Excess Enthalpies of the Binary System Methane–Hydrogen Sulfide by Flow Calorimetry

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Enthalpies of mixing for the binary gaseous system methane–hydrogen sulfide were measured by an isothermal flow calorimeter at temperatures of 293.15, 305.15, and 313.15 K. For each isotherm, the measurements were made at pressures of 0.507, 1.013, and 1.520 MPa (5, 10, and 15 atm, respectively). The experimental results were compared with those predicted from the equation of state of Benedict–Webb–Rubin and Redlich–Kwong and the Redlich–Kwong equation with the modifications proposed by Jacoby and Robinson.

In a preceding article (*1*), the importance of excess enthalpy data in the gas phase has been discussed and a complete review of the data available in the literature has been made.

In the investigation reported in this article, the binary system methane–hydrogen sulfide has been studied. Excess enthalpies were determined at temperatures of 293.15, 305.15, and 313.15 K. For each of these three isotherms, measurements were made at the following pressures: 0.507, 1.013, and 1.520 MPa (5, 10, and 15 atm, respectively). All measurements were made in the gas phase.

Experimental Method

Detailed descriptions of the equipment and the experimental method utilized in these determinations are presented in two previous articles (*2*, *3*). For the case of the binary system methane–hydrogen sulfide, the mixtures are also endothermic like the ones previously reported. Consequently, the mixing of the two gases is accompanied by a temperature drop. To compensate for this drop, a measured quantity of energy is supplied to the system.

The investigation of this system has been particularly difficult owing to the characteristics of the hydrogen sulfide component. The difficulties resided in the toxic and corrosive properties of hydrogen sulfide, as well as its strong and disagreeable odor. In view of these facts, the system of aeration for the laboratory, as well as the setup for elimination of the spent gas in the atmosphere, had to be improved.

All equipment pieces built in bronze (valves) and copper (coils) had to be replaced by stainless-steel (No. 316) components. The operating pressures were limited by the low pressure of the available cylinders of hydrogen sulfide, which was of the order of 1.724 MPa (17.01 atm).

The gas analyses were supplied by Lynde Co. of Canada. The methane had a certified purity of 99%, containing 0.1% of CO_2, 0.2% of O_2, 0.2% of N_2, 0.3% of C_2H_6, and 0.2% of C_3H_8. The hydrogen sulfide had a certified purity of 99.5%, containing 0.2% of N_2, 0.03% of CO_2, 0.05% of SO_2, 0.03% of COS, 0.01% of CS_2, 0.06% of C_3H_8, 0.1% of C_3H_8, 0.01% of CH_4S, and 0.05% of hydrocarbons. The effect of the impurities in the gases upon the values of the excess enthalpies was evaluated by utilizing the technique recommended by Hejmadi (*4*).

Analysis of Results

The network of equations utilized in the analysis of the experimental results has been represented in ref *1*. For the case of the system methane–hydrogen sulfide, the pressure drops $\Delta P = P_1 - P_0$ and $\Delta P_2 = P_2 - P_0$ were negligible, as well as the temperature difference $(T_1 - T_2)$ and pressure difference $(P_1 - P_2)$ of gases A and B at the calorimeter inlet.

Mean values for the Joule–Thomson coefficients $\bar{\Phi}_A$ and $\bar{\Phi}_B$ and for the heat capacities $\bar{C}_{P,A}$ and $\bar{C}_{P,B}$ were utilized in the evaluation of eq 3 and 4 of ref *1* for the primary corrections. Equation 11 of ref *1* was utilized for the evaluation of the secondary corrections. For the case of the system methane–hydrogen sulfide the fluctuations $\Delta T_n = T_n - T_0$ and $\Delta P_n = P_n - P_0$ are very slight; thus, it is feasible to utilize mean values of the Joule–Thomson coefficients Φ^E and the heat capacities C_P^E for the mixture. These excess properties were calculated from eq 35 and 36 of ref *1*.

Summary

The equations from ref *1* are as follows:

$$H_0^E = \Delta H_m = \frac{Q}{F} + x_A(H_{A,1} - H_{A,0}) + x_B(H_{B,2} - H_{B,0}) - \Delta E_k \quad (2)$$

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

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

$$\Delta E_k = E_{k,A-B,0} - (x_A E_{k,A,1} + x_B E_{k,B,2}) \quad (5)$$

$$H_0^E = \frac{Q}{F} + x_A\bar{C}_{P,A}(T_1 - T_0) + x_B\bar{C}_{P,B}(T_2 - T_0) + x_A\bar{\Phi}_A(P_1 - P_0) + x_B\bar{\Phi}_B(P_2 - P_0) + x_A E_{k,A,1} + x_B E_{k,B,2} - E_{k,A-B,0} \quad (10)$$

$$H_n^E = H_0^E + \int_{T_0}^{T_n} C_P^E\, dT + \int_{P_0}^{P_n} \Phi^E\, dP \quad (11)$$

Experimental Results

The experimental results for the system methane–hydrogen sulfide are presented in Table I for the temperatures of 293.15, 305.15, and 313.15 K. For each isotherm the pressures selected were 0.507, 1.013, and 1.520 MPa (5, 10, and 15 atm, respectively).

Figures 1–3 present the same data in graphical form.

The heat capacities utilized in the calculation of eq 3 and 4, for the case of methane, were those reported by Tester (*5*). For the hydrogen sulfide, the heat capacities utilized were those tabulated by Lee and Kesler (*6*). The contribution of the primary corrections, calculated from eq 3, 4, and 7 of ref *1* as well as the corrections attributable to gas impurities upon H_0^E

$$\left(\frac{H_0^E - Q/F}{Q/F}\right)100$$

and the secondary corrections (eq 12, ref 1)

$$\left(\frac{H_0^E - H_n^E}{H_0^E}\right)100$$

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Table I. Excess Enthalpies H_n^E for $xCH_4 + (1 - x)H_2S$ Where x Denotes Mole Fraction

	H_n^E			
x	H^E_{exptl}	BWR	RK1	RK2
Nominal Conditions: T_n = 293.15 K; P_n = 0.507 MPa				
0.203	28.3	33.3	31.5	31.9
0.399	43.6	48.7	46.0	46.5
0.560	44.8	49.5	46.7	47.2
0.672	41.2	44.0	41.6	42.0
0.710	40.5	41.0	38.8	39.1
0.777	38.8	34.4	32.5	32.8
Nominal Conditions: T_n = 293.15 K; P_n = 1.013 MPa				
0.265	79.8	89.3	83.2	85.6
0.431	101.1	109.5	102.0	104.7
0.659	97.1	97.3	90.9	92.9
Nominal Conditions: T_n = 293.15 K; P_n = 1.520 MPa				
0.184	123.6	121.1	116.5	110.5
0.245	149.5	146.2	133.5	140.5
0.483	190.8	185.1	169.5	176.8
0.594	184.6	174.4	160.0	166.3
0.793	138.8	114.4	105.4	108.9
Nominal Conditions: T_n = 305.15 K; P_n = 0.507 MPa				
0.206	23.8	30.1	29.6	29.6
0.456	39.7	44.9	44.2	44.1
0.621	40.7	42.2	41.6	41.5
0.738	37.0	34.5	34.0	33.9
Nominal Conditions: T_n = 305.15 K; P_n = 1.013 MPa				
0.184	60.4	61.3	59.8	60.5
0.392	90.8	94.4	92.1	92.9
0.449	95.0	97.3	94.9	95.6
0.782	69.8	64.7	63.2	63.4
Nominal Conditions: T_n = 305.15 K; P_n = 1.520 MPa				
0.274	148.8	134.1	129.0	132.3
0.443	163.8	160.0	154.1	157.3
0.568	167.5	155.3	149.5	152.3
0.847	83.3	78.5	76.9	76.9
Nominal Conditions: T_n = 313.15 K; P_n = 0.507 MPa				
0.324	34.6	37.3	37.7	37.2
0.386	42.5	40.2	40.6	40.1
0.446	43.9	41.7	42.2	41.7
0.693	33.2	35.5	35.9	35.4
Nominal Conditions: T_n = 313.15 K; P_n = 1.013 MPa				
0.237	68.0	67.6	67.8	67.8
0.351	78.8	83.9	84.1	84.0
0.483	90.4	90.5	90.8	90.5
0.692	83.6	75.7	75.9	75.5
0.780	64.7	60.3	60.7	60.3
Nominal Conditions: T_n = 313.15 K; P_n = 1.520 MPa				
0.272	119.2	121.8	121.0	122.3
0.324	139.0	143.2	142.1	143.3
0.602	135.5	138.5	137.5	138.2
0.778	97.3	97.3	96.8	96.3

are of the order of 3%, 2.6%, and 2% at 293.15, 305.11, and 313.15 K, respectively.

The corrections due to the variations of kinetic energy and pressure drops are practically negligible, the order of magnitude being estimated at 10^{-5} J mol^{-1}.

Precision of the Experimental Results

The technique utilized in the evaluation of errors was that described in ref *1*. By summation of the experimental errors, and those owing to the primary and secondary corrections, the precision of the excess enthalpies H_n^E is estimated between 2% and 3%.

Comparison of Experimental Data with Predictions from Equations of State

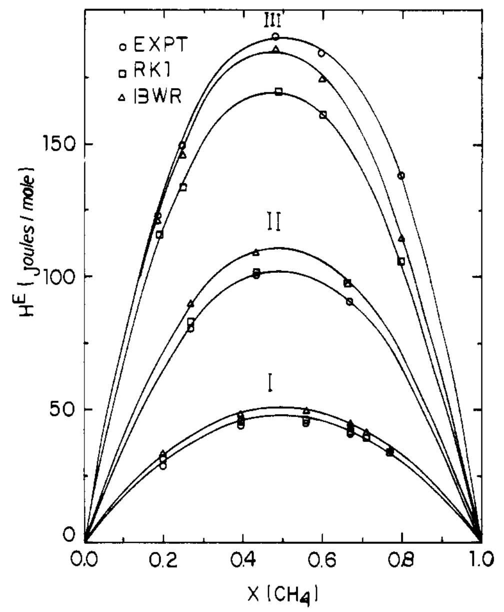

Figure 1. Enthalpy of mixing, $H^E/(J\ mol^{-1})$, of methane-hydrogen sulfide system at 293.15 K. (I, 0.507 MPa; II, 1.013 MPa; III, 1.520 MPa.)

Table II. Constants Utilized in RK1 and RK2 Equations of State

	CH_4	H_2S	ref
Ω_a, dimensionless	0.4546	0.4546	*10*
Ω_b, dimensionless	0.0872	0.0872	*10*
T_c, K	190.6	373.2	*11*
P_c, MPa	4.6	8.94	*11*
V_c, $cm^3\ mol^{-1}$	99.0	98.5	*11*
ω, dimensionless	0.013	0.100	*11*
α, $K^{2.5}\ MPa^{-1}$	44648	136225	*8*
β, $K^{1.5}\ MPa^{-1}$	−24.969	−158.895	*8*
γ, K MPa^{-1}	3.375	3.77	*8*
$10^4\delta$, MPa^{-1}	0.00	−50.33	*8*
k_{12}(RK1)	0.27 (by optimization)		
k_{12}(RK2)	0.30 (by optimization)		

Table III. Constants Utilized in BWR Equation of State (*12*)

	CH_4	H_2S
A_0, MPa $dm^6\ mol^{-2}$	0.1896036	0.3815186
10^3B_0, dm mol^{-1}	4.320305	5.276859
C_0, MPa $dm^6\ mol^{-2}\ K^2$	23811.516	20547.508
10^4b, $dm^6\ mol^{-2}$	3.9787382	6.435567
a, MPa $dm^9\ mol^{-3}$	0.007011487	0.026005757
$10^{-4}c$, MPa $dm^9\ mol^{-3}\ K^2$	0.3057917	0.29471473
$10^6\alpha$, $dm^9\ mol^{-3}$	9.6835765	5.342140
$10^4\gamma$, $dm^3\ mol^{-2}$	5.71181250	4.634509
k_{12}	0.13 (by optimization)	

Since experimental data for this system were not available in the literature, the only possible comparison that could be made was with predictions based upon equations of state. The same equations of state utilized for the study of the system methane–carbon dioxide (*1*) were employed for the case of the system methane–hydrogen sulfide. These were the equations of state of Redlich–Kwong (*7*), henceforth referred to as RK1, that of Redlich–Kwong with Jacoby–Robinson (*8*) modifications, henceforth referred to as RK2, and the Benedict–Webb–Rubin (*9*) equation, henceforth referred to as BWR. A detailed description of the calculation of the excess enthalpies H_n^E from these equations of state is presented in ref *1*.

Tables II and III present the values of the constants for hydrogen sulfide and methane for these equations. The iteration constant k_{12} was obtained by successive iterations leading to the best possible fit for the excess enthalpy data. The values for k_{12} were 0.13, 0.27, and 0.30 for the BWR, RK1, and RK2 equations, respectively.

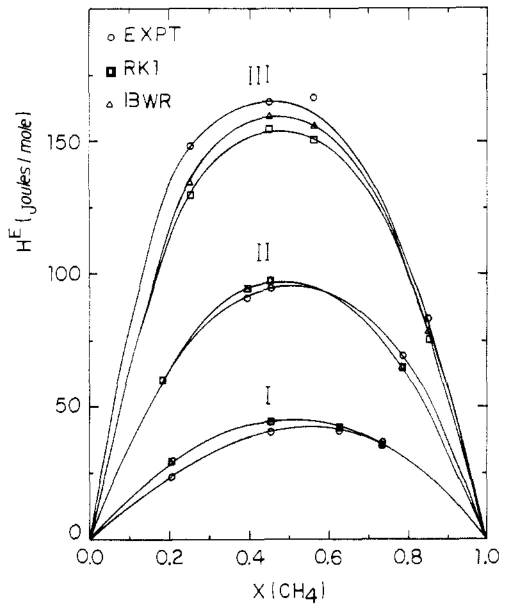

Figure 2. Enthalpy of mixing, H^E/(J mol^{-1}), of methane-hydrogen sulfide system at 305.15 K. (I, 0.507 MPa; II, 1.013 MPa; III, 1.520 MPa.)

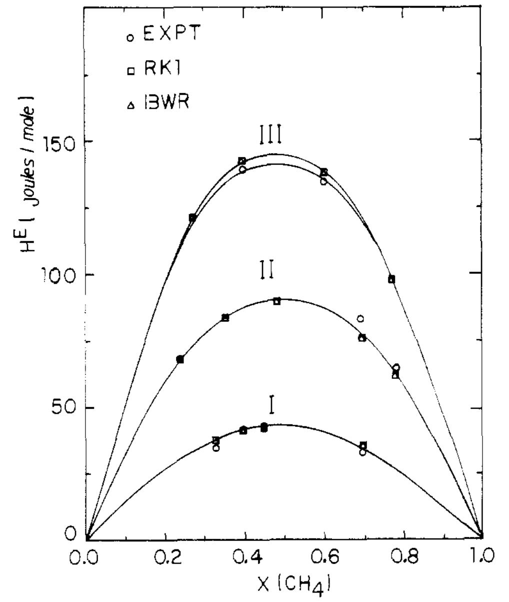

Figure 3. Enthalpy of mixing, H^E/(J mol^{-1}), of methane-hydrogen sulfide system at 313.15 K. (I, 0.507 MPa; II, 1.013 MPa; III, 1.520 MPa.)

Table I presents the excess enthalpy values obtained from these equations. These data are presented in graphical form in Figures 1-3 at the three temperatures of 293.15, 305.15, and 313.15 K.

Table IV presents a summary of the percentage deviation of the calculated and experimental values, according to the expression

$$100\left[\frac{H_{n\ \mathrm{exptl}}^{E} - H_{n\ \mathrm{theo}}^{E}}{H_{n\ \mathrm{exptl}}^{E}}\right]$$

Conclusion

A comparison of excess enthalpy data for the two binary systems, CH_4-CO_2, which we have studied recently (*1*), and CH_4-H_2S, from the present study, shows that the CH_4-H_2S mixture is more endothermal than the CH_4-CO_2 system.

Table IV. Comparison of Experimental Results with Predictions from Equations of State for Methane-Hydrogen Sulfide

T, K	293.15	305.15	313.15
BWR Equation			
$10^2[\{H_n^E - H_n^E(\mathrm{BWR})\}/H_n^E]$	7.6	8.1	4.1
RK1 Equation			
$10^2[\{H_n^E - H_n^E(\mathrm{RK1})\}/H_n^E]$	7.8	8.0	4.0
RK2 Equation			
$10^2[\{H_n^E - H_n^E(\mathrm{RK2})\}/H_n^E]$	8.3	7.3	5.0

Indeed for identical experimental conditions (same temperature and same pressure), differences in excess enthalpies range from 90% to 196%, 132% to 179%, and 137% to 166% at temperatures 293.15, 305.15, and 313.15 K, respectively.

Simultaneously, the excess enthalpies calculated from equations of state of BWR, RK1, and RK2 are in better agreement with the experimental determinations for the binary system CH_4-H_2S over the whole range under study, and a maximum of 8.3% was observed with the CH_4-H_2S mixture, compared to a 10% value for the CH_4-CO_2 mixture on the same range of temperature and pressure. However, the interaction parameters k_{ij} which best fit our experimental results, in the mixing rules utilized with the three equations of state aforementioned, are all higher than the corresponding values found previously (*1*) for the CH_4-CO_2 mixture.

The BWR equation gives slightly better predictions of our experimental results than the two Redlich-Kwong equations utilized, although for the CH_4-H_2S binary mixture the three equations yielded estimations within a 1% deviation range.

Glossary

C_P	molar heat capacity at constant pressure, J mol^{-1} K^{-1}
E_k	kinetic energy, J mol^{-1}
F	flow rate, mol s^{-1}
H	molar enthalpy, J mol^{-1}
k_{12}	characteristic binary constant, dimensionless
P	pressure, MPa
Q	heat supplied to gas system by the power supply, J s^{-1}
T	temperature, K

Superscripts

E	Denotes an excess thermodynamic property, namely, excess enthalpy, H^E
—	denotes mean values (for Joule-Thomson coefficient and for heat capacities at constant pressure)

Greek Letters

α, γ	constants in BWR equation of state, dimensions listed in Table III
α, β, γ, δ	constants in RK2 equation of state (refer to eq 30-32 of ref *1*), dimensions listed in Table II
ΔH	enthalpy change, J mol^{-1}
ΔH_m	heat of mixing for a real solution, J mol^{-1}
Ω_a, Ω_b	constants in eq 19-21 of ref *1*, dimensionless
ω	acentric factor, eq 26 of ref *1*, dimensionless (ω_1 and ω_2 refer to acentric factors for CH_4 and H_2S, respectively)
x	mole fraction, dimensionless

Subscripts

A	denotes pure gas A (CH_4)
B	denotes pure gas B (H_2S)
A-B	denotes gas mixture (CH_4-H_2S)
c	denotes critical temperature or critical pressure: namely, P_{c1} and P_{c2}, critical pressures for gases

	1 and 2; T_{c1} and T_{c2}, critical temperatures for gases 1 and 2, respectively
i	denotes component i
m	denotes mixture
n	denotes a nominal outlet condition, in conjonction with $H_n{}^E$, P_n, or T_n
P, T	denotes constant temperature and pressure
1	denotes inlet conditions (P_1, T_1) for gas 1
2	denotes inlet conditions (P_2, T_2) for gas 2
0	denotes outlet conditions (P_0, T_0) for mixture

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Excess Isobaric Heat Capacities of Water–*n*-Alcohol Mixtures[†]

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Excess isobaric heat capacities of binary mixtures of water with methanol, ethanol, and 1-propanol, obtained from flow microcalorimetric measurements at 288.15 and 308.15 K, are reported.

In several recent papers (*1–3*) we described investigations of the thermodynamic properties of aqueous alcohol mixtures. One of these (*2*) dealt with measurements of the heat capacities of binary mixtures of water with methanol, ethanol, and 1-propanol over the entire mole fraction range at 298.15 K. The present paper reports similar measurements for the same systems at 288.15 and 308.15 K.

Experimental Section

The samples of the alcohols were the same as used in our previous work (*2*). Densities were determined with an Anton Paar densimeter and corrected for water content (usually less than 0.1% by mass) on the basis of analysis by the Karl Fischer method. The results at 288.15 and 308.15 K are listed in Table I along with values from the literature (*4*) for comparison.

Mixtures with deionized distilled water were prepared by mass. The water content of the alcohol was taken into account in calculating the mole fraction. The error of the mole fraction is estimated to be less than 5×10^{-5}.

Differences of volumetric heat capacity were measured between pairs of liquids flowing in the test and reference cells of a Picker microcalorimeter. This apparatus and its operation have been described previously (*5*, *6*). A temperature interval of about 1.6 K centered on the nominal operating temperatures of 288.15 and 308.15 K was adopted. Mixtures were studied in order of their compositions, following a stepwise procedure. Starting with water as the initial reference liquid, each mixture after measurement was used as the reference for the subsequent mixture. Corrections were applied for power losses, and measurements were repeated with the test and reference liquids interchanged to cancel mixing effects (*6*). The latter are relatively large for the present systems since the excess volumes of equimolar mixtures are approximately -1 cm^3 mol^{-1}. The values adopted for the properties of water are summarized in Table I; these were calculated from equations recommended by Kell for the density (*7*) and heat capacity (*8*).

Table I. Physical Properties of Component Liquids

		density/(kg m^{-3})		$C_p{}^*{}_m$/(J K^{-1} mol^{-1})	
component	T/K	measd	lit.	measd	lit.
methanol	288.15	795.84	795.99 (*4*)	78.90	78.72 (*9*)
	308.15	777.02	777.29 (*4*)	83.74	82.59 (*9*)
ethanol	288.15	793.52	793.62 (*4*)	108.07	108.63 (*9*)
	308.15	776.41	776.45 (*4*)	117.75	116.61 (*9*)
1-propanol	288.15	807.55	807.71 (*4*)	138.40	138.49 (*9*) 138.28 (*10*)
	308.15	791.56	791.62 (*4*)	151.93	149.78 (*9*) 148.97 (*10*)
water	288.15		999.10 (*7*)		75.403 (*8*)
	308.15		994.04 (*7*)		75.266 (*8*)

Molar isobaric heat capacities, $C_{p,m}$, were obtained from the experimental results for the volumetric heat capacities, $C_{p,m}/V_m$, using molar volumes, V_m, calculated from the molar excess volumes of the mixtures (*1*) and the densities of the pure components given in Table I. Molar excess isobaric heat capacities were calculated from the relation

$$C_p{}^E{}_m = C_{p,m} - xC_p{}^*{}_1 - (1 - x)C_p{}^*{}_2 \tag{1}$$

where x is the mole fraction of water in the mixture, and $C_p{}^*{}_1$ and $C_p{}^*{}_2$ are the molar isobaric heat capacities of pure water and *n*-alcohol, respectively. The error of $C_p{}^E{}_m$ is estimated to be less than 0.05 J K^{-1} mol^{-1}.

Results and Discussion

The molar isobaric heat capacities measured for the pure alcohols are listed in Table I, where the values recommended in the survey of literature data by Sriskandarajah (*9*) and the recent results for 1-propanol by Kalinowska et al. (*10*) are also shown. The agreement at 288.15 K is good (within ~0.5%)

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