Fortunately, even at low pressure the overall uncertainty was found no greater than 5% which is satisfactory.

4.6 The Binary Interactions Parameters in Wilson's Equation

After knowing activity coefficient at infinite dilution, the binary interactions parameters g_{11}, g_{22} and g_{12} in Wilson's equation were computed for all SO_2 systems using equations (B-10, B-11, B-19). A computer program was written to calculate these interactions using trial-and-error method and further calculate the activity coefficient at different concentration. The final values of binary interactions are tabulated on table 6. Since activity coefficient at infinite dilution values were determined with a certain uncertainty, these values present here are also subjected to these uncertainties.

4.7 Vapor-Liquid Equilibrium Data

The vapor-liquid equilibrium (VLE) Data, or the partial pressure of SO_2 and NO over each solvent at different liquid concentration can now be easily calculated use equations (C-2) and (4-2) after knowing the activity coefficient and

Table 6

Binary Interactions Parameters of Wilson's Equation (cal/g-mole) of SO_2

CHP

Temp °C	g_{11}	g_{22}	g_{12}
343	-5027.9	-15007.4	-10971.1
373	-4862.2	-14940.4	-10913.9
403	-4714.6	-14874.7	-10787.7

TETA

Temp °C	g_{11}	g_{22}	g_{12}
343	-5027.9	-11587.0	-8179.1
353	-4970.3	-11953.9	-8346.9
363	-4915.1	-12316.5	-8509.9
373	-4862.2	-12674.9	-8668.5
383	-4811.2	-13028.9	-8823.2

TABLE 6 (Cont.)

DETA

Temp °C	g_{11}	g_{22}	g_{12}
333	-5088.1	-12105.0	-8444.9
343	-5027.9	-11232.1	-7910.7
353	-4970.3	-10483.6	-7385.1
363	-4915.1	-9834.9	-6923.4

Henry's law constants. The vapor-liquid-equilibrium at other temperature can be obtain by the same method with different values of γ^{∞}.

4.8 NO Diffuses Through Liquid Membrane

With the apparatus described before, several runs of NO diffusing through an immobilized liquid membrane were carried out. The operating conditions of each run are summarized below:

Run	Top Chamber Pressure	Inert Gas in Bottom Chamber	FeCl2	Initial Diffusion Rate
1	10 psig	Air	No	3.50E-2 mmHg/min
2	2 psig	N2	No	1.20E-2 mmHg/min
3	2 psig	He	No	1.73E-2 mmHg/min
4	2 psig	He	Yes	1.38E-2 mmHg/min

The pressure change of the bottom chamber with time is plotted in figure 21. The initial pressure in the bottom chamber of each run was equal to the ambient atomsphere. The initial diffusion rate is taken as the rate of manometer level changs before leveling off. As shown in the figure, the pressure of bottom chamber decreased from time zero for every run, with the pressure of NO in the top chamber always higher. No indication was shown that the pressure in the bottom chamber would rise. To explain this phenomena, several conjectures are described below:

It was possible that a small amount of oxygen was present in the bottom chamber. As soon as NO diffused through to the bottom, it reacted with O_2 to become NO_2 according to the following equation:

$$2\ NO + O_2 \rightarrow 2\ NO_2 \qquad (4-5)$$

The NO_2, being very easy absorbed by triethylenetetramine, dissolves in the solvent as soon as it formed. Therefore, the number of moles of gas decreased. According to the calculation, even 6.0×10^{-5} g-mole of gas change can make liquid rise or fall 10 cm in the monameter.

In addition NO reacts with O_2 reducing the total number of moles of gas. There is also a possiblility that O_2 itself is dissolves in the solvent. O_2 itself is dissolves in the solvent. (It was noticed that if

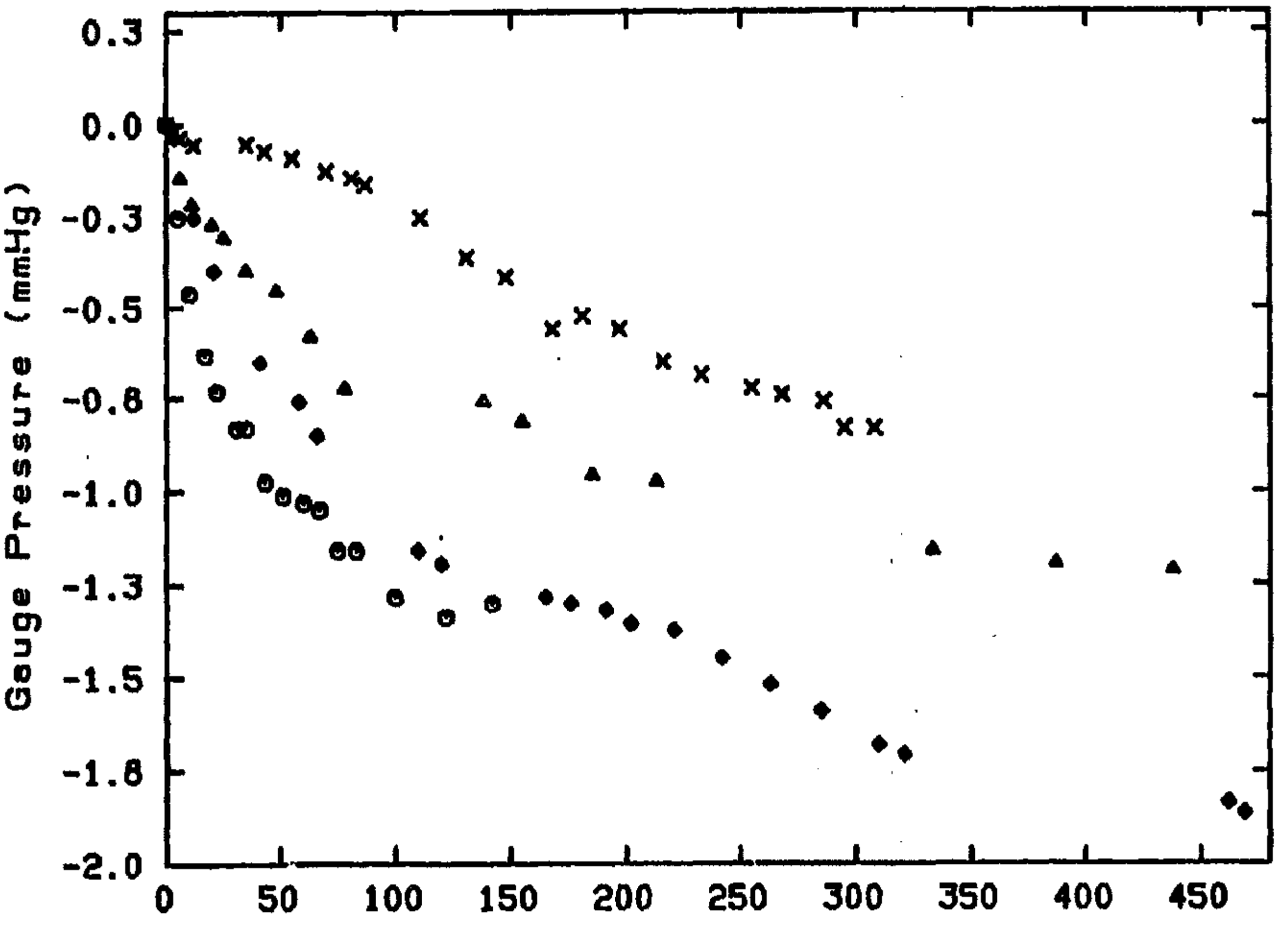

Fig. 21 Pressure In the Lower Chamber

triethylenetetramine is exploed to air for a few days, the solvent changes from colorless to yellow.)

With the above assumptions, it may be possible to explain why when comparing run no. 1, with the bottom chamber filled with air, and no. 2, with the bottom chamber purged and filled with N_2, that the pressure decrease in the bottom chamber was slower for run no. 2.

However, these are not all the reasons why the pressure decreased in the bottom chamber. From run no. 2 and 4, a decrease in pressure is still found even thought the bottom chamber was well purged with N_2 or He. Therefore, besides NO reacted with O_2 or O_2 being dissolved in the solvent, causing the pressure decreased, there was a possibility that the inert gas was diffusing from bottom to top due to concentration gradient. From the chemistry point of view, the bonding energy of TETA and the inert gas, He or N_2, is much smaller than the energy of TETA and NO. Therefore, NO is more difficult to be released from solvent, so the diffusion rate of inert gas from the bottom to top is faster than the diffusion rate of NO from top to bottom even though both of the gases have roughly same concentration gradient.

The above 3 conjectures are not fully established from the data. It is necessary to carry out more experiments to confirm any one of them.

There is a drawback in the whole experiment that must also be addressed. The monameter, ebing at only a 15° inclined angle, and filled with water, is very sensitive. According to calculation, a 0.7 K of temperature change can make water level change 10 cm. Although the more sensitive of the monameter, the better it is for the experiment, the present apparatus is not well insulated from temperature variation. The reading is thus subject to a great uncertainty if operating time is long.

5.0 CONCLUSION

It has been clearly show that gas-liquid chromatography is an easy and fast way to determine activity coefficient at infinite dilution as well as Henry's law constant. The tests on different solvents, different gases and different temperatures were obtained fairly quickly. N-cyclohexane-2-proyrdine, triethylenetetramine, diethylenetriamine, 2-amino-2-methyl-1-propanol, N,N,N',N'-tetraethylethylenediamine and N,N-dipropylacetamide were solvents tested in this work. It was found that SO_2, the most activity gas of the three pollutants (SO_2, NO, NO_2), is absorbed by N-cyclohexane-2-proyrdine, triethylenetetramine and diethylenetriamine and chemically absorbed by 2-amino-2-methyl-1-propanol, and no experiments were preformed with N,N,N',N'-tetraethylethylenediamine and N,N-dipropylacetamide. NO, the most unreactive gas, is absorbed by triethylenetetramine and N,N,N',N'-tetraethylethylenediamine and weakly absorbed by diethylenetriamine and 2-amino-2-methyl-1-propanol.

To help to design the absorber-stripper tower with the vapor-liquid equilibrium data a few computer prgorams have been proposed for this purpose. Designing the absorber-stripper tower for removing acid gases by the solvent found in this study was not include in this work.

Removing acid gases via facilitated transport through liquid membrane is a more economic way of separation as mentioned eariler. However, this technique also requires a trial-and-error procedure in finding a suitable solvent. Due to the time limitation, not much work has been done in this area.

6.0 RECOMMENDATION

6.1 Gas Chromotraphy

Several solvents tested in this work were found weakly absorbed by the acid gases. Seperation of absorbed and non-absorbed gases using these solvents were not possible with the present apparatus. However, there are a few improvements that can be done to this equipment in order have a better separation of the gases.

According to the equation (A-1)

$$Y \cdot P_t = X \cdot \gamma \cdot P^S$$

If the total pressure increases, the solubility of gas in liquid, i,e, X, will also increase. Therefore, for weak absorption of gases, it is recommended to install a flow rate controller at the outlet of the column. By adjusting the flow rate at this point, the pressure inside the column can be controlled and operated at pressure greater than ambient pressure.

Another way to improve the seperation of gases is attach a cooler to the apparatus so the experiment can operate below the ambient temperature and thus increase the solubility of gases.

Besides increasing the pressure or decreasing the temperature, another relative simple way is to increase the length of column. It is obvious that the longer the time the mixture of gases pass over the solvent, then the larger separation that can be completed.

6.2 Liquid Membrane Apparatus

To have better and more accurate result, a few improvments of apparatus are suggusted:

1. It is recommed to keep the bottom chamber at vacuum condition so that no gas can diffuse from the bottom to top thus elimininting the pressure decrease problem and would also eliminate the reaction between NO and O_2. A senstitive vacuum gauage is needed for improved measurements.

2. It is necessary to have an apparatus that is easier to assemble and well insulated from temperature variation.

3. It would be better to have an instrument that is

able to analysis the component and concentration of the gases in the bottom chamber.

APPENDIX A

APPENDIX A

A.1 Activity Coefficients at Infinite Dilution from Gas-Liquid Chromatography Measurements

This appendix shows how athe ctivity coefficient at infinite dilution, γ^{∞}, can be determined using the gas-liquid-chromatography (GLC). The basic theory of the GLC and the equations for calculating γ^{∞} are discussed in this section.

To calculate the vapor-liquid equilibrium (VLE) data, equation (4-1), a basic equilibrium equation from thermodaynamic can be applied:

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

In this equation, ϕ can be assumed to be 1 when the pressure is low, such as ambient pressure as one of conditions set in this work. Consquently, the activity coefficient becomes the major concern.

As approaching to solve for the activity coefficient at different concentration, equation (A-1) can be rearrange as:

$$\frac{X}{Y} = \frac{P_t}{\gamma P^s} \quad \text{(A-2)}$$

With slight modification, this ratio has been named the partition coefficient K:

$$K = \frac{\text{conc. of solute in liquid phase}}{\text{conc. of solute in vapor phase}}$$

or in terms of moles of solute:

$$K = \frac{n_{1\ell}/V_\ell}{n_{1g}/V_g} \quad \text{(A-3)}$$

where $n_{1\ell}$ = total no. of mole of solute in liquid phase in the column

n_{1g} = total no. of mole of solute in vapor phase in the column

V_ℓ = volume of liquid phase in the column

V_g = volume of gas phase in the column

furthermore,

$$n_{1\ell} = X_1 \cdot n_\ell \quad \text{(A-4)}$$

$$n_{1g} = Y_1 \cdot n_g \qquad (A-5)$$

where n_ℓ = no. of mole in V_ℓ

n_g = no. of mole in V_g

Substitute equations (A-4) and (A-5) into equation (A-3) gives:

$$K = \frac{X \cdot n_\ell / V_\ell}{Y \cdot n_g / V_g} \qquad (A-6)$$

or

$$\frac{X}{Y} = \frac{n_g V_\ell K}{n_\ell V_g} \qquad (A-7)$$

combining equations (A-7) and (A-2) we obtain:

$$\frac{P_t}{\gamma P^s} = \frac{n_g V_\ell K}{n_\ell V_g} \qquad (A-8)$$

or

$$\gamma = \frac{P_t n_\ell V_g}{P^s n_g V_\ell K} \qquad \text{(A-9)}$$

Since the pressure is low as discussed earlier, it can be assumed ideal, i,e,

$$P_t \cdot V_g = n_g \cdot R \cdot T \qquad \text{(A-10)}$$

and the activity coefficient can be expressed in more measurable parameters:

$$\gamma = \frac{n_\ell RT}{P^s V_\ell K} \qquad \text{(A-11)}$$

To solve for the partition coefficient, K, the GLC is employed to measure the net retention volume, V_n, which is a parameter directly relate to K. The relation is explained as follows:

As a mixture of absorbed and non-absorbed gases is injected into a column coated with solvent, the non-absorbed gas travels with carrier gas without any delay, and the absorbed gas, being retarded by the stationary liquid, comes out afterwards. If one let T_m be the time needed for the nonabsorbed gas to travel from inlet to the outlet of column, and T_r be the time needed for absorbed gas, multipling these two times, T_r and T_m, with the carrier gas flow rate observed at the pressure at the column outlet, F, then the retention volume, V_r, and gas holdup, V_m, are obtained respectively. However since these value are measured at outlet pressure, they are corrected by multiplying a pressure-correct-factor J. Thus a corrected retention volume, V_r° is:

$$V_r^\circ = J \cdot F \cdot T_r = J \cdot V_r \qquad \text{(A- 12)}$$

and corrected gas holdup, V_m° is:

$$V_m^\circ = J \cdot F \cdot T_m = J \cdot V_m \qquad \text{(A- 13)}$$

$$J = 1.5 \cdot \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \qquad \text{(A- 14)}$$

where P_i = inlet pressure of column

P_o = outlet pressure of column

and net retention volume, an expression of how strong a gas being held by liquid, is defined as:

$$V_n = V_r^\circ - V_m^\circ = J(V_r - V_m) \tag{A-15}$$

It is the net retention volume from which equilibrium thermodynamic parameters, such as activity coefficient in solution and absorption coefficient, are calculated.

Furthermore, consider a solute molecule traveling along the column, it is absorbed and released by the solvent repeatly, one can define the retention ratio S as a fraction of time (< 1) spent by a solute molecule in the mobile (gas) phase, and it can be written as:

$$S = \frac{T_m}{T_r} = \frac{V_m}{V_r} \tag{A-16}$$

This ratio, which is also equal to the fraction of the total number of solute molecules in the mobile phase at equilibrium:

$$S = \frac{C \cdot V_m}{C \cdot V_m + Q \cdot V_\ell} = \frac{V_m}{V_m + K_s \cdot V_\ell} \qquad \text{(A-17)}$$

where D = conc. of solute in vapor phase

Q = conc. of solute in liquid phase

comparing equations (A-16) and (A-17) obtains

$$V_r = V_m + K_s \cdot V_\ell \qquad \text{(A-18)}$$

i,e,

$$V_n = K_s \cdot V_\ell \qquad \text{(A-19)}$$

In deriving the above equations, it is assumed that the partition coefficient is constant, this is only valid at infinite dilution. Therefore, substituting equation (A-19) into equation (A-10) yields:

$$\gamma^{\infty} = \frac{n_{\ell}RT_{C}}{P^{S}V_{\ell}K} = \frac{WRT_{C}}{P^{S}MV_{n}} \qquad \text{(A-20)}$$

where W = total weight of liquid phase, the solvent

M = molecule weight of solvent

The net retention volume, V_n, after measured from GLC , γ^{∞} can be determined.

A.2 Henry's Law Constant from Gas-Liquid Chromatography Measurements

Determining the Henry's law constants does not need any more data than determining the activity coefficient at infinite dilution. The equation for the Henry's law constants is:[17,18]

$$H = \frac{WRT_{C}}{MV_{n}} \qquad \text{(A-21)}$$

which is vary similar to equation (A-20) except not including vapor pressure.

The equations for deriving activity coefficient at infinite dilution and Henry's law constant agree with the thermodynamic definition:

$$\lim_{x_i \to 0} \gamma_i = \frac{H_{i,j}}{f_{\text{pure } i}} \qquad \text{(A-22)}$$

where i stands for solute, j stands for solvent. As X_i approaches zero, γ_i is at infinite dilution; and since operating pressure is low, fugacity of pure solute, $f_{\text{pure } i}$, is equal to the vapor pressure of solute.

A.3 Net Retention Volume and Specific Retention Volume

The net retention volume, as described in equation (A-23) is usually obtained by measuring the difference of time that comes from the column between absorbing and nonabsorbing gases. However, since the flow rate is often determined with a soap film meter, correction for both of the vapor pressure of the soap solution(equal to the vapor pressure of pure water) and the temperature (when the flowmeter temperature and column temperature are not equal) are needed. The final expression for V_n is then:

$$V_n = t \cdot F \cdot (1 - \frac{P_w}{P_o}) \cdot 1.5 \cdot \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \cdot \frac{T_c}{T_r} \qquad \text{(A-23)}$$

where t = retention time difference

P_w = vapor pressure of water at room temperature

T_c = temperature of column

T_r = temperature of flow meter

The net retention volume in above equation, however, is dependent on the solvent weight, and temperature of flow meter and pressure of atomsphere. Littlewood and his co-workers[19] converted this volume to a standard value calculated at standard temperature and pressure per unit weight of solvent, and is called the specific retention volume V_s. This specific retention volume, related to the net retention volume as:

$$V_g = \frac{273.2 \cdot V_n}{T_c \cdot W} \qquad \text{(A-24)}$$

and the γ^{∞} written in terms of V_s is:

$$\gamma^{\infty} = \frac{273.2 \cdot R}{P^{s} M V_g} \qquad \text{(A-25)}$$

If expressing the gas constant, R as:

$$R = 62365.6 \ \frac{\text{cc} \cdot \text{mmHg}}{\text{K} \cdot \text{g-mol}}$$

we obtain the expression of γ^{∞} first derived by Martire in 1961.[20]

$$\gamma^{\infty} = \frac{1.704 \times 10^{7}}{P^{s} M V_g} \qquad \text{(A-26)}$$

where P_s = the vapor pressure of solute in mmHg at the column temperature.

V_s = specific retention volume (cc of carrier gas per gram of solvent)

The expression of specific retention volume, V_s in terms of GLC measurements is obtained by combining euqation (A-20) and (A-21):

$$V_s = t \cdot \frac{F}{W} \cdot \frac{273.2}{T_r} \cdot \left(1 - \frac{P_w}{P_o} \right) \cdot 1.5 \cdot \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \qquad \text{(A-27)}$$