

# Solubility of Hydrogen in Toluene at Elevated Temperatures and Pressures

James J. Simnick, Herbert M. Sebastian, Ho-Mu Lin, and Kwang-Chu Chao\*

School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907

Solubility of hydrogen in toluene is reported at four temperatures (188.7, 229.0, 269.0, 302.0 °C) and seven pressures from 20 to 250 atm. A flow apparatus is used to determine the new data.

## Introduction

Solubility of hydrogen in a number of organic liquid solvents has been reported in the literature. Simnick et al. (7) reported a survey of the data which showed that past work was mostly limited to temperatures below 200 °C. Investigations of Connolly and co-workers (1) and Grayson and Streed (2) were the major exceptions. Recent intensified development of hydrotreating processes has heightened interest in data at elevated temperatures and pressures. In this work we report vapor-liquid equilibrium in hydrogen/toluene mixtures at temperatures of 190–300 °C and pressures 20–250 atm. The present study is a continuation of our investigation of gas-liquid equilibria at elevated temperatures and pressures (5–10).

## Experimental Section

The equilibrium apparatus used in this study is of the flow type to reduce the residence time of the two-phase fluid mixture in the high temperature zone, thus minimizing possible thermal decomposition of the organic solvent. Detailed descriptions of the apparatus, the experimental procedure, accuracy, and the attainment of equilibrium have been presented (5–10).

Hydrogen gas used in this work was supplied by Air Products Co. with a minimum purity of 99.95%. Toluene of "high purity reagent grade" was purchased from Fisher Scientific Co. No impurities were detected from gas chromatographic analysis.

Samples of toluene were taken from the cell effluents at all conditions studied. Chromatographic analysis of the samples showed that the sum of the peak areas of the impurities never amounted to more than 0.2% of the total peak areas. The liquid samples were colorless. Therefore, all toluene collected from the cell effluents was recycled back to the apparatus without further purification. The rate of thermal decomposition of toluene was studied by Johns et al. (3). Their data indicate negligible decomposition at the conditions of this investigation.

## Results

Figure 1 shows the solubility isotherms of hydrogen in toluene at four temperatures from 188.7 to 302.0 °C. At each temperature, measurements were made at seven pressures from 20 to 250 atm. However, no data are reported at 20 atm and 269.0 °C and at pressures below 50 atm at 302.0 °C due to excessive vaporization of toluene. The isotherms extend smoothly to  $x_H = 0$  at a pressure equal to the vapor pressure of toluene taken from ref 4. The equilibrium vapor compositions are shown in Figure 2. At least two samples were taken for each of the cell effluents at a given condition of temperature and pressure. Individual data points are shown in the figures, where possible. A single point in the figures at a fixed temperature and pressure represents graphically indistinguishable multiple samples. In general the multiple samples agreed to within 1% in mole fraction of hydrogen except at the highest

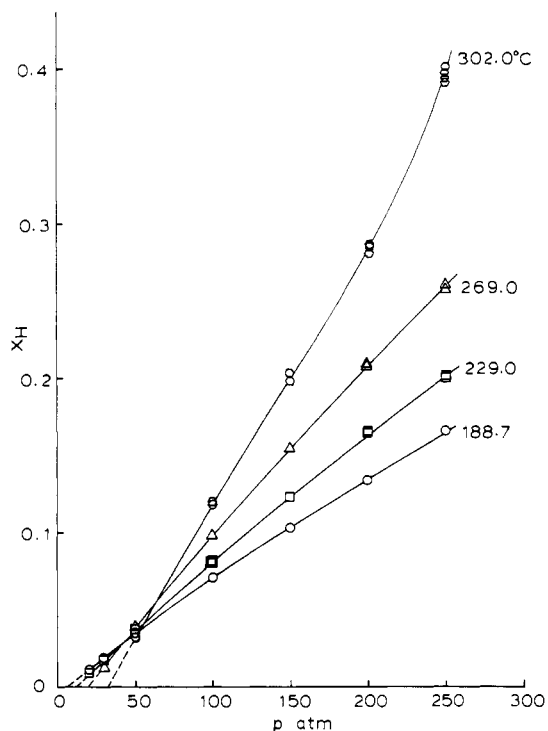


Figure 1. Solubility of hydrogen in toluene.

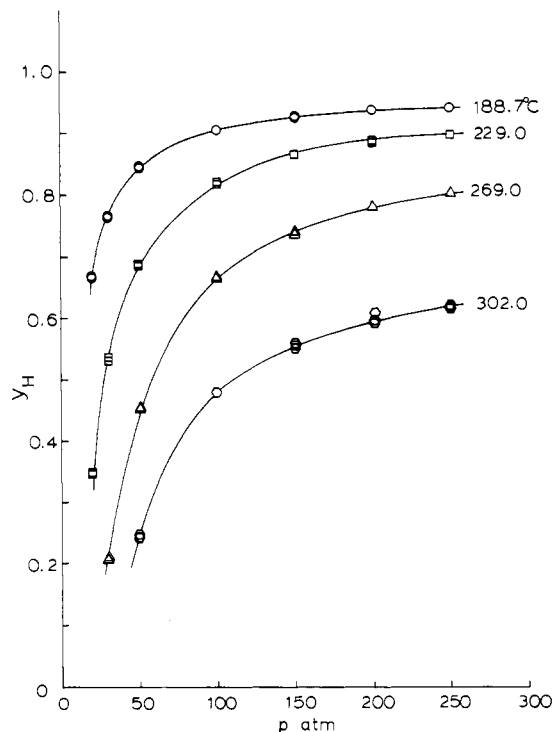


Figure 2. Mole fraction of hydrogen in saturated gas in H<sub>2</sub>/toluene.

temperature studied where a sharp upward curvature in the solubility of hydrogen is observed in the high-pressure region as shown in Figure 1. There is a corresponding sharp drop of the  $K$  value of hydrogen in Figure 3 and an abrupt rise in the

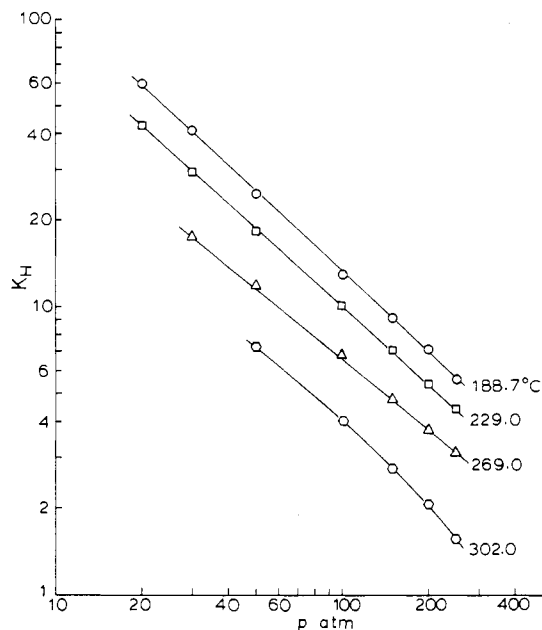


Figure 3. Vaporization equilibrium ratio of hydrogen in H<sub>2</sub>/toluene.

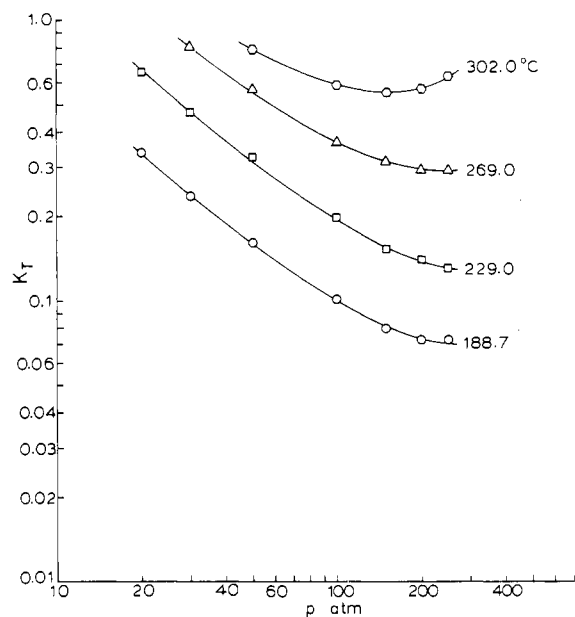


Figure 4. Vaporization equilibrium ratio of toluene in H<sub>2</sub>/toluene.

$K$  value of toluene in Figure 4. These are consistent indications of the approach to the critical state of the mixture. In this region differences larger than 1% among liquid samples taken at the same temperature and pressure were observed. Deviations among liquid samples at the highest pressure amounted to 5% in mole fraction of hydrogen. The vapor samples did not show the same abnormal variations. This is shown in Figure 2.

Table I presents the equilibrium saturated gas and liquid compositions. Each value in the table is the mean of multiple samples. These averaged values of  $x_H$  and  $y_H$  were used to compute the  $K$  values of hydrogen and toluene which are also shown in Figures 3 and 4.

Table I. Vapor-Liquid Equilibrium Data of Hydrogen/Toluene Mixtures

$p$ , atm	$x_H$	$y_H$	$K_H$	$K_T$
188.7 °C				
20.0	0.0113	0.6674	59.1	0.336
29.9	0.0187	0.7678	41.0	0.237
49.7	0.0342	0.8425	24.6	0.163
99.8	0.0704	0.9064	12.9	0.101
149.9	0.1023	0.9284	9.08	0.0798
200.2	0.1331	0.9374	7.04	0.0722
250.4	0.1645	0.9430	5.73	0.0682
229.0 °C				
19.9	0.0082	0.3491	42.6	0.656
29.9	0.0181	0.5356	29.6	0.473
50.0	0.0375	0.6863	18.3	0.326
99.3	0.0812	0.8182	10.1	0.198
150.2	0.1227	0.8645	7.04	0.154
200.3	0.1649	0.8831	5.36	0.140
249.3	0.2015	0.8905	4.42	0.137
269.0 °C				
30.0	0.0120	0.2100	17.5	0.800
50.4	0.0385	0.4555	11.8	0.566
99.5	0.0977	0.6668	6.83	0.369
149.6	0.1545	0.7357	4.76	0.313
200.1	0.2088	0.7789	3.73	0.279
249.8	0.2581	0.7986	3.09	0.271
302.0 °C				
49.5	0.0332	0.2410	7.26	0.785
99.9	0.1196	0.4824	4.03	0.588
149.7	0.2005	0.5527	2.76	0.559
202.4	0.2844	0.5890	2.07	0.574
250.2	0.3935	0.6145	1.56	0.636

#### Glossary

$K_i$	vaporization equilibrium ratio $\equiv y_i/x_i$
$p$	pressure, atm
$T$	temperature, K
$x_i$	mole fraction of component $i$ in liquid phase
$y_i$	mole fraction of component $i$ in gas phase

#### Subscripts

H	hydrogen
T	toluene

#### Literature Cited

- (1) Connolly, J. F., *J. Chem. Phys.*, **36**, 2897 (1962); Connolly, J. F., Kandalic, G. A., Preprint No. 14-63, 28th Midyear Meeting of API, Philadelphia, Pa., May 13, 1963.
- (2) Grayson, H. G., Streed, C. W., Sixth World Petroleum Congress in Frankfurt/Main, Section VII, paper 20, June 19-26, 1963.
- (3) Johns, I. B., McElhill, E. A., Smith, J. O., *J. Chem. Eng. Data*, **7**, 277 (1962).
- (4) Krase, N. W., Goodman, J. B., *Ind. Eng. Chem.*, **22**, 13 (1930).
- (5) Sebastian, H. M., Simnick, J. J., Lin, H. M., Chao, K. C., submitted for publication in *J. Chem. Eng. Data*.
- (6) Sebastian, H. M., Yao, J., Lin, H. M., Chao, K. C., *J. Chem. Eng. Data*, **23**, 167 (1978).
- (7) Simnick, J. J., Lawson, C. C., Lin, H. M., Chao, K. C., *AIChE J.*, **23**, 469 (1977).
- (8) Simnick, J. J., Liu, K. D., Lin, H. M., Chao, K. C., *Ind. Eng. Chem. Process Des. Develop.*, **17**, 204 (1978).
- (9) Simnick, J. J., Sebastian, H. M., Lin, H. M., Chao, K. C., submitted for publication in *J. Chem. Thermodyn.*
- (10) Yao, J., Sebastian, H. M., Lin, H. M., Chao, K. C., *Fluid Phase Equilib.*, **1**, 293 (1978).

Received for review April 14, 1978. Accepted July 19, 1978. This research was supported by the Electric Power Research Institute through research project No. RP-367.