

Application of the Principle of Corresponding States for Polar Substances

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THE PRACTICING ENGINEER requires reliable procedures for estimating unknown thermodynamic properties of pure gases and their mixtures. The principle of corresponding states provides a procedure for representing the volumetric behavior of substances in generalized form. Derived thermodynamic properties have been presented in the familiar two-parameter reduced temperature-pressure diagrams (8). More recently, third parameters have been proposed and have resulted in more precise predicting procedures (4, 5, 12, 17, 19). These procedures have been most successful over a wide range of conditions for predicting the properties of hydrocarbons and their mixtures. When chemically dissimilar systems are encountered, predictions are much less reliable in the few instances where data are available to make a comparison. This article presents a procedure for estimating the enthalpy of a binary mixture containing a hydrocarbon and a chemically dissimilar substance which associates. Enthalpy data for hydrocarbon mixtures with alcohols are used to demonstrate the procedure.

Enthalpy data for mixtures of benzene-methanol have been reported by McCracken and Smith (13). They proposed a correlating procedure based on the formation of methanol dimers. Benzene-ethanol and *n*-pentane-ethanol data were obtained by Storvick and Smith (21). The experimental equipment and procedures are described in detail in these articles.

PURE ASSOCIATING SUBSTANCES

Association has been used to explain anomalous behavior of many strongly polar substances. Lambert (11) used dimerization to obtain agreement between predicted values of second virial coefficients of polar substances as compared to nonpolar. In an enthalpy predicting procedure, it would be desirable to isolate the effect of association. The effect could then be added to the enthalpy deviations for equi-structural nonpolar substances to give the total effect for the associated substance. Bondi and Simkin (3) have successfully applied this procedure to isolate the effect of hydrogen bonding on the heat of vaporization of substances containing —OH groups.

The isothermal enthalpy behavior of any substance can be calculated from its *P-V-T* properties which may be represented by the residual volume equation of state

$$V = \frac{RT}{P} - \alpha \quad (1)$$

If orientational forces were not present in a polar molecule, its volumetric behavior would be represented very nearly by a hydrocarbon homomorph (a compound of similar molecular geometry—e.g., propane is a hydrocarbon homomorph of ethanol). The kinetic energy of the homomorph molecule would be nearly the same as the polar molecule with no orientational forces present at equal thermodynamic temperatures. The residual volume in Equation 1 could then be split into two parts:

The residual volume of the hydrocarbon homomorph.
The contribution due to association, α_{assoc} .

By an analysis similar to that of Pitzer and others (16, 17)

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it is possible to show that the hydrocarbon portion of the residual volume may be split again into α_s , the contribution of a "perfect fluid" comprised of spherically symmetrical molecules and α_g , the additional contribution due to the "acentric" forces between nonspherical molecules. Equation 1 then becomes

$$V = \frac{RT}{P} - (\alpha_s + \alpha_g + \alpha_{\text{assoc}}) \quad (2)$$

This equation of state can be used to calculate the isothermal effect of pressure on the enthalpy and integrated from zero pressure to any pressure *P*.

$$(H^* - H) = \int_0^P \left[T \left(\frac{\partial \alpha_s}{\partial T} \right)_P - \alpha_s \right] dP + \int_0^P \left[T \left(\frac{\partial \alpha_g}{\partial T} \right)_P - \alpha_g \right] dP + \int_0^P \left[T \left(\frac{\partial \alpha_{\text{assoc}}}{\partial T} \right)_P - \alpha_{\text{assoc}} \right] dP \quad (3)$$

or

$$(H^* - H) = \Delta H_s + \Delta H_g + \Delta H_{\text{assoc}} \quad (4)$$

The first two terms in Equation 4 can be evaluated using the generalized correlation of Curl and Pitzer (4) since only the factors pertaining to molecular geometry are included in these terms. The temperature and pressure of the associating substances and the critical constants and vapor pressure of the hydrocarbon homomorph are used in this calculation.

The third term in Equation 4 may be evaluated by assuming association accounts for all orientational and association effects in the substance not accounted for by molecular geometry. Although several assumptions are made to evaluate ΔH_{assoc} , this quantity is not a large contribution to $(H^* - H)$ in Equation 4 and the errors introduced by the assumptions are not as serious as might be expected.

The association may be represented by the reaction



Assuming that the mole fraction of the polymers, A_n , is much less than one, the association effect is obtained from the individual heats of reaction for the formation of each polymer from monomer units, ΔH_{A_n} , by the sum

$$\Delta H_{\text{assoc}} = \sum_{n=2}^{\infty} -x_n \Delta H_{A_n} \quad (6)$$

The equilibrium constants for the various polymers formed in Equation 5 in terms of the fugacities are given by

$$K_n = f_n / f_1^n \quad (7)$$

(Although $A + A_{n-1} \rightleftharpoons A_n$ is the path to trimers and higher polymers, the same expression is obtained for the equilibrium constant in Equation 7.)

If the gaseous mixture of monomers and polymers is assumed an ideal solution and the ratio of the fugacity coefficients is approximately one, the mole fraction of each polymer is given by

$$x_n = K_n x_1^n P^{n-1} \quad (8)$$

Table 1. Differences between Predicted and Experimental Enthalpy Deviations from the Ideal Gas Values

Temp., ° F.	P, P.S.I.A.	$(H^* - H)_{\text{calcd.}} - (H^* - H)_{\text{exptl.}}$				Temp., ° F.	P, P.S.I.A.	$(H^* - H)_{\text{calcd.}} - (H^* - H)_{\text{exptl.}}$			
		Hougen, Watson (8)	Lyderson, others (12) ^a	Equations 4 and 12 b c				Hougen, Watson (8)	Lyderson, others (12) ^a	Equations 4 and 12 b c	
Methanol						Ethanol					
350	100	-6	-5	-1	0	350	100	-6	-6	-2	0
	200	-12	-12	0	0		200	-12	-15	0	-1
	300	-19	-19	0	4	400	100	-3	-4	-2	1
400	100	-5	-4	-2	0		200	-8	-9	-2	0
	200	-10	-8	-2	1		300	-12	-13	-1	0
	300	-14	-11	-3	-1		400	18	-20	-2	-2
	400	-18	-13	-2	0	450	100	-3	-2	-1	1
	500	-22	-16	-1	0		200	-6	-5	-1	1
	600	-28	-20	-1	2		300	-9	-8	-1	1
450	100	-2	-2	0	2		400	-13	-13	0	-1
	200	-5	-3	-1	2		500	-19	-17	0	-4
	300	-8	-5	-1	3		600	-27	-25	-2	-11
	400	-10	-6	0	3	500	100	-1	-1	0	1
	500	-14	-7	1	3		200	-4	-4	-1	1
	600	-16	-8	2	0		300	-6	-5	-1	2
	700	-22	-12	-1	-1		400	-7	-8	1	2
	800	-30	-17	-5	-7		500	-11	-11	0	0
475	100	0	0	1	3		600	-14	-13	0	-3
	200	-2	-1	1	4		700	-17	-16	0	-7
	300	0	1	3	6		800	-21	-19	-1	-12
	400	-3	-2	5	7	Error					
	500	-5	-2	6	8	Absolute,					
	600	-7	-2	8	8	B.t.u./lb.	217	214	18	51	
	700	-10	-4	6	5	Average,					
	800	-14	-8	3	1	B.t.u./lb.	10.85	10.70	0.90	2.55	
	900	-23	-14	-4	-8	Per cent ^d	32.1	31.6	2.7	7.5	
	1000	-30	-24	-13	-19						
Error						1-Propanol ^e					
Absolute,						391	100	2	2	0	
B.t.u./lb.	335	225	73	98			200	4	3	0	
Average,						445	100	2	2	0	
B.t.u./lb.	12.41	8.33	2.70	3.62			200	2	3	0	
Per cent ^d	26.4	17.8	5.8	7.8			300	6	5	-1	
							400	10	4	-3	
						499	100	1	1	0	
							200	1	3	1	
							300	5	5	1	
							400	2	6	1	
						Error					
						Absolute,					
						B.t.u./lb.	37	34	7		
						Average,					
						B.t.u./lb.	3.70	3.40	0.70		
						Per cent ^d	29.4	27.0	5.5		

^a $z_c = 0.222$ for methanol, 0.248 for ethanol, 0.251 for 1-propanol.

^b ΔH_{A_n} and ΔS_{A_n} from Table IV.

^c For methanol (22) $\Delta H_{A_2} = -5796$, $\Delta H_{A_4} = -43,560$ B.t.u./lb. mole, and $\Delta S_{A_2} = -16.5$, $\Delta S_{A_4} = -81.3$ e.u. For ethanol (2) $\Delta H_{A_2} = -6120$, $\Delta H_{A_4} = -44,640$ B.t.u./lb. mole, and $\Delta S_{A_2} = -16.57$, $\Delta S_{A_4} = -81.48$ e.u.

^d Calculated by dividing absolute error by sum of experimental deviations from an ideal gas.

^e Experimental enthalpy deviations for 1-propanol calculated from P-V-T data (18).

The equilibrium constant in Equation 8 is related to the heat of formation of the various polymers by the equation

$$\frac{\partial \ln K_n}{\partial T} = \frac{\Delta H_{A_n}}{RT^2} \quad (9)$$

Over relatively short ranges of temperature, ΔH_{A_n} may be assumed independent of temperature and Equation 9 integrated to give

$$\ln K_n = \frac{\Delta H_{A_n}}{RT} + C \quad (10)$$

Through the relationship between the equilibrium constant and the free energy of formation, the integration constant, C , in Equation 10 can be identified with the entropy of formation of the n th polymer, $\Delta S_{A_n}/R$. The expression for the equilibrium constant is then

$$K_n = \exp. \left[\frac{\Delta S_{A_n}}{R} - \frac{\Delta H_{A_n}}{RT} \right] \quad (11)$$

Substituting Equations 8 and 11 into 6, the expression for $\Delta H_{\text{assoc.}}$ becomes

$$\Delta H_{\text{assoc.}} = \sum_{n=2}^n -x_1^n P^{n-1} \Delta H_{A_n} \exp. \left[\frac{\Delta S_{A_n}}{R} - \frac{\Delta H_{A_n}}{RT} \right] \quad (12)$$

Inspection of Equation 12 indicates that $\Delta H_{\text{assoc.}}$ can be represented as a power series in pressure

$$\Delta H_{\text{assoc.}} = \beta(T, x_1) P + \gamma(T, x_1) P^2 + \dots \quad (13)$$

where

$$\beta(T, x_1) = -x_1^2 \Delta H_{A_2} \exp. \left[\frac{\Delta S_{A_2}}{R} - \frac{\Delta H_{A_2}}{RT} \right] \quad (14)$$

$$\gamma(T, x_1) = -x_1^3 \Delta H_{A_3} \exp. \left[\frac{\Delta S_{A_3}}{R} - \frac{\Delta H_{A_3}}{RT} \right] \quad (15)$$

Additional terms may be added to account for higher association polymers. The parameters can be evaluated from pure component enthalpy data of associating substances.

Application of Equations 4 and 13 for the prediction of the effect of pressure on the enthalpy of a pure associating substance will be limited to pressures below 0.9 of the critical pressure in the vapor region. The pressure-enthalpy isotherms above the critical pressure and temperature become decreasing functions of pressure. This cannot be explained by the association model and the region above $P_r = 0.9$ is not included in this treatment.

The effect of pressure on the enthalpy of associating substances can be predicted with literature values of the heats and entropies of formation. Such values have been obtained by Weltner and Pitzer (22) for methanol and by Barrows (2) for ethanol. From an analysis of low pressure P - V - T and heat capacity data, Weltner and Pitzer postulated that dimers and tetramers of methanol were formed. This suggests that Equation 12 should be applied with values of $n = 2$ and 4, neglecting the term $n = 3$. The results calculated from Equations 4 [using ethane as the hydrocarbon homomorph and the Curl and Pitzer (4) correlation to calculate $\Delta H_s + \Delta H_e$] and 12 are shown in Table I. The homomorph properties, $\Delta H_s + \Delta H_e$, were calculated at the temperature of the alcohol and reduced with respect to the homomorph critical constants to maintain nearly equal kinetic energies between the homomorph and the alcohol. The enthalpy data of McCracken and Smith (13) are used as the basis of comparison. Values calculated by other correlations are also listed. The representation is considerably better with Equations 4 and 12.

Similar calculations were made for ethanol using the heat and entropies of formation for dimers and tetramers obtained by Barrows. These calculated values are compared to the data of Storvick and Smith (21) in Table I.

These predicted values are independent of the measured enthalpy values for methanol and ethanol. To improve the representation of the alcohol data, Equation 4 can be written

$$\Delta H_{\text{assoc.}} = (H^* - H) - (\Delta H_s + \Delta H_e) \quad (16)$$

to obtain $\Delta H_{\text{assoc.}}$ data from the calorimetric enthalpy data. Isothermal values of $\Delta H_{\text{assoc.}}$ from Equation 16 were fitted to Equation 13 by a least squares procedure to obtain β , γ , and other coefficients.

These coefficients for different isotherms were in turn fitted to Equations 14 and 15 to obtain values of ΔH_{A_n} and ΔS_{A_n} . In all cases the mole fraction of the monomer, x_1 , was assumed to be one. Equation 13 best represented the alcohol data up to 0.9 P_c when only the terms up to $n = 3$ were retained in Equation 12.

Inspection of Equation 13 shows that as the pressure approaches zero, the slope of the $\Delta H_{\text{assoc.}}$ vs. pressure curve equals $\beta(t, x_1)$. Therefore, the value of the heat and entropy of formation for the dimer should compare favorably with literature values obtained by other measurements. This is confirmed by the values listed in Table II.

The calculated dimer constants for methanol from the data of McCracken and Smith did not compare favorably with the literature values. When the enthalpy data of Smith (20) and the low pressure P - V - T data of Foz Gazulla, Moricillo, and Mendez (7) were used to calculate the dimer constants, the results were in much better agreement with the literature values. Analysis of the McCracken and Smith data indicated points on the high temperature isotherms in the low pressure region were not obtained. Adjustment of the initial slopes of the high temperature isotherms would bring the values for the dimer constants into agreement with the literature and still do justice to the high pressure data.

Additional confirmation of the dimerization constants was obtained by evaluating the enthalpy deviations for 1-propanol from the P - V - T data of Ramsey and Young (18). The constants obtained are also listed in Table II.

Interpretation of the constants $\gamma(T, 1)$ as representing only the heat and entropy of formation for the various alcohols is risky. Equation 12 was terminated at $n = 3$ to give the best fit of the data. Any orientational effects and high order polymerization would affect the values obtained.

A general procedure for calculating $\Delta H_{\text{assoc.}}$ for various alcohols is suggested by the fact that the dimerization

Table II. Heats and Entropies of Formation for Alcohol Dimers from Monomer (Literature values)

Alcohol Investigated	Description of Data	ΔH_{A_2} , B.t.u. per Lb. Mole	ΔS_{A_2} , E.U.
Methanol vapor (22)	Low pressure P - V - T , heat capacity, spectroscopic	-5800	-16.5
Ethanol vapor (2)	Low pressure P - V - T , heat capacity, spectroscopic	-6120	-16.57
Methanol vapor (9)	Spectroscopic	-5400	...
Various alcohols (10)	Analysis of P - V - T data for several alcohols	-7200	...
Methanol and ethanol (1)	Liquid solutions of methanol and ethanol in carbon tetrachloride at 45° C.	-6340	...
Ethanol (14)	Data for $\Delta H_{\text{assoc.}}$ fitted to Equations 4 and 12 of this work.	-5000	-16.04

constants are nearly the same for all three alcohols. To predict $\beta(T, 1)$, the heat of dimerization would be chosen as -5000 B.t.u. per pound mole and the entropy of dimerization evaluated for the particular alcohol. No reliable procedure is available to predict ΔS_{A_2} , but average values can be obtained from Equation 14 and the values listed in Table III for each alcohol. Table IV gives the general magnitude of the entropy terms.

The effect of temperature on the heat of formation of the dimer, has not been accounted for, as it was assumed constant in integrating Equation 9. The range of temperatures over which the dimer constants were evaluated was sufficiently narrow to make the evaluation of this third-order effect impossible without more precise data. Finch and Lippencott (6) have evaluated the temperature dependence of ΔH_{A_2} from spectroscopic data. These data show a varia-

Table III. Coefficients $\beta(T, 1)$ and $\gamma(T, 1)$ Obtained from Equation 13 for Ethanol, Methanol, and 1-Propanol^a

Alcohol	Temp., ° F.	$\beta(T, 1)$, B.t.u. per Lb. Mole-Atm.	$\gamma(T, 1)$, B.t.u. per Lb. Mole-Atm. ²
Ethanol	350	34.88	3.984
	400	29.00	1.357
	450	25.88	0.882
	500	20.99	0.483
Methanol	350	50.82	0.881
	400	36.80	0.532
	450	17.91	0.554
	475	12.49	0.440
1-Propanol	391	18.50	0.412
	445	13.54	0.429
	499	12.28	0.050

^a Mole fraction of monomer, x_1 , was set equal to one. Methanol data are from McCracken and Smith (13). 1-Propanol data calculated from P - V - T data of Ramsey and Young (18). Ethanol data from Storvick and Smith (21).

Table IV. Average Entropies of Formation for Dimers and Trimers of Methanol and 1-Propanol^a

Alcohol	ΔS_{A_2} , E.U.	ΔS_{A_3} , E.U.
Ethanol	-16.04	-42.99
Methanol	-16.11	-44.55
1-Propanol	-17.13	-45.48

^a Average values of entropy obtained from Equations 14 and 15, using the heats of formation of the dimer and trimer for ethanol from Table III and the $\beta(T, 1)$ and $\alpha(T, 1)$ data from Table III. $\Delta H_{A_2} = -5000$ B.t.u./lb. mole and $\Delta H_{A_3} = -20,800$ B.t.u./lb. mole.

tion of about 10% in ΔH_{A_2} per 100° F. temperature change at room temperature.

The same procedure can be used to obtain the constant for the trimer and higher order terms. The values of ΔS_{A_3} for the three alcohols are also listed in Table IV, based upon a value of $\Delta H_{A_3} = -20,800$ B.t.u. per pound mole.

The parameters listed in Table IV were used in Equations 4 and 12 to calculate the enthalpy deviations from ideality for each alcohol. The results are compared with experimental values in Table I. The average absolute error of 1 B.t.u. per pound for ethanol and 1-propanol is within the experimental error in obtaining the data. The larger error for methanol is due primarily to the poor representation of the 450° and 475° F. isotherms. Adjustment of these isotherms as discussed previously would improve this representation.

VAPOR PHASE ENTHALPY OF MIXTURES

The methods for predicting the thermodynamic properties of mixtures are based on two general procedures. In one, the pure component properties are evaluated and then combined according to a prescribed procedure. The other involves combining pure component parameters, such as the critical constants or constants in an equation of state, and using these in a procedure developed for pure components. Both methods have been successfully applied to hydrocarbon mixtures.

When a mixture contains a hydrocarbon and an associating substance, generalized procedures give unreliable results. The generalized correlation of Hougen and Watson (8) using the true mixture critical constants listed in Table V and the pseudo-critical constants obtained by Kay's method were used to predict the enthalpy deviations for the benzene-methanol data of McCracken and Smith (13) and

Table V. True Critical Constants for Mixtures of Benzene-Ethanol, *n*-Pentane-Ethanol, and Benzene-Methanol^a

Mole % alcohols	25		50		75	
	$T_{cm},$ ° F.	$P_{cm},$ p.s.i.a.	$T_{cm},$ ° F.	$P_{cm},$ p.s.i.a.	$T_{cm},$ ° F.	$P_{cm},$ p.s.i.a.
Benzene-ethanol	502	693	478	756	479	906
<i>n</i> -Pentane-ethanol	378	550	390	657	432	826
Benzene-methanol	480	680	472	908	468	1115

^a Benzene-ethanol and *n*-pentane-ethanol data from McCracken, Storvick, and Smith (13).

Table VI. Average Absolute and Per Cent Absolute Error of Difference between Predicted and Experimental Enthalpy Deviations from Ideal Gas Values

Mole % alcohol	25		50		75		
	Abs., B.t.u./lb.	%	Abs., B.t.u./lb.	%	Abs., B.t.u./lb.	%	
Benzene-ethanol ^a	1	6.3	46.3	4.2	25.5	0.6	3.3
	2	3.9	28.8	3.2	19.4	2.5	12.7
	3	2.8	21.0	1.5	9.1	0.9	4.6
<i>n</i> -Pentane-ethanol ^a	1	2.8	10.8	4.0	18.2	1.4	5.4
	2	4.2	16.5	1.3	6.1	7.6	30.8
	3	2.3	8.9	1.4	6.5	1.2	4.9
Benzene-methanol ^b	1	4.2	25.1	4.9	35.7	4.8	31.3
	2	3.8	22.8	3.1	22.1	1.8	12.0
	3	4.0	23.7	2.6	19.1	3.4	22.5

1. Hougen and Watson (8) correlation using pseudo-critical constants.

2. Hougen and Watson correlation using true critical constants listed in Table V.

3. Proposed Equation 17.

^a Benzene-ethanol and *n*-pentane-ethanol data from Storvick and Smith (21).

^b Benzene-methanol data from McCracken and Smith (13).

the benzene-ethanol and *n*-pentane-ethanol data of Storvick and Smith (21). The results are tabulated in Table VI.

Although excellent agreement was obtained in a few instances, the general agreement is poor. No pattern was established to allow a prediction of which mixture, or mixture composition, would give good agreement. This was equally true for the predictions based on the true or the pseudo-critical constants.

In the previous section, the enthalpy deviation of pure associating substances was based on isolating the effect of association for the molecular geometry. An extension of this procedure to mixtures is possible, provided an adequate method is available to evaluate the geometric effect of a mixture of an associating substance and hydrocarbons. The total enthalpy would be obtained by adding the association effect to the geometric contribution for the mixture.

The geometric contribution to the mixture can be determined by combining the pure-component enthalpy deviations for the hydrocarbon and the hydrocarbon homomorph of the associating substance. Mayer (15) has shown that the second virial coefficient for a binary mixture is a second-degree polynomial in terms of the mole fraction of each component. Calculation of the enthalpy deviation from the virial equation of state for the mixture retaining only the second coefficients leads to the following expression for the mixture enthalpy deviation in terms of the pure component values:

$$\Delta H_m = x_1^2 \Delta H_1 + 2x_1x_2 \Delta H_{12} + x_2^2 \Delta H_2 \quad (16)$$

Equation 16 can be evaluated for a mixture by calculating ΔH_1 , the enthalpy deviation for the hydrocarbon homomorph of the associating substance and ΔH_2 for the hydrocarbon. The generalized correlation of Curl and Pitzer (4) was used for this calculation. The geometric mean, $(\Delta H_1 \Delta H_2)^{1/2}$, was employed to evaluate ΔH_{12} .

Adding the association effect, ΔH_{assoc} , to the geometric contribution gives the total deviation from ideality for the binary containing an associating substance and a hydrocarbon. This is expressed

$$\Delta H_m = x_1^2 \Delta H_1 + 2x_1x_2 \Delta H_{12} + x_2^2 \Delta H_2 + \Delta H_{\text{assoc}} \quad (17)$$

The value of ΔH_{assoc} was obtained from Equation 12. The quantity x_1 in Equation 12 was taken as the mole fraction of the alcohol in the mixture. As in the case of the pure component data, this assumes the degree of polymerization to be small.

Equation 17 was used to calculate the enthalpy deviations for the benzene-ethanol, *n*-pentane-ethanol and benzene-methanol mixtures. The heats and entropies of formation of the alcohol polymers given in Table IV were used in this calculation. The results are given in Table VI.

The average error is less than 3 B.t.u. per pound for all mixtures of benzene- and *n*-pentane-ethanol and the results are generally more precise than the generalized correlations. The mixtures containing the higher percentages of alcohol are more reliably predicted, suggesting that the presence of a nonassociating substance tends to decrease the degree of association of the alcohol.

The benzene-methanol data are not as reliably predicted as the other mixtures. Improved representation of the pure methanol data as discussed would be expected to improve these results.

The advantage of Equation 17 as a predicting procedure for mixtures containing an associating substance is that it requires no mixture properties. The necessary interaction parameter, ΔH_{12} , is calculated from the pure component data.

Alternative procedure may be used which adequately predict the geometric contribution to the nonpolar-polar mixture enthalpy deviations given by Equation 16. This is due to the additive nature of the association effect as shown in Equation 17.

CALCULATIONS

Sample. Calculate the enthalpy deviation from ideality for a mixture containing 75 mole % ethanol and 25 mole % *n*-pentane at 450° F. and 600 p.s.i.a.

Data

Critical temperature, <i>n</i> -pentane	469.8° K.	(12)
Critical pressure, <i>n</i> -pentane	33.3 atm.	(12)
Acentric factor, ω	0.233	(17)
Critical temperature, propane	369.9° K.	(12)
Critical pressure, propane	42.0 atm.	(12)
Acentric factor, ω	0.152	(17)

From Table IV, for ethanol:

$$\Delta H_{A2} = -5000 \text{ B.t.u./lb. mole} \quad \Delta S_{A2} = -16.04 \text{ e.u.}$$

$$\Delta H_{A3} = -20,800 \text{ B.t.u./lb. mole} \quad \Delta S_{A3} = -42.99 \text{ e.u.}$$

Pure Component. The enthalpy deviation from ideality for *n*-pentane is estimated from the tables of Curl and Pitzer (4) using linear interpolation and represents ΔH_2 in Equation 17. The same calculation for propane (the hydrocarbon homomorph of ethanol) gives ΔH_1 in Equation 17.

n-Pentane.

$$T_r = \frac{910}{1.8} \times \frac{1}{469.8} = 1.076$$

$$P_r = \frac{600}{14.7} \times \frac{1}{33.3} = 1.225$$

From the Curl and Pitzer Tables II

$$\left[\frac{H^* - H}{RT_c} \right] = 1.69 + (0.233)(0.77) = 1.87$$

$$H^* - H = \Delta H_2 (1.99)(1.8)(469.8)(1.87) = 3120 \text{ B.t.u./lb. mole}$$

Propane.

$$P_r = \frac{600}{14.7} \times \frac{1}{42.0} = 0.972$$

$$T_r = \frac{910}{1.8} \times \frac{1}{369.9} = 1.366$$

From the tables

$$\left[\frac{H^* - H}{RT_c} \right] = 0.44 + (0.152)(0.10) = 0.46$$

$$H^* - H = \Delta H_1 = (1.99)(1.8)(369.9)(0.46) = 609 \text{ B.t.u./lb. mole}$$

Interaction Parameter, ΔH_{12}

$$\Delta H_{12} = (\Delta H_1 \Delta H_2)^{1/2} = [(609)(3120)]^{1/2} = 1380 \text{ B.t.u./lb. mole}$$

Association Contribution. Obtain β from Equation 14

$$\beta = -(0.75)^2(-5000) \exp. \left[\frac{-16.04}{1.99} + \frac{5000}{(1.99)(910)} \right]$$

$$\beta = 2810 \exp. [-5.31]$$

$$\beta = 14.00$$

Obtain γ from Equation 15

$$\gamma = -(0.75)^3(-20,800) \exp. \left[\frac{-42.99}{1.99} + \frac{20,800}{(1.99)(910)} \right]$$

$$\gamma = 8770 \exp. (-10.11)$$

$$\gamma = 0.361$$

$\Delta H_{\text{assoc.}}$ is now calculated from Equation 13

$$\Delta H_{\text{assoc.}} = (14.00) \left(\frac{600}{14.7} \right) + (0.361) \left(\frac{600}{14.7} \right)^2$$

$$\Delta H_{\text{assoc.}} = 1172 \text{ B.t.u./lb. mole}$$

The total enthalpy deviation from ideality for the mixture is obtained from Equation 17.

$$\Delta H_{\text{m}} = (0.75)^2(609) + 2(0.75)(0.025)(1380) + (0.25)^2(3120) + 1172$$

$$\Delta H_{\text{m}} = 342 + 517 + 195 + 1172$$

$$\Delta H_{\text{m}} = 2226 \text{ B.t.u./lb. mole}$$

The average molecular weight of the mixture is 52.59. Therefore, $\Delta H_{\text{m}} = 42 \text{ B.t.u./lb.}$ as calculated compares to the experimental value of 43 B.t.u./lb. reported by Storvick and Smith (21).

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NOMENCLATURE

A	= associating molecule in Equation 5
C	= integrating constant in Equation 10
\bar{f}	= fugacity in the mixture
H	= enthalpy at any pressure, P
H*	= enthalpy in the ideal gas state
K	= equilibrium constant
P	= pressure
R	= universal gas constant
S	= entropy
T	= temperature
V	= volume
x	= mole fraction
z_c	= compressibility factor at the critical point, $z_c = RT_c/P_c V_c$
α	= residual volume
β, γ	= coefficients in Equation 13
ω	= acentric factor, $= -\log(P/P_c)_{\text{satd.}} - 1.00$ at $T_r = 0.700$ (4)

Subscripts

An	= property of a polymer of n monomer units
Assoc.	= association contribution
c	= critical property
g	= geometric contribution in addition to spherical contribution
m	= mixture property
ma	= mixture containing an associating substance
n	= number of monomer units in a polymer
r	= reduced property
s	= spherical contribution

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