ACID GAS REMOVAL BY ABSORPTION IN ORGANIC SOLVENTS (Task 2)

1.0 INTRODUCTION

1.1 Acid Gases as Air Pollutants

The combustion of coal produces three major air pollutants; particulates, sulfur dioxide (SO_2) and oxides of nitrogen (NOx). Fly ash particulates can be removed satisfactorily by mechanical filters or electrostatic precipitators. NOx or SO_2, however, can not be removed by these methods. These poisonous gases were liberated into atomsphere without control before the pollution control laws were promulgated in 1963. Estimates were made that in the year of 1970, only in U.S.A., the emmision of SO_2 was more than 35 million tons. If no action is taken to solve these problems, annual emmision of sulfur dioxide can exceed 200 million tons by the year of 2000.[1*]

The study of toxicity of the three major pollutants gases (SO_2, NO, NO_2) indicated that long exposure to these gases can cause respiratory diseases and dangers to human life and plants. Sulfur dioxide, being a corrosive gas, can cause chronic plant injury and damage many structural

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[*] References placed superior to the line of text refer to the bibliography

** Page numbers in the upper right hand corner of this and succeeding pages refers to the page number in the thesis represented by this section.

material. For the oxides of nitrogen, because of their low solubility in water, they are only slightly irritating to respiratory tract. Therefore a dangerous amount of the fumes may be breathed before a workman can sense a discomfort. Continuous exposure to low concentration may also result in coughing and headache etc. Exposure to high concentration (60-100 ppm) with a period of 6 - 24 hours may cause loss of consciousness. Concentration of 100 - 150 ppm may cause death if exposed more than one hour.[2]

1.2 Removal by Solvent Absorption

To prevent the environment from being contaminated by these pollutants, their emission into in atomsphere must be controled. One direct and economic way of removing these acid gases is by the absorption in organic or inorganic solvent before being released into the atomsphere.

The absorption processes can divided into 2 classes -- disposable and regenerable . The disposable processes have been developed over the passed decades. Systems using aquecus slurries of lime, limestone and magnesium hydroxide and other solution based on sodium and ammonia have been known for many years. Some of these processes have been used in industry for gas purification. However, since SO_2 and NOx react with these slurry and produce large masses of waste, (a typical power station will produce several hundred tons of spent slurry per day), an economic disposal of this waste is difficult or impossible. Often it lead to a very serious problem since there are insufficient area avaible for dumping.[3]

Regenerable systems do not pose the previous problems. In these systems, the organic or inorganic solvent is regenerated and recyled for further use. Generally, the interaction between the solvents and acid gases must be either a reversible chemical reaction or the acid gases are physically absorbed. The solvents employed should chose carefully and usually they are decided via a trial-and-error procedure.

In order to have an economic process, it is prefer the physical absorption due to easier recovering of the solvent. Chemical reaction, however, usually require high ultity to make the reactions go reverse. Looking for a solvent that can physically and simulataneously absorbs all these acid gases was major purpose of this study.

Among these three acid gases, NO, the major component of NOx, is the most difficult to be absorbed because of its low reactivity. Although an idea had been presented that NO can be oxidizing slowly to NO_2, which is much easier to be absorbed, by oxygen or by other strong oxidizer such as Cl_2O or O_3, it is still beneficial if NO can be removed directly. If a solvent can absorbes NO, most likely NO_2, SO_2 can also been absorbed by the same solvent. In this work, therefore, several organic solvents were tested for the absorption of NO first, if found to absorb NO, SO_2 was further examined.

If a solvent is found to absorbs NO and SO_2, the vapor-liquid equilibrium (VLE) value of the gases and solvent is needed as a basic data for equipment design such as absorber-stripper tower. In the past, gas-liquid chromatography was used to measure the activity coefficient at infinite dilution , then the single-parameter Wilson equation was applied to calculate the necessary equilibrium data. However, in the present work, due to the critical temperature of NO, (-93°C), being below the lowest possible experimental temperature (ambient temperature), the activity coeffieient of NO can not be calculated. Instead, Henry's law constant is evaluated for use in determining VLE data. Although Henry's constant is valid only for low concentration of solute, it is still acceptable since the concentration of NO from the industrial flue gas is usually less then 1000 ppm.[4]

1.3 Facilitated Transport Through Liquid Membrane

Besides removing acid gases by organic compound absorption, a direct separation of NO from flue gas by diffusing through membrane also has a high potential for use in the future. This area has attracted much attention in recent years because of its simplicity, low capital cost and energy efficiency. Up to present day, however, few membrane process other than reverse osmosis and hydrogen separation have been demonstrated in the industrial field primarily because of the transfer rate and selectivity in the separation. The diffusion rate of most molecules through polymer membrane is so low that exceedingly thin membrane must be constructed in order to have an industrially acceptable flux.[24]

A recent development for membrane separation is to use a liquid as the membrane material. One of advantage of this liquid membrane is that besides ordinary diffusion of a selective molecule through the membrane, it is possible to add an agent which can form complexes with the molecule. The molecular diffusion through the membrane is facilitated by reacting with this agent at one side, then transfer occurs in a form of complex to the other side of membrane and release from the agent.[25] This kind of transport does not depend on the concentration of molecules on both side of membrane alone, but also on the chemical reaction rate in the membrane.[24]

An exploratory experiment of NO transport through an immobilized liquid membrane was carried out in present work. Triethylenetetramine was used as liquid membrane material and $Fe^{II}Cl_2$ was dissolved in this solvent to serve as an agent.[25]

2.0 LITERATURE REVIEW

2.1 Regenerable Systems of Solvents Absorption

2.1.1 Chemical Absorption

In the regenerable acid gas removal system, many studies have been done in the area of reversible chemical reaction in the past decades. In 1935, Johnstone[5,6] published the first work on steam regenerable system regarding SO_2 absorption. He investigated various aqueous absorbents such as alkali sulfite/bisulfite and organic acid buffers. Systems using chemical solvents such as sodium citrate, glyoxylic acid and ammonium sulfite have been developed since then.

Search the solvent for NOx absorption has also began since second half of this century. Ganz and Manon (1953) reported that the solution of $FeSO_4$ and $FeCl_2$ absorb NO. Hikita et al. (1977)[7] carried the experiment further to analysis the reaction mechanism and investigate the reaction rate constants for the same system. In the following year, they also tested two other solutions, $Na_2SO_3/Fe^{III}EDTA\text{-}Na$ and $Na_2SO_3/Fe^{II}EDTA\text{-}Na/Fe_2(SO_4)_3$ and obtained reaction rate constants. In 1983, Uchida and Kobayashi[8] reported the

$KMnO_4/NaOH$ and $Na_2SO_3/FeSO_4$ solutions react with NOx reversibly.

To minimize cost and complexity, it would appear to be advantageous to remove NOx and SO_2 from flue gas simultaneously. Reasearch efforts to find such regenerable solvents have intensified in the passed few years, especially in Japan and many designs have been proposed. These processes either use strong oxidizer such as O_3, ClO_2 or $KMnO_4$ to selectively oxidize the relatively insoluble NO to a more soluble gas -- NO_2, or use the addition of metal chelates such as $Fe^{II}EDTA$ in aqueous solution to promote absorption of NO solution. As studies indicate, the aqueous solution of Fe^{II} chelate can bind NO to form nitrosyl metal chelates according to following equation:

$$NO + Fe^{II}\text{-}R \rightarrow NO\text{-}Fe^{II} + R$$

This nitrosyl metal chelates reacts with another absorbed gas, SO_2, to regenerate the original chelates.[9] Unfortunately, however, all of these processes suffer from problems such as expense of the oxidizing reagent, much too complicated processes for utilities, necessitating taking care of the by product or high energy cost of regeneration.

Up to this day, therefore, these processes have not approached the stage of commerical use.

2.1.2 Physical Absorption

To eliminate all these difficulties, removing SO_2/NOx by physical absorption provides a satisfactory answer. If SO_2 or NOx is absorbed physically, the regeneration step can be done in a stripper tower. Thus using a absorber-stripper towers with absorbing solvent and flue gas fed countercurrently, NOx and SO_2 can be removed. This simplfies the process and also minimize the energy requirement for regerneration. Consequently, looking for a solvent that can absorb NOx and SO_2 is emphasized for developing an economical way to clean the flue gases.

In 1973, Chappel[10] tested several solvents as physical absorbers, such as sulfite solution and concentrated aqueous soluble amines. He found concentrated amine solution were very effective. In 1977[11], Exxon Corporation examined a number of aqueous soluble hindered amine solutions and sterically hindered amino alcohol for their ability in absorbing acid gases, especially CO_2. They claimed that the sterically hindered amino alcohols which containing at least one secondary amino group attached to either a secondary or tertiary carbon atom, or a primary amino group attached to a tertiary carbon atom, have good potential to be the solvent desired. The most preferred sterically hindered amino alcohols include 2-amino-2- methyl-1-propanol, 2-amino-2-methyl-1-butanol, 3-amino-3-methyl-1-butanol and 3-amino-3-methyl-2-pentanol. The hindered amino alcohol, 2-amino-2-methyl-1-propanol was selected as one of several organic solvents to be exaimed in our work becaused of its low toxicity and cost.

2.1.3 Determination of Activity Coefficient at Infinite Dilution from Gas-Liquid Chromatography

The measurement of the activity coefficient at infinite dilution was previously determined by graphical extrapolation of classical vapor-liquid equilibrium data. Not until 1952 did a simple and accurate way using gas-liquid-chromatography was suggested by Jones and Martin.[12] Many experiments were carried out by these investigators and the activity coefficient values obtained were found to be thermodynamically reliable and compared well with those values determine from the extrapolation method.

To determine the activity coefficient at infinite dilution from GLC, the substrate inside the columns have to be coated with solvent before injecting the gases. Formerly the substrate was coated by immersing it in the solvent, leaving it overnight, then drying it with oven before pouring into a column.[13] Not until 1963, was this time consuming method replaced by directly inject the solvent into column as was suggest by Sheets and Marchello.[14] The idea behind this operation is, first the solvent was vaporized in the inject pore, and the vapor is pushed into a cooler column by carrier gas, so the vapor of solvent is condensed as it moves alone the column and the substrate is thus coated.

2.2 Progress of Liquid Membrane Technology

Liquid membranes come in two types: First the immobilized membrane in which the liquid is impregnated into the pores of a solid disk. This disk is sandwiched by two gas premeable polymer sheet on both side to prevent lost of liquid. The selected molecule premeates from one side to the other.[25] The other type of membrane is an emulsion membrane, also called liquid surfactant membrane, which was invented by Norman Li in 1968.[26] It consist of droplets or microspheres (a few microns in diameter) that are mixed with an aqueous solution of material to be treated. These membranes are made by forming an emulsion of two immiscible phases and then dispersing the emulsion in a continuous phase. This kind of liquid membrane, usually contain surfactants to stabilize the membrane. Because of the selectivity of a particular kind of molecules form, liquid membranes are usually tailor-made in order to meet the specific requirements.[27]

Many studied have been carried out in theory and application of liquid membrane up to the present day. These works have been summerized by Schultz et al.[28,29] and Smith et al..[30] Kimura et al.[31] discussed the potential industrial application of the facilitate transport membrane. Goddard[32] treated the application of facilitated transport under reaction equilibrium condition. As far as the application of liquid membranes to remove acid gas is concern, not much work have been done at this point. However, since NO react reversibly with Fe^{II}, Fe^{II} can be used as a carrier to faciliate the transport of NO through solvent. In 1970, Ward[26] carried rried out an experiment and mathematical investigation of this facilitated transport system. He measured the flux of NO through a liquid layer immobilized between two thin polymeric films with and without Fe^{II}. The numerical solution compared favorably with the experimental result.

3.0 EXPERIMENTAL APPARATUS AND PROCEDURE

3.1 Gas-Liquid Chromotography Apparatus

The main part of the apparatus to carry out this study on activity coefficients at infinite dilution was a Hewltt-Packard Model 5750B research gas chromatograph. Two Supleco stainless steel columns (8 ft long, coiled 8 inches in diameter, and 0.04 ID) were employed. The columns were packed with 28.1 grams of chromasorb GAW Mesh 80/100 as substrate. Helium was used as a carrier gas and was kept at 40 psi at the exit of main tank. A pressure gauge was connected just before the entrance of the column to measure the gas inlet pressure. The helium flow rate was measured with soap-flim meter at outlet of the chromatograph. An Hewlett-Packard Model 3380S integrator was used to determine the retention time of exiting gas. At the end of each experiment, a water cooled graduated cylinder was placed at the outlet of chromatograph to recover the solvent. A diagram for the apparatus is shown on figure 1.

3.2 Experimental Procedure

The columns were first conditioned overnight at

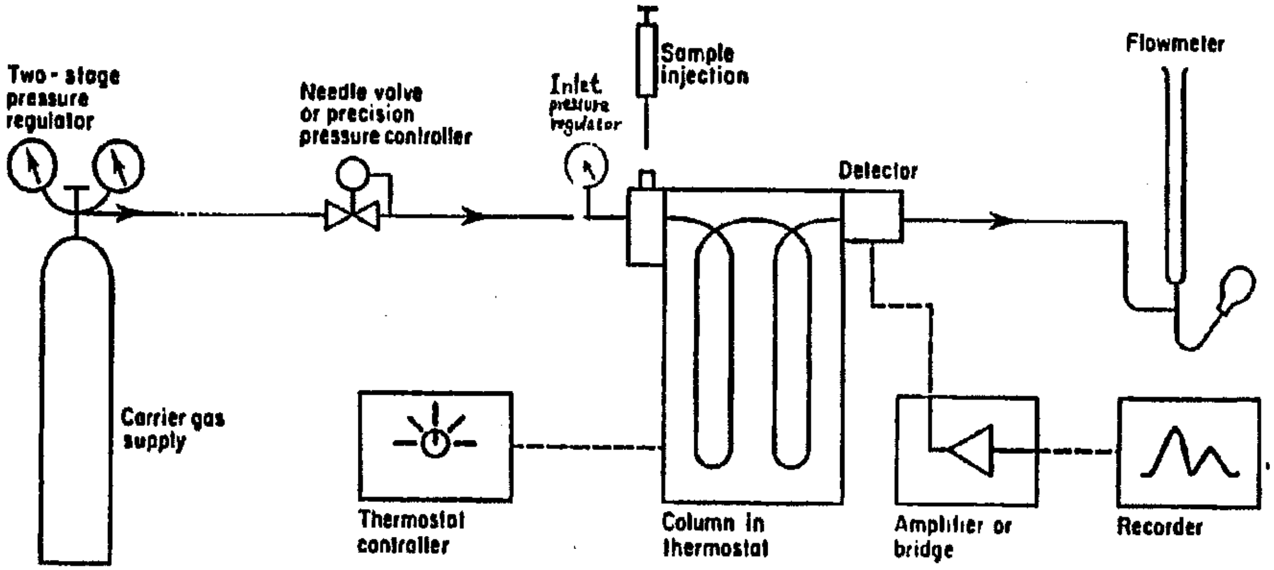

Figure 1 Gas chromatograph for physicochemical measurement

temperature 300^oC^{15} and 10 cc/min of carrier gas flow rate before coating the substrate in order to remove any impurity and dirt that deposit on the column substrate. To coat the substrate with the solvent of interested, the injection port was heated to a temperature well above the boiling point (about 20°C above) of that solvent to assure a complete vaporization. When the solvent was first injected, a huge peak due to the solvent vapor will be shown on the recorder. The temperature of oven was kept at a point so that the peak was at least 30 minutes in width.* After the base line become hornorzontal again, another 30 minutes was allowed to assure an even disturbition of solvent in the column. In all experiments, a flow rate of 10 cc/min of carrier gas and oven temperature in the range of 80 - 120 °C below the boiling point of solvent was employed.

Since the retention time difference between absorbed

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*The even distribution of solvent in the column can be achieved by setting the carrier gas flow rate low and oven temperature at a range so the solvent is not condensing too slow or too fast. The proper oven temperature for each particular solvent is found by trial-and-error in present experiments.

and nonabsorbed gas is independent of the concentration of each gas in the mixture injected, the exact amount of NO or SO_2 taken for each run was not recorded as data. Usually a 0.3CC - 0.5CC mixture of NO or SO_2 with the non-absorbing gas was injected each time. (The NO was mixed with $N_2$and SO_2 was mixed with air).

After obtained the retention times at various temperatures, the solvent is collected by heating the oven with an temperature increment as slow as 1°C/min to 300°C and remaining overnight to completely vaporize the solvent in the column. The purged gaseous solvent passed from the exit port into a graduated cylinder which was placed in an water cooled dewar to minimize the solvent loss. It was found that the collected solvent was greater than 97% wt of the originally liquid injected in all cases.

3.3 Making Liquid Surfactant Membranes

In making liquid surfactant membranes by agitation,[33] the size and quantity of membranes are depended on the viscosity of continuous phase, diameter of impeller and speed of agitation. The first step is rapid stirring of an oil and water mixture to make a water-oil emulsion. The emulsion was stablized by an oil soluble surfactant. When this emulsion was added to second phase with moderate stirring, a water-oil-water liquid surfactant membrane was obtained.

A typical procedure of making water-oil-water membrane is as following:[3] (To make sure liquid membrane exist, an acid-base indicator is added inside membrane and observe the color change of membrane phase by adding acid and base alternately.)

1. Making Emulsion

    A. Mix 200 ml heavy mineral oil with 10 g Span 80 Sorbitan Monooleate (an oil soluble surfactnat) using a turbine impeller (2.5 in diameter) stirred at speed of 1500 RPM for 10 minutes to distribute Span 80 homogeneously in the oil.

    B. After 10 min, add 100 ml 5% wt. of NaOH + phenolphthalein. Allow mixing to take place for 20 minutes. (At end of this 20 minutes, the solution should be in an emulsion phase)

2. Making Membrane

    A. Add 80 ml distilled water to 150 ml of emulsion, using a marine impeller (2.5 in diameter), mix for 60 minutes at 500, 750 or

1000 RPM for different quantities of membrane to form.

After letting the solution settle for more than 5 minutes, it may seperate into 3 phases. The bottom phase is aqueous NaOH, the middle phase is emulsion and the top phase contains the membranes. Under a powerful microscope, the emulsions and membranes are shown on figure 2. The emulsions have average size 5 um and membranes have average size 20 um. The sand or powder-like fine particles abround the membrane were the phenolphthalein.

3.4 Immobilized Liquid Membrane Apparatus

The apparatus for acid gas diffusion through liquid membrane experiment is shown on figures 3 and 4. Twq aluminum disks and one teflon disk were used to immobilize the liquid membrane. Two teflon sheets, 0.2 um in pore size from Gelman Instrument Company, were used as membrane supporter. Each disk has three 5/8" dia holes in order to permet the gas to diffuse through it. These 3 disks were assembled and held together by 6 screws. The liquid is placed in the teflon disk and held by the 2 teflon sheets on either sides.

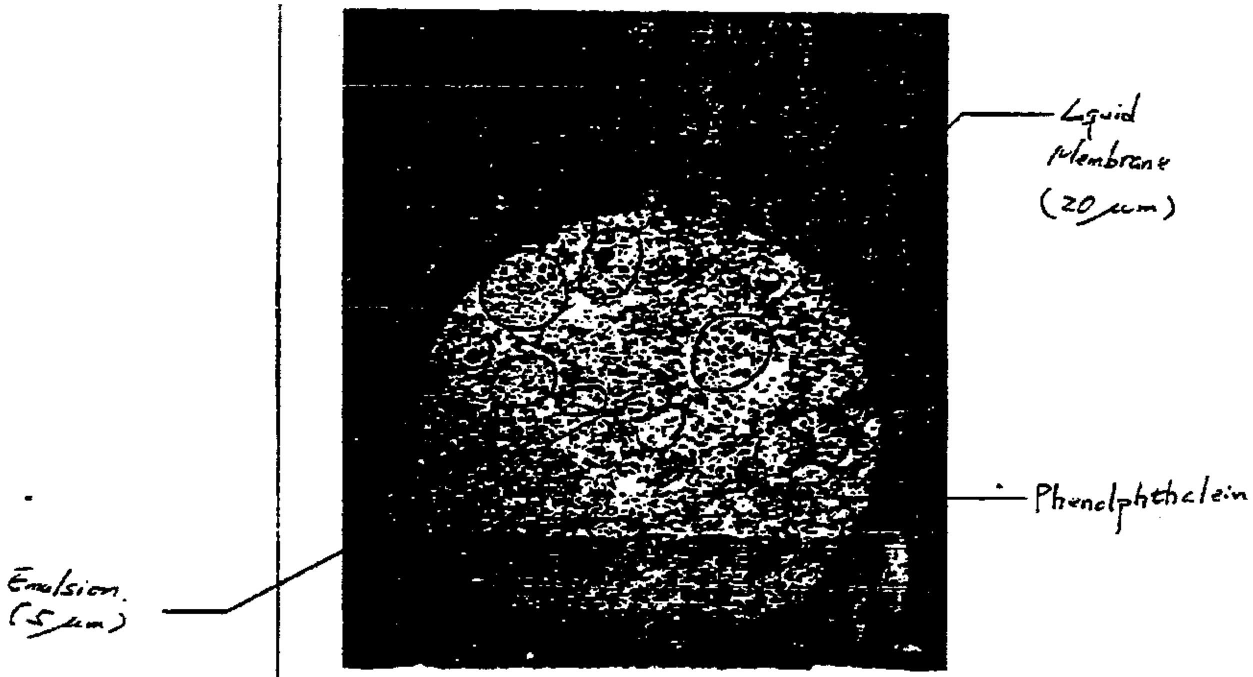

Fig. 2 Liquid Surfactant Membrane Under Microscope

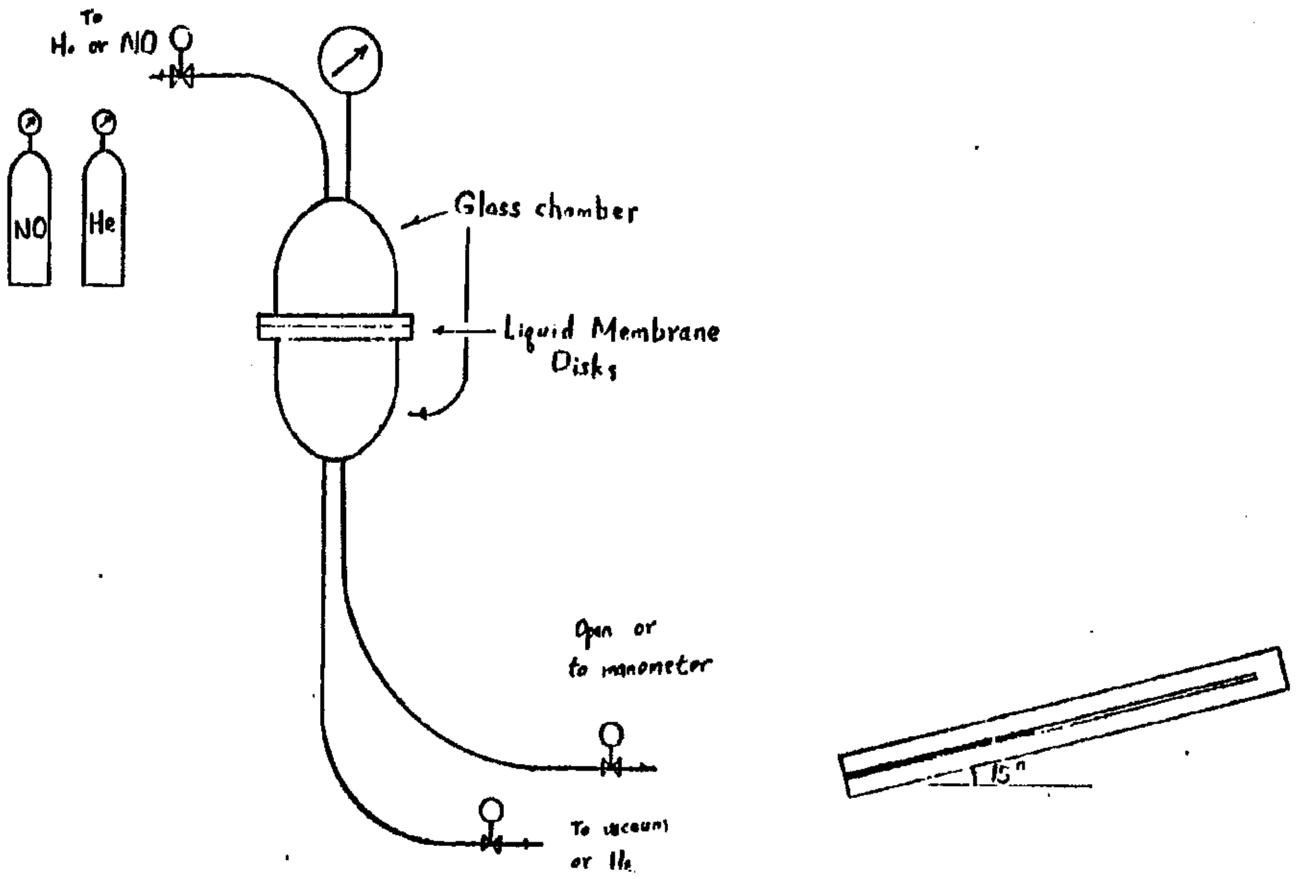

Fig. 3 Diagram of Immobilized Liquid Membrane Apparatus

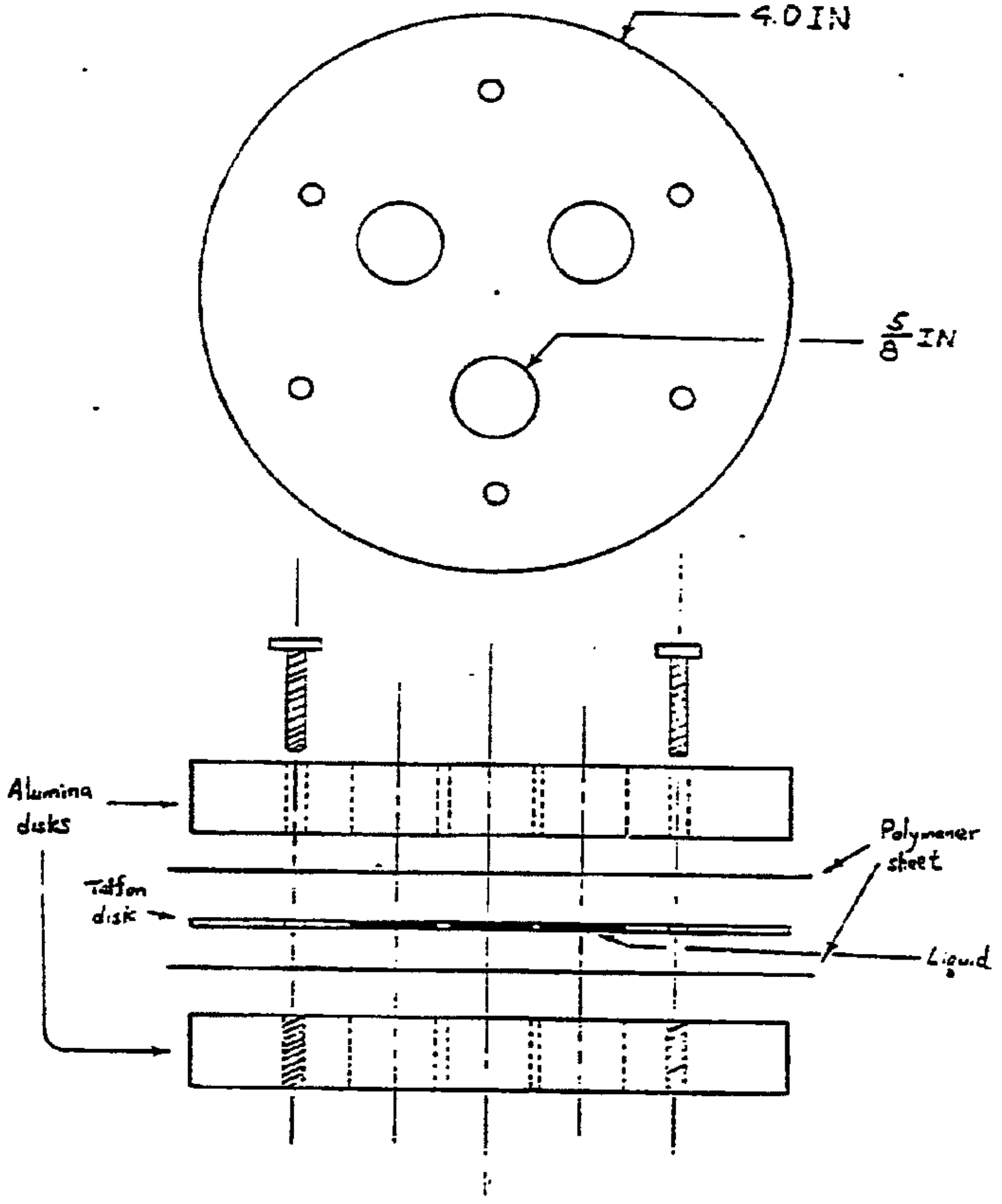

Fig. 4 Liquid Membrane Disks

These disks, after assembled together, are sandwiched between the two chambers. The top chamber contains the gas to be examined and the bottom one contains the inert gas and is connected to an inclined manometer.

3.5 Experiment Procedure for NO Diffusion

In making the immobilized liquid membrane, one has to be careful that no air bubbles exist in the membrane. After assembly, vacuum grease is used to ensure no leaks occure around the bolts.

Before starting the tests, the top and bottom were both purged with helium for 3 minumtes. The top chamber is evacuated before NO is injected. The pressure change on the bottom is shown on the inclined manometer.