Table II. Densities, Refractive Indices, Dielectric Constants, Molar Refractions, and Molar Polarizations of Binary Solutions at 25° and 35° C. (*Continued*)

	25° C.					35° C.				
N_1	d, grams/ml.	n_D	D	R_D, ml.	P, ml.	d, grams/ml.	n_D	D	R_D, ml.	P, ml.
				m-Nitrotoluene–*o*-Nitrotoluene						
1.0000	1.1527	1.5447	26.39	37.60	106.40					
0.8963	1.1536	1.5447	26.61	37.57	106.37					
0.7959	1.1540	1.5446	26.61	37.55	106.37					
0.6948	1.1544	1.5446	26.69	37.53	106.37					
0.5969	1.1547	1.5445	26.77	37.52	106.38					
0.4967	1.1555	1.5444	26.80	37.49	106.32					
0.3897	1.1564	1.5443	26.80	37.45	106.23					
0.2967	1.1568	1.5442	26.78	37.43	106.19					
0.1952	1.1572	1.5441	26.73	37.42	106.13					
0.1014	1.1576	1.5441	26.64	37.40	106.05					
0.0000	1.1584	1.5440	26.52	37.37	105.94					

RESULTS

Table II gives the composition, density, refractive index, dielectric constant, molar refraction (R_D), and molar polarization (P) of the binary solutions of each of the nitrotoluene isomers with each of the sylene isomers and of the *o*- and *m*-nitrotoluene isomers with chloroform and cyclohexane, as well as the solution of *o*-nitrotoluene with *m*-nitrotoluene, in most cases at two temperatures, 25° and 35° C. In the composition column the mole fraction listed is that of the first named of the binary components. The systems containing *p*-nitrotoluene do not cover the complete range of composition due to the limited solubility of this isomer.

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Effect of Polar Components on the Relative Volatility of the Binary System *n*-Hexane–Benzene

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Vapor liquid equilibrium data are presented for the binary systems *n*-hexane–1-propanol, benzene–1-propanol and *n*-hexane–benzene at 760 mm. of mercury pressure. In addition ternary data are presented at selected compositions with respect to the 1-propanol in the 1-propanol, benzene, *n*-hexane system at 760 mm. The results indicate the relative volatility of *n*-hexane relative to benzene increases appreciably with addition of 1-propanol.

THE RAPID growth of the petrochemical industry has led to the wide application of extractive distillation as a means of separating closely boiling compounds. One of the problems in the field of extractive distillation is to find a quantitative method of assessing solvents, in terms of the physical properties of the constituents, in order to select the most efficient solvent for a particular process. This investigation is another in a series (*8, 10, 11, 14, 16, 18*) initiated to determine experimentally the effect of polar components on the relative volatility of binary systems. Anderson (*1*), Gerster (*4*), Prausnitz (*15*), and Pierotti (*13*) have reported some investigations in this area.

The binary system studied in this work was composed of *n*-hexane and benzene. These hydrocarbons are difficult to separate because of closeness of boiling points. 1-Propanol was used as a solvent. Vapor-liquid equilibria of the binary systems *n*-hexane–benzene, *n*-hexane–1-propanol, benzene–1-propanol, and of the ternary system *n*-hexane–benzene–1-propanol were determined at 760 mm. of mercury absolute, using a modified Colburn still (*9*). The change in relative volatility of *n*-hexane relative to benzene, in the presence of 1-propanol, was calculated.

MATERIALS

n-Hexane, 99 mole % (min.) grade, was obtained from Phillips Petroleum Co., the reagent grade benzene was obtained from Merck and Co., and the Baker analyzed reagent grade 1-propanol was obtained from Baker Chemical Co. Table I compares the literature and experimental values of physical properties of these materials.

APPARATUS

A modified Colburn equilibrium still (*9*) was used to obtain the vapor-liquid equilibrium data. The modifications and the general procedure have been reported in earlier articles (*5, 17*). Temperatures were measured using a Copper-Constantan thermocouple and a Type K Leeds & Northrup potentiometer. A Bausch & Lomb precision refractometer was used to measure the refractive index of the vapor and liquid samples using a sodium D line light source. A Cottrell boiling point apparatus was used to check the purity of the compounds and to calibrate the equilibrium still thermocouple. The accuracy of the refractometer was tested by the test pieces supplied by Bausch & Lomb, Inc. Pressure was measured to within +0.5 mm. of mercury using a calibrated mercury manometer.

PROCEDURE

The procedures for determining vapor-liquid equilibrium data for the three binary systems were essentially those described by Haynes and Van Winkle (*5*). For each of the binary hydrocarbon systems, refractive index calibration curves were obtained with samples of 12 to 15 different known concentrations at 30° C. The compositions of vapor and liquid samples were read from the calibration curves. In the case the ternary system, three mixtures of *n*-hexane–benzene in the mole ratios of 25 to 75, 50 to 50, and 75 to 25 were used. 1-Propanol was added to each of the above mixtures to give equivalent mole fractions of 0.33, 0.50, 0.67, 0.75, and 0.80 in the ternary mixture. These mixtures were subjected to equilibrium distillation in the Colburn still and the vapor and liquid samples were obtained. The 1-propanol in these samples was extracted with water. The hydrocarbon layer was dried overnight by adding crystals of Drierite, which removed any traces of water remaining in the hydrocarbon mixture. The composition of the added agent-free samples was determined in the refractometer maintained at 30° C.

DISCUSSION OF RESULTS

Activity coefficients for the components in the binary mixture were calculated by the following equation.

$$\gamma_i = \frac{\nu_i\, y_i\, P_T}{x_i\, P_i} \tag{1}$$

The fugacity coefficient, ν_i, was assumed to be unity for all of the data reported here. Calculation of fugacity coef-

Table II. Vapor-Liquid Equilibrium Data Pressure = 760 mm. of Hg Absolute Hexane-Benzene System

	Experimental				Calculated (*2*)	
	Hexane-Benzene System					
Temp., ° C.	x_H	y_H	γ_H	γ_B	γ_H	γ_B
77.6	0.073	0.140	1.46	1.00	1.53	1.00
75.1	0.172	0.268	1.28	1.03	1.36	1.02
73.4	0.268	0.376	1.22	1.05	1.25	1.05
72.0	0.372	0.460	1.12	1.11	1.16	1.08
70.9	0.462	0.540	1.09	1.15	1.11	1.12
70.0	0.585	0.644	1.06	1.18	1.06	1.18
69.4	0.692	0.725	1.03	1.26	1.03	1.24
69.1	0.792	0.807	1.01	1.32	1.01	1.29
69.0	0.828	0.838	1.00	1.34	1.01	1.32
68.9	0.883	0.888	1.00	1.35	1.00	1.35
68.8	0.947	0.950	1.00	1.36	1.00	1.39
68.8	0.962	0.964	1.00	1.36	1.00	1.40
	Hexane–1-Propanol System					
Temp., ° C.	x_H	y_H	γ_H	$\gamma_{1\text{-}P}$	γ_H	$\gamma_{1\text{-}P}$
89.6	0.024	0.256	6.04	1.03	6.17	1.00
82.0	0.060	0.490	5.46	1.01	5.25	1.01
74.6	0.144	0.662	3.67	1.01	3.74	1.05
71.9	0.236	0.728	2.80	1.02	2.73	1.13
71.2	0.262	0.716	2.53	1.15	2.52	1.16
70.0	0.370	0.760	1.97	1.20	1.90	1.34
68.4	0.476	0.786	1.67	1.39	1.53	1.55
67.7	0.620	0.800	1.33	1.85	1.32	2.01
67.0	0.752	0.836	1.18	2.41	1.09	2.63
66.4	0.784	0.856	1.18	2.49	1.06	2.82
66.2	0.904	0.916	1.10	3.30	1.01	3.71
65.8	0.95	1.10	1.10	3.85	1.00	4.17
67.2	0.975	0.97	1.05	4.32	1.00	4.40
	Benzene–1-Propanol System					
Temp. ° C.	x_B	y_B	γ_B	$\gamma_{1\text{-}P}$	γ_B	$\gamma_{1\text{-}P}$
92.8	0.049	0.142	1.99	1.07	2.34	1.00
88.4	0.104	0.296	2.22	1.12	2.21	1.01
84.75	0.180	0.436	2.10	1.14	2.04	1.02
82.0	0.254	0.530	1.97	1.17	1.88	1.04
79.0	0.398	0.622	1.62	1.33	1.61	1.13
77.4	0.504	0.680	1.47	1.46	1.44	1.24
76.51	0.64	0.728	1.27	1.78	1.25	1.49
76.0	0.764	0.774	1.15	2.31	1.12	1.94
76.05	0.792	0.776	1.11	2.59	1.10	2.10
76.25	0.834	0.812	1.10	2.70	1.06	2.39
76.88	0.916	0.864	1.04	3.75	1.02	3.24
78.25	0.956	0.916	1.01	4.16	1.01	3.89

Table I. Properties of Materials

	n-Hexane		Benzene		1-Propanol	
	Exptl.	Lit. (*3*)	Exptl.	Lit. (*3*)	Exptl.	Lit. (*3*)
Refractive Index, n_D^{30}	1.36996	1.36949	1.49469	1.49460	1.38146	1.38160
Density, d_4^{30}	0.65043	0.65026	0.86839	0.86829	0.7962	0.7960
Boiling point, 760 mm. Hg, ° C.	68.8	68.74	80.1	80.1	97.25	97.29
Antoine Constants						
A		6.87773		6.89745		7.99733
B		1171.53		1206.35		1569.70
C		224.366		220.237		209.5

Where $\log P = A - [B/(C + t)]$, P = mm. Hg., t = ° C.

ficients by the generalized f/P chart (7) indicated the assumption to be valid. The vapor-liquid equilibrium data for the three binaries are reported in Table II and shown graphically in Figures 1 to 3. The data were correlated by the Carlson and Colburn modified van Laar equations (2).

$$\log \gamma_1 = \frac{A}{\left(1 + \frac{A}{B}\frac{x_1}{x_2}\right)^2} \tag{2a}$$

$$\log \gamma_2 = \frac{B}{\left(1 + \frac{B}{A}\frac{x_2}{x_1}\right)^2} \tag{2b}$$

The values of the constants in the correlation were evaluated by trial and error methods to give equations which gave the least deviation between calculated and experimental data and are as follows:

	Modified van Larr Constants	
	A	B
Hexane–benzene	0.23	0.155
Hexane–1-propanol	0.84	0.67
Benzene–1-propanol	0.39	0.69

The values of activity coefficients calculated by Equation 2 are also given in Table II. A defined deviation between the calculated and experimental activity coefficients was evaluated by the formula:

$$\omega = \frac{\sum k^2 - (\sum k)^2\, n^{1/2}}{(n-1)} \tag{3}$$

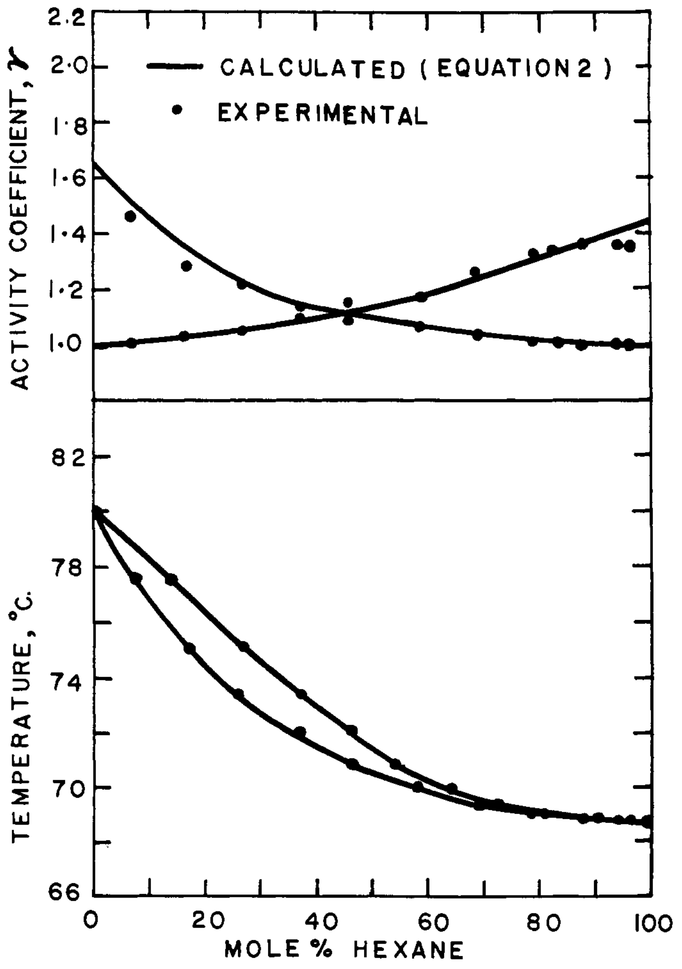

Figure 1. Hexane-benzene system at 760 mm. of Hg

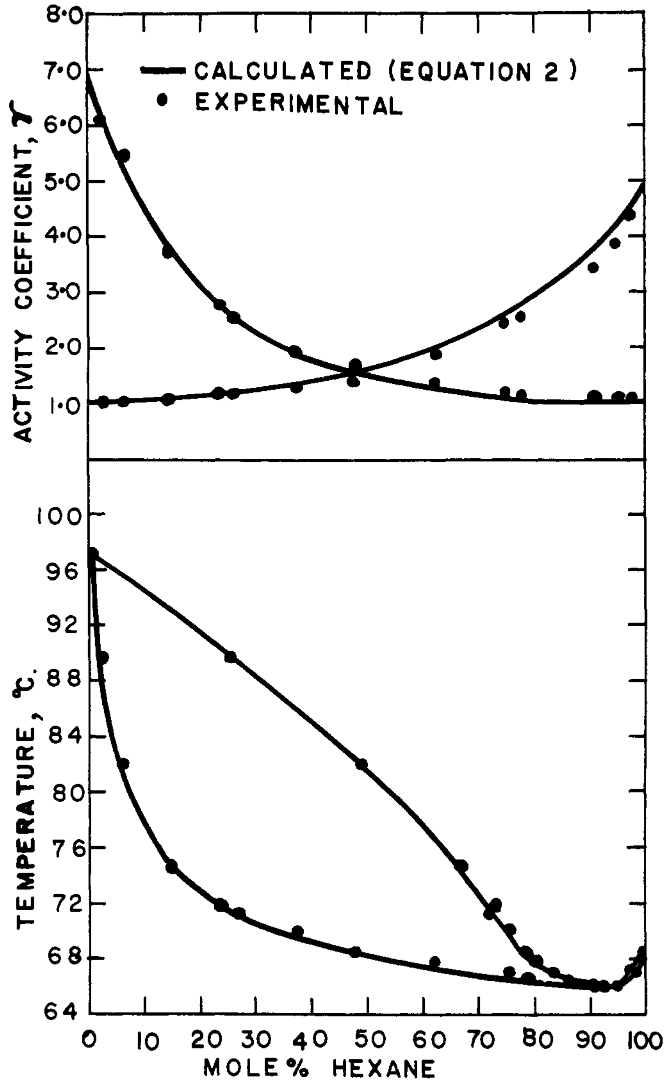

Figure 2. Hexane–1-propanol system at 760 mm. of Hg

where

k = deviation of experimental activity coefficients values from calculated values
n = number of experimental points
ω = defined deviation of k from a mean value of k

The deviations are as follows:

H – B		H-1-P		B-1-P	
H	B	H	1-P	B	1-P
0.029	0.023	0.101	0.137	0.112	0.188

Maximum and minimum values of the activity coefficients were calculated to show the limits of the experimental deviations. Probably refractometer error for the n-hexane–benzene and benzene–1-propanol system was within 0.001 mole fraction and for the n-hexane–1-propanol system, 0.005 mole fraction. Pressure errors were within ±0.5 mm. of Hg. and temperature errors were within ±0.1° C.

$$\gamma_{\max} = \frac{(y_1 + 0.001)(P_T + 0.5)}{(x_1 - 0.001)(P_1 \text{ at } t - 0.1^\circ \text{C.})} \tag{4a}$$

$$\gamma_{\min} = \frac{(y_1 - 0.001)(P_T - 0.5)}{(x_1 + 0.001)(P_1 \text{ at } t + 0.1^\circ \text{C.})} \tag{4b}$$

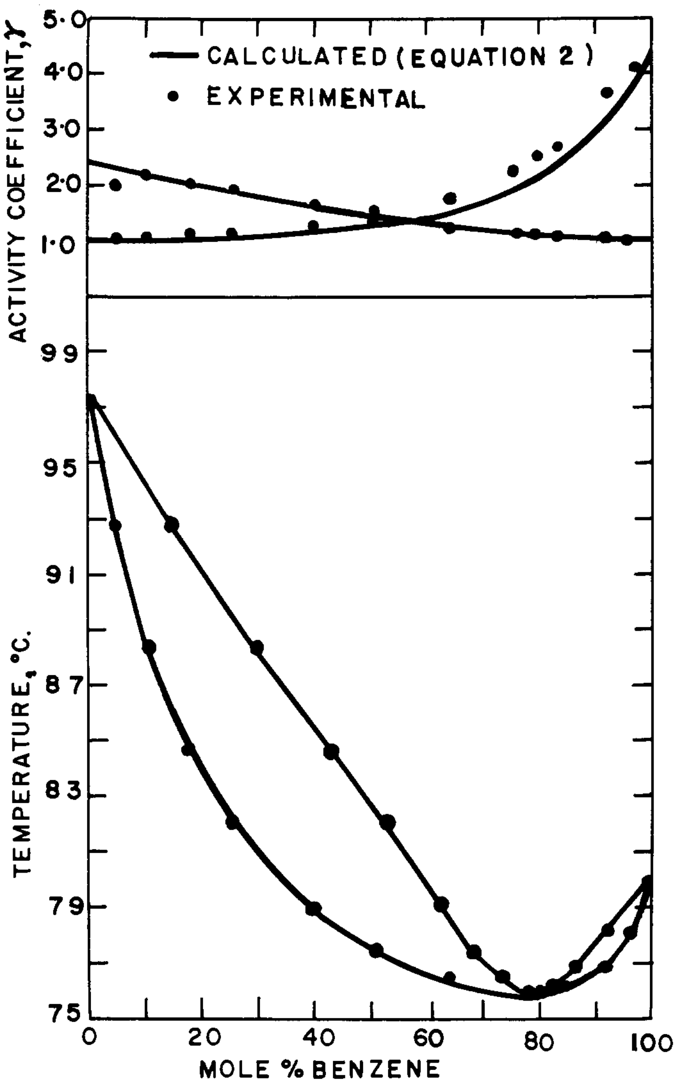

Figure 3. Benzene–1-propanol system at 760 mm. of Hg

The defined deviation between the experimental activity coefficients and the $\gamma_{\min}$ and $\gamma_{\min}$ values calculated by Equation 3, in the range of $x = 0.15$ to $x = 0.85$, are as follows:

	H − B		H-1-P		B-1-P	
	H	B	H	1-P	B	1-P
$\omega_{\max\gamma}$	0.022	0.006	0.034	0.048	0.009	0.013
$\omega_{\min\gamma}$	0.006	0.016	0.026	0.053	0.005	0.012

The defined deviation over the full range will be larger because of the influence of the high errors in the end values of γ's. It may be seen from Table II that the deviation between the calculated (Equation 2) and experimental values of γ's is maximum in the middle range and this deviation depends on the type of equation applied for calcualtion the γ's. It is not necessary that the defined deviation between calculated and experimental γ's be between $\omega_{\max\gamma}$ and $\omega_{\min\gamma}$ values as they are only deviations due to experimenal errors.

The Herrington test (*6*) was applied to the activity coefficient-composition data of the binaries. In accordance with the criterion of the test the data were found to be consistent.

The experimental data for all the three binaries show that they are non-ideal in nature. Tongberg and Johnston (*19*), studying the equilibrium of *n*-hexane–benzene, reported no separation obtainable at concentration above 97 mole % hexane. This is consistent with the observation made in this investigation and also that by Myers (*12*). The *n*-hexane–1-propanol and benzene–1-propanol systems evidence minimum boiling azeotropes. It is indicated by the interpolation of the data that *n*-hexane–1-proponal form an azeotrope at 95 mole % hexane at 65.8° C. and the benzene–1-propanol form an azeotrope at 77.5 mole % benzene at 76° C.

The variation of the relative volatility with the concentration of the solvent in the ternary system is reported in Table III and shown in Figure 4. These data show that the greatest change of relative volatility is obtained at higher concentration of the solvent. As the vapor and

Table III. Variation of Relative Volatility with Solvent Concentration

Ternary System: Hexane–Benzene–1-Propanol at 760 Mm. Hg Absolute

Binary Mixture		Mole Fraction 1-Propanol in Mixture	Temp.,	Mole Fraction Isopropanol-Free Basis				
x'_H	x'_B	$x_{1\text{-}P}$	° C.	x_H	y_H	x_B	y_B	$\alpha(H/B)$
0.25	0.75	0.00	74.1	0.21	0.326	0.79	0.674	1.82
		0.33	27.0	0.193	0.346	0.807	0.654	2.21
		0.50	74.3	0.172	0.332	0.828	0.668	2.39
		0.67	78.7	0.156	0.325	0.884	0.675	2.60
		0.75	82.3	0.154	0.327	0.846	0.673	2.67
		0.80	84.8	1.36	0.300	0.864	0.700	2.72
0.50	0.50	0.00	71.2	0.428	0.528	0.572	0.472	1.50
		0.33	67.5	0.424	0.574	0.576	0.426	1.83
		0.50	70.2	0.400	0.572	0.600	0.428	2.00
		0.67	75.2	0.396	0.593	0.606	0.407	2.23
		0.75	80.3	0.375	0.58	0.625	0.420	2.30
		0.80	83.0	0.368	0.574	0.632	0.426	2.31
0.75	0.25	0.00	69.4	0.684	0.724	0.316	0.276	1.31
		0.33	66.3	0.68	0.776	0.32	0.224	1.63
		0.50	68.2	0.63	0.744	0.37	0.256	1.71
		0.67	72.8	0.658	0.776	0.342	0.224	1.80
		0.75	78.2	0.635	0.766	0.365	0.234	1.88
		0.80	80.7	0.605	0.746	0.395	0.254	1.92

x' = solvent free basis

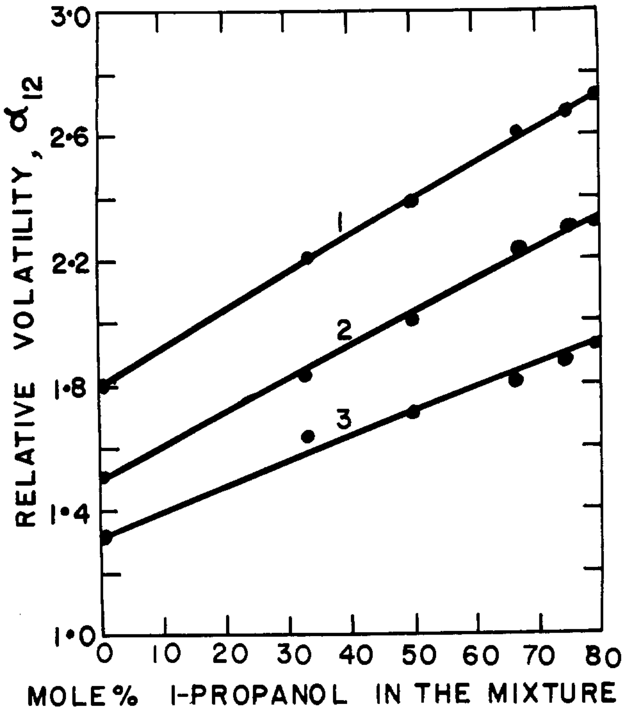

Figure 4. Effect of 1-propanol on relative volatility of binary system hexane-benzene at 760 mm. of Hg

	Mole %	
Curve No.	Hexane	Benzene
1	25	75
2	50	50
3	75	25

liquid samples were extracted with water, it was ensured by laboratory tests that the solvent-free hydrocarbon concentration did not change because of the different solubilities of the hydrocarbons in water. Also, it was found that the drying agent, Drierite, had no selective absorption capacity for the hydrocarbon mixture involved.

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NOMENCLATURE

A, B = Carlson and Colburn modified van Laar constants
d = density, g./cc.
n = refractive index
P_T = total pressure, mm. Hg
P = vapor pressure
t = temperature, ° C.
x_i = mole fraction of component i in liquid phase
y_i = mole fraction of component i in vapor phase
H = hexane
B = benzene
1-P = 1-propanol
α = relative volatility
γ = activity coefficient
ν = fugacity coefficient, f/p

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