

# Solubilities of Carbon Dioxide in Cyclohexane and *trans*-Decalin at Pressures to 10.7 MPa and Temperatures from 323 to 423 K

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Solubility data have been obtained for carbon dioxide in the naphthenic solvents cyclohexane and *trans*-Decalin (decahydronaphthalene). Measurements cover the temperature range from 323 to 423 K (122 to 302 °F) at pressures up to 10.7 MPa (1550 psia). The data can be described with average deviations of less than 0.004 mole fraction by the Soave-Redlich-Kwong or Peng-Robinson equation when two interaction parameters are used in the equation.

## Introduction

The work reported here is part of a continuing study of the phase behavior of CO<sub>2</sub> with hydrocarbon solvents that are of interest in the processing of petroleum products, production of coal liquids, and enhanced oil recovery operations. Measurements have been reported previously (1) on the solubility of CO<sub>2</sub> in *n*-paraffins from *n*-C<sub>20</sub> through *n*-C<sub>44</sub>, and correlations for these systems have been developed (2). In the present study, the solubilities of CO<sub>2</sub> in a single-ring (cyclohexane) and a two-ring (*trans*-Decalin) naphthenic solvent were measured. Work is in progress on CO<sub>2</sub> + aromatic solvents. These combined studies should provide a sound data base for testing/development of correlations to describe the behavior of CO<sub>2</sub> in multicomponent hydrocarbon systems.

## Experimental Method

The experimental apparatus and procedures used in this work are similar to those described by Gasem (1, 3); however, several modifications were made to the apparatus to improve the precision of the data, the rate of data production and the safety of the apparatus. Only the modifications are described here. Complete details of the apparatus and procedures are given elsewhere (4). The general arrangement of the apparatus is illustrated in Figure 1. The major modifications to Gasem's apparatus involved the equilibrium cell, the pressure measurement system, and the fluid injection pumps.

The rocking cell used by Gasem was replaced by the magnetically stirred cell shown in Figure 2. This cell was fabricated from a commercial 304 stainless steel tubular reactor (High Pressure Equipment Co., Inc., Cat. No. TOC-6) of approximately 40 cm<sup>3</sup> internal volume. The top plug (TP, refer to symbols on Figures 1 and 2) on the vessel was fitted with a aluminum stirrer (ST) containing two bar magnets (see inset detail in Figure 2). The stirrer was driven by two external horseshoe magnets (DM) held in a rotating support (MS) which was driven by a variable-speed motor. Hydrocarbon solvent and CO<sub>2</sub> were injected through a three-way valve (TV) attached to the top plug (TP). The volume of the cell could be varied by injecting mercury through the bottom plug of the reactor. The upper 2 1/2 in. of the reactor body was machined from 1 1/2 in. to 1.0 in. o.d. to increase magnetic coupling between the drive magnets and the stirrer. This new cell led to more rapid equilibration than the previous rocking cell and also eliminated the danger of mercury spills caused by breaks in lines (due to metal fatigue resulting from continuous rocking of that cell).

The second modification was installation of low-volume screw pumps (Temco, Inc.) for solute (GIP) and solvent (HIP) injection. Volumes of these pumps were 25 and 10 cm<sup>3</sup>, respectively, with resolution of 0.005 cm<sup>3</sup>. The solute pump was filled directly with CO<sub>2</sub>, while the solvent pump contained mercury and was used for two purposes. It could inject mercury into the solvent storage cylinder (SV), thus displacing an equivalent volume of solvent to the equilibrium cell (SEC), or it could inject mercury directly into the equilibrium cell during the measurement of a pressure-volume traverse on the equilibrium fluid.

The final modification was installation of pressure transducers (Sensotec, Inc., Model STJE 1890) to measure the CO<sub>2</sub> injection (PT2), solvent injection (PT1), and equilibrium (PT1) pressures. The injection pumps and transducers were housed in an air bath (IPAB) in which the temperature was held at 50.0 ± 0.1 °C by a commercial temperature controller (Hallikainen Model 1053A). The modifications described here permitted more precise measurements of the amounts of chemicals injected to the equilibrium cell and more sensitive monitoring of the approach to equilibrium by use of the transducers (0.1 psi resolution). The transducers were calibrated periodically against a dead-weight tester (Ruska Instruments, Inc., Model 2400.1).

A detailed analysis of experimental errors is given elsewhere (4, 5); results indicate expected uncertainties of less than 0.001 in mole fraction and 2 psi in bubble point pressure.

## Materials

The carbon dioxide had a stated purity of 99.99 mol % and was supplied by Linde Specialty Gases. The other chemicals were from Aldrich Chemical Co. with reported purities of 99+ mol %. No further purification of the chemicals was attempted.

## Results

Preliminary measurements were made to evaluate the operation of the modified apparatus. First, vapor pressures were measured at 40 and 50 °C for pure *n*-pentane and benzene; results agreed within 0.5 psi of literature data, confirming the measurements of temperature and pressure. Next, the solubility of CO<sub>2</sub> in benzene at 40 °C was determined, and results appear in Table I. Comparison of these data with previous investigations (3, 6-8) are shown in Figure 3. For purposes of comparison, the various data are displayed in terms of the deviation of the measured solubility from the prediction by the Soave (9) equation (optimized to fit the present data). Agreement among the various data sets is reasonable, with the exception of those of Ohgaki (8) which appear to be in error. These comparisons were taken as confirmation of proper operation of the modified apparatus. Measurements for CO<sub>2</sub> with the solvents cyclohexane and *trans*-Decalin were then performed, and results appear in Table I.

For CO<sub>2</sub> + Decalin, the results at 50 °C are early measurements done on an equilibrium mixture of *cis*- and *trans*-Decalin; the higher temperature data are for *trans*-Decalin. The 50 and 75 °C isotherms overlap previous data by Tiffin, et al. (10), who made measurements from 0 to 75 °C. Comparisons of these data appear in Figures 4 and 5 (expressed in the same format as Figure 3). At 50 °C (Figure 4), agreement is within

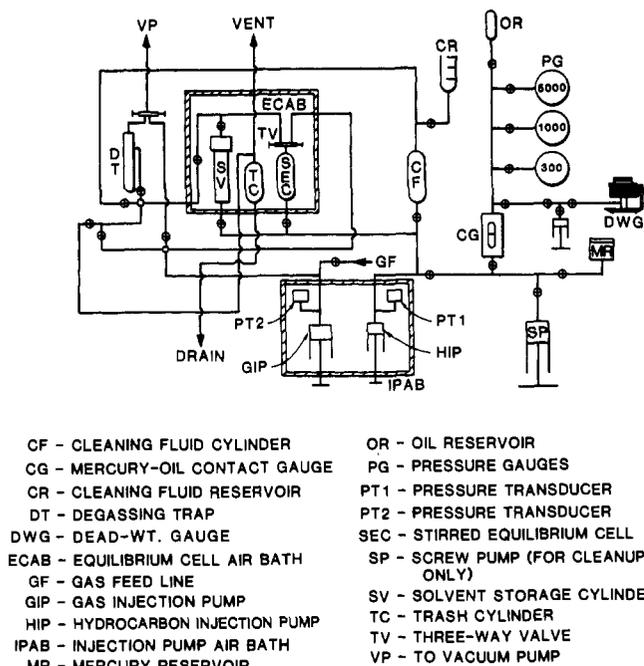


Figure 1. Gas solubility apparatus.

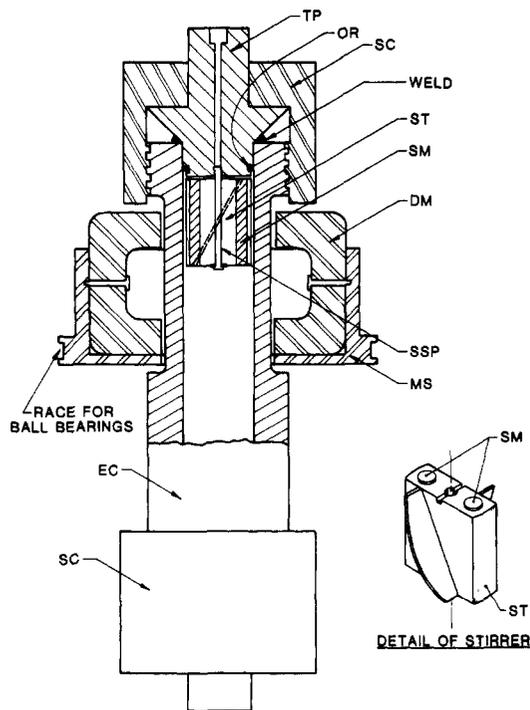


Figure 2. Details of stirred equilibrium cell.

0.005 mole fraction except at the highest pressure. This is within the combined experimental uncertainties in the two data sets. At 75 °C (Figure 5), significant disagreement exists, with differences approaching 0.02 mole fraction at high pressures. No explanation for this difference is evident.

For CO<sub>2</sub> + cyclohexane, data have been reported by Krichevskii and Sorina (11). Their data are at higher temperatures (200 to 260 °C) than the present work, so no direct comparisons are possible.

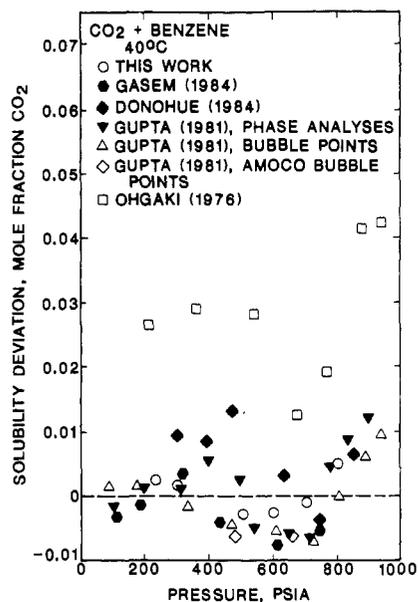


Figure 3. Comparison of solubility data for CO<sub>2</sub> + benzene at 40 °C.

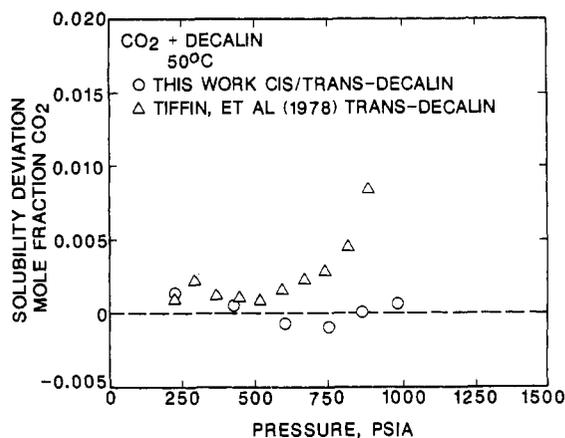


Figure 4. Comparison of solubility data for CO<sub>2</sub> + Decalin at 50 °C.

Correlation

The data from this work were used to evaluate optimum interaction parameters (C<sub>12</sub>, D<sub>12</sub>) for the Soave and Peng-Robinson (12) equations of state and to assess their abilities to represent the data. Table II gives the interaction parameters for the Soave equation as well as root-mean-square (rms) and maximum errors in predicted solubilities. The interaction parameters C<sub>12</sub> and D<sub>12</sub> are defined by the relations

$$a = \sum_{i=1}^N \sum_{j=1}^N y_i y_j a_{ij}$$

$$b = \sum_{i=1}^N \sum_{j=1}^N y_i y_j b_{ij}$$

$$a_{ij} = (a_i a_j)^{1/2} (1 - C_{ij})$$

$$b_{ij} = \frac{1}{2}(b_i + b_j) (1 + D_{ij})$$

where C<sub>ij</sub> and D<sub>ij</sub> are empirical interaction parameters. The values of C<sub>12</sub> and D<sub>12</sub> were evaluated from the bubble-point pressure data by minimizing the sum of squares of errors, SS, in predicted bubble-point pressures:

$$SS = \sum_{i=1}^M (\Delta P)_i^2$$

Table II reveals that when two binary interaction parameters,

Table I. Solubility Data for CO<sub>2</sub>

CO <sub>2</sub> mole fraction	press., MPa (psia)
CO <sub>2</sub> + Benzene at 313.2 K (104 °F)	
0.139	1.644 (238.4)
0.181	2.106 (305.5)
0.325	3.544 (514.0)
0.401	4.186 (607.1)
0.500	4.925 (714.3)
0.602	5.572 (808.1)
CO <sub>2</sub> + Cyclohexane at 348.2 K (167 °F)	
0.103	1.979 (287.0)
0.173	3.283 (476.2)
0.302	5.407 (784.2)
0.399	6.782 (983.7)
0.505	8.150 (1182.0)
0.577	9.000 (1305.4)
CO <sub>2</sub> + Cyclohexane at 373.2 K (212 °F)	
0.126	2.841 (412.1)
0.183	3.994 (579.3)
0.210	4.558 (661.1)
0.308	6.465 (937.7)
0.350	7.244 (1050.6)
0.403	8.209 (1190.6)
0.507	9.995 (1449.5)
CO <sub>2</sub> + Cyclohexane at 423.2 K (302 °F)	
0.112	3.403 (493.5)
0.160	4.616 (669.5)
0.200	5.610 (813.6)
0.257	7.015 (1017.4)
0.300	8.079 (1171.7)
0.350	9.249 (1341.4)
0.401	10.428 (1512.4)
CO <sub>2</sub> + Decalin at 323.2 K (122 °F) <sup>a</sup>	
0.093	1.576 (228.6)
0.170	2.899 (420.5)
0.243	4.137 (600.0)
0.300	5.103 (740.1)
0.351	5.928 (859.8)
0.399	6.729 (976.0)
CO <sub>2</sub> + <i>trans</i> -Decalin at 348.2 K (167 °F)	
0.133	2.553 (370.3)
0.139	2.688 (389.8)
0.214	4.172 (605.1)
0.224	4.337 (629.0)
0.273	5.388 (781.5)
0.310	6.138 (890.2)
0.325	6.453 (935.9)
0.360	7.223 (1047.6)
0.408	8.240 (1195.1)
0.456	9.295 (1348.1)
CO <sub>2</sub> + <i>trans</i> -Decalin at 373.2 K (212 °F)	
0.098	2.184 (316.7)
0.161	3.645 (528.7)
0.193	4.376 (634.7)
0.254	5.932 (860.4)
0.322	7.641 (1108.3)
0.360	8.632 (1252.0)
0.422	10.297 (1493.4)
CO <sub>2</sub> + <i>trans</i> -Decalin at 423.2 K (302 °F)	
0.052	1.469 (213.0)
0.103	2.962 (429.6)
0.144	4.172 (605.1)
0.199	5.861 (850.0)
0.250	7.475 (1084.1)
0.295	8.963 (1300.0)
0.345	10.657 (1545.7)

<sup>a</sup>For the 323.2 K isotherm only, the solvent is a mixture of *cis*- and *trans*-Decalin.

$C_{12}$  and  $D_{12}$ , are employed, the equation of state can fit the data for a specific isotherm within its experimental uncertainty. Even when a single pair of parameters is used to represent all isotherms for a system, rms errors are no greater than 0.004

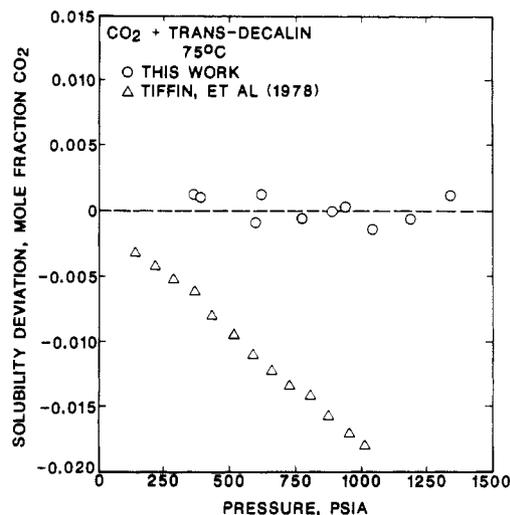


Figure 5. Comparison of solubility data for CO<sub>2</sub> + *trans*-Decalin at 75 °C.

Table II. Soave Correlation of Solubility Data

temp, K	optimum parameters		errors in mole fraction	
	$C_{12}$	$D_{12}$	rms	max
CO <sub>2</sub> + Benzene				
313.2	0.068	0.035	0.003	0.005
	0.090		0.018	0.031
CO <sub>2</sub> + Cyclohexane				
348.2	0.108	0.051	0.002	0.004
	0.136		0.020	0.027
373.2	0.113	0.042	0.001	0.001
	0.141		0.011	0.019
423.2	0.125	0.034	<0.001	0.001
	0.151		0.005	0.007
348.2, 373.2, and 423.2	0.112	0.046	0.003	0.007
	0.141		0.014	0.038
CO <sub>2</sub> + <i>trans</i> -Decalin				
323.2 <sup>a</sup>	0.145	0.030	0.001	0.001
	0.181		0.011	0.015
348.2	0.137	0.025	0.001	0.001
	0.167		0.009	0.012
373.2	0.143	0.022	0.001	0.002
	0.168		0.006	0.008
423.2	0.156	0.020	<0.001	0.001
	0.183		0.003	0.004
348.2, 373.2, and 423.2	0.136	0.029	0.004	0.010
	0.168		0.009	0.020

<sup>a</sup>For the 323.2 K isotherm only, the solvent is a mixture of *cis*- and *trans*-Decalin.

mole fraction. However, when a single interaction parameter  $C_{12}$  is employed ( $D_{12} = 0$ ), errors rise by a factor of 2 for the *trans*-Decalin system and by a factor of almost five for cyclohexane. The Peng–Robinson and Soave equations yield essentially identical prediction errors. The regressed interaction parameter  $D_{12}$  is identical for both equations, while  $C_{12}$  values are uniformly 0.013 lower for the Peng–Robinson equation. In both systems studied, the interaction parameters exhibit a mild temperature dependence, as illustrated for CO<sub>2</sub> + *trans*-Decalin in Figure 6.

#### Glossary

$a, b$	parameters in Soave or Peng–Robinson equation of state
$C_{ij}, D_{ij}$	interaction parameters between components $i$ and $j$ in mixing rules for equation of state
$M$	number of data points
$N$	number of components in the mixture

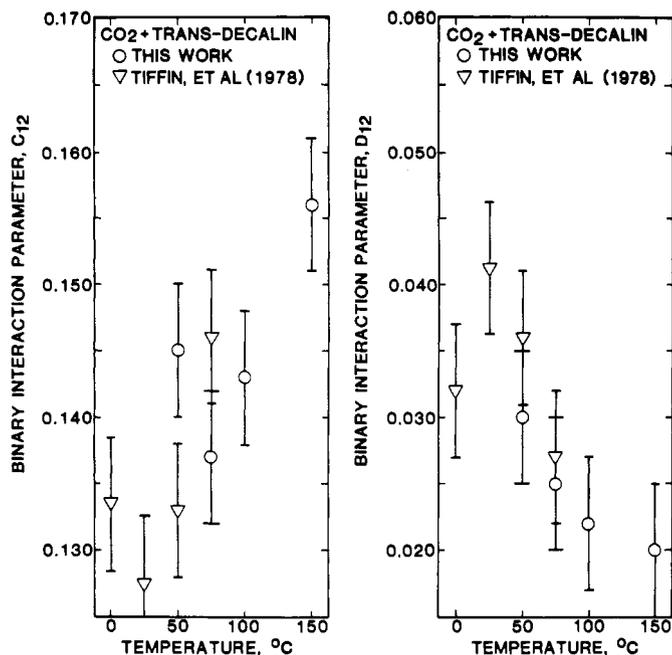


Figure 6. Soave interaction parameters for  $\text{CO}_2 + \text{trans-Decalin}$ .

$P$  bubble-point pressure  
 $y$  mole fraction  
 $\Delta$  difference between calculated and experimental values

Registry No.  $\text{CO}_2$ , 124-38-9;  $\text{C}_8\text{H}_{16}$ , 71-43-2; *trans*-decalin, 493-02-7; cyclohexane, 110-82-7.

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## Solubility of Gases in Liquids. 17. The Solubility of He, Ne, Ar, Kr, $\text{H}_2$ , $\text{N}_2$ , $\text{O}_2$ , $\text{CO}$ , $\text{CH}_4$ , $\text{CF}_4$ , and $\text{SF}_6$ in Tetrachloromethane at 283-318 K<sup>†</sup>

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The Ostwald coefficients  $L_{2,1}(T,P)$  of He, Ne, Ar, Kr,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{CF}_4$ , and  $\text{SF}_6$  in tetrachloromethane have been determined at about atmospheric pressure, and from 283 to 318 K, by a modified Ben-Naim/Baer apparatus. Both pressure control and measurement of the volume of gas dissolved in a given amount of solvent were effected by a microprocessor. This improved, medium-precision design (about  $\pm 1\%$ ) combines easy handling with automated data retrieval, and is totally *mercury-free*. Test measurements for  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  dissolved in pure water showed excellent agreement with recent high-precision results. Henry coefficients  $H_{2,1}(T,P_{s,1})$  are evaluated from the solubility data. Their variations with temperature yield the enthalpy changes upon solution  $\Delta H_2^\circ$ , which are compared with recent calorimetric measurements. Results obtained through application of scaled particle theory are also given.

#### Introduction

Tetrachloromethane ( $\text{CCl}_4$ ) is a pseudospherical molecule of high symmetry with an average molecular polarizability and an effective hard-sphere diameter comparable to that of cyclohexane and benzene (1-3). As such, it plays a central role in assessing the performance of theories of pure liquids and liquid mixtures, as documented by the many measurements reported in the literature on thermodynamic quantities of mixtures containing tetrachloromethane (4-6). Of particular interest are those mixtures where the molecules are of substantially different size, since large size ratios will magnify existing deficiencies in the statistical-mechanical models (7-9). However, aside from Horluti (10), who measured the solubility in tetrachloromethane of five of the gases reported on in this article, the literature contains few reliable gas solubility data for this solvent. Considering the importance of tetrachloromethane from both the theoretical and practical point of view, the paucity of solubility data is surprising. We suspect the reason for this is that most apparatuses used for gas solubility measurements contain mercury which is known to react with tetrachloromethane.

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