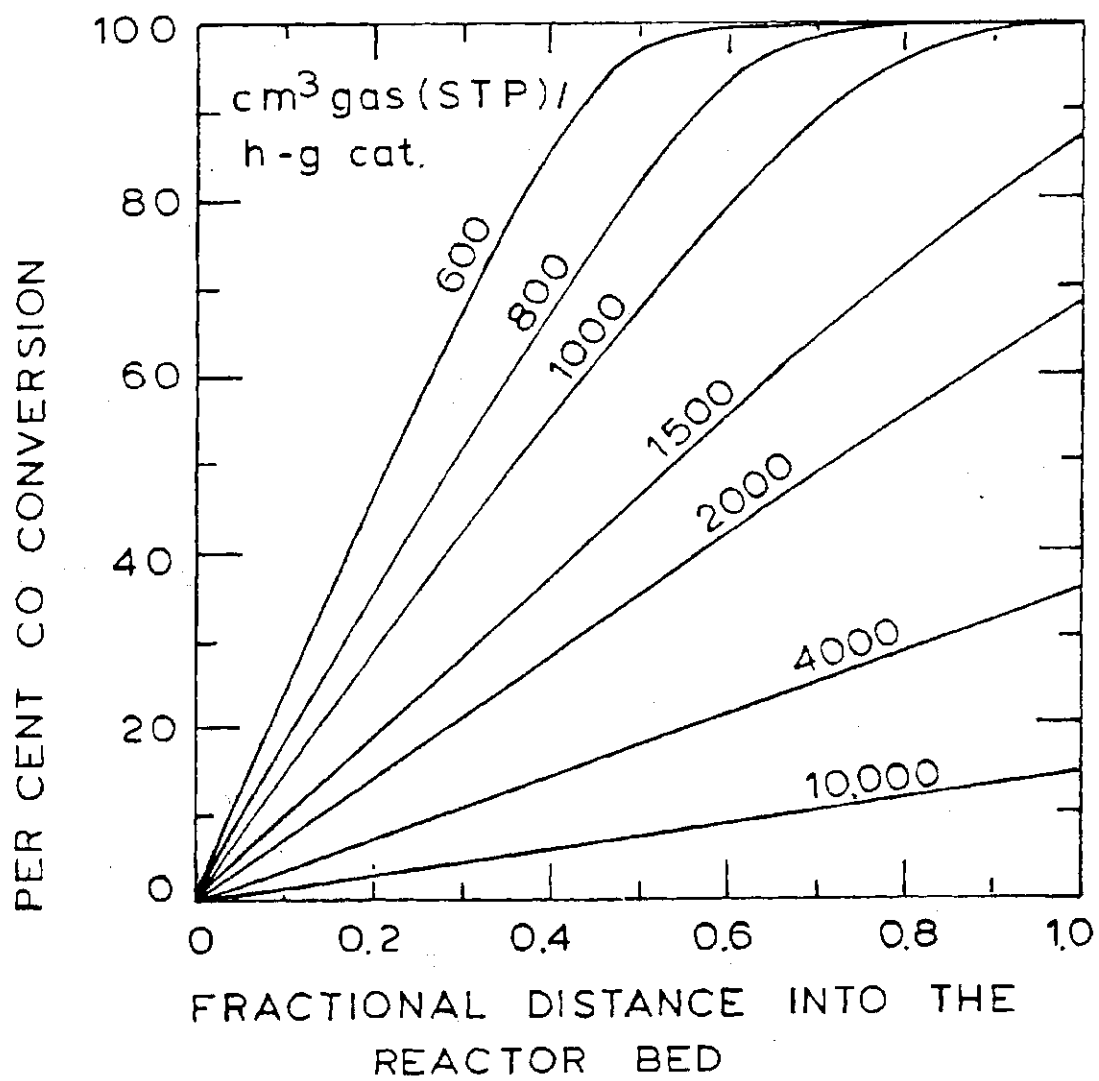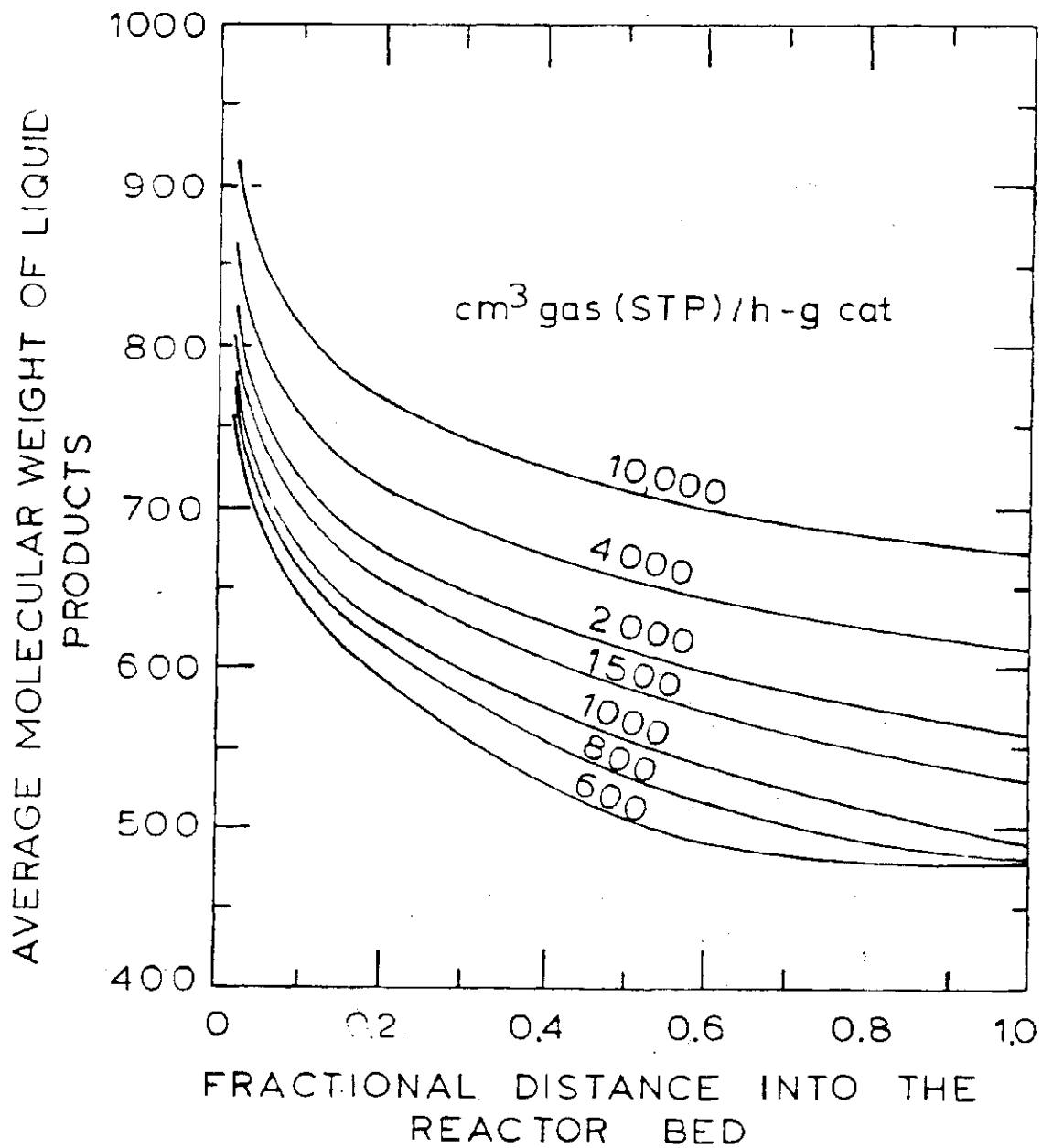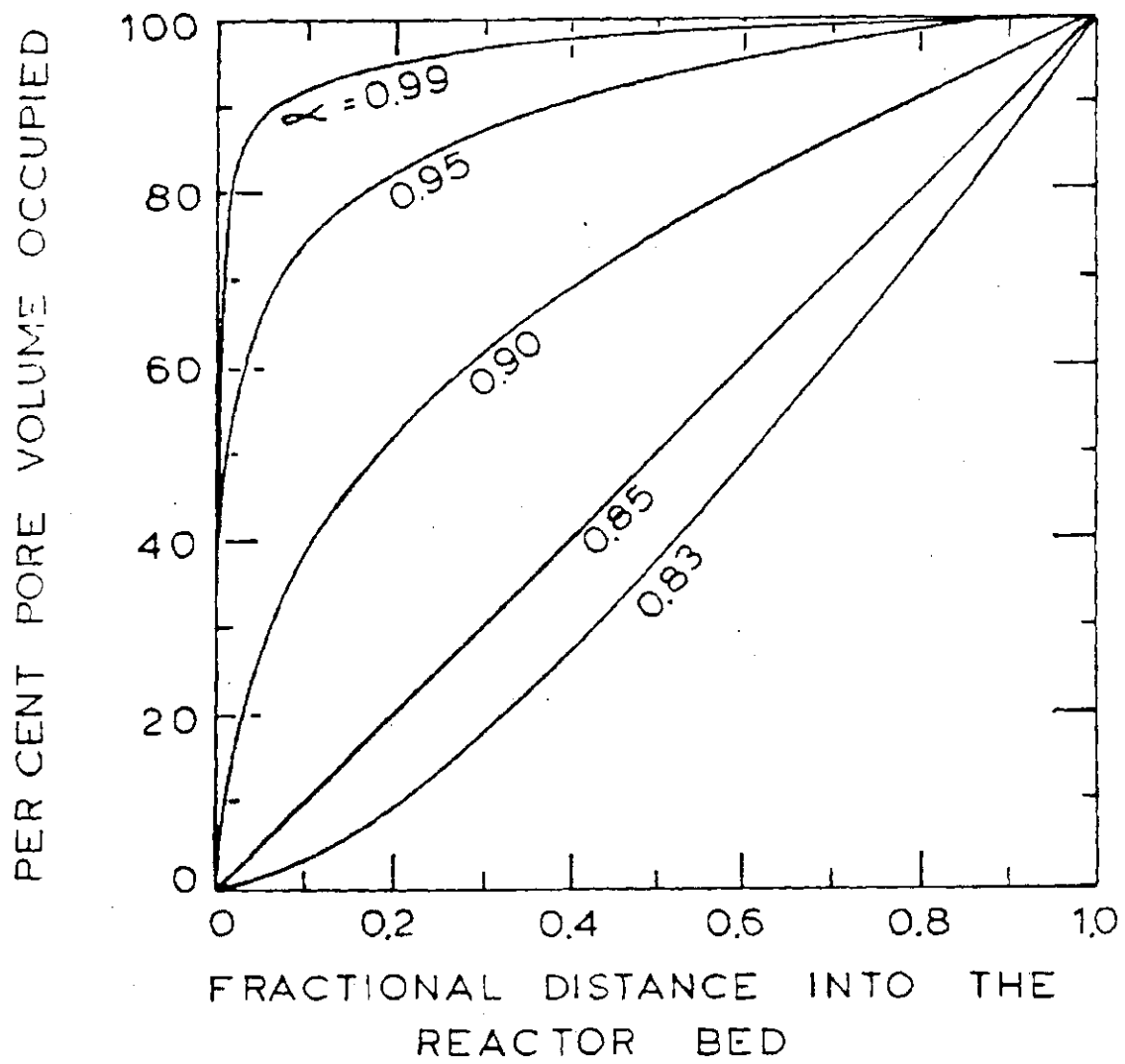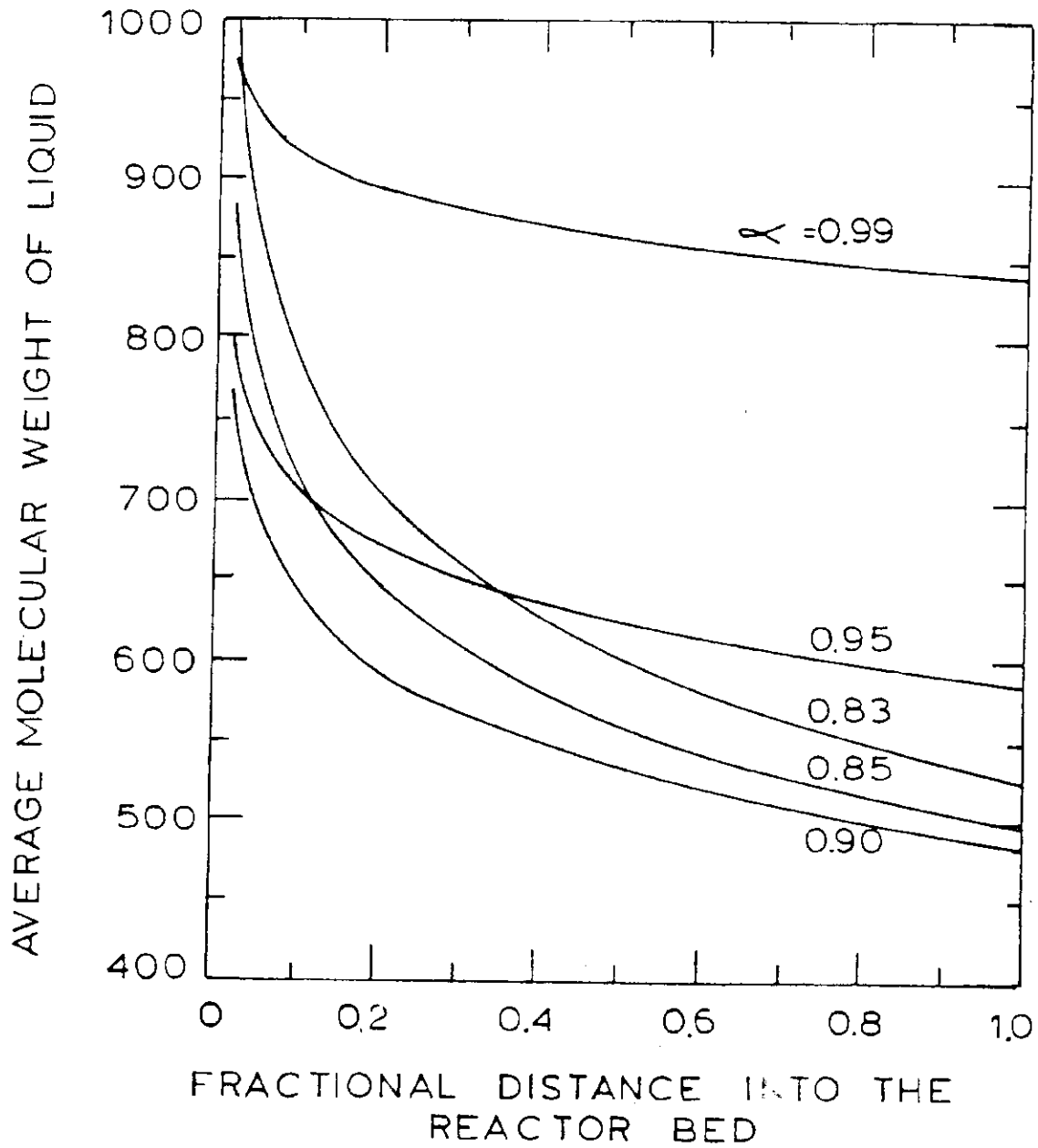FIGURE 9

FIGURE 10

FIGURE 11

FIGURE 12

FIGURE 13
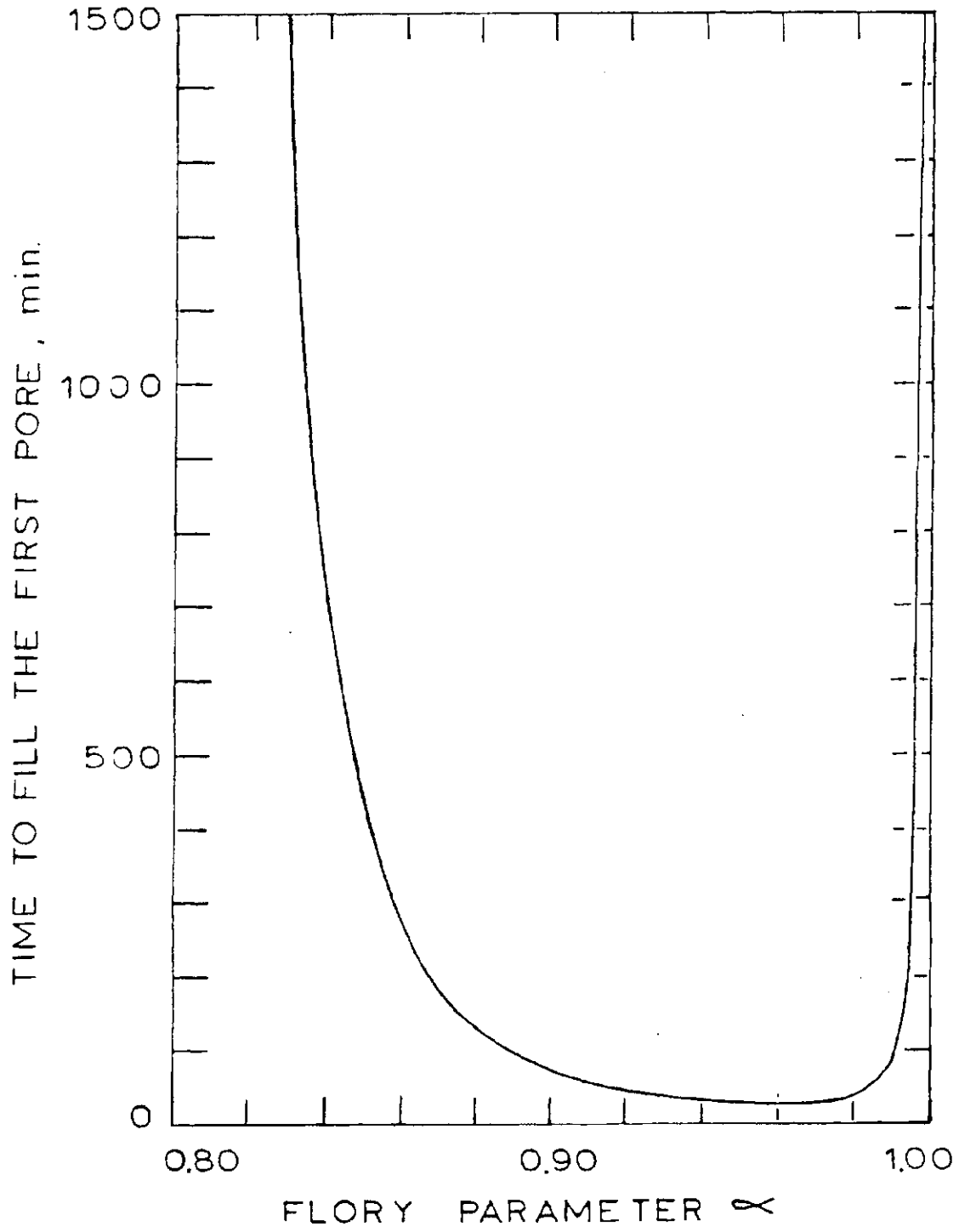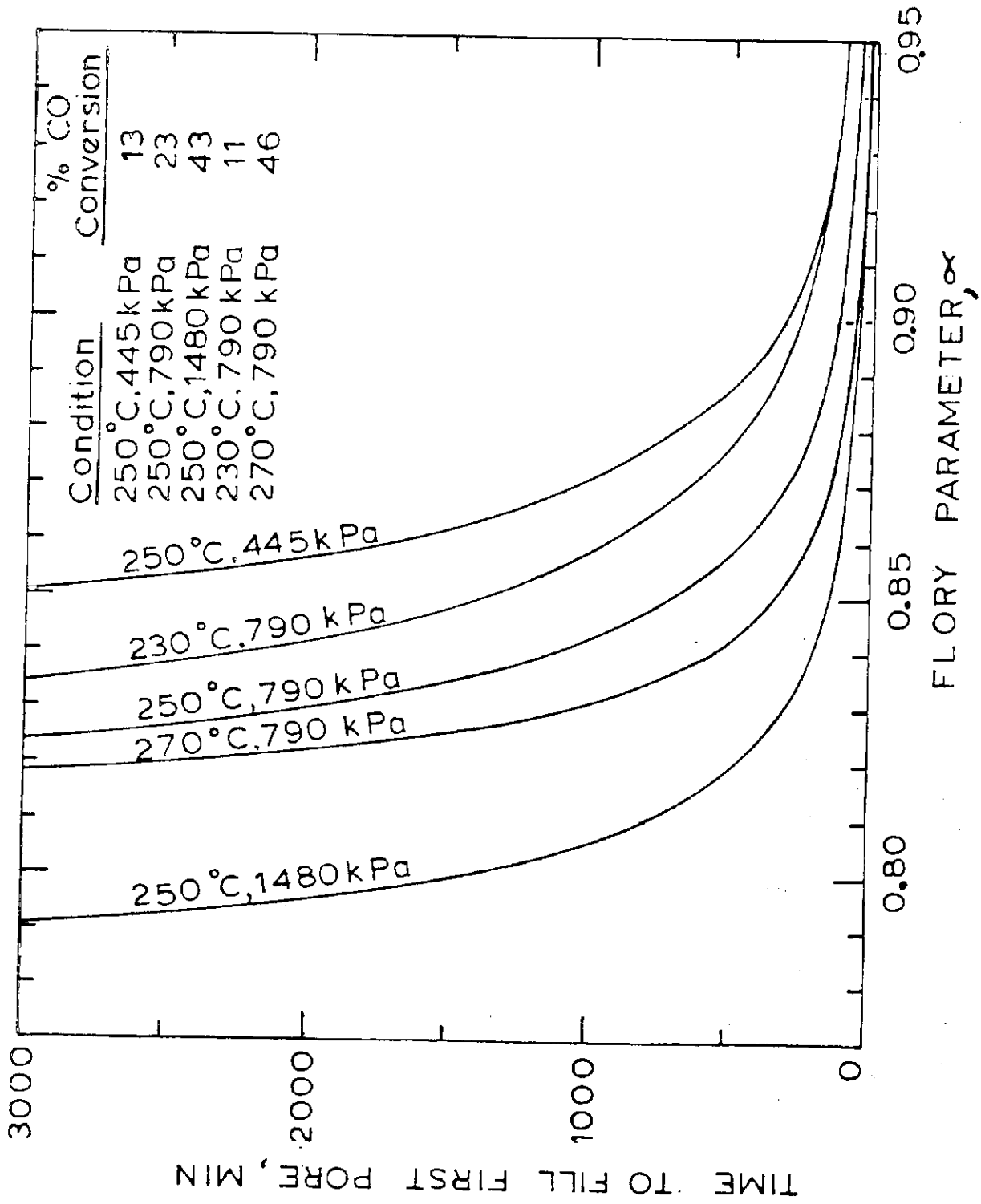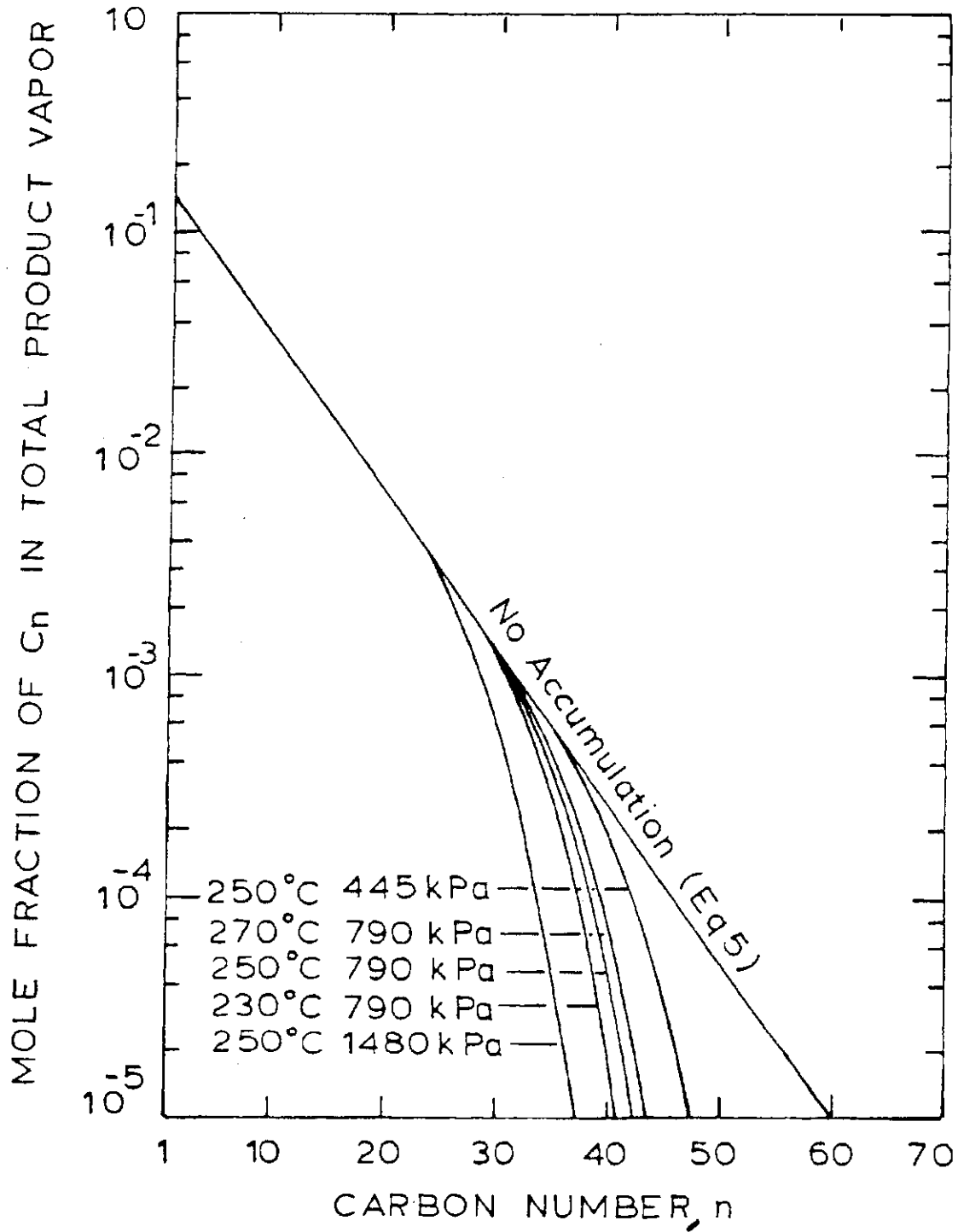
FIGURE 14

FIGURE 15

FIGURE 16
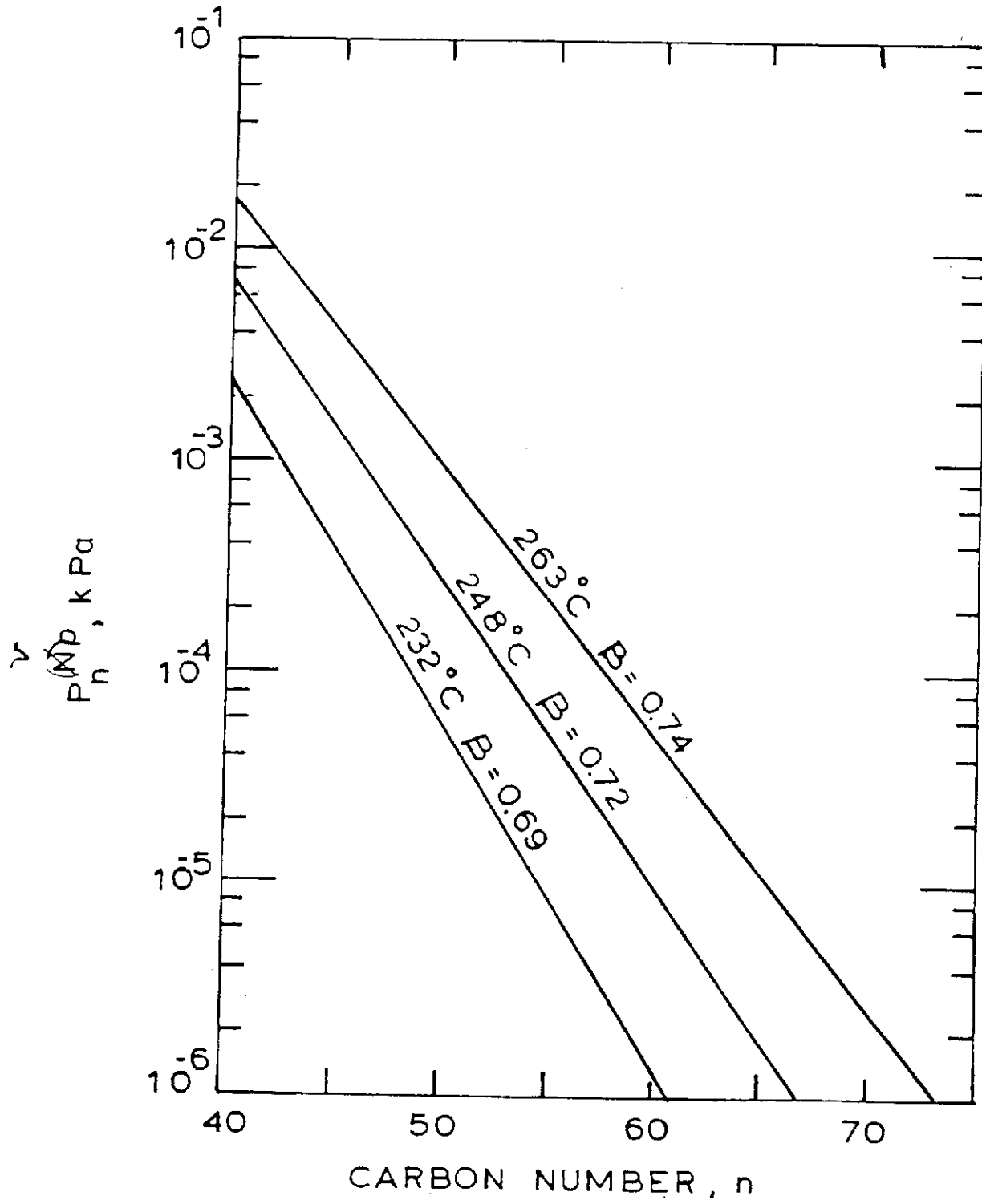
FIGURE 17

SOLUBILITY OF HYDROGEN AND CARBON MONOXIDE

IN SELECTED NON-AQUEOUS LIQUIDS

ABSTRACT

New data at elevated temperatures and pressure are reported for

octacosane, phenanthrene and Fomblin, a perfluorinated polyether, and

compared to previous literature on a variety of liquids. When hydrogen

solubilities are reported on a volumetric basis, substances of a similar

chemical nature have very similar solubilities.

INTRODUCTION

We recently reported studies of the effect of liquid composition on the

rate of reaction and selectivity of the Fischer-Tropsch synthesis in a slurry

reactor system (Satterfield and Stenger, 1984; Stenger and Satterfield, 1984).

For interpretation of studies of this type it is necessary to know the solu-

bility of H_2 and CO in the liquids of interest. Gas solubility information

at elevated temperatures and pressures is also an important parameter in

other pressure processes such as coal liquefaction. Hydrocarbon liquids

are of primary concern but there is also some interest in highly fluorinated

liquids because of the substantially greater solubility of gases in general

in them.

Previous relevant studies on the solubility of hydrogen in hydrocarbons

at elevated temperatures include data on diphenylmethane (Simnick, et al.,

1978; Cukor and Prausnitz, 1972), n-decane (Sebastian, et al., 1980), hexadecane

(Cukor and Prausnitz, 1972), bicyclohexyl (Cukor and Prausnitz, 1972), and

9-methylanthracene (Kobayashi and Nasir, 1981). The only high temperature

data available on carbon monoxide solubility in hydrocarbon liquids appear to

be those by Peter and Weinert (1955) and Albal, et al., (1984), both on paraffin waxes of similar molecular weight.

We present here the results of measurements on three compounds we used in our Fischer-Tropsch synthesis studies. These represent different classes of non-aqueous liquids - n-octacosane, a linear paraffin; phenanthrene, a fused ring polyaromatic; and Fomblin YR, a perfluorinated polyether. Some measurements were also made of the solubility of hydrogen in diphenylmethane for comparison with published data.

EXPERIMENTAL METHOD

It was assumed that the solubilities of hydrogen and carbon monoxide follow Henry's law. From data in the literature, the assumption appears to hold for partial pressures less than about 100 atm for hydrogen. The limited data on the solubility of carbon monoxide seem to indicate the assumption is valid for carbon monoxide as well.

If the partial pressure of the solvent is sufficiently low, then the partial pressure of the solute is a good approximation for its fugacity and Henry's law may be expressed as

$$H_i = \frac{P_i}{x_i} \tag{1}$$

where P_i is the partial pressure of solute i, and x_i is mole fraction of solute i in the solution. In systems previously studied, the mole fraction of hydrogen or carbon monoxide in the liquid phase under conditions of interest here did not exceed 0.1 for partial pressures of less than 100 atm. We can thus approximate x_i by $x_i = N_i/N_L$, where N_i is the number of moles of solute dissolved in the liquid phase and N_L is the number of moles of solvent. Under present conditions the partial pressure of the solute is much greater than the partial pressure of the solvent, the partial pressure of the solute is essentially equal to the total pressure, P, thus,

$$H_i = P \frac{N_L}{N_i} \tag{2}$$

Equation 2 indicates that Henry's law constant can be determined by taking a system at equilibrium at a pressure P_1, increasing pressure to P_2, and then determining the additional number of moles dissolved, i.e.,

$$H_i = N_L \frac{(P_2 - P_1)}{(N_{i,2} - N_{i,1})} \tag{3}$$

This method avoids the extensive degassing procedures required in methods which involve the absolute measurement of the mole fraction of the solute. The method can be used with relatively simple apparatus to obtain reasonably accurate solubility data.

In this study a simple equilibrium cell was used. The cell was filled with a known amount of liquid and heated to the desired temperature. Gas from a calibrated reservoir was added to the cell in which solvent was already at equilibrium under a known initial pressure of gas. When the system came to equilibrium again, a mole balance was calculated given the volume of the cell and the volume of the liquid and assuming the ideal gas law applied. The liquid volume was determined by direct measurement or using Fishtine's correlation for density (Fishtine, 1963). From the mole balance, the number of moles of gas dissolved was determined and the Henry's law constant was calculated.

EXPERIMENTAL APPARATUS

The apparatus consisted of a gas reservoir for the addition of the solute, and an equilibrium cell which contained the solvent (Figure 1). The equilibrium cell was a 1000 ml 316 stainless steel bomb wrapped in heating tapes. Three type J thermocouples were mounted in the bomb to measure the temperature at different locations. A 300 psig (2.14 MPa) Ashcroft test gauge was used to measure the pressure inside the equilibrium cell. The bomb-gauge assembly was mounted on a rocking platform powered by an electric

motor which provided enough agitation in the equilibrium cell to ensure iso-
thermality.

The solute gas reservoir consisted of a bomb (75 ml) equipped with a pres-
sure gauge (550 psig [3.84 MPa], Matheson). The gas reservoir and the equili-
brium cell were connected and disconnected by means of a double-end-shut-off
quick connect coupler.

MATERIALS

The n-octacosane was obtained from the Humphrey Co. (99%). The phenanthrene
(98+%) and the diphenylmethane (99%) were obtained from Aldrich Chemical Company.
The Fomblin YR was obtained from Montedison. The hydrogen and carbon monoxide
were CP grade from Matheson.

EXPERIMENTAL PROCEDURE

The cell was filled with a weighed amount of solvent such that the volume
of the solvent under experimental conditions would be about 800 to 900 ml. This
liquid volume left enough space so that solvent would not splash up into the
pressure gauge assembly. The vessel was then connected to the pressure gauge
assembly and heated to the desired temperature. The voltages to the heating
tapes were adjusted to achieve the same temperature reading at each of the
three thermocouples. The equilibrium cell was pressurized and depressurized
with the solute gas at least five times over a period of three to four hours
to flush impurities from the system. The system was then allowed to come to
temperature and pressure equilibrium, which usually took about three hours.
The initial pressure was usually kept at about 20 psig (0.236 MPa) so that
the solute pressure was much greater than the vapor pressure of the solvent.
Equilibrium was assumed to have been achieved when temperature and pressure
remained constant for a period of at least one-half hour. The gas reservoir
was charged at least a half-hour before use to allow it to thermally equilibrate.

The equilibrium cell was then charged with the solute gas until the pressure in the cell increased by about 0.7 MPa.

After the cell was charged, the gas reservoir was disconnected and the rocking platform was turned on. Pressure and temperature readings were made periodically to watch for equilibration. The period for equilibration was typically about two or three hours; however, the Fomblin YR fluid required as much as 6 hours to equilibrate because of its high viscosity. In a typical run, the pressure in the equilibrium cell would drop about 0.2 to 0.5 MPa. When equilibrium had been achieved, the pressure and temperature were recorded, and a new charge of solute gas was added to the equilibrium cell. A maximum of three charges were added to cell before the system was depressurized. When the solute gas was changed, the same flushing procedure was followed as that for the removal of impurities in the initial run.

RESULTS

The Henry's law constants for hydrogen in diphenylmethane are shown in Figure 2. These data are compared with low pressure data from Cukor and Prausnitz (1972) and high pressure data from Simnick, et al., (1978). Our data agree reasonably well at the higher temperatures but are somewhat low at the lower temperatures. At the lower temperatures the method is inherently less accurate because of the smaller amount of gas dissolved in the liquid.

Henry's law constants for phenanthrene, n-octacosane and Fomblin YR (average Mw = 3500) are presented in Figure 3. Volumetric solubilities defined as

$$S_i = \frac{\rho_i}{H_i \, M_i} \qquad \begin{array}{l} \rho_i = \text{density} \\ \\ M_i = \text{molecular weight} \end{array} \qquad (4)$$

allow comparison of the solubilities of gases in different liquids. Figures 4 and 5 show the solubilities of hydrogen and carbon monoxide, including data for other compounds estimated from the literature. Densities for these

compounds were extrapolated from literature values using Fishtine's correlation (Fishtine, 1963),

$$\rho_2 = \rho_1 \frac{(T_c - T_2)^n}{(T_c - T_1)^n} \tag{5}$$

where n was taken to be 0.29 for all compounds. The average accuracy of the correlation is approximately one percent for $T_r < 0.85$. Critical temperatures for most of the compounds could not be found in the literature. In these cases, critical temperatures were calculated using Lydersen's method (Reid, et al., 1977), a structural group contribution method requiring the normal boiling point. Normal boiling points for 9,10-dihydrophenanthrene and 9-methylanthracene, which were not available in the literature, were estimated to be 320°C and 360°C respectively, based on similar compounds.

Figure 4 shows that hydrogen solubility is very similar for "crude paraffin" (MW = 345) (Peter and Weinert, 1955), "Gulfwax," MW 380 (Albal, 1984), squalane, $C_{30}H_{62}$, (Chappelow and Prausnitz, 1974), and octacosane (present study) $C_{28}H_{58}$. We conclude that paraffins of molecular weight greater than about 300 have similar hydrogen solubility characteristics. Carbon monoxide solubilities (Figure 5) show more scatter among the three paraffin liquids. It is likely that the early data of Peter and Weinert (1955) are slightly high. The Fomblin YR fluid showed much higher solubilities than did the other liquids, as would be expected. Fluorinated compounds in general have low solubility parameters and a high solubility for gases. The aromatic and heterocyclic compounds, on the other hand, demonstrated lower solubilities for hydrogen and carbon monoxide than did the paraffinic compounds.

Much of the solubilty data in the literature appears in the form of Henry's law constants. When solubilities are reported on a volumetric basis, substances of a similar chemical nature have very similar solubilities.

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List of Figure Captions

Figure 1. Solubility apparatus.

HENRY'S CONSTANT FOR
HYDROGEN IN DIPHENYLMETHANE

● CUKOR AND PRAUSNITZ (1972)
▲ SIMNICK, ET AL (1978)
■ THIS WORK
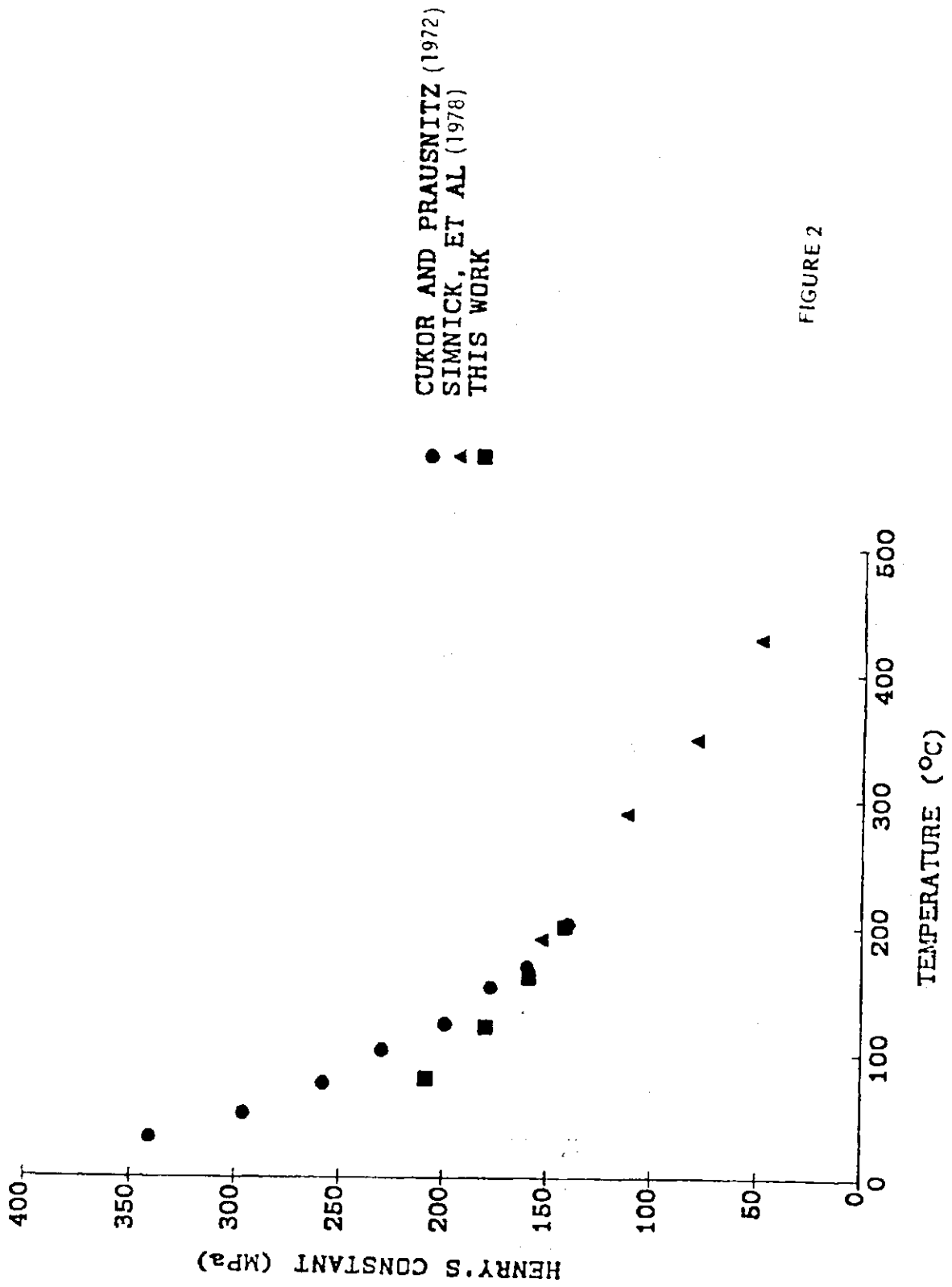
FIGURE 2

HENRY'S CONSTANT FOR
HYDROGEN AND CARBON MONOXIDE

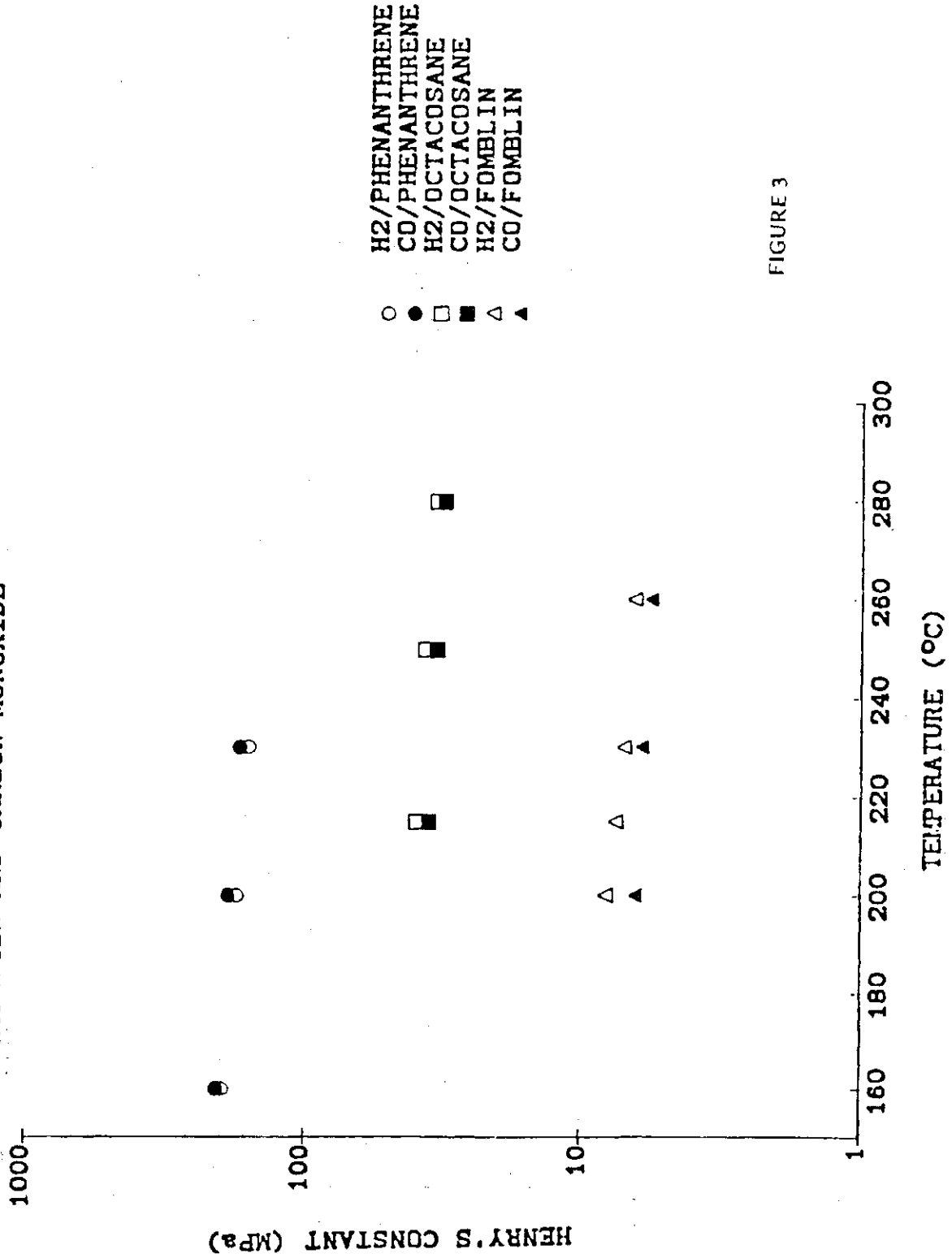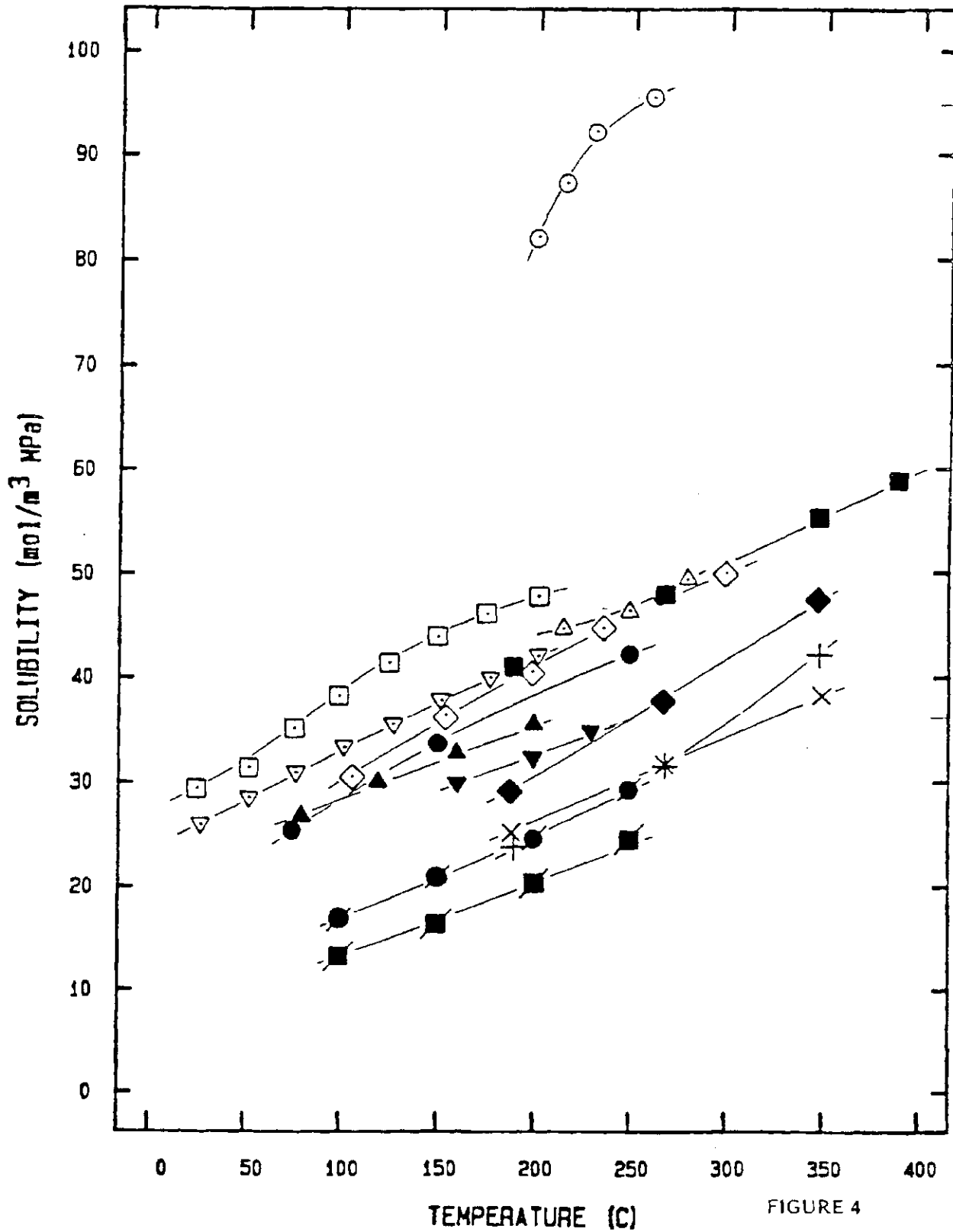|	
○	H2/PHENANTHRENE
●	CO/PHENANTHRENE
□	H2/OCTACOSANE
■	CO/OCTACOSANE
△	H2/FOMBLIN
▲	CO/FOMBLIN

FIGURE 3

SOLUBILITY OF HYDROGEN

FIGURE 4

SOLUBILITY OF CARBON MONOXIDE

FOMBLIN
CRUDE PARAFFIN (Peter and Weinert, 1955)
GULFWAX (Albal, et al., 1984)
OCTACOSANE
PHENANTHRENE

FIGURE 5

TEMPERATURE (°C)

SOLUBILITY (mol/m³ MPa)