Estimation of Enthalpies: Multicomponent Hydrocarbon Mixtures at Their Saturated Vapor and Liquid States

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Based on the data reported by Rossini et al. (9) analytical expressions have been developed for the calculation of enthalpies at zero pressure as functions of temperature for normal paraffins ranging from methane through octane. The coefficients of these equations have been found to correlate linearly with molecular weight, thus allowing the enthalpy relationships for hydrocarbons heavier than octane to be determined by extrapolation. The enthalpy of mixtures at zero pressure can then be obtained by combining the enthalpies of the individual components on an additive basis, weighted by the mole fractions.

Corrections due to nonideal gaseous behavior have been developed in equation form from the work of Lydersen, Greenkorn, and Hougen (7) in terms of the reduced temperature T_R and the critical compressibility factor z_c of the substance. These corrections have been developed for both the saturated vapor and saturated liquid states and can be applied to the determination of the enthalpy of mixtures at these conditions. The results of this method have been compared with the experimental enthalpy data available for three ternary mixtures and were found to be in excellent agreement.

Various methods have been presented in the literature for the determination of heat capacities and enthalpies of individual hydrocarbons. In 1938 Edmister (2) published an excellent compilation and correlation of the information then available. Later the group contribution method of Andersen, Beyer, and Watson (*1*) attempted to predict the heat capacities of organic vapors from their molecular structure. In 1949 Souders, Matthews, and Hurd (*11*) made a systematic study of available information, which enabled the presentation of heat capacities and enthalpies of hydrocarbons in tabular form for temperatures from −250° to 3,000°F. However the enthalpy data of API Project 44, which were published in 1953 (9), appear to be the most comprehensive currently available, and consequently they have been used as the basis for the present study.

ENTHALPY OF HYDROCARBON MIXTURES AT ZERO PRESSURE

In the hypothetical state of zero pressure all gases behave ideally. In addition, if the molecules of a mixture are similar, solution effects are minimized, and the thermodynamic properties of the components of the mixture become additive. In the case of enthalpy it follows that

$$H_m^* = \sum_{n=1}^{N} n_i H_i^* \tag{1}$$

Hence, once the enthalpies of the individual components of the mixture have been established, Equation (1) can be used to determine the enthalpy of the mixture at zero pressure.

This investigation proposes a method which has been particularly slanted toward use in the design of fractionation columns. Therefore only saturated vapor and liquid mixtures have been considered, and the upper temperature limit has been set at 500°F. To establish the dependence of enthalpy at zero pressure upon temperature the following polynomial expression has been applied:

$$H_i^* = a_i + b_i\left(\frac{t}{100}\right) + c_i\left(\frac{t}{100}\right)^2 + d_i\left(\frac{t}{100}\right)^3 \tag{2}$$

Enthalpy values obtained from the work of Rossini et al. (9) gave the coefficients listed in Table 1 with data ranging from 0 to 500°F.

For normal hydrocarbons from methane through octane the temperature coefficients presented in Table 1 can be used in Equation (2) to calculate the enthalpy of each pure component at zero pressure. A correlation of these coefficients with molecular weight has shown that a linear relationship exists for hydrocarbons heavier than propane. Consequently, for hydrocarbons with molecular weights greater than *n*-octane, the coefficients of Equation (2) can be obtained by extrapolation with the following relationships:

$$a_i = 100M_i + 800 \tag{3}$$

$$b_i = 32.15M_i + 186.5 \tag{4}$$

$$c_i = 3.708M_i - 26.42 \tag{5}$$

$$d_i = -0.0859M_i + 0.40 \tag{6}$$

These equations have been tested by calculating the ideal gas enthalpy of *n*-nonane for temperatures between 0 and 500°F. The resulting values were then compared with the enthalpy data presented by Rossini et al. (9). The calculated and literature values are as follows:

Ideal Gas Enthalpy for
n-Nonane, B.t.u./lb.

°F.	Calculated	Rossini et al. (9)
0	106.2	106.6
100	142.6	143.8
200	187.0	187.5
300	236.7	237.2
400	291.9	292.2
500	352.1	352.2

TABLE 1. COEFFICIENTS FOR ENTHALPY POLYNOMIAL FOR NORMAL HYDROCARBONS

$$H_i^* = a_i + b_i\left(\frac{t}{100}\right) + c_i\left(\frac{t}{100}\right)^2 + d_i\left(\frac{t}{100}\right)^3,$$

where t = °F. and H_i^* = B.t.u./lb.-mole

Hydrocarbon	Mol. wt.	a_i	b_i	c_i	d_i
Methane	16	3,682	794	32.2	0.58
Ethane	30	4,216	1,131	84.4	—0.22
Propane	44	5,073	1,501	158.5	—3.46
n-Butane	58	6,637	2,099	162.9	0.28
n-Pentane	72	8,012	2,573	208.8	—0.87
n-Hexane	86	9,483	2,932	301.1	—7.07
n-Heptane	100	10,573	3,311	337.5	—7.83
n-Octane	114	12,270	3,877	395.5	—9.38

Reference state for enthalpy: $H = 0$ at 0°R. and 0 lb./sq. in. abs.

TABLE 2. CRITICAL COMPRESSIBILITY FACTORS AND CRITICAL TEMPERATURES FOR THE NORMAL PARAFFINS

	z_c	T_c, °R.
Methane	0.290	343
Ethane	0.285	550
Propane	0.277	666
n-Butane	0.274	765
n-Pentane	0.269	846
n-Hexane	0.264	914
n-Heptane	0.260	972
n-Octane	0.256	1,025
n-Nonane	0.250	1,069
n-Decane	0.245	1,109
n-Undecane	0.240	1,145
n-Dodecane	0.235	1,177
n-Tridecane	0.230	1,206
n-Tetradecane	0.225	1,233
n-Pentadecane	0.220	1,257

Although Equations (3), (4), (5), and (6) were developed from data for hydrocarbons heavier than propane, they should be used only for hydrocarbons heavier than octane. For normal hydrocarbons up to and including octane the values presented in Table 1 are more accurate and should be employed. The appropriate values for a_i, b_i, c_i, and d_i can then be used in Equation (2) to give the enthalpy at zero pressure for each individual hydrocarbon. These enthalpies can be combined by means of Equation (1) to give the enthalpy of the mixture at zero pressure.

CORRECTIONS FOR SATURATED VAPOR AND LIQUID STATES

The recent thermodynamic studies of Lydersen, Greenkorn, and Hougen (*7*) present corrections for the effect of pressure on the enthalpy of gases, treating in detail both the saturated vapor and liquid states. They present tabular values for the enthalpy correction terms as a function of reduced temperature and critical compressibility factor. Hougen, Watson, and Ragatz (*6*) present this information in a condensed form. Based on the original data of Lydersen, Greenkorn, and Hougen (*7*) equations specific to the saturated vapor and liquid states have been developed. For the saturated vapor state

$$\frac{H^* - H}{T_c} = [mT_R + k]^{\frac{1}{p}} \qquad (7)$$

in which p, m, and k are related to the critical compressibility factor as follows:

$$p = 2.5\,z_c - 0.525 \qquad (8)$$

$$m = -7.424 + 45.65\,z_c - 48.75\,z_c^2 \qquad (9)$$

$$k = 7.401 - 39.65\,z_c + 43.75\,z_c^2 \qquad (10)$$

For the saturated liquid state the relationship is

$$\frac{H^* - h}{T_c} = 10\,[\alpha - \beta\, T_R]^{\frac{1}{r}} \qquad (11)$$

in which r, α, and β are related to the critical compressibility factor as follows:

$$r = 25\,z_c - 2.25 \qquad (12)$$

$$\alpha = -317.49 + 2559.5\,z_c - 5012.5\,z_c^2 \qquad (13)$$

$$\beta = -335.52 + 2686.5\,z_c - 5237.5\,z_c^2 \qquad (14)$$

It should be noted that the coefficients and exponents of Equations (7) and (11) depend only on the critical compressibility factor of the substance. For a mixture z_c', the pseudocritical compressibility factor, and T_c', the pseudocritical temperature, can be used. These are obtained by combining the critical compressibility factors and the critical temperatures of the components as follows:

$$z_c' = \sum_{i=1}^{N} n_i\, z_{c_i} \qquad (15)$$

$$T_c' = \sum_{i=1}^{N} n_i\, T_{c_i} \qquad (16)$$

A more exact representation, especially in the neighborhood of the critical point, results from the use of the actual critical temperature of the mixture, when this information is available. One method for estimating the critical temperature of hydrocarbon mixtures is reported by Grieves and Thodos (*3*).

The critical values for the mixture serve to define a hypothetical pure compound for which Equations (7) and (11) can be applied. In order to make use of Equations (15) and (16) values of z_c and T_c for the pure compounds are needed. Lydersen, Greenkorn, and Hougen (*7*) give values of these properties for the normal paraffins, through octane, which have been extended by Thodos (*12*) to heavier hydrocarbons. These values are presented in Table 2.

APPLICATION OF METHOD

In order to demonstrate the applicability and accuracy of the method developed in this study the enthalpies of three ternary hydrocarbon mixtures, at their saturated vapor and liquid states, have been estimated and compared with experimental data reported by Nelson and Holcomb (*8*). The details of the procedure are presented for one of these mixtures.

Example

Determine the enthalpy of a hydrocarbon mixture in its saturated vapor and liquid states at 280°F. The composition of the mixture is

	Mole Fraction
Propane	0.201
n-Butane	0.298
n-Pentane	0.501
	1.000

Calculation of Enthalpy of Mixture at 280°F. and 0 lb./sq.in.abs. Using the coefficients of Table 1 one can calculate the enthalpies of the individual pure hydrocarbons as follows:

Propane

$$H^* = 5{,}073 + 1{,}501\left(\frac{280}{100}\right) + 158.5\left(\frac{280}{100}\right)^2 - 3.46\left(\frac{280}{100}\right)^3 =$$
$$10{,}443 \text{ B.t.u./lb.-mole}$$

n-Butane

$$H^* = 6{,}637 + 2{,}099\left(\frac{280}{100}\right) + 162.9\left(\frac{280}{100}\right)^2 + 0.28\left(\frac{280}{100}\right)^3 =$$
$$13{,}797$$

n-Pentane

$$H^* = 8{,}012 + 2{,}573\left(\frac{280}{100}\right) + 208.8\left(\frac{280}{100}\right)^2 - 0.87\left(\frac{280}{100}\right)^3 =$$
$$16{,}834$$

By Equation (1) the enthalpy of the mixture at 280°F. and 0 lb./sq.in.abs. is

$$H^* = 10{,}443\ (0.201) + 13{,}797\ (0.298) + 16{,}834\ (0.501) =$$
$$14{,}645 \text{ B.t.u./lb.-mole}$$

Evaluation of Enthalpy Corrections for Deviations from Ideal Gas Behavior. The constants characteristic of this mixture are calculated as follows:

	n	M	z_c	T_c, °R.	nM	$n\,z_c$	$n\,T_c$
Propane	0.201	44	0.277	666	8.84	0.0557	133.9
n-Butane	0.298	58	0.274	765	17.28	0.0816	228.0
n-Pentane	0.501	72	0.269	846	36.07	0.1348	423.8
	1.000				62.19	0.2721	785.7

The critical temperature of this mixture was established as 793°R. by the method of Grieves and Thodos (3).

$$\text{Therefore } T_R' = \frac{460 + 280}{785.7} = 0.942, \text{ and } T_R = \frac{460 + 280}{793} = 0.933$$

The constants for the correction equation for the saturated vapor state are determined from Equations (8), (9), and (10) as follows:

$$p = 2.5\ (0.2721) - 0.525 = 0.155$$

$$m = -7.424 + 45.65\ (0.2721) - 48.75\ (0.2721)^2 = 1.388$$

$$k = 7.401 - 39.65\ (0.2721) + 43.75\ (0.2721)^2 = -0.149$$

Substituting these values in Equation (7), using T_c', one gets

$$H_m^* - H_m = T_c'\,[m\,T_R' + k]^{\frac{1}{p}} =$$
$$785.7\ [1.388\ (0.942) - 0.149]^{\frac{1}{0.155}} = 2{,}027 \text{ B.t.u./lb.-mole}$$

When the actual critical temperature is used, this enthalpy correction becomes

$$H_m^* - H_m = 793\ [1.388\ (0.933) - 0.149]^{\frac{1}{0.155}} = 1{,}911 \text{ B.t.u./lb.-mole}$$

The constants for the correction equation for the saturated liquid state are determined from Equations (12), (13), and (14) as follows:

$$r = 25\ (0.2721) - 2.25 = 4.55$$

$$\alpha = -317.49 + 2559.5\ (0.2721) - 5012.5\ (0.2721)^2 = 7.82$$

$$\beta = -335.52 + 2686.5\ (0.2721) - 5237.5\ (0.2721)^2 = 7.70$$

Substituting these values in Equation (11), using T_c' one gets

$$H_m^* - h_m = 10\,T_c'\,[\alpha - \beta\,T_R']^{\frac{1}{r}} =$$
$$10\ (785.7)\ [7.82 - 7.70(0.942)\,]^{\frac{1}{4.55}} =$$
$$6{,}946 \text{ B.t.u./lb.-mole}$$

When the actual critical temperature is used, this enthalpy correction becomes

$$H_m^* - h_m = 10\ (793)\ [7.82 - 7.70\ (0.933)\,]^{\frac{1}{4.55}} =$$
$$7{,}193 \text{ B.t.u./lb.-mole}$$

Calculation of Enthalpy of Saturated Vapor and Liquid (reference: $H = 0$ at 0°R. and 0 lb./sq.in.abs.) Using the pseudocritical temperature, one obtains

$$H_m = H_m^* - (H_m^* - H_m) = 14{,}645 - 2{,}027 =$$
$$12{,}618 \text{ B.t.u./lb.-mole}$$

$$h_m = H_m^* - (H_m^* - h_m) = 14{,}645 - 6{,}946 =$$
$$7{,}699 \text{ B.t.u./lb.-mole}$$

Using the actual critical temperature one obtains

$$H_m = 14{,}645 - 1{,}911 = 12{,}734 \text{ B.t.u./lb.-mole}$$

$$h_m = 14{,}645 - 7{,}193 = 7{,}452 \text{ B.t.u./lb.-mole}$$

These calculated values of enthalpy may be summarized on a weight basis as follows:

	Saturated enthalpy at 280°F., B.t.u./lb. (H = 0, at 0°R. and 0 lb./sq.in.abs.)	
	H_m	h_m
Pseudocritical temperature	202.9	123.8
Actual critical temperature	204.8	119.8

For this ternary mixture Nelson and Holcomb (8) report experimental saturated enthalpy values of H = 220 B.t.u./lb. and h = 134 B.t.u./lb., referred to the saturated liquid at 80°F. In order to compare the enthalpies calculated by the present method with these experimental values it is essential to utilize the same reference state. The enthalpy of this mixture at 80°F. and the saturated liquid state has been calculated according to the following procedure.

At 80°F. the enthalpies of the individual hydrocarbons at 0 lb./sq.in.abs. are found to be H_3^* = 6,373, H_4^* = 8,420, and H_5^* = 10,204 B.t.u./lb.-mole. Therefore the enthalpy of the mixture at 80°F. and 0 lb./sq.in.abs. is

$$H_m^* = 6{,}373\ (0.201) + 8{,}420\ (0.298) + 10{,}204\ (0.501) =$$
$$8{,}902 \text{ B.t.u./lb.-mole}$$

$$\text{At 80°F., } T_R' = \frac{540}{785.7} = 0.687 \text{ and } T_R = \frac{540}{793} = 0.681$$

Therefore, using the pseudocritical temperature, one obtains

TABLE 3. COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED ENTHALPIES OF SATURATED VAPOR AND LIQUID MIXTURES

Reference State [$H = 0$, saturated liquid at 80°F. as used by Nelson and Holcomb (*8*)]

		Saturated vapor and liquid enthalpies, B.t.u./lb.				
		Experimental	*Calculated*			
		Nelson and Holcomb (*7*)	Holcomb and Brown (*4*)	Scheibel and Jenny (*8*)	This Investigation with T'_c	with T_c
Mixture *A* at 240°F. (T_c = 784°R.)	H	201	207	204	205	207
($C_3 = 0.201, C_4 = 0.399, C_5 = 0.400$)	h	101	102	94	103	102
Mixture *B* at 280°F. (T_c = 793°R.)	H	220	220	220	215	219
($C_3 = 0.201, C_4 = 0.298, C_5 = 0.501$)	h	134	132	122	136	134
Mixture *C* at 280°F. (T_c = 814°R.)	H	229	226	226	218	224
($C_3 = 0.198, C_4 = 0.106, C_5 = 0.696$)	h	134	131	121	130	128

$$\frac{H_m^* - h_m}{785.7} = 10\,[7.82 - 7.70\,(0.687)]^{\frac{1}{4.55}} = 12.26$$

$$h_m = 8{,}902 - 12.26(785.7) = -731 \text{ B.t.u./lb.-mole} = -11.8 \text{ B.t.u./lb.}$$

Similarly, using the actual critical temperature, one obtains

$$\frac{H^* - h}{793} = 10\,[7.82 - 7.70\,(0.681)]^{\frac{1}{4.55}} = 12.32$$

$$h = 8{,}902 - 12.32\,(793) = -868 \text{ B.t.u./lb.-mole} = -14.0 \text{ B.t.u./lb.}$$

These values, when subtracted from the calculated enthalpies, convert them to the reference state of saturated liquid at 80°F. used by Nelson and Holcomb (*8*). Then the following comparison can be made:

	Saturated enthalpy at 280°F., B.t.u./lb. (H = 0, saturated liquid at 80°F.)	
	H_m	h_m
Nelson and Holcomb (*8*)	220	134
Present Method:		
(*a*) pseudocritical temperature	215	136
(b) actual critical temperature	219	134

These comparisons indicate that the present method accurately predicts the enthalpies of this saturated vapor and liquid mixture. It should be noted that the use of the actual critical temperature results in closer agreement between the calculated and experimental values. This agreement should continue as the critical point of the mixture is approached. Similar calculations have been made for the other two ternary mixtures studied by Nelson and Holcomb (*8*). The results of these calculations showed a comparable agreement with the experimental values, as indicated in Table 3.

Enthalpies calculated by the present method can be compared with corresponding values calculated by other available methods. Holcomb and Brown (*4*) present charts of the molar enthalpies of hydrocarbons at zero pressure, which have been corrected by the generalized correlation of Hougen and Watson (*5*) for the isothermal effect of pressure on enthalpy. In addition Scheibel and Jenny (*10*) give a nomograph for the calculation of enthalpies of hydrocarbon mixtures at pressures from 0 to 1,000 lb./sq.in. abs. The enthalpies of the three mixtures studied by Nelson and Holcomb have been calculated by these two methods, and the results are presented in Table 3. It can be seen that the present method gives results at least as accurate as those obtained by the other methods for saturated vapors and produces somewhat better results for saturated liquids.

CONCLUSION

This study has stressed the analytical approach to the problem of estimating enthalpies of saturated hydrocarbon mixtures. Such estimates comprise an important part of all distillation calculations, many of which are now being handled by digital computers. The equations presented can be easily programmed and could form an integral part of any computer program for distillation column design.

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NOTATION

a, b, c, d = coefficients for Equation (2)
h = enthalpy of saturated liquid, B.t.u./lb.-mole
H = enthalpy of saturated vapor, B.t.u./lb.-mole
H^* = enthalpy of ideal gas, B.t.u./lb.-mole
k, m = constants for Equation (7)
M = molecular weight
n = mole fraction
p = exponent for Equation (7)
r = exponent for Equation (11)
t = temperature, °F.
T_c = critical temperature, °R.
T_c' = pseudocritical temperature, °R.
T_R = reduced temperature, $(460 + t)/T_c$
T_R' = pseudoreduced temperature, $(460 + t)/T_c'$
z_c = critical compressibility factor
z_c' = pseudocritical compressibility factor
α, β = constants for Equation (11)

Subscripts

i = ith component
m = mixture

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