Part I

PHASE EQUILIBRIA
MOLECULAR TRANSPORT
THERMODYNAMICS

Vapor-Liquid Equilibria in the Acetylene-Propyne System

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Vapor-liquid equilibrium data for the acetylene-propyne system have been obtained in an equilibrium apparatus designed for operation at elevated pressures. Because of the experimental hazards of working with high concentrations of liquid acetylene, the experimental data for dilute solutions of acetylene in propyne have been extended over the whole range of acetylene-propyne concentrations by the Margules equations (*13*). Because of the relatively high pressures involved, the activity coefficients (*2,3,19*) used in the Margules equations were corrected for the nonideality of the vapors by evaluation of fugacities from literature data for each component of the solution.

The dynamic methods for obtaining equilibrium data (*1,2, 6,7,10,16,18,19*) have certain advantages over the static methods (*21*) at low and moderately high pressures. However, the equilibrium stills used in most of the dynamic methods could not be used for the study of the acetylene-propyne system as they would be hazardous in operation because of the necessity for condensing, under pressure, vapors which were high in acetylene content (*5*). A static equilibrium cell was designed which requires only small volumes of solution and eliminates the major disadvantage of the static methods—i.e., the disturbance of the equilibrium upon sampling the phases. The cell is particularly suitable for the study of phase equilibria at high pressures where only small volumes of each phase are required for analyses.

EXPERIMENTAL

Materials. The propyne and acetylene were manufactured by the Air Reduction Co., Inc. The propyne was purified by low temperature distillation. The purified product analyzed 99.95% propyne by the mass spectrometer. Cylinder acetylene was freed of acetone by passage through water scrubbing towers and drying. Inerts were removed from the acetylene by low temperature flash distillation. Solutions of acetylene in propyne were prepared by passing the acetylene gas into liquid propyne at low temperature.

Apparatus and Procedure. The equilibration of the phases was carried out in the all-brass cell shown in Figure 1. The lower sleeve, *A*, contained a soft iron bar, *B*, to which was attached an aluminum rod, *C*, extending upward to the bottom of a 1-inch ball valve, *D*, situated at the center of the upper chamber. (The valve is manufactured by the Rockland Sprinkler Co., Worcester, Mass.) The rod was moved vertically through the cell by means of the permanent magnet, *J*. Perforated aluminum disks, *E* and *F*, on the rod allowed both the liquid and vapor phases to be stirred without transporting liquid to the vapor section above the ball valve.

The equilibrium cell was immersed in a thermostated bath maintained constant to within ± 0.04 °C. The cell was evacuated and filled under pressure with the acetylene-propyne solution to about 1 inch below the perforated disk, *F*, of the stirring rod. Equilibrium was attained in the cell by passing rod C vertically through the chamber by means of *J* (lift weight, 80 pounds). The magnet was driven by the slow-speed motor, *P*, shown mounted on the square steel frame above the equilibrium cell in Figure 2. The pressure was measured with a Bourdon gage which had been calibrated against a dead weight gage tester. Pressure measurements were both accurate and precise to 0.014 atm.

When equilibrium had been maintained for at least a 0.5-hour period, as indicated by the constancy of the temperature and pressure, the two phases were separated by closing the ball valve. The vapor phase was allowed to expand into an evacuated glass bulb on the vacuum manifold, *O*, shown in Figure 2. Approximately 1 ml. of the liquid phase was forced under the vapor pressure of the liquid into the evacuated space between valves *G* and *H* (Figure 1). After valve *H* had been closed, the liquid sample was completely flash-distilled into a second evacuated bulb on the manifold. The liquid and vapor samples were analyzed for both acetylene and propyne by a Perkin-Elmer infrared spectrometer. Measurements were taken at concentrations below 15% acetylene at 0°, 20°, and 35°C. No measurements

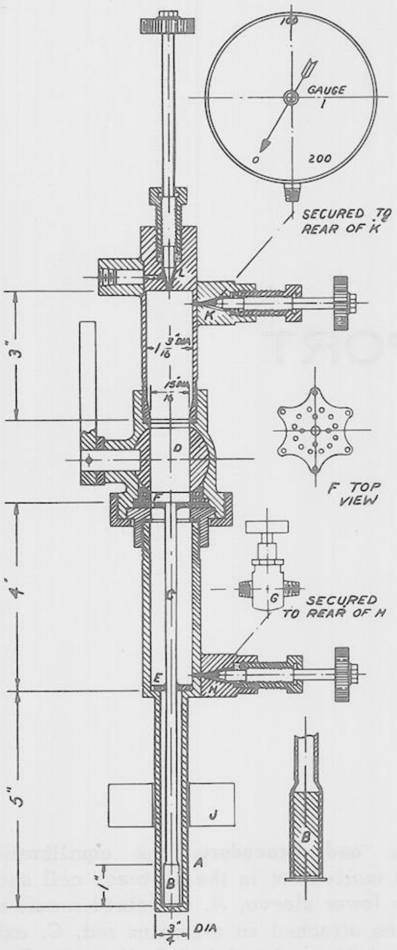

Figure 1. Cell for obtaining liquid-vapor equilibrium data at moderately high pressures

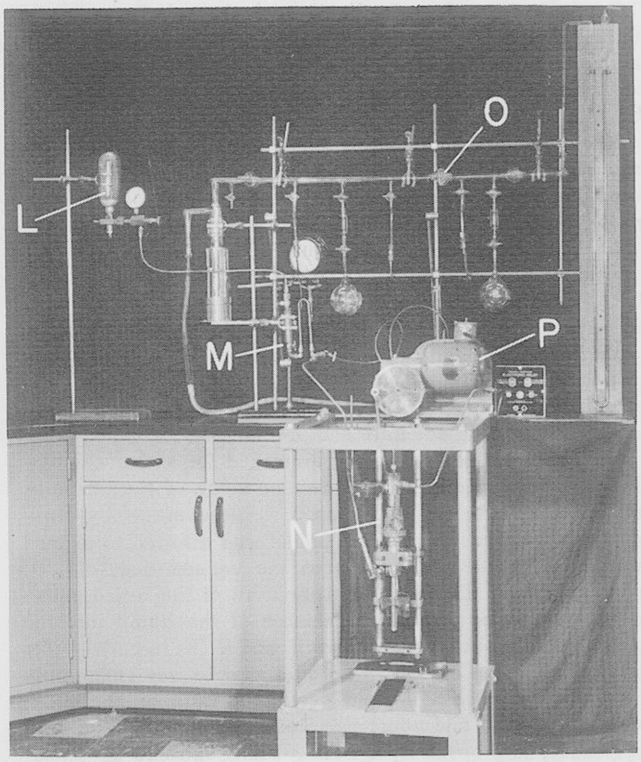

Figure 2. Static vapor-liquid equilibrium cell (*N*) with auxiliary apparatus for filling cell, equilibration and sampling phases

were taken above 15% acetylene because of the possible danger of spontaneous decomposition of the acetylene at higher concentrations and pressures (*5*).

RESULTS

For ideal liquid solutions, the partial fugacity of a component is given by Raoult's law,

$$\bar{f}_i = X_i f_i^0 \tag{1}$$

where f_i^0 is the fugacity of pure component i corrected to the vapor pressure of the solution. A measure of the deviation of a solution from ideal behavior may then be expressed in terms of an activity coefficient for each component,

$$\gamma_i = \frac{\bar{f}_i}{X_i f_i^0} \tag{2}$$

The partial fugacity of a component in the vapor phase is given by the Lewis and Randall rule if the vapors are assumed to form an ideal mixture (*7,12*),

$$\bar{f}_i = Y_i f_i^* \tag{3}$$

where f_i^* is the fugacity of component i in the mixture and in solution at the temperature and pressure of the solution. Equation 2 then becomes

$$\gamma_i = \frac{Y_i f_i^*}{X_i f_i^0} \tag{4}$$

For the evaluation of experimental activity coefficients from Equation 4, it was assumed that: (1) the partial molal volumes of each constituent in the liquid and vapor phases of the solutions were equal to their molal volumes and (2) the equation of state for each component in the vapor phase was:

$$PV_i = RT - \beta_i P \tag{5}$$

where β_i was calculated by graphical integration from zero pressure to the vapor pressure of the pure components and the solutions (*2,9,17,22*). Molal volumes of the pure liquids and the saturated vapors were obtained from the orthobaric densities of acetylene (*14*) and propyne (*11*). The vapor pressures of acetylene were taken from the data of Villard (*10*). The vapor pressures of the propyne were measured in the equilibrium cell and found to agree within 0.01 atm. with the reported values (*8*). A summary of the data used for the calculation of the activity coefficients is given in Table I. The experimental activity coefficients have been calculated from Equation 4 using the fugacities given in Table II.

Table I. Vapor Pressures, Liquid Molal Volumes, and Second Virial Coefficients[a] of Acetylene and Propyne

	Vapor Pressure, Atm.		Liquid Molal Volumes, Liters		Second Virial Coefficients	
Temp., °K.	Propyne,[b] P_1^0	Acetylene, P_2^0	Propyne, V_1	Acetylene, V_2	Propyne, β_1	Acetylene, β_2
223	0.26	5.38	0.0561	0.0461	. . .	0.20
250	1.0	13.5	0.0595	0.0504	2.30	0.363
273.3	2.63	26.0	0.0624	0.0561	2.06	0.277
293.3	4.99	42.6	0.0654	0.0650	0.606	0.248
308.3	7.68	59.1	0.0679	0.0856	0.432	0.285

[a] For equation of state $PV = RT - \beta P$.
[b] Experimental values, this work.

The experimental data were correlated and extended by means of the Margules three-suffix equations (*13*), since the molal volumes of liquid propyne are approximately

Table II. Equilibrium Vapor-Liquid Composition Data, Calculated Fugacities, and Experimental Activity Coefficients for Solutions of Acetylene in Propyne

		Experimental Data, Mole Fractions				Fugacities of Pure Components					
		Propyne		Acetylene		Corr. to Sol. Pressure		In Vapor		Activity Coefficients	
Temp., °K.	Pressure, Atm.	X_1	Y_1	X_2	Y_2	f_1^0	f_2^0	f_1^*	f_2^*	γ_1	γ_2
250	13.5	0		1.0					11.51		
	1.0	1.0		0				0.959			
273.3	26.0	0		1.0				...	20.71		
	2.63	1.0		0				2.47	...		
	3.19	0.959	0.777	0.041	0.223	2.47	19.40	2.96	3.10	0.952	1.04
	3.62	0.931	0.687	0.069	0.313	2.49	19.44	3.32	3.50	0.958	0.967
	3.99	0.911	0.589	0.089	0.411	2.49	19.45	3.56	3.85	0.910	1.08
	5.06	0.865	0.485	0.135	0.515	2.50	19.52	4.50	4.84	0.972	1.09
	5.28	0.863	0.482	0.137	0.518	2.50	19.55	4.66	5.04	1.00	1.12
293.3	42.6	0	...	1.0	...	...	...	...	31.38	...	...
	4.99	1.0	...	0	...	...	...	4.54	...	...	...
	5.71	0.963	0.834	0.037	0.166	4.54	28.3	5.15	5.49	0.978	1.07
	6.66	0.935	0.700	0.065	0.300	4.57	28.3	5.90	6.35	0.970	1.26
	7.11	0.909	0.638	0.091	0.362	4.57	28.3	6.24	6.75	0.961	1.15
	7.59	0.901	0.628	0.099	0.372	4.57	28.3	6.60	7.19	1.01	1.15
308.3	59.1	0	...	1.0	...	...	...	...	41.9	...	...
	7.68	1.0	...	0	...	...	...	6.81	...	...	...
	8.47	0.969	0.882	0.031	0.118	6.84	35.34	7.42	8.06	0.990	1.16
	10.53	0.920	0.708	0.080	0.292	6.88	35.62	8.94	9.92	1.00	1.34
	11.60	0.891	0.602	0.109	0.398	6.90	35.80	9.66	10.82	0.950	1.32

equal to those of liquid acetylene. The equations were used in the form (*3,23*):

$$\begin{aligned} \log \gamma_1 &= X_2^2\,[A + 2\,(B - A)\,X_1] \\ &\text{limit } \log \gamma_1 = A \\ &(X_1 \longrightarrow 0) \\ \log \gamma_2 &= X_1^2\,[B + 2\,(A - B)\,X_2] \\ &\text{limit } \log \gamma_2 = B \\ &(X_2 \longrightarrow 0) \end{aligned} \qquad (9)$$

The experimental activity coefficients given in Table II were used to solve for constants A and B by simultaneous solution of the equations. The Margules equations with the average values of the constants (Table III) were used to smooth the experimental activity coefficients and to extend the activity coefficient data over the whole range of acetylene and propyne concentrations at each temperature. The calculated and experimental activity coefficients are plotted as a function of composition in Figure 3 for 0° and 35 °C.

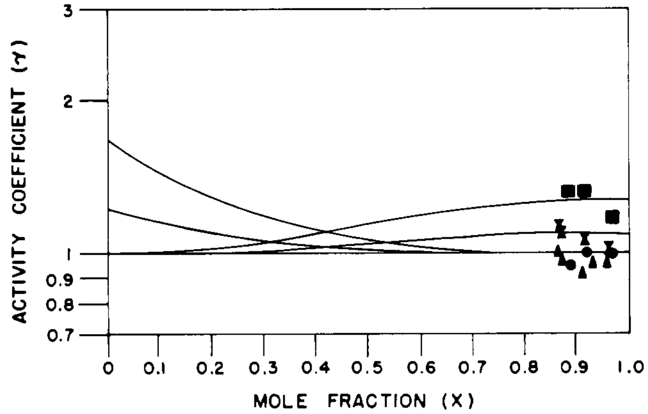

Figure 3. Activity coefficient-concentration curves for acetylene in propyne calculated from Margules equations.
▲, ●. Experimental data for propyne at 0° and 35°C.
X, ■. Experimental data for acetylene at 0° and 35°C., respectively (upper curves)

Table III. Smoothed Equilibrium Vapor-Liquid Composition Data for Acetylene-Propyne System (Correlated and extended from experimental data and Margules equations)

		Average Margules Constants		Activity Coefficients		Mole Fraction Liquid-Phase		Mole Fraction Vapor-Phase	
						Propyne	Acetylene	Propyne	Acetylene
Temp., °K.	Pressure, Atm.	A	B	γ_1	γ_2	X_1	X_2	Y_1	Y_2
223.2	0.483	...	...	...	...	0.95	0.05	0.518	0.483
	0.930	...	...	...	...	0.85	0.15	0.240	0.760
	1.39	...	...	...	...	0.75	0.25	0.141	0.859
250	1.46	...	...	...	...	0.95	0.05	0.653	0.347
	1.92	...	...	...	...	0.90	0.10	0.469	0.531
	2.41	...	...	...	...	0.85	0.15	0.353	0.647
	2.91	...	...	...	...	0.80	0.20	0.275	0.725
	3.94	...	...	...	...	0.70	0.30	0.177	0.823
273.3	3.42	0.08	0.03	1.00	1.083	0.95	0.05	0.732	0.268
	5.11	...	...	1.00	1.082	0.85	0.15	0.438	0.562
	6.93	...	...	1.00	1.075	0.75	0.25	0.284	0.716
293.3	6.13	0.14	0.06	1.00	1.156	0.95	0.05	0.771	0.229
	8.62	...	...	1.00	1.147	0.85	0.15	0.491	0.509
	11.28	...	...	1.00	1.130	0.75	0.25	0.330	0.670
308.3	9.10	0.23	0.10	1.00	1.272	0.95	0.05	0.801	0.199
	12.19	...	...	1.00	1.261	0.85	0.15	0.536	0.464
	15.66	...	...	1.01	1.247	0.75	0.25	0.368	0.632

The activity coefficients were extended to temperatures below the experimental by plotting the values of A and B against $1/T$. The straight lines resulting from this plot indicated that the partial molal heat of solution at infinite dilution is a constant over this temperature interval (*15, 20*). In addition, the intersection of the lines with the abscissa at about $-20°C$. showed that the activity coefficients below this temperature are equal to one—i. e., the solutions are ideal below $-20°C$.

From Equation 4 and the calculated activity coefficients at each temperature, smoothed and extended equilibrium vapor and liquid compositions as well as total pressures were obtained by a series of approximations which were initiated with the assumption that Raoult's law in the usual form of partial pressures could be used to obtain approximate total pressures. Typical smoothed equilibrium composition data and activity coefficients are given for acetylene concentrations below 25% in Table III. The data from Table III were used to construct an $X - Y$ diagram at each temperature (Figure 4). With data obtained from the curves of Figure 4, the graph of Figure 5 was constructed containing loci of constant mole fraction of acetylene in the liquid and vapor phases as a function of the temperature and total pressure of the solutions. For the concentration region covered by Figure 5, the compositions of both the liquid and vapor phases may be obtained by interpolation in Figure 5 when only the temperature and pressure of a mixture have been measured.

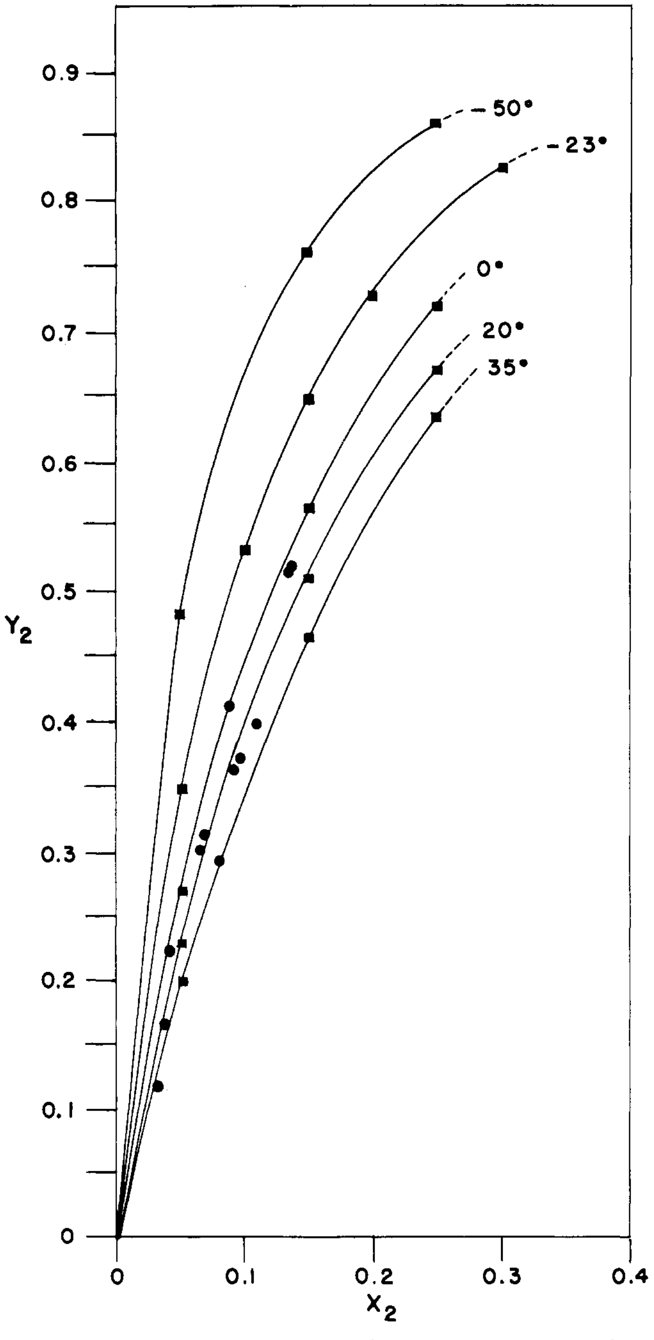

Figure 4. $X - Y$ diagram for acetylene in propyne at several temperatures
●. Experimental data ■. Margules equations

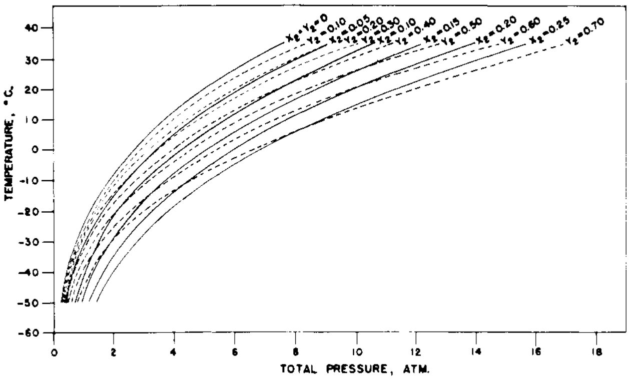

Figure 5. Loci of constant vapor or liquid compositions of acetylene in propyne

Ideal or nearly ideal solutions are formed at moderate temperatures and pressures by homologs which are closely related chemically. Deviations from ideal behavior, where they occur, are usually due to differences in chemical structure or in chemical size and volatility. Deviations from ideal behavior which are due to chemical dissimilarity decrease with increase in temperature, while deviations caused by differences in molecular size or volatility increase as the temperature increases, provided the pressure becomes relatively high (*4*). From the curves of Figure 3 and the data of Table III, it is seen that solutions of acetylene in propyne deviate from ideal behavior at the higher temperatures studied, and approach ideal behavior as the temperature is decreased. This behavior of the solutions suggests that the small positive deviation of the solutions from ideality is due to differences in molecular size and volatility of the components.

NOMENCLATURE

γ = activity coefficient
X = mole fraction in liquid phase
Y = mole fraction in vapor phase
P^0 = vapor pressure of pure component in atmospheres at absolute temperature T
p_i = partial pressure of component i in atmospheres
V = liquid molal volume of pure component in liters per mole
P = total pressure of the solution in atmospheres
β = second virial coefficient of the equation of state, $Pv = RT - \beta P$, where v is the molal volume of vapor
f^0 = fugacity of pure component at P^0 and T, corrected to vapor pressure of solution
$\bar{f}_i$ = partial fugacity of component i in liquid and vapor phases of a solution
f_i^* = fugacity of pure component i in vapor phase at temperature and pressure of solution

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Saturated Liquid Phase Enthalpies for the System *n*-Butane-*n*-Heptane at Elevated Pressures

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Accurate calculations for distillation operations require thermal as well as vapor-liquid equilibrium data. At the present time there are vapor-liquid equilibrium data for a number of binary systems for which thermal data are unavailable. Recently, Stiehl, Hobson, and Weber (*6*) utilized a thermodynamically rigorous method, outlined by Dodge (*3*), by which the saturated liquid phase enthalpies of binary mixtures may be calculated from the differential heats of condensation and vapor phase enthalpy data. As the saturated vapor phase enthalpies can be calculated from the Benedict-Webb-Rubin equation of state (*2*), complete enthalpy composition data are made available.

The method of calculation has been discussed thoroughly (*6*). The basic relationships which apply to the process of condensation for 1 mole of liquid from a large quantity of vapor under equilibrium conditions are

$$\Delta V = V_b - V_d + (y - x)\left(\frac{\partial V_a}{\partial y}\right)_{T,P} \tag{1}$$

$$\left(\frac{\partial P}{\partial T}\right)_y = \frac{\Delta H_c}{T\Delta V} \tag{2}$$

and

$$\Delta H_c = H_b - H_d + (y - x)\left(\frac{\partial H_a}{\partial y}\right)_{T,P} \tag{3}$$

In the previous work enthalpy-composition data were presented for the system methane-ethane at 200, 400, and 600 pounds per square inch absolute and for the systems ethane-*n*-butane and propane-*n*-butane at the two lower pressures. In this work enthalpy composition data are presented for the system *n*-butane-*n*-heptane at 100, 200, 300, and 400 pounds per square inch absolute.

The vapor-liquid equilibrium data and the volumetric behavior of the coexisting phases for the *n*-butane-*n*-heptane system are reported by Kay (*4*). The Benedict-Webb-Rubin equation (2)

$$P = RTd + (B_0RT - A_0 - C_0/T^2)d^2 + (bRT - a)d^3 + a\alpha d^6 + cd^3/T^2[(1 + yd^2)\exp(-yd^2)] \tag{4}$$

was also used to calculate the saturated vapor volumes; the results agreed with the experimental data of Kay within ±1%. The single exception was the calculated value at the critical point at 400 pounds per square inch absolute, 511.8°F., and 1.1% *n*-heptane. In this case the molal volume predicted by the equation was 3.6% greater than the experimental value.

As the validity of the Benedict-Webb-Rubin equation was established for this binary system, this relationship was used to predict volumetric data in the superheated vapor region. Through the use of the calculated data, the experimental results of Kay (*4*), and the volumetric data for pure *n*-butane (*5*), the term $(\partial V/\partial y)_{T,P}$ in Equation 1 can be determined as a function of composition along any given isotherm at the pressure under consideration. The partial differential must be evaluated accurately. This is rendered difficult for three reasons: First, the slope is determined graphically; second, the slope of the isotherm must be determined at its point of intersection with the saturated vapor curve; and third, at high percentage compositions of the