

Solubility of Carbon Monoxide in *n*-Hexane between 293 and 473 K and CO Pressures up to 200 bar

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The solubility of carbon monoxide, CO, in *n*-hexane was measured at 293, 323, 373, 423, and 473 K for CO partial pressures up to 200 bar. The enthalpy of solution was calculated between 293 and 473 K. Using the Krichevsky-Ilinskaya equation of state, the solubility of CO in *n*-hexane can be calculated between 293 and 423 K for CO partial pressures up to 200 bar with an accuracy better than 5%.

Introduction

Carbonylation reactions are widely used in organic industrial processes. Despite this, little is known about the solubility of carbon monoxide, CO, in solvents, especially at elevated temperatures and pressures, where oxo reactions are normally carried out. In this study, the solubility of CO was measured in *n*-hexane, a typical representative of alkanes, the class of solvents often used for spectroscopical investigations involving CO.

As early as 1952, Gjaldbaek (1) postulated an empirical equation for calculating the solubility of different gases at standard conditions in a variety of solvents. For CO in *n*-hexane, the mole fraction solubility x_2° can be calculated at 1.013 bar and 293.15 K as $x_2^\circ = 17.4 \times 10^{-4}$. Until now, its solubility was determined experimentally only by Patyi et al. (2) and Makranczy et al. (3) with $x_2^\circ(293.15\text{K}) = 16.97 \times 10^{-4}$ or $x_2^\circ(293.15\text{K}) = 18.5 \times 10^{-4}$, respectively (the latter was calculated from the reported Kuenen coefficient).

Experimental Section

Apparatus and Procedure. The gas solubility was measured by degassing a CO/*n*-hexane sample, which was before pressurized and equilibrated with CO at the desired temperature and pressure (4) (Figure 1). The 2.5-L Hastelloy B autoclave (A) was first evacuated and then vented several times with CO before filling it with between 1.5 and 2 L of *n*-hexane. Afterward, for at least three times, 5 or more bar of CO was pressurized and decompressed in order to get rid of possible traces of other gases. The CO/*n*-hexane equilibrium was adjusted under vigorous stirring, for at least half an hour, at the desired temperature ($\pm 0.2\%$, measured with a Cr/Ni thermocouple (G)) and pressure ($\pm 1\%$, measured with a 40.0- and 400-bar pressure transducer (F)). The pressure drop due to the equilibration process was recorded and normally completed within 15 min.

Before taking a sample, 5–10 mL of solution was released into flask I in order to flush the tubes. Immediately afterward a sample of the solution, containing at least 5, but normally 40–60 mL, of *n*-hexane was released by opening v_3 and v_6 into the solution buret (K). The liberated CO was collected in a 100-mL (L), 500-mL (M), or 2000-mL (N) gas buret, containing a saturated aqueous NaCl solution, according to the expected amount of gas. All burets were equipped with a cooling mantle

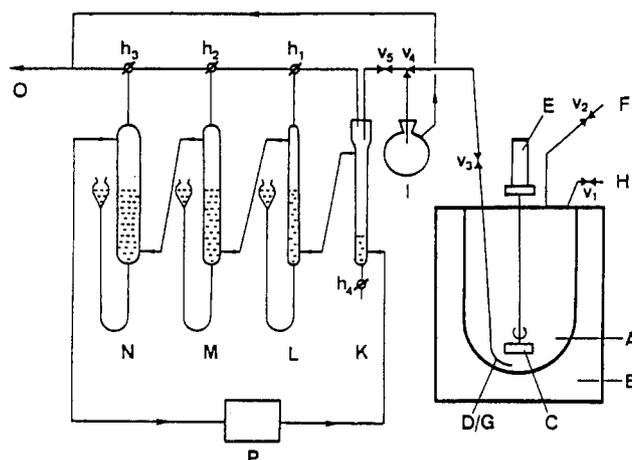


Figure 1. Apparatus to measure the solubility of carbon monoxide at elevated temperatures and pressures: (A) 2.5-L Hastelloy B autoclave; (B) electrical heating mantle; (C) shovel stirrer; (D) sampling tube (contains the thermoelement); (E) stirring motor; (F) piezoresistive pressure transducer; (G) Cr/Ni thermocouple; (H) entrance for sucking in the solvent; (I) flask for the forerun; (K) 70-mL solution buret; (L)–(N) 100-, 500-, and 2000-mL, respectively, gas burets with double glass walls for thermostating; (O) exhaust; (P) thermostat; (h_1)–(h_4) glass stopcocks; (v_1)–(v_6) stainless steel needle valves.

and thermostated to 293.1 ± 0.1 K. The gas volume was measured at both 5 and 30 min after decompression. The latter measurement was not significantly different from the first one, indicating a fast and efficient thermal equilibrium. During the volume measurements, an *n*-hexane film was not observed on any NaCl solution in the gas burets.

The CO solubility in *n*-hexane at the given temperature T and pressure p , expressed as mole fraction x_2 , can be calculated, after decompression, from the volumes of the liquid and the gas phases. In addition to this, the *n*-hexane in the gas phase and the dissolved CO in *n*-hexane had to be considered (vide infra). The latter can be calculated by extrapolating $x_2(p, T)$ to the averaged actual CO pressure at 813 ± 2 mbar as 1.42×10^{-3} . A comparison by IR of a decompressed CO/*n*-hexane sample with one saturated with CO at standard conditions yielded no significant difference in the solubility, revealing that the *n*-hexane is saturated with CO after expansion. This is in contrast to the system CO/H₂O studied by Jung et al. (5). They found a clear

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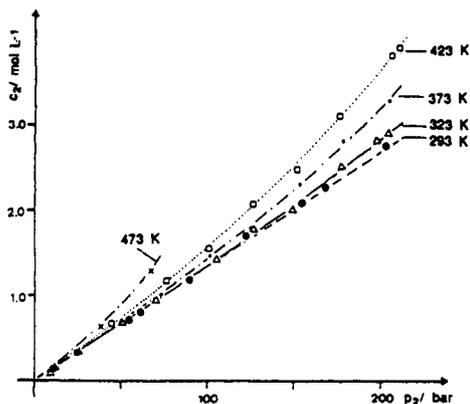


Figure 2. Molar concentration solubility of CO, c_2 , in n -hexane at different temperatures and partial pressures of CO, p_2 .

undersaturation after the sudden decompression of a sample at high temperature and pressure. The values used for the relative density, d_4 , and vapor pressure, p , of n -hexane at 293 K were $d_4 = 0.6603$ and $p = 168.6$ mbar (6).

For the calculation of the partial pressure p_1 of n -hexane, two effects have to be considered: its decrease due to the CO solubility according to Raoult's law (eq 1), and its increase due to the effect of a foreign gas (7) (eq 2), where p_s is the

$$p_1 \approx x_1 p_s = (1 - x_2) p_s \quad (1)$$

$$p_s = p_{0s} \exp\{V_1'(p_{\text{tot}} - p_{0s})/RT\} \quad (2)$$

vapor pressure of the solvent with the influence of an inert gas, p_{0s} the vapor pressure of the pure solvent, p_{tot} the total pressure, and V_1' the molar volume of the condensed n -hexane.

For the latter effect, an inert and ideal behavior of the gas is assumed. Since no mixing is assumed, the values for n -hexane (8) can be taken. Combining eqs 1 and 2 and expressing it for the gas pressure p_2 results in

$$p_2 \approx p_{\text{tot}} - (1 - x_2) p_{0s} \exp\{V_1'(p_{\text{tot}} - p_{0s})/RT\} \quad (3)$$

Purity of the Materials. The purity of the carbon monoxide (Carbagas) was 99.97%. The n -hexane (Merck, p.a.) ($\geq 99\%$) was first dried over a Na/K alloy and distilled under argon. Before the autoclave was filled with it, n -hexane was frozen under vacuum.

Results and Discussion

The accuracy of the measurements was checked with the known system H_2/n -hexane (3, 10–16). The obtained molar fractions $x_{H_2}^\circ$ ($\times 10^4$) are, at 298 K, 7.08; at 323 K, 8.06; and, at 373 K, 10.63. These experimental values are in good agreement with Brunner's (16) data (where other literature is discussed as well) and differ by 0.6% (at 298 K), 0.4% (at 323 K), and 0.1% (at 373 K) only slightly. Also, the enthalpy ΔH_2° , 5.14 ± 0.25 kJ/mol, and entropy ΔS_2° , -42.2 ± 0.84 J/mol K, of solution are close (within 0.1% and 0.3%, respectively) to Brunner's data and are within the experimental error. For further data and discussion see ref 17.

The extrapolation of the measured CO solubility, x_2 , at different pressures to 1.013 bar and its calculation to 298 K (vide infra) give a x_2° (298 K) of 17.68×10^{-4} . This value is 4.2% higher than Patyi's (2), but 4.6% lower than Makranczy's (3) measurements. The value calculated from the empirical equation from Gjaldbaek (1) is 1.6% lower than the one of the present work. A three-term Clarke Glew (18) regression of the x_2° values (for a CO partial pressure of 1.013 bar),

Table I. Experimentally Determined Mole Fraction Solubilities of CO, x_2 (exptl), in n -Hexane as well as Calculated Mole Fractions, x_2 (calcd), and Molar Concentration, c_2 , Solubilities at Various Temperatures and Pressures

T (K)	p (bar)	p_2^a (bar)	x_2^b (exptl)	x_2^c (calcd)	Δx_2^d (%)	c_2^e (mol/L)
293	12.6	12.4	0.0213	0.0213	0.0	0.164
	12.8	12.6	0.0217	0.0216	-0.3	0.167
	22.6	22.4	0.0380	0.0381	0.4	0.297
	55	54	0.0893	0.0887	-0.7	0.725
	61	61	0.0993	0.100	1.2	0.812
	90	90	0.141	0.144	2.2	1.18
	123	123	0.192	0.191	-0.7	1.68
	155	155	0.229	0.232	1.4	2.07
	169	169	0.248	0.250	0.7	2.25
	198	198	0.291	0.284	-2.6	2.76
	203	203	0.289	0.290	0.3	2.73
323	12.3	11.7	0.0207	0.0205	-1.0	0.154
	12.8	12.2	0.0220	0.0214	-2.9	0.164
	25.6	25.0	0.0439	0.0435	-1.0	0.333
	52	51	0.0870	0.0871	0.2	0.680
	71	70	0.119	0.118	-0.7	0.951
	106	105	0.170	0.173	1.6	1.413
	128	127	0.207	0.205	-0.8	1.77
	150	149	0.233	0.237	1.7	2.03
	178	177	0.278	0.273	-1.7	2.51
	199	198	0.303	0.300	-1.0	2.80
	204	203	0.312	0.306	-1.9	2.90
373	14.5	12.0	0.0232	0.0232	0.0	0.159
	14.9	12.4	0.0239	0.0240	0.4	0.167
	28.7	26.1	0.0503	0.0503	0.0	0.350
	54	51	0.0984	0.0981	-0.3	0.707
	77	74	0.139	0.142	2.3	1.03
	105	102	0.191	0.195	2.0	1.46
	128	125	0.226	0.237	4.8	1.78
	158	154	0.277	0.285	3.0	2.31
	179	175	0.326	0.318	-2.4	2.75
	183	179	0.330	0.324	-1.8	2.80
	205	200	0.364	0.352	-3.4	3.16
209	205	0.376	0.361	-4.0	3.26	
423	16.6	8.7	0.0213	0.0202	-5.1	0.130
	17.3	9.4	0.0224	0.0218	-2.7	0.136
	31.0	22.8	0.0512	0.0521	1.8	0.317
	54	45	0.104	0.103	-0.5	0.682
	86	77	0.177	0.181	2.2	1.17
	111	101	0.234	0.239	2.2	1.55
	137	127	0.292	0.303	3.6	2.07
473	162	152	0.346	0.361	4.2	2.47
	187	177	0.408	0.409	0.4	3.09
	217	207	0.489	0.454	-7.1	3.85
	223	213	0.523	0.457	-12.6	3.91
	28.4	9.8	0.0288	0.0293	1.6	0.154
	59	39	0.123	0.105	-14.7	0.631
	88	68	0.225	0.173	-23.3	1.28
	105	86	0.321	0.206	-35.9	1.86

^a Calculated according to eq 3. ^b The value of the mole fraction of CO in n -hexane, x_2 , can be calculated from the number of moles in the liquid and gaseous phases of n -hexane, n_1' and n_1'' , and of CO, n_2' and n_2'' , respectively. They were obtained from the measured volumes in the gas and liquid burets at 293.1 K and 982 ± 29 mbar: $x_2 \approx \{n_2''/(n_2'' + n_1' + n_1'')\} + 1.42 \times 10^{-3}$. The value 1.42×10^{-3} represents the mole fraction solubility of CO ($n_2/(n_2' + n_1')$) in the decompressed n -hexane for an averaged CO pressure, p_2 , of 813 ± 2 mbar at 273.1 K. ^c Calculated using eqs 2, 4, 10–13. ^d $\Delta x_2 = 1 - x_2(\text{calcd})/x_2(\text{exptl})$. ^e The molar concentration solubility of CO, c_2 , can be calculated from the mole fractions, if the molar volumes of the solution at the given temperatures and pressures, $V_m'(p, T)$, are known: $c_2 = x_2/V_m'(p, T)$. The data for the present work are obtained from density measurements and taken from refs 9 and 17.

obtained at 293, 323, 373, 423, and 473 K (Table II), leads with good accuracy (± 0.012) to

$$\ln x_2^\circ = a + b/(T/K) + c \ln (T/K) \quad \text{at } 293\text{--}473 \text{ K} \quad (4)$$

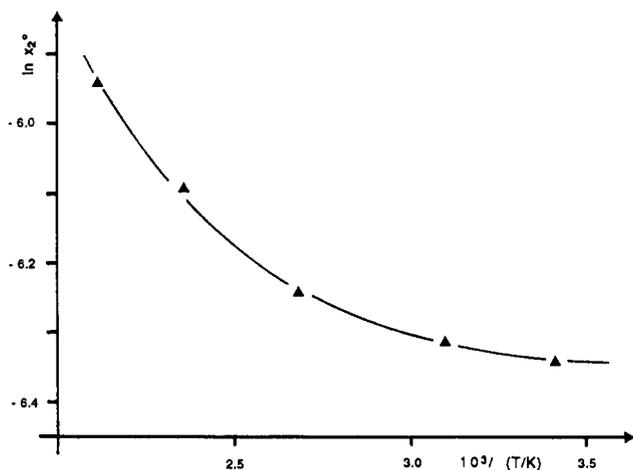
with

$$a = -34.2 \pm 2.0 \quad (4a)$$

Table II. Thermodynamic Parameters for CO Solubilities in *n*-Hexane

<i>T</i> (K)	293	323	373	423	473
x_2° (exptl) $\times 10^4$ ^a	17.55	18.10	19.38	22.55	26.23
x_2° (calcd) $\times 10^4$ ^b	17.62	17.92	19.59	22.42	26.26
$H_{2,1}^c$ (bar)	577.3	559.8	523.0	449.3	386.3
$H_2^{\infty'}$ ^d (kJ/mol)	-0.0733	0.967	2.70	4.43	6.17
$H_2^{\circ\prime}$ ^e (kJ/mol)	-0.0103	-0.0376	-0.219	-1.01	-5.12
ΔH_2° ^f (kJ/mol)	-0.0591	1.01	2.92	5.44	11.28
$V_2^{\infty'}$ (exptl) ^g (cm ³ /mol)	51.6	59.1	93.9	150	
$V_2^{\infty'}$ (calcd) ^h (cm ³ /mol)	48.1	60.1	93.1	165.6	414.5
A (exptl) ⁱ (J/mol)	1078	1428	2573	4408	8596
A (calcd) ^h (J/mol)	1058	1471	2546	4407	7628

^a Obtained from experimental Henry constants, $H_{2,1}$, by applying eq 10. ^b From eq 4. ^c Obtained from a regression ($\ln(f_2/x_2) - V_2^{\infty'}(p_{\text{tot}} - p_s)/RT$ vs $x_1^2 - 1$); see Figure 5. ^d Partial molar enthalpy of solution of carbon monoxide at infinite dilution; see eq 5. ^e Molar enthalpy of pure carbon monoxide in the perfect-gas reference state; see eq 5. ^f From eq 7. ^g Taken from ref 17. At 473 K no data are available. ^h From eq 13. ⁱ Experimental value, obtained from regression as shown in Figure 5. ^j From eq 12.

**Figure 3. Mole fraction solubility of CO, x_2° , in *n*-hexane at a CO partial pressure of 1.013 bar as a function of temperature T .**

$$b = 1230 \pm 100 \quad (4b)$$

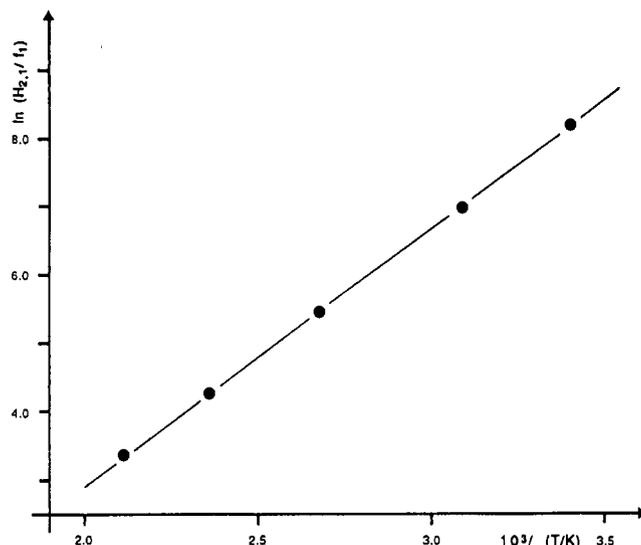
$$c = 4.17 \pm 0.28 \quad (4c)$$

The calculated minimal solubility (where $\partial \ln x_2^\circ / \partial T = 0$) is at 295.1 K, explaining its weak temperature dependence around room temperature (Figure 3). Below this temperature, the solution of CO in *n*-hexane is exothermic; above it, it is endothermic (see below). However, it rises quite rapidly close to the critical temperature of *n*-hexane. Thus, it increases from 293 to 323 K about 3%, and to 373 K, 10%. At 423 K, however, the solubility rises dramatically by 28%, and at 473 K by as much as 49%.

The enthalpy of solution ΔH_2° is equal to the difference between the partial molar enthalpy of the gas at infinite dilution in the solvent, $H_2^{\infty'}$, and the molar enthalpy of pure gas in the perfect-gas reference state, $H_2^{\circ\prime}$. It also can be calculated (19) from the temperature dependences of the gas solubility x_2 and the solvent vapor pressure according to

$$\Delta H_2^\circ = (H_2^{\infty'} - H_2^{\circ\prime}) = RT^2(\partial \ln x_2^\circ / \partial T) + TV_2^{\infty'} \partial p_s / \partial T \quad (5)$$

The vapor pressure from *n*-hexane, p_s , can be described with

**Figure 4. Quotient of the Henry constant, $H_{2,1}$, of the CO solubility in *n*-hexane, and the fugacity of solvent vapor, f_1 , as a function of temperature T .**

the Antoine equation from constants in ref 20 as

$$\ln(p_s/\text{Pa}) = A - B/[C + (T/K)] \quad \text{at } 293\text{--}473 \text{ K} \quad (6)$$

with $A = 20.725$, $B = 2696.8$, and $C = -48.752$.

Using eqs 4 and 6, eq 5 can be written as

$$\begin{aligned} (\Delta H_2^\circ / (\text{J mol}^{-1})) = & -bR + cR(T/K) + \\ & B(V_2^{\infty'} / (\text{m}^3 \text{mol}^{-1}))(T/K) / [(T/K) + C]^2 \times \\ & \exp\{A - B / [(T/K) + C]\} \quad (7) \end{aligned}$$

Above room temperature, the enthalpy of solution for CO in *n*-hexane is negative (see Table II). With increasing temperature, it rises exponentially from -0.0591 (293 K) to 11.3 kJ/mol at 473 K.

Henry's law (eq 8) describes the proportionality of the mole fraction of a dissolved gas to its partial pressure (21, 22),

$$p_i = H_{i,j} x_i \quad (8)$$

$$p_i \gamma_i = H_{i,j} x_i \alpha_i \quad (8a)$$

where $H_{i,j}$ is the Henry constant (component i dissolved in component j), γ_i the fugacity, and α_i the activity coefficient.

Equation 8 is exactly valid only for ideal dilute solutions. For real systems, γ_i and α_i have to be considered (eq 8a). Unfortunately, the latter are often unknown. However, the Jonah (23) correlation $\ln(H_{2,1}/f_1)$ vs $1/T$ leads, as in most systems, to a straight line (Figure 4):

$$\ln(H_{2,1}/f_1) = -4.448 + 3696/(T/K) \quad \text{at } 293\text{--}473 \text{ K} \quad (9)$$

where f_1 is the fugacity of the solvent vapor. The Henry coefficients can be calculated as

$$\ln(H_{2,1}/\text{bar}) = -\ln x_2^\circ + 0.01316 \quad (10)$$

with x_2° given by eq 4.

Krichevsky and Kasarnovsky (24) took the pressure dependence of the chemical potential into consideration by using the molar volume of the dissolved gas at infinite dilution, $V_2^{\infty'}$. Later, Krichevsky–Ilinskaya (25) proposed eq 11, where mixing and concentration effects were introduced.

$$\ln(f_2/x_2) = \ln H_{2,1} + \{V_2^{\infty'}(p_{\text{tot}} - p_s)/RT\} + A/RT(x_1^2 - 1) \quad (11)$$

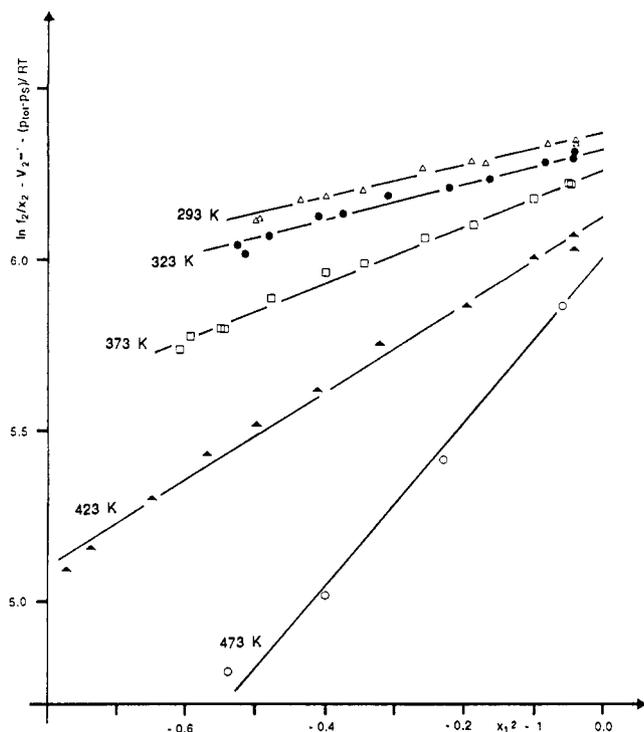


Figure 5. Difference between the quotient of fugacity and solubility of CO in *n*-hexane, expressed as $\ln(f_2/x_2)$, and $V_2^\infty - (p_{\text{tot}} - p_s)/RT$, as a function of the mole fraction of *n*-hexane, x_1 .

Henry constants, $H_{2,1}$, as well as the Krichevsky–Ilinskaya parameter A , both dependent on temperature and the system (see eq 11 and Table II), can be obtained with good accuracy by a regression (Figure 5), while the molar volumes of CO, V_2^∞ , were taken from density measurements (9).

$H_{2,1}$ can be computed between 293 and 473 K for any temperature using eqs 4 and 10. The Krichevsky–Ilinskaya parameter A can be calculated for any temperature in the measured range according to (see Table II)

$$\ln(A/(\text{J mol}^{-1})) = 1.097 \times 10^{-2}(T/\text{K}) + 3.747 \quad (12)$$

and, in analogy to the Rackett equation for liquids (26), the molar volumes of the dissolved gas at infinite dilution as

$$\ln(V_2^\infty/(\text{cm}^3 \text{mol}^{-1})) = -6.761[1 - (T/\text{K})/(T_{c,1}/\text{K})]^{2/7} + 9.158 \quad (13)$$

where $T_{c,1}$ is the critical temperature of *n*-hexane.

The method of calculating the fugacity coefficients influences slightly the calculated data. The modified Redlich Kwong equation of state (27), which is used therefore in the present work, leads to a smaller deviation in eq 11 than the virial equation of state (calculated with the Tsionopoulos method (28–30)).

Using eqs 2, 4, and 10–13, the gas solubility of CO in *n*-hexane can be calculated for the temperature range between 293 and 423 K for CO pressures up to 200 bar. The differences between the calculated and measured data are mostly lower than 4%. At 473 K as well as above 200 bar of CO at 423 K the deviations become larger due to the proximity to the critical point of the mixture.

Acknowledgment

The supportive interest in this work and the helpful discussions with the late Prof. P. Pino and with PD Dr. G. Bor are gratefully acknowledged.

Glossary

A Krichevsky–Ilinskaya parameter, J/mol

c molar concentration, mol/L
f fugacity, bar
 ΔH_2 enthalpy of solution, kJ/mol
 $H_{i,j}$ Henry constant of component *i* dissolved in component *j*, bar
p pressure, bar
 p_{0s} vapor pressure of the pure solvent, bar
 p_s vapor pressure of the solvent with the influence of an inert gas, bar
R molar gas constant, J/(mol K)
T temperature, K
V molar volume, L/mol
 x_i mole fraction of *i* in the condensed phase

Superscripts

$^{\circ}$ at a pressure of 1.013 bar
 $^{\infty}$ at infinite dilution
 $'$ liquid phase
 $''$ gas phase

Subscripts

1 *n*-hexane
2 carbon monoxide

Registry numbers supplied by author. *n*-hexane, 110-54-3; carbon monoxide, 630-08-0; hydrogen, 1333-74-0.

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