

# Fugacity Coefficients, Enthalpy, and Second Virial Coefficients of Boron Trifluoride

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Fugacity coefficients and isothermal changes of enthalpy have been calculated and reported. The calculations cover a temperature range of 0° to 75° C. up to gas densities of 1.0 gram per cc. The generalized Benedict-Webb-Rubin constants evaluated from generalized PVT relations is found to predict the experimental data with an over-all absolute deviation of 3.1%. Second virial coefficients and potential energy parameters for Lennard-Jones (12-6) potential energy function are reported also.

WITH THE ADVENT of nuclear technology, boron compounds are finding an important place. The special consideration of boron trifluoride ( $B^{10}F_3$ ) is that it is a stable gas, and its fairly high absorption coefficient (4000 barns) makes it a suitable material to be used as a neutron-absorbing medium.

The generalized equation of state developed by Su and Chang (7) has been used by Smith (6) to predict the PVT behavior of  $BF_3$  gas. The predicted data are compared with the experimental data of Burton and Swinehart (6). Thermodynamic functions have been reported by Wilkins (10). The critical constants for boron trifluoride are

$$\begin{aligned} P_c &= 49.2 \text{ atm. (1)} \\ T_c &= 261.0^\circ \text{ K. (1)} \\ V_c &= 114.7 \text{ cc./ (gram-mole)} \end{aligned}$$

## CALCULATION OF $f/P$ VALUES

The PVT data as reported by Smith (6) were employed in this study. Graphical integration was used to evaluate  $f/P$  values from the relation

$$\ln f/P = \int_0^P \frac{(1-Z)}{P} dP \quad (1)$$

Extrapolation of PVT data was necessary for pressures below 25 atm. The calculated values are tabulated in Table I.

## EQUATION OF STATE FOR $BF_3$ GAS

Smith (6) has utilized the Su and Chang generalized equation of state to predict the PVT behavior of  $BF_3$ , and was able to predict the PVT data nearly up to twice the critical density with an average absolute deviation of 3%. A set of generalized constants obtained for Benedict-Webb-Rubin (8, 9) equation is used to predict the PVT behavior of  $BF_3$  and compared with the experimental data reported by Smith (6). Although the set of generalized constants determined from a set of generalized PVT properties in a  $\theta$  range of 1.0 to 15.0 and  $\zeta$  of 0.25 to 6.5, reproduced the data with an over-all absolute deviation of 1.8%, the error in predicting the PVT data of  $BF_3$  was found to be of the same order of magnitude as obtained with the Su and Chang equation. The over-all absolute deviation is found to be 3.1%, using the generalized Benedict-Webb-Rubin (9)

Table I. Fugacity Coefficients,  $f/P$  for  $BF_3$  Gas

$\pi$	$P$ , atm.	0° C.	10° C.	20° C.	25° C.	40° C.	50° C.	60° C.	75° C.
0.0	0.0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.1	4.92	0.9759	0.9763	0.9797	0.9804	0.9817	0.9856	0.9887	0.9922
0.4	19.68	0.8964	0.9061	0.9181	0.9232	0.9268	0.9401	0.9570	0.9685
0.6	29.52	0.8418	0.8584	0.8758	0.8780	0.8932	0.9128	0.9342	0.9510
0.8	39.36	0.7830	0.8110	0.8345	0.8486	0.8598	0.8853	0.9105	0.9340
1.0	49.20	0.7263	0.7640	0.7949	0.8121	0.8283	0.8574	0.8859	0.9137
1.2	59.04	0.6713	0.7173	0.7553	0.7752	0.7980	0.8424	0.8610	0.8962
1.4	68.88	0.6142	0.6707	0.7155	0.7375	0.7678	0.8149	0.8366	0.8756
1.6	78.72	0.5611	0.6252	0.6764	0.7009	0.7381	0.7884	0.8125	0.8549
1.8	88.56	0.5174	0.5830	0.6396	0.6664	0.7099	0.7630	0.7894	0.8345
2.0	98.40	0.4817	0.5464	0.6039	0.6342	0.6834	0.7381	0.7676	0.8147
2.2	108.24	0.4522	0.5147	0.5720	0.6052	0.6588	0.7147	0.7466	0.7692
2.4	118.08	0.4273	0.4881	0.5454	0.5789	0.6359	0.6931	0.7273	0.7787
2.6	127.92	0.4060	0.4658	0.5226	0.5552	0.6148	0.6728	0.7092	0.7628
2.8	137.76	...	0.4475	0.5025	0.5342	0.5960	0.6545	0.6924	0.7485
3.0	147.60	...	0.4310	0.4852	0.5158	0.5788	0.6380	0.6770	0.7352
3.2	157.44	...	0.4166	0.4697	0.4998	0.5632	0.6227	0.6625	0.7230
3.4	167.28	...	0.4037	0.4553	0.4855	0.5493	0.6087	0.6492	...
3.6	177.12	...	0.3924	0.4427	0.4729	0.5365	0.5960	0.6369	...
3.8	186.96	...	...	0.4313	0.4614	0.5250	0.5843	0.6259	...
4.0	196.80	...	...	0.4211	0.4512	...	0.5740	0.6160	...
4.2	206.64	...	...	0.4121	0.4420	...	0.5645	...	...
4.4	216.48	...	...	0.4043	0.4337	...	...	...	...
4.6	226.32	...	...	...	0.4261	...	...	...	...
4.8	236.16	...	...	...	0.4195	...	...	...	...
5.0	246.00	...	...	...	...	...	...	...	...

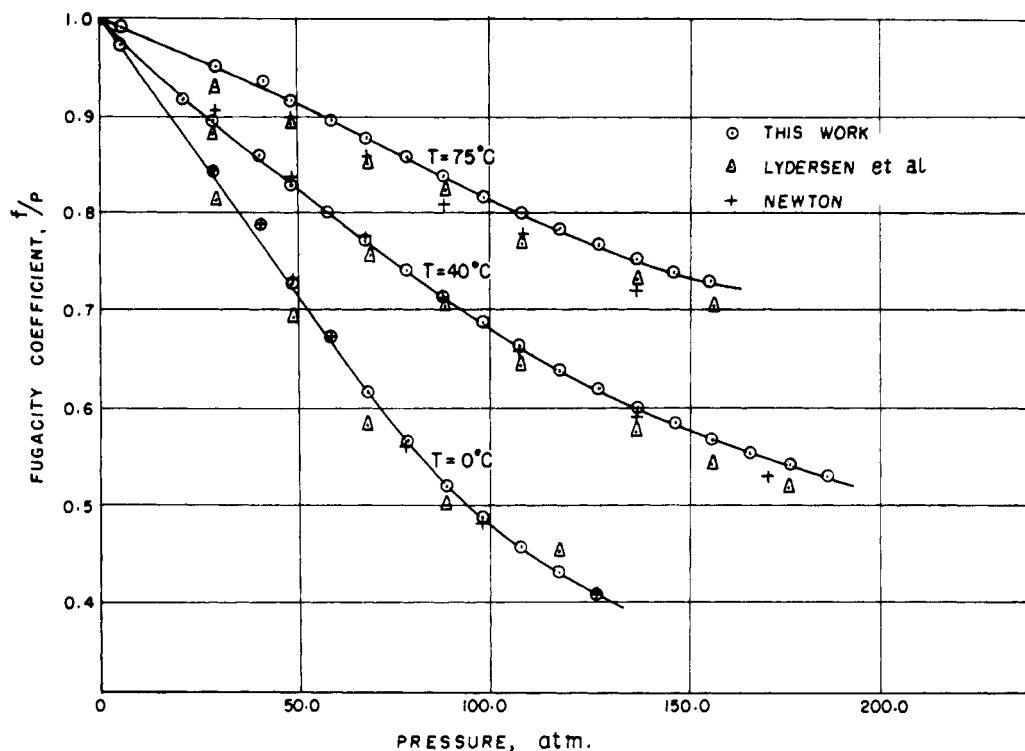


Figure 1. Fugacity correlation

equation. The generalized constants utilized in the equation are

$$\pi = \theta \zeta + \zeta^2 \theta B'(\zeta) - A'(\zeta) - \frac{C'(\zeta)}{\theta^2} \quad (1a)$$

where

$$A'(\zeta) = A'_0 + a' \zeta (1 - \alpha' \zeta^3)$$

$$B'(\zeta) = B'_0 + b' \zeta$$

$$C'(\zeta) = C'_0 - c' (1 + \gamma'_0 \zeta^2) e^{-\gamma'_0 \zeta^2}$$

$$a' = 0.044070594 \quad c' = 0.064480014$$

$$A'_0 = 0.24180980 \quad C'_0 = 0.21217005$$

$$b' = 0.037151710 \quad \alpha' = 0.0025798311$$

$$B'_0 = 0.076431013 \quad \gamma'_0 = 0.06$$

The values of the constants for the Benedict-Webb-Rubin equation

Table II. Enthalpy Changes  $(H^* - H)/T_c$  for  $\text{BF}_3$  Gas

Units: B.t.u./ (lb. mole) ( $^{\circ}$  R.) or Cal./ (gram-mole) ( $^{\circ}$  K.)

P, atm.	0 $^{\circ}$ C.	10 $^{\circ}$ C.	20 $^{\circ}$ C.	40 $^{\circ}$ C.	50 $^{\circ}$ C.	60 $^{\circ}$ C.	75 $^{\circ}$ C.
USING SU-CHANG EQUATION OF STATE							
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4.92	0.1270	0.1200	0.1120	0.0860	0.0690	0.0530	0.0240
24.60	0.8563	0.8229	0.7402	0.7159	0.6461	0.5321	0.5034
36.90	1.4347	1.3069	1.1942	1.0757	0.9668	0.8998	0.7545
49.20	2.2069	1.9566	1.9153	1.4468	1.3226	1.1984	1.0673
73.80	5.2812	4.1991	3.1858	2.4607	2.0924	1.8950	1.6753
98.40	6.7572	5.7579	4.8819	3.5328	3.0966	2.7991	2.3692
123.00	7.2430	6.5034	5.7403	4.4689	3.9082	3.5611	3.2114
147.60	...	6.8244	6.2416	5.0695	4.5300	4.1156	3.5491
172.20	...	7.2024	6.5925	5.4491	4.9547	4.5085	...
196.80	...	...	6.7910	...	5.2740	4.8569	...
USING BENEDICT-WEBB-RUBIN EQUATION OF STATE							
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4.92	0.247	0.234	0.225	0.103	0.051	0.025	...
24.60	0.1313	1.0554	0.9354	0.8466	0.7678	0.6287	...
36.90	1.8792	1.6739	1.5033	1.2953	1.1547	1.0546	0.8850
49.20	2.8558	2.4696	2.1577	1.7392	1.5825	1.4135	1.2356
73.80	6.6628	4.9164	3.7986	2.8939	...	2.1902	1.9005
98.40	7.5812	6.4024	5.4546	3.9919	3.4893	3.1296	2.6166
123.00	8.1723	7.5490	6.2664	4.8704	4.2611	3.8586	3.2803
147.60	...	8.0128	6.7779	5.4159	4.8240	4.3617	3.7356
172.20	...	...	7.1568	5.7693	5.2057	4.7076	...
196.80	...	...	7.4147	...	5.4996	5.0173	...

Table III.<sup>a</sup> Values of  $V(PV - RT)$  for Boron Trifluoride

Temp., °K.	Density, Gram-Moles/Liter											
	1.47445	2.94898	4.42282	5.89796	7.37246	8.84721	10.32151	11.79593	13.27052	14.74491		
273.16	1	-2.783400	-2.564579	-2.041212	-1.840879	-1.648237	-1.480877	-1.323897	-1.146278	-0.921355		
	2	+0.008658	-0.030423	+0.031579	-0.011086	-0.001694	+0.002525	+0.000990	+0.001318	-0.001158		
283.16	1	-2.511985	-2.336908	-2.136261	-1.938872	-1.738767	-1.585795	-1.429539	-1.285493	-1.1578309		
	2	+0.001962	-0.003839	+0.000181	-0.001295	+0.006180	-0.002550	-0.016868	+0.019990	-0.006262		
293.16	1	-2.424633	-2.178209	-2.035058	-1.830784	-1.632970	-1.500281	-1.35127	-1.2105127	-1.083425		
	2	-0.007982	+0.026445	-0.024911	-0.003217	+0.019502	-0.021638	+0.000146	-0.010312	+0.004291		
298.16	1	-2.242943	-2.110355	-1.985203	-1.773866	-1.578239	-1.403313	-1.227174	-1.049826	-0.838618		
	2	-0.004941	+0.018071	-0.020701	+0.002909	+0.007699	-0.001339	+0.017676	-0.002452	-0.001156		
313.16	1	-2.249793	-1.975800	-1.812689	-1.603095	-1.417709	-1.231213	-1.049826	-0.861916	-0.641752		
	2	-0.006997	+0.023515	-0.021964	-0.001266	+0.003254	+0.007961	-0.000885	+0.003784	-0.0003784		
323.16	1	-1.978377	-1.863117	-1.682342	-1.506503	-1.319275	-1.116996	-0.932208	-0.735999	-0.574774		
	2	+0.001647	-0.006718	+0.008802	-0.001299	+0.006256	+0.004692	-0.000653	-0.000214	+0.000546		

<sup>a</sup> In second column, 1 refers to observed values of  $V(PV - RT)$ , and 2 refers to (observed - calculated).

$$P = \frac{RT}{V} + \frac{B_c RT - A_c - C_c/T^2}{V^2} + \frac{bRT - a}{V^3} + \frac{a^\alpha}{V^8} + \frac{c}{V^3 T^2} (1 + \gamma/v^2) e^{-\gamma/v^2} \quad (1b)$$

are

$$\begin{aligned} a &= 0.178868868 & c &= 17827.5635 \\ A_c &= 2.254513473 & C_c &= 134754.73383 \\ b &= 0.0070403239 & \alpha &= 0.0002128198 \\ B &= 0.03327181808 & \gamma &= 0.01137012095 \end{aligned}$$

### ISOTHERMAL CHANGE OF ENTHALPY

The isothermal change of enthalpy with pressure is given by the expression

$$\left(\frac{\partial H}{\partial P}\right)_T = -\frac{RT^2}{P} \left(\frac{\partial Z}{\partial T}\right)_P \quad (2)$$

Equation 2 can be written in terms of the reduced variables  $\pi$  and  $\theta$  as

$$\left(\frac{\partial H}{\partial \pi}\right)_\theta = -\frac{RT\theta}{\pi} \left(\frac{\partial Z}{\partial \theta}\right)_\pi \quad (3)$$

Since  $Z = (\pi V_R/\theta)$ , Equation 3 can be rewritten and integrated to give the expression

$$\frac{H^* - H}{R\theta T_c} = \int_{\pi^*}^{\pi} \left(\frac{\partial V_R}{\partial \theta}\right)_\pi d\pi - \int_{\pi^*}^{\pi} \frac{Z}{\pi} d\pi \quad (4)$$

where \* indicates a suitable reference point. Equation 4 when coupled with Equation 1, eliminates the error due to graphical differentiation involved in Equation 2. Equation

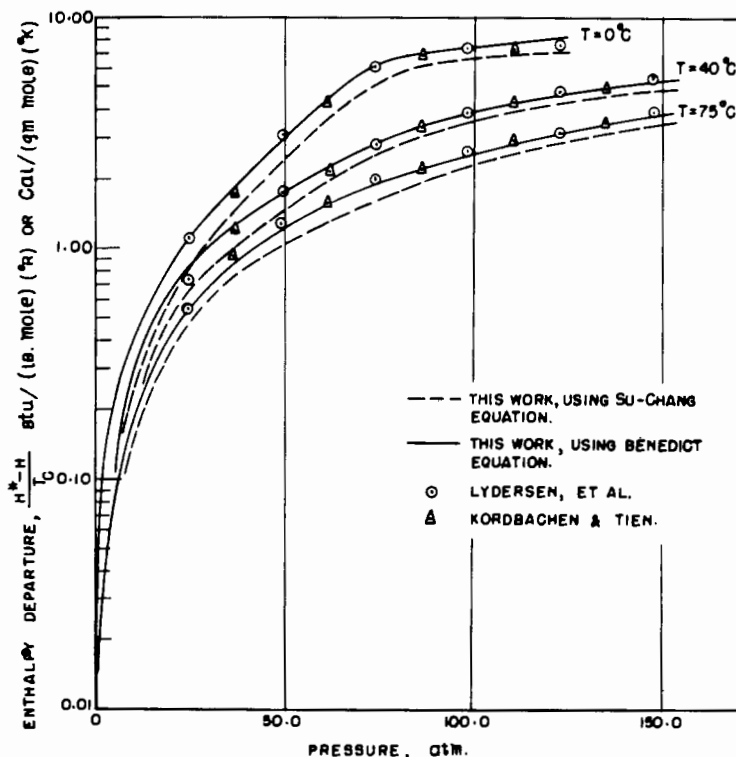


Figure 2. Enthalpy correlation

Table IV. Values of Coefficients in Equation 6

Temp., ° K.	$B_1$ , Liter <sup>2</sup> -Atm./Mole <sup>2</sup>	$B_2$ , Liter <sup>3</sup> -Atm./Mole <sup>3</sup>	$B_3$ , Liter <sup>4</sup> -Atm./Mole <sup>4</sup>	$B_4$ , Liter <sup>5</sup> -Atm./Mole <sup>5</sup>
273.16	-3.0273355	0.14499808	0.01252189	-0.00189648
283.16	-2.6596217	0.08154628	0.01371774	-0.00144017
293.16	-2.6478155	0.16392921	-0.00498374	0.00007676
298.16	-2.3520296	-0.03393579	0.03361208	-0.00294462
313.16	-2.5390655	0.22341454	-0.01691872	0.00117240
323.16	-2.0337714	0.00519855	0.02402277	-0.00200932

4 which involves pseudoreduced volume  $V_R$  can be transformed to an equation involving pseudoreduced density as

$$\frac{H^* - H}{R\theta T_c} = \int_{\pi^*}^{\pi} \frac{1}{\zeta^2} \left( \frac{\partial \pi}{\partial \theta} \right)_{\zeta} d\zeta - \int_{\pi^*}^{\pi} \frac{Z}{\pi} d\pi \quad (5)$$

As the variation of enthalpy with pressure is almost zero at and below  $\pi = 0.01$  ( $P_c = 0.492$  atm.), this was taken as the reference point. The expression

$$\int \frac{1}{\zeta^2} \left( \frac{\partial \pi}{\partial \theta} \right)_{\zeta} d\zeta$$

was evaluated using the Su-Chang equation of state and  $\int (Z/\pi) d\pi$  by graphical integration. The results are shown in Table II. The isothermal change of enthalpy calculated using the generalized Benedict-Webb-Rubin equation is tabulated and, also, shown in Table II. The values are listed in terms of pressure at various temperatures as Equation 5 in terms of  $P$ ,  $V$ , and  $T$  reduces to

$$\frac{H^* - H}{T_c} = \frac{T}{T_c} \left[ \int \left( \frac{\partial P}{\partial T} \right)_{\zeta} dv - \int \frac{Z}{P} dP \right] \quad (5a)$$

## SECOND VIRIAL COEFFICIENTS AND FORCE CONSTANTS

Second virial coefficients were evaluated by fitting the  $PVT$  data to the relation

$$V(PV - RT) = B_1 + B_2/V + B_3/V^2 + B_4/V^3 \quad (6)$$

The polynomial was fitted using a weighted least-squares method without the use of matrix inversion—thus avoiding illconditioning of the equations. Table III gives the experimental and calculated values of  $V(PV - RT)$ . The values of the coefficients for Equation 6 are given in Table IV. Table V gives the experimental and calculated second virial coefficients using the Lennard-Jones(12-6) potential energy function. These values are obtained by reducing  $B_1$  values of Table IV with  $RT$ . The values of the collision diameter  $\sigma$ , and the minimum potential energy  $\epsilon/k$  are 6.04 Å. and 124° K., respectively.

## DISCUSSION

The values of Table II shown also in Figure 2 for three isotherms are in better agreement with certain other generalized charts (2, 3, 4). This is not surprising, as the three-constant Su-Chang equation is reduced to a two-constant equation, whereas the Benedict-Webb-Rubin equation is reduced to a six-constant equation when used in Equation 5. The rather large slopes of  $PV$  isotherms, especially near the critical region, can be better taken into account with higher degree polynomial. The results are shown in Figure 2.

From Figure 1, although  $\text{BF}_3$  has a  $Z_c = 0.264$ , using  $V_c = 114.7$  cc./ (gram-mole) as given by Smith (6), at  $\theta = 1.2$  and above, the calculated  $f/P$  values differ considerably from Lydersen, Greenkorn, and Hougen (2, 4) values. At  $T = 75^\circ \text{C}$ ., these authors' values are even less than Newton's values (5), who did not classify gases according to  $Z_c$ .

Table V. Second Virial Coefficients of  $\text{B}^{10}\text{F}_3$ 

Temp., ° K.	$B_1$ , cc./Mole	
	Exptl.	Calcd.
273.16	-135.05	-139.00
283.16	-117.90	-118.00
293.16	-110.67	-112.00
298.16	-98.10	-101.00
313.16	-97.50	-89.00
323.16	-78.55	-74.50
333.16	-65.00	-66.00

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## NOMENCLATURE

- $a', A', b', B', c', C', \alpha', \gamma'$  = constants in the generalized Benedict-Webb-Rubin equation, Equation 1a  
 $a, A, b, B, c, C, \alpha, \gamma$  = constants in the Benedict-Webb-Rubin equation, Equation 1b  
 $B_1, B_2, B_3, B_4$  = virial coefficients  
 $V_R$  =  $1/\zeta$  = pseudoreduced volume =  $(P_c V / RT_c) = (V / V_c)$   
 $f$  = fugacity, atm.  
 $H$  = enthalpy at given temperature and pressure  
 $H^*$  = enthalpy in ideal state at given temperature  
 $P$  = pressure, atm.  
 $R$  = Universal gas constant, atm. liters/(g. mole) (° K.)  
 $T$  = temperature, ° K.  
 $V$  = volume, liters/(g. mole)  
 $Z$  = compressibility factor =  $(PV/RT)$

## Greek

- $\pi$  = reduced pressure,  $P/P_c$   
 $\theta$  = reduced temperature,  $T/T_c$   
 $\sigma$  = collision diameter, Å.  
 $\epsilon$  = minimum potential energy, ergs  
 Subscript  $c$  refers to critical property, except in  $V_c$ .

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## Critical Temperatures and Critical Pressures of the Ethane-*n*-Pentane-*n*-Heptane System

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Critical temperatures and critical pressures were established experimentally for three mixtures consisting of ethane, *n*-pentane, and *n*-heptane. These determinations were carried out in a visual liquid piston type *PVT* cell which utilized mercury as the pressurizing medium. These critical measurements served as the basis necessary for the development of the critical temperature and critical pressure behavior over the entire composition range of this ternary system. The final relationships are presented on triangular plots and permit the establishment of the critical temperature and critical pressure of any composition for this ternary system. Based on the linear behavior of the critical temperature, analytical relationships are developed that permit the direct calculation of this critical property from a knowledge of the critical behavior of the corresponding binaries.

**E**XPERIMENTAL critical temperature and critical pressure measurements available in the literature mostly are restricted to binary hydrocarbon systems. For systems containing more than two components, critical temperature and pressure measurements are rather scarce, and consequently present an inconvenience to the development of a method capable of predicting these critical properties for systems containing more than two components. Furthermore, attempts to utilize such experimental measurements, of necessity, require that such information become available for three- and four-component systems. Such information will assist in the general understanding of the critical state behavior of multicomponent hydrocarbon systems.

In this study the system ethane-*n*-pentane-*n*-heptane was investigated. This ternary system was selected particularly because the critical temperature and critical pressure behavior of the corresponding binary systems are presented in the literature. This information, coupled with measurements on this ternary system, was utilized for the development of relationships for the critical temperature and critical pressure of this ternary system over its complete range of composition.

### EXPERIMENTAL PROCEDURE

The experimental procedure used in this investigation is identical to that described elsewhere for the ethane-*n*-heptane system (3). The basic feature of the experimental unit was represented by a visual *PVT* cell of the liquid piston type which utilized mercury as the displacing fluid.

Visual observations of the vapor-liquid meniscus at constant temperature conditions and varying pressures permitted the establishment of the phase behavior of the ternary mixture confined in the *PVT* cell. This approach was utilized for three different ethane-*n*-pentane-*n*-heptane mixtures, which yielded relationships comparable to those presented in Figure 1. The hydrocarbons used in this

investigation were research grade and were claimed to have the following purities:

	Mole %
Ethane	99.96
<i>n</i> -Pentane	99.84
<i>n</i> -Heptane	99.78

The components first were introduced into a charging cell preceding the visual *PVT* cell where they were solidified with liquid nitrogen and then were exposed to vacuum. To ensure complete removal of any noncondensables, the charging cell and its contents were warmed to room temperature, then resolidified with liquid nitrogen, and evacuated. This procedure was repeated at least three times.

In Figure 1 are presented the isothermal relationships of liquid volume per cent *vs.* pressure for temperatures ranging from 237.9° to 266.1° F. for a mole fraction composition consisting of the following: ethane = 0.801, *n*-pentane = 0.064, and *n*-heptane = 0.135. Compositions were established with a mass spectrometer. In Figure 1, the isotherms 237.9° and 241.8° F. indicate conventional behavior and exhibit complete liquefaction at the highest pressures. On the other hand, the isotherms 248.6°, 251.6°, and 266.1° F. exhibit a retrograde behavior and are characterized with complete vaporization at their highest pressure. The experimental information presented in Figure 1 was crossplotted for constant values of liquid volume per cent to produce the pressure *vs.* temperature relationships presented in Figure 2. The point of convergence of these relationships represents the critical point of this mixture, which, for charge A, was  $t_c = 245^\circ \text{F.}$  and  $P_c = 1175 \text{ p.s.i.a.}$  A similar procedure was adopted for two additional ternary mixtures for which critical temperatures and critical pressures were established. The experimental values used to obtain the relationships for the ternary mixture of Figures 1 and 2 and for the other two mixtures of this study are available elsewhere (2). The uncertainty in these measurements is 2 p.s.i.a. for pressure and 1° F. for temperature. The mass spectroscopy analyses should be reliable to

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