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THE STUDY OF THE VOLATILITY OF ETHYLENE GLYCOL IN SUB- AND
SUPER-CRITICAL CARBON DIOXIDE

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THE STUDY OF THE VOLATILITY OF ETHYLENE GLYCOL IN
SUB- AND SUPER-CRITICAL CARBON DIOXIDE

by

Yukihiko Adachi

A THESIS SUBMITTED IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

Master of Science

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HOUSTON, TEXAS
March, 1986

ABSTRACT

THE STUDY OF THE VOLATILITY OF ETHYLENE GLYCOL IN CARBON DIOXIDE AT SUB- AND SUPER-CRITICAL CARBON DIOXIDE PRESSURES.

by
Yukihiko Adachi

The volatility of ethylene glycol in carbon dioxide at sub- and super-critical conditions was studied. Four isotherms at 35, 40, 50 and 60°C were studied at pressures ranging from 2.76 MPa to 22.06 MPa. A constant flow gas saturation technique employing a flame ionization detector for gas mixture analysis was applied for the direct measurement of very low concentrations.

The flame ionization detector was calibrated by injecting known rates of ethylene glycol into carbon dioxide carrier gas.

The results reported in this work consist of (1) calibration data for CO_2-ethylene glycol mixtures over several decades of concentration for the flame ionization detector, (2) experimental volatility data showing the temperature inversion of the volatility of ethylene glycol in the pressure range between 6.21 MPa and 15.17 MPa, (3) demonstration that the enhancement factor along isotherms behave in an orderly fashion, (4) the correlation of the volatility of ethylene glycol in CO_2 by the method proposed by Dewan[5] for carbon dioxide-water systems.

DEDICATION

To my wife, Yoko, and our two children, Masatoshi and Nao, whose cheerfulness, encouragement, and concern conspired to make this work thoroughly enjoyable.

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I. OBJECTIVES

The specific objectives of this study were to:

A. Obtain experimental concentrations of ethylene glycol in the carbon dioxide-rich fluid phase in the carbon dioxide-ethylene glycol system..

B. Develop an experimental technique which would yield reliable data of the volatility of ethylene glycol in compressed carbon dioxide.

C. Develop a calibration technique for the mixture of ethylene glycol and carbon dioxide by steady-state elution method using a flame ionization detector.

D. Provide accurate data for ethylene glycol-carbon dioxide system using a steady-state elution technique.

E. Evaluate the experimental data in terms of the pressure dependence of the enhancement factor.

F. Correlate the experimental data to predict the volatility of ethylene glycol at any temperature and pressure as a function of the density of carbon dioxide.

II. SURVEY OF PREVIOUS EXPERIMENTAL WORK

No data for the volatility of ethylene glycol in compressed carbon dioxide has been reported.

Mantor[7] measured the solubility of carbon dioxide in ethylene glycol at 78, 100, 160 and 220°F and at pressures up to 1057 psia (7.288 MPa) and correlated his data using the Krichevsky-Kasarnovsky[6] equation.

Several binary gas-glycol systems have been studied in which only the solubility of the gaseous component in the glycols were measured and reported.[2,14].

Takahashi et. al.[10] studied the water content of the CO_2-rich fluid phase in equilibrium with 3.5 and 7.0 weight percent water in diethylene glycol and triethylene glycol at 75, 100 and 120°F and at pressures up to 1165 psia (8.032 MPa). The solubility of carbon dioxide in the liquid solutions were also measured at the same conditions.

The Dow Chemical Company[13] reported the solubilities of carbon dioxide in diethylene glycol and in triethylene glycol at 60°F and at pressures 0.10, 0.51, 1.01, 2.03 MPa (1, 5, 10 and 20 atmospheres, respectively).

III. EXPERIMENTAL

A. General Description

The gas saturation flow method employing a flame ionization detector (FID) for gas mixture analysis whose appratus and technique were established by Carruth et. al.[3] was chosen for this work.

The flame ionization detector (FID) was calibrated for the detection of carbon dioxide-ethylene glycol mixtures with high precision. A flow method which was also established by Carruth et. al. [3] was applied for calibration of the FID. A flow calibration method minimizes wall adsorption which frequently can cause serious errors in batch calibration techniques.

B. Major Equipment

1. Flame Ionization Detector Calibration Apparatus

a. Micropump

The 10 cc micropump built for a previous study[3,9] was used to prepare the calibration mixture by metering known flow rates of ethylene glycol into a carbon dioxide carrier gas stream. The flow rates used varied from 0.36 cc/min and 4×10^{-8} cc/min. A rapid traverse speed, 0.702 cc/min, was available to flush the system, etc. Suitable limit switches were provided to prevent possible jamming of the piston against the extremities of the pump at the end of the plunger strokes.

Desired discharge rates were obtained through the use of a positive gear transmission with 24 fixed speeds and an overall gear ratio of 4.5 million to 1. Volumetric flow rates possible with this

pumping system are tabulated in Table 1.

The pump was contained in a constant temperature enclosure controlled by the following system as shown schematically in Figure 1: (1) a Prinsco mercury contact thermometer which fixed nominally at 100°F (37.78°C) and activated by a relay which in turn energized a 25 watt incandescent lamp serving as a heat source, (2) a Ripley 10 CFM blower providing air circulation.

Pump pressure was measured by a Kulite Model VQ-500-200 miniature pressure transducer. A stable 5VDC energizing potential for the transducer was applied by a Kepco Model ABC power supply. The signal from the pressure transducer was fed to a Keithley 192 programmable DMM multimeter and converted to pressure units, psig, by the use of a calibrated conversion equation. The signal was recorded by a Commodore 64 computer.

b. Ethylene Glycol Injection

The metered flow of ethylene glycol was injected through a specially manufactured valve into the carrier gas. A schematic diagram of this valve is shown in Figure 2. The valve which has 0.007 inch orifice and 60 degree V-shaped needle was designed and constructed by Mr. R. J. Martin of this laboratory. This valve was specially designed in order to minimize the dead volume and to control the flow down to very low flow rate. The lowest flow rate which was achieved by this valve was 1.3×10^{-6} cc/min.

The valve was contained in a constant temperature bath controlled by the following system. A main electrical heater whose heat was varied by a Powerstat kept the bath temperature at 115°C. A Bayley Model 123 precision temperature controller connected to a

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heater was used to control the temperature precisely.

c. Gas Analysis Equipment

An ANTEK 464 Gas Chromatograph with a hydrogen flame ionization detector (FID) was used to determine the amount of ethylene glycol passing the detector per unit time. The FID was operated at 117°C. Union Carbide "Zero Hydrogen Gas" (<0.5 ppm hydrocarbon) and "Hydrocarbon Free Air" (<0.1 ppm hydrocarbon) were used to supply the FID flame. A Matheson Company model 7642 rotameter was attached just prior to injection point of each gas supplied to the FID. The signal from the FID through the electrometer of the ANTEK 464 Gas Chromatograph was fed to a Leeds & Northrup Speedmax model W/L recorder and a Keithley 192 Programmable DMM multimeter. The signal was recorded by a Comodore 64 computer.

2. Volatility Measurement Apparatus

a. Carrier Gas Metering Pump

The carbon dioxide carrier gas was metered with a 500 cc positive displacement plunger pump capable of operating up to 86.18 MPa (12500 psi) which was built for a previous study[3].

Various flow rates were obtained through a reducing gear and a transmission. The available volumetric flow rates for this pump are presented in Table 2. The pump is equipped with a rapid traverse speed of about 575 cc/min. Both the rapid traverse and pump drives are equipped with forward and reverse controls and limit switches.

The pressure of the metered carrier gas was measured directly by a Heise gauge with range of 0 to 4000 psi (27.58 MPa). The gauge has dials of 12 inch in diameter with a calibrated accuracy stated by the manufacturer to be 0.1% of full scale.

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The temperature of the pump was controlled nominally at 24.5°C. The measured temperature never varied by more than ±0.1°C during a run. The pump was enclosed in a box constructed of particle board. Two Chromolox 250 watt heaters, a 50 CFM Dayton 1C9139 blower and a Fenwal 17300-0 thermoswitch were installed to control the temperature in a box.

b. Equilibrium Cell

The cell was made from a heat-treated 410 stainless steel cylinder for a previous study[4]. The windows were installed to observe the vapor-liquid/or fluid-liquid level in the cell. The material of the windows was Schott Lithium Glass AS-8000 Herculite supplied by Schott Optical Glass, Inc. This glass was strengthened by a chemical treatment by the Optical Instrument Laboratories of Houston. The cell with this windows could be used for pressures up to 55.16 MPa (8000 psi).

The saturated gas proceeded through a WHITEY SS22RS2 Micro Metering Valve which was installed to control the back pressure in the cell and to expand the gas mixture to atmospheric pressure and thence to an ANTEK 464 Gas Chromatograph through an insulated and heated line.

A magnetic pump for the circulation of the gas or fluid was installed in the system in order to establish equilibrium more rapidly. Also, a preheater and a presaturator were installed prior to the equilibrium cell for the same purpose.

The pressure in the cell was measured by a set of two Heise gauges with ranges of 0 to 13.79 MPa (0 to 2000 psi) and 0 to 27.58 MPa (0 to 4000 psi). The gauges have dials of 12 inch in diameter

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with a calibrated accuracy stated by the manufacturer to be 0.1% of full scale and frequently checked versus Ruska Dead Weight Gages.

The temperature of the cell was measured with an Omega Engineering model PR-11-3-500- $\frac{1}{4}$ "-24 $\frac{1}{2}$ -E Platinum Resistance Thermometer (PRT) inserted vertically approximately 7 inches into a well bored in the wall of the cell. The signal was fed to a Keithley model 192 Programmable DMM multimeter. The signal was converted to the Centigrade temperature scale and recorded by a Commodore 64 computer. Calibration of the PRT with the DMM multimeter is discussed in Appendix B.

c. Gas Analysis Equipment

The amount of ethylene glycol passing the detector per unit time was determined by the same apparatus as that was described in establishing the calibration curve.

d. Cryostat

The cryostat consisted of a preheater, a presaturator, equilibrium cell, a magnetic pump, temperature measurement and control equipment, a refrigeration coil, bath fluid, bath fluid stirrer, appropriate valves and tubing, and a cryostat to hold the bath fluid. The 10 inch diameter by 22 inch deep glass Dewar mounted in a metal box filled with a moldable Urethane foam served as the cryostat.

The preheater consisted of a 1/8 inch stainless steel tubing 10 feet long. The presaturator consisted of three 3/8 inch stainless steel tubing 36 inches long.

The cryostat temperature was controlled by balancing refrigeration against a continuously controlled heat input. A

Bayley Model 123 precision temperature controller received its input from an attached resistance thermometer which was placed directly in the bath fluid and provided an electronic output to a 200 watt immersion heater. A 115V R-12 refrigeration unit was installed for this purpose. A 250 watt electrical heater with a Powerstat was used as a continuous heat input to counteract the refrigeration load.

The cryostat bath fluid was stirred by a propeller driven by a 1/40 h.p., 1725 rpm Bodine motor.

A silicone oil in the cryostat bath served as the bath fluid.

C. Experimental Procedure

1. Flame Ionization Detector Calibration

A schematic diagram of the apparatus for the Flame Ionization Detector (FID) calibration is shown in Figure 3.

The calibration curve was prepared by metering known flow rates of ethylene glycol into the carbon dioxide carrier gas which was conveyed to it for analysis by the FID. The variables recorded were the volumetric flow rates of ethylene glycol and carbon dioxide, temperature of the pump, pressure of the pump, temperature of carbon dioxide at the flow meter and the FID signal. Since the liquid density of ethylene glycol is known accurately in the temperature range used, the molar flow rate of ethylene glycol can readily be calculated. The molar flow rate of ethylene glycol was plotted versus detector signal on log-log coordinates. Analytical curve was fitted to the data by a linear least square regression technique.

Since ethylene glycol is much less volatile than CO_2, calibration data in the low molar flow rate region were necessary.

Extreme difficulty in maintaining a steady injection of ethylene glycol in a lower flow rate region, less than 1.3×10^{-6} cc/min, was encountered. Therefore, a stream splitting technique was utilized to obtain calibration data in this region. A relatively higher flow rate of carbon dioxide was initially fed at the mixing point to ethylene glycol. Since the injection rate of ethylene glycol was not changed by the CO_2 flow rates, the latter was changed in accordance with the ethylene glycol concentration desired. The lower molar flow rates of CO_2 were obtained by splitting the relatively higher flow rate of carbon dioxide by halving, quartering, etc. the CO_2 stream prior to entering the FID.

Each data point was taken when the FID response and the pressure of the ethylene glycol injection pump were steadied simultaneously for at least one hour. Since small fluctuation of the FID signal was observed, the signal was integrated over a period of time for a single data point and averaged over the length of the run by a Commodore 64 computer.

The carbon dioxide carrier gas was supplied directly from the cylinder via a Matheson Company Model 8H-350 pressure regulator at 0.14 MPa (20 psia).

2. Volatility Measurement

A schematic diagram for volatility measurement system is shown in Figure 4.

Airco Industrial Gases grade 4 carbon dioxide (<10ppm hydrocarbon) was used as the carrier gas. Carbon dioxide was charged to the carrier gas metering pump in a liquid state. Then it was compressed/or expanded to the desired pressure. After thermal

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equilibrium in the pump was attained, the carrier gas which was metered by the pump passed through the bypass line for a period of time in order to clear out all impurities in the system. The carrier gas was then switched from the bypass line and introduced into the bottom of the equilibrium cell through the preheater and the presaturator. The saturated gas was expanded to atmospheric pressure through a micro metering valve and was introduced into the FID.

The variables recorded were the pressure, temperature and the volumetric flow rate of the pump, the resulting FID signal and the pressure and temperature of the cell.

From the least square calibration curve, the flow rate of ethylene glycol was determined and the flow rate of carbon dioxide was known from the metering information. Consequently, the vapor concentration of ethylene glycol was readily calculated.

IV. PRESENTATION AND DISCUSSION OF RESULTS

A. Calibration

1. Optimum Operating Condition of the Flame Ionization Detector

The carrier gas flow rate, 28 cc/min at 1 atm and 34.7°C was employed. The system was designed so that the carrier gas was in direct contact with the liquid in the cell for more than a minute at the flow rate 12 cc/min[3] at 1 atm. The maximum flow rate employed for this research was 0.448 cc/min at the cell condition. Preliminary experiment proved this flow rate, together with the operation of the magnetic pump, was slow enough to insure complete saturation.

The optimum flow rate of hydrogen and air were determined. Figure 5a and 5b support the choice of optimum conditions with respect to the carrier gas flow rate at 28 cc/min. The flow rate of each gas employed in this research was as follows:

Hydrogen 35 cc/min

Air 350 cc/min

These flow rates were used throughout the experiment.

2. Calibration Data

The calibration data taken are tabulated in Table 3. The table gives the molar flow rate of ethylene glycol, the observed detector signal, the coefficients of the fitted least squares expressions, the percentage deviation of each experimental point from the fitted curve and the average absolute percent deviation.

Figure 6, which in fact represents the FID signal displacement above the "pure CO_2", is a plot of these data using log-log coordinate. The data were fitted to the following expression:

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$$Y = A + B \times X$$

where $Y = \ln F = \ln$ (molar flow rate)

         $X = \ln V = \ln$ (detector signal voltage) over reference

value provided by pure CO_2.

The data did not deviate from the curve by more than -1.7 to

+1.0 percent.

The concentration covered a range from 2.6×10^{-6} to 2.49×10^{-3}

mole fraction of ethylene glycol in carbon dioxide.

The response of the detector was linear throughout the

concentrations studied.

As mentioned in the experimental procedure section, the stream

splitting technique was applied to obtain the molar flow rate of

ethylene glycol lower than 2.308×10^{-3} moles/min. The data at lower

flow rate in Table 3 show that the stream splitting technique was

succesfully utlized within the accuracy expected.

B. Volatility Data

Four isotherms at 35, 40, 50 and 60°C were taken at pressures

between 2.76 MPA (400 psia) and 22.06 MPa (3200 psia). Experimental

data are tabulated for each isotherm in Tables 4-7. The figures

plotting the ethylene glycol concentration against pressure at each

isotherm are also shown in Figure 7. Inversion of the volatility of

ethylene glycol at each isotherm was observed at pressures between

6.21 MPa (900 psia) and 15.17 MPa (2200 psia).

The enhancement factor E of ethylene glycol is given by the

following expression (Takahashi et. al.[11])

$$E = \frac{\pi y_{E.G.}}{P^0_{E.G.}} \tag{1}$$

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where $Y_{E.G.}$ =   mole faction of ethylene glycol in carbon dioxide

E   =   enhancement factor of ethylene glycol

$P_{E.G.}^{0}$ =   vapor pressure of ethylene glycol at each temperature

π =   total pressure

Vapor pressures of ethylene glycol at 35, 40, 50 and 60°C were obtained from the following expression:

$$\log P_{E.G.}^{0} = A - \frac{B}{t+C} \tag{2}$$

where $P_{E.G.}^{0}$ =   vapor pressure of ethylen glycol in mmHg

A, B and C =   Antoine constants respectively

t   =   temperature in C

The Antoine constants A, B and C is reported to be:

A = 7.84522

B = 1914.951

C = 188.154

respectively[8]. Figure 8 presents the enhancement of the concentration of ethylene glycol at each isotherm while Figure 9 presents the same factor versus 1/T along isobars. Vapor pressures at each isotherm are enhanced abruptly when the system pressure approaches the critial pressure of carbon dioxide which is 7.375 MPa (1069.66 psia)[1]. Therefore, it could be said that so called "supercritical extraction" took place particularly at pressures exceeding the critical pressure of carbon dioxide when the pressure exceeded its critical pressure.

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At equilibrium, the fagacity, the pressure and temperature and component in the equilibrium phases must be equal. The fugacity of ethylene glycol in the carbon dioxide-rich phase (denoted by the superscript g) is expressed by definition as follows:

$$(f_{E.G.}^g)_p = (\Phi_{E.G.}^g)_p (y_{E.G.})_p P \tag{3}$$

where $(f_{E.G.}^g)$ = fugacity of ethylene glycol at system pressure

$(\Phi_{E.G.}^g)_p$ = fugacity coefficient of ethylene glycol at system pressure

$(y_{E.G.})_p$ = mole fraction of ethylene glycol in carbon dioxide at system pressure

P = system pressure

For the ethylene glycol rich phase (denoted by superscript 1), the fugacity of ethylene glycol is given as follows:

$$(f_{E.G.}^1)_p = (f_{E.G.})_{vp} \exp [\frac{\overline{V}_{E.G.}}{R T} (P - P_{E.G.})] a_{E.G.} \tag{4}$$

where $(f_{E.G.})_p$ = fugacity of ethylene glycol in ethylene glycol rich phase at system pressure.

$(f_{E.G.})_{vp}$ = fugacity of ethylene glycol at its vapor pressure

$\overline{V}_{E.G.}$ = molar volume of ethylene glycol

P = system pressure

$P_{E.G.}$ = vapor pressure of ethylene glycol

$a_{E.G.}$ = activity of ethylene glycol

$\overline{V}_{E.G.}$ was assumed to be incompressible to obtain the equation (4). $(f_{E.G.})_{vp}$ can further be expressed as follows:

$$(f_{E.G.})_{vp} = (\Phi_{E.G.})_{vp} P_{E.G.} \tag{5}$$

where $(\Phi_{E.G.})_{vp}$ = fugacity coefficient of pure ethylene glycol at its vapor pressure.

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From equations (3), (4) and (5) the following expression was obtained:

$$(y_{E.G.})_p = [\frac{(\Phi_{E.G.})_{vp}\; a_{E.G.}}{(\Phi_{E.G.}^g)_p}] \frac{P^o_{E.G.}}{P} \exp\{\frac{\overline{V}_{E.G.}}{RT}(P - P_{E.G.})\}$$

$$= [\Phi rat] \frac{P^o_{E.G.}}{P} \exp\{\frac{\overline{V}_{E.G.}}{RT}(P - P_{E.G.})\} \qquad (6)$$

where Φrat = fugacity coefficient ratio times the activity coefficient for ethylene glycol defined by equation (6).

Dewan[5] obtained equation (6) to predict the water concentration in carbon dioxide by correlating the calibration constant Φrat in equation (6) as a function of the density of carbon dioxide only, probably because the vapor pressures of the glycols were not always known. Tables 12-15 show the fugacity ratio times the ethylene glycol activity (see equation (6)) obtained vs. density of carbon dioxide at each isotherm. Figure 10 demonstrates the relation between the calibration constant and the density of carbon dioxide in ethylene glycol-carbon dioxide system at four isotherms. It is also proved in this system that the calibration constant is a function of the density of carbon dioxide but slightly dependent on the temperature. No further analysis was done in this study.

The calculation of $(y_{E.G.})_p$ is not practically possible since detailed interactive forces between compressed CO_2 and E.G. and even the vapor pressure are not always available. Therefore, the fugacity ratio times the activity for E.G. in equation (6) is correlated versus CO_2 density for use in equation (6) to estimate the ethylene glycol concentration for the CO_2-rich phase.

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V. SUMMARY AND RECOMMENDATIONS

This investigation involved the measurement of the volatility of ethylene glycol in sub- and super-critical carbon dioxide at pressures and temperatures exceeding the critical endpoint of the system. The range of measurements was as follows:

temperature   35, 40, 50, 60°C

pressure   2.76 - 22.06 MPa (400 - 3200 psia)

A steady state gas saturation flow technique employing a flame ionization detector for gas mixture analysis was applied. The stream splitting technique was utilized to obtain the lower molar flow rate of ethylene glycol for the flame ionization detector calibration.

Results reported in this study consist of the

1. FID calibration data

2. Experimental volatility data

3. Correlation of the volatility data using the enhancement factor.

4. Demonstration that the relation between the density of carbon dioxide and the calibration constant which appeared in the thermodynamical equation, equation (6), as a coefficient can be used to predict the volatility of ethylene glycol at higher pressures. The relation demonstrated that the calibration constant was strongly dependent on the density of carbon dioxide but only slightly dependent on the temperature at higher pressures. However, at lower pressures, the relation mentioned above cannot be said to apply with the same degree of fidelity.

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As the future work, the measurement of the solubility of carbon dioxide in the ethylene glycol at each isotherm is recommended in order to obtain K-Values. Tentative K-Values are shown in Appendix A using calculated liquid phase compositions based on experimental solubility data. Furthermore, fundamental density measurements of the mixture, which will also be highly useful for industrial applications, are also recommended.

APPENDIX A

K-VALUE CALCULATION

K-Values were calculated from the volatility data using Mantor's[7] data for liquid phase carbon dioxide compositions measured at lower pressures and the thermodynamic properties of CO_2. Mantor correlated the data using the following expression:

$$\log \left(\frac{\overline{f}_{CO_2}}{x_{CO_2}} \right) = \log H + \frac{\overline{V}_{CO_2}(P - P_{E.G.})}{2.303\ RT} \qquad (1)$$

where $\overline{f}_{CO_2}$ = fugaciy of carbon dioxide in the vapor phase, assumed equal to $f^0_{CO_2}$, the fugacity of pure carbon dioxide

x_{CO_2} = mole fraction of carbon dioxide

H = Henry's law constant

$\overline{V}_{CO_2}$ = partial molar volume of CO_2 in the liquid phase

P = system pressure

$P^0_{E.G.}$ = vapor pressure of ethylene glycol

R = gas constant

T = absolute temperature of the system

The above equation is known as a Krichevsky-Kasarnovsky Equation[6]. Log H and $\overline{V}_{CO_2}$ were obtained at 78, 100, 160 and 220°F respectively. The constants obtained are tabulated in Table 16. Both constants were graphically interpolated at the temperature conditions in this study. The interpolated log H and $\overline{V}_{CO_2}$ are

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tabulated in Table 17. Since $\overline{V}_{CO_2}$ at 160°F was determined from only two experimental data, when it was plotted on a graph, it showed significant inconsistencies from the other isotherms. Therefore, the 160°F isotherm was ommitted from the interporation. Using the remaining constants, liquid phase carbon dioxide compositions were calculated from equation (1) and thus the liquid compositions of ethylene glycol were obtained by a systematic extrapolation of Mantor's data[7]. Calculated liquid compositions, and experimental vapor compositions of ethylene glycol at each isotherm are tabulated in Tables 18-21. Figure 10 shows the plotted πK-Value data where π is the system pressure.

APPENDIX B

CALIBRATION OF THE PLATINUM RESISTANCE THERMOMETER

A Leeds & Northrup 8167-25-B Platinum Resistance Thermometer was used as the primary temperature reference standard in this work. The PRT (Serial 1843602) was calibrated in May 1967 by Leeds & Northrup against their reference PRT which is calibrated at regular intervals by the National Bureau of Standards. Calibration points used were:

Triple point of Water

Tin point

Zinc point

Boiling point of oxygen

The resistance versus temperature data are fitted to the following equation by the International Practical Temperature Scale of 1968 (IPTS-68):

$$t = t' + 0.045 \left(\frac{t'}{100}\right)\left(\frac{t'}{100} - 1\right)\left(\frac{t'}{419.58} - 1\right)\left(\frac{t'}{630.74} - 1\right)$$

$$t' = \frac{1}{\alpha}\left[\frac{R(t')}{R(o)} - 1\right] + \delta\left(\frac{t'}{100}\right)\left(\frac{t'}{100} - 1\right)$$

where
t = temperature (°C)

R_t = resistance at temperature t

R_0 = resistance at 0°C

Values for the parameters supplied by Leeds & Northrup for the temperature range -183°C to 649°C were:

$$R_0 = 25.5160 \text{ ohms}$$

$$\alpha = 0.003925505$$

$$\delta = 1.496675$$

$$A_4 = -4.615 \times 10^{-7}$$

$$C_4 = 2.332 \times 10^{-14}$$

The Omega platinum resistance thermometer with a Keithley Model 192 Programmable DMM multimeter was calibrated against the Leeds & Northrup PRT.

The values obtained by calibration were:

$$R_0 = 499.913 \text{ ohms}$$

$$\alpha = 0.003846827$$

$$\delta = 1.604270$$

APPENDIX C

PURITY OF MATERIALS USED

Ethylene glycol used in this study was obtained from Fisher Scientific Company. The suppliers actual lot analysis data is listed below:

            Lot No.   730469
            Boiling Range   196.5-198.0°C
            Acidity (as CH_3COOH)   0.002%
            Water (H_2O)   0.2%
            Specific Gravity at 25°C/25°C   1.113
            Color (APHA)   5

Ethylene glycol was further dehydrated by DAVISON CHEMICALS 4 A effective pore size Molecular Sieves prior to use to effectively eliminate the water. The grade 4 carbon dioxide carrier gas was obtained from Airco Industrial Gases. The hydrogen zero gas and hydrocarbon free air were obtained from Union Carbide. The suppliers' purity analysis are given below:

            Grade 4 Carbon Dioxide   < 10 ppm hydrocarbon
            Hydrogen Zero Gas   < 0.5 ppm hydrocarbon
            Hydrocarbon Free Air   < 0.1 ppm hydrocarbon

APPENDIX D

DENSITY MEASUREMENT

The experimental apparatus is equipped with density measurement capabilities for liquid mixture which was not utilized in this study. The device consists of a VALCO Instrument Co. Model 26UW (Serial No. 000203) switching valve which holds up to 4000 psia at 100°C and 10 cc sampling loop. The sampling loop was prepared from 1/8 inch stainless steel tubing. A calibration of its volume is necessary to obtain the exact volume.

The density of the liquid mixture can be measured as follows by:

1) Evacuating the whole sampling line to be used.

2) Setting the switching valve to a sampling mode and introducing the liquid mixture to the sampling loop.

3) After the entire sampling loop is filled with liquid, switching the valve to the elution mode. Eluting the entire liquid out of the loop using Helium gas and measuring the weight of carbon dioxide and ethylene glycol, respectively by the method described in Appendix E.

Since the exact volume of the sample is known from the sampling loop calibration, and also exact weight of each component is obtained by gravimetric analysis, the density of the mixture can readily be calculated.

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APPENDIX E

COMPOSITION ANALYSIS BY GRAVIMETRIC METHOD

The experimental apparatus is equipped with compositional analysis capabilities by a gravimetric method in order to obtain the liquid composition and vapor/or fluid composition when the concentration is beyond the range of the calibrated flame ionization detector. This method, however, was not applied in this study since the objective of this study was to measure the volatility of ethylene glycol in sub- and super-critical carbon dioxide, and the volatility never exceeded the calibrated detector range for the experimental conditions studied.

This method was developed by Charoensombut-amon[12]. The device consists of a WHITEY SS22RS2 Micro Metering Valve, liquid sampling trap which was made of 1/4 inch Kovar tube sealed to a pyrex tube sealed on one end, and an Ascarite column for carbon dioxide absorption. The liquid mixture which is expanded from an operating pressure to an atmospheric pressure by a metering valve is vented for a period of time, bypassing the trap and absorbption tube in order to attain constant composition in the sampling line. The three-way switching valve is installed for this purpose. After the composition in the sampling line becomes constant, the liquid mixture is first introduced to the liquid trap where ethylene glycol is trapped while carbon dioxide is released from the top of the trap. Carbon dioxide is then absorbed by an Ascarite column. A rotameter is attached after the Ascarite column and no flow of gas should be detected,

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since the only gaseous component in the sampling line is carbon dioxide and it must be completely absorbed by the Ascarite column. The sample flow rate should be controlled by the metering valve in order not to detect any flow of carbon dioxide at the rotameter. Both trap and column are weighed prior to use. The amount of ethylene glycol and carbon dioxide in the sample can be obtained by weighing the trap and the column with samples and subtracting their empty weight. The composition can be calculated by dividing the measured weight by the molecular weight of each component.

TABLE 1 - MICROPUMP FLOW RATES FOR AVAILABLE GEAR SETTINGS (cc/min)

Flow Rate Is Determined by Settings of Decade Gear, Two Position Gear, and Norton Gear Positions Times Indicated Multiplier

Decade Gear Multiplier	A x 1.0		B x 0.1		C x 0.01		D x 0.001		E x 0.0001		F x 0.00001		G x 0.000001	
Two Position Gear	I	II	I	II	I	II	I	II	I	II	I	II	I	II
Norton Gear														
1	0.360	0.144	0.360	0.144	0.360	0.144	0.360	0.144	0.360	0.144	0.360	0.144	0.360	0.144
2	0.320	0.128	0.320	0.128	0.320	0.128	0.320	0.128	0.320	0.128	0.320	0.128	0.320	0.128
3	0.300	0.120	0.300	0.120	0.300	0.120	0.300	0.120	0.300	0.120	0.300	0.120	0.300	0.120
4	0.280	0.112	0.280	0.112	0.280	0.112	0.280	0.112	0.280	0.112	0.280	0.112	0.280	0.112
5	0.260	0.104	0.260	0.104	0.260	0.104	0.260	0.104	0.260	0.104	0.260	0.104	0.260	0.104
6	0.240	0.096	0.240	0.096	0.240	0.096	0.240	0.096	0.240	0.096	0.240	0.096	0.240	0.096
7	0.220	0.088	0.220	0.088	0.220	0.088	0.220	0.088	0.220	0.088	0.220	0.088	0.220	0.088
8	0.200	0.080	0.200	0.080	0.200	0.080	0.200	0.080	0.200	0.080	0.200	0.080	0.200	0.080
9	0.180	0.072	0.180	0.072	0.180	0.072	0.180	0.072	0.180	0.072	0.180	0.072	0.180	0.072
10	0.160	0.064	0.160	0.064	0.160	0.064	0.160	0.064	0.160	0.064	0.160	0.064	0.160	0.064
11	0.150	0.060	0.150	0.060	0.150	0.060	0.150	0.060	0.150	0.060	0.150	0.060	0.150	0.060
12	0.140	0.056	0.140	0.056	0.140	0.056	0.140	0.056	0.140	0.056	0.140	0.056	0.140	0.056
13	0.130	0.052	0.130	0.052	0.130	0.052	0.130	0.052	0.130	0.052	0.130	0.052	0.130	0.052
14	0.120	0.048	0.120	0.048	0.120	0.048	0.120	0.048	0.120	0.048	0.120	0.048	0.120	0.048
15	0.110	0.044	0.110	0.044	0.110	0.044	0.110	0.044	0.110	0.044	0.110	0.044	0.110	0.044
16	0.100	0.040	0.100	0.040	0.100	0.040	0.100	0.040	0.100	0.040	0.100	0.040	0.100	0.040

TABLE 2

AVAILABLE VOLUMETRIC FLOW RATES OF THE GAS METERING PUMP

Flow   Rate (cc/min)

	1	2	3	4	5	6	7	
	0.008	0.009	0.010	.0.11	0.012	0.013	0.014	A
	0.016	0.018	0.020	0.022	0.024	0.026	0.028	B
A	0.032	0.036	0.040	0.044	0.048	0.052	0.056	C
B	0.064	0.072	0.080	0.088	0.096	0.104	0.112	D
C	0.128	0.144	0.160	0.176	0.192	0.208	0.224	
D	0.256	0.288	0.320	0.352	0.384	0.416	0.448	

4:1 DRIVE   WORM SETTING

1:1 DRIVE   WORM SETTING

TABLE 3

ETHYLENE GLYCOL FID CALIBRATION DATA

A = 11.05949

B = 1.00357

F(Calc) (mol/min)	$\overline{V}$(Exp) (V)	F(Exp) (mol/min)	DIF (-)	DEV (%)
2.850×10^{-6}	4.882×10^{-11}	2.843×10^{-6}	7.0×10^{-9}	0.25
1.436×10^{-6}	2.465×10^{-11}	1.422×10^{-6}	1.4×10^{-8}	0.96
3.279×10^{-7}	5.660×10^{-12}	3.336×10^{-7}	-5.7×10^{-9}	-1.71
9.222×10^{-8}	1.599×10^{-12}	9.234×10^{-8}	-1.2×10^{-10}	-0.13
2.313×10^{-8}	4.030×10^{-13}	2.308×10^{-8}	5.0×10^{-11}	0.21
1.171×10^{-8}	2.046×10^{-13}	1.168×10^{-8}	3.0×10^{-11}	0.29
2.647×10^{-9}	4.648×10^{-14}	2.644×10^{-9}	3.0×10^{-12}	0.11

Absolute Average Deviation = 0.52%

Constants A and B refers to

$$Y = A + B \times X$$

where $Y = \ln F = \ln$ (molar flow rate)

$X = \ln V = \ln$ (detector signal voltage)

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TABLE 4

ETHYLENE GLYCOL VOLATILITY DATA AT 35°C

Pressure (psia)	Pressure (MPa)	Vapor Mole Fraction of Ethylene Glycol
400	2.76	3.34×10^{-5}
800	5.52	5.11×10^{-5}
1000	6.89	8.00×10^{-5}
1200	8.27	1.97×10^{-4}
1600	11.03	7.83×10^{-4}
2000	13.79	1.26×10^{-3}
2400	16.55	1.36×10^{-3}
2800	19.31	1.44×10^{-3}
3200	22.06	1.47×10^{-3}

TABLE 5

ETHYLENE GLYCOL VOLATILITY DATA AT 40°C

Pressure (psia)	Pressure (MPa)	Vapor Mole Fraction of Ethylene Glycol
400	2.76	4.22×10^{-5}
800	5.52	6.54×10^{-5}
1000	6.89	9.72×10^{-5}
1200	8.27	2.38×10^{-4}
1600	11.03	5.64×10^{-4}
2000	13.79	1.17×10^{-3}
2400	16.55	1.39×10^{-3}
2800	19.31	1.53×10^{-3}
3200	22.06	1.61×10^{-3}

TABLE 6

ETHYLENE GLYCOL VOLATILITY DATA AT 50°C

Pressure (psia)	Pressure (MPa)	Vapor Mole Fraction of Ethylene Glycol
400	2.76	7.22×10^{-5}
800	5.52	9.68×10^{-5}
1000	6.89	1.20×10^{-4}
1200	8.27	2.19×10^{-4}
1400	9.65	3.42×10^{-4}
1600	11.03	6.11×10^{-4}
2000	13.79	1.18×10^{-3}
2400	16.55	1.54×10^{-3}
2800	19.31	1.83×10^{-3}
3200	22.06	1.96×10^{-3}

TABLE 7

ETHYLENE GLYCOL VOLATILITY DATA AT 60°C

Pressure (psia)	Pressure (MPa)	Vapor Mole Fraction of Ethylene Glycol
400	2.76	1.18×10^{-4}
800	5.52	1.31×10^{-4}
1000	6.89	1.91×10^{-4}
1200	8.27	2.32×10^{-4}
1600	11.03	5.31×10^{-4}
2000	13.79	1.03×10^{-3}
2400	16.55	1.54×10^{-3}
2800	19.31	1.93×10^{-3}
3200	22.06	2.13×10^{-3}

TABLE 8

ENHANCEMENT FACTOR AT 35°C

Pressure (MPa)	E
2.76	3.766
5.52	11.522
6.89	22.516
8.27	66.550
11.03	352.788
13.79	709.759
16.55	919.418
19.31	1135.850
22.06	1324.644

TABLE 9

ENHANCEMENT FACTOR AT 40°C

Pressure (MPa)	E
2.76	3.086
5.52	9.564
6.89	17.742
8.27	52.143
11.03	164.805
13.79	427.432
16.55	609.438
19.31	782.692
22.06	940.911

TABLE 10

ENHANCEMENT FACTOR AT 50°C

Pressure (MPa)	E
2.76	2.345
5.52	6.288
6.89	9.729
8.27	21.313
9.65	38.837
11.03	79.306
13.79	191.485
16.55	299.921
19.31	415.835
22.06	508.803

TABLE 11

ENHANCEMENT FACTOR AT 60°C

Pressure (MPa)	E
2.76	1.817
5.52	4.035
6.89	7.344
8.27	10.707
11.03	32.684
13.79	79.262
16.55	142.227
19.31	207.971
22.06	262.209

TABLE 12

E.G. FUGACITY RATIO x E.G. ACTIVITY IN EQN. 6 <u>VS.</u> CO_2 DENSITY AT 35°C

Pressure (MPa)	ϕrat	CO_2 Density (g/cm³)
2.76	3.251	5.39×10^{-2}
5.52	9.346	1.36×10^{-1}
6.89	17.779	2.43×10^{-1}
8.27	50.970	4.79×10^{-1}
11.03	254.238	7.59×10^{-1}
13.79	480.579	8.17×10^{-1}
16.55	588.538	8.52×10^{-1}
19.31	682.756	8.69×10^{-1}
22.06	748.194	8.88×10^{-1}

TABLE 13

E.G. FUGACITY RATIO X E.G. ACTIVITY IN EQN. 6 <u>VS.</u> CO_2 DENSITY AT 40°C

Pressure (MPa)	ϕrat	CO_2 Density (g/cm^3)
2.76	2.728	5.30×10^{-2}
5.52	7.954	1.28×10^{-1}
6.89	14.400	1.92×10^{-1}
8.27	41.148	3.54×10^{-1}
11.06	122.468	6.66×10^{-1}
13.79	299.394	7.62×10^{-1}
16.55	402.290	8.14×10^{-1}
19.31	484.973	8.44×10^{-1}
22.06	549.437	8.66×10^{-1}

TABLE 14

E.G. FUGACITY RATIO X E.G. ACTIVITY IN EQN. 6 <u>VS.</u> CO_2 DENSITY AT 50°C

Pressure (MPa)	ϕrat	CO_2 Density (g/cm^3)
2.76	2.013	5.07×10^{-2}
5.52	5.092	1.17×10^{-1}
6.89	7.663	1.67×10^{-1}
8.27	16.300	2.32×10^{-1}
9.65	28.845	3.50×10^{-1}
11.03	57.202	4.81×10^{-1}
13.79	130.271	6.46×10^{-1}
16.55	192.215	7.35×10^{-1}
19.31	251.854	7.81×10^{-1}
22.06	290.220	8.12×10^{-1}

TABLE 15

E.G. FUGACITY RATIO X E.G. ACTIVITY IN EQN. 6 <u>VS.</u> CO_2 DENSITY AT 60°C

Pressure (MPa)	Φrat	CO_2 Density (g/cm^3)
2.76	1.716	4.82×10^{-2}
5.52	3.599	1.11×10^{-1}
6.89	6.374	1.50×10^{-1}
8.27	9.031	2.06×10^{-1}
11.03	23.438	3.53×10^{-1}
13.79	59.633	5.36×10^{-1}
16.55	101.074	6.54×10^{-1}
19.31	139.609	7.11×10^{-1}
22.06	166.347	7.51×10^{-1}

TABLE 16

CONSTANTS FOR USE IN THE KRICHEVSKY-KASARNOVSKY EQUATION

Temperature ($^\circ$F)	Temperature ($^\circ$C)	log H	$\overline{V}$ CO_2 (ft^3/lb. mole)
78	25.56	3.820	-1.21
100	37.78	3.928	-0.97
160	71.11	4.175	-1.50*
220	104.44	4.251	-0.72

*discarded

TABLE 17

INTERPOLATED CONSTANTS FOR USE IN THE KRICHEVSKY-KASARNOVSKY EQUATION

Temperature (°C)	log H	$\bar{V}$ CO_2 (ft^3/lb. mole)	$\bar{V}$ CO_2 ($ft.^3$/g. mole)
35	3.902	-1.02	-63.68
40	3.944	-0.94	-58.68
50	4.016	-0.85	-53.07
60	4.076	-0.78	-48.70

TABLE 18

EXPERIMENTAL VAPOR COMPOSITIONS AND CALCULATED LIQUID COMPOSITIONS OF ETHYLENE CLYCOL AT 35°C

Pressure (MPa)	$y_{E.G.}$(exp)	$x_{E.G.}$ (Calc)
2.76	3.44×10^{-5}	0.9529
5.52	5.11×10^{-5}	0.9126
6.89	8.00×10^{-5}	0.8959
8.27	1.97×10^{-4}	0.8831
11.03	7.83×10^{-4}	0.8663
13.79	1.26×10^{-3}	0.8478
16.55	1.36×10^{-3}	0.8271
19.31	1.44×10^{-3}	0.8044
22.06	1.47×10^{-3}	0.7801

TABLE 19

EXPERIMENTAL VAPOR COMPOSITIONS AND CALCULATED

LIQUID COMPOSITIONS OF ETHYLENE GLYCOL AT 40°C

Pressure (MPa)	$y_{E.G.}$ (Exp)	$x_{E.G.}$ (Calc)
2.76	4.22×10^{-5}	0.9572
5.52	6.54×10^{-5}	0.9204
6.89	9.72×10^{-5}	0.9046
8.27	2.38×10^{-4}	0.8918
11.03	5.64×10^{-4}	0.8731
13.79	1.17×10^{-3}	0.8564
16.55	1.39×10^{-3}	0.8385
19.31	1.53×10^{-3}	0.8183
22.06	1.61×10^{-3}	0.7958

TABLE 20

EXPERIMENTAL VAPOR COMPOSITIONS AND CALCULATED

LIQUID COMPOSITIONS OF ETHYLENE GLYCOL AT 50°C

Pressure (MPa)	$y_{E.G.}$ (Exp)	$x_{E.G.}$ (Calc)
2.76	7.22×10^{-5}	0.9635
5.52	9.68×10^{-5}	0.9316
6.89	1.20×10^{-4}	0.9174
8.27	2.19×10^{-4}	0.9049
9.65	3.42×10^{-4}	0.8942
11.03	6.11×10^{-4}	0.8849
13.79	1.18×10^{-3}	0.8685
16.55	1.54×10^{-3}	0.8531
19.31	1.83×10^{-3}	0.8352
22.06	1.96×10^{-3}	0.8155

TABLE 21

EXPERIMENTAL VAPOR COMPOSITIONS AND CALCULATED

LIQUID COMPOSITIONS OF ETHYLENE GLYCOL AT 60°C

Pressure (MPa)	$y_{E.G.}$ (Exp)	$x_{E.G.}$ (Calc)
2.76	1.18×10^{-4}	0.9680
5.52	1.31×10^{-4}	0.9396
6.89	1.91×10^{-4}	0.9268
8.27	2.32×10^{-4}	0.9149
11.03	5.31×10^{-4}	0.8947
13.79	1.03×10^{-3}	0.8784
16.55	1.54×10^{-3}	0.8628
19.31	1.93×10^{-3}	0.8468
22.06	2.13×10^{-3}	0.8291

TABLE 22

K-VALUES AT 35°C

Pressure	K (E.G.)	πK (E.G.)	K (CO_2)	πK (CO_2)
2.76	3.505×10^{-5}	9.674×10^{-5}	21.231	58.596
5.52	5.599×10^{-5}	3.091×10^{-4}	11.441	63.155
6.89	8.930×10^{-5}	6.153×10^{-4}	9.605	66.175
8.27	2.231×10^{-4}	1.845×10^{-3}	8.553	70.733
11.03	9.038×10^{-4}	9.969×10^{-3}	7.474	82.434
13.79	1.486×10^{-3}	2.049×10^{-2}	6.562	90.490
16.55	1.644×10^{-3}	2.721×10^{-2}	5.776	95.590
19.31	1.790×10^{-3}	3.457×10^{-2}	5.105	98.580
22.06	1.884×10^{-3}	4.157×10^{-2}	4.541	100.171

TABLE 23

K-VALUES AT 40°C

Pressure (MPa)	K(E.G.)	πK (E.G.)	K (CO_2)	πK (CO_2)
2.76	4.338×10^{-5}	1.211×10^{-4}	23.363	64.482
5.52	7.106×10^{-5}	3.922×10^{-4}	12.562	69.342
6.89	1.075×10^{-4}	7.403×10^{-4}	10.481	72.215
8.27	2.669×10^{-4}	2.207×10^{-3}	9.240	76.414
11.03	6.460×10^{-4}	7.125×10^{-3}	7.876	86.870
13.79	1.366×10^{-3}	1.884×10^{-2}	6.956	95.918
16.55	1.658×10^{-3}	2.744×10^{-2}	6.183	102.334
19.31	1.870×10^{-3}	3.610×10^{-2}	5.495	106.111
22.06	2.023×10^{-3}	4.463×10^{-2}	4.889	107.857

TABLE 24

K-VALUES AT 50°C

Pressure (MPa)	K (E.G.)	πK (E.G.)	K (CO_2)	πK (CO_2)
2.76	7.494×10^{-5}	2.068×10^{-4}	27.395	75.610
5.52	1.039×10^{-4}	5.735×10^{-4}	14.618	80.691
6.89	1.308×10^{-4}	9.012×10^{-4}	12.105	83.404
8.27	2.420×10^{-4}	2.001×10^{-3}	10.513	86.945
9.65	3.825×10^{-4}	3.691×10^{-3}	9.449	91.179
11.03	6.905×10^{-4}	7.616×10^{-3}	8.683	95.771
13.79	1.359×10^{-3}	1.874×10^{-2}	7.596	104.743
16.55	1.805×10^{-3}	2.988×10^{-2}	6.797	112.488
19.31	2.191×10^{-3}	4.231×10^{-2}	6.057	116.958
22.06	2.403×10^{-3}	5.302×10^{-2}	5.409	119.332

TABLE 25

K-VALUES AT 60°C

Pressure	K (E.G.)	πK (E.G.)	K (CO_2)	πK (CO_2)
2.76	1.219×10^{-4}	3.364×10^{-4}	31.246	86.239
5.52	1.394×10^{-4}	7.695×10^{-4}	16.554	91.378
6.89	2.061×10^{-4}	1.420×10^{-3}	13.659	94.111
8.27	2.536×10^{-4}	2.097×10^{-3}	11.748	97.156
11.03	5.940×10^{-4}	6.552×10^{-3}	9.492	104.697
13.79	1.173×10^{-3}	1.618×10^{-2}	8.215	113.849
16.55	1.785×10^{-3}	2.954×10^{-2}	7.277	120.434
19.31	2.279×10^{-3}	4.401×10^{-2}	6.515	125.805
22.06	2.569×10^{-3}	5.667×10^{-2}	5.839	128.808

1. Pump
2. Constant Temp. Enclosure
3. Mercury Contact Thermometer
4. Relay
5. Incandescent Lamp
6. Blower
7. Charging Vessel
8. Precision Thermometer
9. Pressure Transducer
10. Synchronous Motor
11. Transmission
12. Motor Reversing Switch
13. Variable Voltage Control
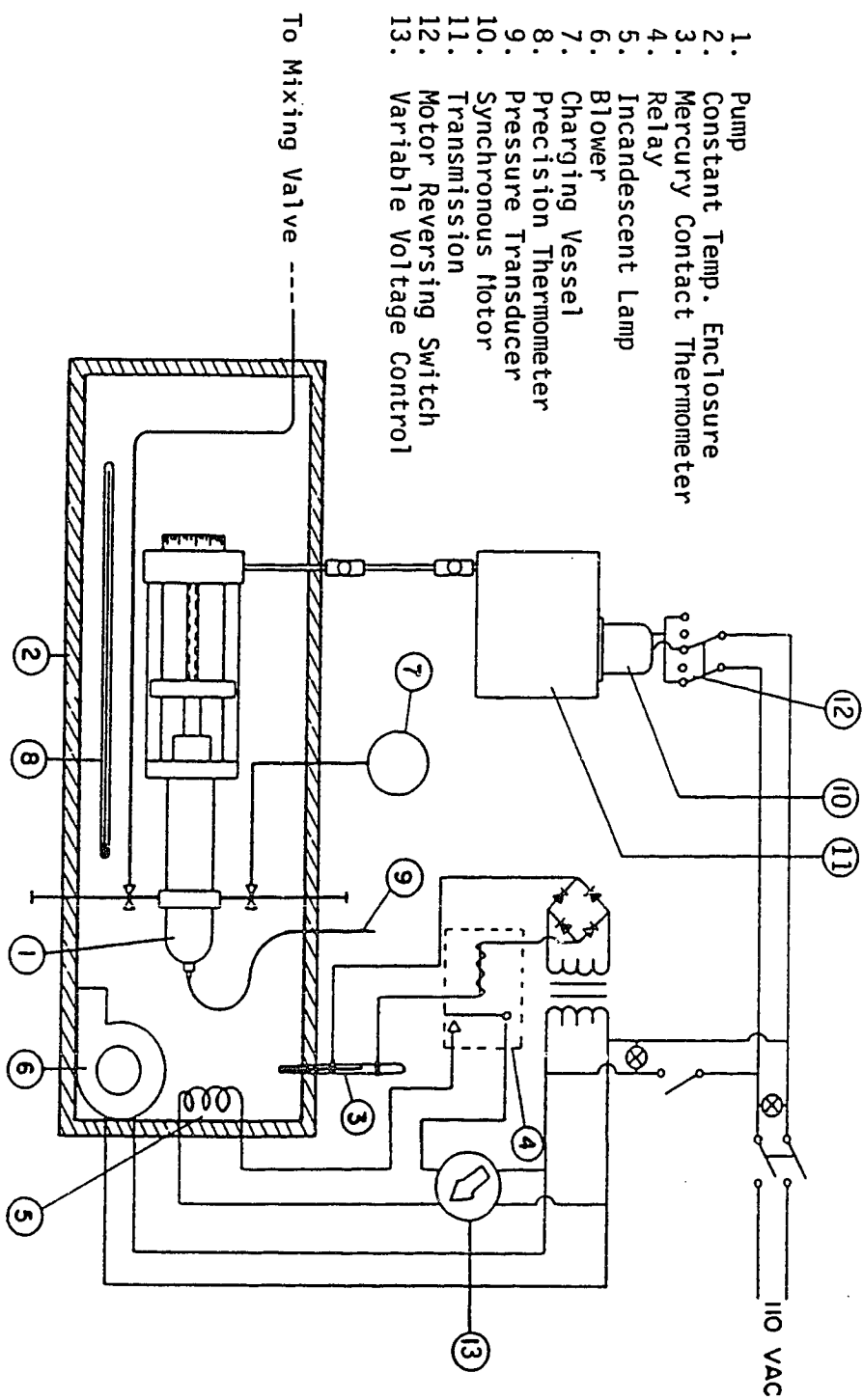
To Mixing Valve ----

FIGURE 1   MICROPUMP AND AUXILIARY EQUIPMENT FOR CALIBRATION OF DETECTOR

110 VAC

CO$_2$

ETHYLENE GLYCOL
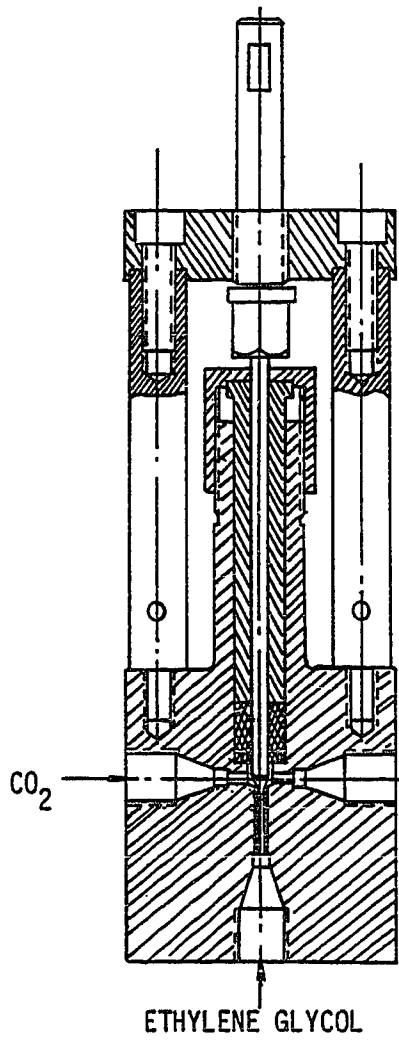
FIGURE 2   MIXING VALVE

FIGURE 3   SCHEMATIC DIAGRAM OF THE APPARATUS FOR FID CALIBRATION

NOTE: TS = TEMPERATURE SENSOR
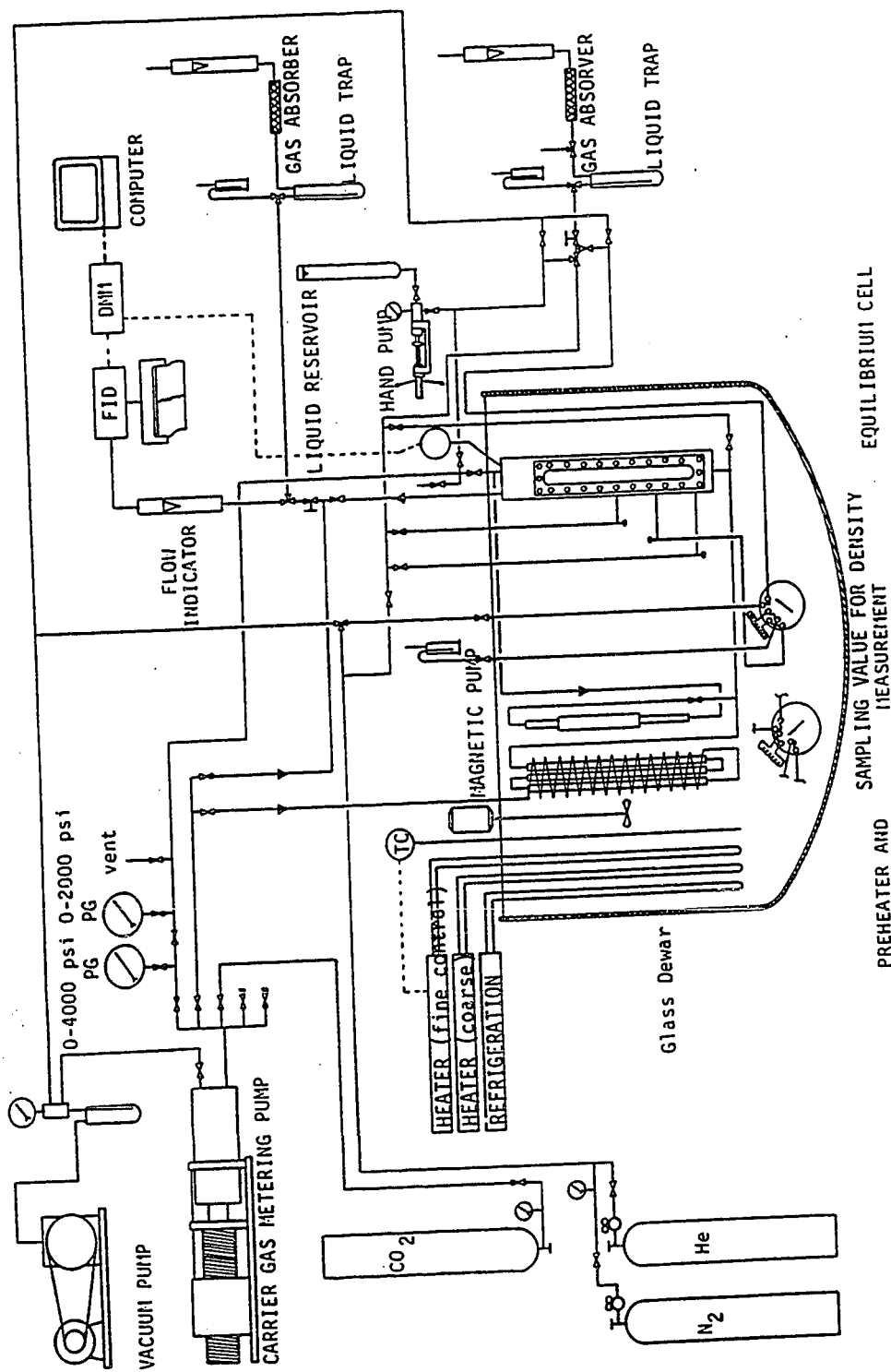
FIGURE 4   SCHEMATIC DIAGRAM OF THE APPARATUS FOR VOLATILITY MEASUREMENT
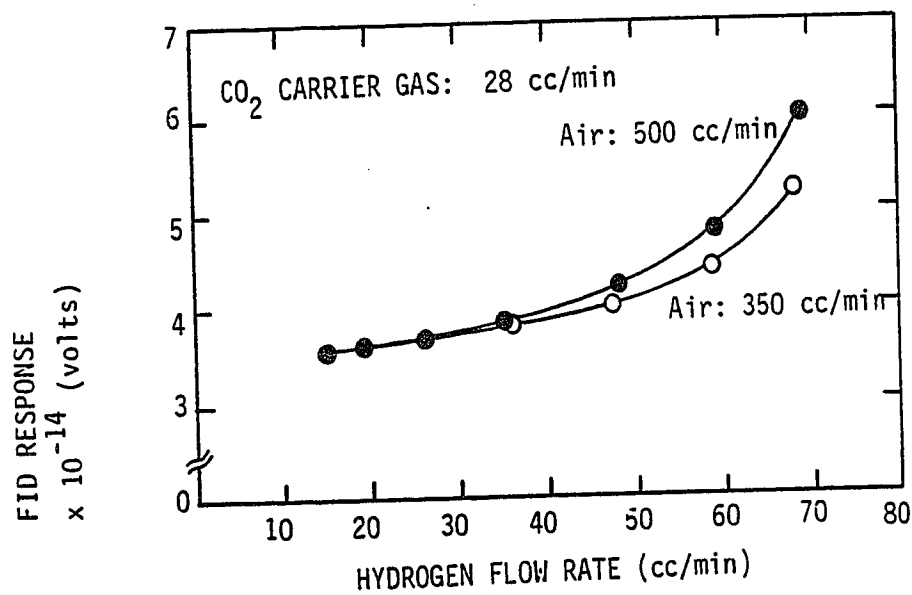
FIGURE 5a   OPTIMIZATION OF HYDROGEN FLOW RATE
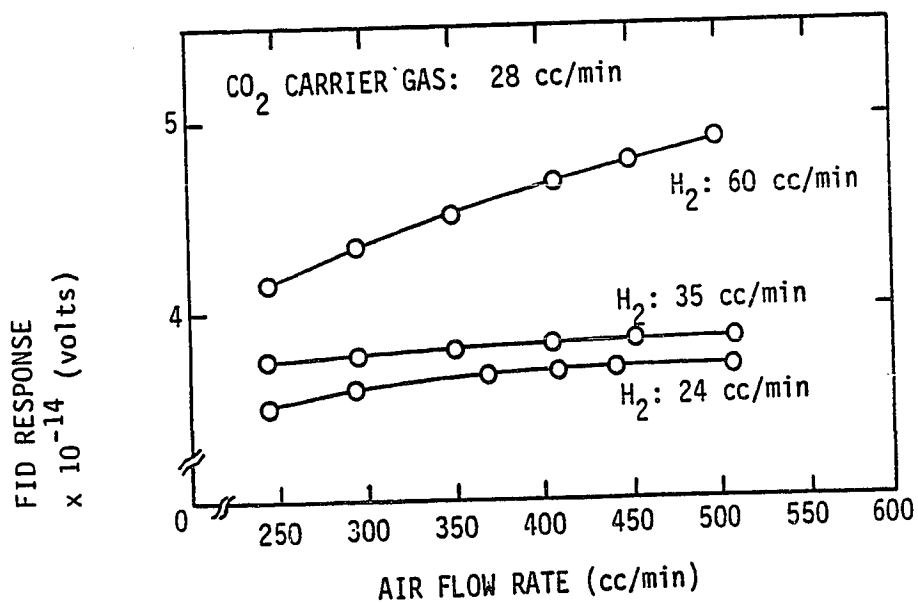
FIGURE 5b   OPTIMIZATION OF AIR FLOW RATE
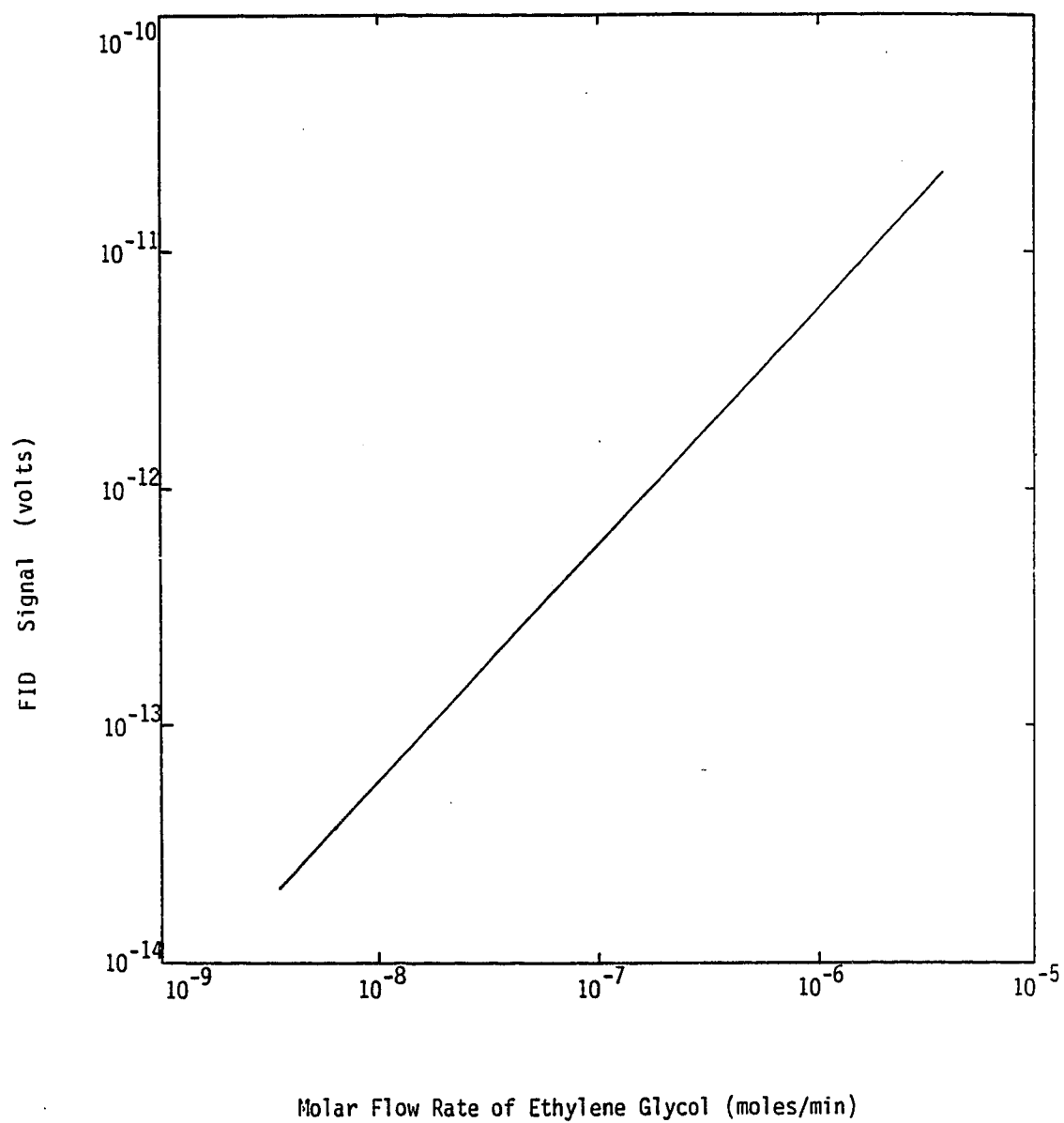
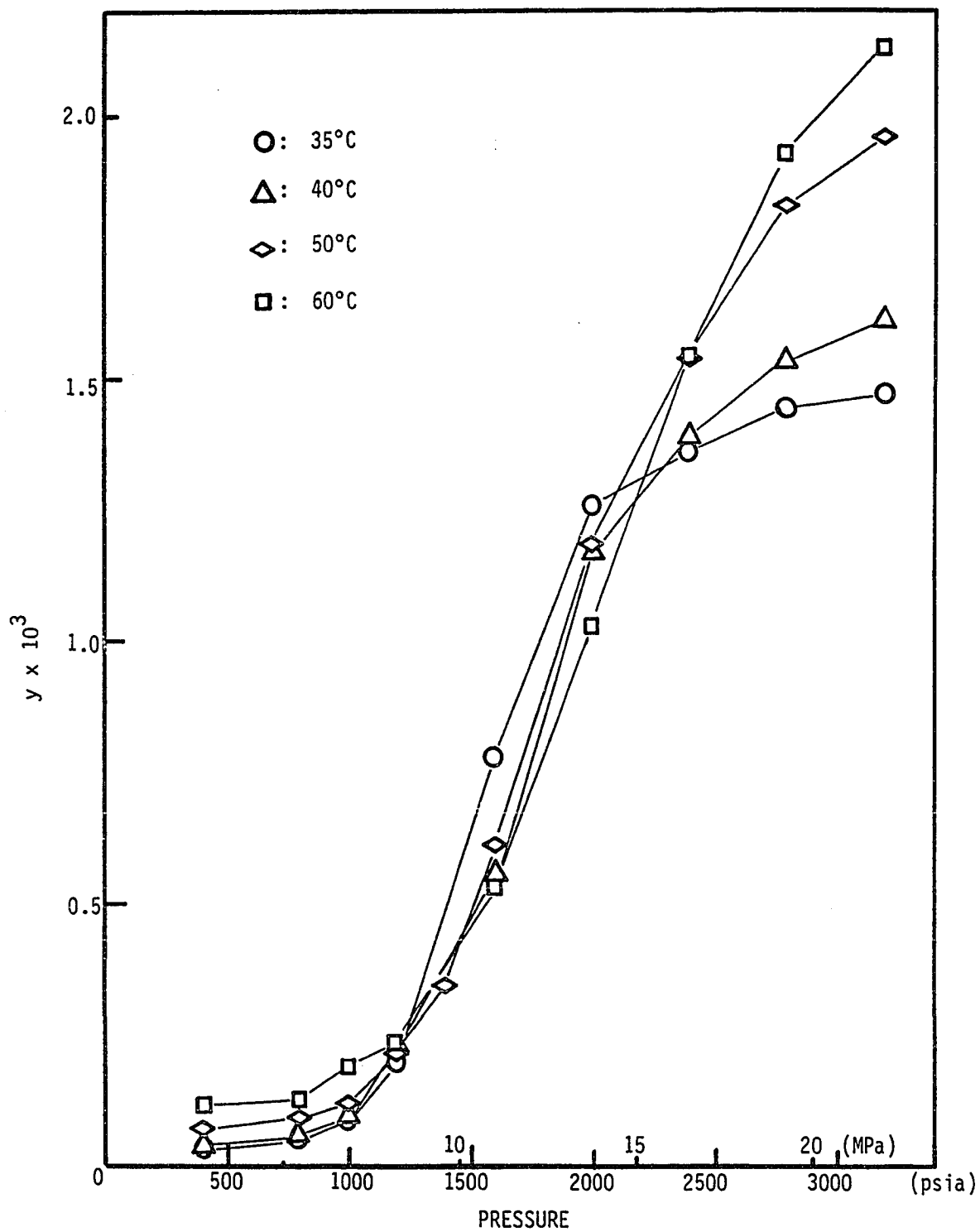FIGURE 6   CALIBRATION CURVES FOR FLAME IONIZATION DETECTOR

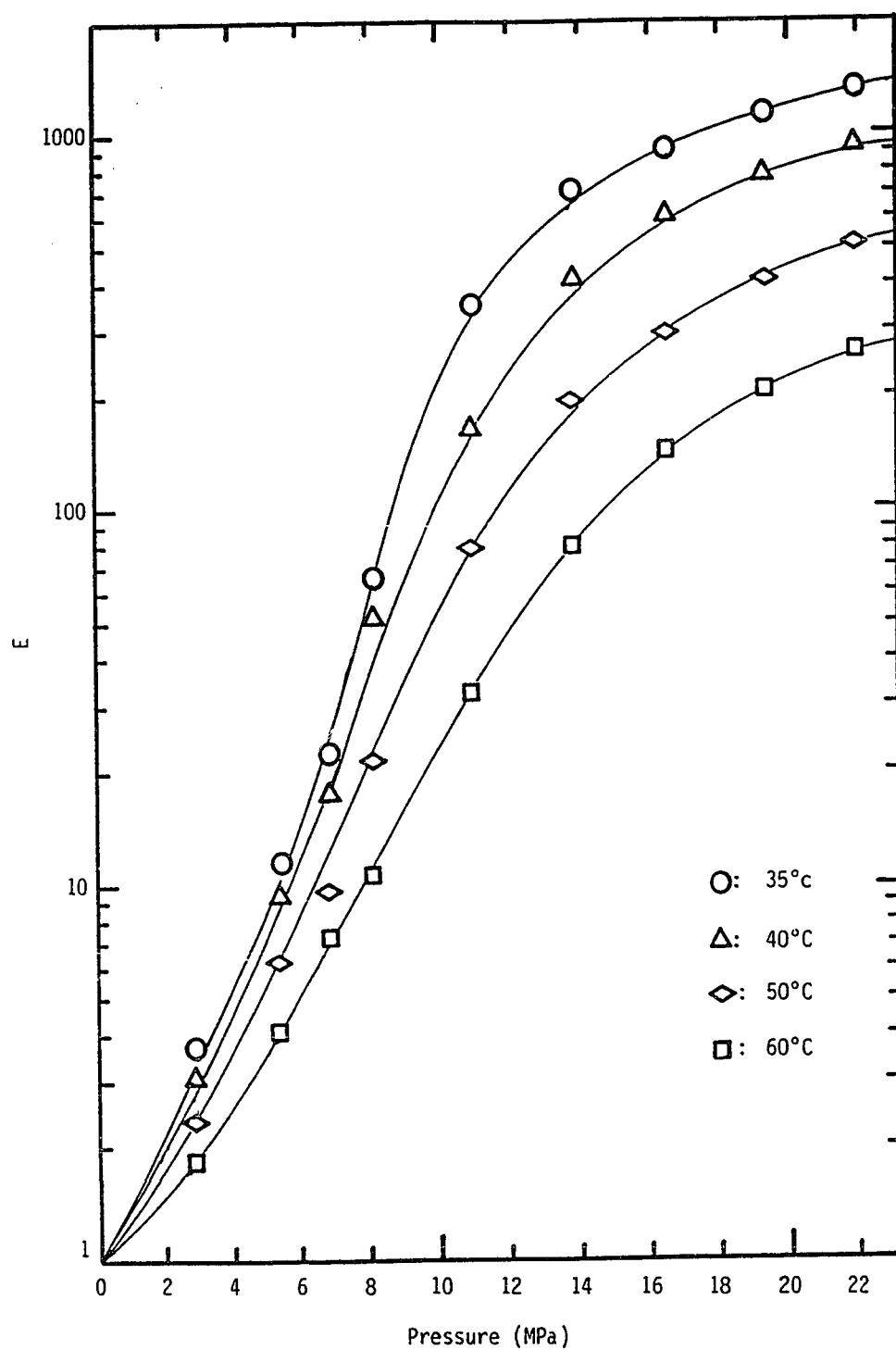FIGURE 7.   ETHYLENE GLYCOL CONCENTRATION <u>VS.</u> PRESSURE AT 35, 40, 50 and 60°C

FIGURE 8   ENHANCEMENT OF THE CONCENTRATION OF ETHYLENE GLYCOL AT
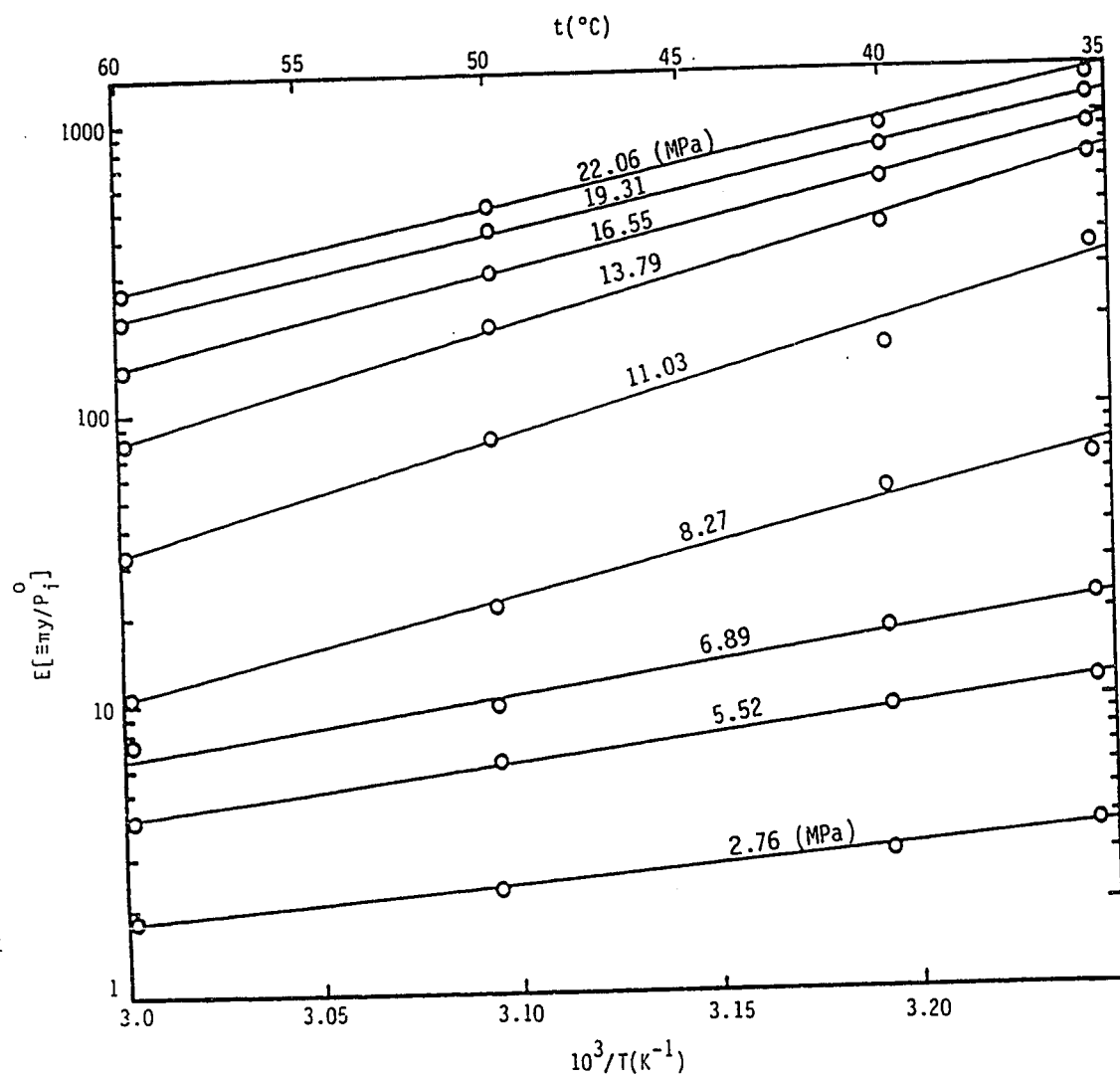35, 40, 50 and 60°C

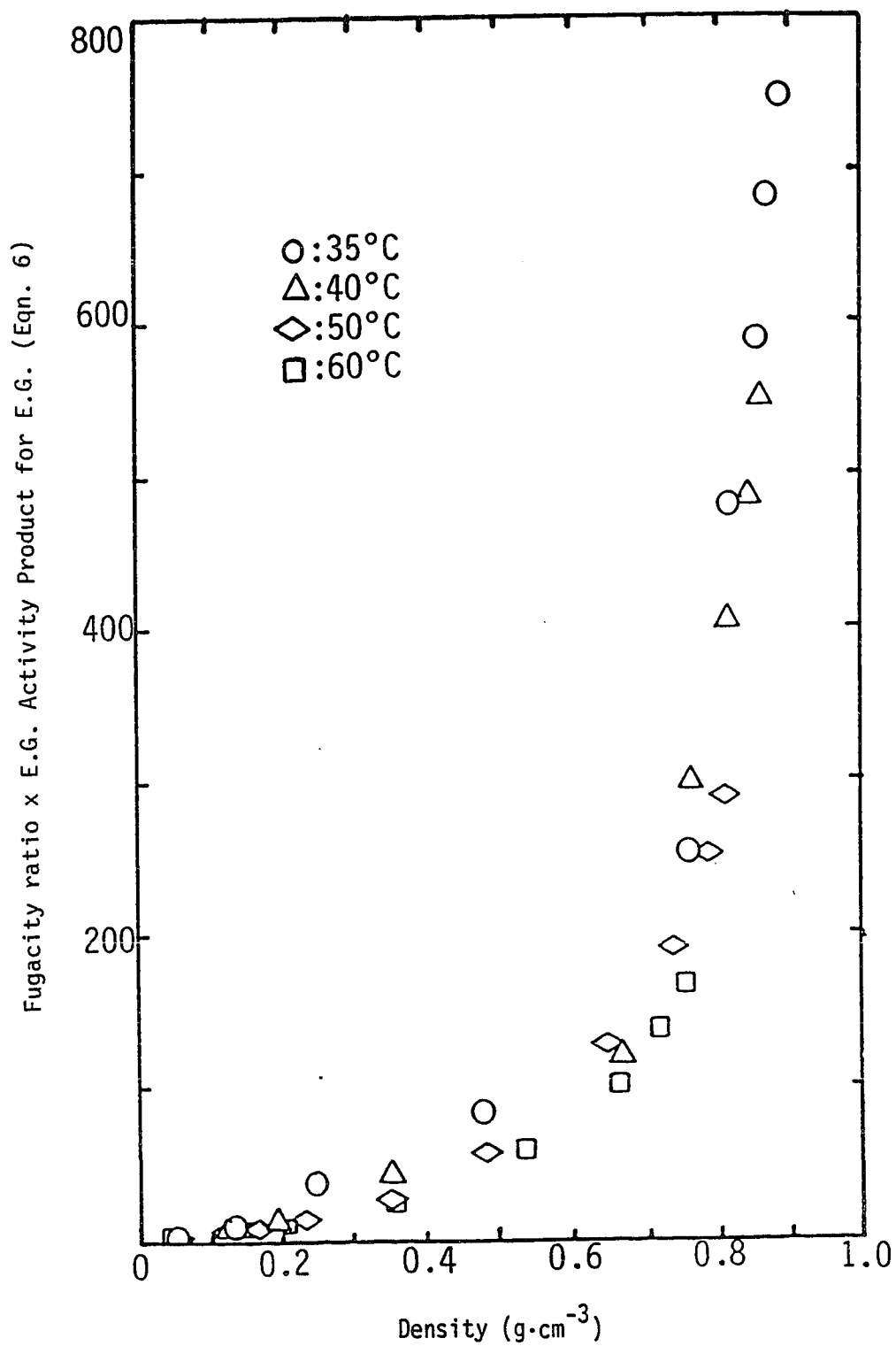FIGURE 9   ENHANCEMENT FACTOR VS. TEMPERATURE ALONG ISOBARS

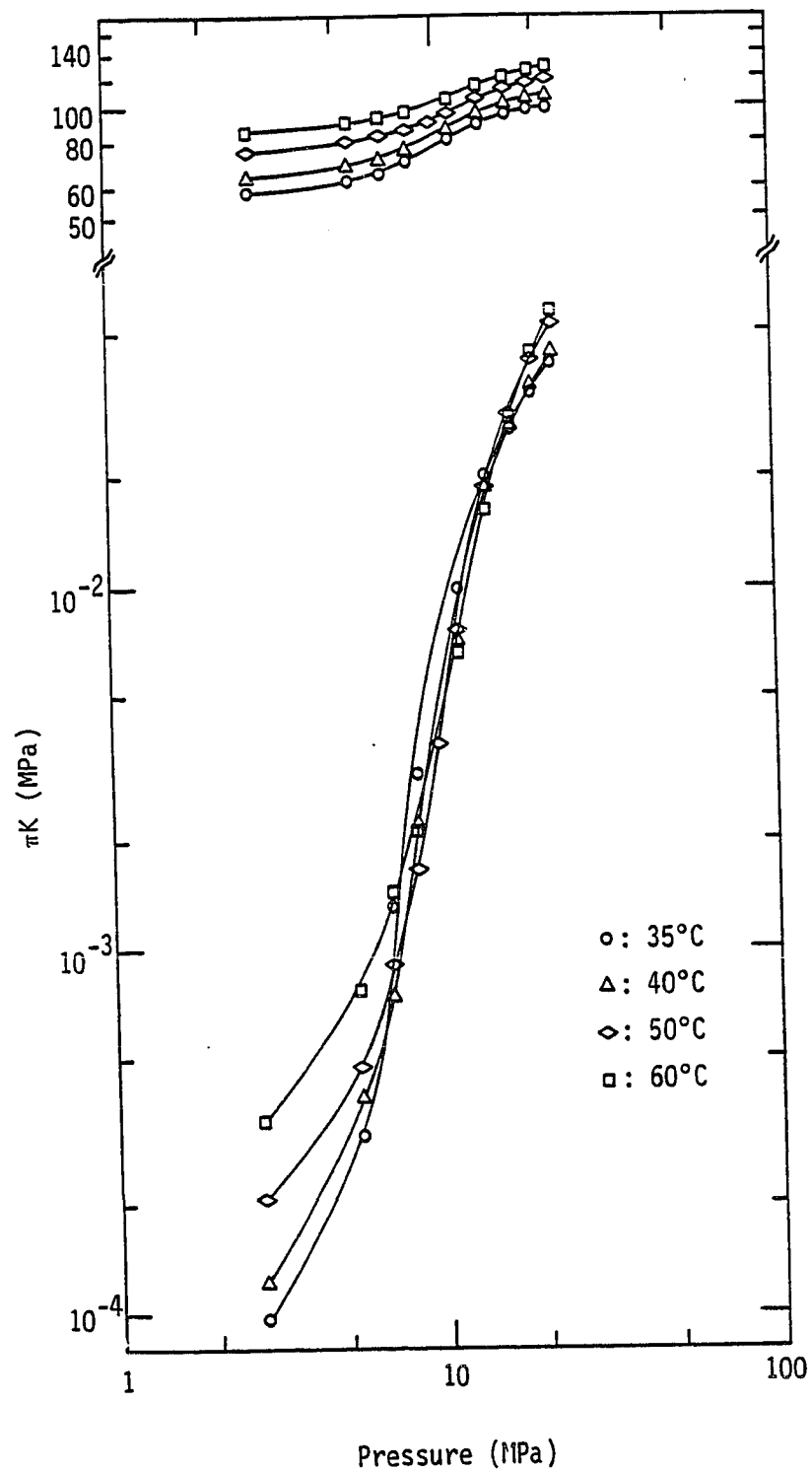FIGURE 10   CALIBRATION CONSTANT VS. CARBON DIOXIDE DENSITY

FIGURE 11   πK-VALUES AT 35, 40, 50 and 60°C

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