Table III. Measured Equilibrium Tie-Line Compositions (in Mole Fractions) for Ethanol–Water–CO_2 Mixtures at 50 and 60 °C

fluid phase			liquid phase		
H_2O	ETOH	CO_2	H_2O	ETOH	CO_2
T = 50 °C, P = 10.2 MPa					
0.004	0.004	0.992	0.946	0.032	0.022
0.012	0.048	0.940	0.410	0.371	0.219
T = 50 °C, P = 13.6 MPa					
0.006	0.005	0.989	0.945	0.031	0.023
0.027	0.083	0.890	0.408	0.356	0.236
T = 50 °C, P = 17.0 MPa					
0.006	0.006	0.988	0.945	0.031	0.024
0.037	0.104	0.859	0.401	0.346	0.253
T = 65 °C, P = 10.2 MPa					
0.005	0.005	0.990	0.948	0.031	0.021
0.007	0.020	0.973	0.417	0.389	0.194
T = 65 °C, P = 13.6 MPa					
0.006	0.006	0.988	0.948	0.030	0.022
0.019	0.060	0.921	0.400	0.355	0.245
T = 65 °C, P = 17.0 MPa					
0.006	0.007	0.987	0.946	0.030	0.024
0.042	0.106	0.852	0.390	0.340	0.270

of the measured value or 0.1 mol % whichever is greater. Mixture critical points or plait points have also been estimated from the experimental data by using a graphical method (*7*), and are included in these figures. These estimated plait points are listed in Table II. Equilibrium tie-line compositions measured at the same three pressures but higher temperatures, 50 and 65 °C, are presented in Table III.

The experimental results can be used to characterize the solvent properties of dense CO_2 in the extraction of ethanol from aqueous solutions. At all conditions studied, fluid-phase ethanol solubilities are appreciably higher than water solubilities, which indicates that compressed CO_2 at moderate temperatures and pressures would be a reasonably selective solvent for the extraction of ethanol from aqueous solutions. However, the results also show that ethanol concentrations greater than that corresponding to the ethanol–water azeotrope would not be obtained by extraction with CO_2 at the temperatures and pressures studied. This finding is in agreement with the experimental observations of Baker and Anderson (*3*).

The effect of solvent density on the solvent properties of CO_2 is also evident from the effect of pressure on plait point compositions at 35 °C (Table II). Ethanol mole fractions at the plait point increase from 0.163 to 0.212 as pressure is increased from 10.2 to 17.0 MPa. Water mole fractions also increase from 0.062 to 0.102 over the same pressure range. The higher solubilities correspond to greater solvent capacities at higher CO_2 densities. However, reduced ethanol selectivities are also obtained with greater solvent capacities. A similar effect can be found by examining ethanol–water solubilities in the fluid phase as a function of isobaric temperature changes.

Although the observed changes in solvent properties of CO_2 are appreciable for this ternary mixture, much more dramatic changes have been observed for 2-propanol–water–CO_2 mixtures (*8*). The phase behavior for this latter ternary mixture in the vicinity of the critical point of CO_2 is also much more complex. This suggests that the solvent properties of supercritical CO_2 cannot be correlated with CO_2 density alone; the phase behavior for the ternary mixture is an important factor. This phase behavior is the subject of a subsequent paper (*9*).

Registry No. CO_2, 124-38-9; ethanol, 64-17-5.

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Experimental Study of Excess Enthalpies for the Binary Gaseous System Methane–Ethylene by Flow Calorimetry

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Excess enthalpies for the binary system methane–ethylene were measured in an isothermal flow calorimeter. The experimental study has been made at three temperatures, 293.15, 305.15, and 313.15 K, and pressures of 1.114, 1.520, and 3.445 MPa (11, 15, and 34 atm). The experimental results were compared with those predicted from Redlich–Kwong and Benedict–Webb–Rubin equations of state. The binary interaction coefficient, k_{ij}, has been determined from experimental data by an optimization procedure. A single value independent of temperature and pressure was sufficient to represent all the network of data.

Introduction

Excess enthalpies are very important for solving engineering problems. They are very useful in equipment design, heat of solution calculations, and energy balances. Excess enthalpies are also particularly important from a scientific point of view since they are useful to verify prediction of thermodynamic properties of mixtures by equations of state. These predictive equations are usually based upon theories of molecular interaction.

The excess enthalpy of a mixture at constant temperature and pressure is defined as

$$H^E_{T,P} = \Delta H_m - \Delta H_m^{id} = [H_m - \sum x_i H_i]_{T,P} \qquad (1)$$

For an ideal solution, the heat of mixing is zero ($\Delta H_m^{id} = 0$), so either of the terms excess enthalpy or heat of mixing can be used, since these two quantities are numerically equal ($H^E_{T,P} = \Delta H_m$).

Although many experimental studies of excess enthalpies for liquids are reported in literature, few data for gas mixtures are

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Table I. Excess Enthalpies for the Binary Gaseous System Methane-Ethylene

T_0, K	P_0, MPa	x_A	Q/F, J/mol	H^E_0, J/mol	H^E_n, J/mol exptl	RK	BWR
Nominal Conditions: T_n = 293.15 K, P_n = 1.114 MPa							
293.172	1.099	0.209	22.6	22.3	22.6	20.5	21.9
293.160	1.098	0.462	32.8	33.0	33.6	30.0	32.1
293.150	1.097	0.622	30.5	30.5	31.1	27.9	29.9
293.153	1.098	0.812	21.0	21.5	21.8	17.8	19.1
Nominal Conditions: T_n = 293.15 K, P_n = 1.520 MPa							
293.180	1.515	0.217	35.4	35.0	35.1	32.1	33.7
293.157	1.454	0.430	46.7	46.8	49.5	44.7	47.2
293.175	1.498	0.612	51.3	50.8	51.6	42.1	44.7
293.153	1.535	0.801	31.5	31.6	31.2	27.5	29.3
Nominal Conditions: T_n = 293.15 K, P_n = 3.445 MPa							
293.190	3.465	0.228	123.8	122.7	120.9	148.8	142.7
293.152	3.416	0.449	150.3	150.1	153.3	184.2	180.5
293.137	3.402	0.613	147.7	148.0	151.9	163.5	162.2
293.170	3.437	0.788	92.5	91.3	91.9	107.4	107.6
Nominal Conditions: T_n = 305.15 K, P_n = 1.114 MPa							
305.162	1.099	0.252	24.0	23.2	23.6	21.2	21.6
305.142	1.072	0.436	25.3	25.4	26.6	27.2	27.7
305.155	1.105	0.621	31.1	30.4	30.7	25.6	26.2
305.158	1.080	0.792	19.0	19.1	19.7	17.7	18.1
Nominal Conditions: T_n = 305.15 K, P_n = 1.520 MPa							
305.170	1.493	0.203	33.3	32.2	32.9	27.5	27.6
305.134	1.528	0.425	40.6	41.1	40.8	40.2	40.6
305.176	1.458	0.642	39.7	39.5	41.4	36.7	37.3
305.131	1.473	0.791	24.0	25.1	26.1	25.9	26.4
Nominal Conditions: T_n = 305.15 K, P_n = 3.445 MPa							
305.178	3.450	0.245	112.1	111.5	111.2	121.8	113.8
305.170	3.472	0.431	129.5	129.7	129.7	148.4	140.9
305.177	3.416	0.625	125.5	124.6	126.5	131.7	126.6
305.167	3.430	0.784	81.1	80.4	81.1	90.2	87.4
Nominal Conditions: T_n = 313.15 K, P_n = 1.114 MPa							
313.191	1.057	0.218	20.3	18.9	20.0	18.2	17.9
313.167	1.061	0.452	28.9	28.5	30.0	25.8	25.6
313.150	1.072	0.645	26.6	26.4	27.4	23.5	23.4
313.147	1.058	0.785	15.0	15.5	16.5	17.2	17.1
Nominal Conditions: T_n = 313.15 K, P_n = 1.520 MPa							
313.153	1.465	0.259	31.7	31.4	32.8	30.3	29.6
313.191	1.506	0.456	42.3	40.8	41.3	38.1	37.4
313.181	1.500	0.666	35.7	34.3	34.8	33.3	32.9
313.184	1.440	0.816	24.1	23.2	24.6	22.1	21.9
Nominal Conditions: T_n = 313.15 K, P_n = 3.445 MPa							
313.189	3.416	0.216	97.2	95.8	93.5	99.2	90.7
313.179	3.457	0.435	113.4	112.1	111.0	131.6	122.4
313.162	3.464	0.602	125.9	125.6	125.0	121.2	113.9
313.150	3.491	0.793	67.5	67.9	68.9	78.5	74.4

available. Complex and expensive apparatus, experimental difficulties, and high cost of purified gases are the main reasons for the scarcity of data.

A complete literature review of excess enthalpy data for binary gas systems is presented as follows. The first determinations have been made by Beenakker et al. (*1*, *2*) on the following systems: H_2–N_2, Ar–H_2, Ar–N_2, and CH_4–Ar. Knoester et al. (*3*) published data for H_2–N_2, Ar–N_2, Ar–H_2 and H_2–N_2–Ar. Van Eijnsbergen and Beenakker (*4*) presented data for CH_4–Ar, CH_4–N_2, CH_4–H_2, CH_4–He, and He–Ar. Klein (*5*, *6*) studied the system CH_4–N_2. Hejmadi et al. (*7*, *8*) presented data on N_2–O_2, N_2–CO_2, and N_2–C_2H_6. Lee and Mather (*9*, *10*) studied the systems H_2–N_2, N_2–CO_2, and CH_4–CO_2 and Altunin et al. (*11*–*13*) the systems N_2–CO_2, He–CO_2, and He–Ar. Glowacki and Waluga (*14*) studied the system CH_4–N_2 and Wormald et al. (*15*) investigated the systems CH_4–H_2, CH_4–N_2, CH_4–Ar, N_2–H_2, and N_2–Ar. Kotousov and Baranyuk (*16*) presented data for the system H_2–N_2, Kotousov and Popov (*17*–*19*) studied the systems He–Ar, He–N_2, He–CO_2, H_2–Ar, and H_2–CO_2. Powers et al. (*20*) investigated the systems CH_4–C_2H_6 and CH_4–C_2H_6–C_3H_8. In our laboratory, Ba et al. (*21*–*23*) presented data for the systems N_2–O_2, N_2–C_2H_4, and C_2H_4–CO_2. Barry et al. (*24*–*28*) obtained data for the systems CH_4–CO_2, CH_4–H_2S, and CO_2–H_2S and the ternary system CH_4–CO_2–H_2S. This article presents data for the system CH_4–C_2H_4 at temperatures of 293.15, 305.15, and 313.15 K and pressures of 1.114, 1.520, and 3.445 MPa with mole fraction of methane in the range of approximately 0.2–0.8.

Experimental Method

The experimental procedure and a complete description of the equipment utilized in this study have been reported in previous articles (*21*–*28*).

The two gaseous streams (CH_4 and C_2H_4) arrive independently at the calorimeter inlet, at temperature and pressure conditions T_1,P_1 and T_2,P_2 which are essentially the same ($T_1 \approx T_2$, $P_1 \approx P_2$). The two gases are thoroughly mixed and since the mixing is endothermic, a temperature drop occurs. To compensate for this temperature drop a measured quantity of energy is supplied to the mixture by a power supply to bring the outlet temperature T_0 at approximately the same as the inlet

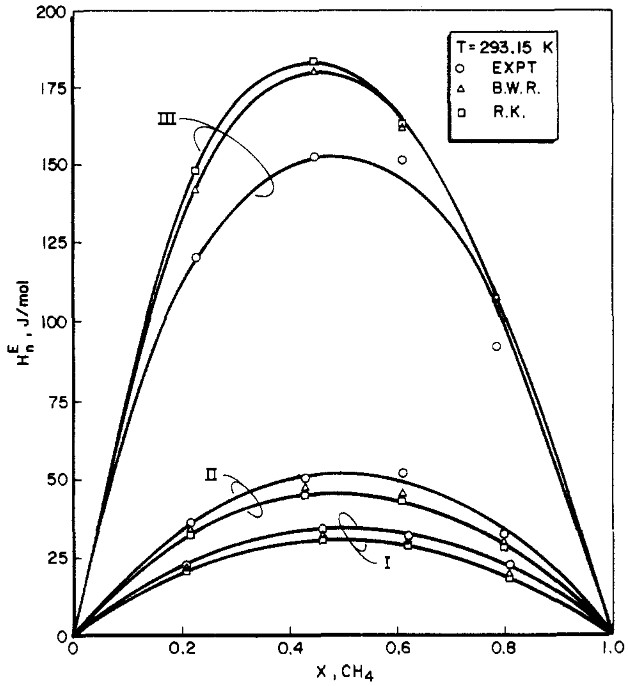

Figure 1. Excess enthalpies (J/mol) for the binary gaseous system methane–ethylene at 293.15 K: (I) 1.114, (II) 1.520, and (III) 3.445 MPa.

Table II. Effect of the Primary and Secondary Corrections on the Excess Enthalpies for the Binary Gaseous System Methane–Ethylene

	T, K		
	293.15	305.15	313.15
$100(H^E_0 - Q/F)/(Q/F)$	0.8	1.5	2.3
$100(H^E_n - H^E_0)/H^E_0$	1.9	2.2	3.3

temperature (T_1, T_2) of the two gases.

Some improvements have been made on the equipment described in previous articles. The two flowmeters have been insulated with fiberglass wool surrounded by a Styrofoam jacket to reduce external heat effects, which might affect the signal output. The micrometer valves and pressure regulators on the two lines have been slightly heated to prevent condensation of the gases at high pressures.

The methane and ethylene were supplied by Linde Co. of Canada. The methane has a certified purity of 99%, containing 0.1% CO_2, 0.2% O_2, 0.2% N_2, 0.3% C_2H_6, and 0.2% C_3H_8. The ethylene has a certified purity of 99.5%, the main impurities being 0.25% C_2H_6, 0.02% C_3H_8, 0.02% CH_4, and 0.01% air.

Experimental Results

Application of the first law of thermodynamics to the system previously described leads to

$$H^E_0 = \Delta H_m = Q/F + x_A(H_{A,1} - H_{A,0}) + x_B(H_{B,2} - H_{B,0}) - \Delta E_k \quad (2)$$

In eq 2

$$H_{A,1} - H_{A,0} = \int_{T_0}^{T_1} C_{P,A}\, dT + \int_{P_0}^{P_1} \phi_A\, dP \quad (3)$$

$$H_{B,2} - H_{B,0} = \int_{T_0}^{T_2} C_{P,B}\, dT + \int_{P_0}^{P_2} \phi_B\, dP \quad (4)$$

where

$$\phi = (\delta H/\delta P)_T \quad (5)$$

$$C_P = (\delta H/\delta T)_P \quad (6)$$

$$\Delta E_k = E_{kA-B,0} - (x_A E_{kA,1} + x_b E_{kB,2}) \quad (7)$$

Equations 3 and 4 yield the primary corrections on Q/F to obtain H^E_0 at conditions T_0 and P_0 at the calorimeter outlet. Notice that only thermodynamic properties of the pure gases A and B are required in the calculation of the primary corrections.

For the system CH_4–C_2H_4, within the experimental range encompassed in this investigation, the pressure drops across the calorimeter ($\Delta P_1 = P_0 - P_1$ and $\Delta P_2 = P_0 - P_2$) are negligible. Also, the two inlet temperatures T_1 and T_2 are nearly indentical ($T_1 \approx T_2$), and $T_1 - T_0 < 0.05$ K. Consequently, mean values for the heat capacities $\bar{C}_{P,A}$ and $\bar{C}_{P,B}$ and for the Joule–Thomson isothermal coefficients $\bar{\phi}_A$ and $\bar{\phi}_B$ were utilized in the evaluation of the integrals in eq 3 and 4. Then

$$H_{A,1} - H_{A,0} = \bar{C}_{P,A}(T_1 - T_0) + \bar{\phi}_A(P_1 - P_0) \quad (8)$$

$$H_{B,2} - H_{B,0} = \bar{C}_{P,B}(T_2 - T_0) + \bar{\phi}_B(P_2 - P_0) \quad (9)$$

Substitution of eq 7–9 into eq 2 leads to

$$H^E_0 = Q/F + x_A\bar{C}_{P,A}(T_1 - T_0) + x_B\bar{C}_{P,B}(T_2 - T_0) + x_A\bar{\phi}_A(P_1 - P_0) + x_B\bar{\phi}_B(P_2 - P_0) + x_A E_{kA,1} + x_B E_{kB,2} - E_{kA-B,0} \quad (10)$$

Since it is practically impossible to adjust the outlet pressure and temperature precisely to the nominal conditions desired, the following equation must be used:

$$H^E_n = H^E_0 + \int_{T_0}^{T_n} C^E_P\, dT + \int_{P_0}^{P_n} \phi^E\, dP \quad (11)$$

$$C^E_P = (\delta H^E/\delta T)_{P,x} \quad (12)$$

$$\phi^E = (\delta H^E/\delta P)_{T,x} \quad (13)$$

The two integral terms in eq 11 are called secondary corrections. Notice that contrary to the case of primary corrections, the calculation of secondary corrections requires thermodynamic properties for the gas mixture. For the primary corrections, the molar heat capacities for methane and ethylene utilized were those tabulated by Tester (*29*). The Joule–Thomson isothermal coefficients for the two gases were calculated from an equation derived from the Benedict–Webb–Rubin equation of state for pure components (*30*). In the case of the secondary corrections, C^E_P and ϕ^E were determined by application of BWR equation of state. The mixing rules required to calculate C^E_P and ϕ^E were those reported by Bishnoi and Robinson (*31*).

The effect of the impurities in the gases has been evaluated by Hejmadi's technique (*7*), and found to be less than 0.7 J/mol, but not entirely negligible.

Corrections relative to the variation of kinetic energy of the gases are of the order of 10^{-6} J/mol, which is negligible.

The experimental results of the excess enthalpy for the system CH_4–C_2H_4 are presented in Table I. These data are also shown in graphical form in Figures 1–3.

The effects of the primary and secondary corrections on the excess enthalpies values have also been calculated, and average values for these corrections are reported in Table II.

Accuracy of the Experimental Results

The same technique as in previous articles (*24–28*) was utilized for estimation of errors. The summation of experimental

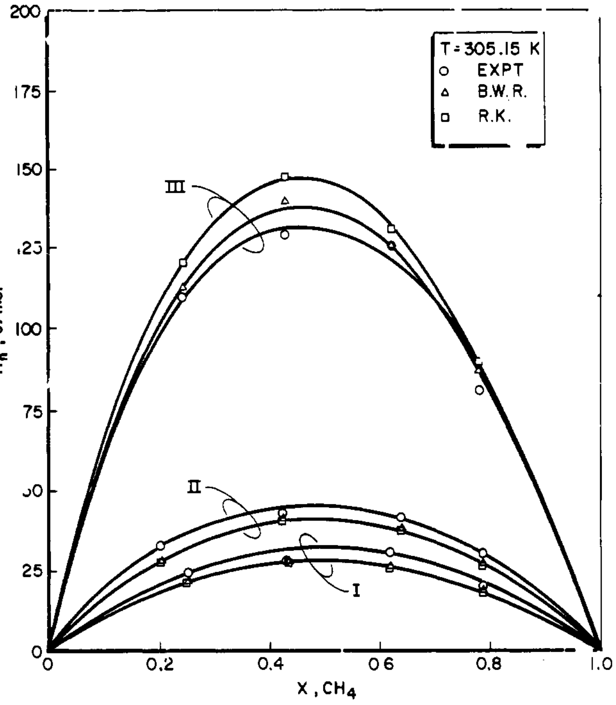

Figure 2. Excess enthalpies (J/mol) for the binary gaseous system methane-ethylene at 305.15 K: (I) 1.114, (II) 1.520, and (III) 3.445 MPa.

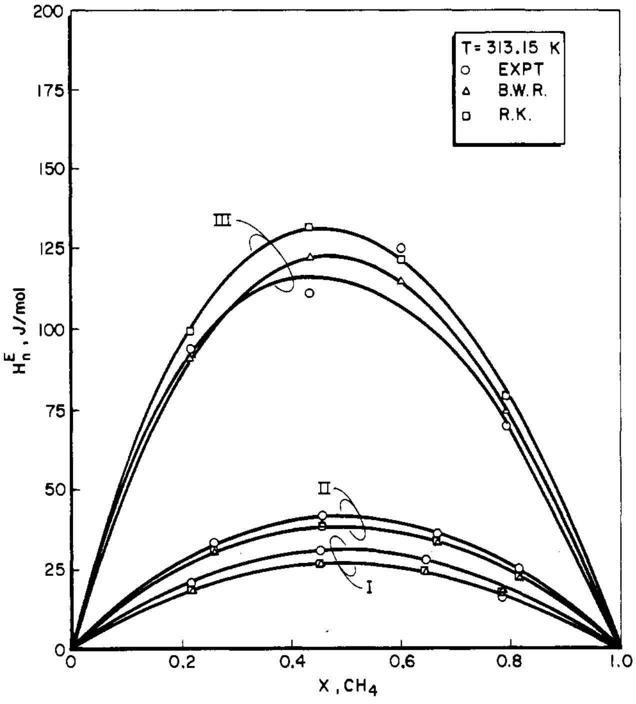

Figure 3. Excess enthalpies (J/mol) for the binary gaseous system methane-ethylene at 313.15 K: (I) 1.114 (II) 1.520, and (III) 3.445 MPa.

errors and those due to primary and secondary corrections yields a precision between 3 and 5% of the excess enthalpies H_n^E for the system methane-ethylene.

Table III. Comparison of Experimental Values of the Excess Enthalpies for the Binary Gaseous System Methane-Ethylene with Predictions from Equations of State

	T, K		
	293.15	305.15	313.15
$100(H^E_{n,exptl} - H^E_{n,RK})/H^E_{n,exptl}$	13.8	9.2	9.4
$100(H^E_{n,exptl} - H^E_{n,BWR})/H^E_{n,exptl}$	9.3	6.9	9.1

Table IV. Constants Utilized in RK Equation of State

	CH$_4$	C$_2$H$_4$	ref
Ω_a, dimensionless	0.4546	0.4290	*34*
Ω_b, dimensionless	0.0872	0.0815	*34*
T_c, K	190.6	282.4	*35*
P_c, MPa	4.60	5.04	*35*
V_c, cm^3/mol	99.0	129.0	*35*
ω, dimensionless	0.0013	0.085	*34*
k_{12}	0.0229 (by optimization procedure)		

Table V. Constants Utilized in BWR Equation of State

	CH$_4$ (*31*)	C$_2$H$_4$ (*36*)
A_0, MPa dm^6/mol^2	0.1896036	0.338383
$B_0 \times 10^2$, dm^3/mol	4.320305	5.56833
C_0, MPa dm^6 K^2/mol^2	2381.152	13287.8
a, MPa dm^9/mol^3	0.007011487	0.0262432
$b \times 10^3$, dm^6/mol^2	3.9787382	8.6000
$c \times 10^{-4}$, MPa dm^9 K^2/mol^3	0.03057917	0.21400
$\alpha \times 10^5$, dm^9/mol^3	9.6835765	17.8000
$\gamma \times 10^3$, dm^6/mol^2	5.7118125	9.23000
k_{12}	−0.0058 (by optimization procedure)	

Comparison of Experimental Data with Prediction from Equation of State

Since experimental data of excess enthalpies for the binary system methane-ethylene were not available in the literature, the only feasible comparison was that with predicted values obtained from equations of state. The Redlich-Kwong (*32*) and Benedict-Webb-Rubin (*30*) equations of state were employed.

The RK equation was utilized to calculate the excess enthalpies H_n^E with the modified mixing rules suggested by Chueh and Prausnitz (*33*). The network of equations required is presented in ref *24*. [See eq 16-27 of ref *24*.]

The enthalpies of the pure components CH$_4$ and C$_2$H$_4$ and of binary mixture were calculated from eq 28 of ref 24.

The excess enthalpy, H_n^E, is calculated as follows:

$$H_n^E = H_{m,n} - \sum x_i H_{i,n} \tag{14}$$

The values for the constants utilized in the calculations are presented in Table IV.

The BWR equation of state is also applied to predict excess enthalpies, Joule-Thomson isothermal coefficients, and heat capacities at constant pressure, utilizing the mixing rules presented by Bishnoi and Robinson (*31*). The network of equations utilized is presented in ref *24*. [See eq 33-35 of ref *24*.]

The values for the constants utilized for calculations in BWR equation are listed in Table V.

The binary interaction coefficient, k_{ij}, has been determined by an optimization procedure in order to have the minimum deviation between the experimental network of data and the values of excess enthalpies predicted by equations of state. The coefficient k_{ij} is usually considered independent of temperature and pressure. A single value of this coefficient for each equation of state was found to be sufficient to represent all the network of experimental data. The values for the k_{ij} are listed in Tables IV and V.

The excess enthalpies predicted by equations of state are presented in Table I and are also shown in graphical form in Figures 1–3. The comparison of experimental values of excess enthalpies for the binary gaseous system methane–ethylene with calculated values from equations of state is presented in Table III.

Conclusion

The largest deviation between experimental data and excess enthalpies values predicted from equations of state was 13.8% at 293.15 K, for the RK equation of state. It was the only deviation above 10%. This deviation can be explained by the fact that a single value of the binary interaction coefficient, k_{ij}, was used. Consequently, the data cannot be represented with the same precision at all temperatures and pressures. Utilization of adjustable binary interaction coefficients should improve the prediction from equations of state.

It is of interest to notice that the RK equation of state, which contains only two constants, represents the data as well as the BWR equation of state, which contains eight constants. Consequently, the RK equation seems preferable to BWR equation, because of its relative simplicity.

Glossary

a, b, c, A_0, B_0, C_0	coefficients in BWR equation of state, dimensions listed in Table V
C_P	molar heat capacity at constant pressure, J/(mol K)
E_k	kinetic energy, J/mol
F	flow rate, mol/s
H	molar enthalpy, J/mol
k_{ij}	binary interaction coefficients, dimensionless
P	pressure, MPa
Q	energy supplied to gas system by the power supply, J/s
T	temperature, K
x	mole fraction, dimensionless

Superscripts

E	denotes an excess thermodynamic property
$-$	denotes mean values for thermodynamic properties (for Joule–Thomson isothermal coefficients, ϕ, and heat capacities at constant pressure, C_P)

Subscripts

A	denotes pure gas A (CH_4)
B	denotes pure gas B (C_2H_4)
A–B	denotes gas mixture (CH_4–C_2H_4)
c	denotes critical temperature, critical pressure or critical volume (T_{c_1} and T_{c_2}, critical temperatures for gases 1 and 2, respectively; P_{c_1} and P_{c_2}, critical pressures for gases 1 and 2, respectively; V_{c_1} and V_{c_2}, critical volumes for gases 1 and 2, respectively)
i	denotes component i
j	denotes component j
m	denotes mixture
n	denotes a nominal outlet condition
P, T	denotes constant temperature and pressure
1	denotes inlet conditions (P_1, T_1) for gas A (CH_4)
2	denotes inlet conditions (P_2, T_2) for gas B (C_2H_4)
0	denotes outlet conditions (P_0, T_0) for gas mixture (CH_4–C_2H_4)

Greek Letters

α, γ	constants in BWR equation of state, dimensions listed in Table V
ΔE_k	change of kinetic energy for gaseous system across calorimeter, J/mol
ΔH	change of molar enthalpy, J/mol
ΔH_m	heat of mixing for a real solution, J/mol
ΔH_m^{id}	heat of mixing for an ideal solution ($\Delta H_m^{id} = 0$), J/mol
ϕ	Joule–Thomson isothermal coefficient, J/(mol MPa)
Ω_a, Ω_b	dimensionless constants, listed in Table IV
ω_1, ω_2	acentric factor, dimensionless, listed in Table IV (ω_1 and ω_2 refer to acentric factors for CH_4 and C_2H_4, respectively)

Registry No. CH_4, 74-82-8; C_2H_4, 74-85-1.

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