4.0 RESULTS AND DISCUSSION

4.1 Nitrogen Dioxide and Methanol Sysytem

The $NO_2$and Methanol system was conducted to gain the confidence in using the experimental apparatus. Comparing the activity coefficient at infinite dilution between Mohamed's study and the present work, one finds a value of 15.5 for activity ceofficient at infinite dilution at temperature 28°C in Mohamed's work and a value of 12.8 at temperature 26°C was found in present work. The comparsion between the two values can be seen clearly in Figure 5.

This agreement was felt adequate to proceed with other systems.

4.2 Equilibrium Within the Column

The calculation of activity coefficients and Henry's constants based on the chromatography measurements are derived from the equations:

$$\phi \cdot Y \cdot P_t = X \cdot \gamma \cdot P^S \qquad (4-1)$$

$$Y \cdot P_t = X \cdot H \qquad (4-2)$$

where ϕ = fugacity coefficient

Y = mole fraction of solute in vapor phase

P_t = total pressure of system

X = mole fraction of solute in liquid phase

γ = activity coefficient

P^S = vapor pressure of solute at that temperature

H = Henry's law constnat

These equations are valid under equilibrium condition. This means that the experimental measurements can only be meaningful when the equilibrium condition is established within the column.

Sulfur dioxide, since it can be easily absorbed, is believed to reach equilibrium condition before it exits the 8-ft column, but for the nitric oxide, equilibrium can only be established at the low carrier gas flow rate. Therefore, to find out if reaches equilibrium, the flow rate was decreased until the net retention volume did not increase further.[16] A plot of net retention volume versus reciprocal of flow rate of the system NO and triethylenetetramine is show on Figure 6. An asymptotic value is approached as flow rate decreases. Once a flow rate is low enough to have equilibrium at one temperature, the same flow rate is applied for higher temperature, because at the higher temperature, the equilibrium condition are established easier.

4.3 Physical and Chemical Absorption

The solvents found to absorb SO_2 or NO are believed to be physical absorbed simply because the second peak (the peak for SO_2 or NO) were detected. This means NO or SO_2 gave evidence of being delayed and released in the column. It was also assumed that the acid gases were released completely or the gases remaining in the liquid were in such small quantity that they did not affect the result of other samples of mixture gases which were injected afterwords. The activity coefficients or the Henry's constants therefore were determined in such a way that for each liquid loading, several temperatures were explored. For each temperature a variety of flow rates were carried out.

One of the solvent tested in this work, 2-amino-2-methyl-1-propanol, was found to react chemically with SO_2.

A mixture of 0.1 cc air and 0.1 cc SO_2 was first injected into the column, and under the same conditions (same flow rate and temperature) another mixture of 0.1 cc air and 0.3 cc SO_2 was also injected. The area of the peaks, which are related to the number of moles of gas come out, were found to be equal in both cases, and no indication was noted of the second peak. This means only the non-absorbed gas, air, is released. The same phenomena was observed at higher temperatures. Even when the temperature reached 100°C which caused the solvent to vaporize, SO_2 was still being absorbed by the liquid. Intiutively, a gas should not be physically absorbed by a liquid while the liquid itself is vaporizing.

An experiment was carried out outside the chromatograph which gave other envidence of a chemical reaction. When SO_2 was passed through this solvent, a white precipitate formed, and this precipitate was found to have a higher melting point than the orginial solvent.

4.4 Chromatography Results

The Henry's law constants of NO and the activity coefficients at infinite dilution of SO_2 in each solvent were determined for several different temperatures at each particular liquid loading in the column.*

There were at least three different liquid loadings tested in order to find the true Henry's law constants and the true activity coefficient at infinite dilution cases. Figure 7 to Figure 12 show the Henry's law constants as well as the activity coefficient at infinite dilution at different loadings for each solvent.

These figures all show an asymptotic value (the true infinite dilution values) is approached as the liquid loading increases. Both the Henry's law constants and activity coefficients of SO_2 reached the infinite dilution at 45%, 40% and 10% of loading in solvent triethylenetetramine, diethylenetriamine and N-cyclohexane-2-pyrroldine respectively.

It is worth mentioning that, from Figure 7 that the true Henry's law constant is reached earlier (i,e, at smaller liquid loading) at higher temperatures than at lower temperatures.

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*Liquid loading = $\frac{\text{weight of liquid in the column}}{\text{weight of column packing}}$

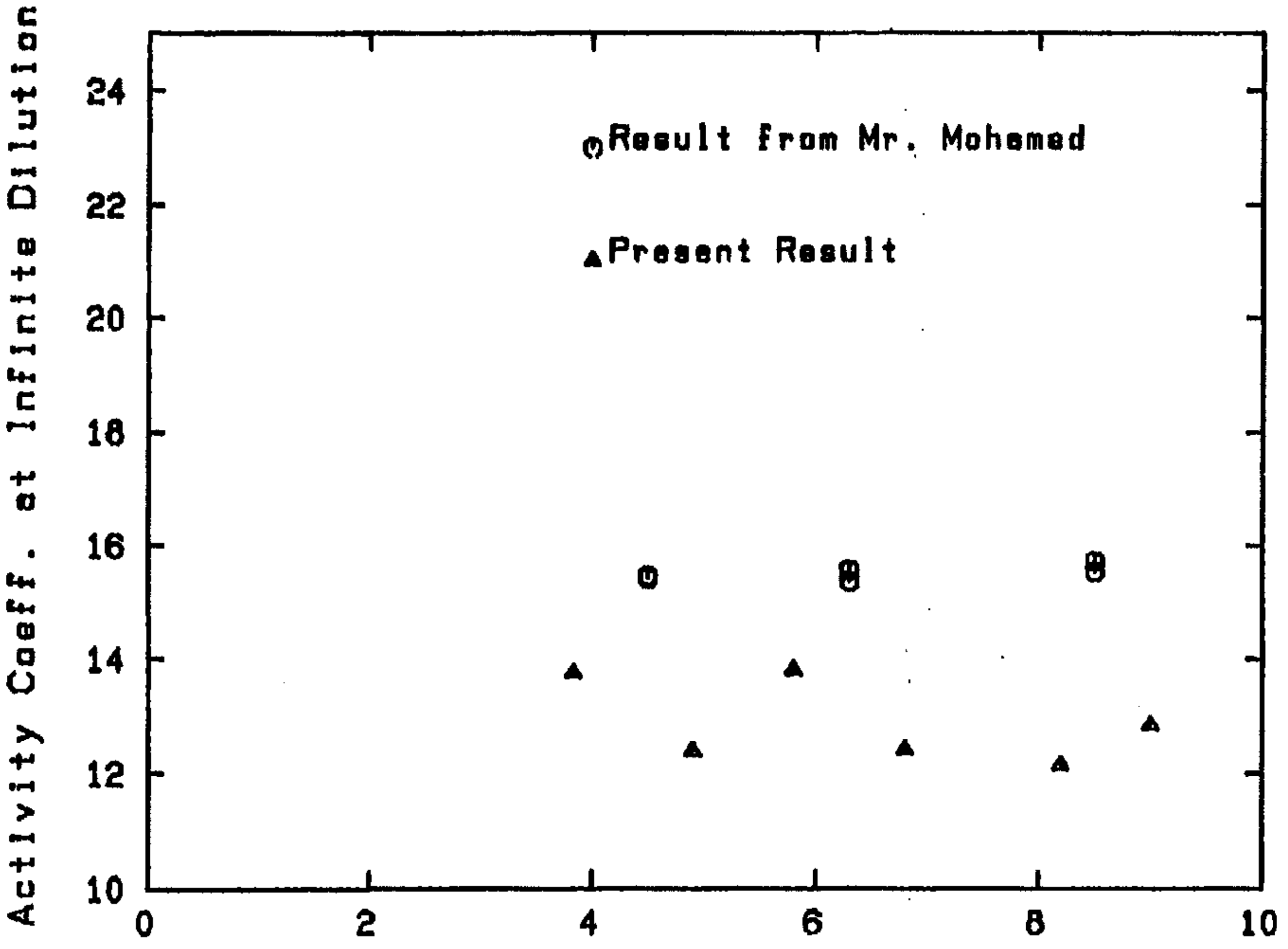

Fig. 5 Act Coeff Inf Dilut of NO2 In MEOH

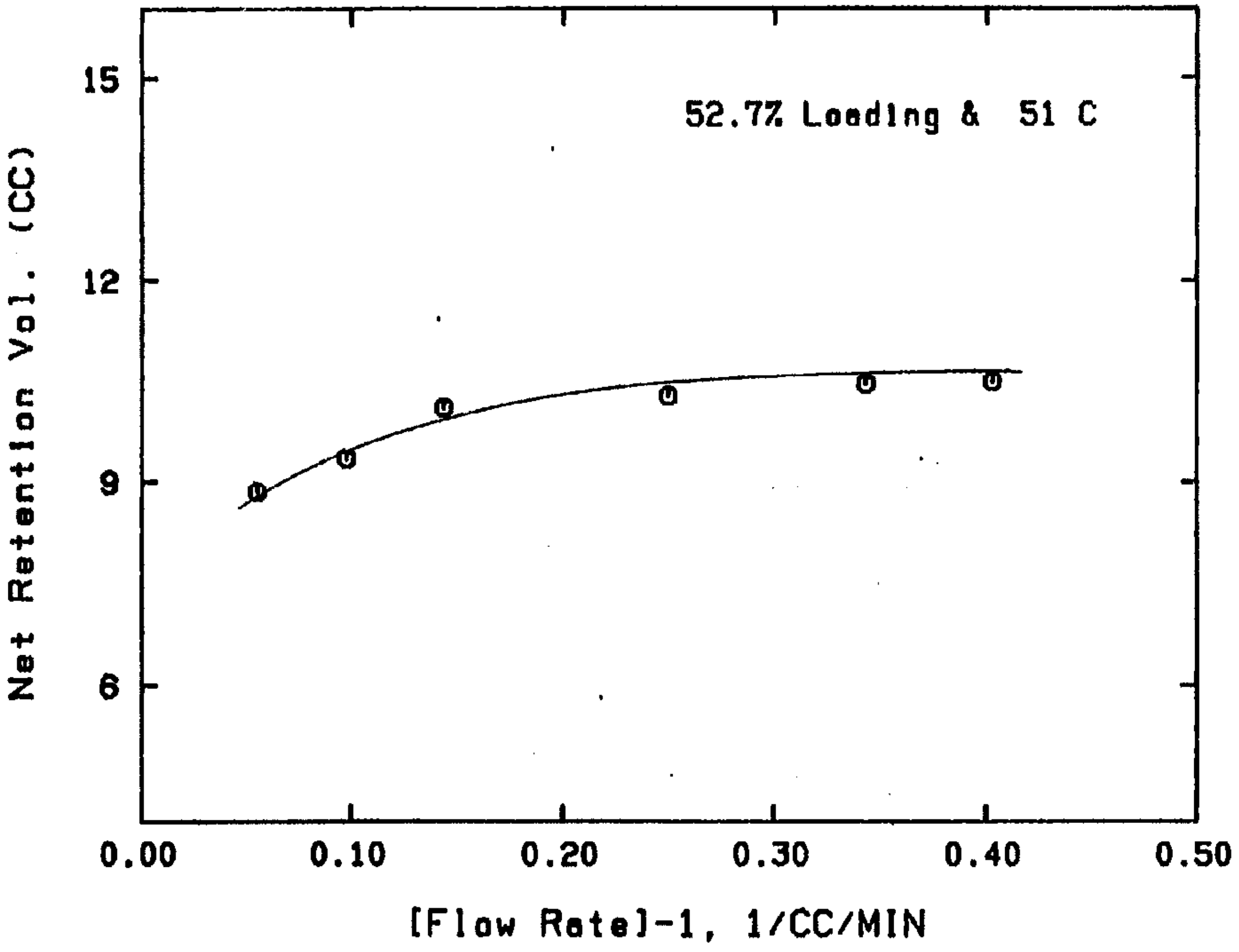

Fig. 6 Net Retention Vol. of NO Over TETA

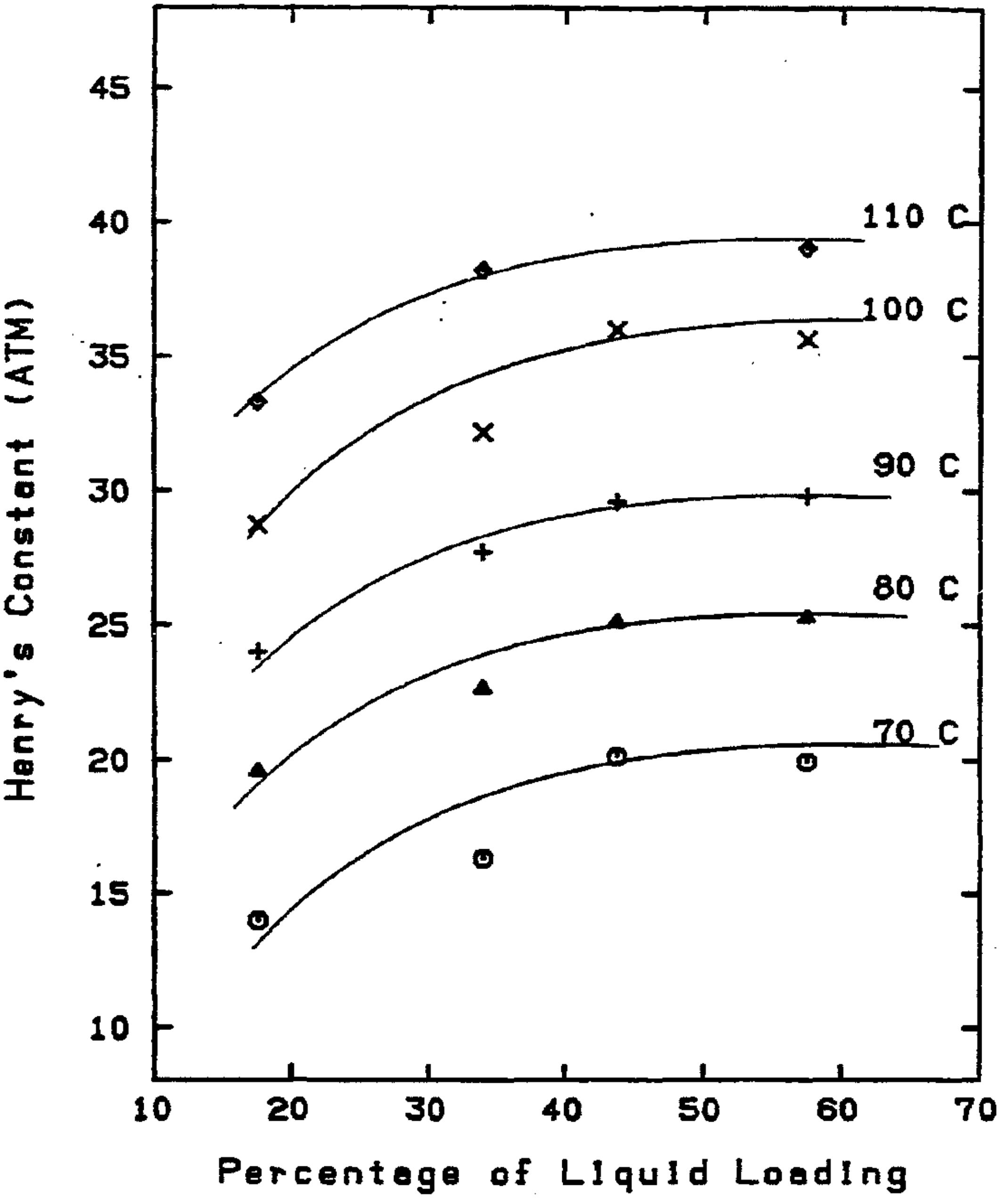

Fig. 7 Henry's Constants of SO2 in TETA

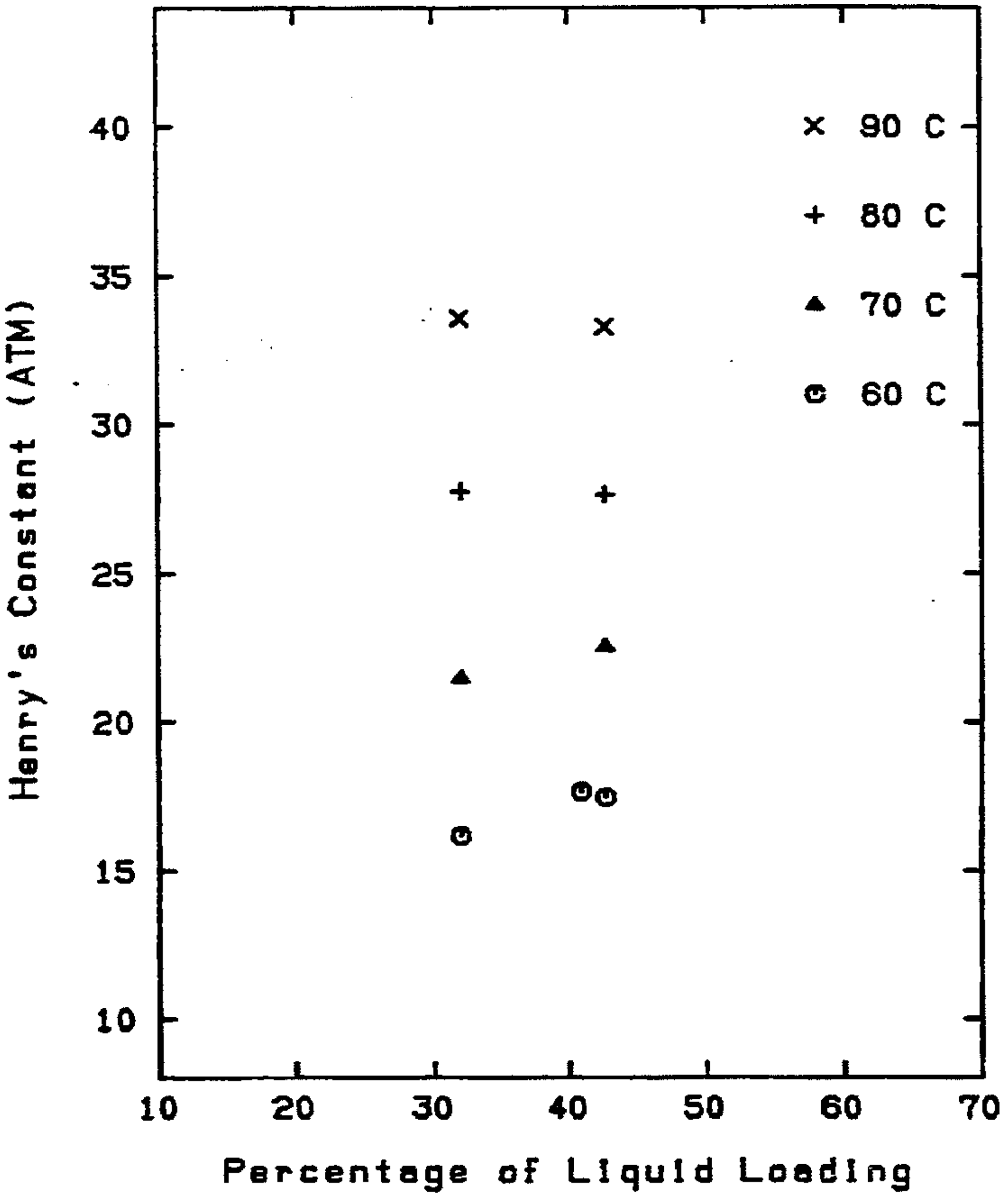

Fig. 8 Henry's Constants of SO2 In DETA

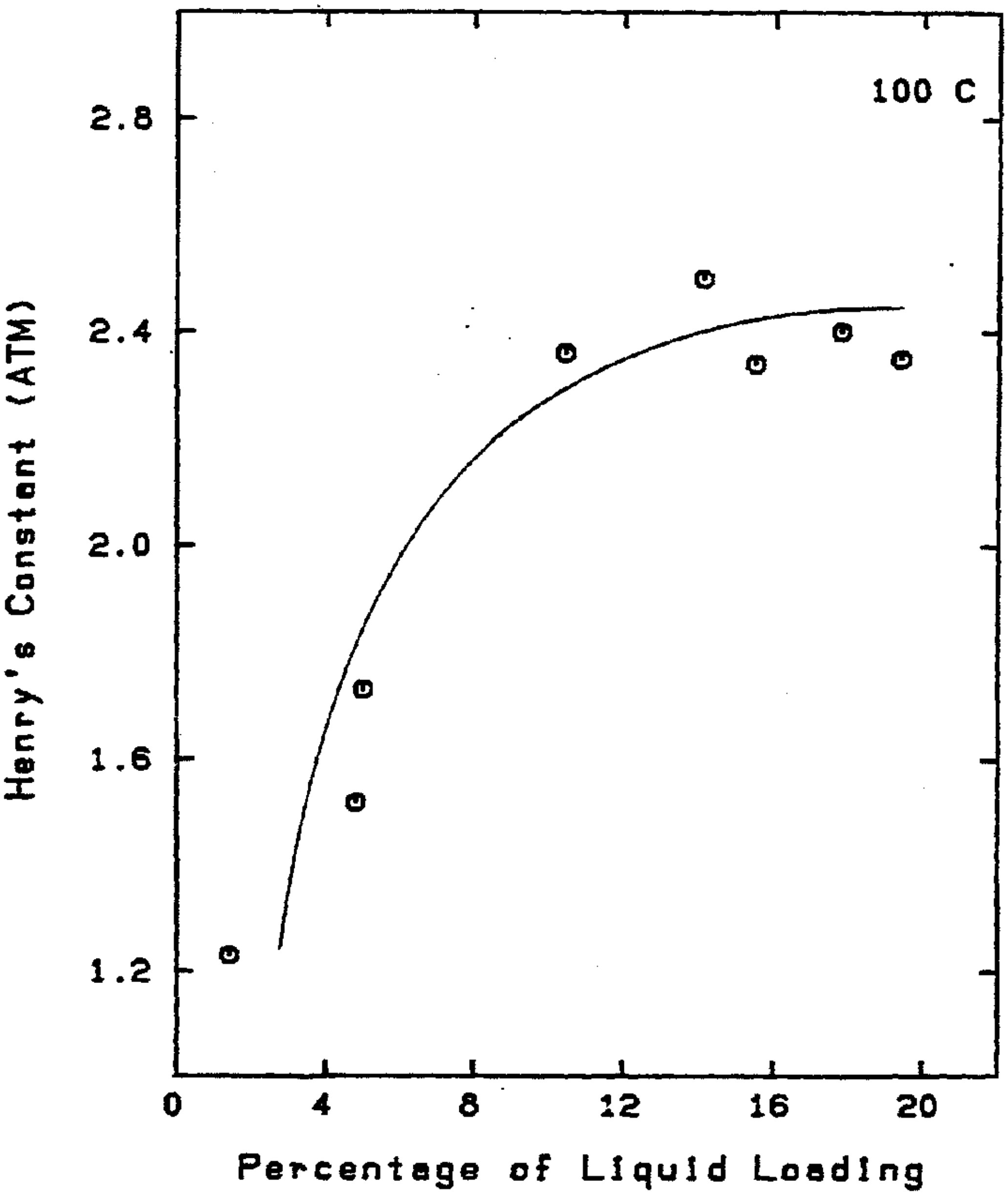

Fig. 9 Henry's Constants of SO2 in CHP

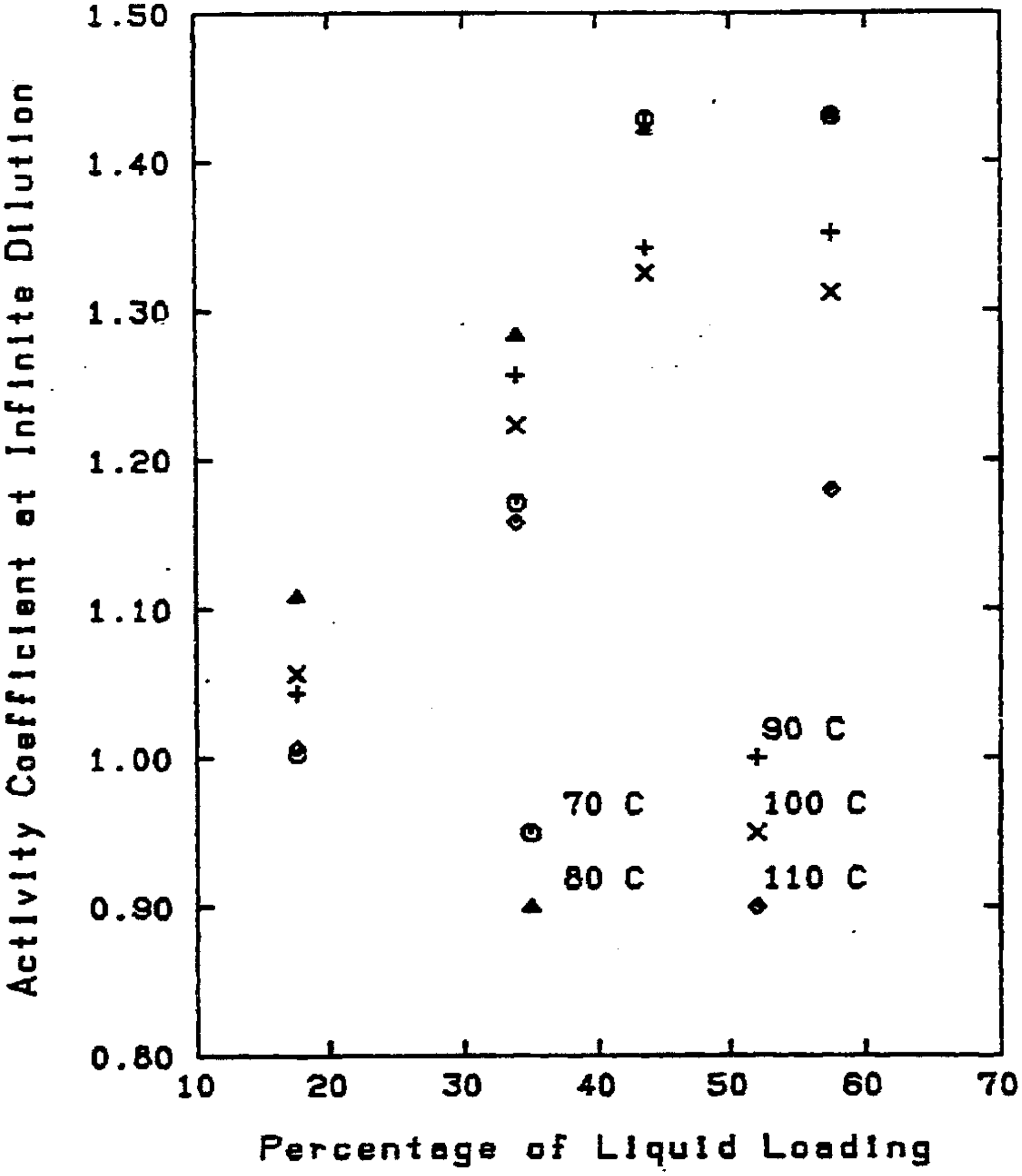

Fig. 10 Activity Coeff. of SO2 in TETA

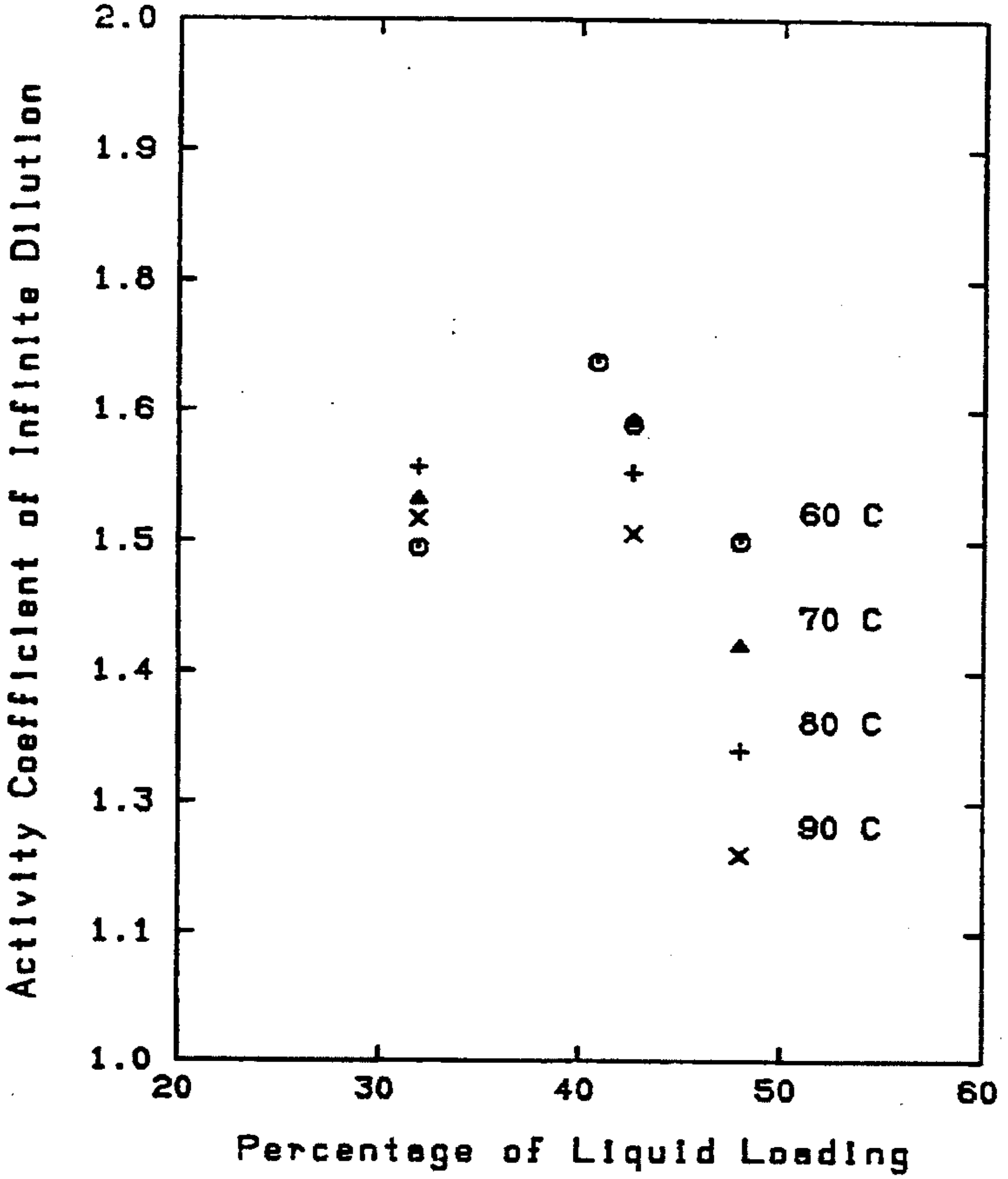

Fig. 11 Activity Coeff. of SO2 in DETA

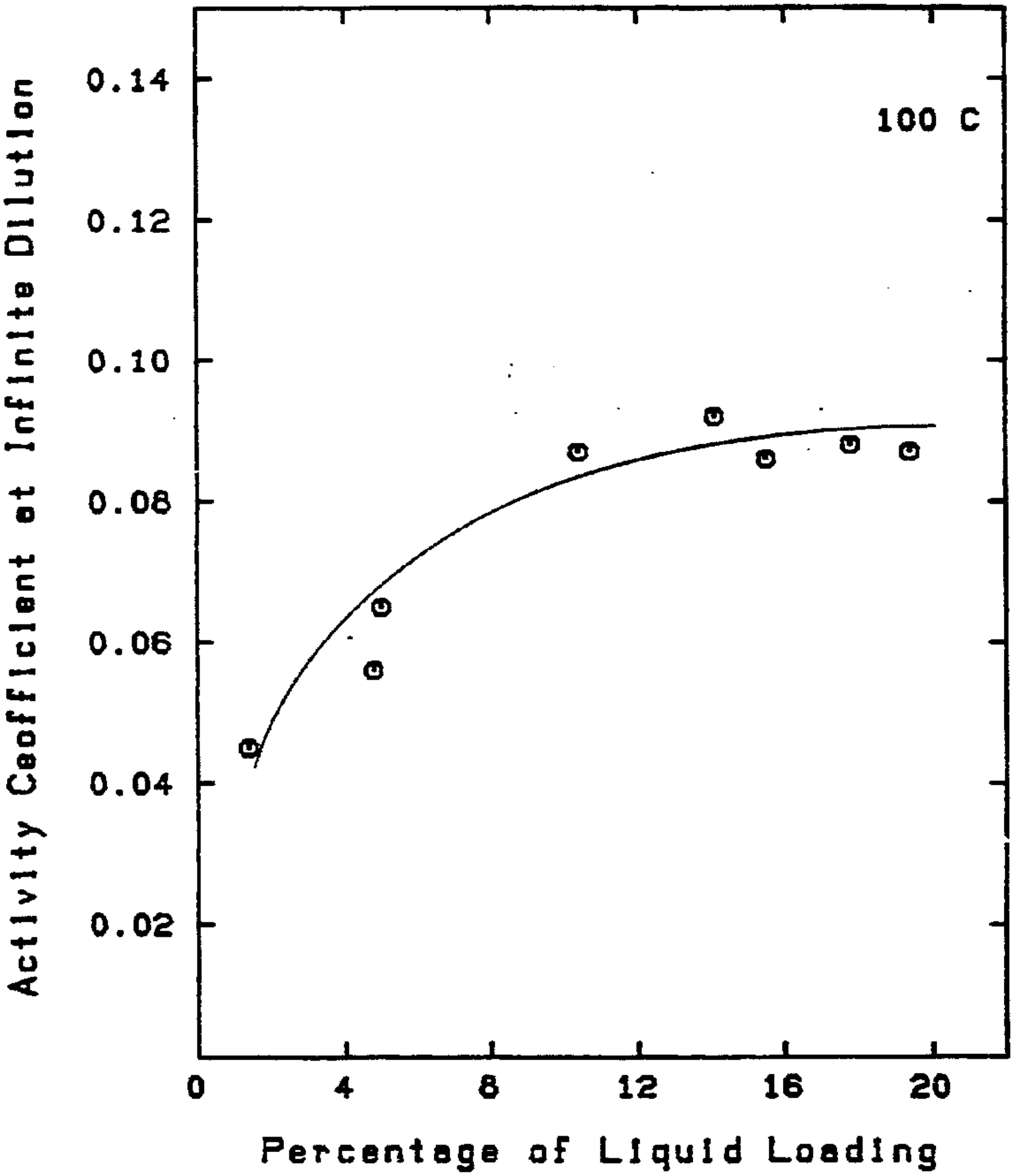

Fig. 12 Act Coeff Inf Dilute of SO2 in CHP

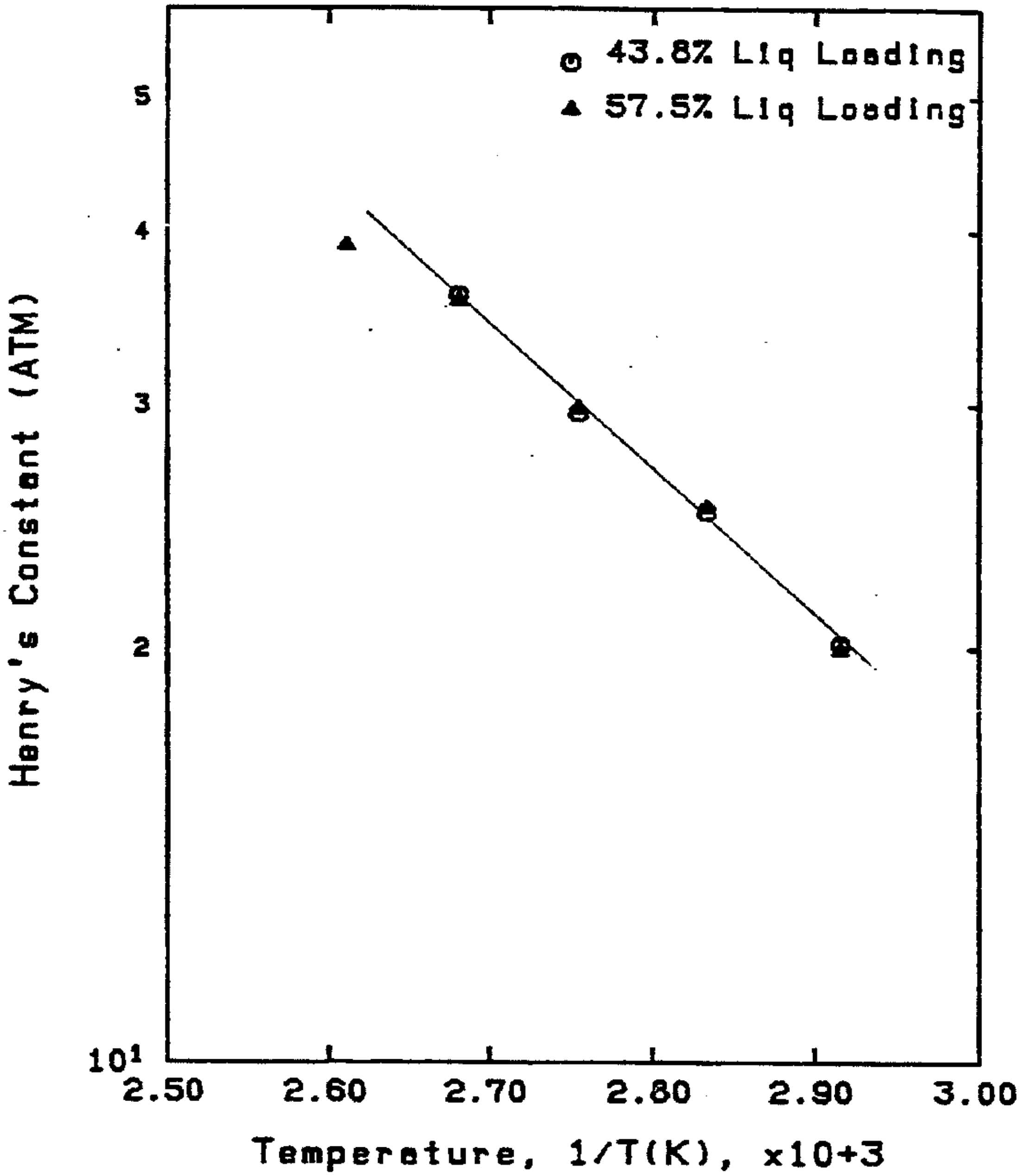

Fig. 13 Henry's Constants of SO2 in TETA

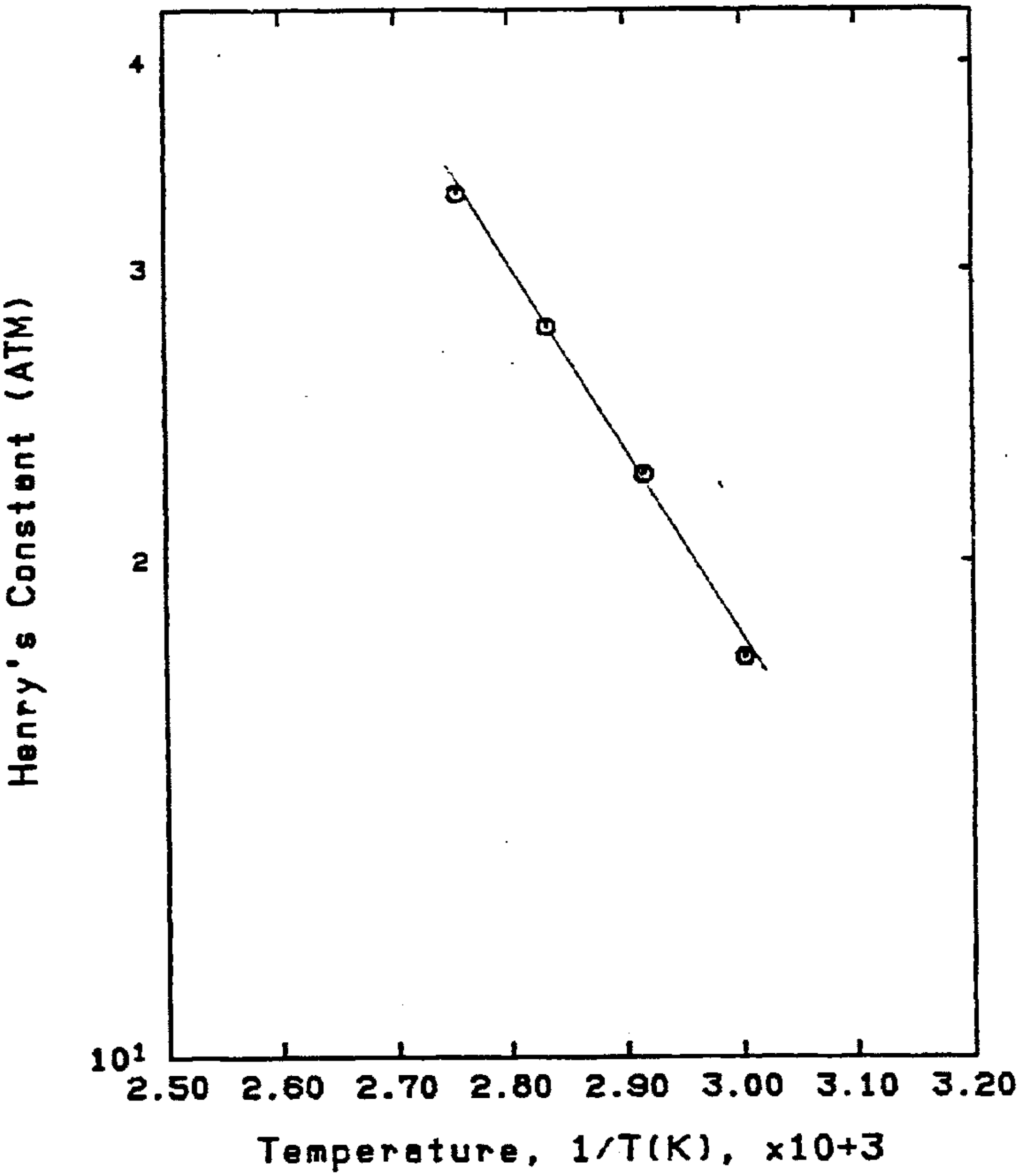

Fig. 14 Henry's Constants of SO2 in DETA

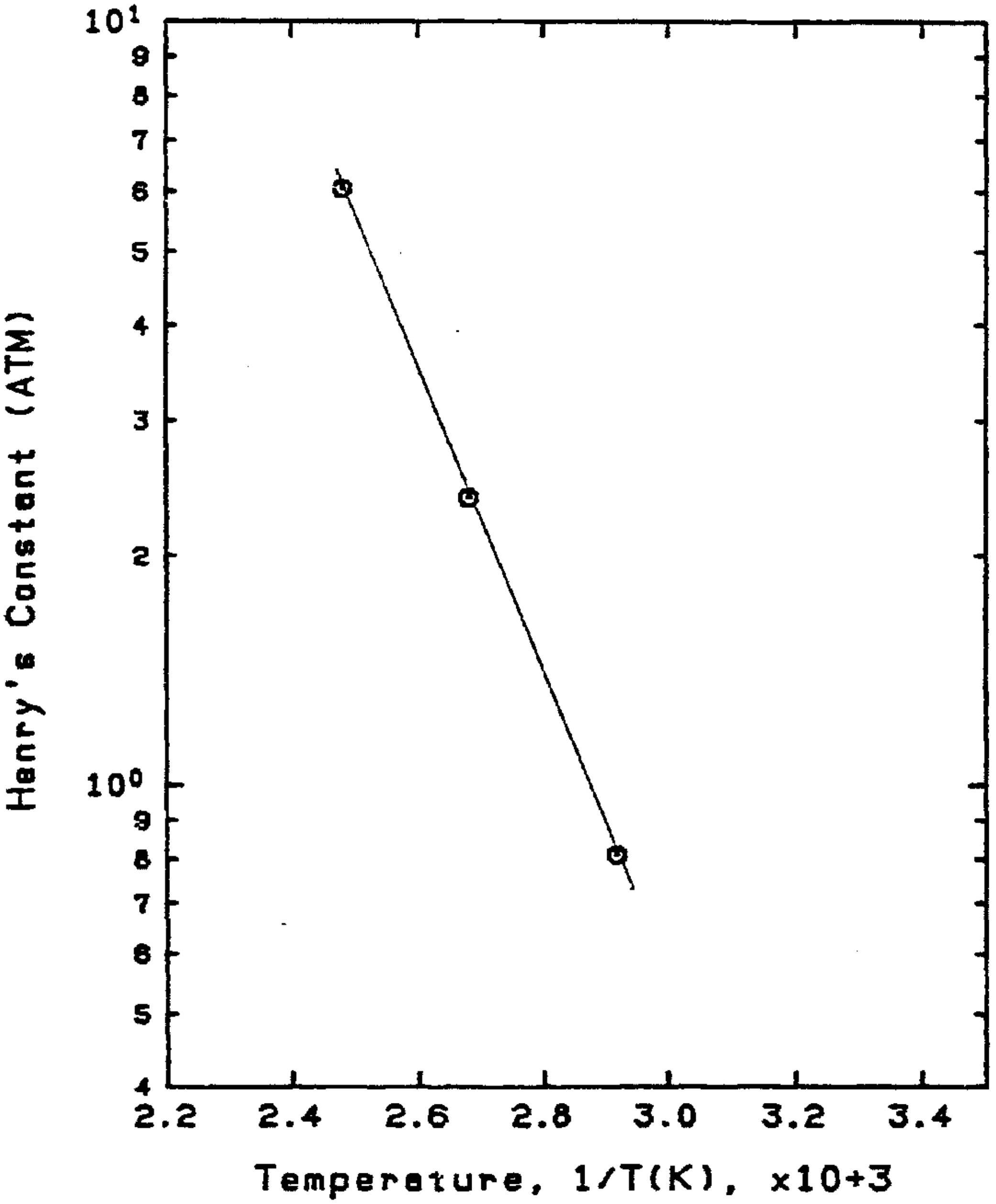

Fig. 15 Henry's Constants of SO2 in CHP

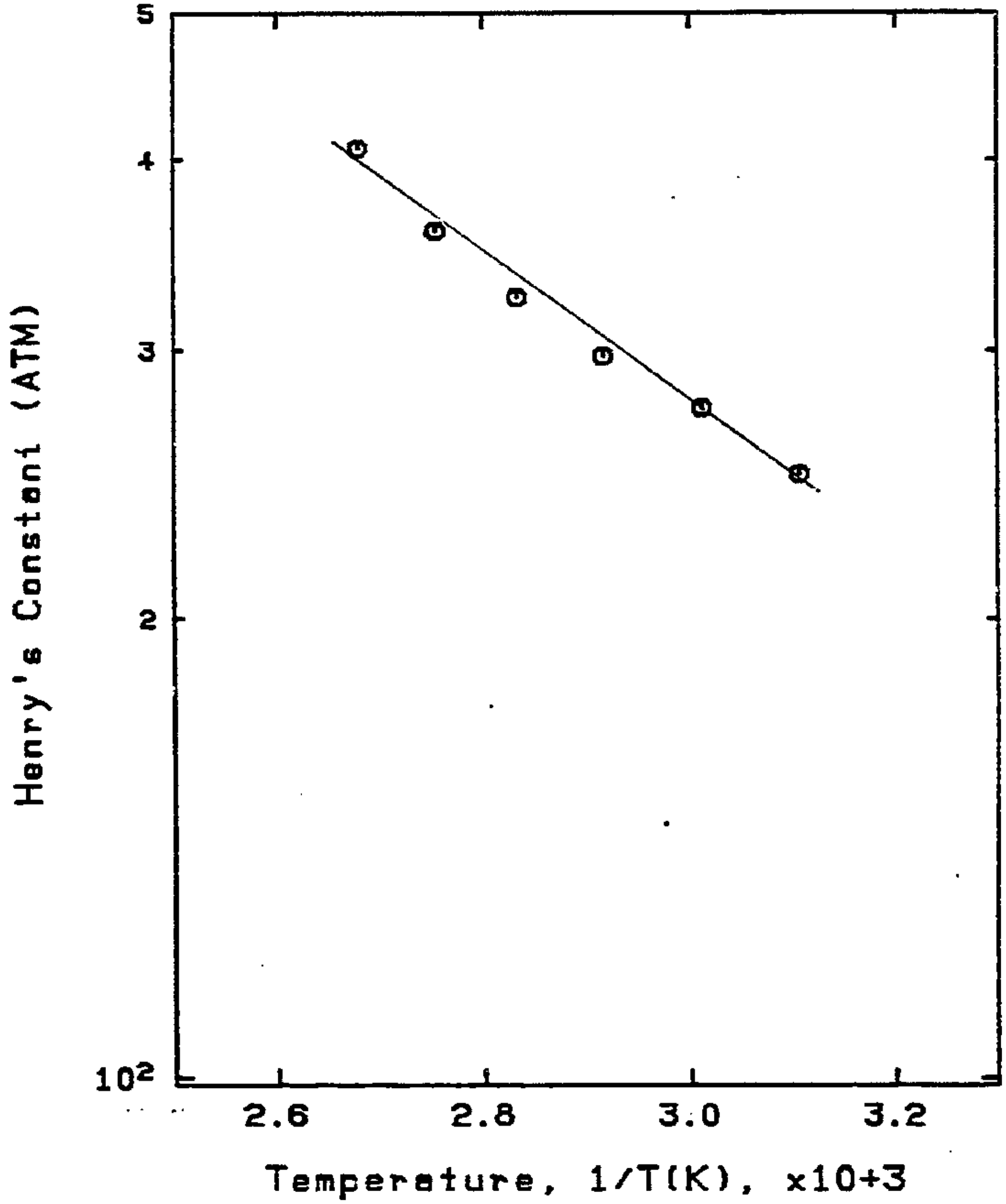

Fig. 16 Henry's Constants of NO in TETA

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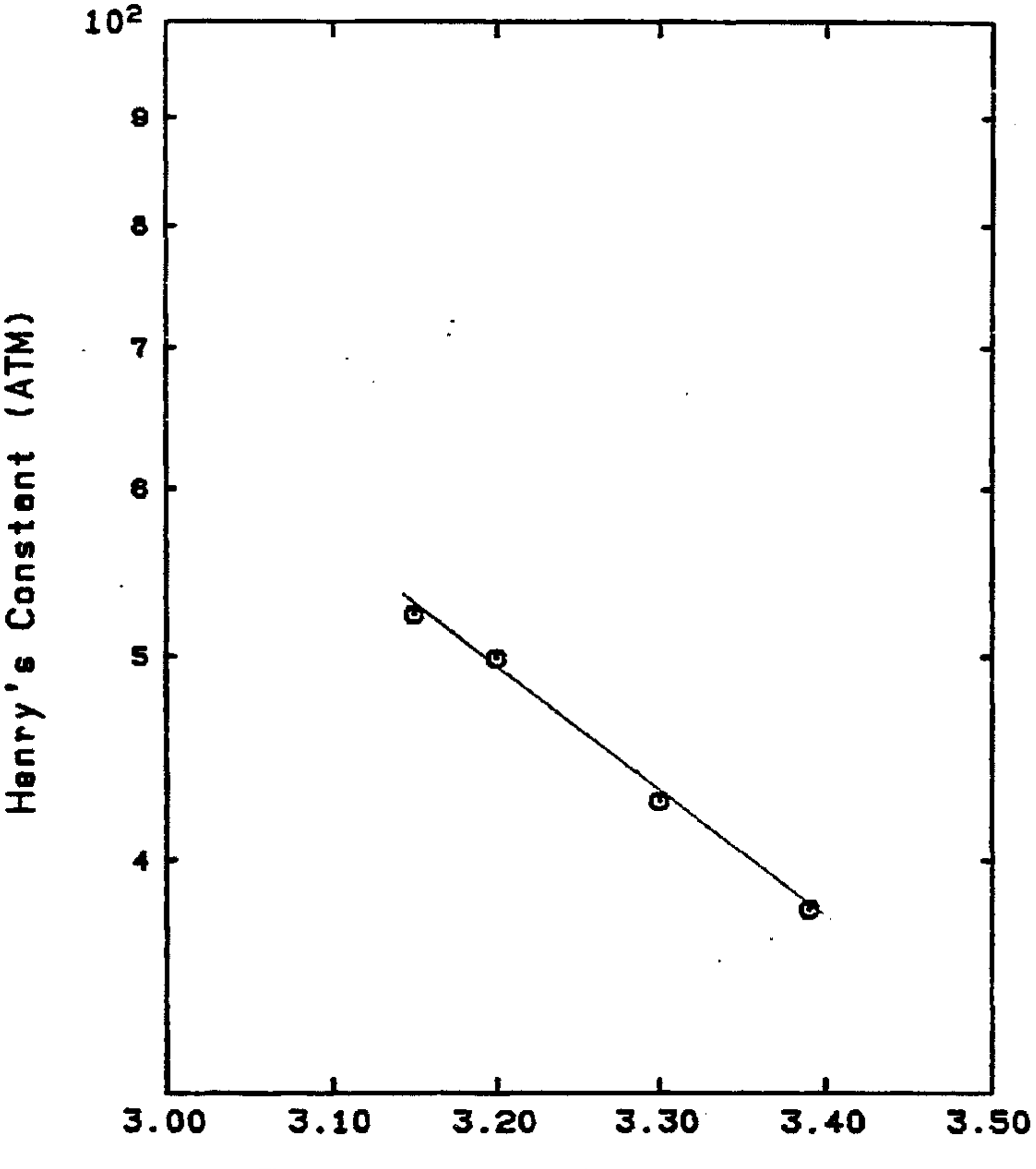

Fig. 17 Henry's Constants of NO in TEEDA

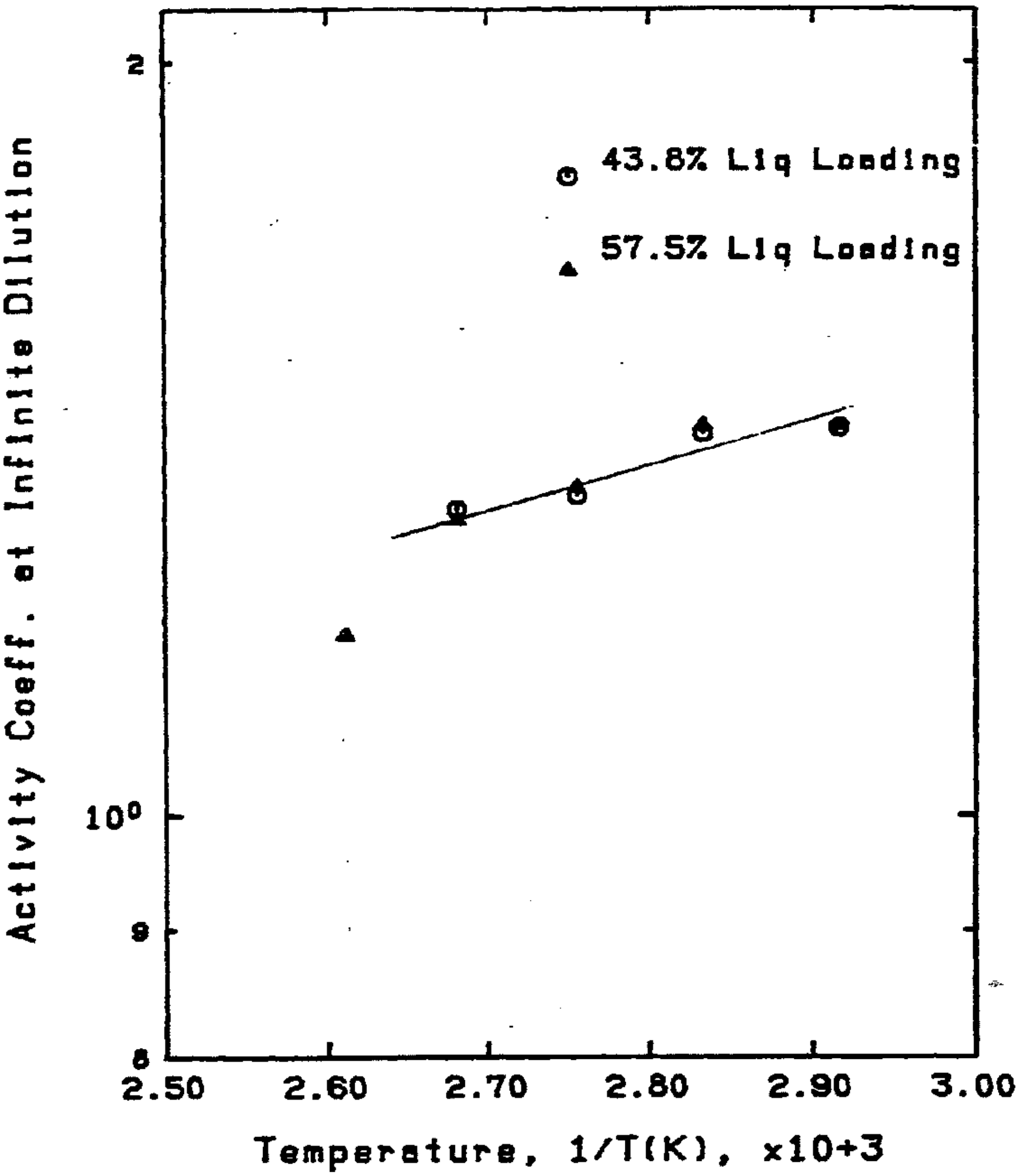

Fig. 18 Act Coeff Inf Dilut of SO2 in TETA

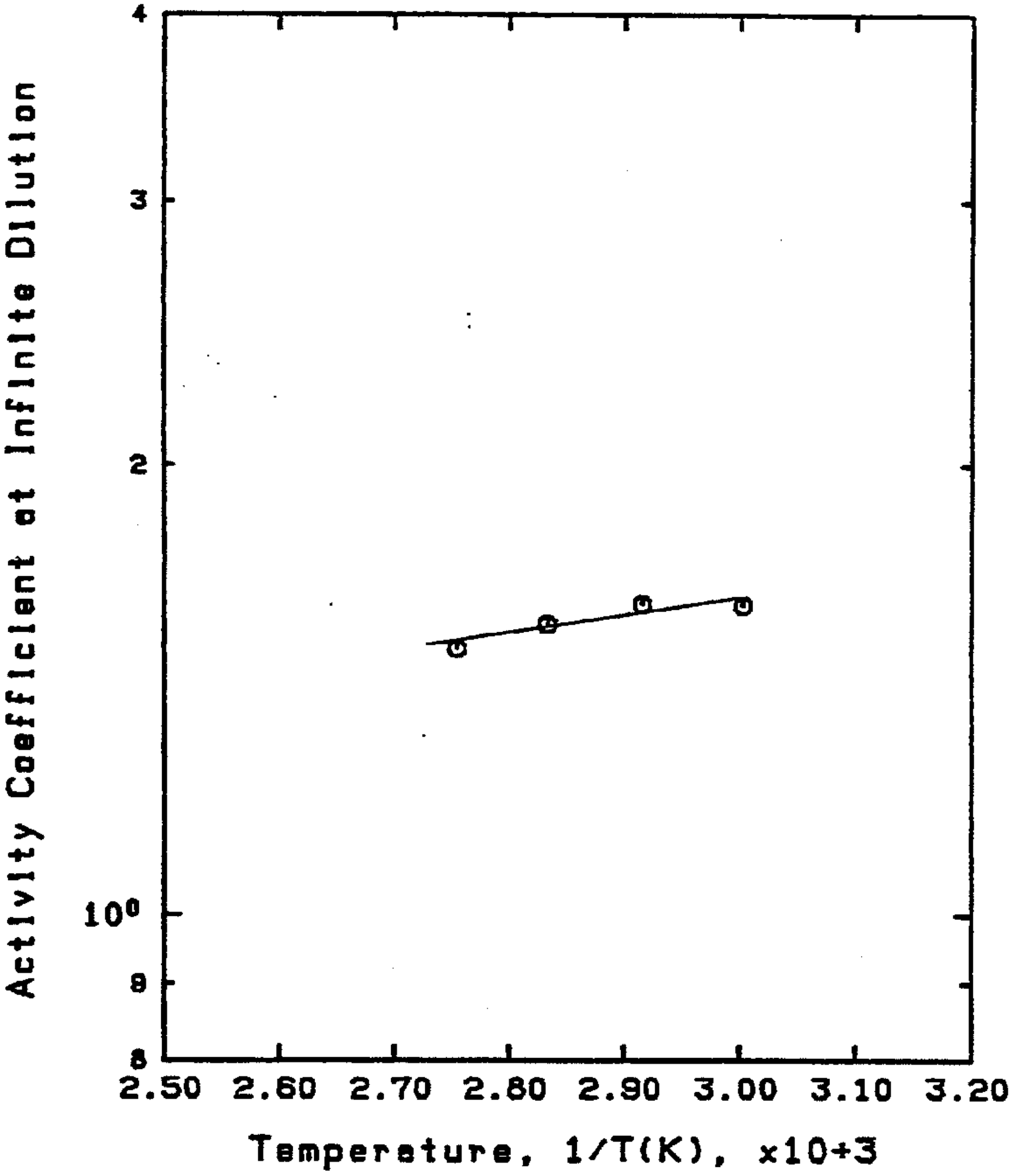

Fig. 19 Act Coeff Inf Dilut of SO2 in DETA

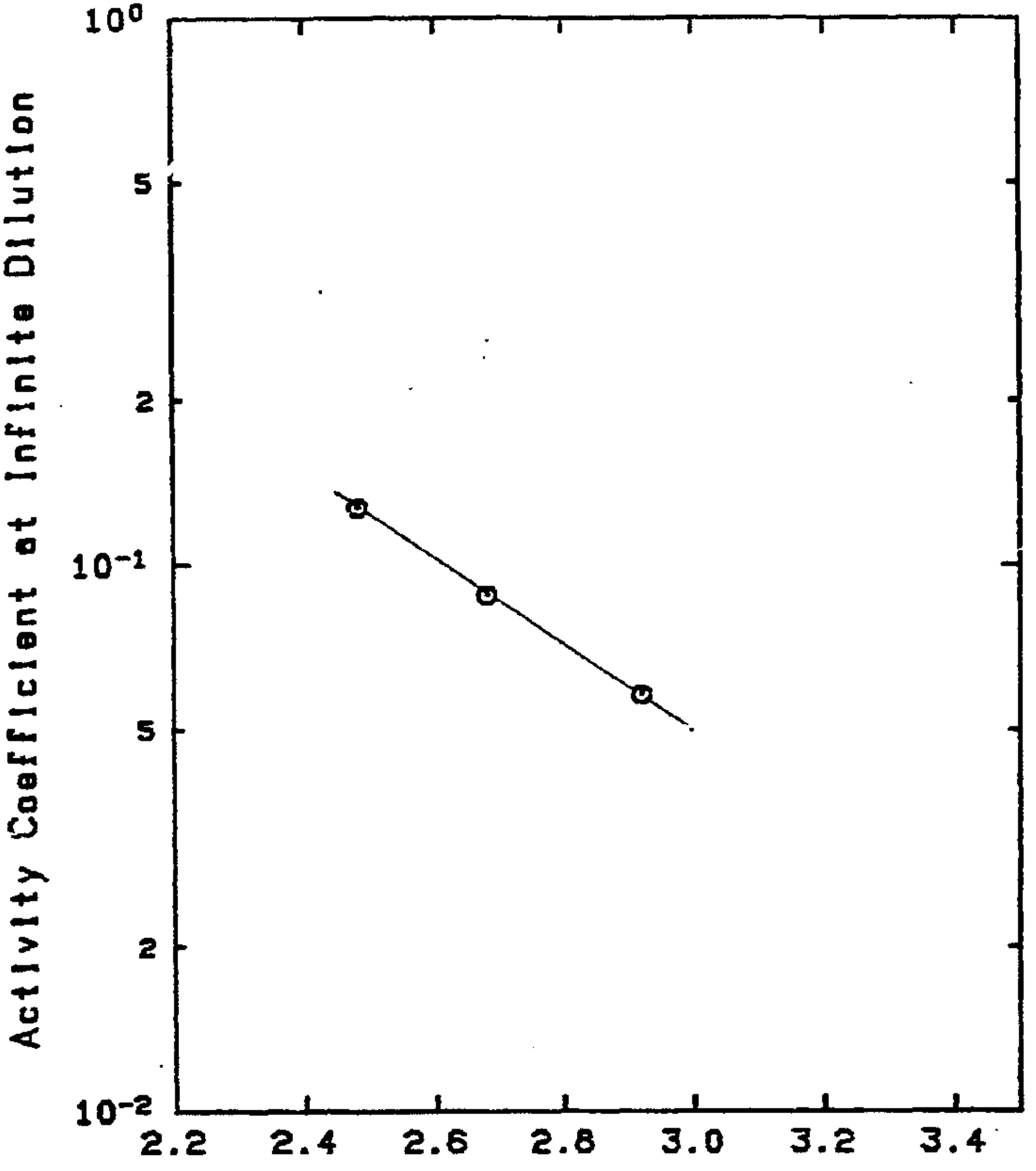

Fig. 20 Act Coeff Inf Dilut of SO2 in CHP

Figure 13 to Figure 20 are the plots of the logarithm of Henry's law constants or activity coefficients at infinite dilution versus recropical of the temperatures. These values are all taken from the highest liquid loading, and they show good linearities as expected. A best-fit line is determined by least-squares method. At high temperature (110°C) the values for Henry's law constants or activity coefficients at infinite dilution in triethylenetetramine seem are a bit off the linearity. This is because this solvent was vaporizing at this temperature. Table 1, 2 and 3 are the list of the Henry's constants of NO and SO_2 and the activity coefficients at infinite dilution of SO_2 in different solvents at various temperatures.

The equations describe the relations of Henry's constants or activity coefficients at infinite dilution and absolute temperatures are easily found from analyses. The general form of them is:

$$H \text{ (or } \gamma^{\infty}) = A \cdot \exp(B/T) \qquad (4-3)$$

where T is in Kelvin, H is in atm., A and B are constants which are tabulated in Table 4 and 5.

One notes that the lower of Henry's law constant of a gas in a solvent, the better solubility of the gas is in that solvent. According to the values found, within the same temperature range, N-cyclohexyl-2-pyrrodine can absorbs SO_2 better than triethylenetatramine and diethylenetriamine. The diethylenetriamine has weakest absorption among the three solvents found to absorbs SO_2. In ranking the strength of the solvents found to absorbs NO, N,N,N',N'-tetraethylethylenediamine absorbs roughly 4 times stronger than triethylenetetramine. However, since N,N,N',N'-tetraethylethylenediamine start to vaporize when temperature reaches 50°C as found during the experiment, it can used for absorbing NO only at lower temperature.

Consquently, it is suggested that if all three gases, NO, NO_2 and SO_2, need to be absorbed simultaneously, N,N,N',N'-tetraethylethylenediamine should be used below 45°C and triethylenetetamine for higher temperature (but not higher than 110°C). But if only SO_2 need to be removed, N-cyclohexane-2-pyrrodine is a far better solvent to used than triethylenetetramine or N,N,N',N'-tetraethylethylenediamine for the ability of absorption and temperature range available.

For NO_2 in N-cyclohexane-2-prodine, NO in diethylenetriamine and NO in 2-Amino-2-methyl-1-propanol systems it was found that little absorption of each gas by the solvents was seen. This was shown on the integrator by a tail of the peak being elongated. Lowering the temperature (to 25°C), and reducing the flow rate (to 2 cc/min) was attempted to separated the gases further so two peaks could obtain for these systems. Unfortunately, these procedures failed. As the result, although these solvents are capable of absorbing these acid gases, the absorption are too weak to be measured with present equipment.

4.5 Uncertainty Analysis

The uncertainity determined for the Henry's law constants and the activity coefficient at infinite dilution in this work is based on the uncertainity experienced in measuring certain parameter in the laboratory. For the variables used in equation (A-26), there are five different parameters which can be assigned an interval of uncertainity dictated by the accuracy of each measurement. These five different parameters and the estimated uncertainty ranges are summarized as follows:

TABLE 1

Acitivity Coefficients at Infinite Dilution of Sulfur Dioxide in Several Solvents at Various Temperatures

Temp °C	TETA	DETA	CHP
60.	---	1.612	---
70.	1.430	1.615	0.058
80.	1.431	1.566	---
90.	1.352	1.508	---
100.	1.312	---	0.088
110.	1.180	---	---
120.	---	---	---
130.	---	---	0.127

TABLE 2

Henry's Constants (ATM)
of Sulfur Dioxide
in Several Solvents at Various Temperatures

Temp °C	TETA	DETA	CHP
60.	---	17.46	--
70.	19.94	22.52	0.81
80.	25.27	27.65	--
90.	29.82	33.27	--
100.	35.65	---	2.38
110.	39.04	---	--
120.	---	---	--
130.	---	---	6.05

TABLE 3

Henry's Constants (ATM)
of Nitric Oxide
in Several Solvents at Various Temperatures

Temp °C	TETA	TEEDA
22.	---	37.92
30.	---	42.69
40.	---	49.89
45.	---	52.32
49.	248.9	---
59.	275.2	---
70.	297.4	---
80.	325.0	---
90.	359.3	---
100.	407.0	---

Table 4

Constants of Equation (4-3)
Henry's Law Constants

Gas: SO_2

Solvent	A	B	Temp Range °C
CHP	498969.4	-4567.4	70 - 130
TETA	24874.5	-2440.4	70 - 110
DETA	42230.6	-2590.2	60 - 90

Gas: NO

Solvent	A	B	Temp Range °C
TEEDA	4054.6	-1378.4	22 - 45
TETA	12643.9	-1287.6	50 - 100

Table

Constants of Equation (4-3)
Activity Coefficient at Infinite Dilution

Gas: SO_2

Solvent	A	B	Temp Range °C
CHP	10.4456	-1779.7	70 - 130
TETA	0.4513	-399.8	70 - 110
DETA	0.7108	-276.5	60 - 90

Ω_{P_t} = range in inlet pressure, ± 0.5 psi

Ω_t = range in retention time, ± 0.01 min

Ω_w = range in solvent weight, ± 0.001 gm

Ω_T = range in temperature, ± 5 K

Ω_F = range in carrier gas flow rate, ± 5% of flow rate

A root mean square (RMS) technique proposed by Kline and McClintock is used to obtain the overall uncertainty of the dependent valuable, which is the Henry's law constants and the activity coefficient at infinite dilution in this case, by the following equation:

$$\Omega_{\gamma^\infty} = \left| \sum_{i=1}^{5} \left(\frac{\partial \gamma^\infty}{\partial i} \Omega_i\right)^2 \right|^{1/2} \qquad (4\text{-}4)$$

where i stands for each measurement variable. The functions of Henry's law constant and activity coefficient at infinite dilution are obtained by combining equations (A-21) and (A-23) and equations (A-20) and (A-23) respectively.

Since it was found that the weight of solvent is the major part of the uncertainty from previous works, a mechanical analytical balance was then used for measuring the weight of solvent during the experiment in order to reduce this uncertainty. The carrier gas flow rate was measured for each run with a stop watch with an accuracy to 0.01 sec. On the average, the uncertainty of time measured is about 5%. Therefore, this uncertainty is taken to be 5% of the flow rate of each run. The result shows the uncertainty is 3% to 5% for activity coefficient at infinite dilution and exactly the same range for Henry's law constant. (This is because the Henry's law constant depends on these five measurements in same way as activity coefficient does.) The pressure, after the uncertainty of solvent weight and flow rate is reduced, becomes the major source of uncertainty which accounts for 30% of the total uncertainty. It was intended to increase the accuracy of the measurement by increasing the inlet pressure so that the uncertainty range of the pressure can be reduced. This idea works fine for SO_2 which still remains in equilibrium even at high flow rate, but not for NO, since it is necessary to keep flow rate down in order to obtain equilibrium.