag{15}$$
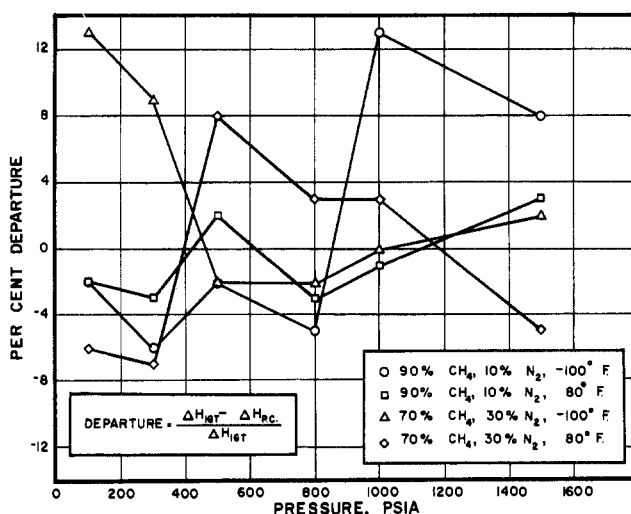

Figure 1. Per cent departure of enthalpies calculated by the pseudocritical method

Table I. Summary of Enthalpy Calculation by the Virial and Pseudocritical Methods

Temp., °F.	Pressure, P.S.I.A.	$(H^* - H)$ in B.t.u./Lb. Mole			% Departure from I.G.T.	
		I.G.T.	Virial	Pseudo-critical	Virial	Pseudo-critical
90% Methane–10% Nitrogen						
−100	100	94	89.5	96	+5	−2
	300	294	291	313	+1	−6
	500	545	538	554	+1	−2
	800	1082	1084	1133	0	−5
	1000	1652	1601	1475	+3	+13
	1500	2159	2218	1977	−3	+8
80	100	42	42.5	43	−1	−2
	300	126	129	130	−2	−3
	500	210	216	205	−3	+2
	800	339	350	331	−3	−3
	1000	423	440	428	−4	−1
	1500	641	662	621	−3	+3
70% Methane–30% Nitrogen						
−100	100	78	76.5	68	+2	+13
	300	248	244	225	+2	+9
	500	437	437	445	0	−2
	800	776	792	790	−2	−2
	1000	1043	1083	1046	−4	0
	1500	1640	1678	1608	−2	+2
80	100	35	37	37	−6	−6
	300	107	111	115	−4	−7
	500	177	186	162	−5	+8
	800	286	298	279	−4	+3
	1000	356	373	344	−5	+3
	1500	523	554	549	−6	−5

from which dB_{11}/dT and dB_{22}/dT were calculated. The temperature derivative of the cross-coefficient dB_{12}/dT in Equation 13 was calculated from the Lennard-Jones potential, tabulated by Hirschfelder, Curtiss, and Bird (4), using empirical combining laws for σ_{12} and $(\epsilon/k)_{12}$.

The temperature derivative of the second virial coefficient for a mixture was then calculated by combining the calculated values for each of the above temperature derivatives in accordance with Equation 13.

The temperature derivative of the third virial coefficient dC_m/dT was estimated by differentiating Equation 11 to yield the following

$$\frac{dC_m}{dT} = X_1^3 \frac{dC_{111}}{dT} + 3X_1^2 X_2 \frac{dC_{112}}{dT} + 3X_2^2 X_1 \frac{dC_{122}}{dT} + X_2^3 \frac{dC_{222}}{dT} \quad (16)$$

The temperature derivatives dC_{111}/dT and dC_{222}/dT for the pure components were evaluated from the Lennard-Jones potential in a straightforward manner. The cross-coefficient temperature derivatives dC_{112}/dT and dC_{122}/dT were estimated from the Lennard-Jones potential using the empirical combining laws recommended by Hirschfelder, Curtiss, and Bird (4).

The summary of the virial method for calculating the enthalpy function of a mixture is as follows: At a given temperature and composition the second and third virial coefficients and their temperature derivatives are determined. The molar volume, V, is evaluated at the required pressure, using Equation 7. The value of the enthalpy correction $(H^* - H)$ is then obtained from Equation 12.

The enthalpy corrections for methane-nitrogen mixtures were calculated using the virial method at the same 24 conditions used for the pseudocritical method. The results are summarized in Table I, showing an average deviation of 2.8% from experimental data. The per cent deviation is shown graphically in Figure 2.

COMPARISON WITH OTHER METHODS

The two proposed methods for calculating enthalpies of gaseous mixtures were compared with four methods:

Total Pressure: $\sum_i X_i H_i$ where H_i is evaluated at the temperature and total pressure of the mixture.

Partial Pressure: $\sum_i X_i H_i$ where H_i is evaluated at the temperature and partial pressure of each component.

Hougen and Watson (5).

Edmister (3).

The enthalpies of methane-nitrogen mixtures for 10 of the 24 conditions used in the previous calculations had been calculated using the above four methods. The results are summarized in Table II. These methods were compared with experimental data in Figure 3, and the proposed pseudocritical and virial methods were compared with the same experimental data in Figure 4.

For calculations restricted to the 10 conditions of temperature and pressure common to Tables I and II, the average deviations from the experimental data were:

	%		%
Pseudo-critical	3	Partial Pressure	20
Virial	3	Hougen & Watson	7
Total Pressure	12	Edmister	5

The partial pressure method is very sensitive to composition and is unsatisfactory. Errors in enthalpies calculated by the partial pressure method were very large and were always positive. Errors in enthalpies calculated from the simple total pressure method were serious and generally negative. The method recommended by Hougen and Watson (5) yielded errors which were moderate, although several large errors were noted at the low temperatures. The method of Edmister (3) gave moderately low errors which were all negative. The proposed pseudocritical and virial
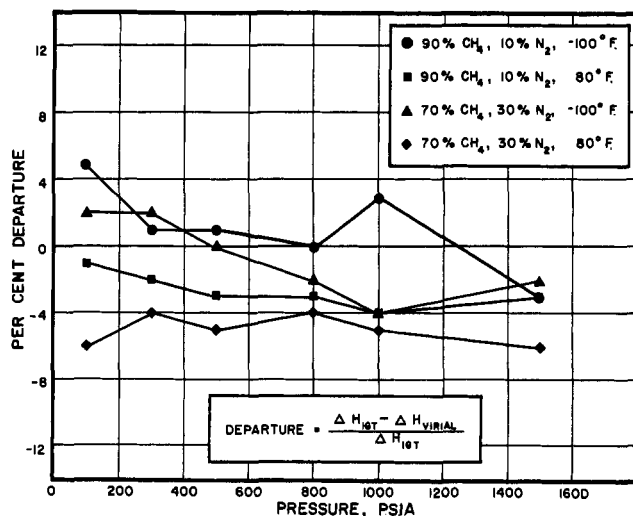
Figure 2. Per cent departure of enthalpies calculated by the virial method

Table II. Enthalpy Calculations by Other Methods

Enthalpy, B.t.u./Lb. Mole

Temp., °F.	Pressure, P.S.I.A.	At Total Pressure		At Partial Pressure		Hougen, Watson		Edmister		
		$H^* - H$	% dev.	$H^* - H$	% dev.	$H^* - H$	% dev.	$H^* - H$	% dev.	I.G.T.[a]
				90% Methane–10% Nitrogen						
−100	300	316	−7	269	+9	254	+14	319	−8	294
−100	500	571	−5	487	+11	468	+14	572	−5	545
80	300	133	−5	115	+8	130	−8	133	−4	126
80	500	235	−12	203	+3	218	−3	223	−6	210
80	1000	470	−10	409	+4	416	+2	432	−2	423
				70% Methane–30% Nitrogen						
−145	500	723	−9	413	+38	574	+13	726	−10	661
−100	500	491	−12	301	+31	396	+9	460	−5	437
−100	800	1007	−30	524	+32	721	+7	803	−4	776
80	500	204	−15	127	+28	183	−4	188	−7	177
80	800	326	−14	212	+26	279	+3	296	−4	286
80	1000	405	−14	264	+26	344	+3	368	−4	356

[a] Institute of Gas Technology (1).

Figure 3. Comparison of other calculation methods
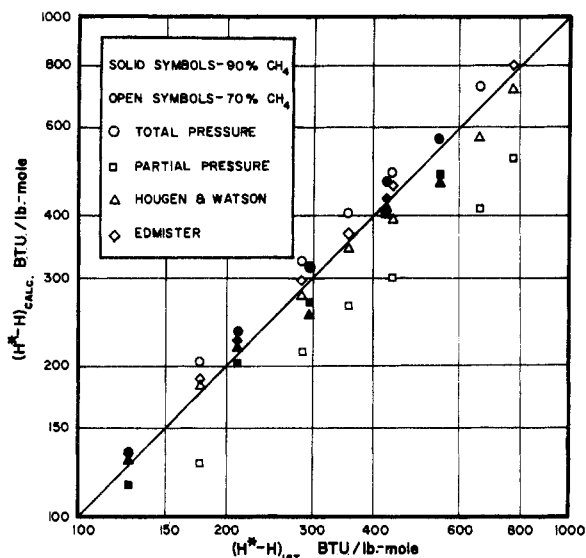with experimental data

Figure 4. Comparison of proposed calculation methods
with experimental data

methods had the smallest deviations, 3%, in this region of comparison, were free of large errors, and were both positive and negative.

Comparison of the virial and pseudocritical methods in a broader range of pressure conditions, from 100 to 1500 p.s.i.a. as shown in Table I, shows that the virial method appears to be slightly superior, with an average deviation of 2.8%; the pseudocritical method has an average deviation of 4.5%. Furthermore, the results calculated by the virial method did not have erratic values, but the pseudocritical method did; the pseudocritical method is more rapid, and the virial method is more tedious. The advantage is less important when a digital computer is used.

NOMENCLATURE

B = second virial coefficient
C = third virial coefficient
H = enthalpy at given temperature and pressure
H^* = enthalpy in ideal state at given temperature
k = Boltzmann constant
n = number of components
P = pressure
R = gas constant
T = absolute temperature
V = molar volume
X = mole fraction
Z = compressibility factor
ϵ = maximum energy of attraction in Lennard-Jones potential
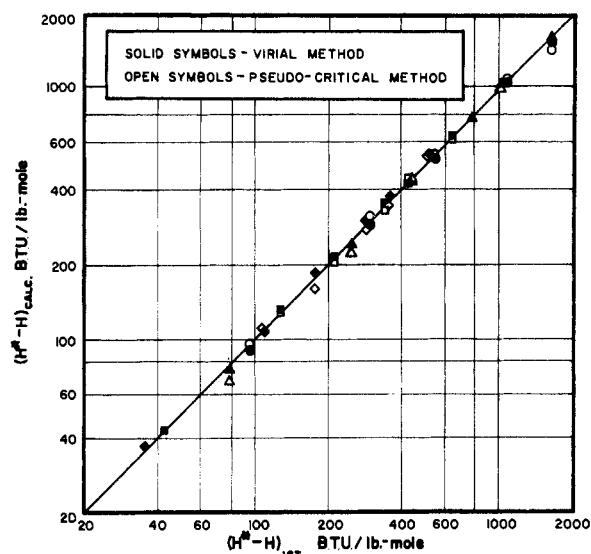σ = distance at which Lennard-Jones potential is zero
ω = acentric factor

Subscripts

c = critical
i, j, k = components i, j, and k
$1, 2$ = components 1 and 2
r = reduced, dimensionless property
m = property for a mixture

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