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B.J. Schwarz and J.M. Prausnitz

October 1986

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SOLUBILITIES OF METHANE, ETHANE AND CARBON DIOXIDE IN HEAVY FOSSIL-FUEL FRACTIONS

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ABSTRACT

Measurements are reported for the solubilities of methane, ethane and carbon dioxide in six characterized fossil-fuel fractions. The fractions from crude oils and coal liquid have initial boiling points between 589 and 700 K. Solubilities were measured in a semibatch equilibrium cell at pressures between 5.8 and 21 bar and temperatures from 374 to 575 K. An equation of state was used to determine Henry's constants from the solubility data. These solubility data may be useful for testing correlations used in process-design calculations.

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INTRODUCTION

Sometime, perhaps by the end of the century, the supply of light, easily accessible, high-quality crude oils will be nearing depletion. When high-quality oil becomes scarce, it will become necessary to turn to other hydrocarbon sources to fill energy needs. Alternative fuels include heavy crude oil, coal liquids, shale oil, and tar sands. The molecules in these fuels tend to be larger, more aromatic, and contain more oxygen, nitrogen, and sulfur than those in light crudes. To process these heavy fossil fuels, it is necessary to know their thermodynamic properties. Presently available correlations for properties of light crudes are often not reliable for heavier fossil fuels (1); new correlations must be developed. This work presents experimental data for the solubilities of methane, ethane, and carbon dioxide in heavy fossil fuels. These experimental studies provide some of the data necessary to construct the needed correlations.

In the past decade, several articles have reported data for vapor liquid-equilibria (VLE) for mixtures of known components which serve as models for mixtures of heavy fossil fuels and light gases (2-10). These articles avoid the problem of characterizing the heavy component; they are useful for constructing correlations but they do not provide a convincing test for the ability of a correlation to predict properties of a complex mixture. Several authors have published VLE data for mixtures of fossil fuels and light gases (11-13); however, the characterization data provided in these studies vary widely depending on the preference of the author. Often, these characterization data are incomplete.

This work presents measurements of pressure, temperature and liquid-composition for mixtures containing methane or ethane or carbon dioxide with various crude-oil and coal-liquid fractions. Data were obtained between 375 and 574 K and pressures between 5.8 and 21 bar. The fractions come from two different crude oils from proprietary sites (Exxon A and B), and from Wilsonville (Alabama) coal liquefaction product (W CLP). Table I shows a list of samples and their normal boiling points, as estimated from subatmospheric distillations.

These samples have been characterized by Rodgers et al. (14). The characterization data include elemental analysis, hydrogen-atom distribution, molecular weight and concentrations of groups containing heteroatoms. Experimental vapor pressures and densities of these samples have been reported previously. (15).

EXPERIMENTAL APPARATUS AND PROCEDURE

Gas was contacted with the heavy hydrocarbon liquid in an equilibrium cell at controlled temperature and pressure. A liquid sample of the equilibrium mixture was obtained and flashed under vacuum. The amount of gas in the sample was determined by measuring pressure and temperature changes in a gas burette. The quantity of liquid in the sample was determined gravimetrically.

To minimize contamination due to cracking and to conserve scarce fossil-fuel samples, a semibatch equilibrium cell was used, as shown in Figure 1. The cell was built entirely of stainless steel. Prior to an experiment, approximately 40 cm^3 of the heavy hydrocarbon liquid is loaded in the bottom of the cell through flange (E). Liquid samples are taken through a 1/16-inch, 0.19-inch ID line which extends through fitting G to roughly 1 cm from the middle of the cell. Gas flows through the spargers (F) and out through the condenser at a rate between 20 and 40 $\text{cm}^3/\text{min.}$ Heavy hydrocarbon vapors are refluxed in the condenser as the solute gas stream and light cracking products leave the cell. Water flows counter-currently in the condenser to keep temperatures at the bottom of the condenser relatively high to minimize crystallization from the exit stream. The lower sparger mixes and contacts gas with the fossil fuel. The upper sparger, above the liquid level, maintains pressure during sampling. Both spargers were fabricated from sintered stainless steel with 0.5-micron pores. To avoid contamination, spargers were discarded when samples were changed.

Figure 2 shows the apparatus around the equilibrium cell. All connections shown in Figure 2 are of stainless steel except for the gas cylinders, manometer (X) and flash vessel (R).

Equilibrium pressure is controlled by a Veriflo IR-500 regulator (E) and measured by a

0-300 psig Heise gauge (P). Flow is controlled using needle valves (G). The three-way valve (H) directs the gas to the top or bottom sparger. Before entering the cell, gas is heated in 1.2 m of 1/16-inch-diameter tubing coiled around the equilibrium cell. The gas lines between the cell and check valves (J) are heated to prevent clogging of viscous samples. The check valves and cold trap (F) prevent backflow to the regulator.

Equilibrium temperature is maintained by immersing the cell in a fluidized sand-bath (N) which reaches to roughly 1 cm below the condenser's water jacket. The sand-bath temperature is controlled by a Hallikainen-model-1053 controller. Since the gas flowrate and pressure affect the equilibrium temperature slightly, temperatures may vary by at most one Kelvin among points on a measured isotherm. Temperatures are measured with a copper-constantan thermocouple calibrated against NBS traceable thermometers.

Liquid samples were analyzed using a gas burette consisting of three (approximately 300 cm^3) bulbs (S) and a 25 cm^3 bulb (U), flash vessel (R) and manometer (X). The amount of gas was determined from changes in the temperature and pressure in the burette. To obtain desirable final gas burette pressure with a variety of gases and samples, the burette volume is varied by opening or closing ball valves (V). With both mercury columns in the manometer at the same height, the volume of the burette varies between 388 and 1045 cm^3 . Burette volumes are corrected for movement of mercury in the manometer. The volume of the gas burette is calibrated with air by measuring pressure changes as air expands from bulb U into the burette. The capacity of bulb U is found gravimetrically using water. The gas burette is kept at room temperature.

Samples are drawn into flash vessel (R), shown in Figure 3, through heat-traced 0.019-inch ID sample lines and the Valco zero-dead-volume valve (Q). Small sample lines and zero-dead-volume fittings are used to avoid contamination of samples and to reduce the amount of sample used to purge the lines. The sample lines and valve are heat-traced to prevent clogging and flashing in the lines. Temperatures of the lines are maintained near the equilibrium temperature using 120-V variacs. The flash vessel is cooled by a fan following

sampling. A glass-wool plug is placed in the flash vessel to prevent entrainment of liquid when the sample flashes. Boiling stones facilitate the evolution of gas into the burette.

All of the light gases from Matheson Gas Products have high purity: 99.99% (Coleman grade) for carbon dioxide; 99% (chemical purity) for ethane; and 99.99% (Matheson grade) for methane.

To obtain nearly isothermal data, a sample is loaded in the equilibrium cell. Gas enters the cell's bottom sparger at the highest desired pressure. The sandbath, preheated on a jack below the cell until it reaches the desired temperature, is raised to engulf the cell. To minimize solvent loss from the cell and upon flashing in the gas burette, temperatures are chosen such that the solvent vapor pressure is less than 0.2 bar. While the cell is heating to a steady temperature, the gas burette is evacuated. After a steady temperature is obtained (about one and a half hours), the gas flow is switched to the top sparger. After approximately fifteen minutes, measurements are recorded for manometer mercury heights, temperatures in the open burette bulbs, equilibrium temperature and pressure. An approximately 1-cm³ purge is drawn through the sampling valve before obtaining a 0.5 to 2.5-gram sample in a tared flash vessel. Following sampling, the gas flow is switched to the bottom sparger and the pressure is changed using the regulator. After conditions are steady in the gas burette (about fifteen minutes), the final mercury heights and burette temperatures are recorded. Final burette pressures range between 5 and 30 torr. These are kept under one four hundredth of the equilibrium pressure to avoid the need to correct for gas remaining in the liquid following flashing. The burette is then vented to atmospheric pressure and the vial is removed and weighed. A new vial is attached to the burette which is then evacuated. After about one hour, the equilibrium conditions are stable and the procedure is repeated.

To provide corrections for data reduction, measurements were recorded for boiling-stone and glass-wool weights, manometer reference pressures and temperatures of the manometer and at the top of the flash vessel.

The primary data acquired are: equilibrium temperature and pressure; initial and final burette pressures, temperatures and mercury heights; liquid sample weight, boiling-stone weights, and glass-wool weights. Temperatures are accurate to ± 0.2 K and equilibrium pressures to ± 0.03 bar. Mercury-height uncertainties are about 0.04 mm resulting in burette pressure errors of about 0.06 torr. Weights are measured with an analytical balance to ± 0.3 mg.

DATA REDUCTION

For calculations of solubilities from the primary data, the major problem is to calculate accurately the quantity of gas in the sample. Using the known volume of the gas burette, the initial and final temperatures and pressures in the burette and the ideal-gas law, the number of moles of gas in a sample can be determined. To increase accuracy, several adjustments are made to the temperature and volumes. Manometer readings are corrected for temperature and for gravitational effects as well as for nonzero reference pressures. Appendix 1 gives details of other corrections for the volume vacated by mercury in the manometer; temperature gradients in the burette; and volumes occupied by glass-wool, boiling-stones and liquid samples. All corrections are usually less than one percent.

The number of moles of liquid in the sample is determined from the measured mass of the liquid and from the molecular weight of the fossil-fuel fraction as determined by Rodgers et al (14) using mass spectroscopy. Liquid mole fractions are calculated from the known moles of liquid and gas in the sample.

Henry's constants for the light gas in the fossil-fuel samples are calculated from experimental data using the perturbed-hard-chain equation of state presented by Cotterman et al (16,17). Pure-component parameters for the heavy fractions were fit to vapor-pressure and density data. Segment volumes (v_{seg}^*) for the fossil fuel were taken to be $10 \text{ cm}^3/\text{mole}$ as recommended by Cotterman et al (17). The attractive energy per segment (ϵ/k) was 110 K. Table II shows pure-component parameters for the fossil-fuel samples. Parameters for the light gases are given in references 15 and 16. Using the new experimental data, interaction parameter k_{ij} is obtained for every isotherm using a maximum-likelihood method (In this

calculation high-density interaction parameter $k_{ij} = k_{ji}$, and low-density parameter, $k^B = 0$.) In the maximum-likelihood method, estimated errors are set: temperature ± 0.2 K, pressure ± 0.03 bar, solubility the larger of $\pm 5 \times 10^{-8}$ moles per gram or $\pm 2\%$. After fitting the pressure-composition data, Henry's constants were calculated.

RESULTS AND DISCUSSION

To check the apparatus and experimental procedure, measurements were obtained for the solubility of carbon dioxide in hexadecane near 296.7 K and in eicosane near 322.7 K. Both heavy components are 99+% pure. Because of the relatively high solubility of carbon dioxide in hexadecane, there is a need to correct for gas remaining in the liquid. This was done by assuming that the Henry's constant of carbon dioxide was 72 bar and calculating the amount of gas dissolved in the liquid at the final burette pressure. The solubility did not change when using the Henry's constant calculated from the data (66 bar) to correct for the carbon dioxide remaining in the liquid. The correction was always less than one percent of the solubility. Table II shows equation-of-state parameters for hexadecane and eicosane.

Table III shows the measured solubilities, derived interaction parameters and Henry's constants, H , for the *n*-alkane-carbon dioxide isotherms. Using parameters obtained from fitting data at 296.7 K, the equation of state was used to calculate a Henry's constant of 67.4 bar for carbon dioxide in hexadecane at 298.6 K. At 298.6 K, Chai and Paulaitis (4) report a Henry's constant of approximately 73.6 bar. Figure 4 shows the solubility of carbon dioxide in eicosane near 323 K as measured here and by two other authors (3,5). For eicosane, the data reported here are in good agreement with those reported previously. Table III gives the data shown in Figure 4, as well as interaction parameters and Henry's constant for carbon dioxide in eicosane. At 321.0 K, the calculated Henry's constant is 76.6 bar, compared to approximately 82.0 bar reported by Chai and Paulaitis (4).

For typical solubility data, Henry's constants can vary by about ten percent depending on the method used to extrapolate the solubility data to the Henry's-constant limit. The differences between Henry's constants reported here and those from previous publications are

most likely due to the extrapolating procedure. In this work, the perturbed-hard-chain equation of state was chosen as the extrapolating function because of its ability to smooth and extrapolate solubility data over a range of temperatures as well as compositions using few parameters.

Tables IV to VII show solubility data and calculated Henry's constants for methane, ethane and carbon dioxide in six fossil-fuel fractions. Estimated errors for the solubility data are the same as those given previously for use in fitting equation-of-state parameters. The worst reproducibility error in solubility was a difference of 1.2×10^{-5} moles/gram, or approximately 11%. Figures 6 to 8 compare Henry's constants for gases in the fractions and those in model solvents as reported in references 6,7 and 8. The magnitude of the Henry's constants of methane and ethane in the model solvents seems to be strongly dependant on the hydrogen-to-carbon ratio, with higher Henry's constants corresponding to lower hydrogen-to-carbon ratios. The location of the maximum Henry's constant as a function of temperature is shifted to higher temperatures by higher molecular-weight solvents. Henry's constants of methane and ethane in fossil-fuel fractions generally follow the same trends as those in the model solvents. The hydrogen-to-carbon ratio of the solvent has less effect on the Henry's constant of carbon dioxide than on those for methane and ethane. For carbon dioxide dissolved in hydrocarbons, the location of the maximum in the Henry's constant is determined primarily by the solvent's molecular weight.

Henry's constant of carbon dioxide in WCLP cut 8 is high, possibly due to acidic heteroatom groups in the coal liquid.

ACKNOWLEDGMENTS

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APPENDIX 1

CORRECTIONS FOR GAS-BURETTE VOLUMES AND TEMPERATURES

The uncorrected volume of the gas burette (including the flash vessel) is determined from the volume calibration for the open bulbs. The corrected volume of the burette is given by

$$V_b = V_b^{\text{cal}} - V_{bs} - V_{gw} - V_l + A\Delta h \quad (\text{A1})$$

where V_b^{cal} is the burette volume from the calibration and V_{bs} , V_{gw} and V_l are the volumes of the boiling stones, glass wool and liquid sample, respectively, A is a constant and Δh is the mercury-height difference across the manometer; Δh is positive when the burette pressure is higher than the reference pressure. V_{bs} , V_{gw} and V_l are determined upon dividing weight by density. The densities for boiling stones, glass wool and liquid sample are taken to be 3.4, 2.2 and 1.0 g/cm³, respectively. A is determined from the diameter of the manometer (0.4 cm):

$$A = \pi \times 0.4^2 \text{ cm}^2 \times (1 \text{ cm} / 10 \text{ mm}) / 8 = 0.00628 \text{ cm}^3 / \text{mm} \quad (\text{A2})$$

The volume of the flash vessel V_f is given by

$$V_f = V_f^{\text{cal}} - V_{bs} - V_{gw} - V_l \quad (\text{A3})$$

where V_f^{cal} is the volume of the empty flash vessel (6.4 cm³).

The uncorrected temperature of the burette, T^u is taken to be the average of the temperatures in the open large bulbs. This average temperature is corrected for temperature gradients in the flash vessel caused by the heat-traced sample lines at the top of the vessel. The average temperature in the flash vessel T^f is estimated from

$$T^f = 0.25T^t + 0.75T^u \quad (\text{A4})$$

where T^t is the temperature at the top of the flash vessel. The average burette temperature is then calculated as a volume-weighted average:

$$T^v = \frac{(V_b - V_f)T^u + V_f T^f}{V_b} \quad (\text{A5})$$

Table IV.

Solubilities of Gases in Exxon A Cut 1							
T (K)	P (bar)	$10^4 s$ (moles/gram)	$10^2 x$	T (K)	P (bar)	$10^4 s$ (moles/gram)	$10^2 x$
Methane							
473.4	19.65	2.23	4.3	573.1	20.53	2.31	5.0
473.0	15.81	1.75	3.8	571.0	16.01	1.67	3.7
473.0	15.69	1.74	3.8	570.6	13.64	1.50	3.3
472.6	12.66	1.38	3.1	570.6	12.44	1.29	2.9
472.8	8.77	1.00	2.2	570.4	10.23	1.06	2.4
473.0	6.09	0.67	1.5				
	$k_v = 0.0116$				$k_v = 0.0322$		
	H (473.0 K) = 393 bar				H (571.1 K) = 404 bar		
Ethane							
474.6	18.88	5.17	11.5	571.8	19.09	4.01	8.4
474.6	14.98	4.03	8.4	572.0	15.26	3.12	6.6
474.2	12.24	3.21	6.8	573.7	13.30	2.82	6.0
474.4	12.19	3.10	6.6	572.0	12.50	2.48	5.4
473.0	12.13	3.29	7.0	573.7	11.07	2.33	5.0
473.6	10.60	2.88	6.2	573.5	9.99	2.13	4.6
474.0	9.15	2.40	5.2	572.9	9.20	1.83	4.0
473.0	8.86	2.34	5.1	572.3	8.50	1.71	3.8
473.0	8.86	2.40	5.2	572.0	5.98	1.21	2.7
474.0	5.86	1.58	3.5	572.0	5.97	1.09	2.4
	$k_v = 0.0028$				$k_v = 0.0040$		
	H (473.8 K) = 167 bar				H (572.6 K) = 213 bar		
Carbon Dioxide							
474.8	18.53	3.08	6.8	571.0	19.06	2.84	6.1
474.2	14.07	2.30	5.0	570.2	15.89	2.31	5.0
474.2	11.66	1.86	4.1	570.7	12.74	1.81	4.0
474.4	8.09	1.30	2.9	570.6	9.54	1.39	3.1
474.4	8.09	1.29	2.9	570.2	6.66	0.93	2.1
474.2	6.06	0.97	2.2				
	$k_v = 0.0573$				$k_v = 0.0532$		
	H (474.4 K) = 271 bar				H (570.5 K) = 301 bar		

Table V.

Table V. Solubilities of Gases in Exxon A Cut 5							
T (K)	P (bar)	10 ⁴ s (moles/gram)	10 ² x	T (K)	P (bar)	10 ⁴ s (moles/gram)	10 ² x
Methane							
473.8	20.79	2.00	5.2	570.6	19.71	1.99	5.2
473.6	18.09	1.71	4.5	570.8	16.69	1.62	4.3
473.6	15.13	1.46	3.9	570.4	13.40	1.31	3.5
473.5	11.99	1.15	3.1	570.8	10.61	0.98	2.6
473.4	8.74	0.82	2.2	570.8	7.72	0.72	1.9
$k_y = 0.0169$ H(473.6 K) = 382 bar				$k_y = 0.0093$ H(570.7 K) = 373 bar			
Ethane							
475.0	15.84	3.60	9.0	574.1	19.79	3.59	9.0
474.8	12.72	2.84	7.2	574.5	16.01	2.86	7.3
474.8	9.37	2.14	5.5	574.1	12.81	2.30	5.9
474.8	6.32	1.41	3.7	574.5	9.67	1.71	4.5
$k_y = 0.0062$ H(474.9 K) = 163 bar				574.1	6.49	1.09	2.9
				$k_y = -0.0012$ H(574.3 K) = 206 bar			
Carbon Dioxide							
474.2	18.33	2.66	6.8	575.1	18.52	2.37	6.1
473.8	14.46	2.05	5.3	574.9	15.03	1.91	5.0
473.6	11.45	1.65	4.3	574.7	11.77	1.46	3.8
473.6	8.30	1.18	3.1	574.7	9.02	1.15	3.1
473.6	5.75	0.82	2.2	574.9	6.05	0.75	2.0
$k_y = 0.0555$ H(473.8 K) = 255 bar				573.3	6.04	0.75	2.0
				$k_y = 0.0459$ H(574.6 K) = 289 bar			

Table VI.

Solubilities of Gases in Exxon B Cut 1							
T (K)	P (bar)	10^4s (moles/gram)	10^2x	T (K)	P (bar)	$s \times 10^4$ (moles/gram)	10^2x
Methane							
375.3	20.38	2.59	4.9	423.6	19.07	2.28	4.4
375.1	17.18	2.18	4.2	423.4	15.66	1.86	3.6
375.1	14.26	1.81	3.5	423.2	12.57	1.48	2.9
375.1	10.59	1.32	2.6	423.0	9.31	1.10	2.2
375.3	7.31	0.95	1.9	423.2	6.34	0.73	1.5
$k_y = 0.0302$ H(375.2 K) = 391 bar				$k_y = 0.0201$ H(423.3 K) = 419 bar			
Ethane							
375.3	19.53	9.75	16.4	424.0	20.44	7.22	12.7
375.5	16.03	7.92	13.7	424.0	16.91	5.87	10.6
375.5	12.60	6.04	10.8	423.6	13.82	4.79	8.8
375.3	9.11	4.29	7.9	423.4	10.54	3.57	6.7
374.8	6.07	2.74	5.2	423.8	7.00	2.24	4.3
$k_y = 0.0218$ H(375.3 K) = 108 bar				$k_y = 0.0168$ H(423.8 K) = 150 bar			
Carbon Dioxide							
375.6	18.11	4.64	8.5	425.0	18.60	3.73	7.0
375.5	14.18	3.56	6.7	425.0	15.15	2.98	5.7
375.5	11.08	2.68	5.1	424.4	12.16	2.50	4.8
374.9	8.17	1.99	3.8	424.0	9.19	1.80	3.5
374.8	6.21	1.52	3.0	423.8	6.25	1.23	2.4
$k_y = 0.0728$ H(375.3 K) = 203 bar				$k_y = 0.0630$ H(424.4 K) = 252 bar			

Table VII.

Solubilities of Gases in Exxon B Cut 4							
T (K)	P (bar)	10^4s (moles/gram)	10^2x	T (K)	P (bar)	$s \times 10^4$ (moles/gram)	10^2x
Methane							
474.2	20.94	1.96	5.0	572.2	19.70	1.79	4.6
474.4	19.64	1.79	4.6	572.2	16.42	1.59	4.1
473.8	18.99	1.76	4.5	571.6	13.78	1.25	3.3
474.0	18.22	1.70	4.4	572.2	11.39	1.06	2.8
474.4	16.87	1.56	4.0	572.0	8.86	0.77	2.0
474.0	15.71	1.49	3.9	571.6	8.85	0.78	2.1
474.2	14.68	1.32	3.4	$k_y = 0.0273$			
473.8	12.57	1.12	2.9	$H(572.0\text{ K}) = 403\text{ bar}$			
473.6	10.56	0.93	2.4				
473.6	10.54	0.92	2.4				
$k_y = 0.0236$							
$H(474.0\text{ K}) = 404\text{ bar}$							
Ethane							
474.2	19.32	4.41	10.6	573.9	15.93	2.43	6.1
474.4	15.60	3.52	8.6	573.5	11.58	1.69	4.3
474.0	12.65	2.74	6.9	573.3	10.38	1.64	4.2
473.6	8.62	1.74	4.5	573.5	7.34	1.10	2.9
473.8	8.60	1.86	4.8	572.7	7.34	1.11	2.9
473.4	6.40	1.26	3.3	$k_y = 0.0343$			
$k_y = 0.0148$				$H(573.4\text{ K}) = 255\text{ bar}$			
$H(473.9\text{ K}) = 173\text{ bar}$							
Carbon Dioxide							
473.2	18.25	2.84	7.1	571.0	18.17	2.43	6.1
472.2	15.67	2.41	6.1	571.0	14.17	1.85	4.7
472.4	12.71	1.91	4.9	570.4	11.32	1.42	3.7
471.6	9.65	1.41	3.7	570.6	8.01	1.04	2.7
471.6	7.52	1.15	3.0	570.0	6.97	0.87	2.3
$k_y = 0.0450$				$k_y = 0.0376$			
$H(472.0\text{ K}) = 245\text{ bar}$				$H(570.6\text{ K}) = 285\text{ bar}$			

Table VIII.

Solubilities of Gases in W CLP Fractions							
T (K)	P (bar)	10 ⁴ s (moles/gram)	10 ² x	T (K)	P (bar)	sx10 ⁴ (moles/gram)	10 ² x
Methane in W CLP cut 8							
474.0	18.97	1.62	3.4	549.7	19.62	1.82	3.8
474.0	18.93	1.62	3.4	549.5	19.62	1.81	3.7
473.6	14.07	1.15	2.4	549.3	14.98	1.36	2.8
473.8	16.20	1.38	2.9	549.3	12.48	1.14	2.4
473.8	13.77	1.22	2.6	549.2	10.93	0.98	2.1
473.6	11.59	0.97	2.0	548.9	9.06	0.80	1.7
473.4	9.58	0.77	1.6			$k_y = 0.0260$	
		$k_y = 0.0395$				$H(549.3 \text{ K}) = 506 \text{ bar}$	
		$H(473.7 \text{ K}) = 547 \text{ bar}$					
Ethane in W CLP cut 7							
376.3	18.89	7.67	13.8	424.6	19.01	5.84	10.9
375.9	15.55	6.30	11.6	424.4	15.73	4.62	8.8
375.9	12.66	5.04	9.5	424.4	15.73	4.56	8.7
375.3	8.04	3.06	6.0	424.6	12.30	3.68	7.1
375.3	5.52	2.09	4.2	424.4	9.01	2.66	5.3
		$k_y = 0.0274$		424.4	6.49	1.76	3.5
		$H(375.7 \text{ K}) = 124 \text{ bar}$				$k_y = 0.0194$	
						$H(424.5 \text{ K}) = 166 \text{ bar}$	
Carbon Dioxide							
in W CLP cut 7				in W CLP cut 8			
376.1	17.67	4.01	7.7	547.9	17.03	1.86	3.8
376.1	14.36	3.24	6.3	547.7	14.53	1.56	3.2
376.1	11.41	2.42	4.8	547.9	12.61	1.29	2.7
375.7	8.43	1.76	3.5	547.7	10.43	0.96	2.0
375.5	5.80	1.15	2.3	548.1	10.42	0.95	2.0
375.9	5.78	1.10	2.2	548.7	8.13	0.70	1.5
		$k_y = 0.0739$		548.2	8.11	0.80	1.7
		$H(375.9 \text{ K}) = 205 \text{ bar}$				$k_y = 0.0995$	
						$H(548.0 \text{ K}) = 453 \text{ bar}$

Figure 1. Equilibrium Cell

Key to Figure 1

- A** Thermocouple Housing
- B** Connection to Pressure Gauge and Vent
- C** Connection to Rupture Disk
- D** Small Flange
- E** Large Flange
- F** Sparger
- G** Connection to Sampling Line

Figure 2. Schematic of Solubility Apparatus

Key to Figure 2

A	Vacuum Pump
B	Liquid-Nitrogen Trap
C	Thermocouple Vacuum Gauge
D	McCleod Vacuum Gauge
E	Pressure Regulator
F	Ice Trap
G	Metering Valve
H	Three-way Ball Valve
I	Rotameter
J	Check Valve
K	3500-cm ³ Dead Volume
L	2-micron Filter
M	Equilibrium Cell
N	Fluidized Sand Bath
O	Rupture Disk
P	0-300 psig Pressure Gauge
Q	Zero Dead Volume Three-way Valve
R	Flash Vessel
S	300-cm ³ Sample Bomb
T	Thermocouple
U	25-cm ³ Sample Bomb
V	Ball Valve
W	Purge Vessel
X	Mercury Manometer
≡	Heat Traced Line

1/16", 0.02" ID tube
to three way valve

1/16", 0.02" ID
tube to gas buret

Figure 3. Flash Vessel

Figure 4. Solubility of Carbon Dioxide in Eicosane Near 323 K

Figure 5. Solubilities of Gases in Exxon A Cut 1 Near 573 K

- EICOSANE, MW = 283, H/C = 2.10
 - - 1-METHYLNAPHTHALENE, MW = 142, H/C = 1.09
 - . - BICYCYCLOHEXYL, MW = 166, H/C = 1.83
 $\triangle$ EXXON A CUT 1, MW = 228, H/C = 1.70
 ∇ EXXON A CUT 5, MW = 274, H/C = 1.65
 $\blacksquare$ EXXON B CUT 1, MW = 201, H/C = 1.63
 $\square$ EXXON B CUT 4, MW = 269, H/C = 1.55
 $\bullet$ WCLP CUT 8, MW = 215, H/C = 1.38

Figure 6. Henry's Constants for Methane in Model Solvents and in Fossil Fuels

- EICOSANE, MW = 283, H/C = 2.10
- - - 1-METHYLNAPHTHALENE, MW = 142, H/C = 1.09
- · - BICYCYCLOHEXYL, MW = 166, H/C = 1.83
- △ EXXON A CUT 1, MW = 226, H/C = 1.70
- ▽ EXXON A CUT 5, MW = 274, H/C = 1.65
- EXXON B CUT 1, MW = 201, H/C = 1.63
- EXXON B CUT 4, MW = 269, H/C = 1.55
- WCLP CUT 7, MW = 209, H/C = 1.43

Figure 7. Henry's Constants for Ethane in Model Solvents and in Fossil Fuels

Figure 8. Henry's Constants for Carbon Dioxide in Model Solvents and in Fossil Fuels

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