ENTHALPIES OF THE HYDROGEN-LIGHT HYDROCARBON BINARY MIXTURES AT ELEVATED PRESSURES AND LOW TEMPERATURES

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The enthalpies of hydrogen-methane, hydrogen-ethane, and hydrogen-propane mixtures were measured by flow calorimetry at several temperatures from 120 K to 210 K and 6.8 atm and 13.6 atm. The experimental data ranged in the vapor and vapor-liquid coexisting regions.

By adopting the previously proposed estimation method of hypothetical liquid properties of hydrogen, the regular solution theory could be successfully applied to predict the enthalpies of hydrogen-light hydrocarbon mixtures in vapor-liquid coexisting region.

Introduction

Accurate enthalpy data of hydrogen-light hydrocarbon mixtures at elevated pressures and low temperatures are particularly important in the design of low temperature gas separation or liquefaction processes. However, as reviewed by Yesavage *et al.*¹⁹⁾ and one of the authors¹⁶⁾, enthalpy data for fluid mixtures under such conditions are scarce except for light hydrocarbon mixtures, such as methane and propane^{20,21)}. The purpose of the present study is to obtain enthalpy data for hydrogen and light hydrocarbon mixtures in the gas and vapor-liquid coexisting regions and to propose a reliable prediction method. The calorimeter used in this work was of a flow type and liquid nitrogen was chosen as reference fluid. As has been shown previously¹⁶⁾, enthalpies of gaseous mixtures can be well predicted by the BWR equation¹⁾ while enthalpies of liquid mixtures can scarcely be predicted. Therefore, the regular solution theory¹⁰⁾ in connection with the previously proposed hypothetical liquid properties of hydrogen¹³⁾ was applied to predict the enthalpies of the hydrogen-hydrocarbon mixtures in vapor-liquid coexisting and liquid regions.

1. Experimental Apparatus and Procedure

The enthalpies of hydrogen-methane, hydrogen-ethane, and hydrogen-propane binary systems were measured by flow calorimetry at temperatures ranging from 120 K to 210 K and pressures at 6.8 atm and 13.6 atm. The purity of each component is the same as

that described in a previous paper¹²⁾.

The calorimeter is shown in Fig. 1 and a flow scheme is seen in Fig. 2. This type of a calorimeter has been used by several workers^{2,6,8,9,15,17,18)}. The present apparatus was designed according to Sahgal *et al.*¹⁵⁾ As shown in Fig. 1, the fluid mixture enters at the inlet and passes the heat exchanger ④. The heat transferred from the fluid to the liquid nitrogen evaporates some of the latter. The amount of vaporized liquid nitrogen was measured by a wet gas flow meter ㉑ as shown in Fig. 2. A level sensor ⑩ was used to detect decrease of the liquid nitrogen and to maintain its level at a constant value. Heat leak from the surroundings to the calorimeter was eliminated by the vaporization of liquid nitrogen in an outer vessel ①. The heat exchanger was surrounded by double-walled radiation shield plates ⑦ and was placed in a container which was evacuated to about 10^{-8} atm. Pressurized hydrogen and light hydrocarbon mixtures were prepared in a surge tank ⑫. The pressure and flow rate of the fluid mixture were regulated by valves ⑮ and ⑯. The flow rate of the mixture was determined by a wet gas flow meter ㉑. The temperatures of the fluid at the inlet and the outlet were measured by copper-constantan thermocouples. It took 4 to 5 hours to reach a state in which the temperature and the vaporization rate of the liquid nitrogen remained constant. The inlet and outlet temperatures of the fluid and the flow rate of the vaporized liquid nitrogen were measured at that point. The flow rate and pressure of the fluid were also measured. The experimental accuracies were $\pm 0.2^{\circ}\text{C}$ for temperature, $\pm 0.2\%$ for flow rate, and ± 0.1 atm for pressure.

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Fig. 1 Details of the calorimeter

Fig. 2 Flow scheme of the experimental apparatus

The enthalpy difference at constant pressure can be calculated from the following energy balance equation:

$$\Delta h = [h(T_A, P) - h(T_B, P)]_z = (F_{N_2} - F_Q) \lambda_{N_2} / F \quad (1)$$

where F_{N_2} is the flow rate of vaporized nitrogen due to the heat transferred from the fluid, F_Q the heat inleak from the surroundings, F the flow rate of the fluid, and λ_{N_2} the heat of vaporization of nitrogen under atmospheric pressure whose values are taken from Sahgal *et al.*¹⁵⁾ F_Q was found by comparing measured enthalpies of nitrogen gas with those calculated from the equation of state of Jacobsen *et al.*⁴⁾ This was found to be a function of the flow rate of the vaporized

Fig. 3 Enthalpies of methane

Fig. 4 Enthalpies of the hydrogen-methane system at 6.8 atm

nitrogen:

$$\left. \begin{aligned} F_Q \lambda_{N_2} / F_{N_2} \lambda_{N_2} &= -0.04416 + 10.75 / F_{N_2} \lambda_{N_2} \\ &\quad (F_{N_2} \lambda_{N_2} \leq 243 \text{ cal/min}) \\ F_Q \lambda_{N_2} / F_{N_2} \lambda_{N_2} &= 0 \quad (F_{N_2} \lambda_{N_2} > 243 \text{ cal/min}) \end{aligned} \right\} \quad (2)$$

2. Experimental Result

To ascertain the reliability and accuracy of the experimental procedure, enthalpies of methane were measured and compared with the literature value. A good agreement between the present data and those of Jones *et al.*⁵⁾ is shown in Fig. 3. In this figure, the enthalpy of gas at 25°C was selected as zero ($h_{25^\circ\text{C}}^V = 0$), that is, $\Delta h = (h_{25^\circ\text{C}}^V - h_T)_{P,z} = 0$ at 25°C. The enthalpy

Fig. 5 Enthalpies of the hydrogen-methane system at 13.6 atm

Fig. 7 Enthalpies of the hydrogen-ethane system at 13.6 atm

Fig. 6 Enthalpies of the hydrogen-ethane system at 6.8 atm

Fig. 8 Enthalpies of the hydrogen-propane system at 6.8 atm and 13.6 atm

at the inlet temperature T_A was corrected to that at 25°C by use of the BWR equation. Experimental enthalpies, $\Delta h = (h_{T_A}^V - h_{T_B}^L)_{P,z}$, for hydrogen-methane, hydrogen-ethane, and hydrogen-propane mixtures at 6.8 atm and 13.6 atm are shown in **Tables 1 to 3** and are graphically represented in **Figs. 4 to 8** by choosing $h_{25^\circ\text{C}}^V = 0$.

3. Prediction of Enthalpies of Hydrogen and Hydrocarbon Mixtures

Enthalpies of fluid mixtures in the vapor-liquid co-existing region, $h(T, P)$, are represented by

$$[h(T, P) - h(T, 0)]_z = [h^{SV}(T, P) - h(T, 0)]_y F^V + [h^{SL}(T, P) - h(T, 0)]_x F^L \quad (3)$$

Table 1 Enthalpies of the hydrogen-methane system

P=6.8 atm			P=13.6 atm		
T _A [K]	T _B [K]	Δh [cal/mole]	T _A [K]	T _B [K]	Δh [cal/mole]
0.213 mole fraction H ₂					
292.1	170.2	998.8	289.5	163.2	1058.5
292.8	159.2	1093.8	289.0	153.1	1151.6
289.7	153.8	1112.2	284.5	147.3	1298.5*
283.9	145.4	1132.1	281.5	141.3	1956.9*
281.2	133.7	1332.1*	280.9	139.0	2119.5*
0.455 mole fraction H ₂					
291.8	167.5	941.4	290.5	165.8	964.4
289.7	158.0	1008.7	283.5	151.6	1027.3
285.1	152.7	1014.3	279.3	139.9	1087.4
278.6	138.3	1080.3	276.9	133.8	1421.5*
278.8	130.8	1148.9			
0.671 mole fraction H ₂					
286.5	163.9	881.0	286.3	164.0	888.9
282.1	154.2	924.5	282.8	154.7	915.5
282.9	148.4	961.2	282.7	149.3	969.6
279.1	134.5	1045.4	279.5	135.4	1060.2
277.6	129.2	1088.1	277.6	125.7	1223.7*

* two-phase region

Table 2 Enthalpies of the hydrogen-ethane system

P=6.8 atm			P=13.6 atm		
T _A [K]	T _B [K]	Δh [cal/mole]	T _A [K]	T _B [K]	Δh [cal/mole]
0.472 mole fraction H ₂					
291.1	198.1	1972.4	291.5	198.3	2209.6
288.3	181.0	2535.0	288.1	184.3	2512.1
283.6	174.1	2681.8	283.8	174.6	2692.0
282.4	167.3	2826.0	281.6	170.0	2804.6
280.5	163.8	2903.6	280.7	165.5	2891.2
0.757 mole fraction H ₂					
286.7	183.2	1186.2	287.4	186.0	1331.8
281.2	173.9	1403.7	281.8	176.6	1486.4
278.9	167.4	1568.7	278.6	167.8	1617.9
280.7	160.9	1731.8	282.4	161.6	1746.8
278.7	155.0	1811.7	278.8	159.3	1760.6
277.4	153.7	1824.9	276.9	156.1	1851.2
0.910 mole fraction H ₂					
286.0	170.0	903.8	287.1	172.3	985.8
282.7	161.3	1048.5	283.4	163.6	1087.0
280.3	156.2	1137.7	280.0	156.9	1164.2
279.6	154.0	1125.4	280.6	154.7	1176.4
278.6	145.4	1249.9	279.4	149.7	1250.4
277.8	143.7	1297.2	277.3	146.4	1301.6

Table 3 Enthalpies of the hydrogen-propane system

P=6.8 atm			P=13.6 atm		
T _A [K]	T _B [K]	Δh [cal/mole]	T _A [K]	T _B [K]	Δh [cal/mole]
0.742 mole fraction H ₂					
290.5	207.3	1779.0	289.9	205.1	1811.7
286.7	190.9	2040.2	285.8	192.8	1973.6
287.8	175.6	2135.1	287.5	175.8	2067.9
282.9	170.0	2222.6	278.5	174.9	2240.2
279.4	166.7	2286.2	282.9	169.8	2160.0

where F^L and F^V denote moles of liquid and moles of vapor per mole of fluid mixture, respectively. h^{SV} and h^{SL} are molar enthalpies of the saturated vapor and liquid at a given composition. As shown in the previous review¹⁶⁾ h^{SV} can be calculated by the BWR equation. On the other hand, h^{SL} can scarcely be

predicted by the BWR equation. Therefore, h^{SL} was evaluated by using the following procedure.

The liquid phase enthalpy of binary mixture is expressed as

$$[h^L(T,P) - h(T,0)]_x = \sum_{i=1}^2 x_i [\bar{h}_i^L(T,P) - h_i(T,0)] \quad (4)$$

The partial molar enthalpy, $\bar{h}_i^L$, is related to the liquid phase fugacity by the following equation¹⁰⁾:

$$\bar{h}_i^L(T,P) - h_i(T,0) = -RT^2 \left(\frac{\partial \ln f_i^L}{\partial T} \right)_{P,x} \quad (5)$$

The liquid phase fugacities of the supercritical (1) and subcritical (2) components are approximately given as^{10,11)}

$$f_1^L = x_1 \gamma_1^{*(P,0)} H_1^{(P,0)} \exp \left[\frac{v_1^{0L} P}{RT} \right] \quad (6)$$

and

$$f_2^L = x_2 \gamma_2^{*(P,0)} f_2^{0L(P,0)} \exp \left[\frac{v_2^{0L} P}{RT} \right] \quad (7)$$

where $H_1^{(P,0)}$ is Henry's constant and $\gamma_1^{*(P,0)}$ the activity coefficient defined by the unsymmetric convention for the supercritical component. In the present study, hydrogen is the supercritical component and hydrocarbon is the subcritical component. From Eqs. (3) to (7), enthalpies of a hydrogen and hydrocarbon binary mixture are obtained as

$$\begin{aligned} [h^L(T,P) - h(T,0)]_x &= -[x_1 RT^2 (\partial \ln H_1^{(P,0)} / \partial T) + x_2 RT^2 (\partial \ln f_2^{0L(P,0)} / \partial T)] \\ &\quad - [x_1 RT^2 (\partial \ln \gamma_1^{*(P,0)} / \partial T)_x + x_2 RT^2 (\partial \ln \gamma_2^{(P,0)} / \partial T)_x] \\ &\quad + \left[x_1 P \left(v_1^{0L} - T \frac{\partial v_1^{0L}}{\partial T} \right)_P + x_2 P \left(v_2^{0L} - T \frac{\partial v_2^{0L}}{\partial T} \right)_P \right] \end{aligned} \quad (8)$$

The second term on the right hand side of Eq. (8) is the excess enthalpy, h^E . As shown in the previous papers^{13,14)}, the nonideality of the hydrogen-hydrocarbon system can successfully be represented by the regular solution theory. Thus, the excess enthalpy, h^E , was evaluated from the following equation:

$$h^E = (x_1 v_1^{0L} + x_2 v_2^{0L}) \phi_1 \phi_2 \left(1 - \frac{\phi_1}{\phi_2} \right) (\delta_1 - \delta_2)^2 \quad (9)$$

The liquid phase fugacity of the pure hydrocarbon, $f_2^{0L(P,0)}$, in the first term on the right hand side of Eq. (8), is usually calculated by

$$f_2^{0L(P,0)} = \phi_2^S P_2^S \exp \left[-v_2^{0L} P_2^S / RT \right] \quad (10)$$

where ϕ_2^S is the fugacity coefficient of the saturated vapor. This can be obtained from the correlation of Lyckman *et al.*⁷⁾. The vapor pressure, P_2^S , can be calculated from the equation of Prausnitz *et al.*¹¹⁾ and the liquid molar volume, v_2^{0L} , can be obtained from the Francis' equation³⁾. Henry's constant for hydrogen in Eq. (8) can be predicted by the regular solution theory:

$$\ln H_1^{(P0)} = v_1^L (\delta_1 - \delta_2)^2 / RT + \ln f_1^{(P0)} \quad (11)$$

The solubility parameter, the molar volume, and the fugacity of the hypothetical liquid hydrogen were obtained by the previous method¹³⁾. Finally, F^L and F^V were determined from the vapor-liquid equilibrium relation in which vapor and liquid fugacities were obtained from the BWR equation and Eqs. (6) and (7). Consequently, the enthalpies of hydrogen-hydrocarbon mixtures in the vapor-liquid coexisting region can be calculated from Eq. (3).

The calculated results are shown by solid lines in Figs. 4 to 8. For comparison, the calculated results by the BWR equation are shown in the same figures with dotted lines. As seen in these figures, the calculated results by the present procedure show good agreement with experiments, while those calculated by the BWR equation deviate from the experimental data in the vapor-liquid coexisting region. For comparison, the present calculation method was applied to the methane-propane system investigated by Yesavage *et al.*²¹⁾ which covers vapor, two-phase, and liquid regions. The results are presented in Fig. 9. As seen again, the present calculation gives good agreement over a wide range of temperature. However, the results obtained from the BWR equation, represented by the dotted line, show a discrepancy in the two-phase and liquid phase regions.

Conclusion

By using a flow type calorimeter, enthalpies of the hydrogen-methane, hydrogen-ethane, and hydrogen-propane mixtures were measured at several temperatures from 120 K to 210 K and at 6.8 atm and 13.6 atm. The measured enthalpy data could readily be predicted by the regular solution theory coupled with the properties of the hypothetical liquid hydrogen.

Nomenclature

F	= flow rate of fluid	[mole/min]
F^L	= moles of liquid per unit mole of fluid mixture	[mole]
F_{N_2}	= flow rate of vaporized liquid nitrogen	[mole/min]
F_Q	= flow rate of vaporized liquid nitrogen due to heat inleak from surroundings	[mole/min]
F^V	= moles of vapor per unit mole of fluid mixture	[mole]
f	= fugacity	[atm]
H	= Henry's constant	[atm]
h	= molar enthalpy	[cal/mole]
$\bar{h}$	= partial molar enthalpy	[cal/mole]
Δh	= enthalpy difference	[cal/mole]
h^L	= liquid phase molar enthalpy	[cal/mole]
h^V	= vapor phase molar enthalpy	[cal/mole]
P	= pressure	[atm]
R	= gas constant, 0.08205 [l·atm/mole·K], 1.987 [cal/mole·K]	
T	= absolute temperature	[K]

Fig. 9 Enthalpies of the methane-propane system at 17.0 atm

v	= molar volume	[l/mole]
x	= mole fraction of liquid phase	[—]
y	= mole fraction of vapor phase	[—]
z	= mole fraction of fluid mixture	[—]
γ	= activity coefficient	[—]
δ	= solubility parameter	[atm ^{1/2}]
λ_{N_2}	= heat of vaporization of nitrogen under atmospheric pressure	[cal/mole]
ϕ	= volume fraction	[—]
φ	= fugacity coefficient	[—]

<Subscripts and Superscripts>

1, 2	= component 1, 2
A	= inlet condition
B	= outlet condition
E	= excess property
i	= component i
L	= liquid phase
$0L$	= pure liquid state
$P0$	= zero pressure
S	= saturation
SL	= saturated liquid
SV	= saturated vapor
V	= vapor phase
*	= unsymmetric convention

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