Table II. Solubility of CO_2 in Binary Mixtures

system	mole fraction of A	K_p,[a] mol/cm^3	K_H,[b] 1/atm
$NaNO_3$(A)-$LiNO_3$(B) (350 °C)	0	3.86×10^{-6}	1.54×10^{-4}
	0.07	4.70×10^{-6}	1.89×10^{-4}
	0.20	3.68×10^{-6}	1.52×10^{-4}
	0.25	4.67×10^{-6}	1.93×10^{-4}
	0.50	2.79×10^{-6}	1.19×10^{-4}
	0.52	3.18×10^{-6}	1.37×10^{-4}
	0.66	2.34×10^{-6}	1.03×10^{-4}
	1.00	1.04×10^{-6}	4.68×10^{-5}
$NaNO_3$(A)-$RbNO_3$(B) (350 °C)	0	1.88×10^{-6}	1.13×10^{-4}
	0.25	1.36×10^{-6}	7.66×10^{-5}
	0.50	1.18×10^{-6}	6.15×10^{-5}
	0.75	1.07×10^{-6}	5.27×10^{-5}
	1.00	1.04×10^{-6}	4.68×10^{-5}
NaCl(A)-KCl(B) (1000 °C)	0	9.08×10^{-7}	4.85×10^{-5}
	0.25	7.24×10^{-7}	3.65×10^{-5}
	0.50	8.17×10^{-7}	3.86×10^{-5}
	0.75	9.66×10^{-7}	4.23×10^{-5}
	1.00	1.01×10^{-6}	4.07×10^{-5}

[a] mol/cm^3 of CO_2 in molten salt at 1 atm. [b] mol of CO_2/mol of salt at 1 atm.

of K_p in Figure 3. The solubility data for the alkali halides in this work show fairly good agreement with the values predicted by eq 1. The data for the alkali nitrates, by contrast, are much larger than the predicted values. These deviations in the alkali nitrates may be attributed to the nonspherical shape of the NO_3^- ion, the negative energy of interaction between the ions and the CO_2 quadrupole, and the low temperature range of the measurements.

Figure 4 shows Henry's-law constants K_H mol of gas/(mol of salts atm) plotted against the mole fraction of $NaNO_3$ on semilogarithmic coordinates for the $NaNO_3$-$LiNO_3$ and $NaNO_3$-$RbNO_3$ systems. The Henry's-law constant of a gas in a binary solvent is expressed by the following equation (*9*):

$$\ln K_{H(a+b)} = X_a \ln K_{H(a)} + X_b \ln K_{H(b)} - \alpha_{ab} X_a X_b \qquad (2)$$

where X_a and X_b are mole fractions of a and b components, respectively. In the case of an ideal mixture, α_{ab} is equal to zero, and a plot of ln K_H against the mole fraction of one component of the mixture gives a straight line. Such a linear relation is observed in the $NaNO_3$-$RbNO_3$ system. The $NaNO_3$-$LiNO_3$ system, however, shows a slight positive deviation from ideal behavior, especially at high mole fraction of $LiNO_3$. This might be attributed to the small ionic radius of Li^+ in comparison with those of Na^+, Rb^+, and NO_3^-. A linear relation is also observed in the NaCl-KCl system at 1000 °C. These results are summarized in Table II.

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Vapor-Liquid Equilibrium in Ternary Mixtures of Hydrogen + Carbon Dioxide + Tetralin

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Vapor-liquid equilibrium was determined for the ternary system hydrogen + carbon dioxide + tetralin at 543 and 663 K, and 50-250 atm. The relative concentrations of hydrogen to carbon dioxide were systematically varied from 75 to 95 mol % of hydrogen at each condition of temperature and pressure. The effect of composition upon the *K* values was studied.

Introduction

Recent developments in coal hydrotreating processes have created a need for phase-equilibrium data of mixtures containing hydrogen and heavy hydrocarbons at high temperatures and pressures. We report in this work experimental data on vapor-liquid equilibrium in ternary mixtures of hydrogen + carbon dioxide + tetralin at the two temperatures of 543 and 663 K and pressures to 250 atm. The relative concentrations of hydrogen to carbon dioxide were varied, and three observations were made at each condition of temperature and pressure in order to determine the response of the *K* values to changing compositions.

The equilibrium data for this ternary system are not available in the literature. However, the constituent binary mixtures of hydrogen + tetralin (*2*) and carbon dioxide + tetralin (*1*) have been reported.

Experimental Section

For the study of binary mixtures of a light gas and a heavy solvent, the experimental apparatus and procedure have been described (*2*) in detail. Modification has been made of the apparatus and procedure for the study of ternary mixtures of two light gases and a heavy solvent such as the present mixture system. The modification has also been described (*3*). Briefly, a mixed gas stream is prepared of the two light gases at a specified composition. The binary gas mixture is compressed and mixed with a liquid stream of the heavy solvent. The combined gas and liquid heterogeneous mixture is heated to the desired temperature. The saturated phases are separated in

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Table I. Hydrogen + Carbon Dioxide + Tetralin Vapor-Liquid Equilibrium Data

T, K	p, atm	x_H	x_{CD}	x_T	y_H	y_{CD}	y_T
					0.9229[a]	0.0771[a]	
543.3	50.0	0.03516	0.00946	0.95538	0.8432	0.0747	0.0821
543.3	100.3	0.07021	0.01771	0.91208	0.8818	0.0724	0.0458
543.2	149.9	0.1042	0.0257	0.8701	0.8932	0.0726	0.0342
543.3	198.8	0.1345	0.0302	0.8353	0.8989	0.0713	0.0298
543.2	248.5	0.1638	0.0352	0.8010	0.9043	0.0691	0.0266
					0.8290[a]	0.1710[a]	
543.2	50.1	0.0321	0.0201	0.9478	0.7551	0.1612	0.0837
543.3	99.8	0.0633	0.0374	0.8993	0.7861	0.1655	0.0484
543.2	150.5	0.0946	0.0541	0.8513	0.7968	0.1661	0.0371
543.3	200.8	0.1254	0.0653	0.8093	0.8108	0.1570	0.0322
543.3	250.4	0.1542	0.0745	0.7713	0.8176	0.1527	0.0297
					0.7620[a]	0.2380[a]	
543.2	50.2	0.0293	0.0274	0.9433	0.6755	0.2372	0.0873
543.1	101.1	0.0588	0.0544	0.8868	0.7094	0.2388	0.0518
543.2	151.4	0.0874	0.0775	0.8351	0.7194	0.2399	0.0407
543.2	201.4	0.1162	0.0982	0.7856	0.7304	0.2340	0.0356
543.2	249.5	0.1422	0.1122	0.7456	0.7341	0.2318	0.0341
					0.9144[a]	0.0856[a]	
663.2	50.0	0.04340	0.00722	0.94938	0.4679	0.0432	0.4889
663.3	100.4	0.10605	0.01616	0.87779	0.6529	0.0569	0.2902
663.3	149.9	0.1640	0.0235	0.8125	0.7187	0.0617	0.2196
663.4	200.7	0.2229	0.0311	0.7460	0.7499	0.0641	0.1860
663.4	249.9	0.2723	0.0390	0.6887	0.7627	0.0694	0.1679
					0.8359[a]	0.1641[a]	
663.2	49.8	0.04028	0.01379	0.94593	0.4219	0.0825	0.4956
663.2	100.5	0.0997	0.0335	0.8668	0.5782	0.1164	0.3054
663.1	150.7	0.1566	0.0485	0.7949	0.6481	0.1222	0.2297
663.2	200.4	0.2081	0.0622	0.7297	0.6711	0.1275	0.2014
663.3	247.8	0.2559	0.0776	0.6665	0.6784	0.1368	0.1848
					0.7451[a]	0.2549[a]	
663.1	49.6	0.0356	0.0217	0.9427	0.3702	0.1377	0.4921
663.0	100.3	0.0897	0.0509	0.8594	0.5269	0.1758	0.2973
663.2	151.2	0.1425	0.0784	0.7791	0.5726	0.1933	0.2341
663.0	201.0	0.1931	0.1026	0.7043	0.5768	0.2112	0.2120
663.3	248.9	0.2470	0.1267	0.6263	0.5669	0.2229	0.2102

[a] Feed gas.

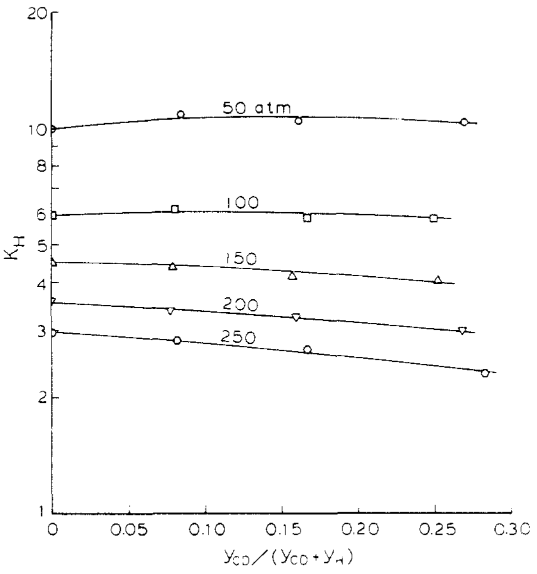

Figure 1. K values of hydrogen at 663 K.

an equilibrium cell, from which the effluents are withdrawn and sampled for analysis.

Tetralin was purchased from Aldrich Chemical Co. with a purity of 99+%. Carbon dioxide obtained from Matheson was Coleman Instrument grade of 99.99% purity. The purity of hydrogen as supplied by Airco was claimed to be 99.95+%. Matheson primary standard mixtures of hydrogen and carbon dioxide at carbon dioxide concentrations of 0.997, 9.932, 25.017, and 49.749 mol % were used for the calibration of the gas chromatograph.

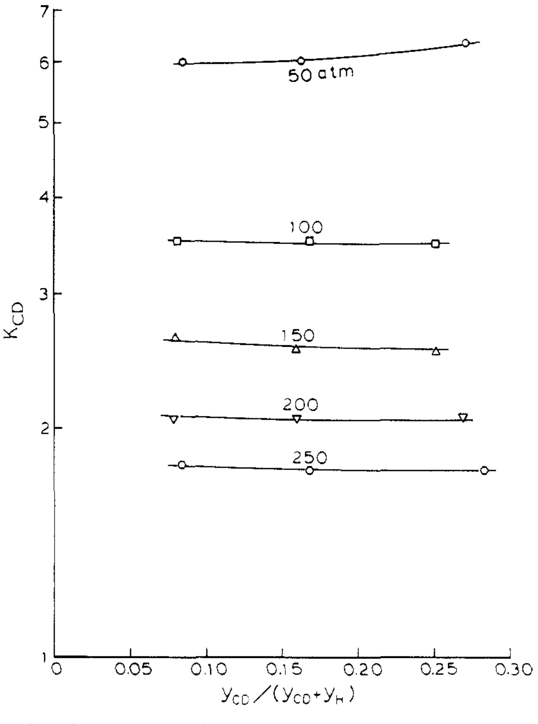

Figure 2. K values of carbon dioxide at 663 K.

Gas-chromatographic analyses of the condensate from the cell effluents showed no products from chemical reactions at any of the conditions studied, but the effluent tetralin was purified by distillation under a reduced nitrogen atmosphere before being reused.

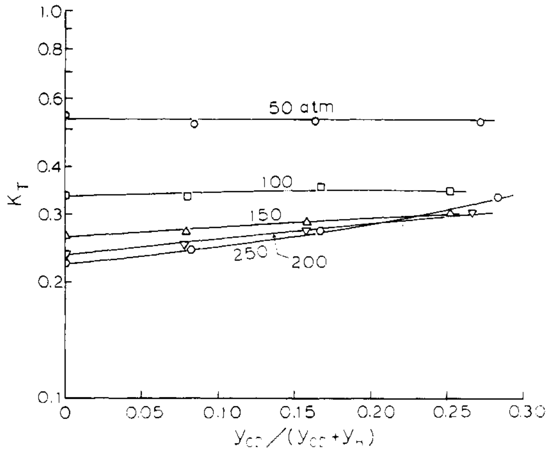

Figure 3. *K* values of tetralin at 663 K.

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 senstivity 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

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