Figure 3. K values of tetralin at 663 K.

Results and Discussion

Table I presents the compositions of both saturated vapor and liquid phases determined at two temperatures, 543 and 663 K, and at total pressures from 50 to 250 atm. Three binary gas feed mixtures of ca. 75, 80, and 90 mol % of hydrogen were used successively at each condition of temperature and pressure. The binary feed gas mixtures were kept lean in carbon dioxide in order to avoid condensation when compressed.

At least two samples were taken for each cell effluent stream during one experiment at a fixed temperature, pressure, and feed gas composition. The volumetric measurements of the multiple samples agreed to within 1%, while the gas-chromatographic analyses for the gas composition from multiple samples were reproducible to within 1.5%. The reported values in Table I are the averages of the multiple samples.

Figures 1–3 show the variation of K values of hydrogen, carbon dioxide, and tetralin, respectively, with the tetralin-free mole fraction of carbon dioxide in equilibrium gas mixture at 663 K. The end points at $y_{CD} = 0$ in Figures 1 and 3, which correspond to binary mixtures of hydrogen + tetralin, were taken from Simnick et al. (2). There is substantial variation of the K values of tetralin to changing compositions at the higher pressures. The K values of carbon dioxide show the least sensitivity to the variation of the gas compositions. Similar results were observed at 543 K.

Glossary

K	equilibrium vaporization ratio, $K \equiv y/x$
p	pressure, atm
T	temperature, K
x	mole fraction in liquid phase
y	mole fraction in vapor phase

Subscripts

CD	carbon dioxide
H	hydrogen
T	tetralin

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Isothermal Compressibility and Derived Properties of the Benzene + Toluene System at Various Temperatures

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The isothermal compressibility κ_T has been determined for benzene + toluene mixtures at 298.15, 308.15, 318.15, and 333.15 K. A direct measurement piezometric technique has been used. From our own results and supplementary literature data, we have calculated the isentropic compressibility κ_s and the heat capacity at constant volume C_v. The corresponding excess functions $-V^{-1}(\partial V^E/\partial p)_T$, $-V^{-1}(\partial V^E/\partial p)_s$, and C_v^E have been also calculated in every case. From this detailed effort we expected to achieve a better understanding of the behavior of these excess functions as a function of the variables mole fraction and temperature.

Introduction

The isothermal compressibility κ_T and the isentropic compressibility κ_s defined respectively as $\kappa_T = -V^{-1}(\partial V/\partial p)_T$ and $\kappa_s = -V^{-1}(\partial V/\partial p)_s$ are related by

$$\kappa_T = \kappa_s + \alpha^2 TV/C_p \qquad (1)$$

A correlation between the heat capacities and the compressibilities is

$$C_v/C_p = \kappa_s/\kappa_T \qquad (2)$$

The heat capacity ratio γ is defined as

$$\gamma = C_p/C_v \qquad (3)$$

In this work from our own κ_T measurements and the literature reported values of α and C_p for the corresponding mixtures, we have calculated κ_s, C_v, and γ at four temperatures for the benzene (1) + toluene (2) system.

Experimental Section

Isothermal compressibility has been measured by a piezometric technique allowing direct reading of volume changes occurring as pressure varies at constant temperature. This technique, which has been described in great detail previously (1–3), allows κ_T to be measured with a precision better than 0.5%. Liquid volume values required to obtain κ_T were calculated from the liquid weight and density values. These densities

Table I. Experimental Densities (ρ) at Various Temperatures and Comparison Data at 298.15 K

		$\rho/(\text{g cm}^{-3})$				
		expt				
compd	source	298.15 K	308.15 K	318.15 K	333.15 K	lit.,[a] 298.15 K
benzene	Carlo Erba R.S.	0.873 67	0.862 96	0.852 20	0.835 94	0.873 70
toluene	Merck z.a.	0.861 89	0.852 58	0.843 18	0.828 95	0.862 30

[a] Reference 4.

Table II. Comparison of Toluene Values with Literature Data

	κ_T/TPa^{-1}	
T/K	this work	lit.
298.15	911.5	916,[a] 920[b]
308.15	977.9	979[b]
318.15	1053.9	1051[b]
333.15	1183.6	1172,[c] 1200,[d] 1172[e]

[a] From ultrasonic velocity measurements (6). [b] Interpolated from ultrasonic velocity measurements (7). [c] From P-V measurements (8). [d] From P-V measurements (9). [e] From P-V measurements (10).
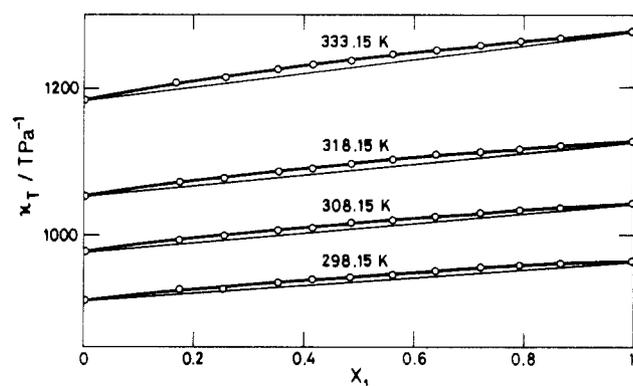
Figure 1. Isothermal compressibilities κ_T against the mole fraction x_1 of benzene.

were measured by a picnometric technique for benzene and toluene at four temperatures. Table I reports the chemical source and the densities as determined by us. For the sake of comparison, we included in the last column the corresponding literature data at 298.15 K.

The procedure to purify the mercury used in the sealing piezometer is described elsewhere (3).

The mixture volume V is given by eq 4, where V_1 and V_2

$$V = x_1 V_1 + x_2 V_2 + V^{\text{E}} \tag{4}$$

are the molar volumes for the pure substances. The excess volume V^{E} has been taken from data at various temperatures by Nigam and Singh (5).

Results and Discussion

The isothermal compressibility for the benzene (1) + toluene (2) system was determined at 298.15, 308.15, 318.15, and 333.15 K at negligible pressures.

Measurements on the pure substances were run twice. The values of κ_T for toluene are given in Table II, where corresponding literature data are included for the sake of comparison. A similar comparison for benzene has been reported previously (3).

Experimental κ_T values for various mole fractions are given in Table III. For each temperature these values were fitted against the benzene mole fraction x_1 by polynomials of the type

$$Y(x_1) = \sum_{0}^{2} A_i x_1{}^i \tag{5}$$

assigning double weight to results for the pure substances. The

Table III. Experimental Values of Isothermal Compressibility κ_T, $\kappa_T{}^{\text{E}}$, and $(\partial V^{\text{E}}/\partial p)_T$ at Negligible Pressures

x_1	κ_T/TPa^{-1}	$\kappa_T{}^{\text{E}}/\text{TPa}^{-1}$	$10^{-3}(\partial V^{\text{E}}/\partial p)_T/$ $(\text{cm}^{-3}\,\text{mol}^{-1}\,\text{TPa}^{-1})$
		$T = 298.15$ K	
0	911.5	0	0
0.1749	926.5	7.1	−0.74
0.2551	927.1	3.9	−0.40
0.3549	936.0	7.9	−0.80
0.4176	940.3	9.0	−0.90
0.4877	943.3	8.2	−0.82
0.5612	946.2	7.2	−0.71
0.6414	951.0	7.4	−0.72
0.7234	955.9	7.7	−0.73
0.7935	958.8	6.3	−0.59
0.8687	962.3	5.0	−0.47
1	966.0	0	0
		$T = 308.15$ K	
0	977.9	0	0
0.1749	993.1	5.4	−0.56
0.2551	999.0	6.8	−0.70
0.3549	1005.9	7.8	−0.79
0.4176	1008.9	6.9	−0.69
0.4877	1017.4	10.7	−1.07
0.5612	1021.0	9.5	−0.94
0.6414	1025.5	8.6	−0.83
0.7234	1030.1	7.3	−0.69
0.7935	1034.1	6.2	−0.57
0.8687	1037.7	4.2	−0.38
1	1044.0	0	0
		$T = 318.15$ K	
0	1053.9	0	0
0.1749	1071.4	6.8	−0.71
0.2551	1078.0	8.0	−0.83
0.3549	1086.2	9.5	−0.98
0.4176	1091.0	9.9	−1.01
0.4877	1098.0	11.8	−1.19
0.5612	1101.9	10.4	−1.04
0.6414	1110.6	12.9	−1.27
0.7234	1113.1	8.8	−0.84
0.7935	1115.9	6.1	−0.57
0.8687	1121.3	5.1	−0.47
1	1128.0	0	0
		$T = 333.15$ K	
0	1183.6	0	0
0.1749	1206.8	9.4	−1.00
0.2551	1213.8	9.9	−1.04
0.3549	1224.9	12.3	−1.29
0.4176	1230.9	12.8	−1.33
0.4877	1238.4	14.0	−1.43
0.5612	1245.9	14.6	−1.48
0.6414	1250.8	12.0	−1.18
0.7234	1256.9	9.8	−0.95
0.7935	1261.8	7.6	−0.72
0.8687	1266.3	4.0	−0.36
1	1277.0	0	0

fitting A_i coefficients and the standard deviations σ are reported in Table IV.

Values of κ_T vs. x_1 are plotted in Figure 1. The curved line corresponds to eq 5. Obviously κ_T increases with temperature at fixed mole fraction.

To get κ_s from κ_T through eq 1, one requires knowledge of α and C_p. The values of α were obtained from volume change measurements as a function of mole fraction and temperature

Table IV. Coefficients A_i for the Adjustment of κ_T, κ_s, and C_v in Eq 5

function	A_0	A_1	A_2	σ
	$T = 298.15$ K			
κ_T/TPa^{-1}	911.7	75.0	−20.3	1.2
	±0.7	±3.3	±3.2	
κ_s/TPa^{-1}	679.2	16.1	−23.9	
$C_v/(\text{J K}^{-1}\text{ mol}^{-1})$	117.14	−24.18	0.98	
	$T = 308.15$ K			
κ_T/TPa^{-1}	977.9	88.4	−22.2	0.8
	±0.5	±2.4	±2.3	
κ_s/TPa^{-1}	734.2	21.8	−26.9	
$C_v/(\text{J K}^{-1}\text{ mol}^{-1})$	120.22	−25.45	1.01	
	$T = 318.15$ K			
κ_T/TPa^{-1}	1053.8	103.2	−29.2	1.0
	±0.6	±2.9	±2.7	
κ_s/TPa^{-1}	798.5	28.0	−35.4	
$C_v/(\text{J K}^{-1}\text{ mol}^{-1})$	123.59	−26.80	0.88	
	$T = 333.15$ K			
κ_T/TPa^{-1}	1184.1	127.3	−35.4	1.1
	±0.7	±3.0	±2.9	
κ_s/TPa^{-1}	910.6	33.9	−43.9	
$C_v/(\text{J K}^{-1}\text{ mol}^{-1})$	128.97	−28.96	0.92	

(5, 11), and those of C_p were calculated from corresponding pure-component molar values, $C_{p,i}$, and the excess function, C_p^E, by using eq 6.

$$C_p = x_1 C_{p,1} + x_2 C_{p,2} + C_p^E \qquad (6)$$

Values of C_p for benzene were obtained by interpolating measurements by Staveley et al. (12), whereas those for toluene were calculated by interpolation measurements by Scott et al. (13). Recently Fortier and Benson (14) measured C_p^E for the benzene + toluene system at 298.15 K. In the region around the maximum, they obtained the value of −0.31 J K^{-1} mol^{-1}, whereas the C_p value was −146.08 J K^{-1} mol^{-1}. We have used their measurements. Because the rather small C_p^E values (~0.2% of C_p at the most), we may accept as negligible the error involved assuming C_p^E independent of temperature.

Values of all of the quantities calculated for the pure substances are reported in Table V. In all cases eq 1–3 were used to calculate κ_s, C_v, and γ, respectively, and the κ_s and C_v values thus obtained were fitted to polynomial equations like eq 5. The corresponding A_i coefficients are in Table IV.

Differentiating eq 4 with respect to pressure at constant temperature and rearranging terms, we get eq 7, where

$$(\partial V^E/\partial p)_T = (\partial V/\partial p)_T - x_1(\partial V_1/\partial p)_T - x_2(\partial V_2/\partial p)_T \qquad (7)$$

$(\partial V^E/vp)_T$ stands for the difference between the real and ideal values of the system and is therefore an excess function. Some authors (15) consider it the most important quantity in this kind of study. Therefore we have calculated it, and the results are given in Table III.

Still the most utilized "excess" function is the one defined by Orwoll and Flory (16) as

$$\kappa_T^E = -V^{-1}(\partial V^E/\partial p)_T = \kappa_T - \phi_1\kappa_{T,1} - \phi_2\kappa_{T,2} \qquad (8)$$

where ϕ_i is the corresponding volume fraction defined as

$$\phi_i = x_i V_i / V \qquad (9)$$

V being the mixture volume calculated from eq 4. "Excess" isothermal compressibility, κ_T^E, is not a proper excess function but is widely used (16, 17). Therefore, we have calculated it, and its values at the four temperatures reported in Table III are fitted to eq 10. The B_0 coefficients and the standard deviations

$$Y^E = x_1 x_2 B_0 \qquad (10)$$

σ are given in Table VI.
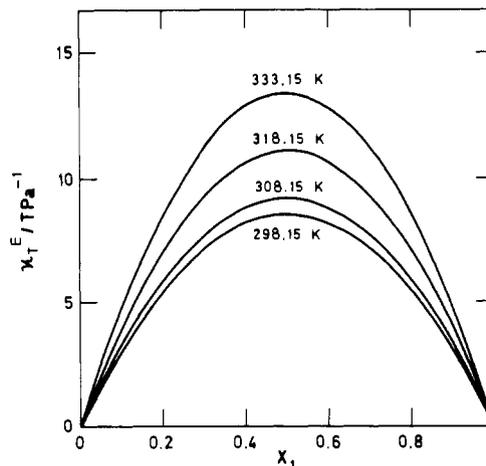
Figure 2. "Excess" isothermal compressibilities κ_T^E against the mole fraction x_1 of benzene.
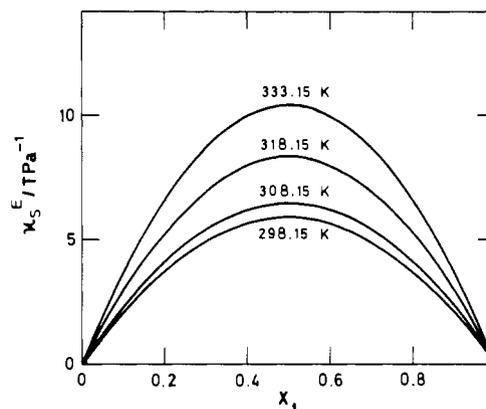
Figure 3. "Excess" isentropic compressibilities κ_s^E against the mole fraction x_1 of benzene.
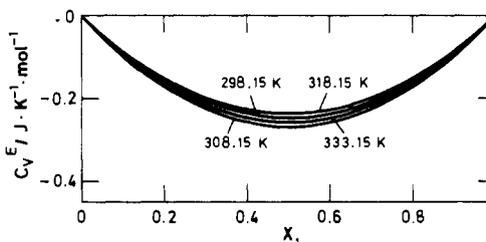
Figure 4. Excess heat capacities at constant volume C_v^E against the mole fraction x_1 of benzene.

We have also calculated the "excess" isentropic compressibility, κ_s^E, and the excess heat capacity at constant volume, C_v^E, applying respectively eq 11 and 12, where $C_{v,i}$ is the molar

$$\kappa_s^E = -V^{-1}(\partial V^E/\partial p)_s = \kappa_s - \phi_1\kappa_{s,1} - \phi_2\kappa_{s,2} \qquad (11)$$

$$C_v^E = C_v - x_1 C_{v,1} - x_2 C_{v,2} \qquad (12)$$

heat capacity at constant volume for the pure component i. Similary, results at the four temperatures for both excess functions were fitted to equations like eq 10. The B_0 coefficients are in Table VI.

Plots of the three excess functions κ_T^E, κ_s^E, and C_v^E against x_1 are given in Figures 2–4, respectively. The two "excess" quantities κ_T^E and κ_s^E are positive throughout, whereas C_v^E is negative. Also, the three excess functions are symmetric in this representation, their maxima or minima being located at x_1 = 0.5.

The plots show that κ_T^E and κ_s^E increase with temperature at a constant mole fraction, whereas no simple definite trend could be ascribed to C_v^E. Worth mentioning is that C_v^E values

Table V. Values of Compressibilities κ_T and κ_s, Thermal
Expansivity α, Heat Capacities C_p and C_v, and Heat Capacity
Ratio γ for Pure Components

function	298.15 K	308.15 K	318.15 K	333.15 K
κ_T/TPa^{-1}		Benzene		
κ_T/TPa^{-1}	966.0	1044.0	1128.0	1277.0
κ_s/TPa^{-1}	671.1	729.2	791.3	901.7
α/kK^{-1}	1.223^a	1.244^a	1.268^a	1.313^a
$C_p/(\text{J K}^{-1}\text{ mol}^{-1})$	135.22^b	137.14^b	139.26^b	143.00^b
$C_v/(\text{J K}^{-1}\text{ mol}^{-1})$	93.94	95.79	97.69	100.97
γ	1.439	1.432	1.425	1.416
		Toluene		
κ_T/TPa^{-1}	911.5	977.9	1053.9	1183.6
κ_s/TPA^{-1}	679.1	734.2	798.5	910.1
α/kK^{-1}	1.071	1.083	1.095	1.113
$C_p/(\text{J K}^{-1}\text{ mol}^{-1})$	157.24^c	160.13^c	163.10^c	167.68^c
$C_v/(\text{J K}^{-1}\text{ mol}^{-1})$	117.14	120.22	123.58	128.94
γ	1.342	1.332	1.320	1.300

^{a} Interpolated from ref *11*. ^{b} Interpolated from ref *12*.
^{c} Interpolated from ref *13*.

Table VI. Values of Coefficient B_0 for the Adjustment of
κ_T^E, κ_s^E, and C_v^E in Eq 10

function	B_0	σ
	$T = 298.15$ K	
$\kappa_T^E/\text{TPa}^{-1}$	34.0 ± 9.8	1.4
$\kappa_s^E/\text{TPa}^{-1}$	23.5	
$C_v^E/(\text{J K}^{-1}\text{ mol}^{-1})$	0.98	
	$T = 308.15$ K	
$\kappa_T^E/\text{TPa}^{-1}$	36.5 ± 6.3	0.9
$\kappa_s^E/\text{TPa}^{-1}$	25.8	
$C_v^E/(\text{J K}^{-1}\text{ mol}^{-1})$	1.06	
	$T = 318.15$ K	
$\kappa_T^E/\text{TPa}^{-1}$	44.5 ± 8.5	1.2
$\kappa_s^E/\text{TPa}^{-1}$	33.3	
$C_v^E/(\text{J K}^{-1}\text{ mol}^{-1})$	0.94	
	$T = 333.15$ K	
$\kappa_T^E/\text{TPa}^{-1}$	53.5 ± 8.5	1.2
$\kappa_s^E/\text{TPa}^{-1}$	41.3	
$C_v^E/(\text{J K}^{-1}\text{ mol}^{-1})$	1.00	

around the minima are only $\sim 0.15\%$ of the corresponding C_v
values, and that is within the experimental error.

Glossary

A_0, A_1, coefficients of adjustment in eq 5
..., A_i

B_0	coefficient of adjustment in eq 10
C_p	heat capacity at constant pressure, J K^{-1} mol^{-1}
C_p^E	excess heat capacity at constant pressure, J K^{-1} mol^{-1}
C_v	heat capacity at constant volume, J K^{-1} mol^{-1}
C_v^E	excess heat capacity at constant volume, J K^{-1} mol^{-1}
p	pressure, TPa
T	temperature, K
V	molar volume, cm^3 mol^{-1}
V^E	molar excess volume, cm^3 mol^{-1}
x_i	mole fraction of component i

Greek Letters

α	coefficient of thermal expansion, kK^{-1}
γ	heat capacities ratio
κ_s	isentropic compressibility, TPa^{-1}
κ_s^E	"excess" isentropic compressibility, TPa^{-1}
κ_T	isothermal compressibility, TPa^{-1}
κ_T^E	"excess" isothermal compressibility, TPa^{-1}
ρ	density, g cm^{-3}
σ	standard deviation
ϕ_i	volume fraction of component i

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