

Glossary

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|---------------------------|--|
| $c_1, c_2,$..., c_j | coefficients in representation of molar excess heat capacity by eq 3 |
| C_p | molar heat capacity |
| C_p^E | molar excess heat capacity |
| $C_{p,i}$ | molar heat capacity of component i |
| P | heating power |
| r | reference liquid |
| s | sample liquid |
| V | molar volume |
| x_i | mole fraction of component i |

Greek Letters

| | |
|----------|---------------------------------------|
| σ | calculated standard deviation in eq 1 |
|----------|---------------------------------------|

Subscripts

| | |
|---|--------------|
| 1 | benzene |
| 2 | cycloalkanes |

Registry No. Benzene, 71-43-2; cyclopentane, 287-92-3; methylcyclohexane, 108-87-2; cyclooctane, 292-64-8.

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Solubility of Hydrogen in 10 Organic Solvents at 298.15, 323.15, and 373.15 K

Erwin Brunner

BASF Aktiengesellschaft, D-6700 Ludwigshafen/Rhein, Federal Republic of Germany

The solubility of hydrogen in *n*-hexane, *n*-octane, *n*-decane, toluene, acetonitrile, acetone, *N,N*-dimethylformamide, tetrahydrofuran, 1,4-dioxane, and 1-methylpyrrolidone-2 was determined with two different measuring methods at 298.15, 323.15, and 373.15 K and, in general, at up to 10 MPa. The error of measurements is estimated to be less than $0.02x_2$, where x_2 is the mole fraction of dissolved hydrogen.

Introduction

A knowledge of the solubility of gases in liquids is important in a wide range of scientific and technological disciplines. Although the repeatability of the methods adopted today for its measurement is frequently 1% or even less, great differences sometimes exist between sets of results obtained by different working groups on the same system at the same temperature and pressure, despite the fact that the methods and apparatus adopted are reliable and the data are consistent. It is evident that, even if the layout and instruments are checked with the utmost care, systematic errors occur that are very difficult to trace and eliminate. Hence, in the light of the current state of the art in instrumentation, it is indeed desirable to improve the precision of measurements, but it would appear more important to obtain consistent sets of results by different methods on a few representative systems than to improve the repeatability or even the reproducibility.

The solubility of hydrogen at near-atmospheric and high pressures in a few organic compounds is known with sufficient accuracy. In the course of our studies, we measured its solubility in 10 organic solvents at 298.15, 323.15, and 373.15 K, and partially at pressures of up to 14 MPa.

Literature data on the solubility of hydrogen in liquids has been critically evaluated by Young (1). Table I lists all refer-

ences that have reported experimental results obtained on the solvents investigated in this paper.

Experimental Section

Apparatus and Procedure. Method 1. The apparatus is essentially the same as that described for earlier measurements (27-29). Vapor-liquid phase equilibrium is established in a static cell fitted with a stirrer; afterwards, a liquid sample is withdrawn and analyzed by stripping. The solvent is saturated with hydrogen in a 1000-cm³ high-pressure autoclave with vigorous stirring, and a sample of the saturated liquid is taken through high-pressure capillaries and decompressed to atmospheric pressure at constant temperature. The mass of the sample depends on the solubility of the gas and varies between 30 and 200 g. The hydrogen mole fraction x_2 in the solution is calculated by eq 1,

$$x_2 = (n_2^v + n_2^l) / (n_1^v + n_1^l + n_2^v + n_2^l) \quad (1)$$

where n_1^v and n_1^l are the moles of solvent and vapor, and n_2^v and n_2^l are the moles of hydrogen in the vapor and liquid phases of the decompressed sample, n_1^v and n_2^l being merely correction terms.

The liquid should be degassed at as low a temperature as possible in order to restrict the correction term n_1^v to a minimum, particularly since the actual vapor density of the solvent is not always known with sufficient accuracy. The decompression apparatus (27, 29) consists of the variable-volume gas buret and the liquid sampler, and care must be taken to ensure that the pressure at which the vapor is flashed is kept as constant as possible during the entire sampling operation. If the pressure changes during sampling, solvent vapor may condense in the gas buret, or the gas sample may not be completely saturated with solvent vapor. As a result, the errors incurred in determining the moles of gas and liquid in the entire

Table I. References on the Solubility of Hydrogen in the Solvents Investigated

| solvent | T/K | p/MPa | ref | |
|-------------------------------|----------------|-------------------|--------|----|
| <i>n</i> -hexane | 263.15–293.15 | 0.1013 | 2 | |
| | 293.15, 298.15 | 0.1013 | 3 | |
| | 213.15–298.15 | 0.1013 | 4 | |
| | 298.15 | 0.1013 | 5 | |
| | 298.15 | 1.0–11.0 | 6 | |
| | 308.35 | 5.10–15.17 | 7 | |
| | 277.59–477.59 | 3.45–68.95 | 8 | |
| | 248.15–308.15 | 0.1013 | 9 | |
| <i>n</i> -octane | 298.15 | 0.1013 | 5 | |
| | 298.15 | 0.1013 | 10 | |
| | 298–323 | 5–30 | 11 | |
| | 298.15 | 0–19 | 6 | |
| | 463.15–553.15 | 0–138 | 12 | |
| | 298.15–324.65 | 0.1013 | 13 | |
| | 298.15 | 0.1013 | 10 | |
| | 298.15 | 0.1013 | 5 | |
| <i>n</i> -decane | 358.15–483.15 | 4.05–30.4 | 14 | |
| | 462.5–583.5 | 0.14–25.2 | 15 | |
| | 298.15–323.15 | 0.1013 | 13 | |
| | 263.15–293.15 | 0.1013 | 2 | |
| | 293.15–298.15 | 0.1013 | 16 | |
| | 258.15–308.15 | 0.1013 | 9 | |
| toluene | 298.15 | 0.1013 | 17 | |
| | 291.25–305.25 | 0.1013 | 18 | |
| | 283.15–313.15 | 0.1013 | 19 | |
| | 208.15–573.15 | 4.9–29.4 | 20 | |
| | 461.83–575.15 | 2–25 | 21 | |
| | 269.0, 295.0 | 3.5–32.7 | 22 | |
| | acetone | no data available | | |
| | acetone | 293.15, 298.15 | 0.1013 | 16 |
| <i>N,N</i> -dimethylformamide | 191.25–313.15 | 0.1013 | 23 | |
| | 298.15 | 0.10 | 24 | |
| | 277.15–313.15 | 0.05–0.12 | 25 | |
| tetrahydrofuran | 293.15, 298.15 | 0.1013 | 3 | |
| 1,4-dioxane | 293.15, 298.15 | 0.1013 | 3 | |
| | 283.15–313.15 | 0.1013 | 19 | |
| 1-methylpyrrolidone-2 | 283.15–323.15 | 6.0–13.7 | 26 | |

sample may be quite significant.

It is estimated that the values of x_2 determined by this method are correct to within $0.02x_2$. This figure includes the experimental error involved in the measurement of pressure ($\Delta p/p = 0.002$) and temperature ($\Delta T = 0.1$ K) and in the determination of n_1^v , n_1^l , n_2^v , and n_2^l (eq 1). The figure taken for the molar volume of hydrogen at 273.15 K and 101.325 kPa is 22 428 cm³ mol⁻¹.

Method II. The apparatus for method II has been described in great detail by Brunner et al. (30). The measurements are made in a 30-cm³ high-pressure optical cell with a magnetic stirrer. Hydrogen of known pressure is admitted at a given temperature, and degassed solvent is metered with a high-pressure screw press into the cell and simultaneously stirred intensely until the last gas bubble has not quite disappeared; in other words, the transition from the two-phase state into the single-phase is observed. The gas solubility is easily

obtained from the moles of hydrogen determined from PVT data, the moles of solvent metered, and the bubble point pressure at a given temperature. Method II yields values for the mole fraction of hydrogen x_2 in the solution that are estimated to be correct to within $0.02x_2$. This figure includes the experimental errors involved in the measurement of pressure ($\Delta p/p = 0.002$) and temperature ($\Delta T = 0.1$ K) and the determination of cell volume ($\Delta v/v = 0.001$) and the moles of hydrogen and solvent introduced into the cell ($\Delta m/m = 0.001$). The greatest error occurs in determining the equilibrium point by visual observation, and it has been estimated to be 0.005, expressed in terms of $\Delta p/p$, at 10 MPa. This error is larger at smaller equilibrium pressures and may be as high as 0.02 at 0.5 MPa.

Purity of the Materials. The mole fraction purity of the hydrogen produced by Messer-Griesheim is 99.999%. The corresponding figures for the solvents used in our studies were determined by gas chromatography with two stationary phases and are listed in Table II. The suppliers were Merck for the *n*-hexane, toluene, acetonitrile, 1,4-dioxane, and 1-methylpyrrolidone-2, Baker for the *n*-decane and *n*-octane, and BASF for the acetone, tetrahydrofuran, and *N,N*-dimethylformamide. Before they were taken into use, the *n*-hexane and the acetone were distilled in a packed column with about 30 theoretical plates. The other solvents were not additionally purified.

Results

Table II lists the densities and vapor pressures of the solvents at 298.15, 323.15, and 373.15 K. The results of the gas solubility measurements are presented in Table III, in which p stands for the total pressure and x_2 for the mole fraction of dissolved hydrogen. The activity coefficient of the solvent is very close to unity at low solubilities. Hence, its partial pressure p_1 can be calculated with sufficient accuracy from the vapor pressure of the pure solvent p_1^0 and x_2 with the aid of Raoult's law, especially since the solvent partial pressure is very small compared with the total pressure p . Thus, the hydrogen partial pressure p_2 is given by

$$p_2 = p - p_1^0(1 - x_2) \quad (2)$$

Figure 1 shows the solubilities x_2 of hydrogen in *n*-hexane, toluene, tetrahydrofuran, 1,4-dioxane, and *N,N*-dimethylformamide at 298.15 K, and Figure 2 the solubilities in *n*-hexane and *N,N*-dimethylformamide at 298.15, 323.15, and 373.15 K by way of example. Within the limits of experimental accuracy involved in the measurement of $0.02x_2$, it may be considered that a linear relationship has been satisfactorily established between p_2/x_2 and p_2 .

The solubilities of hydrogen x_2^0 at a hydrogen partial pressure of 101.325 kPa were obtained by linear extrapolation of the x_2/p_2 values to $p_2 = 101.325$ kPa. The results are listed in Table IV. Owing to the small temperature range investigated

Table II. Mass Fraction Purities w , Molar Masses M , Densities ρ , and Vapor Pressures p of the Solvents

| solvent | formula/ w | $M/g \cdot mol^{-1}$ | $\rho/kg \cdot m^{-3}$ | | | $p/10^5 \cdot Pa$ | | |
|-------------------------------|---|----------------------|------------------------|------------|------------|------------------------|------------------------|---------------------------|
| | | | 298.15 K | 323.15 K | 373.15 K | 298.15 K | 323.15 K | 373.15 K |
| <i>n</i> -hexane | C ₆ H ₁₄ /0.999 | 86.178 | 664.7 (31) | 631.5 (31) | 581.7 (31) | 0.202 (31) | 0.541 (31) | 2.459 (31) |
| <i>n</i> -octane | C ₈ H ₁₈ /0.998 | 114.230 | 698.6 (31) | 678.0 (31) | 635.0 (31) | 0.0186 (31) | 0.0671 (31) | 0.468 (31) |
| <i>n</i> -decane | C ₁₀ H ₂₂ /0.995 | 142.285 | 726.4 (31) | 707.3 (31) | 667.8 (31) | 0.0017 (31) | 0.0087 (31) | 0.0957 (31) |
| toluene | C ₇ H ₈ /0.995 | 92.141 | 873.6 (31) | 838.8 (31) | 789.9 (31) | 0.0380 (32) | 0.123 (32) | 0.742 (32) |
| acetonitrile | C ₂ H ₃ N/0.995 | 41.053 | 779.5 (33) | 754.0 (33) | 699.0 (33) | 0.118 (32) | 0.338 (32) | 1.744 (32) |
| acetone | C ₃ H ₆ O/0.9999 | 58.080 | 784.4 (34, 35) | 756.4 (34) | 691.8 (36) | 0.3080 (32) | 0.8199 (32) | 3.725 (32) |
| <i>N,N</i> -dimethylformamide | C ₃ H ₇ NO/0.999 | 73.095 | 944.5 (37) | 920.5 (37) | 873.0 (37) | 0.0050 (32) | 0.021 (32) | 0.193 (32) |
| tetrahydrofuran | C ₄ H ₈ O/0.998 | 72.108 | 882.5 (38, 39) | 855 (38) | 800 (38) | 0.216 (40–42) | 0.586 (40–42) | 2.722 (40–42) |
| 1,4-dioxane | C ₄ H ₈ O ₂ /0.996 | 88.107 | 1028.0 (43) | 999.4 (43) | 941.7 (43) | 0.0488 (41, 42, 44) | 0.0159 (41, 42, 44) | 0.974 (41, 42, 44, 45) |
| 1-methylpyrrolidone-2 | C ₅ H ₉ NO/0.994 | 99.133 | 1028 (45, 47) | 1006 (45) | 962 (45) | 0.00046 (46, 47) | 0.0025 (46) | 0.0338 (46) |

Table III. Mole Fraction Solubilities of Hydrogen in Named Solvents^a

| <i>p</i> /MPa | 10 ² <i>x</i> ₂ | <i>p</i> /MPa | 10 ² <i>x</i> ₂ | <i>p</i> /MPa | 10 ² <i>x</i> ₂ | <i>p</i> /MPa | 10 ² <i>x</i> ₂ | <i>p</i> /MPa | 10 ² <i>x</i> ₂ | <i>p</i> /MPa | 10 ² <i>x</i> ₂ | <i>p</i> /MPa | 10 ² <i>x</i> ₂ |
|------------------|---------------------------------------|--------------------|---------------------------------------|---------------|---------------------------------------|---------------|---------------------------------------|-----------------|---------------------------------------|-----------------------|---------------------------------------|-------------------------------|---------------------------------------|
| <i>n</i> -Hexane | | <i>n</i> -Octane | | Toluene | | Acetonitrile | | 5.41 | 1.520 | 1,4-Dioxane | | <i>N,N</i> -dimethylformamide | |
| 298.15 K | | 298.15 K | | 298.15 K | | 298.15 K | | 7.34 | 2.091 ^a | 298.15 K | | 298.15 K | |
| 0.020 | 0 | 0.0019 | 0 | 0.0038 | 0 | 0.0118 | 0 | 8.81 | 2.455 | 0.0049 | 0 | 0.0005 | 0 |
| 1.53 | 1.076 ^a | 2.89 | 1.961 ^a | 0.874 | 0.2709 | 1.594 | 0.280 | 9.48 | 2.657 ^a | 1.895 | 0.345 ^a | 0.0005 | 0 |
| 1.62 | 1.135 | 6.91 | 4.472 ^a | 1.40 | 0.4362 ^a | 3.59 | 0.619 | 323.15 K | | 6.585 | 1.205 ^a | 3.28 | 0.473 ^a |
| 1.92 | 1.338 | 10.89 | 6.806 ^a | 1.83 | 0.5708 | 3.66 | 0.647 ^a | 0.0820 | 0 | 9.46 | 1.707 ^a | 4.56 | 0.671 |
| 2.61 | 1.832 | 14.77 | 9.073 ^a | 4.27 | 1.320 | 6.08 | 1.067 ^a | 1.762 | 0.589 | 323.15 K | | 6.53 | 0.942 ^a |
| 3.79 | 2.641 | 323.15 K | | 5.02 | 1.550 | 6.77 | 1.161 | 4.05 | 1.378 | 0.0016 | 0 | 7.23 | 1.035 |
| 4.29 | 2.907 | 0.0067 | 0 | 5.53 | 1.689 | 9.72 | 1.690 ^a | 4.24 | 1.435 ^a | 2.86 | 0.648 ^a | 9.68 | 1.361 |
| 6.00 | 4.113 | 2.40 | 1.861 ^a | 7.01 | 2.138 ^a | 10.25 | 1.736 | 6.70 | 2.286 ^a | 5.71 | 1.297 ^a | 9.77 | 1.406 ^a |
| 8.07 | 5.467 | 6.36 | 4.841 ^a | 7.60 | 2.322 | 323.15 K | | 6.71 | 2.258 | 9.94 | 2.248 ^a | 323.15 K | |
| 8.31 | 5.620 | 10.39 | 7.600 ^a | 9.63 | 2.993 | 0.0338 | 0 | 9.96 | 3.371 ^a | 373.15 K | | 0.0021 | 0 |
| 9.19 | 6.117 ^a | 14.37 | 10.220 ^a | 10.12 | 3.03 | 1.554 | 0.324 | 373.15 K | | 0.0974 | 0 | 2.75 | 0.490 |
| 323.15 K | | 373.15 K | | 323.15 K | | 2.92 | 0.620 ^a | 0.3725 | 0 | 2.78 | 0.896 ^a | 3.32 | 0.600 ^a |
| 0.054 | 0 | 3.05 | 2.860 ^a | 0.0123 | 0 | 3.83 | 0.794 | 3.14 | 1.370 ^a | 6.38 | 2.049 ^a | 4.28 | 0.758 |
| 1.38 | 1.075 | 7.01 | 6.582 ^a | 1.02 | 0.3724 | 5.78 | 1.225 ^a | 4.63 | 2.107 | 9.12 | 2.914 ^a | 6.63 | 1.185 ^a |
| 2.00 | 1.532 ^a | 11.51 | 10.491 ^a | 1.92 | 0.7242 | 7.61 | 1.558 | 6.97 | 3.236 | 1-Methylpyrrolidone-2 | | 6.99 | 1.206 |
| 5.28 | 4.182 | 15.27 | 13.701 ^a | 2.23 | 0.8248 ^a | 8.68 | 1.829 ^a | 8.44 | 3.914 ^a | 298.15 K | | 7.29 | 1.263 |
| 5.92 | 4.555 | <i>n</i> -Decane | | 3.94 | 1.440 | 10.05 | 2.049 | Tetrahydrofuran | | <0.0001 | 0 | 8.25 | 1.416 |
| 7.44 | 5.711 | 298.15 K | | 4.85 | 1.820 | 373.15 K | | 298.15 K | | 0.0193 | 0 | 10.06 | 1.760 ^a |
| 8.26 | 6.315 | 373.15 K | | 6.40 | 2.319 | 0.1744 | 0 | 0.1744 | 0 | 2.78 | 0.387 ^a | 373.15 K | |
| 8.82 | 6.757 ^a | 0.0002 | | 9.15 | 3.318 | 0.946 | 0.233 | 0.946 | 0.233 | 5.47 | 0.778 ^a | 0.0193 | 0 |
| 373.15 K | | 0.0002 | | 9.88 | 3.601 ^a | 2.11 | 0.582 ^a | 2.11 | 0.582 ^a | 8.34 | 1.164 ^a | 2.43 | 0.610 |
| 0.256 | 0 | 2.37 | 1.582 ^a | 373.15 K | | 4.12 | 1.166 | 3.71 | 0.996 ^a | 8.34 | 1.164 ^a | 3.03 | 0.756 |
| 2.05 | 1.909 ^a | 2.38 | 1.579 ^a | 0.0742 | 0 | 8.48 | 2.391 | 6.11 | 1.650 ^a | 323.15 K | | 3.24 | 0.812 ^a |
| 2.08 | 1.913 ^a | 10.35 | 6.661 ^a | 0.981 | 0.4544 | 10.39 | 2.939 | 9.66 | 2.614 ^a | 0.0003 | 0 | 4.81 | 1.184 |
| 2.52 | 2.400 | 323.15 K | | 2.19 | 1.057 | Acetone | | 323.15 K | | 2.17 | 0.372 ^a | 6.44 | 1.615 ^a |
| 4.03 | 3.998 | 0.0009 | | 2.36 | 1.138 ^a | 298.15 K | | 0.0620 | 0 | 4.34 | 0.739 ^a | 6.50 | 1.585 |
| 6.62 | 6.514 | 2.82 | | 5.70 | 2.748 | 0.0308 | | 2.95 | 0.950 ^a | 8.72 | 1.459 ^a | 9.73 | 2.409 ^a |
| 8.18 | 8.102 | 5.64 | | 9.11 | 4.384 ^a | 0 | | 8.61 | 2.789 ^a | 373.15 K | | | |
| 9.81 | 9.388 | 9.42 | | 9.47 | 4.489 | 1.473 | | 1.473 | 0.418 | 0.0034 | | | |
| | | 373.15 K | | 9.79 | 4.710 | 2.75 | | 2.75 | 0.787 | 0.2722 | | | |
| | | 0.0096 | | | | 3.23 | | 3.23 | 0.910 ^a | 0 | | | |
| | | 2.04 | | | | 4.73 | | 4.73 | 1.321 | 3.38 | | | |
| | | 4.69 | | | | 5.28 | | 5.28 | 1.494 ^a | 6.53 | | | |
| | | 8.845 ^a | | | | | | | | 9.58 | | | |
| | | | | | | | | | | 4.284 ^a | | | |
| | | | | | | | | | | 9.74 | | | |
| | | | | | | | | | | 2.297 ^a | | | |

^aMeasurements with high-pressure optical cell (method II); all other measurements are performed with the degassing apparatus (method I).

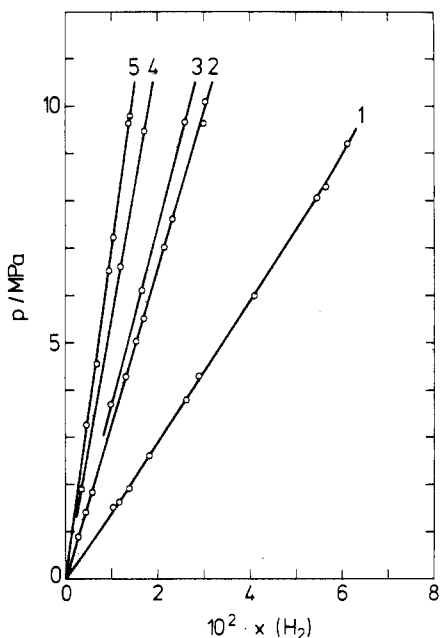


Figure 1. Solubility of hydrogen in (1) *n*-hexane, (2) toluene, (3) tetrahydrofuran, (4) 1,4-dioxane, and (5) *N,N*-dimethylformamide at 298.15 K.

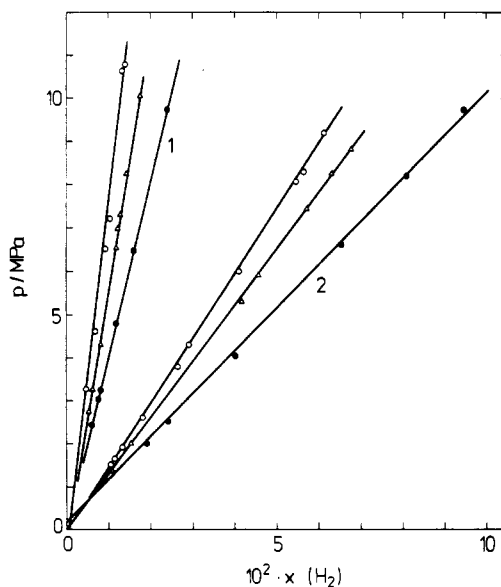


Figure 2. Solubility of hydrogen in (1) *n*-hexane and (2) *N,N*-dimethylformamide at (O) 298.15, (Δ) 323.15, and (●) 373.15 K.

perature suffices for smoothing and evaluating the hydrogen solubility x_2° at a hydrogen partial pressure of 101.325 kPa:

$$\Delta G_2 / \text{J} \cdot \text{mol}^{-1} = -RT \ln x_2^\circ \quad (3)$$

$$\ln x_2^\circ = -\Delta H_2 / RT + \Delta S_2 / R \quad (4)$$

where ΔG_2 is Gibbs energy of solution, ΔH_2 and ΔS_2 are the

and to the fact that only three isotherms have been determined, a two-constant Gibbs energy of solution equation linear in tem-

Table IV. Mole Fraction Solubilities x_2° of Hydrogen at a Hydrogen Partial Pressure of 101.325 kPa in Named Solvents at Temperature T^a

| T/K | $10^4 x_2^\circ$ | $\Delta H_2^a/kJ\cdot mol^{-1}$ | $-\Delta S_2^b/J\cdot mol^{-1}\cdot K^{-1}$ |
|-------------------------------|------------------|---------------------------------|---|
| <i>n</i> -Hexane | | | |
| 298.15 | 7.13 | 5.134 | 43.09 |
| 323.15 | 8.20 | | |
| 373.15 | 10.78 | | |
| <i>n</i> -Octane | | | |
| 298.15 | 6.76 | 4.494 | 45.57 |
| 323.15 | 7.88 | | |
| 373.15 | 9.75 | | |
| <i>n</i> -Decane | | | |
| 298.15 | 6.73 | 5.105 | 43.56 |
| 323.15 | 8.00 | | |
| 373.15 | 10.20 | | |
| Toluene | | | |
| 298.15 | 3.15 | 5.773 | 47.68 |
| 323.15 | 3.75 | | |
| 373.15 | 5.05 | | |
| Acetone | | | |
| 298.15 | 2.87 | 6.794 | 45.06 |
| 323.15 | 3.50 | | |
| 373.15 | 4.97 | | |
| Tetrahydrofuran | | | |
| 298.15 | 2.70 | 6.888 | 45.26 |
| 323.15 | 3.30 | | |
| 373.15 | 4.71 | | |
| 1,4-Dioxane | | | |
| 298.15 | 1.84 | 7.176 | 47.46 |
| 323.15 | 2.29 | | |
| 373.15 | 3.29 | | |
| 1-Methylpyrrolidone-2 | | | |
| 298.15 | 1.41 | 6.582 | 51.69 |
| 323.15 | 1.71 | | |
| 373.15 | 2.40 | | |
| <i>N,N</i> -Dimethylformamide | | | |
| 298.15 | 1.47 | 6.729 | 50.78 |
| 323.15 | 1.83 | | |
| 373.15 | 2.54 | | |
| Acetonitrile | | | |
| 298.15 | 1.78 | 6.539 | 49.89 |
| 323.15 | 2.16 | | |
| 373.15 | 3.02 | | |

^a Enthalpy of solution. ^b Entropy of solution.

temperature-independent changes in enthalpy and entropy on the transfer of 1 mol of hydrogen from the gas at 101.325 kPa to the infinitely dilute solution, and R is the gas constant $8.31441 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The figures calculated for ΔH_2 and ΔS_2 are summarized in Table IV. They are shown as four-digit numerals in order to allow the mole fraction solubility x_2° to be represented to within three significant figures. This does not imply that the values for the changes in enthalpy and entropy of solution are significant to within more than two or three digits.

Since x_2° is estimated to be correct to within $0.02x_2^\circ$, the largest error that can be calculated from eq 4 for ΔH_2 is 0.04 (at 298.15 K) to 0.06 (at 373.15 K) $\text{kJ}\cdot\text{mol}^{-1}$. It can be seen from the typical examples shown in Figure 3 that $\ln x_2^\circ$ is, in fact, a linear function of $1/T$ with a slope of $-\Delta H_2/R$; in other words, ΔH_2 is constant in the temperature range investigated within the limits of accuracy of the measurements.

Comparison with Data in the Literature

***n*-Hexane.** Seven laboratories have reported values for the solubility in *n*-hexane (2–8). Four sets of measurements were performed at or near a hydrogen partial pressure of 101.325

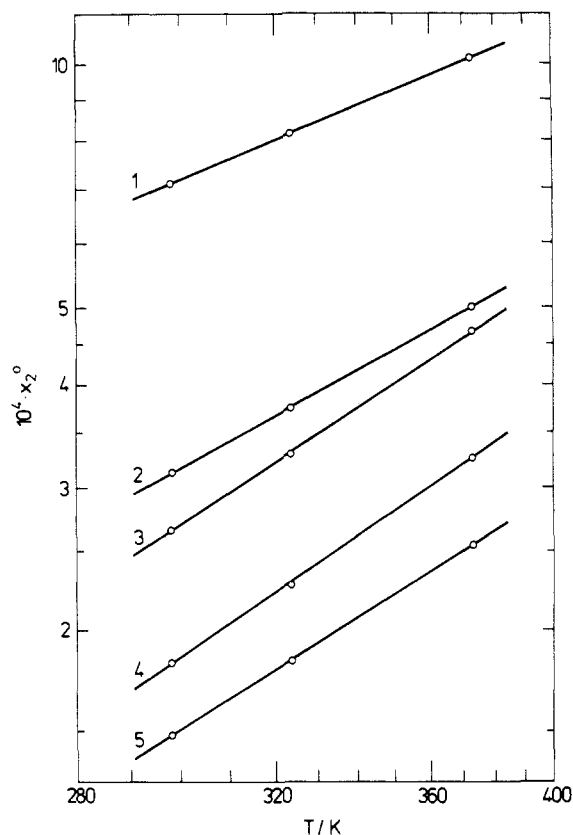


Figure 3. Temperature dependence of the solubility of hydrogen x_2° at a hydrogen partial pressure of 101.325 kPa in (1) *n*-hexane, (2) toluene, (3) tetrahydrofuran, (4) 1,4-dioxane, and (5) *N,N*-dimethylformamide.

kPa; the values that come closest to our results are those determined by Katayama and Nitta (4) at 213.15–298.15 K. The value determined by Katayama et al. at 298.15 K is 2% less than that which we obtained by extrapolation for a partial hydrogen pressure of 101.325 kPa. The values determined at 293.15 and 298.15 K by Guerry (3) and at 298.15 K by Makranczy et al. (5) are about 8% lower; and those extrapolated to 298.15 K by Waters et al. (2) are about 11% lower.

This system has been studied at high pressures by three laboratories. The data obtained by Frolich et al. (6) at 298.15 K and up to 11 MPa are 40% higher than ours and are incorrect. The figures determined by Sattler (7) at 308.35 K and 5.10–15.17 MPa are about 11% lower than those that we obtained by interpolating to 308.35 K, and the data submitted by Nichols et al. (8) for temperatures of 277.59, 310.93, and 344.26 are 20% higher than our interpolated values for these temperatures. Nichols et al. (8) submitted 377.59 K values that are 0–6% higher, and the data that they extrapolated to 101.325 kPa are about 25% higher than the reliable data of Katayama and Nitta (4).

***n*-Octane.** The low-pressure data for Cook et al. (9) agree well with those that we obtained by extrapolation to a hydrogen partial pressure of 101.325 kPa; those of Makranczy et al. (5) for 298.15 K are 5% lower; those of Ene et al. (13) for 298.15 and 324.65 K are 3.6% and 5% lower; and those of Ijams (10) are 2.5% higher. The high-pressure data presented in graphical form by Frolich et al. (6) are about 35–40% higher than ours. The temperature range studied by Connolly (12), viz., 463–553 K, differs too much from ours to allow a significant comparison. Data on the solubility of hydrogen and deuterium at 298.15, 310.65, and 325.15 K and between 5 and 30 MPa have been presented by Lachowicz et al. (11) in graphical form and in terms of linear equations. Extrapolated to a partial

hydrogen pressure of 101.325 kPa, they agree well with our own results and with those of Cook et al. (9).

n-Decane. The low-pressure data obtained at 298.15 K by Makranzy et al. (5) are 3% lower than our own extrapolated to 101.325 kPa, those of Ene et al. (13) for 298.15 and 323.15 K 1% and 6% lower, and those of Ijams (10) 25% less. The high-pressure data compiled by Sokolov et al. (14) are very difficult to compare with ours, and those of Sebastian et al. (15) do not provide any basis at all for a comparison, because the temperature range studied was higher, viz., 462.5–583.5 K. If the Sokolov et al. (14) data are extrapolated to a hydrogen partial pressure of 101.325 kPa and the values obtained are interpolated on a plot of $\ln x_2^\circ$ against $1/T$, the results will be slightly less than ours.

Toluene. The results obtained by Cook et al. (9) and Saylor and Battino (17) at 293.15 K agree to within 0.5% with those that we obtained by extrapolating to a hydrogen partial pressure of 101.325 kPa. The Just (6) and de Wet (18) values are about 20% higher, and those of Waters et al. (2) and Krauss and Gestrich (19) are about 4–8% lower. The first two figures obtained at high pressures and 298.15 K by Ipatiev and Levina (20) differ from ours at the same temperature by +1.5% and –2%, and the two values determined at 373.15 K are about 15% lower. The temperature ranges studied by Simnick et al. (21) and Laugier et al. (22) are substantially higher and cannot, therefore, be adopted for a comparison.

Acetone. Figures for the solubility of hydrogen in acetone at low pressures have been presented by three different authors. Our 298.15 K value extrapolated to a hydrogen partial pressure of 101.325 kPa agrees to within 0.5% with that of Puri and Ruether (25). Horiuti's figure (23) is 5% higher, and Just's (16) 20% lower.

N,N-Dimethylformamide. In the literature we only found some very unreliable low-pressure data of the solubility in *N,N*-dimethylformamide for 278.15–313.15 K obtained by Haidegger et al. (25). Because only one figure is given for the solubility, the uncertainty of the values is at least 20–50%.

Tetrahydrofuran. Guerry (3) measured the solubility at 293.15 and 298.15 K. His value for x_2° at 298.15 K agrees to within 1% with the figure that we obtained by extrapolating to a hydrogen partial pressure of 101.325 kPa.

1,4-Dioxane. The low-pressure value obtained at 298.15 K by Guerry (3) is 5% higher than our value determined by extrapolating to a hydrogen partial pressure of 101.325 kPa. Those published by Krauss and Gestrich (19) were measured in the 283.15–313.15 K temperature range and are about 3–5% lower than our corresponding figures for x_2° .

1-Methylpyrrolidone-2. Shakhova et al. (26) measured the solubility of hydrogen in 1-methylpyrrolidone-2 at 298.15 and 323.15 K. The figures that they obtained are about 4–8% lower than ours.

Acetonitrile. No data on the solubility of hydrogen in acetonitrile could be found in the literature.

Registry No. *n*-Hexane, 110-54-3; *n*-octane, 111-85-9; *n*-decane, 124-18-5; toluene, 108-88-3; acetonitrile, 75-05-8; acetone, 67-64-1; *N,N*-dimethylformamide, 68-12-2; tetrahydrofuran, 109-99-9; 1,4-dioxane, 123-91-1; 1-methyl-2-pyrrolidone, 872-50-4; hydrogen, 1333-74-0.

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