Table II. Refractive Indices (Relative to Air) of Aqueous Solutions for $\lambda = 6328$ Å and $\theta = 25°C$

Molarity	Refractive indices			
	$CuSO_4$[a]	$ZnSO_4$[b]	$AgNO_3$[b]	KCl[c]
0.000	1.33126	1.33126	1.33126	1.33126
0.010	1.33156			1.33134
0.025	1.33198			
0.050	1.33276	1.33269		1.33174
0.100	1.33421	1.33403	1.33298	1.33227
0.125	1.33486			
0.250	1.33840	1.33817	1.33560	
0.400	1.34250			
0.500	1.34518	1.34464	1.33992	
0.750			1.34421	
1.000			1.34843	

[a] Solution prepared from Titrisol Merck. [b] Solution prepared from anhydrous Prolabo R.P. salt. [c] Solution prepared from anhydrous Merck p.a. salt.

Table III. Refractive Indices (Relative to Air) of Sulfuric Acid Solutions for $\lambda = 6328$ Å and $\theta = 25°C$

Normality	H_2SO_4[a]
0.000	1.33126
0.100	1.33186
0.250	1.33275
0.500	1.33411
0.750	1.33543
1.000	1.33671

[a] Solution prepared from Titrisol Merck.

where n is the relative refractive index of the dilute aqueous solution, the molarity of which is C (in mol/l.), and k is a constant for a given solute. Table IV gives values of k corresponding to the four salt solutions investigated and also the values of the regression coefficients R calculated by means of an Olivetti desk computer.

Table IV. Values of Coefficient k in (0; 0.100 mol/l.) Range and Corresponding Values of Regression Coefficient R

Solute	k, mol^{-1}/l.	R
$CuSO_4$	2.96 10^{-2}	0.9999
$ZnSO_4$	2.77 10^{-2}	0.9998
$AgNO_3$	1.74 10^{-2}	0.9999
KCl	1.02 10^{-2}	0.9996

Discussion

During solution diffusion studies, the difference between the refractive index of pure water and the refractive index of potassium chloride at 0.100 mol/l. was measured directly by holographic interferometry. Accuracy in this case is $1 \cdot 10^{-5}$ RI unit.

$$n(\text{KCl; 0.1 mol/l.}) - n(\text{water}) = (101 \pm 1) \cdot 10^{-5}$$

for $\lambda = 6328$ Å and $\theta = 25°C$, a result which agrees well with that obtained by Pulfrich refractometer measurements. However, interferometry cannot directly give the refractive index, only the refractive index variations. To obtain the absolute value of the refractive index of dilute aqueous solution with the same precision (10^{-5}), one can measure the difference in refractive index Δn between this solution and pure water, which gives

$$n_{\text{solution/air}} = n^{II}{}_{\text{water/air}} + \Delta n$$

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Solubility of Water in Benzene

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The solubility of water in benzene was measured over the temperature range 15–35°C by use of a coulometric method for the determination of water. The accuracy of the solubility determinations was about ±0.3% over the whole range. Some thermodynamic functions of solutions were also calculated.

The low solubility of water in many nonpolar organic liquids is difficult to determine, especially that of water in benzene, which is apparently the most widely investigated system. The methods published are either based on those directly worked out for the solubility determinations of water in nonpolar solvents or on conventional methods for the determination of water. There are, however, large variations among the results published. In most of the cases, this depends on too low an accuracy of the method for water determination and, in some cases, on too short a time for ensuring complete equilibrium between the two phases, water and benzene.

The method presented here for the determination of the solubility of water in benzene in the range 15–35°C is based on an accurate method for the determination of small amounts of water by use of coulometrically generated iodine at controlled potential in a Karl Fischer reagent previously described (*6, 7*).

Experimental

Two 100-ml Erlenmeyer flasks, each containing 10 ml of water (twice distilled) and 40 ml of benzene (Fisher Scientific Co., thiophene-free and twice recrystallized), were placed in a specially built temperature bath containing about 8 liters of water, with a low heat exchange with the surroundings. The solutions were agitated in the bath for 2 hr and then left another 3 hr in the bath to allow the liquid layers to separate completely. Solutions agitated more than 2 hr and left overnight in the bath showed no observable difference from the former. The minimum time for the solutions to stand after agitation is about 1 hr in the actual temperature range with the technique used.

When equilibrium was reached, samples were taken from the benzene phase with an Agla microsyringe dried with nitrogen before every filling. The syringe was equipped with a 100-mm long injection needle, bent about 90°, with which a membrane in the electrolysis cell could be punctured at the sample additions to prevent contamination from water in the atmosphere. The fillings of the syringe were made under a nitrogen atmosphere. From the syringe the samples were immediately added to the electrolysis cell where an approximately fivefold excess of iodine (to the water in the sample) was generated. After 60-sec mixing for complete reaction, the remainder of the iodine was reduced. The whole analysis was completed in about 300 sec, and blanks were run between every analysis.

Three samples were taken (50, 100, and 200 μl) from each flask at every temperature, starting from the lowest temperature. The temperatures were measured by a platinum resistance thermometer. When the highest temperature was reached, the same procedures were repeated, now starting from the highest temperature. The results from the two series of measurements agreed well within 0.1%, which indicated that the phases were completely separated and that equilibrium was reached at every measured temperature.

Results and Discussion

The results for the solubility of water in benzene are shown in Table I and in Figure 1, where the solubilities are plotted as a function of temperature. Each value is the mean of three double determinations. The temperature was controlled to ±0.03°C which gave an uncertainty of about 0.1% in the solubility results. Temperature differences between the temperature bath and the microsyringe and volume-weight calculations at different temperatures gave a maximum error of 0.1%. Together with the uncertainty in the water determination step, a total error of about 0.3% is reasonable for each single determination.

In Table II some available references from the literature are listed, where the solubility of water in benzene was determined by some of the most common methods. Some of the values have been interpolated to 25°C, which may have caused small errors. The solubility found in this work agrees well with the value given by Moule and Thurston (*8*), whereas the others reported here lie more or less lower, with the exception of the result given by Roddy and Coleman (*9*), which lies somewhat higher. The low value obtained by Joris and Taylor (*5*) is probably due to incomplele exchange or isotopic fractionation.

If we consider the solubility of water in benzene expressed as mole fractions (x) at varying temperatures and use the following equation:

$$\ln x = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (1)$$

and assume that ΔH° and ΔS° for the transfer of 1 mole of water from the water phase to the benzene phase are independent of the temperature in this relatively small interval (25 ± 10°C), a plot of $\ln x$ vs. the reciprocal of the absolute temperature will give a straight line (Figure 2). The line was evaluated by means of a least-squares fit with the data given in Table III. From the slope, ΔH° was determined to 23.34 kJ mol^{-1}. From the intercept on the ordinate, ΔS° was determined to 30.49 J mol^{-1} K^{-1}.

The enthalpy and entropy for the following reaction have thus been calculated:

$$H_2O\ (l) \rightleftharpoons H_2O\ (\text{benzene}) \qquad (2)$$

Table I. Solubility of Water in Benzene as Function of Temperature

°C	H_2O, ppm
14.97	533.0
17.94	591.3
20.05	631.4
22.95	686.7
24.90	724.8
27.97	803.2
29.95	853.5
31.96	915.8
35.06	1021.1

Table II. Some Literature Data on Solubility of Water in Benzene at 25°C (Expressed in *M*)

Ref.	Molar solubility, *M*	Method
(*5*)	0.025	Tritium
(*4*)	0.032	Karl Fischer titration
(*2*)	0.033	Cloud point
(*10*)	0.033	CaH_2
(*3*)	0.035	$AgClO_4$
(*8*)	0.0359	Isotope dilution
(*9*)	0.0363	Tritium-monitored gravimetric
This work	0.0355	Karl Fischer coulometric

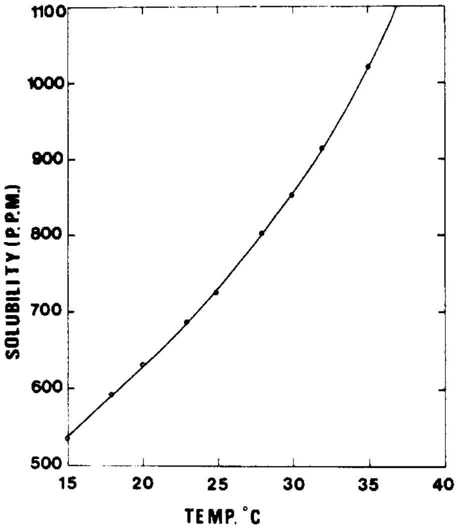

Figure 1. Solubility of water in benzene as function of temperature

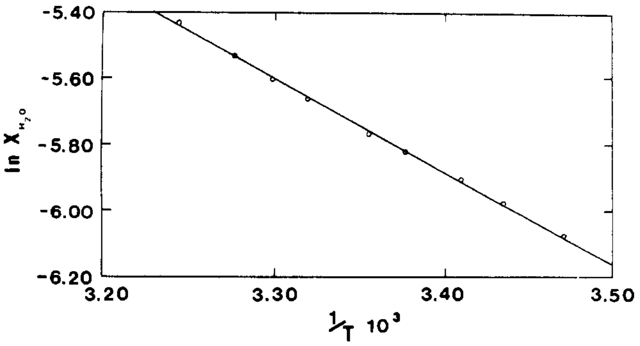

Figure 2. Logarithm of mole fraction of solubility of water in benzene vs. reciprocal absolute temperature

Table III. Logarithm of Mole Fraction of Solubility of Water in Benzene Vs. Reciprocal Absolute Temperature

ln x	$1/T \cdot 10^3$
−6.0726	3.4707
−5.9690	3.4352
−5.9036	3.4105
−5.8199	3.3771
−5.7685	3.3550
−5.6637	3.3208
−5.6031	3.2991
−5.5329	3.2774
−5.4246	3.2444

The low solubility of benzene in the water phase has been corrected for by using data published by Franks et al. (*1*) The enthalpy value of 23.34 kJ mol^{-1} for the heat of solution of water in benzene supports the assumption that hydrogen bonds are involved as the order of magnitude in hydrogen-bonding systems is about 21–25 kJ mol^{-1}.

The high accuracy in the solubility determinations and the small samples required indicates that the coulometric method for determination of water used is convenient for this determination. In a later study, an extended temperature range will be investigated and also the solubility of water in some other interesting solvents.

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Correction

In the paper, "Thermodynamic Properties of Compressed Gaseous Methane," by Roland H. Harrison, Richard T. Moore, and Donald R. Douslin [*J. Chem. Eng. Data*, **18** (2), 131 (1973)], Equation 3 should read:

$$G - G° = {}_T\int_0^{\rho} \frac{[P - RT\rho]d\rho}{\rho^2} + P/\rho - RT + RT \ln RT\rho \qquad (3)$$

and in Table I the block of data under 225.00°C and 250.00°C should be moved down one row so that the functions are tabulated from 0.80 through 8.5 mol dm^{-3} as follows:

Table I. Gram-Molal Thermodynamic Properties

	225.00°C				250.00°C			
Density, mol dm^{-3}	P, atm	−(H − H°), cal	− (S − °S), cal K^{-1}	G − G°, cal	P, atm	−(H − H°), cal	− (S − °S), cal K^{-1}	G − G°, cal
0.80	32.7054	44.1	7.0180	3452.0	34.4191	41.1	7.1139	3680.5
1.0	40.8922	54.8	7.4836	3673.1	43.0580	51.1	7.5790	3913.9
1.5	61.4192	80.8	8.3449	4076.2	64.7539	75.2	8.4395	4339.9
2.0	82.0793	105.6	8.9725	4364.0	86.6447	98.2	9.0663	4644.9
2.5	102.907	129.6	9.4724	4589.1	108.762	120.3	9.5654	4883.8
3.0	123.988	152.4	9.8917	4775.2	131.189	141.2	9.9838	5081.8
3.5	145.361	174.1	10.2556	4934.8	153.994	160.9	10.3469	5252.1
4.0	167.103	194.7	10.5792	5075.3	177.233	179.6	10.6698	5402.3
4.5	189.293	214.1	10.8722	5201.9	200.982	197.0	10.9620	5537.8
5.0	211.999	232.2	11.1412	5317.8	225.336	213.2	11.2304	5662.0
5.5	235.232	249.5	11.3911	5425.0	250.303	228.3	11.4797	5777.3
6.0	259.163	265.3	11.6253	5525.8	276.064	242.0	11.7133	5885.8
6.5	283.826	280.0	11.8466	5621.4	302.611	254.6	11.9340	5988.7
7.0	309.404	293.0	12.0570	5713.2	330.154	265.5	12.1439	6087.6
7.5	335.858	304.8	12.2582	5801.6	358.720	275.1	12.3446	6183.0
8.0	363.407	315.1	12.4516	5887.7	388.438	283.1	12.5375	6275.9
8.5	392.088	323.9	12.6383	5971.9				