limited number of experimental measurements it is impossible for us to conclude which of these explanations is most probable. Recent vapor pressure measurements by Grant et al. (*2*) on γ-butyrolactone + isooctane mixtures do suggest very weak specific interactions between γ-butyrolactone molecules. Although the vapor pressure data could be described by a monomer/pentamer association model, the authors cautioned that their results did not definitively prove the existence of pentameric species in solution. As in all cases, the presence of molecular complexes should be supported by independent measurements involving spectroscopy, calorimetry, etc.

Registry No. Cyclohexane, 110-82-7; benzene, 71-43-2; toluene, 108-88-3; *p*-xylene, 106-42-3; *m*-xylene, 108-38-3; γ-butyrolactone, 96-48-0.

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Solubility of Hydrogen in Well-Defined Coal Liquids

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The solubility of hydrogen in Tetralin and several coal liquids was measured at high temperatures and pressures. A four-component synthetic recycle solvent containing 43% Tetralin, 38% 2-methylnaphthalene, 17% *p*-cresol, and 2% 4-picoline was studied in a 2-L, stirred autoclave at temperatures of 125, 200, 275, 350, and 400 °C and at pressures of 5, 10, 15, 20, and 25 MPa. The solubility of hydrogen in middle and heavy distillates from the Solvent Refined Coal II process (SRC II) was measured at the same temperatures and pressures. Densities of the liquid phases were measured at operating conditions. Analyses of small, thermally induced, changes in the compositions of the mixtures are presented. The occurrence of a hydrogen disproportionation reaction is indicated for the four-component mixture. There appeared to be a greater conversion of aromatic hydrocarbons to saturated hydrocarbons than heteroatom compounds to hydrocarbons and other products in the middle and heavy distillate mixtures. Additional properties of SRC II liquids, such as results of Bureau of Mines routine method distillation, viscosity, specific gravity, detailed elemental and chemical-type analyses, and enthalpies of combustion, are presented as supplementary material.

Introduction

The liquefaction of coal to produce fuels and possibly chemical feedstocks requires much research in chemical and phase equilibrium for suitable design, product distribution, and energy utilization. Thus, the Bartlesville Energy Technology Center of the U.S. Department of Energy conducted a research program in support of the program for development of the Solvent Refined Coal II process. The coal liquids studied in this project were produced during run 77SR-12 (*1*) at the Fort Lewis pilot plant which charged Pittsburgh seam coal from the Blacksville (WV) Mine No. 2. That run produced yields (weight percent moisture–ash-free coal) of 5.9% naphtha, 17.9% middle distillate, and 5.8% heavy distillate. Samples from that run were labeled 1007, 1008, and 1009, respectively. The solubility of hydrogen in samples 1008 and 1009 is reported in this report along with the densities of the phases at equilibrium. Physical and chemical properties for all three samples have been reported by Brinkman and Bowden (*2*).

The naphtha, middle distillate, and heavy distillate fractions showed some overlap by simulated distillation chromatography. Thus, a blending was made in the ratio 5.9:17.9:5.8, and a more precise distillation using a 75-plate spinning-band still provided fractions of 200, 200–325, and 325–425 °C distillates and a 425+ °C residuum. The distribution of the new fractions was 28.0%, 58.8%, 8.6%, and 2.7% with a loss of 1.9%. A standard crude petroleum analysis on the blended stock and analyses on the distillation fractions such as elemental and chemical type are given as supplementary material (see paragraph at end of text regarding supplementary material).

The project to measure the solubility of hydrogen in coal liquids was developed through the phases of design, construction, testing by measurements of hydrogen solubility in Tetralin, measurements of the solubility of hydrogen in a four-component synthetic recycle solvent mixture, and measurements of hydrogen solubility in middle and heavy distillates from the SRC II process. The methods were extended to measure the composition of the vapor phase at equilibrium for the hydrogen–Tetralin system.

Apparatus

A static system with a 2-L autoclave was selected for this project because (1) it was simple to operate, (2) the cost was relatively low, (3) design, assembly, and operation were possible in shortest time, (4) it gives reasonable accuracy, and (5) it was deemed best suited for study of coal liquids and complex systems containing water, ammonia, and hydrogen sulfide as well as hydrogen. The static system suffers most from increased probability of sample reactions at high temperatures owing to the long exposure times. That problem will be discussed later in the paper.

The high-pressure equipment was located in a special-purpose laboratory for hydrogen solubility and coal hydrogenation projects. The autoclave and sampling system are shown in Figure 1. All parts of the autoclave and sampling system that contacted the fluids were made with type 316 stainless steel except the short tubing between the autoclave and valve 1, which was made from type 347 stainless steel. The studies were made with 1300 cm^3 of liquid in the vessel at operating

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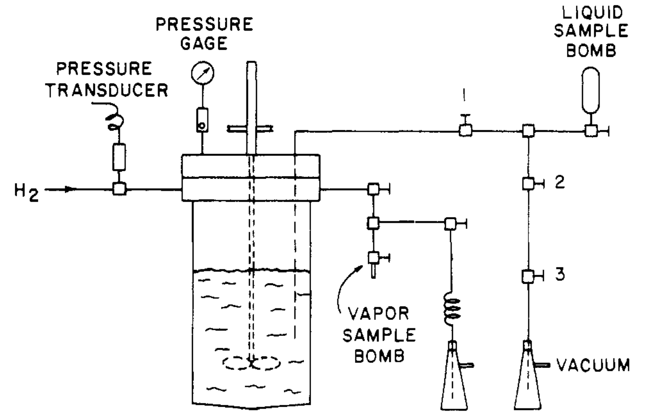


Figure 1. Equilibrium vessel and sampling system.

conditions. Gases from their supply cylinders were compressed to 3700 psi with a Whitey Model LC-105 compressor. Mixing and contact between the gas and liquid phases were effected by the hollow shaft mixer which drew gas down the tube and dispersed it in the liquid. Samples of the vapor were taken through the evacuated manifold into the evacuated bomb. To compensate for the pressure reduction of about 1% from the vapor sampling, the autoclave was repressured with hydrogen and subsequently reequilibrated before the liquid samples were taken through the dip tube into the evacuated bomb. The volume of the tubing from the bottom of the dip tube to valve 1 was minimized to reduce holdup and was about 1.5 cm^3. Liquid in this tubing was first drawn off and isolated in the 1.5-cm^3 volume between valves 2 and 3 of Figure 3. Liquid samples were then taken into the sample bomb while maintaining the autoclave at constant pressure by addition of hydrogen to the vapor phase; the sample bombs were left open to the autoclave for $1^1/_2$ min after they were initially charged to ensure complete filling and recondensation. With the valves to the bomb and autoclave closed, the line was depressured to vacuum, and the sample bomb was easily removed.

The autoclave body was heated with a standard 2.7-kW furnace, and the head was heated with two 500-W heaters. The sample bombs were fitted with custom-made Gas-Col heating jackets, and the temperature was controlled automatically. Heaters on the lines and other valves were adjusted manually to maintain the system at isothermal conditions. Temperatures were measured with thermocouples that had been calibrated against a platinum thermometer. At 125 °C the thermocouples indicated about 1.2 °C high but were accurate within 0.5 °C at all temperatures from 200 to 400 °C. The temperature of the autoclave was maintained to within 0.5 °C of its set point, so $\sigma(T) = 0.5$ K. Pressures were measured with a 7500-psi-range Bourdon-type pressure gage and a 5000-psi-range pressure transducer which were made of type 316 stainless steel and had stated accuracies of 0.5% of full scale. Calibrations against a dead-weight gage decreased the imprecision to about $\sigma(P) = 0.07$ MPa.

The apparatus for measuring the gas evolved from the sample bombs is shown in Figure 2. The sample bombs of accurately measured internal volume were weighed on a large double-pan analytical balance with a sensitivity of 0.2 mg. The bombs weigh about 1300 g and the masses of the 8-cm^3 liquid samples were 4–8 g. The bombs were weighed to an accuracy of ±1–2 mg. The gas was expanded from the bomb through a 0.040-in.-i.d. metal tube and a glass trap into the buret. The gas was then transferred into the bulb for analysis by gas chromatography. Some liquid is often transferred with the vapor into the trap where a twisted steel ribbon produced centrifugal flow and helped to prevent carry-over of any liquid to the buret. The trap was cooled to prevent evaporation of the liquid. Between 10 and 30 expansions were necessary to remove all dissolved gases from the bomb liquid down to a pressure of 10 mmHg. The remaining liquid was analyzed by mass spectrometry.

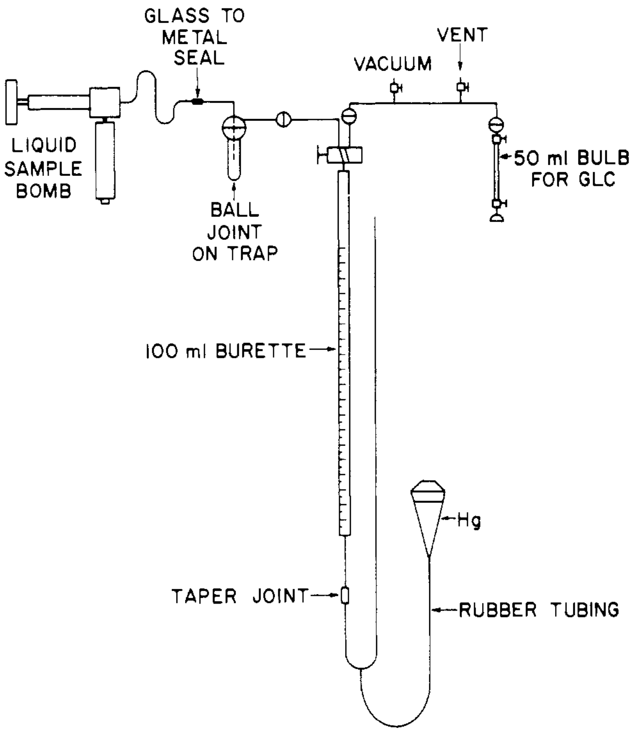


Figure 2. Apparatus for determination of dissolved-gas volume.

The accuracy of the mole fraction of hydrogen, X_H, in the liquid phase depends primarily on the accuracy of reading the gas buret. The buret can be read to 0.1 cm^3. Thus, at the lowest temperature and pressure, where only about 10 cm^3 was dissolved in the liquid, the imprecision was on the order of about 1%. The imprecision in the measurement of X_H, the mole fraction of hydrogen in the liquid phase, can be expressed as

$$\sigma(X_H) = (1 \times 10^{-6})(1 - X_H)^2(MW_l/\rho) \text{ for } X_H\rho \leq 0.14$$

$$\sigma(X_H) = 0.0002 \text{ for } X_H\rho \geq 0.14$$

where MW_l is the molecular weight of the solvent or coal liquid, and ρ is the density of the liquid phase at equilibrium in g/cm^3.

The densities of the samples were determined from the sample masses and from the internal volume of the sample bombs. The imprecision of the densities was $\sigma(\rho) = 0.01\rho$.

Hydrogen–Tetralin Mixture

The system was tested by measuring the solubility of hydrogen in Tetralin. These data are tabulated in Table I and compared with the data of Chao and his associates (*3*). Fisher purified-grade Tetralin was used without further purification. No impurity was detected in the starting material nor after use in the autoclave at 390 °C. The initial measurements were at 189.6 °C and 150 atm. The liquid phase was sampled while the impeller was turning at 300, 600, and 1000 rpm and also after the impeller was stopped following rotation at 300 rpm. No effect was noted on the values of the mole fraction of hydrogen dissolved in Tetralin, X_H. The four values varied from 0.081 to 0.082. The average value of 0.0814 agreed with the value of Chao, 0.0823. Subsequent sampling of the liquid phase was made after the impeller was stopped following rotation at 600 rpm. Good agreement between our data and those of Chao was also obtained at 268.7, 348, and 389.1 °C. Nasir, Martin, and Kobayashi (*4*) studied the same system. The agreement between their values and those reported in this work

Table I. Vapor-Liquid Equilibria of Hydrogen in Tetralin

P,[a] atm	X_H(Chao)	BETC X_H	BETC ρ[b]
	189.6 °C		
50	0.0297		
150	0.0823	0.0814	0.79
250	0.1289		
	268.7 °C		
50	0.0373	0.0395	0.70
100	0.0732	0.0701	0.71
150	0.1046	0.1079	0.71
250	0.1640	0.1733	0.70
	348 °C		
50	0.0452	0.0470	0.61
100	0.0925	0.0975	0.62
150	0.1390	0.1504	0.62
250	0.2314	0.2389	0.61
	389.1 °C		
50	0.0482	0.0471	0.55
100	0.1170	0.1154	0.56
150	0.1760	0.1759	0.58
250	0.2824	0.2762	0.57

[a] 1 atm = 0.101325 MPa. [b] ρ = density of liquid phase at equilibrium in g/cm^3.

is even better than the agreement with Chao's results.

After the measurements on all of the systems reported here were completed, modifications to the apparatus were completed so that vapor samples could be taken and $K = Y/X$ values calculated. New measurements on the Tetralin-hydrogen system were made, and the agreement of the mole fraction of hydrogen in the vapor phase, Y_H, between our values and those of Chao (*3*) was good. The new solubility data, X_H, agree with our previous data and those of Chao along the 189.6 °C isotherm, as well as for the 50-atm points at 268.7 and 389.1 °C. However, the new solubility data are about 10% higher than previously measured at 250 atm at both 268.7 and 389.1 °C. The modifications to the apparatus should have made the system more nearly isothermal and the data more accurate. Additional measurements are planned to resolve the differences.

Four-Component Mixture

Experimental measurements were made of the solubility of hydrogen in a four-component, synthetic recycle solvent consisting of 43% Tetralin, 38% 2-methylnaphthalene, 17% *p*-cresol, and 2% 4-picoline. This mixture was chosen because it was used previously in short contact time coal liquefaction by Mobil Research at Princeton, NJ (*5*), and it offered the possibility of studying the reactions of the molecules subjected to high temperature for about 6 h in the present system. The extent of chemical change is discussed later in the Chemical Analysis section. Sample materials were either reagent or practical grade. The results of this study are presented in Table II and Figure 3.

Duplicate measurements were made at 125 and 275 °C to check the repeatability of the measurements, and they were given equal weight when the lines were drawn in Figure 3. Duplicate measurements were also made at 400 °C but are not of equal value because, during run 8, the liquid phase expanded and almost filled the autoclave, and the proper mixing of the phases was impaired. Nevertheless, the data for run 8 have been included in Table II to show the relatively good agreement with run 9, where proper mixing and equilibrium were achieved. Thus, hydrogen dissolves readily in the liquid at high temperature, and equilibrium is easy to attain in the autoclave.

A gas-chromatographic (GC) analysis of the gases that had dissolved in the liquid at 400 °C showed a concentration of about 0.5% methane. Values of the liquid-phase densities in g/mL at system conditions are also given in Table II.

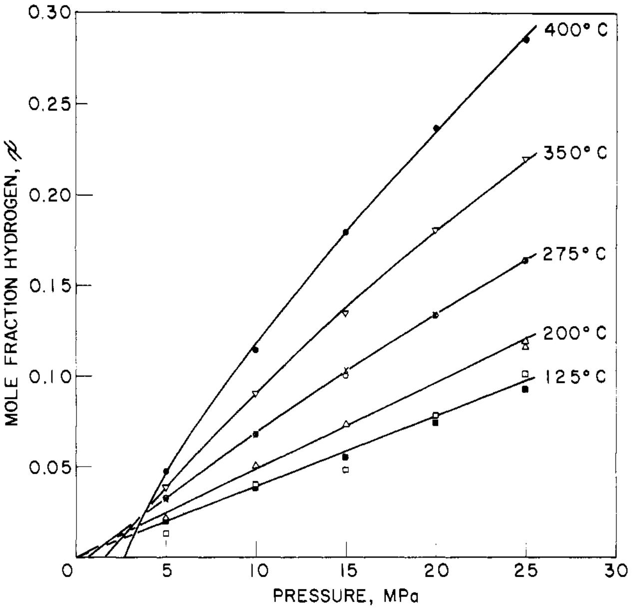


Figure 3. Solubility of hydrogen in a synthetic recycle solvent: 43% Tetralin, 38% 2-methylnaphthalene, 17% *p*-cresol, and 2% 4-picoline.

Table II. Solubility of Hydrogen in Four-Component Mixture of 43% Tetralin, 38% 2-Methylnaphthalene, 17% *p*-Cresol, and 2% 4-Picoline

P, MPa	125 °C X run 2	125 °C X run 3	125 °C ρ[a]	200 °C X(run 4)	200 °C ρ[a]
5	0.0131	0.0187	0.86	0.0216	0.79
5		0.0206	0.87		
10	0.0398	0.0387	0.86	0.0499	0.79
15	0.0482	0.0556	0.88	0.0731	0.80
20	0.0783	0.0743	0.88		
25	0.1010	0.0924	0.86	0.1192	0.81
25				0.1154	0.79

P, MPa	275 °C X run 5	275 °C X run 6	275 °C ρ[a]	350 °C X(run 7)	350 °C ρ[a]
5	0.0319	0.0329	0.72	0.0387	0.59
10	0.0676	0.0680	0.72	0.0904	0.61
15	0.1030	0.1003	0.72	0.1350	0.61
20	0.1339	0.1331	0.72	0.1807	0.62
25	0.1641	0.1642	0.73	0.2199	0.62

P, MPa	400 °C X run 8	400 °C X run 9	400 °C ρ[a]
5	0.0481	0.0475	0.52
10	0.1113	0.1145	0.54
15	0.1704	0.1793	0.54
20	0.2261	0.2370	0.54
25	0.2791	0.2853	0.55

[a] Units: g/cm^3.

The vapor pressure of the four-component mixture was determined at each temperature in a separate experiment and used in Figure 3 at $X = 0$. The data at the highest temperature are only approximate because of thermal decomposition in the absence of hydrogen. Detailed analytical data are in a following section.

SRC II Middle Distillate

The results of the measurements of the solubility of hydrogen in a middle distillate from the SRC II process are presented in

Table III. Solubility of Hydrogen in a Middle Distillate from the SRC II Process, Sample 1008

	125 °C		200 °C		275 °C		350 °C		400 °C	
P, MPa	X	ρ^a	X	ρ^a	X	ρ^a	X	ρ^a	X	ρ^a
5	0.0227	0.87	0.0334	0.77	0.0494	0.67	0.0534	0.60	0.0617	0.50
10	0.0375	0.88	0.0589	0.78	0.0788	0.70	0.1036	0.62	0.1293	0.54
15	0.0595	0.88	0.0883	0.79	0.1256	0.70	0.1577	0.62	0.1942	0.54
20	0.0797	0.88	0.1143	0.79	0.1583	0.70	0.2045	0.61	0.2439	0.53
25	0.0987	0.87	0.1412	0.78	0.1944	0.70	0.2472	0.62	0.3201	0.53

[a] Units: g/cm^3.

Table IV. Solubility of Hydrogen in a Heavy Distillate from the SRC II Process, Sample 1009

	125 °C		200 °C		275 °C		350 °C		400 °C	
P, MPa	X	ρ^a	X	ρ^a	X	ρ^a	X	ρ^a	X	ρ^a
5	0.0157	1.00	0.0240	0.95	0.0483	0.84	0.0460	0.78	0.0470	0.74
10	0.0345	1.01	0.0426	0.96	0.0792	0.86	0.0828	0.80	0.0906	0.75
15	0.0457	1.02	0.0689	0.96	0.0978	0.86	0.1290	0.78	0.1332	0.74
20	0.0609	1.01	0.0910	0.95	0.1268	0.88	0.1603	0.80	0.1765	0.74
25	0.0761	1.01	0.1099	0.96	0.1524	0.88	0.1933	0.80	0.2087	0.74

[a] Units: g/cm^3.

Table III. The dissolved hydrogen gas was expanded from the sample bombs, measured, collected, and tested by GC for the presence of hydrogen and any decomposition products. The stripped SRC II liquid was separated into aromatic and saturated fractions by high-performance liquid chromatography (HPLC). An average molecular weight of 146.1 was determined by mass-spectroscopic (MS) analysis of the aromatic fraction and gas-chromatographic (GC) analysis of the saturated fraction. Thus, the values of solubility, X, given in Table III, are for the mole fraction of hydrogen dissolved in the liquid. Also shown in Table III are the densities of the liquid phase. The solubility data are shown graphically in Figure 4. The lines are extrapolated to an assumed vapor pressure. Vapor pressures were not obtained because the sample was unstable in the absence of hydrogen. The data at 400 °C were adjusted for a concentration of about 1.5% methane, as determined by GC, and an average molecular weight shift from 146.1 to 149.9 during the run as discussed in a following section. The small change in molecular weight and composition would be expected to cause little change in the gas solubility.

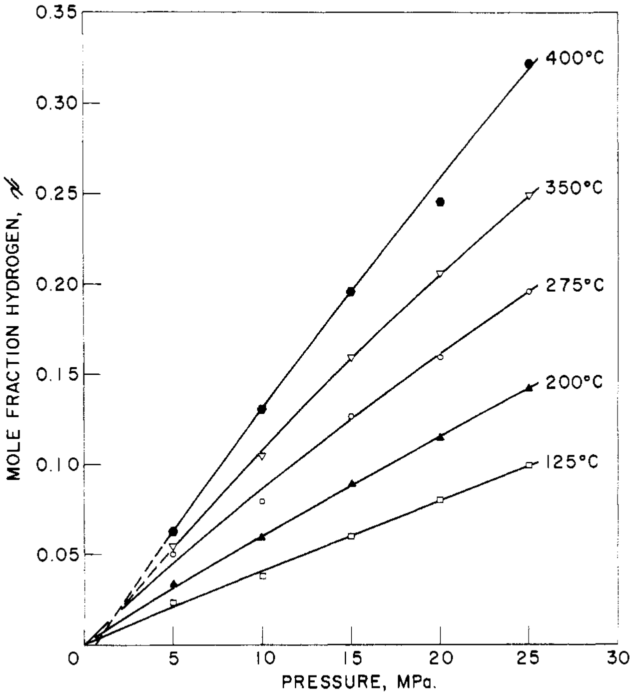


Figure 4. Solubility of hydrogen in a middle distillate from the SRC II process: sample 1008.

SRC II Heavy Distillate

The results of the measurements on the solubility of hydrogen in a heavy distillate from the SRC II process are presented in Table IV and Figure 5. This material had a 5% point at 96 °C and an end point of 247 °C at a pressure of 0.4 mmHg as measured by an ASTM D1160 distillation. An average molecular weight of 203.6 was determined in the same manner as for the middle distillate. The solubility data at 400 °C were adjusted for a concentration of about 3.5% methane, as determined by GC, and an average molecular weight shift to only 204.4 during the run as discussed in the next section. The small change in molecular weight and composition would be expected to cause little change in the gas solubility in the heavy distillate by reference to Figure 6, which compares the solubility of hydrogen in several fluids.

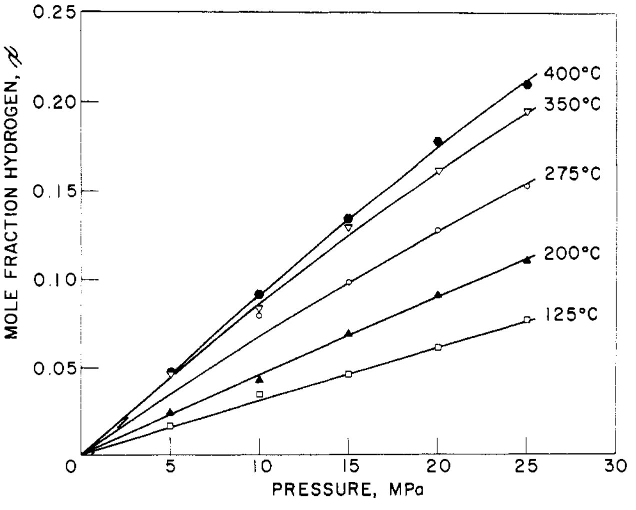


Figure 5. Solubility of hydrogen in a heavy distillate from the SRC II process: sample 1009.

Chemical Analysis

Four-Component Mixture. The extent of chemical change occurring during the hydrogen-solubility studies and the average molecular weights of the liquid phase in the autoclave were determined by low-voltage electron-impact (LV/EI) mass spectrometry. Mass spectra were acquired at an electron energy in the nominal range 10–10.5 eV which produced a ca. 10:1 ratio of the m/z 106 and 91 ions from ethylbenzene and at a resolution of ca. 1500 with a Kratos MS-30 mass spectrometer (6). Samples were introduced into the ion source (300

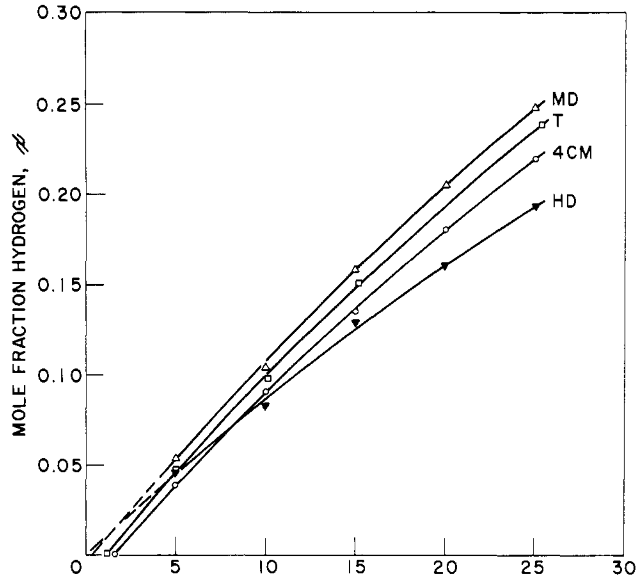


Figure 6. Comparison of the solubility of hydrogen in several fluids at about 350 °C: (△) middle distillate, SRC II; (▽) heavy distillate, SRC II; Tetralin at 348.6 °C; (○) four-component mixture.

Table V. Compositional Data for Four-Component Mixture and for Mixture from Autoclave Following Solubility Studies

compd		concn in mixture, wt %		
		initial		
name	formula	weights	MS	autoclave[a]
methyltetralin[b]	$C_{11}H_{14}$			1.9 ± 0.1[c]
2-methylnaphthalene	$C_{11}H_{10}$	38.0	36.8 ± 0.1	35.5 ± 0.1
Tetralin	$C_{10}H_{12}$	43.0	43.1 ± 0.3	43.1 ± 0.2
naphthalene	$C_{10}H_8$			1.4 ± 0.1
p-cresol	C_7H_8O	17.0	18.0 ± 0.4	16.2 ± 0.1

[a] Liquid from autoclave after 400 °C runs. [b] MS spectra indicate but do not conclusively prove presence of 2-methyl isomer. [c] Calculated by assuming that 2-methyl- and 6-methyl-1,2,3,4-tetrahydronaphthalenes have identical LV/EI sensitivities. The error introduced into the results by this assumption should be small since the relative sensitivity for the 2-methyl isomer should be bounded by the values for Tetralin (1.02) and its 6-methyl homologue (1.09).

°C) via a reservoir inlet (325 °C), and the LV/EI/MS were recorded in triplicate. Conversion of molecular-ion intensities into quantitative distributions incorporated LV/EI-ionization sensitivities. Consequently, sensitivities for LV/EI ionization of 4-methylpyridine, 4-methylphenol, naphthalene, Tetralin, 2-methylnaphthalene, and 6-methyl-1,2,3,4-tetrahydronaphthalene were determined relative to the sensitivity for LV/EI of ethylbenzene. The average deviation in these sensitivities was 4.7%. The relative LV/EI gram sensitivities for naphthalene (1.74), Tetralin (1.02), 2-methylnaphthalene (2.12), and 6-methyl-1,2,3,4-tetrahydronaphthalene (1.09) are in excellent agreement with the corresponding values of 1.73, 0.94, 2.11, and 1.12 reported by Lumpkin and Aczel (*7*, *8*). The relative LV/EI gram sensitivities for 4-picoline and *p*-cresol were 0.72 and 1.23. The ratio of the *m/z* 128 to *m/z* 132 intensities (0.0122) in the spectra of Tetralin was incorporated into the quantitative analysis of the MS data for the mixtures.

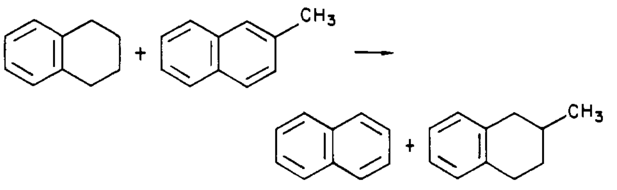
Table VI. Composition of SRC II Middle Distillate Aromatic Fractions from Sample 1008

		composn, wt %			
		fraction basis[a]		distillate basis[b]	
Z series	C no. range	initl	after 400 °C run	initl	after 400 °C run
−6 (H)	7–15	3.3	2.9	3.0	2.7
−8 (H)	8–17	12.5	13.3	11.5	12.2
−10 (H)	9–16	3.6	3.6	3.3	3.3
−12 (H)	10–16	34.8	34.6	32.0	31.7
−14 (H)	12–16	8.3	8.2	7.6	7.5
−16 (H)	12–18	0.9	1.3	0.8	1.2
−18 (H)	14–15	0.3	0.2	0.3	0.2
−22 (H)	16–17	0.1	0.1	0.1	0.1
−5 (N)	6–13	3.4	3.0	3.1	2.8
−7 (N)	8–14	0.5	1.7	0.5	1.6
−9 (N)	8–15	2.5	3.5	2.3	3.2
−11 (N)	9–15	1.4	2.0	1.3	1.8
−13 (N)	13–18	0.1	0.4	0.1	0.4
−15 (N)	12–17	0.1	0.1	0.1	0.1
−6 (O)	6–14	19.5	16.3	17.9	14.9
−8 (O)	8–14	5.5	5.6	5.1	5.1
−10 (O)	9–14	0.3	0.4	0.3	0.4
−12 (O)	10–11	0.0	0.0	0.0	0.0
−14 (O)	12–16	1.2	1.3	1.1	1.2
−16 (O)	12–14	0.8	0.8	0.7	0.7
−4 (O2)	10–11	0.1		0.1	
−6 (S)	8–10	0.1	0.1	0.1	0.1
−8 (S)	9–10		0.1		0.1
−10 (S)	8–12	0.7	0.6	0.6	0.6
		100.0	100.1	91.9	91.9

[a] Calculated on basis of mass-spectral analysis on the aromatic fraction of the distillate only. [b] Normalized to the total distillate.

The results obtained from the mass-spectrometric analyses are summarized in Table V. Comparison of the values in columns 3 and 4 reveals that the weight percent values obtained for the original mixture by MS are in good agreement with the values calculated from the weights taken. The presence of a residual intensity at *m/z* 128 and an intensity at *m/z* 146 in the spectra of the liquid from the autoclave following completion of the hydrogen-solubility studies and the absence of these ions in the spectra of the original mixture demonstrate the formation of naphthalene and methyltetralin during heating of the mixture. The absence of an ion at *m/z* 118 and the presence of an ion at *m/z* 104 in the spectra of the autoclave liquid indicate that the methylated Tetralin corresponds to the 2-methyl isomer rather than the 6-methyl isomer.

The weight percent values in column 5 of Table V reveal that the thermally induced formation of naphthalene and assumably 2-methyltetralin at elevated temperatures accounts for 3.3% of the liquid recovered from the autoclave after the hydrogen-solubility studies. Formation of these compounds is most easily rationalized by the disproportionation reaction



(1)

The average molecular weight of the initial mixture calculated from the weights of the compounds taken is 129.6 amu. The weight percent values of the four components from the mass-spectrometric analysis of this mixture result in an average molecular weight of 129.0 ± 0.6 amu. The weight percent values in column 5 of Table V yield an average molecular weight of 129.8 ± 0.5 amu for the liquid in the autoclave at the end of the solubility studies. The three values are seen to agree within the limits of data precision.

In conclusion, the occurrence of chemical change during the heating of a four-component mixture under static conditions and high hydrogen pressures at temperatures up to 400 °C for extended times has been demonstrated. However, the chemical reaction and the difference in volatility of the components altered the composition of the liquid in the autoclave at the end of the solubility studies from that of the initial mixture by only 3.3%. In addition, it is important to note that these phenomena

Table VII. Elemental Analysis of SRC II Middle Distillate Sample 1008

	composn, wt %				
	tot. distillate as received[c]	aromatic fractions			
		fraction basis[a]		distillate basis[b]	
		as received[d]	after 400 °C run[d]	as received[d]	after 400 °C run[d]
carbon	86.28	87.5	87.7	80.5	80.4
hydrogen	9.05	8.1	8.1	7.5	7.4
nitrogen	0.98	0.9	1.1	0.8	1.0
oxygen	3.36	3.4	2.9	3.1	2.7
sulfur	0.32	0.2	0.2	0.2	0.2

[a] Calculated on basis of mass-spectral analysis on the aromatic fraction of the distillate only. [b] Normalized to the total distillate; aromatic fraction as received = 92% of total, aromatic fraction after 400 °C run = 91.7% of total. [c] SWRI data (2). [d] BETC MS.

affected the average molecular weight of the liquid by less than 0.6 amu.

SRC II Distillates. Standard mass-spectrometric methods for the analysis of saturates (*9*) do not provide carbon-number distributions which are prerequisites to calculation of average molecular weights. Consequently, chemical analysis of the SRC II middle and heavy distillates before and after the 400 °C hydrogen-solubility experiments involved separation of samples into saturate and aromatic fractions using high-performance liquid chromatography prior to analysis. The compositions and average molecular weights of the saturate fractions were determined by gas chromatography. Known mixtures of saturated hydrocarbons were used for calibration in these analyses. LV/EI mass spectra of the aromatic fractions were acquired at ca. 12 500 resolving power as described above. The conversion of ion intensities to carbon-number distributions assumed equal relative LV/EI mole sensitivities for all components.

Results from the LV/EI/MS analysis of the SRC II middle distillate aromatic fractions are summarized in Table VI. The first column lists Z-series values for the compound types where Z is defined by the general formula $C_nH_{2n+z}N_aO_bS_c$. For hydrocarbon compound types, the value of Z is followed by the letter H. Heteroatomic compound types are designated by the Z value followed by the heteroatom symbol and the number of heteroatoms per molecule. For example, the Z-series designations for alkylbenzenes, alkylphenols, and alkylthienobenzothiophenes are -6(H), -6(O), and -14(S2), respectively. The assignment of compound types was not completely unambiguous as the MS resolving power, although sufficient to resolve most multiplets, was not sufficient to resolve ions differing in composition by $^{12}C_3/^{32}SH_4$, $^{12}CH_2/^{14}N$, or $^{13}CH/^{14}N$ over the observed mass range. Inclusion of intensity corrections for heavy-isotope contributions effectively eliminated problems with $^{13}CH/^{14}N$ multiplets. Problems arising from the $^{12}CH_2/^{14}N$ doublet, which reflects the presence of hydrocarbon fragments and nitrogen-containing molecular ions possessing the same mass numbers, were minimized by use of low-voltage electrons. In regard to analysis of sulfur compound types, ambiguity in assignments does not exist at carbon numbers below those of the initial member of the unresolved hydrocarbon homologous series.

Comparison of the data in Table VI for each Z series indicates relatively small differences in composition between the distillate aromatic fractions before and after the 400 °C hydrogen-solubility experiment. Some of the larger variations observed for the nitrogen-containing compound types [-5(N) through -15(N)] may be due to interference from hydrocarbon fragment ions rather than actual sample differences. Nevertheless, the total amounts of nitrogen compounds observed are reasonably consistent with the nitrogen contents of the original sample as shown in Table VII, columns 2 and 5, assuming all heteroatomic compounds are separated into the aromatic fractions. In fact, the agreement between the elemental compositions for nitrogen, oxygen, and sulfur calculated from the MS analysis of the aromatic fractions and normalized to the distillate basis (columns 5 and 6) and the values from conventional elemental analysis of the original distillate (column 2) is quite good considering the assumption of equal molar sensitivities in the mass-spectral analaysis. Comparison of the data in columns 5 and 6 indicates only small changes in elemental composition of the aromatic fractions after the 400 °C hydrogen-solubility experiment.

Analysis of the SRC II heavy distillate samples gave results very similar to those obtained for the middle distillate (see supplementary material). The most significant dfference was the conversion of more aromatics to saturates in the 400 °C hydrogen-solubility experiment with the heavy distillate compared to the middle distillate. However, the extent of conversion was not very significant as the weight percent of saturates increased only from 4.0% to 5.2% of the heavy distillate.

Average molecular weights for the two middle distillate and two heavy distillate samples were determined by combining the average molecular weights of the saturated fractions determined by GC with the corresponding weights of the aromatic fractions calculated from the mass-spectral analysis. The equation is

$$MW = MW_sX_s + MW_AX_A \qquad (2)$$

where MW_s and MW_A are the average molecular weights of the saturated fraction and aromatic fraction, and X_s and X_A are the mole fractions of the saturate fraction and aromatic fraction in the combined, total distillate sample, respectively. X_s and X_A are calculated from the weight fractions g_s and g_A by the following equations:

$$X_s = g_s/[MW_s(g_s/MW_s + g_A/MW_A)] \qquad (3)$$

$$X_A = g_A/[MW_A(g_s/MW_s + g_A/MW_A)] \qquad (4)$$

Only small shifts in molecular weight were indicated by the data for the middle distillate (146.1 to 149.9) and the heavy distillate (203.6 to 204.4) before and after the 400 °C hydrogen-solubility experiments.

In conclusion, analysis of the SRC II middle distillate samples before and after the 400 °C hydrogen-solubility experiments indicates some small, but not very significant, changes in composition. There appeared to be a greater conversion of aromatic hydrocarbons to saturated hydrocarbons than heteroatomic compounds to hydrocarbons and other products, especially in the heavy distillate samples.

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Registry No. H_2, 1333-74-0; Tetralin, 119-64-2; 2-methylnaphthalene, 91-57-6; *p*-cresol, 106-44-5; 4-picoline, 108-89-4; methyltetralin, 31291-71-1; naphthalene, 91-20-3; 2-methyltetralin, 3877-19-8.

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Supplementary Material Available: Two tables showing *Z*-series composition (Table VIII) and elemental analysis (Table IX) of SRC II heavy distillate 1009, three tables showing enthalpy of combustion results for samples 1007, 1008 and 1009 and the reconstituted whole crude (Tables X–XII), one table of crude distillation of blended coal liquid (Table XIII), and two tables of compositional and elemental analyses (Tables XIV and XV) of distillates from the blended coal liquid (8 pages). Ordering information is given on any current masthead page.

Diffusion Coefficient of Chlorine in Water at 25–60 °C

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The molecular diffusivity of chlorine in water was measured over the temperature range 25–60 °C and at atmospheric pressure by using a laminar jet apparatus. Experimental results are compared to values reported in the literature and with correlations. The diffusivity was found to vary from 1.38 × 10^{-5} cm^2/s at 25 °C to 3.11 × 10^{-5} cm^2/s at 60 °C.

Introduction

The purpose of this note is to report experimental values of the diffusion coefficient for chlorine in water measured over the temperature range 25–60 °C. A laminar liquid jet device was used in these experiments, and the experimental results are compared to values reported in the literature (Spalding (*1*), Ibrahim and Kuloor (*2*), Kramers et al. (*3*)) and with correlations (Wilke and Chang (*4*), Scheibel (*5*), Othmer and Thakar (*6*), Akgermann and Gainer (*7*)).

In this study we have followed Spalding (*1*) and used 0.1 N HCl rather than pure water in order to suppress the hydrolysis reaction

$$Cl_2(aq) + H_2O \rightleftarrows HOCl + H^+ + Cl^- \qquad (1)$$

It is necessary to suppress the hydrolysis reaction so that this reaction will not affect the rate of absorption and give a diffusion coefficient that is larger than the true value. For 0.1 N HCl at 25 °C, only 5.8% of the chlorine is hydrolyzed at equilibrium. Since the contact time in the jet device is short (less than 0.025 s) and the rate of hydrolysis is slow, the reaction has little effect on the rate of absorption. The addition of 0.35 wt % HCl to give a 0.1 N solution is expected to have little effect on the physical properties of the solution. For example, a falling-ball viscosimeter was used to measure the viscosity of the 0.1 N HCl solution and the viscosity was found to be 0.919 cP at 25 °C. This value may be compared to the pure-water viscosity of 0.890 cP at 25 °C. The viscosity is therefore only increased 3% by the addition of HCl. The Stokes–Einstein relation ($D\mu/T$ = a constant) normally overpredicts the effect of electrolytes on the diffusion coefficient and can be used to estimate a maximum effect on the diffusion coefficient by the addition of HCl. Thus, it is expected that the diffusion coefficient measured in this work for 0.1 N HCl is within 3% of the value for pure water.

Raimondi and Toor (*8*) did an extensive study on different jet designs and their characteristics. Using the CO_2–water system they found that jets formed by flow through thin, square-edged orifice plates produced absorption rate results closest to the theoretical values for rodlike flow and no interfacial resistance. In our work we have followed the results of Raimondi and Toor and have used a jet nozzle consisting of a square-edged orifice 5.1 × 10^{-4} m in diameter drilled in a 8.0 × 10^{-5} m thick stainless steel sheet. The face of the nozzle was coated with a thin layer of wax to prevent wetting.

For an ideal cylindrical jet the contact time for the liquid is given by

$$t = \pi d^2 l / 4q \qquad (2)$$

Application of penetration theory to predict the rate of gas absorption with the contact time given by eq 2 gives

$$R = 4(Dql)^{1/2} C^* \qquad (3)$$

In eq 3 R, q, and l can be measured, and the gas solubility, C^*, is available from the literature. The diffusion coefficient, D, can thus be calculated from eq 3.

Experimental Apparatus and Procedure

A schematic drawing of the jet apparatus is shown in Figure 1. The temperature of the system is monitored by thermometers in the constant-temperature bath, in the jet chamber, and in the fluid stream.

The liquid feed is pumped through a rotameter and through a coil in the constant-temperature bath. It is then fed into a

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