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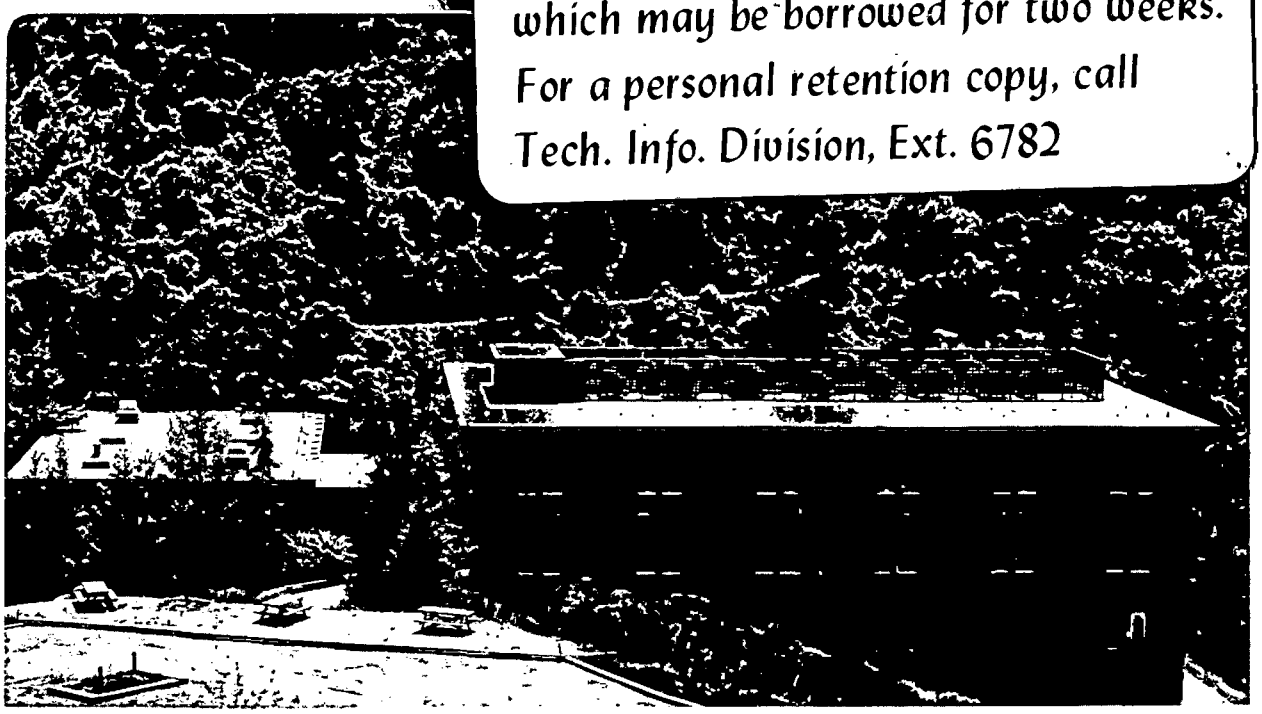

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AN EXPERIMENTAL METHOD FOR MEASURING SOLUBILITIES OF HEAVY FOSSIL-FUEL FRACTIONS IN COMPRESSED GASES TO 100 BAR AND 300° C

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ABSTRACT

A new experimental method has been developed to measure solubilities of narrow-boiling, heavy fossil-fuel fractions in compressed gases. Solubilities are determined from the volume of gas required to vaporize completely a small, measured mass of fossil-fuel sample. This method has been used successfully for several heavy solutes dissolved in compressed methane.

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INTRODUCTION

The high cost of energy has led to a search for new process technologies which allow more efficient utilization of energy resources. As a result, there has been growing interest in processing or upgrading of coal, heavy crudes, heavy petroleum fractions, tar sands, shale, etc. Development of such processes requires quantitative information for equilibrium properties of these materials under processing conditions at elevated temperatures and pressures. Of particular interest here is the solubility of a heavy fossil-fuel mixture in a compressed gas. This solubility is needed for the design of extraction processes with supercritical or near-critical fluids, (e.g. deasphalting, deashing and general upgrading of petroleum fractions); for petroleum-reservoir pressurization with light gases, toward removal of high-molecular-weight hydrocarbons left behind after primary recovery; and for coal-gasification process steps (condensation and quenching) where product gas streams often contain high-boiling coal tars.

Fossil-fuel mixtures typically contain very many components. The wide range of properties of the components and the analytical problem to identify these components makes phase equilibrium predictions and experimental measurement extremely difficult. A common procedure is to "divide" the mixture into fractions with fewer components and smaller ranges of properties. Phase equilibrium predictions and process design are then based on average or effective properties of the fractions.

This work reports an experimental technique for measuring

vapor-liquid equilibria in systems containing narrow-boiling fossil-fuel fractions and compressed gases. The total solubility of a fossil-fuel fraction in a compressed gas is determined by measuring the quantity of gas required to vaporize completely, under equilibrium conditions, a measured sample of that fraction. Because stripping effects cause the composition and total solubility of the fraction to change during the vaporization process, a computer simulation of the vaporization process is used to relate the experimentally determined gas volume to the total solubility of the heavy fraction before its composition and solubility have changed. Total solubility is defined as the sum of the solubilities, or vapor-phase compositions of the heavy fraction's individual components. Approximate characterization of the heavy mixture, required for computer simulation, is obtained from the average molecular weight, hydrogen-to-carbon ratio, and approximate chromatographic analysis of the heavy mixture.

This experimental technique differs from those used previously to measure compressed-gas solubilities of pure heavy hydrocarbons (eg. Kaul 1978, Paulitis 1980, Kurnik 1981, Johnston 1981). First, the total-vaporization technique requires only semi-quantitative analysis of the gas phase. For measuring solubilities of complex mixtures, such as coal-tar fractions which are difficult to analyze quantitatively, this represents an important advantage over conventional methods which require precise quantitative analysis. Second, because only semi-quantitative analysis of the gas phase is required, water vapor can be introduced into the gas phase without significantly affecting the

experimental and data-reduction procedures. Third, the total-vaporization method allows experiments to be performed with small liquid samples, such as those obtained from fractionation of coal tars or petroleum crudes into narrow-boiling fractions. Whereas sparged gas-liquid contactors, used in conventional methods, often require on the order of 100 cm^3 of liquid, the packed-bed equilibrium cell used here requires less than 0.5 cm^3, per measurement.

Our technique has been tested by measuring solubilities of hexadecane, and tetradecane/1-methylnaphthalene mixtures in compressed methane. It has also been used to measure solubilities of coal-tar fractions produced from a coal-tar sample obtained from SASOL's Lurgi coal gasifier in South Africa.

EXPERIMENTAL APPARATUS

Presented in Figure 1 is the experimental apparatus to determine the solubility of a narrow-boiling, heavy-hydrocarbon liquid mixture in a compressed gas. The solubility is determined from the measured volume of compressed gas required to vaporize completely, under equilibrium condition, a known amount of heavy hydrocarbon liquid.

Gas from a compressed gas cylinder is preheated in a constant-temperature air bath and passed through a packed-bed cell where it equilibrates with the hydrocarbon liquid at measured temperature and pressure. Saturated gas leaving the cell is expanded and directed through a heated gas-sampling valve used to

take samples intermittently. Gas samples are analyzed with a flame-ionization detector in a gas chromatograph; the results are recorded by an electronic integrator. The saturated gas is then cooled to room temperature and its cumulative volume is measured using a wet test meter. Completion of the vaporization of the hydrocarbon liquid is signaled by a sharp decrease in the chromatogram peak area corresponding to the heavy liquid.

We use two packed-bed cells in parallel. These packed-bed cells are stainless-steel tubes, 16 cm in length and 0.5-cm ID, packed with 30/60-mesh Chromosorb-P column support, coated with the hydrocarbon liquid of interest. The hydrocarbon liquid is dispersed throughout the cell by syringing into the cell at five evenly spaced points. The mass of hydrocarbon liquid introduced into the cell is determined by weighing the syringe before and after loading.

A specially designed high-temperature, high-pressure, fine-metering valve is used to expand the compressed-gas mixture from the packed-bed cell so that the gas can be sampled and metered. The gas-sampling valve is a VALCO 10-port, high-temperature sampling valve with 0.75-cm^3 sample loops. A 10-port valve with two sample loops is used so that gas streams from two different packed-bed equilibrium cells can be sampled alternately. Sampling is automated using a VALCO digital valve interface, a VALCO 2-position helical-drive air actuator and a simple mechanical timer.

Gas samples are analyzed using a Perkin-Elmer 990 gas chromatograph with a hydrogen-flame ionization detector under constant-temperature, single-column operation. The

chromatographic column used is a 2-m long, 3.2-mm OD stainless-steel tube packed with 3% OV-101 on 80/100-mesh Chromosorb W-HP column support (supplied by Varian). The output from the gas chromatograph is measured and recorded using a Spectra-Physics single-channel, computing integrator, operating in the "simulated distillation" mode (cumulative integration at regular intervals).

Temperature measurements in the constant-temperature air bath are made with an accuracy of 0.2°C using Brooklyn precision thermometers calibrated against primary N.B.S.-certified thermometers. The uniformity of the temperature within the baffled, air-stirred bath is better than 0.2°C. Thermocouples are used for temperature measurements outside the air bath to insure that condensation of heavy hydrocarbon does not take place. Pressure measurements are made using two Heise bourdon-tube gauges with accuracies of 0.2 psi in the 0-200 psi range and 2.0 psi in the 200-2000 psi range. The pressure drop through the system is negligible at gas flow rates (less than 5 cm^3/min) used in this work.

DATA REDUCTION

Figure 2 presents experimental results of a total-vaporization experiment with normal-hexadecane in methane. The results of intermittent gas-phase analysis are plotted against the corresponding cumulative gas volume having passed through the equilibrium cell. For this simple case, where a pure heavy liquid is vaporized, the vapor-phase solubility in methane can be

obtained directly from the weight of n-Cl6 vaporized, Wcl6, and from that of methane, Wcl, required to vaporize completely the n-Cl6 sample. The equilibrium weight fraction, w, is given by

$$w = Wcl6 / (Wcl + Wcl6)$$

Results obtained for this system are in close agreement with those obtained by conventional techniques. However, experimental results from the vaporization of a multicomponent liquid mixture from a packed bed cannot be interpreted as easily. Stripping effects cause the composition of the heavy liquid to change during the experiment.

Figure 3 shows a typical set of data from a total-vaporization experiment with a Lurgi coal-tar fraction and methane. Figure 3 indicates four features characteristic of experiments with multi-component mixtures:

1. Non-equilibrium start-up: the heavy-hydrocarbon content of the gas increases steeply from zero to the steady equilibrium value.
2. Steady equilibrium plateau: gas leaving the cell is saturated with heavy liquid whose composition has not changed from the original composition.
3. Transient equilibrium: during this period of gradually decreasing heavy hydrocarbon content, the gas is equilibrating with liquid whose composition is changing due to stripping effects where light components are preferentially removed from the equilibrium cell.

4. Non-equilibrium residual liquid vaporization: during the sharp decrease of this final stage, too little liquid remains in the equilibrium cell to provide sufficient gas-liquid contact to saturate the gas completely. This period is distinguished from period 3 by the sharp increase (generally doubling) in the magnitude of the slope.

Experimental conditions (e.g. initial load of heavy liquid) can be chosen to reduce to less than 2%, uncertainties arising from end effects of Stages 1 and 4.

During Stage 3, equilibration takes place with a heavy liquid whose composition has been altered by preferential stripping of lighter components. Since the composition and overall properties of the mixture have been altered, the vaporization process is now more complex. The experimentally observed gas volume required for total vaporization, V, does not provide a direct measure of the solubility of the original heavy liquid. To relate exactly the experimentally observed V to y, the total solubility of the original, unaltered heavy liquid, we require detailed information about the individual components in the heavy liquid, their relative compositions, and the stripping process. Since the heavy liquids of interest here are poorly defined, a procedure has been developed based on approximate characterization and on an idealized stripping process.

The vaporization process is assumed to occur in stages as shown in Figure 4 for the simple case of a ternary liquid. The gas is assumed to be in equilibrium with liquid of constant,

unchanged composition until the most volatile component, 1, is completely stripped from the cell. At that point, its concentration in the liquid goes to zero and it disappears from the vapor, as indicated by Step 1. The next step occurs when the next most volatile component in the liquid, 2, is completely stripped from the cell, and so on.

A simulation of the entire vaporization process and the relationship between V and the desired y (the solubility of the original, unaltered fraction), can be found using simple material balances according to the above model. However, to do so, it is necessary to estimate the number of moles of heavy liquid in the equilibrium cell at the start of the experiment and the vapor-phase composition of the individual components in the heavy liquid mixture.

To determine the number of moles of heavy liquid present at the start of an experiment, it is necessary to determine the molecular weight of the heavy liquid. Number-average molecular weights were determined using a Model 5008 Petroleum Cryoscope (freezing point depression apparatus) obtained from Precision Systems Inc..

The individual quantities which must be approximated to calculate the individual vapor phase compositions, (y_i) are (Prausnitz, 1969);

$$y_i = \frac{x_i P_{sat_i} \gamma_i POY}{\Phi_i P}$$

As a reasonable approximation for narrow-boiling fractions (less than 100° C), the activity coefficient, γ_i, the fugacity

coefficient, Φ_i, and the Poynting correction, POY, are assumed to be the same for all components in the fraction; they are grouped into one constant, PI;

$$y_i \simeq \frac{x_i P_{sat_i}}{P} \cdot PI$$

The relative compositions of the individual components in the heavy liquid, (x_i), are approximated from chromatographic data for the heavy liquid at conditions that separate the "key" components into distinct peaks or groups of peaks with areas, (a_i);

$$X_i \simeq \frac{a_i}{\sum a_i}$$

The vapor pressures, (Psat), were calculated from approximate normal boiling points, TNB, obtained by comparing individual chromatographic peak retention times to retention times for a calibration mixture containing compounds with known boiling points. In general, for aliphatics the calibration curve for retention time versus normal-boiling-point differs from that for aromatic compounds. For compounds of unknown aromaticity, a convenient parameter for interpolating between the two curves is the hydrogen-to-carbon ratio, H/C. This was obtained from standard elemental analysis of the fraction and assumed to be the same for the individual components. The method of Smith et. al. (1976), is especially well suited for approximating vapor pressures of poorly-defined heavy hydrocarbons. The parameters required were estimated from TNB and FA, the fraction of carbon atoms in aromatic rings. FA was determined from H/C using the approximate relationship;

$$FA = \begin{cases} 1 & H/C < 1 \\ 2 - H/C & 1 < H/C < 2 \\ 0 & 2 < H/C \end{cases}$$

The procedure for calculating y from V is an iterative one. Parameter PI is adjusted until the V obtained from the simulation of the vaporization process agrees with that obtained experimentally. The desired y is the sum of the individual "key" component solubilities calculated in the simulation before any change has occured in the liquid composition due to stripping.

Figure 5 summarizes this procedure for data reduction. It has been tested on experimental results of total-vaporization experiments for a synthetic mixture of n-tetradecane and 1-methylnaphthalene in compressed methane. Results uncorrected for stripping effects differ by 20% from those predicted from literature values for the properties of the individual components. Application of the proposed data reduction procedure reduces this to 5%.

In Figure 6 the results of a converged simulation are compared to experimental results for a Lurgi coal-tar fraction in compressed methane.

CONCLUSIONS

An experimental method has been developed for measuring solubilities of narrow-boiling heavy fossil-fuel fractions in compressed gases. The total-vaporization method, apparatus and data-reduction procedure have been tested with heavy synthetic mixtures in methane. Experimental results for pure liquids and

binaries agree, to within 5%, with those calculated. Further tests are required for synthetic mixtures with more components and greater boiling-point range to determine their effect on experimental error. Table 1 shows the results of experimental measurements for two coal-tar fractions in compressed methane.

The experimental apparatus has been modified to allow the introduction of water vapor into the gas phase. Shown in Figure 7 is the addition of two water-containing sparged cells upstream of the original packed-bed equilibrium cells. Experimental measurement of solubilities of heavy fossil-fuel fractions in gaseous mixtures of water and light hydrocarbons will begin in the near future.

Acknowledgments

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LITERATURE CITED

Johnston, K. P. and Eckert, C. A., "An Analytical-Carnahan-Starling-van der Waals Model for Solubility of Hydrocarbon Solids in Supercritical Fluids," AIChEJ., 27,773 (1981)

Kaul, B. K. and Prausnitz, J. M.,"Solubilities of Heavy Hydrocarbons in Compressed Methane, Ethane, and Ethylene: Dew-Point Temperatures for Gas Mixtures Containing Small and Large Molecules," AIChEJ., 24,223 (1978)

Kurnik,R. T., Holla, S. J., and Reid, R. C., "Solubilities of Solids in Supercritical Carbon Dioxide and Ethylene," J. Chem. Eng. Data, 26,47 (1981)

Prausnitz, J. M., Molecular Thermodynamics of Fluid-Phase Equilibria, Prentice-Hall, Englewood Cliffs, N.J. (1969)

Smith, G.,Winnick, J.,Abrahms, D. S.,Prausnitz, J. M., "Vapor Pressures of High-Boiling Complex Hydrocarbons," Can. J. Chem. Eng., 54,337 (1976)

Van Leer, R.A. and Paulitis, M. E., "Solubilities of Phenol and Chlorinated Phenols in Supercritical Carbon Dioxide," J. Chem. Eng. Data ,25,257 (1980)

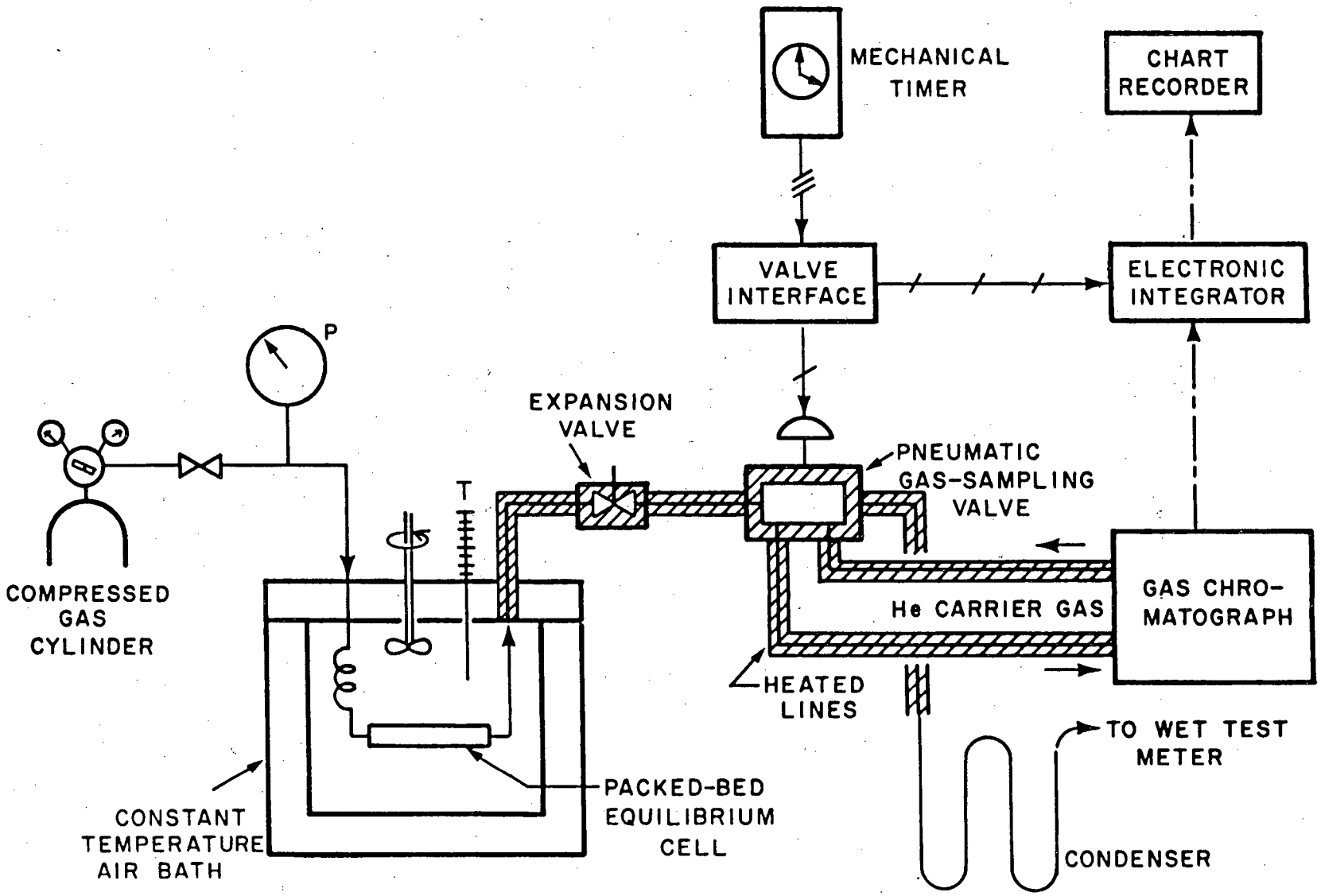


FIGURE 1

TOTAL-VAPORIZATION APPARATUS FOR MEASURING SOLUBILITY HEAVY FOSSIL-FUEL FRACTION IN COMPRESSED GAS

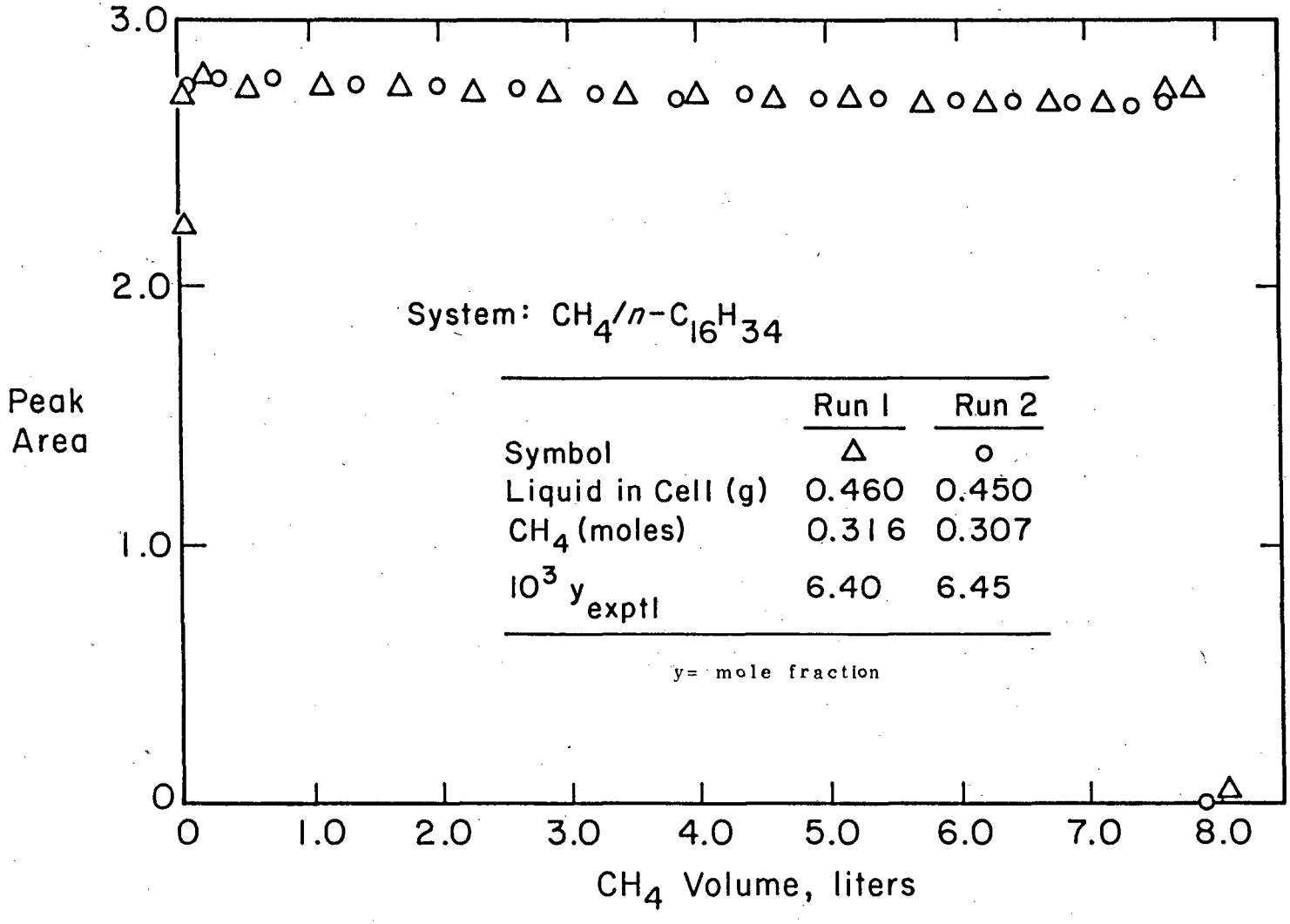


FIGURE 2

TOTAL-VAPORIZATION MEASUREMENTS AT 150°C AND 2.36 BAR

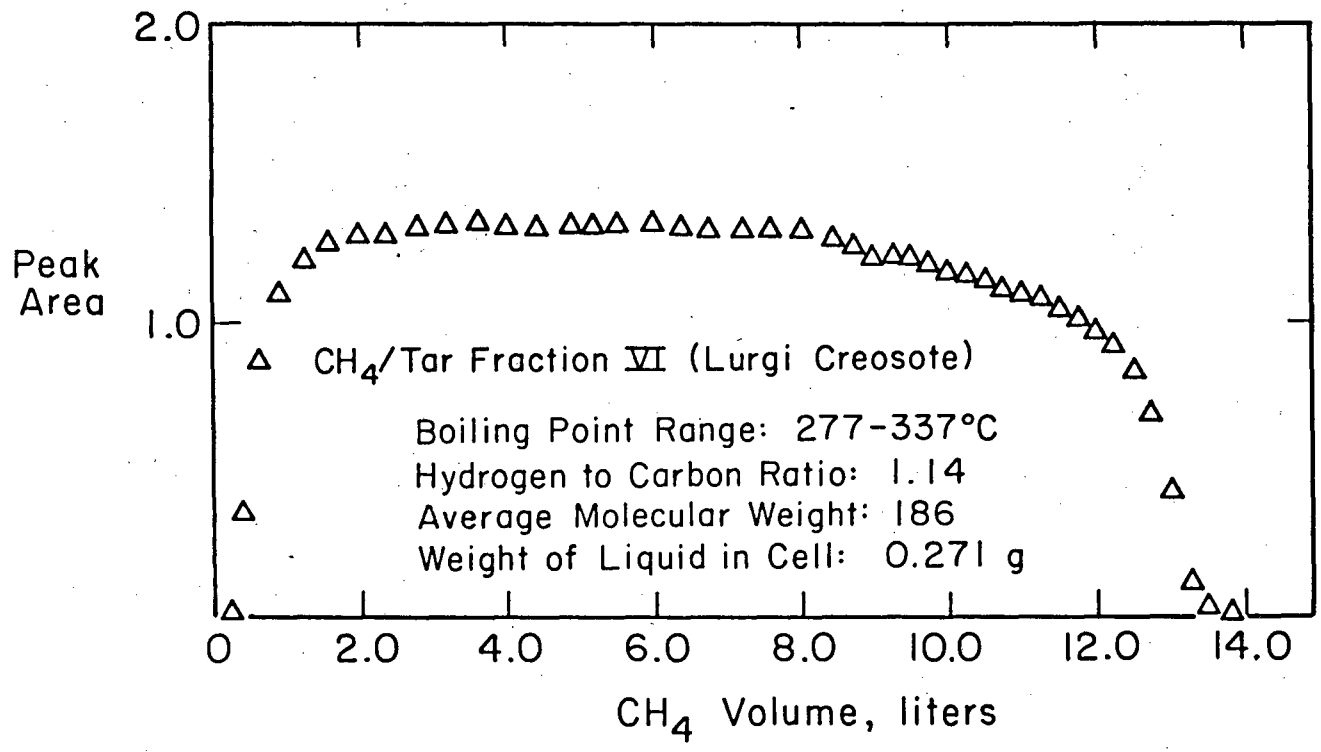
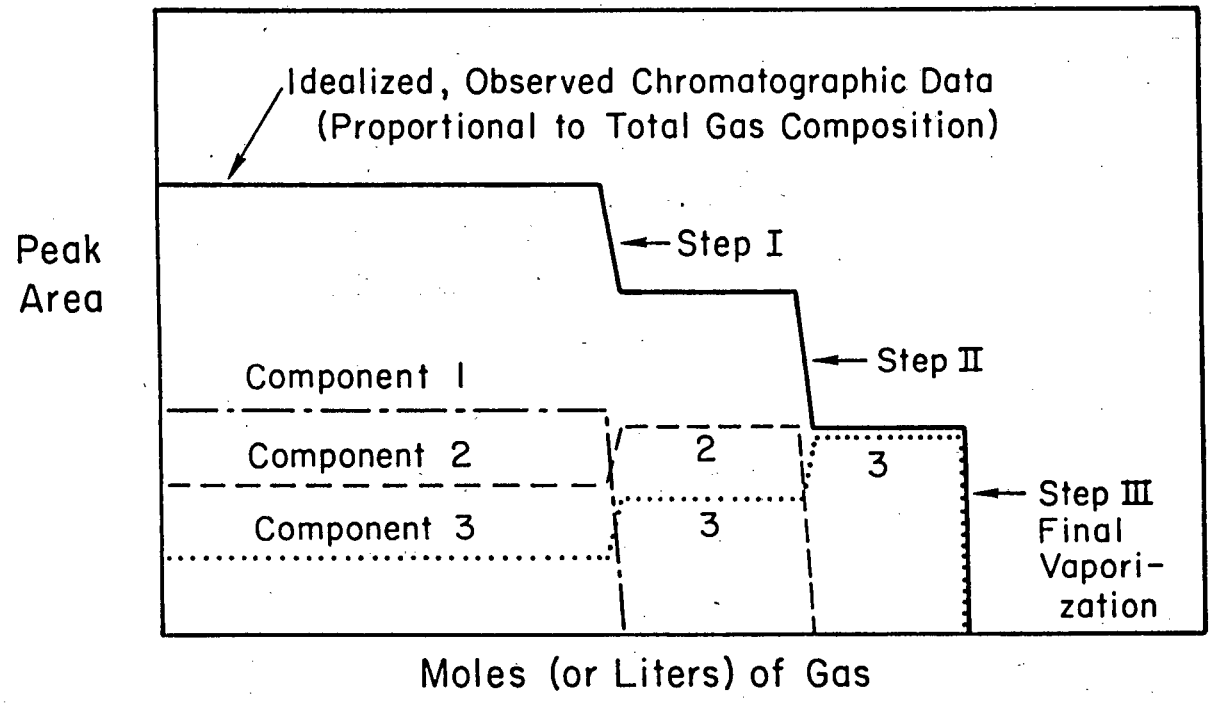


FIGURE 3

TOTAL-VAPORIZATION MEASUREMENT

AT 200°C AND 40.8 BAR



DATA REDUCTION: IDEALIZED, PACKED-BED STRIPPING MODEL FOR A TERNARY LIQUID MIXTURE

FIGURE 4

DATA REDUCTION

CHARACTERIZATION OF FOSSIL-FUEL FRACTION

- NORMAL BOILING POINT (GAS CHROMATOGRAPHY)
- H/C RATIO (ELEMENTAL ANALYSIS)
- COMPOSITION OF "KEYS" (GAS CHROMATOGRAPHY)
- MOLECULAR WEIGHT (FREEZING PT. DEPRESSION)

TOTAL-VAPORIZATION DATA

- TEMPERATURE
- PRESSURE
- WEIGHT OF FRACTION
- VOLUME OF GAS

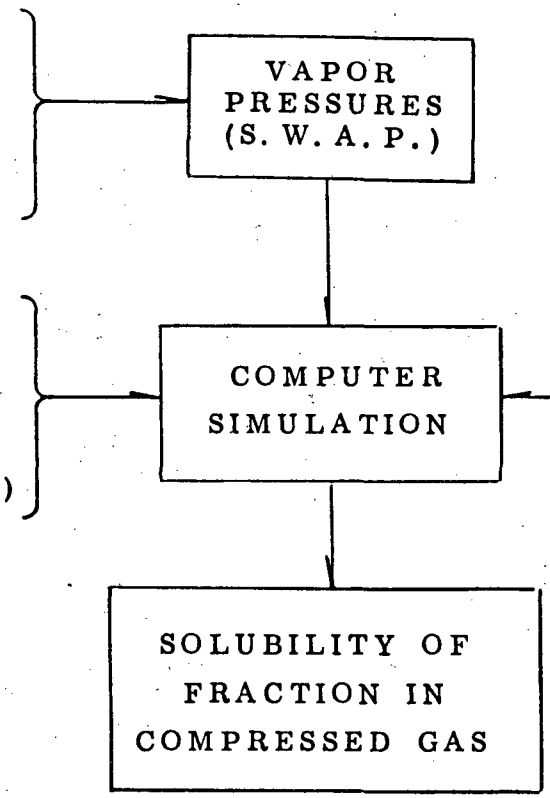
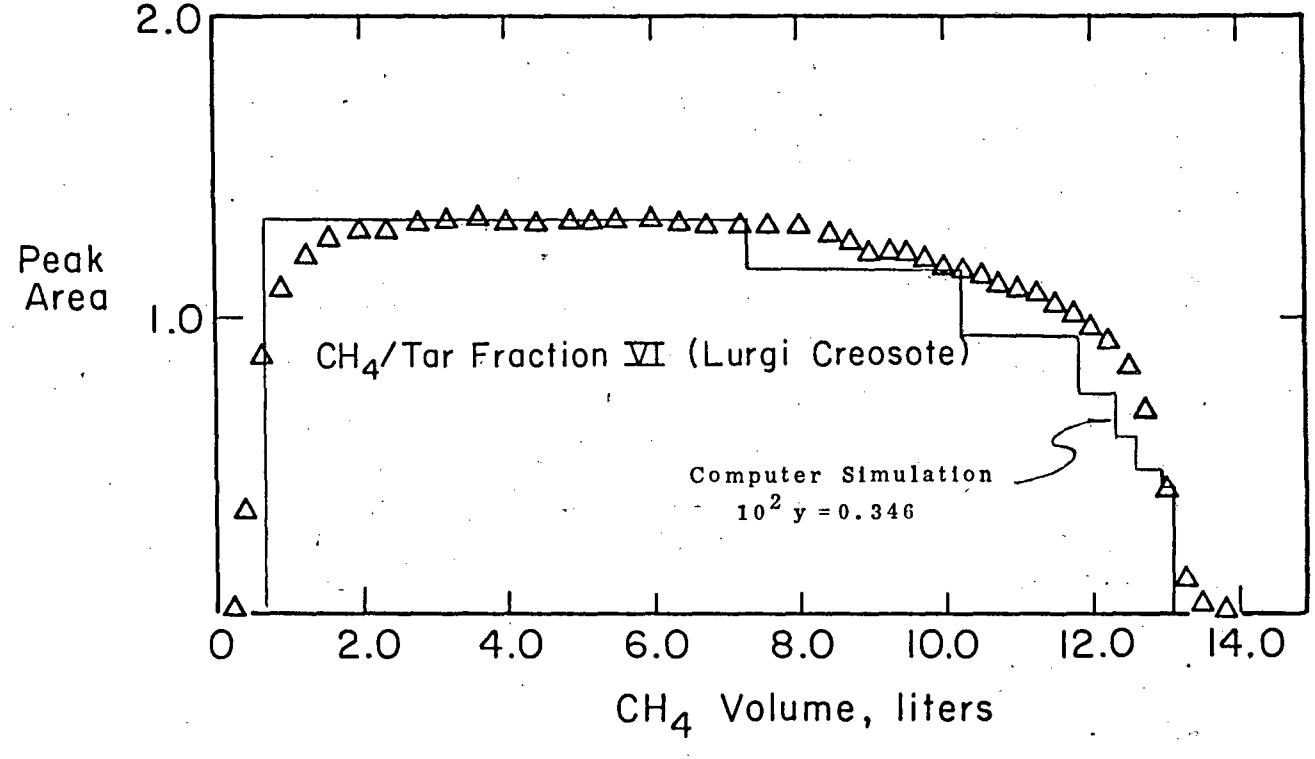


FIGURE 5



TOTAL-VAPORIZATION MEASUREMENT

AT 200°C AND 40.8 BAR

FIGURE 6

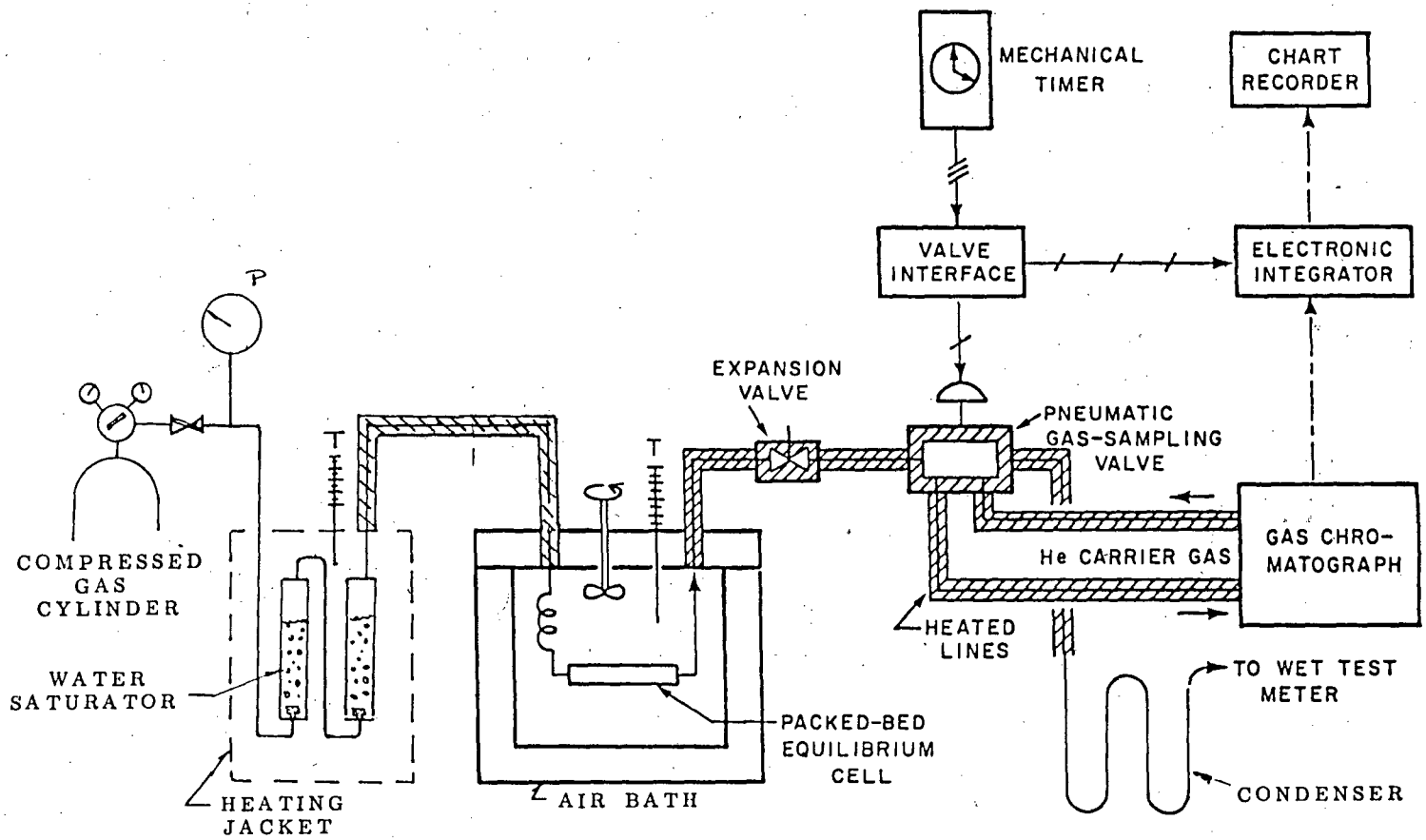


FIGURE 7 APPARATUS FOR MEASURING SOLUBILITY OF FRACTION IN COMPRESSED GAS CONTAINING WATER VAPOR

TABLE 1

SOLUBILITY OF COAL-TAR FRACTIONS IN METHANE

FRACTION*	T, °C	P, BAR	$10^2 y$
1	150	3.77	0.389
	170	42.4	0.152
		70.0	0.135
	200	3.77	2.45
		42.4	0.346
		70.0	0.273
2	210	3.77	0.917
	250	3.77	3.52
		42.4	0.448
		70.0	0.360

*COAL TAR FROM LURGI GASIFIER (SASOL, S. AFRICA)

FRACTION	BOILING PT. RANGE, °C	AVERAGE MOLEC. WT.	H/C RATIO
1	277-337	187	1.14
2	327-402	227	1.18

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