Table I. Thermal Pressure Coefficients of Carbon Tetrachloride

Temp (P = 0), °C	$(\partial P/\partial T)_{\text{graph}}$, atm °C^{-1}	γ_{corr}, atm °C^{-1}	γ (*2*), atm °C^{-1}
21.90	11.84	11.56 ± 0.2	11.45 ± 0.06
27.00	11.48	11.21 ± 0.2	11.08 ± 0.06
31.35	10.95	10.70 ± 0.2	10.78 ± 0.06
32.95	10.73	10.49 ± 0.2	10.60 ± 0.06

Table II. Thermal Pressure Coefficients of Ethers

Substance	Temp (P = 0), °C	$(\partial P/\partial T)_{\text{graph}}$, atm °C^{-1}	γ_{corr}, atm °C^{-1}
Diethyl ether	17.40	9.02	8.93
	22.00	8.61	8.53
	27.15	8.20	8.13
	31.80	7.82	7.76
Di-*n*-butyl ether	21.25	9.68	9.52
	28.35	9.10	8.96
	32.50	8.85	8.72
	37.40	8.67	8.55
Di-*n*-amyl ether	20.90	10.08	9.87
	25.00	9.69	9.51
	30.95	9.36	9.19
	35.15	9.23	9.07
Di-*n*-hexyl ether	20.25	10.50	10.27
	24.90	10.01	9.80
	28.80	9.67	9.48
	33.85	9.29	9.12

Table III. Smoothed Values of Thermal Pressure Coefficients

Substance	Mol wt	$\gamma_{20°C}$	$\gamma_{25°C}$	$\gamma_{30°C}$	$\gamma_{35°C}$
Diethyl ether	74.1	8.71	8.29	7.90	7.51
Di-*n*-propyl ether	102.1	9.80	8.78	8.41	8.09
Di-*n*-butyl ether	130.1	9.64	9.20	8.85	8.63
Di-*n*-amyl ether	158.2	9.95	9.50	9.23	9.07
Di-*n*-hexyl ether	186.2	10.29	9.78	9.38	9.06

content was under 1% except for the dibutyl ether where it was estimated to be just under 4%.

It was considered that these levels of impurity would not significantly alter the thermal pressure coefficients.

RESULTS

As a test of the apparatus and technique, we have measured γ for carbon tetrachloride. The overall accuracy of the measurements is estimated to be ±0.2 atm °C^{-1}. The agreements between our results and those of Benninga and Scott (*1*) is shown in Table I. Table II shows the experimental data for the ethers. Table III shows values at rounded temperatures obtained by smoothing the experimental data and values for di-*n*-propyl ether obtained by interpolation from the data for other ethers.

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Solubility of H_2O and D_2O in Carbon Tetrachloride, Toluene, and Cyclohexane at Various Temperatures

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The solubilities of H_2O and D_2O in carbon tetrachloride, toluene, and cyclohexane have been determined at various temperatures by means of a Karl Fischer titration. The solubility of both solutes is greatest in toluene and least in cyclohexane. The ratio of solubility H_2O/D_2O at 25°C is 1.19 for toluene, 1.14 for carbon tetrachloride, ane 1.10 for cyclohexane. The heat of solution is greatest for CCl_4, least for cyclohexane. There is no significant difference in $\Delta H°$ for H_2O and D_2O in a given solvent.

In the course of some work on the infrared spectra of D_2O in carbon tetrachloride solution, it became necessary to know the solubility of D_2O in carbon tetrachloride. The data available were limited to two references (*2*, *6*). In the first of these, the data had been obtained for only two samples and only at 25°C. In the second, the value was expressed as having been obtained at "room temperature."

The solubilities of D_2O in carbon tetrachloride were measured at several temperatures using the Karl Fischer method with a "dead stop" end-point determination (*9*). At the same time, the solubility of H_2O in carbon tetrachloride was measured as a check on the procedure.

The study was extended to a measurement of the solubility of D_2O and H_2O in toluene and in cyclohexane because it has been suggested that these solvents, together with CCl_4, form a series with differing degrees of association with a polar solute. Allen et al. (*1*) have suggested that the differences in the degree of dimerization of benzoic acid in cyclohexane, carbon tetrachloride, and benzene can be attributed to solvation, increasing in that order. Toluene could be expected to occupy the same position as benzene in this series. In connection with other work in this laboratory on the differences in the behavior of hydrogen and deuterium compounds, it was of interest to see whether any difference in the ΔH° of solutions of H_2O and D_2O in these solvents might be detectable.

EXPERIMENTAL

The reagent-grade solvents were all purified by distillation and the purity was checked by measurement of the refractive index and by ir spectra. The solvents were dried over Drierite (CCl_4) or molecular sieve (toluene and cyclohexane). The ir spectra of the dried solvents were checked for total absence of any OH bands. The water used was distilled in a pyrex system and the D_2O, which was >99.8% D_2O, was used without additional purification.

The dried solvent was saturated with the solute by allowing it to stand in contact with water or D_2O in a closed system, protected from atmospheric moisture.

This two-phase system was kept in a pyrex storage bottle which was part of a conventional Squibb Automatic Zero Burette assembly (Will Scientific Cat. No. 7111). The storage bottle was in a constant temperature water bath. This apparatus is equipped with a side tube on the storage bottle to which a rubber bulb was connected. This bulb was used to increase the pressure on the surface of the liquid in the bottle, forcing the solution up the center tube and into a 50-ml buret.

The titration vessel was a three-neck 500-ml flask. In the center opening of this flask was the tip of a 10-ml microburet which delivered the Karl Fischer reagent. This buret was part of an all-glass assembly (Corning No. 2082) attached to a storage bottle in which the Karl Fischer reagent was kept.

One of the side necks of the flask held the tip of a 50-ml buret. This buret could be filled from the storage bottle in the constant temperature bath. A side arm at the top of this buret was connected to the atmosphere through two wash bottles, each of which contained the same two-phase system being analyzed. As solution was delivered to the flask from the buret, air was drawn in through the solution in the wash bottles, thus eliminating loss of solute from the solution in the buret. The air drawn into the wash bottles had been passed through drying tubes.

The other side neck of the reaction flask held two platinum electrodes which projected into the solution being titrated. These electrodes were connected to a conventional "dead stop" end-point apparatus containing a 1.35-V battery, a 150-Ω variable resistor, and a 0–100 μ-amp ammeter. In this apparatus, a small potential (15–20 mV) is impressed across the electrodes by means of the battery and the resistance. The end point is indicated by a sudden change in the reading on the microammeter.

The Karl Fischer reagent, having a titer in the vicinity of 2.5 mg H_2O/ml of reagent, was standardized using standard sodium tartrate. To perform a standardization, 50 ml of absolute methanol was placed in the 500-ml flask and titrated to the end point with KF reagent using the standard "dead stop" technique. This titration took a considerable time because the balance point continued to change as water was extracted from the glass system. When the balance point was stable, the sodium tartrate was added and titrated to the end point. After the first slow titration, a stable end point was much more quickly obtained in the following titrations.

The first few titrations of a new sample of solution always gave low titers, but a constant value was finally obtained after several titrations had been made. Other work in this laboratory had shown that significant amounts of water is adsorbed from a CCl_4 solution by the walls of a glass vessel. In order to avoid these low values for the first titrations of a new solution, the first sample put in the buret was allowed to stand for about 5 hr. This sample was then discarded, the buret was refilled with solution, and a measured volume was run into the titration flask. As the sample was added to the flask from the 50-ml buret, KF reagent was also added from the microburet in an amount below that required to reach the end point. After all the sample (for CCl_4 and cyclohexane 50 ml) had been added to the flask, additional KF reagent was added to the end point. It was important to standardize carefully on the reading of the ammeter at the end point if reproducible results were to be obtained.

The titrated sample was then removed from the flask, and 50 ml of absolute methanol was added and titrated to the end point. A second sample of test solution was added and the process repeated.

The data are the result of a minimum of 15 trials for each solution at each temperature. The precision of the results was best for toluene in which the solubility was highest. The titration of the cyclohexane solutions required only about 1 ml of reagent, and the precision of the measurements in this solution is not so good. Nevertheless, the precision seems to be as good or better than the other literature values.

RESULTS

The solubilities are tabulated in Table I. The error limits are average deviations based on 15 trials for each solution. The values obtained agree, in general, with those found in the

Table I. Solubilities of H_2O and D_2O in Carbon Tetrachloride, Toluene, and Cyclohexane at Various Temperatures in Moles per Liter

T, °C	CCl_4–H_2O		CCl_4–D_2O	
15	0.0062 ± 0.0001	0.0067 (*6*)	0.0057 ± 0.0001	
25	0.0086 ± 0.0003	0.0087 ± 0.0003 (*3*) 0.00828 (*6*)	0.0075 ± 0.0002	0.0076 (*4*), 0.0071 (*2*)
30	0.0093 ± 0.0003	0.0095 (*6*), 0.0102 (*7*)	0.0084 ± 0.0003	
35	0.0114 ± 0.0003	0.0114 (*6*)	0.0103 ± 0.0003	
45	0.0156 ± 0.0008	0.0154 (*6*)		
	Toluene–H_2O		Toluene–D_2O	
15	0.0200 ± 0.0006	0.0189 (*6*), 0.0131 (*8*)	0.0162 ± 0.0004	
25	0.0261 ± 0.0004	0.0274 ± 0.0005 (*3*) 0.0250 (*6*), 0.021 (*8*)	0.0213 ± 0.0004	0.0222 (*4*)
30	0.0293 ± 0.0004	0.0285 (*6*), 0.025 (*8*)	0.0240 ± 0.0004	
	Cyclohexane–H_2O		Cyclohexane–D_2O	
15	0.0026 ± 0.0001	0.0026 (*8*)	0.0024 ± 0.0001	
25	0.0032 ± 0.0002	0.0024 ± 0.0003 (*3*) 0.0056 (*8*), 0.00345 (*5*)	0.0029 ± 0.0002	0.0026 (*4*)
30	0.0037 ± 0.0002	0.0073 (*8*)	0.0034 ± 0.0001	

Table II. $\Delta G°$, $\Delta H°$, and $\Delta S°$ for Solutions of H_2O and D_2O in Carbon Tetrachloride, Toluene, and Cyclohexane

(T = 298°K)

	$\Delta G°$, kcal/mol	$\Delta H°$, kcal/mol	$\Delta S°$, cal/deg mol
H_2O in CCl_4	-1.27 ± 0.01	5.4 ± 0.4	23 ± 1
D_2O in CCl_4	-1.19 ± 0.02	4.8 ± 0.4	20 ± 1
H_2O in toluene	-1.92 ± 0.01	4.4 ± 0.1	21.2 ± 0.3
D_2O in toluene	-1.81 ± 0.01	4.5 ± 0.1	21.3 ± 0.3
H_2O in cyclohexane	-0.67 ± 0.04	4.0 ± 0.6	15 ± 2
D_2O in cyclohexane	-0.62 ± 0.03	4.0 ± 0.8	15 ± 2

literature. There is a marked discrepancy between our values for H_2O in cyclohexane and those in ref. *8* at 25° and 30°C. However, our value at 25°C checks well with the most recent value of 0.00345 mol/l. given in ref. *5*.

Values for the log of the solubility and the corresponding value of $1/T$ were analyzed with a least-squares program on an IBM 1130 computer to determine the best slope for the straight line. From the relation $\log K_s = \Delta H°/2.3\ RT +$ constant, where K_s is the solubility in mol/l., the slope of the $\log K_s$ vs. $1/T$ plot is equal to $\Delta H°/2.3\ R$. Values for $\Delta H°$ were calculated using the value $\Delta H° = 2.303 \times 1.987 \times$ slope. Values for $\Delta G°$ were calculated from the relation $\Delta G° = -2.303RT \log K_s$. Values for $\Delta S°$ were calculated from the relation $\Delta S° = (\Delta G° - \Delta H°)/T$. These values are given in Table II. By use of the root-mean-square deviations of the values for $\log K_s$, the maximum and minimum values for the slopes of $\log K_s$ vs. $1/T$ were determined, and from these the limits of the $\Delta H°$ values were set. The limits of $\Delta G°$ were based on the root-mean-square deviations of the values of K_s and the limits of $\Delta S°$ were determined from the variation of $\Delta G°$ and $\Delta H°$.

Differences in the values of $\Delta H°$ are of the same order as the precision in $\Delta H°$ and there appears to be no significant difference in the values for H_2O and D_2O. There is a significantly lower value for $\Delta S°$ for cyclohexane which seems to be the result of a low value for $\Delta G°$ rather than an effect due to $\Delta H°$.

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Solubility of Carbon Dioxide in Mixed Paraffinic Hydrocarbon Solvents at Cryogenic Temperatures

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The solubility of carbon dioxide in mixed paraffinic hydrocarbon solvents of methane, ethane, propane, and *n*-butane below the carbon dioxide triple point is reported for several temperatures of industrial interest. The solubility of carbon dioxide in ethane–propane mixtures can be computed as the molal average of the two constituent binary solubility limits. On the other hand, all ternary and quaternary systems containing methane show significant deviations from this molal average solubility, having a larger solubility in a mixture than that in one or in both pure hydrocarbons separately. With parameters determined from binary-system equilibrium data alone, the solubility of solid carbon dioxide in multicomponent systems can be predicted by the Wilson equation to an overall accuracy of ±4.0 mol % over the entire range of the solubility curve, or to an accuracy of ±1.0 mol % up to 10 mol % carbon dioxide solubility. The predictive accuracy of the Wilson equation is primarily dependent on the accuracy with which each binary parameter pair describes the carbon dioxide solubility relationship in pure hydrocarbons.

Cryogenic processes for separation of hydrocarbons from natural gas or for removal of carbon dioxide from other process streams require accurate knowledge of the solubility of solid carbon dioxide in hydrocarbons, particularly in multicomponent systems. However, the experimental data for the solubility of carbon dioxide below its triple point in hydrocarbons have been very limited.

Clark and Din (*5*) measured the solubility of carbon dioxide in ethane–ethylene mixtures and Cheung and Zander (*4*) reported limited data on the solubility of carbon dioxide in methane–ethane mixtures. By far the most complete and thorough study of the solubility of solid carbon dioxide in methane–ethane mixtures was made by Jensen (*13*), who also deter-

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