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Isobaric Integral Heats of Vaporization for Methane-Ethylene System

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An isobaric calorimeter has been built for measuring the integral heat of vaporization at high pressures and low temperatures simultaneously with vapor-liquid equilibria data. The methane-ethylene system was studied at 20 and 40 atm., with data obtained on three mixtures and the two pure components. The experimental results are compared with three different calculation methods.

The industrial and theoretical importance of the heats of vaporization of mixtures is well established. The most useful form of these data is the isobaric integral heat of vaporization. Dana (*2*) built the first calorimeter for determining these enthalpy differences experimentally at atmospheric pressure and cryogenic temperatures.

Schroeder (*16*, *20*) modified the Dana calorimeter to operate above room temperature for his investigation of methanol-benzene mixtures. Tallmadge (*18* to *20*) improved Schroeder's apparatus by adding a heater to compensate for heat lost to the surroundings. By calibrating this heater, he was able to obtain reproducible results on acetone-chloroform, acetone-benzene, and benzene-methanol mixtures. Schnelle (*14*, *15*) rebuilt the Tallmadge apparatus by utilizing ground-glass joints throughout. He also added a hypodermic probe to sample the acetone-chloroform mixtures without opening the calorimeter. Recently, Kumar (*7*) modified the Schnelle apparatus by adding a bubble cap above the heater for improved vapor-liquid contact of benzene-chloroform mixtures. More thermowells and sampling probes were also added.

Concurrent with the work of Schroeder and Tallmadge, Plewes et al. (*10* to *12*) were working on their own version of the Dana calorimeter to operate under vacuum. The calorimeter heater was encapsulated to study corrosive mixtures. Data were obtained on water binaries of methanol, ethanol, *n*-propanol, acetone, and formic acid.

Stein and Martin (*17*) made a glass, adiabatic flow, Dana calorimeter with a unique modification to eliminate the heat-leak problem. Instead of immersing the vacuum-jacketed bulb in the bubble point mixture as was done by the other investigators, they placed it in a large volume of the dew point mixture, which underwent vaporization simultaneously with the liquid in the bulb. With both

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liquids inside and outside the bulb at the dew point temperature, there was no temperature difference across the vacuum-jacketed bulb and consequently no heat leak. They studied the water binaries of *i*-propanol and acetone.

In summary, all previous investigators have used glass Dana calorimeters at atmospheric pressure or below. All studies except that of Dana were above ambient temperature. The present investigation was made in a stainless steel calorimeter at 20 and 40 atm. abs. and low temperatures (116°K. or −161°F.).

EXPERIMENTAL APPARATUS

A schematic diagram of the experimental apparatus is shown in Figure 1 and a detailed drawing of the calorimeter is shown in Figure 2. The calorimeter consists of three independently controlled constant-temperature zones integrated into a single unit. Each temperature zone is equipped with a heater, stirrer, thermocouple, sensor, and controller, and is surrounded by a vacuum jacket. Thermostatic fluid (methanol or iso-octane) is added or withdrawn from each zone through external connections provided for this purpose.

The reservoir, which contains about 700 cc. of the mixture under investigation, is at the base of the calorimeter in the reservoir constant-temperature zone. It is made of stainless steel, is designed for 2,000 lb./sq.in. service, and is equipped with a reflux condenser to prevent the accumulation of vapors there.

The liquid mixture is vaporized by an encapsulated heater in the bottom of the vertical reboiler tube. The top of the reboiler tube opens into the bottom of the equilibrium cell, which is in the equilibrium cell constant-temperature zone. This zone is maintained at a temperature just slightly above the dew point of the mixture, which prevents condensation of the vapor produced by the heater in the reboiler tube.

The equilibrium cell consists of a 2-in. bubble cap mounted on a tray, which is equidistant from the ends of the cylindrical cell. Dew point vapors rising from the heater are brought into contact with the dew point liquid on the tray before passing to the condenser. The cell is equipped with thermocouples and hypodermic sampling probes to determine temperatures and compositions at the heater, just below the tray and on the tray. Essential thermocouples were calibrated along the vapor pressure curve of ethylene.

Samples were collected in an external condenser made from a high-pressure aluminum bomb. The bomb was placed in a thermostatically controlled Dewar that maintained the temperature slightly below that of the condenser constant temperature zone. The thermostatic Dewar was placed in another Dewar that contained a suitable heat sink.

System pressures were measured on a Budenburg dead weight gauge, certified to 0.05% accuracy, as transmitted and nulled by a Ruska differential pressure indicator cell. Thermocouple emf's and voltage drops across the Leeds and Northrup standard resistors were measured by a Tinsley Disselhorst potentiometer equipped with a reversing switch. Power for the calorimeter heater was supplied by a Dressen-Barnes 17 to 22-v., 1.5 amp. d.c. power supply with 0.01% regulation and 1 mv. ripple.

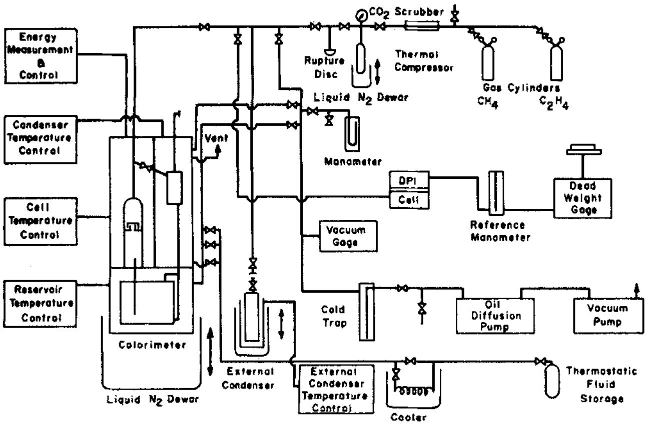

Fig. 1. Schematic flow diagram of apparatus for isobaric integral heat of vaporization.

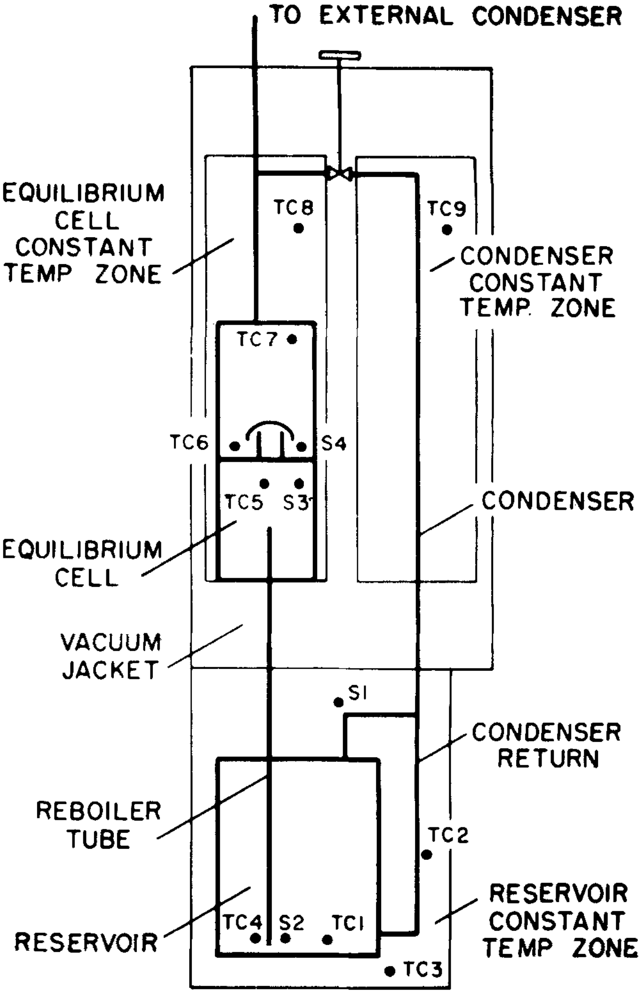

Fig. 2. Schematic diagram of calorimeter.

Materials

The methane and ethylene used in this investigation were pure grade (99 mole % minimum) chemicals. The principal contaminants of the methane were carbon dioxide, nitrogen, and ethane. Most of the carbon dioxide was removed by a scrubber filled with potassium hydroxide flakes. The nitrogen could not be detected on the flame ionization gas chromatograph used for analysis. The major contaminants of the ethylene were methane and ethane. Methane-ethylene mixtures were not analyzed for ethane. Commercial grade iso-octane was used as the thermostatic fluid.

EXPERIMENTAL PROCEDURES

The heats of vaporization of the pure components were determined first to establish the reliability of the calorimeter. The procedure was essentially the same as that for mixtures, which is described later.

The rate of heat leak from the reboiler tube (at the dew point temperature) to its surroundings (at the bubble point temperature) was determined by a special procedure. The dew point–bubble point temperature difference was simulated by filling the reservoir with liquified pure grade ethylene at 20 atm. (244.6°K.) and boiling it in the reboiler tube. When steady state was attained, the system pressure was suddenly raised to about 40 atm. by introducing Grade A (<50 p.p.m. contamination) helium. The liquid ethylene in the reboiler tube warmed to the 40 atm. boiling point (272°K.) and resumed boiling, while the contents of the reservior remained subcooled at 244.6°K. The apparent heat of vaporization under

TABLE 1. HEATS OF VAPORIZATION
(B.t.u./lb.-mole)

Average pressure, atm. abs.	Average composition, mole % methane	Average experimental	Literature	Percent difference	Method I	Calculated Method II	Method III
				Methane			
20.21	99+	2,413	2,405 (*9*)	0.3	—	—	—
40.09	99+	1,195	1,187	0.7	—	—	—
				Ethylene			
19.59	<1	4,029	3,953 (*23*)	1.9	—	—	—
20.15	<1	3,887	3,913	−0.7	—	—	—
38.42	<1	2,408	2,383	1.0	—	—	—
				Mixtures			
19.95	13.7	4,622	—		4,396	4,175	4,365
20.81	43.6	4,170	—		3,325	3,833	4,210
19.94	75.6	3,419	—		2,952	3,206	3,458
			—	Average % difference	−13.0%	−8.0%	−1.2%
39.97	11.2	3,578	—		4,640	3,228	3,047
38.07	32.7	3,445	—		4,237	3,308	3,351
42.44	75.2	2,661			2,853	*	2,678
				Average % difference	20.7%	− 6.9%	−5.6%

*** Program would not converge.**

these conditions was compared with the known heat of vaporization. The difference was attributed to the sensible heat required and the heat lost to the surroundings. The sensible heat was calculated by the Yen-Alexander equations (*22*). The resultant heat leak rate was 1.6 cal./(min.) (°K.), or about 6% of the total heat input.

For a mixture enthalpy determination, pure grade ethylene (99 mole % minimum) was fed from its storage cylinder, through a carbon dioxide scrubber filled with potassium hydroxide flakes, to the thermal compressor, which was submerged in a dry ice and methanol bath. After weighing the condensed ethylene, pure grade methane was condensed in the compressor to make a mixture of the desired composition. The mixture was analyzed after it warmed to room temperature. In the meantime, the calorimeter was cooled down in its cold bath. The mixture was transferred from the thermal compressor to the calorimeter by condensing it in the reservoir. After the liquid level in the reservoir had been adjusted to the correct height and bubble point liquid and vapor samples taken from the reservoir, the calorimeter heater was turned on to vaporize the mixture. The condensate was recycled to the reservoir. Steady state operation was usually attained in about 1 hr., after which dew point liquid and vapor samples were taken from the bubble tray. The flow of overhead vapor was then switched from the internal condenser to the external condenser by closing the valve between the equilibrium cell and condenser constant constant temperature zones (see Figure 2). The condensate was collected in a sample bomb, weighed, and analyzed.

During sample collection (7 to 10 min.) thermocouple emf's, standard resistor voltage drops, and the system pressure were measured.

Following a run, the charge in the reservoir was stripped from the calorimeter back into the thermal compressor, which was in its cold bath. Only one run per day could be made.

EXPERIMENTAL RESULTS

The experimental enthalpy data are given in Table 1. The heats of vaporization were determined for the two pure components and three mixtures at nominal pressures of 20 and 40 atm.

The enthalpy-concentration (*H-x*) diagrams for methane-ethylene at 20 and 40 atm. are plotted in Figures 3 and 4, respectively. The saturated vapor enthalpies were determined by four different methods: an equation given by Edmister et al. (*4*, *6*), which was derived from the Redlich-Kwong (*13*) equation of state; the tables of Pitzer et al. (*8*); the Yen-Alexander (*22*) equations; and the Benedict-Webb-Rubin (*1*) equation of state. The first method was selected, which uses a digital computer to solve

$$-\frac{\Delta H}{RT} = \frac{3}{2}\frac{A^2}{B}\ln\left(1 + \frac{BP}{Z}\right) + 1 - Z \qquad (1)$$

where

$$Z = \frac{1}{1-h} - \frac{A^2}{B}\frac{h}{1+h} \qquad (2)$$

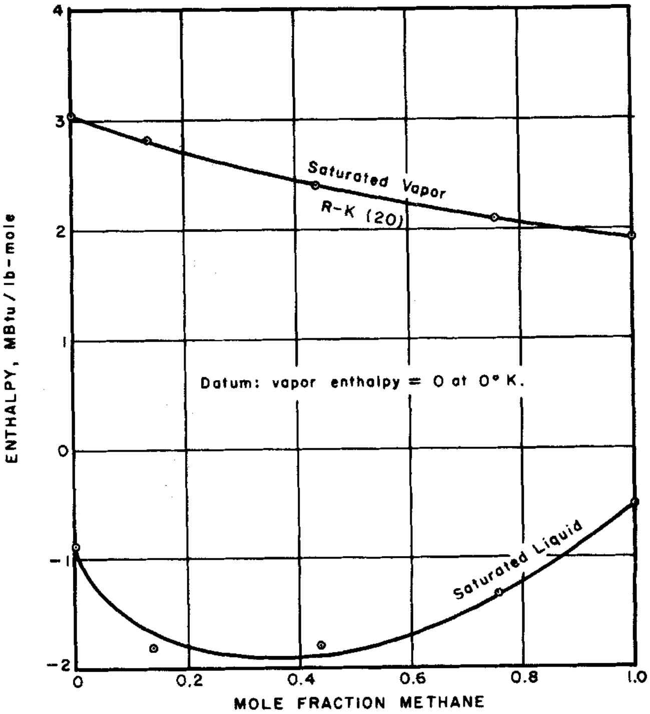

Fig. 3. Enthalpy-concentration diagram for methane-ethylene at 20 atm.

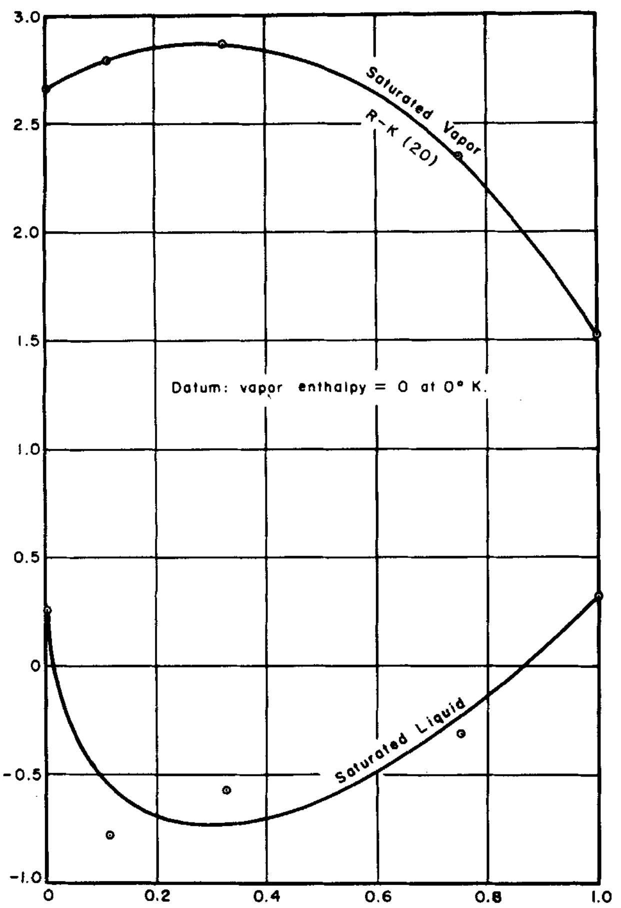

Fig. 4. Enthalpy-concentration diagram for methane-ethylene at 40 atm.

Equation (2) (*13*) can be solved by successive approximations in Z. Saturated liquid enthalpies were determined by subtracting the isobaric integral heats of vaporization from the saturated vapor enthalpies.

The vapor-liquid equilibria data are presented in Table 2 and are plotted on temperature-composition (T-x) diagrams, Figures 5 and 6, at 20 and 40 atm. respectively.

DISCUSSION OF RESULTS

The averages of several replications of pure component heats of vaporization are compared with values found in the literature in Table 1. The combination of individual errors in the enthalpy measurement, that is, standard resistor voltage drops (0.01%), the values of the standard resistances (0.01%), the elapsed time of a run (0.1%), and the weight of a sample (0.01%), amount to only 0.15% and cannot explain these differences entirely. The positive differences are attributed to heat leaks too small to be corrected by the heat leak correction methods used for mixtures. The negative difference is attributed to a slightly flooded equilibrium cell. Early in this investigation it was noted that the combination of a flooded cell plus a small negative temperature gradient between the cell and the external condenser would cause the liquid to vaporize in the cell and condense in the external condenser, without the calorimeter heater being on. Precautions were taken to prevent this action but they were not entirely successful. The negative difference is also indicative of a normal statistical variation. The other errors are pressure measurement, 0.05%; temperature, 0.2%; and sample composition, 1.5 mole %.

The average of the standard deviations of the pure component data is slightly more than 1 B.t.u./lb. This level of precision does not apply to mixture data, however, which require a heat leak correction.

Three replicate enthalpy determinations were made for each of the six mixtures. It was not possible to control pressure and composition very precisely; hence averages are tabulated. The average standard deviation of the enthalpy measurements was 3.1 B.t.u./lb. with a range of 1.9 to 4.5 B.t.u./lb. The precision of the mixture data is not as good as that of the pure component data because of the heat leak calibration. As mentioned, the heat leak correction was determined for a 27.4°K. (272.0 to 244.6) ΔT. The dew point-bubble point ΔT's encountered during the experiments ranged from 9.6° to 29.8° at temperatures ranging from 176.5 to 263.3°K. Better precision could be

TABLE 2. VAPOR-LIQUID EQUILIBRIA DATA

	Bubble point	Composition, mole % methane		Dew point	Composition, mole % methane	
Press, atm. abs.	T, °K.	Liquid	Vapor	T, °K.	Liquid	Vapor
19.95	226.8	13.7	40.8	241.7	2.3	14.1
20.81	199.4	43.6	75.2	226.3	14.0	41.5
19.94	176.5	75.6	94.2	206.3	32.4	69.7
39.97	253.7	11.2	36.4	263.3	6.5	13.1
38.07	235.3	32.7	68.5	252.2	18.9	39.4
42.44	199.4	75.2	92.8	225.2	40.7	75.0

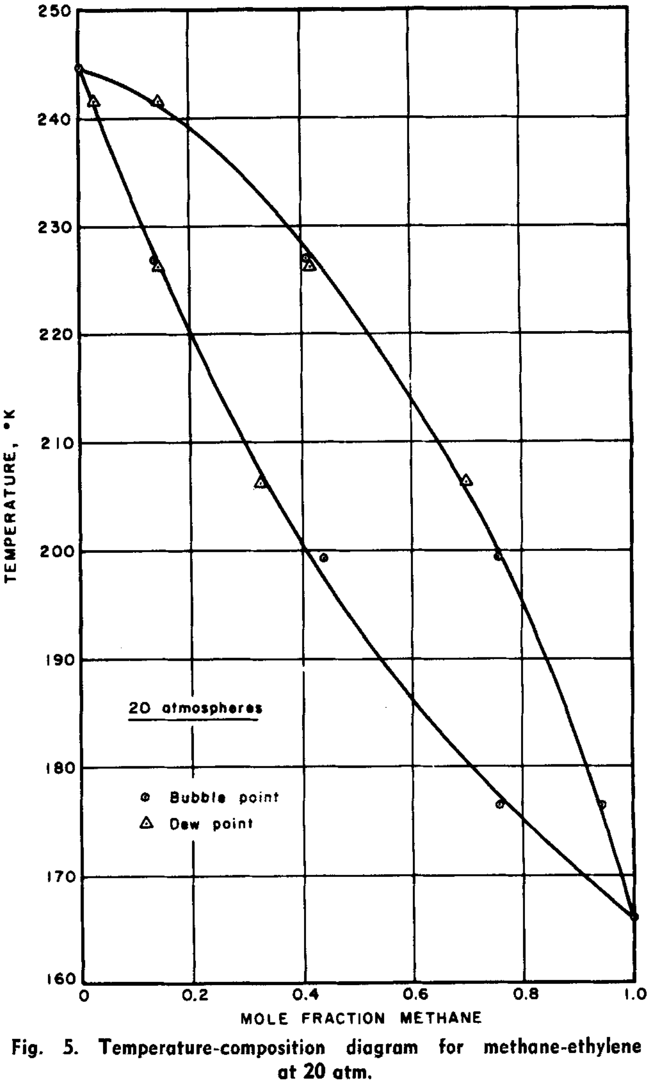

Fig. 5. Temperature-composition diagram for methane-ethylene at 20 atm.

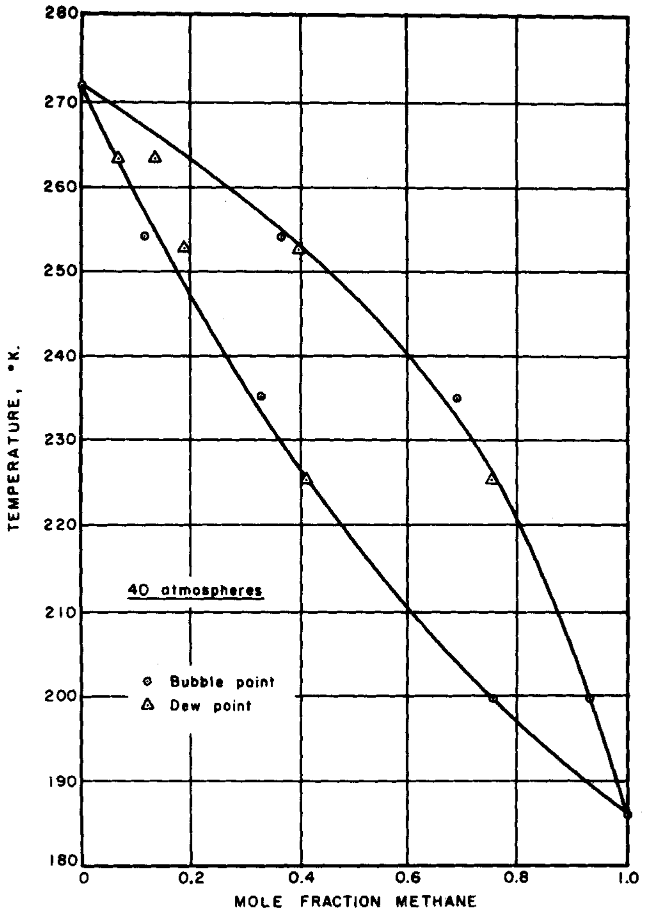

Fig. 6. Temperature-composition diagram for methane-ethylene at 40 atm.

obtained by determining the calibration over the entire range of experimental conditions.

Also given in Table 1 are the isobaric integral heats of vaporization calculated by three different methods. The methods used were: the Edmister (*3*) K value approximation method; the Edmister-Persyn-Erbar (*4, 6*) method; and the Yen-Alexander (*22*) equations. The last method, based on a generalized approach, gave the best agreement with these experimental data. The first method gave the poorest results, as might be expected from its approximate nature. The second method gave results that are consonant with the accuracy expected from the equations used in that computer program.

CONCLUSIONS

It is possible to obtain moderately precise high-pressure integral heats of vaporization in a stainless steel isobaric calorimeter. The precision of the calorimeter can be improved (*21*). Heats of vaporization of pure components studied were within 1% of published values with a precision of about 1 B.t.u./lb.

Isobaric integral heats of vaporization should be calculated by all three methods if possible, and the results evaluated. The Edmister (3) K value approximation can be used for either hand or computer calculations. The Yen-Alexander (22) equations are definitely computer oriented. The Edmister-Persyn-Erbar (*4, 6*) method is strictly for computer solution.

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NOTATION

$A^2 = (\Sigma y_i A_i)^2 = \{\Sigma y_i (a_i/R^2T^{2.5})\}^2$
$a_i = 0.4278\ R^2 T_{ci}^{2.5}/P_{ci}$
$B = \Sigma y_i B_i = \Sigma y_i (b_i/RT)$
$z_i = 0.0867\ RT_{ci}/P_{ci}$
$h = BP/Z$
H = vapor enthalpy
H° = ideal gas enthalpy
$\Delta H = H\text{-}H^\circ$
P = pressure
R = gas constant
T = temperature
V = volume
y = vapor phase mole fraction
$Z = PV/RT$

Subscripts

c = critical property
i = i^{th} component

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