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Authors

Monge, A.
Prausnitz, J.M.

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August 1982

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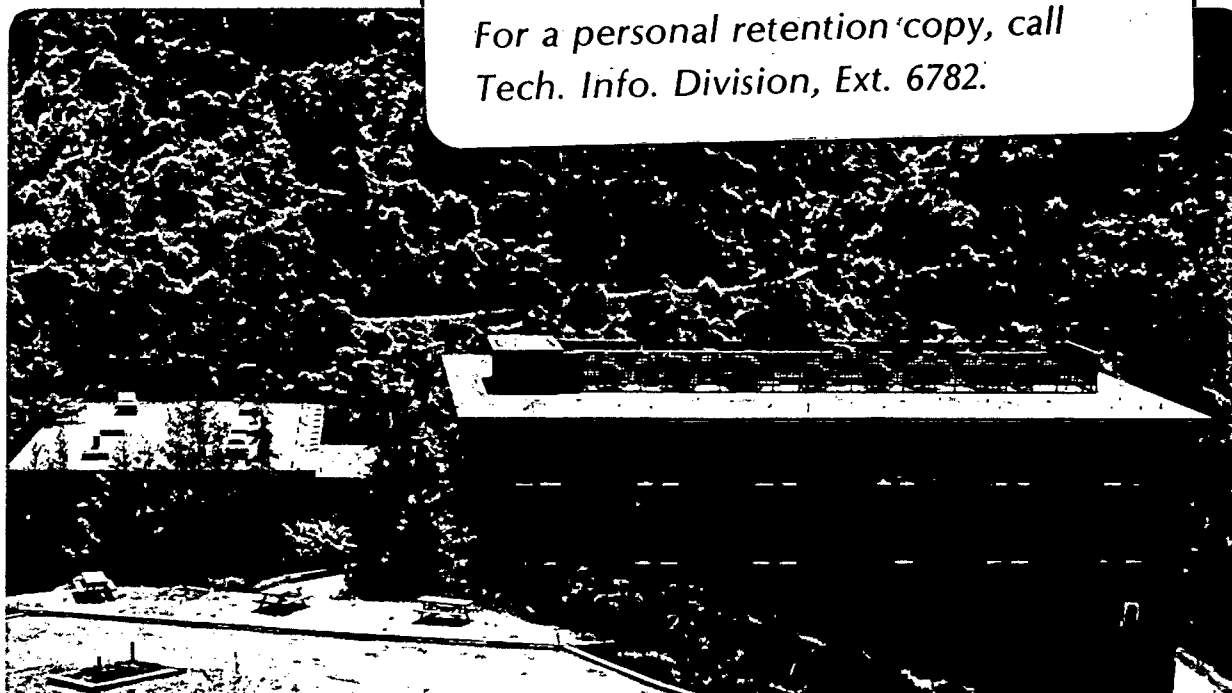
AN EXPERIMENTAL METHOD FOR MEASURING SOLUBILITIES OF HEAVY FOSSIL-FUEL FRACTIONS IN COMPRESSED GASES TO 100 BAR AND 300°C

A. Monge and J. M. Prausnitz

Chemical Engineering Department
and
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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 and in a compressed methane/water mixture.

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, de-ashing 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 solubility of a fossil-fuel fraction in a compressed gas (defined as the sum of the vapor-phase concentrations of the heavy fraction's individual components) 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 solubility of the fraction to change during the vaporization process, a computer simulation of the vaporization process is used to relate the total-vaporization data to the solubility of the heavy fraction before its composition and solubility have changed. 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. A much simpler but less "rigorous" and slightly less accurate procedure is also presented for accounting for stripping effects. The simpler method does

not require computer simulation, chromatographic analysis, or average molecular weight, but gives results (solubilities in terms of weight fractions instead of mole fractions) which are within 5% of those obtained by the more "rigorous" data-reduction procedure.

The experimental technique differs from those used previously to measure compressed-gas solubilities of pure heavy hydrocarbons [e.g. Johnston 1981, Kaul 1978, Kurnik 1981, Paulaitis 1980]. 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. This capability is important because water is so often present during the processing of heavy fossil fuels. 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 a synthetic mixture containing known amounts of naphthalene, 1-methylnaphthalene, 2-ethylnaphthalene, and diphenylmethane, in compressed methane. It has also been used to measure solubilities of two coal-tar fractions produced from a coal-tar sample obtained from SASOL's Lurgi coal gasifier in South Africa. Solubilities were measured in methane and in a methane/water mixture.

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. 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. A typical run lasts two to three days and samples are taken every 30 minutes.

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.

The experimental apparatus has been modified to allow

the introduction of water vapor into the gas phase. Shown in Figure 2 are two water-containing sparged cells upstream of the original packed-bed cells. Otherwise, the apparatus in Figure 2 is identical to that in Figure 1.

The sparged cells are stainless-steel tubes, 18 cm in length and 2.2-cm ID. The spargers are sintered-stainless-steel disks. Two-cm thick layers of pyrex-glass wool, supported by perforated stainless-steel disks, are placed at the outlets of each sparged cell to eliminate possible entrainment. Two sparged cells are connected in series to assure saturation. These cells are placed in a fluidized-bed bath. Temperatures are measured as described previously.

DATA REDUCTION

Figure 3 presents experimental results of two total-vaporization experiments with normal-hexadecane in methane at two different gas flow rates. The results of intermittent gas-phase analysis are plotted against the corresponding cumulative gas volume (at STP) 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 hexadecane vaporized, $W_{C_{16}}$, and from that of methane, W_{C_1}, required to vaporize completely the hexadecane sample. The solubility, expressed as the equilibrium weight fraction, w, is given by,

$$w = \frac{W_{C_{16}}}{W_{C_{16}} + W_{C_1}}. \qquad (1)$$

Results obtained for this system are in close agreement with those obtained by conventional techniques and establish that equilibrium is achieved in the equilibrium cells at flow rates less that 5 cm^3 per minute.

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 4 shows a typical set of data from a total-vaporization experiment with a Lurgi coal-tar fraction and methane. Figure 4 indicates three 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. This feature is

more pronounced at elevated pressures where the effect of the dead volume in the apparatus is significant;

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. This period ends with a sharper decrease in heavy-hydrocarbon content, signaling total vaporization.

Experimental conditions (e.g. initial load of heavy liquid) can be chosen to reduce to less than 2%, uncertainties arising from the start-up effects of Stage 1.

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 the experimentally observed V to y, the solubility of the original, _unaltered_ heavy liquid, we use the results of a computer simulation of the packed-bed multicomponent vaporization process.

In the total-vaporization computer simulation, the packed bed is modeled as 20 mixed cells (well-stirred vessels) in series. Vaporization occurs as about 100 gas increments successively equilibrate with the liquid (distributed equally between the cells initially) in each of the mixed cells. In the required, successive, flash calculations, it is assumed that for the components of a narrow-boiling mixture, the phase-equilibrium nonidealities can be lumped into a single, constant parameter, PI. The vapor-phase mole fraction of each of the mixture components, (y_i) is then

$$y_i = \frac{x_i P_i^s (PI)_i}{P} \qquad (2)$$

and the solubility of the entire mixture, y is;

$$y = \sum_{i=1}^{m} \frac{x_i P_i^S (PI)_i}{P} \qquad (3)$$

where x and P^S are the liquid-phase mole fraction and vapor pressure and P is the total pressure. Details of the computer simulation program and assumptions are presented elsewhere [Monge 1982].

The inputs to the simulation are: (1) a guess for PI or the solubility of the heavy fraction in the gas (an iterative procedure is used to determine the solubility which results in the best fit of the experimentally observed data showing peak area versus gas volume), (2) the area under the data showing observed peak area versus gas volume for the total-vaporization experiment, (3) the weight of the heavy liquid placed in the equilibrium cell, (4) the number-average molecular weight of the fraction, determined from freezing point depression measurements using a Model 5008 Petroleum Cryoscope obtained from Precision Systems Inc. [Alexander 1982], (5) the number and relative composition of the components in the fraction, approximated from gas chromatography of the fraction, as the number and relative areas of the "key" peaks or groups of peaks, and (6) the vapor pressure of the "keys", calculated [Smith 1976] from the aromaticity (assumed to be the same as that for the entire fraction and approximated from the fraction's hydrogen-to-carbon ratio obtained from elemental analysis) and approximate normal boiling points obtained by comparing the "key-peak" retention times to retention times for a calibration mixture containing compounds with known boiling points.

Figure 5 shows an example of the chromatographic analysis described in (5) and (6) for a Lurgi coal-tar fraction. The gas-chromatography column and detector used are those described in the Experimental Apparatus section. For narrow-boiling fractions, the column retention and detector response are assumed not to vary significantly with component normal-boiling point and aromaticity. Tests of the computer simulation indicate that the results are not very sensitive to the assumed number of mixed cells, number of "key" components or the absolute values of component normal-boiling points.

Figure 6 summarizes the procedure for data reduction. It has been tested on the experimental results of a total-vaporization experiment with a synthetic mixture containing known amounts of naphthalene, 2-methylnaphthalene, 1-ethylnaphthalene, and diphenylmethane in compressed methane. The experimental and simulation results are shown in Figure 7. Results uncorrected for

stripping effects differ by 20% from those calculated from literature values for the properties of the individual components. Application of the proposed data-reduction procedure reduces this to less than 2%.

If a slightly less accurate solubility (in terms of weight per volume instead of mole fraction) is acceptable, it can be obtained directly from data showing the observed peak area versus gas volume without the computer simulation, molecular-weight measurement, or chromatographic analysis described above. In the approximate procedure, a simple equal-area analysis is used to determine the volume of gas that would be required for total vaporization of the heavy liquid sample if the composition and solubility of the liquid (and the observed peak area) had not changed from their initial, steady value. In Figure 8 the equal-area procedure has been applied to experimental results for the total-vaporization experiment for the synthetic mixture described previously. The "equivalent" volume of gas, V_e, and the weight of the heavy liquid sample, W_L, can be used to approximate directly the solubility of the heavy liquid (expressed as the weight of heavy liquid per volume of gas, v);

$$v = \frac{W_L}{V_e}. \qquad (4)$$

Solubility v can be converted to mole fraction using the density of the gas and the molecular weight of the heavy liquid if it has been determined.

Although this approximate analysis has little theoretical basis, it has been found to give results which are within 5% of those obtained (for the synthetic mixture and actual coal-tar fractions) using the more rigorous data reduction procedure described earlier.

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 a pure heavy compound and a heavy synthetic mixture in methane. Experimental results for a pure liquid and for a synthetic mixture agree, to within 3%, with those calculated. Figure 9 shows the results of experimental measurements for two Lurgi coal-tar fractions in compressed methane. It also shows predicted results [Monge 1982]. The measurement for Fraction 1 at 42 bar and $200°C$ has been repeated for a gas mixture containing 25 mol % water in methane. The effect of the water on the solubility was found to be negligible compared to

experimental uncertainties. Further measurements are needed to determine the effects of water on solubilities of this and other mixtures at higher pressures and higher water concentrations.

LITERATURE CITED

Alexander, G., and Prausnitz, J. M., AIChE Annual Meeting, November 1981, New Orleans, Louisiana

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)

Monge, A., PhD Dissertation, University of California, Berkeley, 1982

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

Van Leer, R.A. and Paulaitis, M. E., "Solubilities of Phenol and Chlorinated Phenols in Supercritical Carbon Dioxide," J. Chem. Eng. Data ,25,257 (1980)
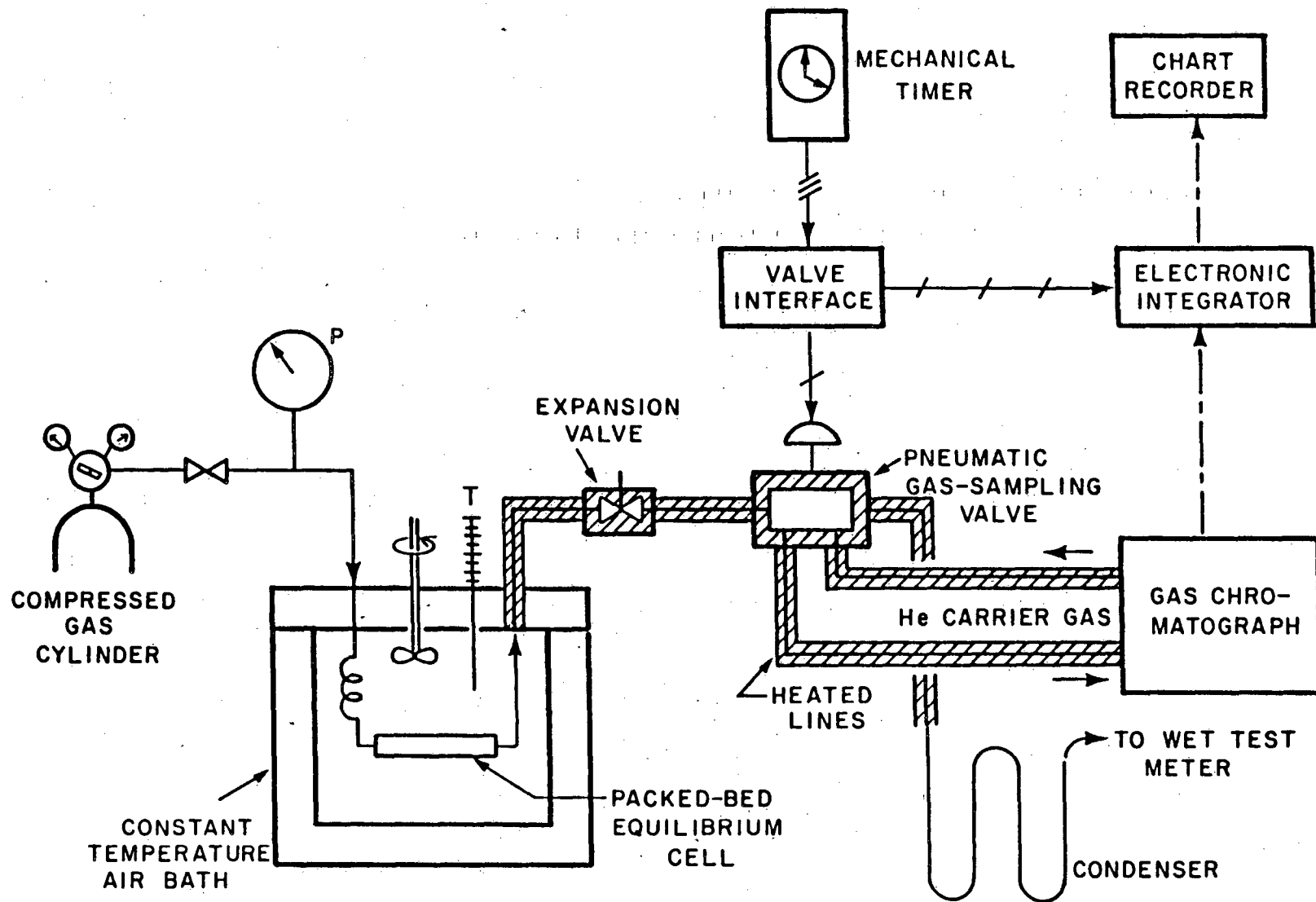
Figure 1. TOTAL-VAPORIZATION APPARATUS FOR MEASURING SOLUBILITY
HEAVY FOSSIL-FUEL FRACTION IN COMPRESSED GAS

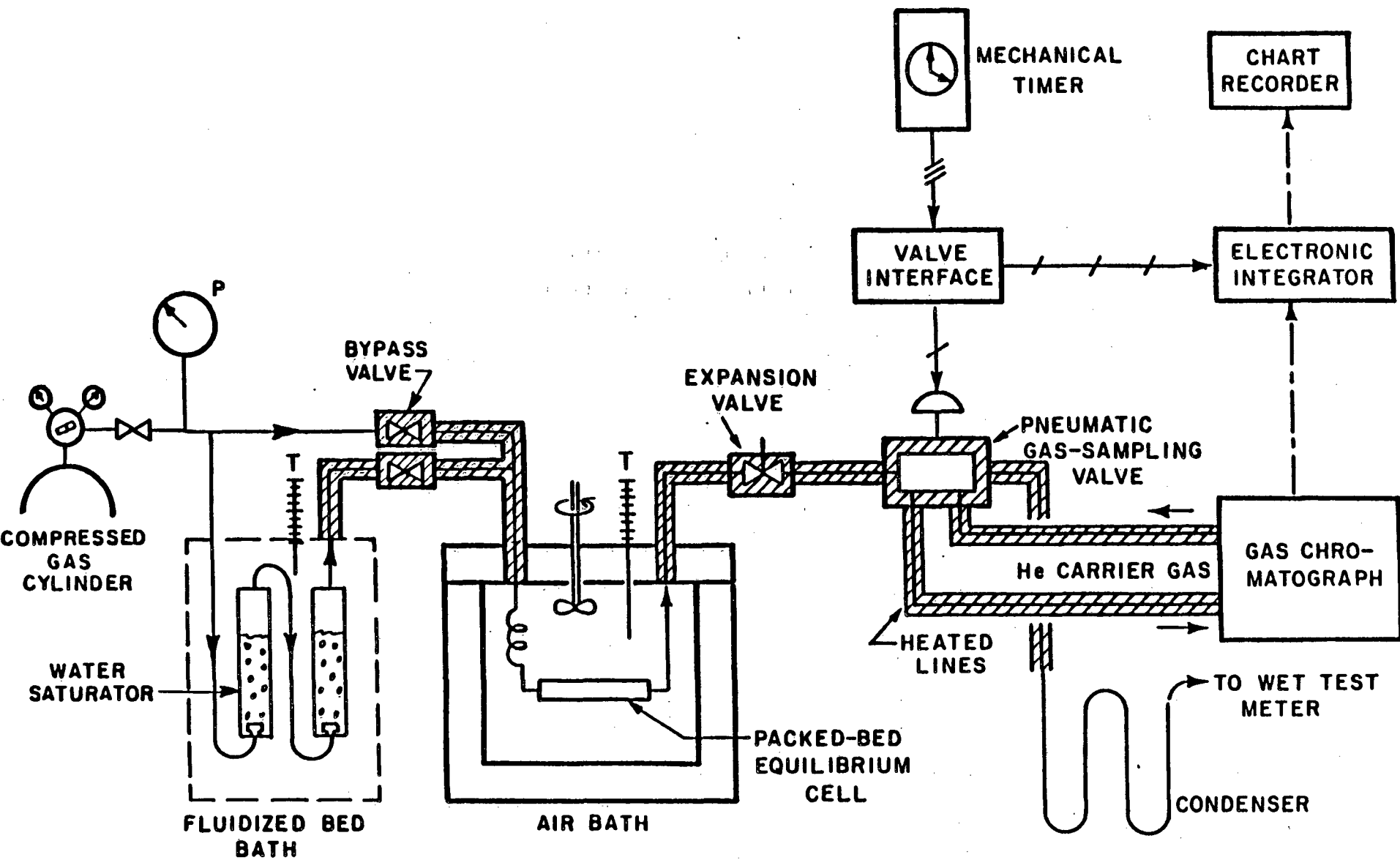Figure 2. **TOTAL-VAPORIZATION APPARATUS FOR MEASURING THE SOLUBILITY OF A HEAVY FOSSIL-FUEL FRACTION IN A COMPRESSED GAS CONTAINING WATER**
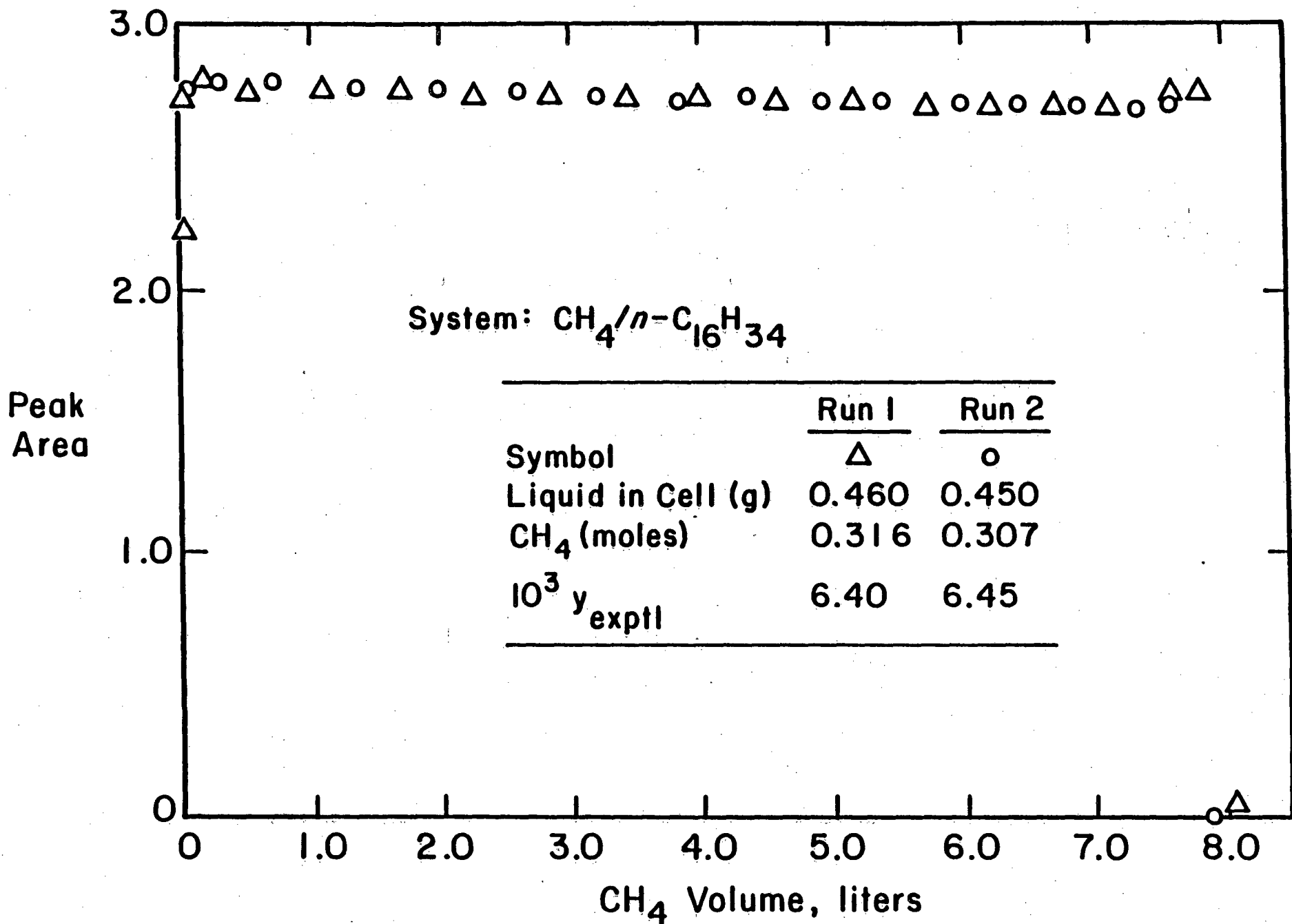
10

System: $CH_4/n\text{-}C_{16}H_{34}$

Symbol	Run 1 $\triangle$	Run 2 $\circ$
Liquid in Cell (g)	0.460	0.450
CH_4 (moles)	0.316	0.307
$10^3 \, y_{exptl}$	6.40	6.45

FIGURE 3. **TOTAL-VAPORIZATION MEASUREMENTS AT 150°C AND 2.36 BAR**
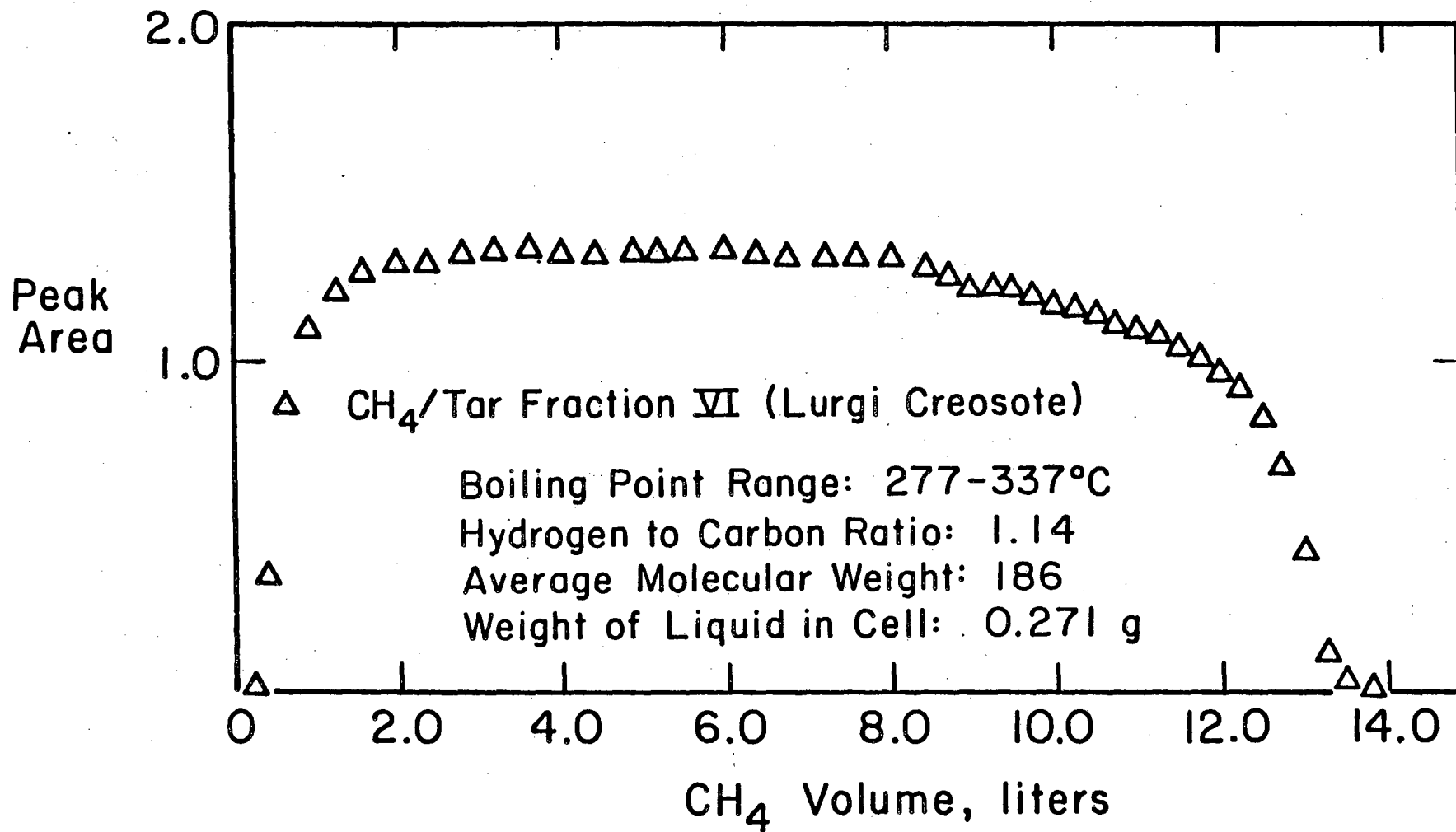
Figure 4. Total-vaporization measurement at 200°C and 42 bar.

FID RESPONSE

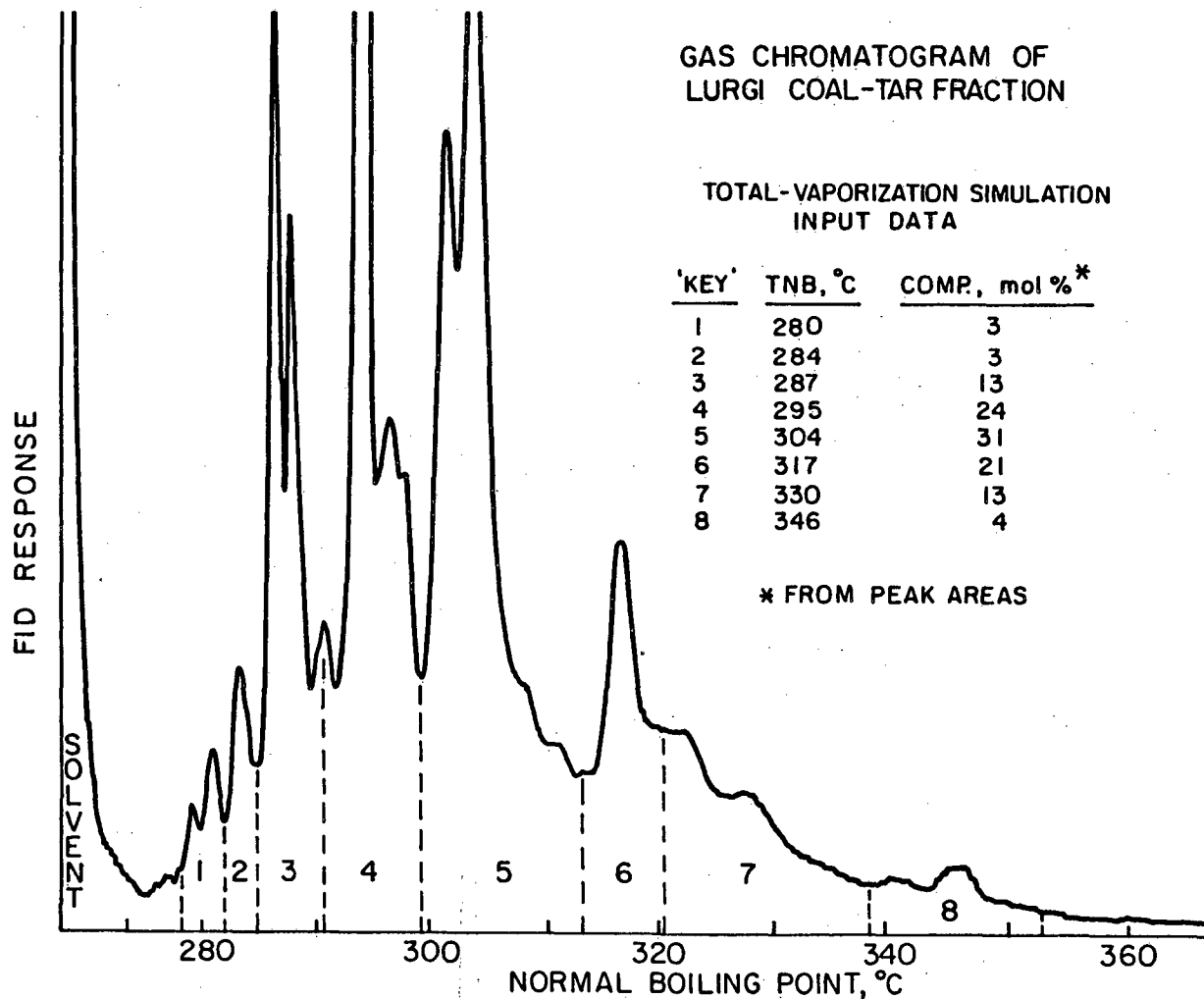SOLVENT

GAS CHROMATOGRAM OF
LURGI COAL-TAR FRACTION

TOTAL-VAPORIZATION SIMULATION
INPUT DATA

'KEY'	TNB, °C	COMP., mol %*
1	280	3
2	284	3
3	287	13
4	295	24
5	304	31
6	317	21
7	330	13
8	346	4

* FROM PEAK AREAS

1 2 3 4 5 6 7 8

280   300   320   340   360

NORMAL BOILING POINT, °C

Figure 5. Gas-chromatography analysis of a Lurgi coal-tar fraction:
input data for total-vaporization simulation and "rigorous" data
reduction procedure.

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

VAPOR PRESSURES (S.W.A.P.)

COMPUTER SIMULATION

SOLUBILITY OF FRACTION IN COMPRESSED GAS

Figure 6.   "Rigorous" data-reduction procedure for obtaining solubilities from total-vaporization data.

Total

Peak Area

30

20

1.0

0

VAPOR-PHASE
MOLE FRACTION

CALCULATED 9.5×10^{-3}
— — TOTAL-VAP. SIMULATION 9.4×10^{-3}

——— EXPERIMENTAL

Mixture Components	Liquid Conc., mole fraction
Naphthalene	0.15
1-Methyl Naphth.	0.35
2-Ethyl Naphth.	0.35
Diphenyl Methane	0.15

0   4   8   12   16   20

CH_4 Volume, L
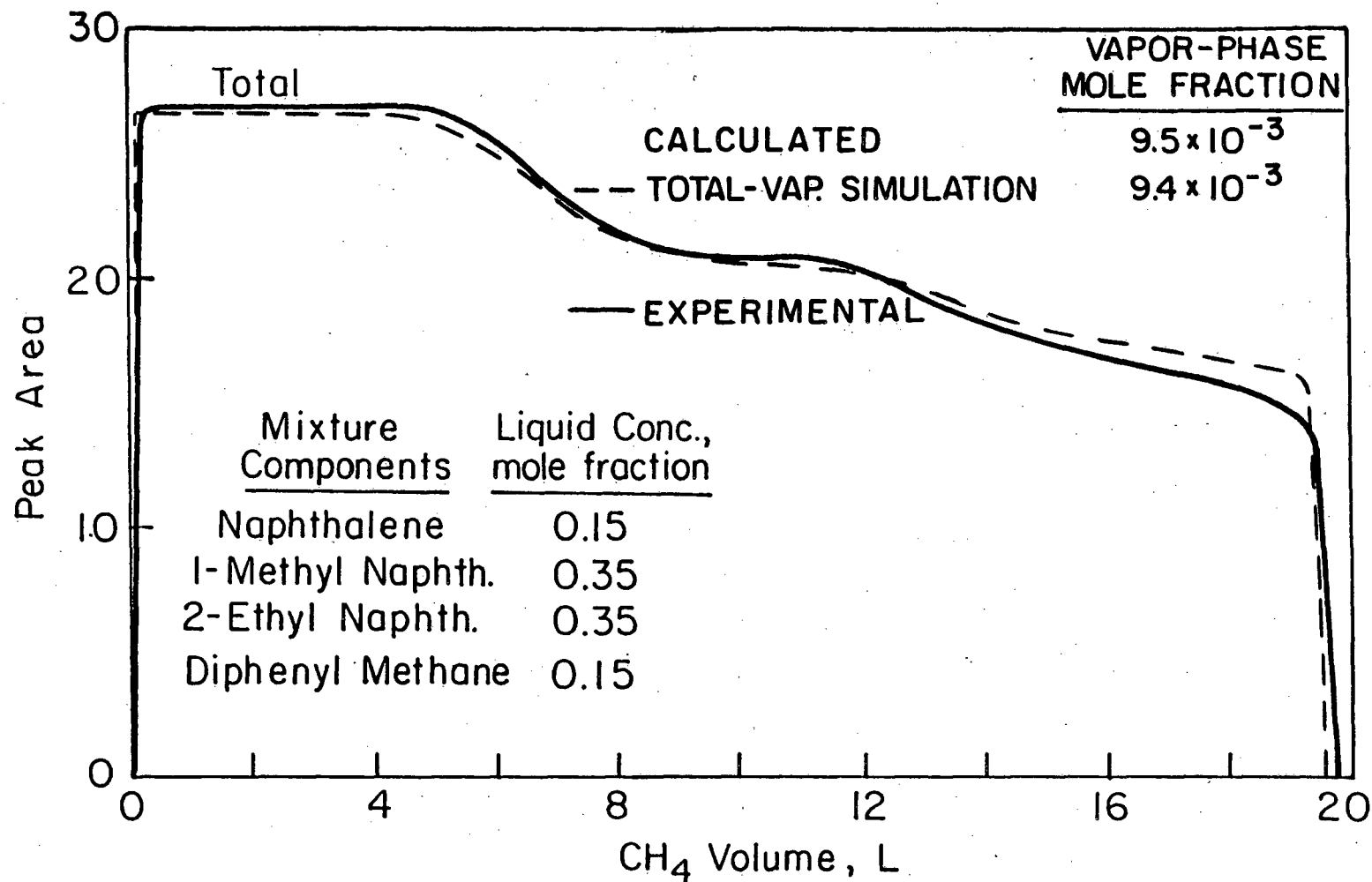
Figure 7.   Comparison of total-vaporization experimental data and simulation
results for a synthetic mixture at 125°C and 3.07 bar.
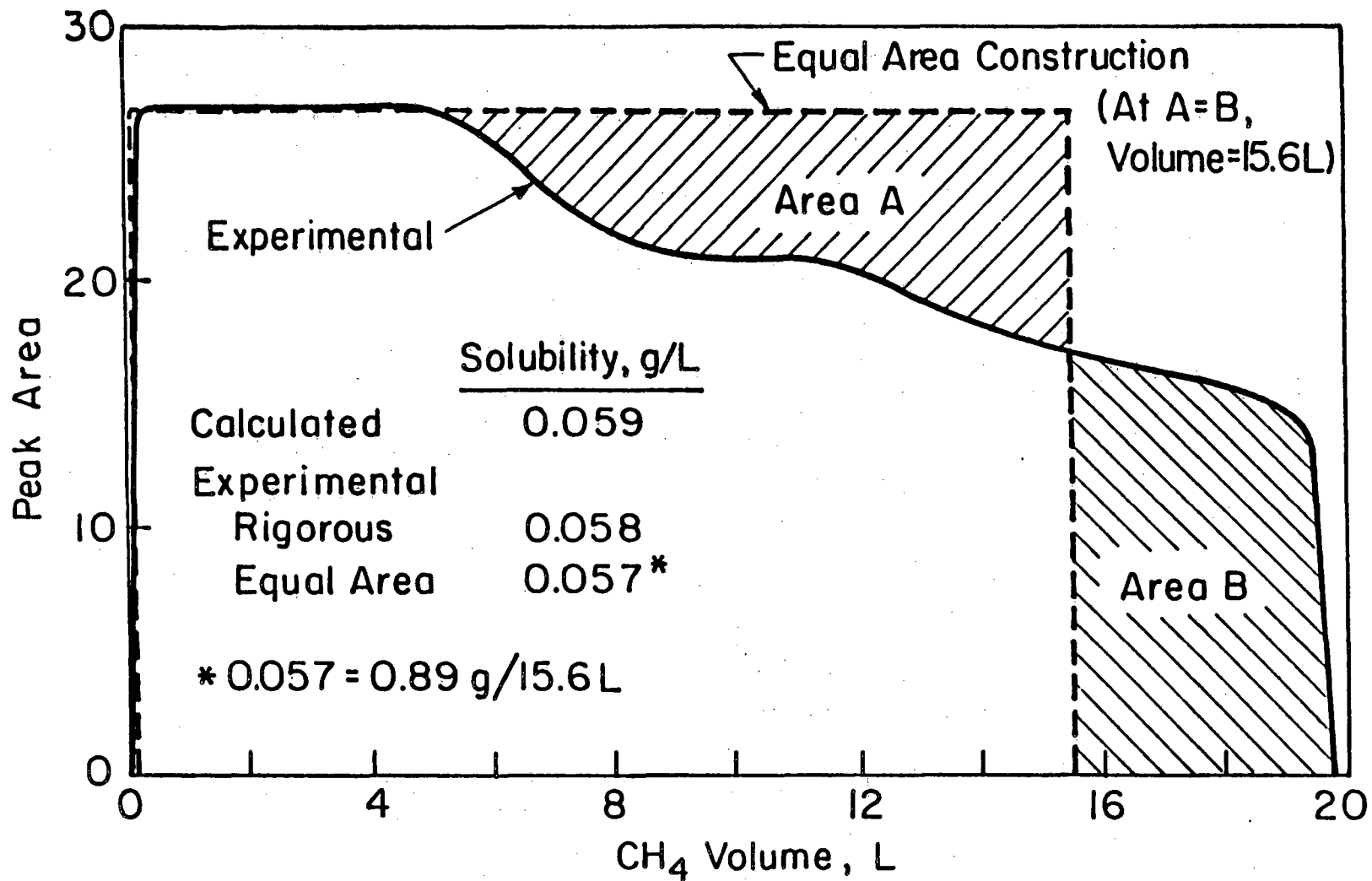
Figure 8. Equal-area construction for approximate reduction total-vaporization data for a synthetic mixture at $125°C$ and 3.07 bar: comparison with results of "rigorous" data reduction and calculated (predicted) results.
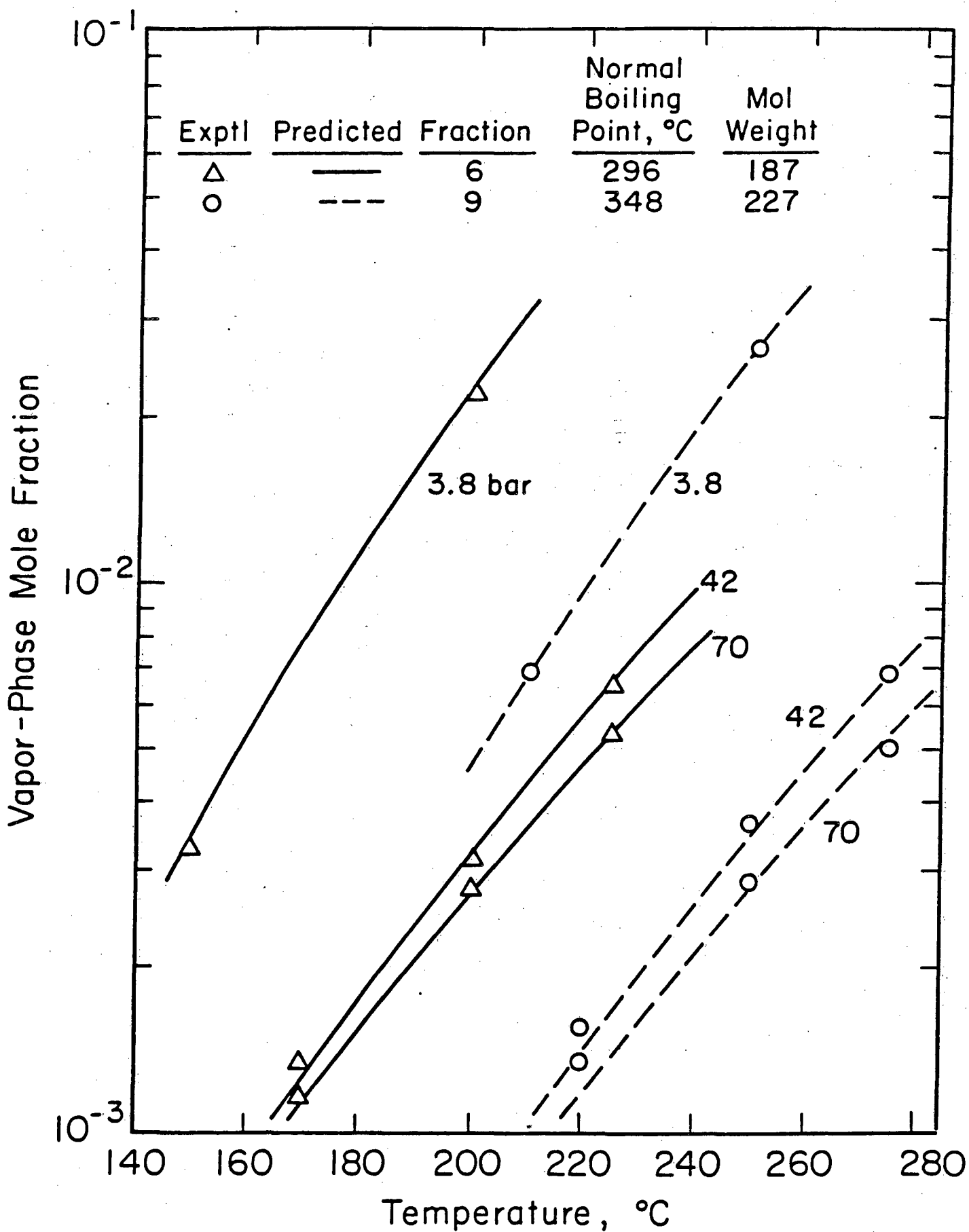
Figure 9. Solubilities of two Lurgi coal-tar fractions in methane.