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GROWTH AND CHARACTERIZATION OF III - V EPITAXIAL FILMS

Parke Mathematical Laboratories

A. Tripathi and J. Adamski

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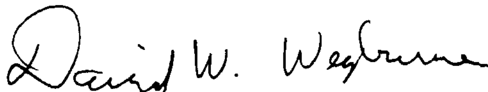
APPROVED: 

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13. ABSTRACT (Maximum 200 words)
Investigations were conducted on the growth of epitaxial layers using Organo Metallic Chemical Vapor Deposition technique of selected III-V materials which are potentially useful for photonics and microwave devices.

RL/ERX's MOCVD machine was leak checked for safety. The whole gas handling plumbing system has been leak checked and the problems were reported to the manufacturer, CVD Equipment Corporation of Dear Park, NY. CVD Equipment Corporation is making an effort to correct these problems and also supply the part according to our redesign specifications.

One of the main emphasis during this contract period was understanding the operating procedure and writing an operating manual for this MOCVD machine.

To study the dynamic fluid flow in the vertical reactor of this MOCVD machine, an experimental apparatus was designed, tested and put together. This study gave very important information on the turbulent gas flow patterns in this vertical reactor. The turbulent flow affects the epitaxial growth adversely. This study will also help in redesigning a vertical reactor so that the turbulent gas flow can be eliminated.

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SUMMARY OF OBJECTIVES

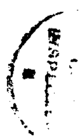
The general subject of this program was that of development of new or adapt existing methods for the preparation, growth and characterization of III-V electronic and optoelectronic materials for MOCVD technique. Investigations were conducted on the growth of epitaxial layers using organometallic chemical vapor deposition method of selected III-V materials which are potentially useful for photonics and microwave devices. The following is a list of specific tasks accomplished during the contract period:

a. Developed new or adapted existing III-V substrate preparation techniques to insure high mobilities and good morphology of the epitaxial layer grown on the substrate.

b. Investigatedthe epitaxial growth characterstics of III-V single crystal epitaxial layers employing RADC metal organic chemical vapor deposition system.

c. Developed new or adapted existing III-V epitaxial layer characterization method to determine the layer mobility, composition, thickness, and carrier concentration.

d. Developed new or adapted existing characterization method to determine the quality of multilayered epitaxial structures for photonics and optoelectronic devices.



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CHAPTER 1

INTRODUCTION

During the life of this contract emphasis was placed on installing the machine, testing for the safety, labelling, and understanding the operating procedures of the different components of the new RADC's Metal Organic Chemical Vapor Deposition (MOCVD) system supplied by the CVD Equipment Corporation. Also, an attempt was made to redesign and write an operating manual for the MOCVD machine.

This report contains the information on safety precautions and operating procedures for safe and efficient handling of the hazardous materials, which is very important for the safe operation of the MOCVD crystal growth laboratory. Even though RADC's main emphasis is on InP, GaInAs, and GaInP based devices, the work done during this contract period was on GaAs epitaxial layer. The reason for doing this is to find the problems existing with the RADC's MOCVD machine. As soon as the leak and fluid flow dynamic problems are solved, work on InP related compounds will begin.

The main emphasis was on installing and tesing the whole MOCVD system for leaks and also finding out which components of this machine did not work. The major problems found were with (1) the donut shaped heater, (2) the feedthrough for the heater, (3) the reactor, and (4) the gas plumbing system. CVD Equipment Corporation was brought in to do final tune-up which turned into a major system change as many problems were uncovered. The major changes included new quartz bell jar shaped reactor design, new heater design and numerous gas plumbing changes.

During this contract period fluid flow dynamics of the MOCVD reactor was studied which helped in understanding the flow patterns in the low pressure MOCVD reactor.

CHAPTER 2

EPITAXIAL GROWTH MECHANISM FOR III-V COMPOUNDS USING MOCVD

MOCVD is a vapor phase process using organometallics as starting materials. For the growth of III-V semiconductors, metal alkyls such as trimethylindium (TMI), Triethylindium (TEI), and Trimethylgallium (TMG) are typically used as the sources of the group III elements. When hydrides from the group V elements like arsine and phosphine are mixed with the metal alkyls at elevated temperatures in the vapor phase, reactions take place resulting in the deposition of single crystal layers of III-V compounds.

General Outline of Epitaxial Growth Mechanism

The most general concept of the growth mechanics which is needed to be outlined is the sequence of events which take place in the reactor. Initially, the group III constituents are introduced into the gas stream by bubbling ultrapure hydrogen carrier gas through a trimethygallium (TMG) (trimethylindium (TMI)) or triethylgallium (TEG) (triethylindium (TEI)) liquied sources. The vapor pressure of the source is exponentially dependant upon the temperature, hence the desired concentration of TMG (TMI) or TEG (TEI) can be controlled by varying the temperature and the hydrogen flow into the bubbler. The actual flow (cc/min.) of TMG (or TEI) into the reactor can be calculated using the formula:

$$F_{TMG/TEI} = \frac{\text{vapor pressure (TMG/TEI)}}{\text{pressure (reactor)}} \text{ (flow } H_2 \text{ into bubbler)}$$

The group V hydride concentration into the reactor can be directly manipulated by regulating the flow of AsH_3 or PH_3 from a 100% AsH_3 or PH_3 cylinder tank respectively. Both the AsH_3 (or PH_3) and TMG (or

TEI) are carried to the reactor by the ultra-pure hydrogen. For a given system, the concentrations of the respective gases can be varied over a range of values; typically the mole fraction of the TMG is in the 10^{-4} range, the mole fraction of the AsH_3 is in the 10^{-3} range and the total flow of gas through the ractor might vary from 1 to 10 liters per minute. The next step requires the reactants to be transferred to the growth site. This takes place by diffusion and/or convection from the main gas stream to the wafer. After the reactants are absorbed at the surface the reaction takes place. At this point, the GaAs (or InP) composes, it attaches to the existing substrate lattice, and the reaction by-products need to be desorbed from the surface and transferred back to the main gas stream. A summary of the steps taking place is given below:

1. Transport of reactants to epitaxial growth region
2. Transfer of reactants to crystal surface
3. Adsorption of reactants
4. Surface reactions
5. Desorption of products
6. Transfer of products to main gas stream
7. Transport of reactants out of epitaxial region

If these steps occur consecutively, then the slowest step will dominate the growth process; this is the rate limiting step. However if some of these steps occur simultaneously, then the fastest sequence will dominate the growth. It is possible that this parallel process occurs during the reaction/incorporation segments since it is not quite certain whether the constituents react and then move to a growth site or if they move to a growth site and then react.

Depending upon which steps of the sequence are dominating the process, the epitaxy can be under one of three different regions of control. The first, mass transport type I, occurs when the process is input rate limited. Here, it is assumed that the surface reactions

and diffusion are in equilibrium and that the growth is governed by the rate at which the species move to and from the reaction site. The second, mass transport type II, is considered to be mass transfer limited. In this case, the diffusion of the reactant to the lattice regulates the growth process. Finally, if the sequence is most dependant upon the surface reactions, the system is under Kinetic control. When this occurs, the transport is occurring at a faster rate than the surface kinetics and therefore, the surface reactions are most important.

By varying the growth parameters, and monitoring the growth rate, one might be able to determine the region of control they are operating in. For instance, if the growth rate is strongly influenced by varying the reaction temperature, then the system is probably in the kinetic control regime. However, if the mole fractions of the gas greatly affect the growth, then the system is mass transport limited. Looking at the effect of varying certain parameters is one technique for investigating the growth mechanics. The growth process will probably shift from one type of control to another, depending upon the gowth parameters.

The three major regions of the growth process are the input stage, where the reactants are introduced, the mixing stage, where possible adduct formation and elimination reactions take place, and the substrate surface, where growth proceeds.

Homogeneous Gas Phase Reactions

The state of the reactants and products in the gas phase has been a topic of vast uncertainty. There are three major phenomena which need to be investigated, adduct formation, polymer formation, and decomposition vs. composition.

An adduct forms when an electron acceptor molecule (Lewis Acid)

combines with an electron donor molecule (Lewis Base). The amount of adduct formation depends primarily on how extensively the two molecules are mixed at low temperatures. However, an important aspect of the adducts in the gas phase is not how it forms, but how it decomposes. Since the bond energy is low, the adduct could just break apart into TMG/TEI and AsH_3/PH_3 as it moves further into the high temperature region in the immediate vicinity of the susceptor. This process would have very little effect on the reaction mechanisms. More importantly though, the adduct could go through an elimination reaction as it approaches the wafer. If this occurs, the $R_3III:R_3'V$ molecule sequentially loses RR' groups until a very strongly bonded, highly reactive RIII:RV polymeric molecule remains (where the R represents the methyl or ethyl group and the R' represents the hydrogen for the GaAs or InP reaction). Since there are two dangling bond sights, the RIII:RV readily forms (RIII:RV)n polymers if possible. Although adduct and polymer formations in MOCVD might be limited, it should be considered since the RIII:R'V molecule could be a source of carbon incorporation into the lattice.

The other aspect of the gas phase reactions involves the decomposition or pyrolisis of the various III-V constituents. Many researchers feel that the TMG and/or TEI molecules and the AsH_3 and/or PH_3 molecules become pyrolised as they enter and pass through the boundary layer. D.H. Reep [1] have calculated that the activation disassociation energies for the three $GaCH_3$ bonds are 59.5, 53.4, and 77.5 Kcal/mole, respectively. Hence, it is thought if there is enough energy, the first two methyl groups will be released and a tightly bonded $GaCH_3$ compex will remain. Much of the general acceptance of this theory lies in the experimental data which presumably supports this concept.

I.R. spectroscopy by various groups has shown there to be no TMG in the boundary layer region. In particular, M.R. Leys and H. Veenliet [2] used in-situ I.R. spectroscopy where the sampling probe

was 0.2 cm above the substrate. It is concluded that at a temperature above approximately 600° C, all the TMG in the boundary layer has been decomposed. Also, Leys and Veenviet point out that the sensitivity of the spectrum for TMG is about 1% of the TMG at the input (P_{TMG} at input = 1 X 10^{-4} atm). J. Kishizawa and T. Kurabyashi [3] have also done extensive I.R. spectroscopy on AsH_3 and TMG + AsH_3. It is shown that the TMG approaches 100% decomposition at about 600°C while the AsH_3 does not decompose nearly as much.

However, when the TMG/TEI is introduced to the AsH_3/PH_3, the AsH_3/PH_3 decomposition is enhanced, and when a GaAs/InP substrate is included, the decomposition of AsH_3/PH_3 progresses even further. The availability of the methyl/ethyl groups seem to be responsible for the increased AsH_3/PH_3 decomposition, while the GaAs/InP substrate seems to act as a catalyst. Much of this data implies that the pyrolisis of the AsH_3/PH_3 and the TMG/TEI is a major step in the growth mechanics.

Finally, it has been found that under the proper growth conditions an appreciable amount of TMG/TEI and AsH_3/PH_3 is still available in the vapor phase at the substrate. Considering the high linear velocities of the gases and the time necessary for 100% decomposition of TMG/TEI and AsH_3/PH_3, the concentration of TMG/TEI and AsH_3/PH_3 in the gas phase must be considered.

Needless to say, the homogeneous gas phase reactions in MOCVD are difficult to precisely predict; given the strong dependence on temperature and the temperature gradient across the reaction chamber, it is difficult to identify which species are dominating the gas phase composition. Some possibilities are, (RIII:R'V)n polymeric compounds, $(GaCH_3)$n polymeric compounds/(InC_2H_5)n polymeric compounds, AsH_2/PH_2, AsH/PH, TMG/TEI, and AsH_3/PH_3. By implementing several sequences of crucial experiments (possibly including some form of spectoscopy), the gas phase compostion could be better defined than it is to date.

Surface Reaction

Given the information on the gas phase composition, there are three genreal theories for the surface reaction. The first two assume that the gas phase is dominated by $GaCH_3/InC_2H_5$ molecules and various forms of As/P constituents as explained by the pyrolisis concept. Here the $GaCH_3/InC_2H_5$ and AsH/PH molecules are absorbed at the surface, then the reactions between the two molecules transpire and the CH_4 by-product is desorbed from the surface.

The second alternative being that the $GaCH_3$ /InC_2H_5 is absorbed at the surface, and then diffuses to the appropriate Gallium/Indium kink site, where it forms GaAs/InP. Hence, this process is enhanced by the concentration of arsenic/Phosphorus. The final possibility postulates that an abundance of TMC/TEI and AsH_3/PH_3 exists at the substrate surface. Now as the TMG/TEI collides with the AsH_3/PH_3 at the surface, the complete reaction occurs, forming GaAs/InP and Methane/Ethane.

All of these surface reactions are assuming ideal thermodynamic conditions. In reality, under certain conditions, the thermodynamics may not be as desirable where upon incomplete reactions may occur.

Boundary Layer Diffusion

In the 600-800°C range, it is generally considered that the reaction mechanisms are not the rate limiting step of the growth process. In this range, the diffusion of the species through the boundary layer to the surface proceeds slower than the surface reaction and is therefore the limiting step of the growth process. Hence, the growth rate is almost entirely controlled by the diffusion mechanisms.

The boundary layer is the sliver of the gas stream above the wafer

that the constituents diffuse through in a very short period of time. It is not actually a stagnant region above the substrate, however, such a concept helps to visualize the diffusion process. Obviously, if the boundary thickness varies over the growth area, then the diffusion time will vary and the growth rate will not be uniform across the substrate.

Since the ratio of the group V partial pressure to the group III partial pressure is usually large (at least 10), then the diffusion of the group III molecules limits the growth rate. The flux of the group III molecules may then be written as:

$$J_{III} = D_{III} (P^{o}_{III} - P_{III})/RTd$$

where D_{III} is the diffusion coefficient in the gas stream and it is dependent upon T^2, P_{III} is the partial pressure at the growth inerface and d is the boundary layer thickness. As the boundary layer thickness is decreased or the reactant partial pressure is increased, the flux will increase, therefore increasing the growth rate.

EFFECTS OF TEMPERATURE, PRESSURE, TOTAL FLOW, MOLE FRACTIONS, AND SUBSTRATE:

In this section the general effect on the growth process of varying the major growth parameters in the MOCVD system is considered.

Varying the temperature of the susceptor can strongly effect both the surface reactions and the gas phase reactions. In the gas phase the temperature greatly influences the amount of TMG/TEI and AsH_3/PH_3 decomposition. Also, the temperature and the magnitude of the temperature gradient can greatly affect the formation of adducts and polymers. At low temperatures, the effect of reduced reaction rates, incomplete reactions, and less decomposition might be so great that the system would shift from diffusion limited growth to kinetically

controlled growth, while at the high temperature end, increased deabsorption from the surface, and extensive decomposition, again might precipitate kinetically controlled conditions.

The direct effects of total pressure probably has very little effect on the reaction mechanisms since the partial pressures are the dominating aspect in the reaction. However, by reducing the total pressure, the linear gas flow velocity is increased. This change in linear velocity definitely will influence the boundary layer thickness and diffusion rate since the flux rate is proportional to the square root of the velocity. Also, increasing the velocity will reduce the amount of time the molecules spend in the high temperature zone. Obviously this should effect both the extent of molecular decomposition and the completion of various gas phase and surface reaction.

Changing the total flow, again, will change the linear velocity of the gases. Hence, changing the total flow should give some similar results to changing the total pressure.

Varying the mole fractions (or partial pressures) of the input gases probably has the strongest influence on the reaction mechanisms. The concentration of the constituents in the gas phase strongly affects the availability of all the different forms of the group III and V reactants at the substrate. These changes will drastically affect both impurity incorporation and growth rates. Also, the partial pressures of the reactants will determine the boundary layer diffusion rates; hence, the mole fractions will strongly affect those systems which are in the mass transport I and II regime.

Finally, the substrate can be considered as a heterogeneous catalyst. Primarily, the substrate acts as a site for the reaction to occur. The large energy liberation of the reaction needs to be transferred to something; the substrate is an ideal sink for the

generated reaction energy. Also, if the molecules lightly bond with the dangling bonds on the substrate surface, the reactants molecular bonds and bond energies will be stretched, and distorted. This would catalyze the reaction, affecting both its rate and completeness.

It must be kept in mind that parameters which effect the reaction mechanisms may be masked out when the system is in the mass transport regime. This is not to say they are not important, since the reaction mechanisms can influence both the growth rate and impurity incorporation.

IMPURITY INCORPORATION:

One of the driving forces in studying MOCVD growth mechanics is the incorporation of impurities. There are many intrinsic impurities which are generally found in MOCVD GaAs/InP; a few of the primary impurities are, silicon, germanium, zinc, and carbon. From the data it appears that the donor incorporation can be controlled by adjusting the temperature and the V/III ratio. On the other hand, the carbon in the films generally increases at low ratios and at elevated temperatures. It is conceivable that the carbon is directly incorporated into the lattice either when incomplete surface reactions occur or when carbon containing polymeric complexes react at the surface. Depending upon which molecules dominate the gas phase reactions as well as which surface reaction is most prevalent, the incorporation of the carbon can be explained. Hence, more experimental research needs to be done to determine the dominating phenomena in the gas phase and at the surface.

CHAPTER 3

APPARATUS

The RADC/ESM'S MOCVD system consists of four major components:

a. The gas handling system which includes the group III source alkyls, group V source hydrides, dopants, all of the valves, plumbing, and instruments necessary to control the gas flows and mixtures.

b. The reaction chamber in which the pyrolysis reaction and deposition occur.

c. The heating system used to obtain pyrolysis temperatures.

d. The exhaust and the low pressure pumping systems.

Each component of the MOCVD system is discussed below:

a. Gas handling system

The purpose of the gas handling system is to deliver precisely metered amounts of uncontaminated reactants without transients due to pressure or flow changes.

Pd-purified hydrogen gas is used as the carrier gas. The inert nitrogen gas is used for purging purposes and also for actuating the air operated valves.

The group III alkyls are held in temperature controlled baths and electronic mass flow controllers are used to regulate the carrier gas. The group V hydrides are introduced as dilute mixtures (5-10%) in hydrogen, but there is a provision for using 100% concentrations of

these hydrides. Again electronic mass flow controllers are used to meter the reactants. The dopants can be used either as alkyls or hydrides.

Each of the reactants is fed into a common manifold, with alkyls, hydrides and dopants separated until introduction into the reactor. The valving provisions are employed to switch the sources from reactor manifold to a bypass manifold. This allows the intervening piping to fully purge before injection into the reactor, and it also allows injection into the reactor to be terminated without flushing excessive lengths of tubings. All the gas handling system is assembled form stainless steel tubing and valves. All the valves are automated and interfaced with computer, as the mass flow controllers. Manual operation is possible, but the requirements of complex multilayered and graded structures make non-automated systems difficult to use reliablly.

The gas handling manifold for the low pressure system has a control valve between the manifold and the low pressure reaction chamber which allows the gas handling system to operate at fixed pressure independent of reaction chamber. This is done because it is essential to maintain a constant pressure over the group III alkyl source since this pressure influences the vapor concentration in the gas phase.

b. Reaction chamber

The RADC MOCVD system has a vertical reaction chamber. In this vertical reaction chamber, the reactants are introduced from the top. The substrate wafer lies flat on top of a moly susceptor which can be rotated at different speeds. The reactor has a 1/4" inject tube made of quartz which is used to spread the flow of the inlet reactants. To decrease the possibility of gas contaminating spent reaction products to recirculate in convection currents and to become entrained in the

inlet stream, the inject tube is placed 1" above the moly susceptor. The reaction chamber is cooled by a chilled water jacket placed around it.

Leak checking of the gas handling system

The source reactants used in the MOCVD system are highly toxic, ultra pure and reactive gases. It is therefore necessary to leak check the system when new, and again after any equipment replacement in the gas distribution system. A helium leak detector capable of detecting leaks in the range of $1X10^{-6}$ cc/sec of helium is used for leak checking the system.

Using the schematic diagram showing gas flows and relative component placement all the gas distribution system is labelled and the flow directions are marked. This marking is used as reference during leak test.

Never use a leak detector on a gas transfer line filled with a reactive gas without purging completely with several purge cycles using Nitrogen as purge gas.

Preliminary leak test of sections of the system is done by checking for pressure decay over 5 minute time periods. Then each section is -tested for leak using helium leak detector.

The procedures of leak checking is given below:

A. Leak check of PH_3-A Line

Note : Close the PH_3 tank.

a. **Source line:**

CLOSE Valve	OPEN Valve
Hand valve (HV) 21	HV 20
HV 6	HV 4
HV 7	HV 5

Pump down using helium leak detector and perform leak test. This procedure tests for leak in the plumbing from PH_3 tank to the MOCVD sytem.

b. **Vent line:**

CLOSE Valve	OPEN Valve
HV 21	HV 20
HV 4	HV 5
HV 6	HV 7
Air operated valve (AOV) 8	AOV 9 (SW9)

Note : AOV 8 ==> SW 8 & AOV 9 ==> SW 9

SET

MFC 9	TO	200 sccm
AOV 38	TO	"VENT"
SWITCh (SW) 54	TO	"OFF" POSITION

Pump down using leak detector and perform the leak test.

c. **Inject line:**

CLOSE Valve	OPEN Valve
HV 21	HV 20
HV 4	HV 5
HV 6	HV 7
AOV 8 (SW 8)	AOV 9 (SW 9)

SET

MFC 9	TO	200sccm
AOV 38	TO	INJECT
SW 54	TO	"OFF" POSITION
SW 51	TO	"OFF" POSITION

Perform the leak test using the helium leak detector.

B. Leak check of PH_3-B line

Note : Close the PH_3 tank.

a. Source line:

CLOSE Valve	OPEN Valve
HV 21	HV 20
HV 10	HV 8
HV 11	HV 9

Perform the leak test.

b. Vent line:

CLOSE Valve	OPEN Valve
HV 21	HV 20
HV 8	HV 9
HV 10	HV 11
AOV 14 (SW 14)	AOV 15 (SW 15)

SET

MFC 12	TO	200 sccm
AOV 41	TO	"VENT"
SW 54	TO	"OFF" POSITION

Test for leak using helium leak detector.

c. **Inject line:**

CLOSE Valve	OPEN Valve
HV 21	HV 20
HV 8	HV 9
HV 10	HV 11
AOV 14 (SW 14)	AOV 15 (SW 15)

SET

MFC 12	TO	200sccm
AOV 41	TO	"INJECT"
SW 54	TO	"OFF"
SW 51	TO	"OFF"

Test for leak.

C. Leak check of AsH_3 line

Note : Close the AsH_3 tank.

a. **Source line:**

CLOSE Valve	OPEN Valve
HV 21	HV 20
HV 14	HV 12
HV 15	HV 13

check for the leak.

b. **Vent line:**

CLOSE Valve	OPEN Valve
HV 21	HV 20
HV 12	HV 13
HV 14	HV 15
AOV 12 (SW 12)	AOV 13 (SW 13)

SET

MFC 11	TO	200 sccm
AOV 40	TO	"VENT"
SW 54	TO	"OFF"

c. **Inject line:**

CLOSE Valve	OPEN Valve
HV 21	HV 20
HV 12	HV 13
HV 14	HV 15
AOV 12 (SW 12)	AOV 13 (SW 13)

SET

MFC 11	TO	200sccm
AOV 40	TO	"INJECT"
SW 54	TO	"OFF"
SW 51	TO	"OFF"

D. Leak check of HCl line

Note : Close the HCl gas tank.

a. **Source line:**

CLOSE Valve	OPEN Valve
HV 21	HV 20
HV 18	HV 16
HV 19	HV 17

Pump down and leak check.

b. **Inject line:**

CLOSE Valve	OPEN Valve
HV 21	HV 20
HV 16	HV 17
HV 18	HV 10
AOV 18 (SW 18)	AOV 19 (SW 19)

SET

MFC 14	TO	100sccm
SW 49	TO	"OFF"

Note : There is no vent line for HCl.

CHAPTER 4

HYDROGEN PURIFIER

OPERATING PRINCIPLES

The Palladium Diffusion Process purifies gaseous hydrogen in a purity beyond the limits of any known means of detection. The purification is accomplished by taking advantage of a property of a palladium-silver alloy which exhibits selective permeability to hydrogen gas. The hydrogen gas will diffuse through the palladium-silver alloy but other gases will not. The metal is impervious to any impurity.

The rate of hydrogen diffusion:

1. Varies directly with the surface area of the palladium alloy.

2. Varies exponentially with the temperature, increasing at a decreasing rate as the temperatue increases.

3. Varies directly with the difference between the square roots of the partial pressures of hydrogen on both sides of the palladium alloy tubes.

4. Varies inversely with the thickness of the palladium alloy septum in the direction of flow.

In service, under operating conditions, the pure hydorgen flow rate is adjusted and controlled by the inlet pressure. The hydrogen puifier contains a fixed length of tubing of definite wall thickness so that the surface area and septum thickness are constant. By controlling the operating temperature to 400°C, the temperature

variable is eliminated. (This temperature of 400°C is the optimum operating temperature which will give the highest output of pure hydrogen consistent with long life of the palladium alloy tubes). The difference between the square roots of the partial pressures of hydrogen on both sides of the tubes is the only remaining variable affecting the pure hydrogen flow rate. The flow rate of pure hydrogen then is adjusted with the pressure of the impure hydrogen entering the purifier. The pressure of pure hydrogen can also adjust the flow rate, however, under operating conditions it is usually held constant. The inlet pressure is limited by the physical strength of the tube wall and should not exceed 200 psig.

Poisoning of the palladium-silver alloy by impurities is of no concern if a commercial cylinder hydrogen source is used. However, when other sources of impure hydrogen are used, which contain large amounts of carbon tetrachloride, hydrogen sulfide, or other gases containing sulpuhr, poisoning takes place at a rapid rate. In these cases, it is necessary to remove the poisoning gases by external means before admitting the gas to the purifier. Poisoned palladium-silver tubes are easily regenerated with air as the inlet gas at operating temperature to oxidize the impurities and then with hydrogen to reduce the metal oxide formed on the tubing wall.

In order to prevent impurities from accumulating on the impure side of the palladium alloy septum and thereby decreasing the partial pressures of hydrogen, they are bled out in a controlled stream of impure hydrogen and either burned or innocuously vented.

The purifier temperature is regulated by an electrical heater which is controlled by the operating thermoswitch.

The cabinet contains a blower which serves the dual purpose of pulling a stream of cool air through the outlet gas cooling coil and of preventing an accumulation of hydrogen within the cabinet in the

event of a leak.

OPERATING INSTRUCTIONS

1. Close valve 2 (SW-2) and valve 5 (SW-5). Open valve 1 (SW-1), valve 3 (SW-3) and valve 4 (SW-4) to purge impure H_2 lines with nitrogen. Make sure that the pure H_2 line has a vacuum of 30".

2. Raise the temperature of the furnace to 385°C with N_2 flowing through it. This helps in getting rid both the impure and pure side of any gases which might form an explosive mixture with hydrogen during start up. The maximum operating temperature should never exceed 400°C.

3. Once the temperature stablizes at 385°C, close valve 1 (SW-1), valve 3 (SW-3) and valve 4 (SW-4). Make sure that the vacuum in pure hydrogen line is 30" and it is holding.

4. Open "inlet" valve 2 (SW-2) to admit the impure hydrogen.

Note : The flow of pure hydrogen may be adjusted by the pressure of the inlet gas since the diffusion rate of pure hydrogen is dependent on the difference between the partial pressures of he hydrogen on both sides of palladium tubes. Therefore the pure hydrogen flow rate can be varied by adjusting the differential between inlet and pure outlet pressure. The recommended inlet pressure is 200 psig or less. The unit should never be subjected to a pressure higher than 250 psig.

5. Open needle valve 1 (NV-1) and adjust it to pass approximately 5% of the "inlet" H_2 gas flow rate.

6. Discard the hydrogen purified during the first few minutes of operation which may be slightly contaminated.

TEMPORARY SHUT-DOWN

If shut down is only for a short time it is advisable not to allow the H_2 purifier to cool down.

1. Close "inlet" valve 2 (SW-2) and needle valve 1 (NV-1) and close valve 5 (SW-5) so that approximately 10 psig of gas pressure is trapped in the purifier.

2. Leave power on so that the furnace temperature is maintained at 385°C.

START-UP FROM TEMPORARY SHUT-DOWN

1. Open "inlet" valve 2 (SW-2), adjust the needle valve 1 (NV-1) and open valve 5 (SW-5).

COMPLETE SHUT-DOWN

1. Close the "inlet" valve 2 (SW-2) and after the gas had dropped to 10 psig close the needle valve 1 (NV-1).

2. Close the pure hydrogen gas valve 5 (SW-5).

3. Purge the purifier by opening the valve 3 (SW-3) and valve 4 (SW-4) so that the pure hydrogen line reads 30" of vacuum.

4. After 10 minutes open valve 1 (SW-1) with venture pump.

5. Switch off the H_2 purifier heater.

SPECIAL PRECAUTIONS

Hydrogen is a highly explosive material when mixed with air. Extreme care should be taken when connecting external fittings to make certain they are leak tight. Periodic checking of the fittings for leak is advisable. The hydorgen diffusion cell should give years of good service provided the following safe operating precautions are taken :

. Never subject the purifier to a pressure higher than 250 psig. The recommended operating pressure is 200 psig or less.

. Never allow the pressure on the pure side of the system to exceed the pressure on the impure side of the system as this may cause the tube to collapse.

. Filter the inlet gas if it contains solid or liquid impurities.

. Never start the hydrogen flow unless all air has been purged out of all impure H_2 lines with nitrogen and the unit has been completely evacuated so as to avoid the possibility of explosive mixtures forming.

. It is very important that the valve 1 (SW-1), valve 3 (SW-3), and valve 4 (SW-4) be closed while hydrogen is being purified.

. The maximum recommended operating temperature is 400°C (750°F). Never operate the purifier at a temperature higher than 400°C.

. The diffusion cell should be operated in well-ventilated area.

. Do not use any instrument containing mercury for any purpose in connection with the hydrogen purifier. Mercury vapor can completely and permanently poison the palladium-silver membrane.

1. In order to avoid corrosive damage to internal parts, insure that corrosive contaminants such as halogens, halides, sulphur compounds, and metal compounds or vapors are absent from the hydrogen feed gas.

2. Oxygen in a concentration greater than 1000 ppm must never be allowed to enter a diffusion cell containing hydrogen. Oxygen can be eliminated by installing a Oxygen Removing Purifier in the feed line upstream from the diffusion cell.

3. Always heat up and cool down your diffusion cell in the absence of hydrogen. This can be done by evacuating or by purging with inert gas.

4. Sulfur compounds, unsaturated hydrocarbons, free carbon, iron, lead, mercury, zinc, halides, oil and grease will poison the precious metal membrane in your diffusion cell and should be entirely eliminated from the feed gas.

TROUBLE SHOOTING

A. NO POWER:

1. Check fuse.

B. OUTPUT OF HYDROGEN DECREASING:

1. Check for proper adjustment of bleed gas valve (Needle valve-1). Too low a bleed gas flow rate will cause accumulation of impurities on the impure side and thereby decrease the pure hydrogen output.

2. Check for a decrease in the hydrogen content of impure gas.

3. Check for poisoning impurities in the feed gas.

4. Regenerate the palladium-silver alloy by passing air through the impure side. Then pass hydrogen through the impure side and original pure hydrogen output should be regained.

Note: It is advisable to keep periodic record of the pure hydrogen output flow rates obtained under the normal operating conditions so that any sign of poisoning can be easily detected by comparison.

REGENERATION PROCEDURE OF PALLADIUM DIFFUSION CELL

During normal operation, it is possible for carbonaceous matter to accumulate on the diffusion cell wall. This may be due to traces of residual oil in commercial cylinders, and various other sources. As palladium is normally a highly active oxidation catalyst, a simple air regeneration will normally bring the diffusion cell back to its initial state. Regeneration would be accomplished in the following steps:

1. Completely evacuate the unit as in normal start-up.

2. Heat the unit up to its normal operating temperature (400°C).

3. Shut off vacuum and run commercial nitrogen through the unit at relatively low pressures, i.e., 10psig.

4. Gradually add air to the nitrogen purge stream. For example, put 20cu. ft./hr. of nitrogen through the diffusion cell and add 1-2 SCFH of air. The exact amount is not a critical matter. After running for 15-30 minutes, gradually increase the air and decrease the nitrogen until air is passing through the diffusion tubes.

5. Shut off air, evacuate the unit, purge with nitrogen, and return to the normal operating procedure.

CHAPTER 5

OXYGEN REMOVING PURIFIERS INSTALLATION AND OPERATION INSTRUCTIONS

Oxygen Removing Purifiers (ORP) catalytically combine hydrogen and oxygen to form water vapor. The water vapor passes off with the purified gas and is removed by Hydrogen Purifier.

THEORY - ORP contain a precious metal catalyst that promotes the reaction of hydrogen and oxygen gases to form water vapor, normally at ambient temperature. The two gases combine in a stoichiometric ratio of two units of hydrogen to one unit of oxygen. In order to completely eliminate hydrogen or oxygen, the other gas must be present in excess (roughly 110%) of the stoichiometric ratio to ensure the reaction is driven to completion.

CONSTRUCTION - ORP is made of seamless stainless steel tubing. The tubing is packed with high-surface-area ceramic pellets coated with a very active precious metal catalyst. The end caps are welded on using an inertia weld, which forms a grain-refined solid-state bond with no grain growth, cast structure, porosity, segregation, or filler materials.

INSTALLATION - ORP must be installed vertically to prevent channeling of the gas after the catalyst has settled. The inlet gas should always enter through the top of the unit. Up-flow may fluidize the catalyst bed and cause attrition of the catalyst. Metallic pipe or tubing should be used to install the OR. Plastic or rubber tubing may allow the purified gas to become recontaminated. An inert material such as Teflon tape should be used for sealing threaded connections.

OPERATION - Both connections to the ORP should be purged and pressure tested for leaks with an inert gas such as argon or nitrogen before placing the unit in service. Once the system has been purged and

pressure tested, the gas flow can be turned on and the OR will begin to work immediately.

The ORP generally operate at room temperature; however, it may be necessary to heat the gas stream if it is near its dewpoint, or if carbon monoxide is in the feed gas. The ORP should not be operated above 1300°F. The ORP is designed to be operated continuously at elevated pressure (see the ORP label for maximum pressure rating). Pressure drop across the ORP is negligible.

The reaction of hydrogen and oxygen is an exothermic reaction (heat releasing). The temperature rise associated with the reaction is apporximately 30 F per 0.1% of oxygen removed from hydrogen or nitrogen and 40 F per 0.1% of oxygen removed from argon or helium. The actual temperature rise depends upon the heat capacity of the gas being processed and on heat losses from the system.

CHAPTER 6

MPS-190 SPECIALTY GAS HANDLING SYSTEMS

INTRODUCTION:

The handling of the process gases used in the semiconductor industry presents a technical challenge because of the special characteristics of those gases: toxic, reactive, corrosive, high purity. This has empasized the importance of improving the handling methods with a view to providing safety to personnel, protection of the physical process, efficiency of the operation by preserving the high purity of the process gas.

Typical phases involved in the handling of the process gases include:

- Attaching a gas cylinder to the manifold of a delivery system.
- Putting the cylinder in service to supply the manifold.
- Isolating the process from the delivery system.
- Disconnecting a gas cylinder from the manifold.

A common purpose through those phases is to achieve the following goals:

- Prior to disconnecting a cylinder from the manifold, exhaust in a safe manner the process gas contained in the manifold and purge the manifold with an inert gas until the concentration of the process gas is reduced to the required safety limit.
- Prior to putting a new cylinder in service (opening the

cylinder valve to supply the manifold), purge the manifold with an inert gas to insure that the concentration of the remaining impurities is not detrimental to the level of purity required for the process gas.

This establishes the need for an effective purging method which will remove the process gas from the manifold and substitute for it a high grade inert purge gas free of impurities.

Two basic approaches are used in practice. One consists in flushing by applying the purge gas at one end of the manifold and creating a continuous flow which is exhausted at the other end of the manifold. This removes the process gas by displacement and entrainment. The other approach uses the principle of dilution: the manifold is successively vented to a low pressure (atmospheric level or below atmospheric level), pressurized with purge gas to a pressure equivalent to several atmospheres, then vented again to the low pressure level. The cycle is repeated several times. At the end of each cycle the concentration of the process gas is diluted by a factor which is directly related to the ratio of the vent pressure to the purge gas pressure. The principle suggests that the combination of number of cylcles and dilution factor will allow to reduce the concentration of the process gas to a very small value. It suggests also that it is independent of the configuration of the manifold and of the path taken by the purge gas flow.

DESCRIPTION:

1. Purge by Dilution:

A manifod which is filled with a process gas is vented to atmospheric or subatmospheric level. A purge gas is applied to the manifold until the pressure in the manifold reaches a nominal preset pressure, then the manifold is again vented to atmospheric or

subatmospheric level. The successive phases of pressurizing and venting consititute a purging cycle. In the course of the cycle the concentration of the process gas has been reduced by "injecting" into the manifold a greater volume of purge gas than the initial volume of process gas. If the addition of purge gas brings the pressure from atmospheric level to 60 psi, the manifold will contain one volume of process gas and four volumes of purge gas: the concentration of the process gas will be reduced to 1/5 of its initial value. The dilution factor is 1/5: it is equal to the ratio of the vent absolute pressure over the absolute pressure created by the purge gas.

The purging cycle is repeated several times. At the conclusion of each cycle the process gas concentration is reduced to 1/5 of its previous value. At the end of N cycles the concetration will be reduced to $(1/5)^N$ of its starting value.

It is apparent that the total dilution is directly related to the number of cycles N and to the dilution factor obtained at each cycle. The dilution factor can be increased by pressurizing at a higher pressure and venting at a lower pressure.

2. Purge by Flush-Flow:

One end of the manifold is connected to a purge gas supply, the other end is connected to the vent line. The purging operation consists in applying a continuous flow through the manifold for a given length of time to displace the process gas and replace it with purge gas. The removal of the process gas proceeds through a combination of turbulent mixing and entrainment . It is evident that direct contact between the two gases is required for an effective operation. It suggests that the effectiveness will be seriously affected by any dead ended side capacity.

3. MPS-190 Purge Panel Operating Instructions:

The following procedures have been devised for the safe operation and manipulation of the hazardous gas purge panels which are installed in the laboratory for handling arsine and phosphine.

In general, changing of hazardous gas cylinder (or metalorganic bubblers) will be done by the "buddy" system and with appropriate safety apparatus and precautions employed at all times.

It is necessary to purge the system with an inert gas after it has been exposed to air, and before it is used for any hazardous process gas such as PH_3 and AsH_3. Purging is also required to remove the process gas before opening the system to air again.

Purging is not necessary or desirable at other times. Each time a transition is made from purge gas to process gas or process gas to purge gas, there is a mixing of the two gases throughout the system; any oxygen or moisture in the purge gas may react and can be left behind as contamination. The parctice of purging lines between runs gives two of these mixing events per run, causing a cumulative buildup of contamination which may eventually create problems. With a leak-tight system, there is no reason not to leave the process gas in the lines and avoid the buildup caused by the repetitive purging ritual.

It is necessary to thoroughly purge the cylinder connection line before and after opening it to the air while changing cylinders. It is not necessary to expose the entire system to purge gas during this operation. The procedures outlined in the following sections permit cylinder changing with a minimum of system exposure to purge gas.

3.1 Procedure to Connect a Gas Cylinder at Initial Start Up Following Facilities Installation of Purge System:

1. Connect the 316SS tubing connection to the gas cylinder outlet valve and tighten the CGA nut.

2. The air-operated **main shut off valve** located downstream of the flow limiting valve is normally closed (NC). Open the air-operated main shut off valve by applying nitrogen pressure (60-80 psi) to the actuator. The actuator is triggered by manually pushing the corresponding MPS-190 reset button on the annunciator panel.

3. Open the by-pass of the **flow limiting valve** as follows: turn counter-clockwise (CCW) one half turn from closed position. Use the Allen key knurled knob attached to the face of the purge panel.

4. Open the DV26 isolation valve at the inlet to the **pressure regulator.** This valve is shaped to indicate clearly the two operating positions: open when the lever is in line with the ports; closed when the lever is at right angle with ports line.

5. Turn the knob of the TDR 450 pressure regulator clockwise (CW) against its stop.

3.2 Procedure to Helium Leak Check MPS-190 Purge System:

1. Open the **process valve** at the outlet to the **pressure regulator.**

2. Open **isolation valve, flow limit valve,** and **main shut off valve.**

3. Close the AsH_3/PH_3 gas tank.

4. Initiate evacuation of the MPS-190 purge panel by applying a source of "clean" vacuum through the process valve. Helium leak check the MPS-190 system components at maximum sensitivity.

3.3 Procedure to Pressurize MPS-190 Purge Panel with N_2:

1. Isolate MPS-190 purge system from vacuum source.

2. Supply regulated N_2 (80 PSI) to purge inlet (i.e., through **purge valve**).

3. Make 20 purge cycles, each cycle consisting of the following steps:

   a. Open **purge valve**, hold open until the pressure reaches 1 atmosphere.

   b. Hold open for 10 additional seconds.

   c. Close **purge valve**.

   d. Open **vent valve**, hold open for 10 seconds.

   e. Close **vent valve**.

   f. Repeat (b-c) 20 times.

4. Close **process valve** at the outlet to the **pressure regulator**.

3.4 Procedure to Pressurize MPS-190 Purge Panel With Cylinder Gas Supply:

1. Turn the knob of the **pressure regulator** counterclock-wise (CCW) to zero setting.

2. Open slowly the valve on the gas cylinder.

3. Close the by-pass of the **flow limiting valve:** turn screw clockwise (CW) to shut tight.

3.5 Procedure to Disconnect a Gas Cylinder to An Operative MPS-190 Purge Panel Installation:

1. Close the valve on the gas cylinder.

2. Close the **isolation valve.**

3. Open the air-operated **main shut off valve** (if not already open).

4. Open the by-pass of the **flow limit valve.**

5. Make 20 purge cycles.

6. Disconnect the flexible connection from the valve of the gas cylinder by unscrewing the CGA fitting slowly.

7. Remove the gas cylinder.

8. Replace cylinder valve safety cap.

9. Call for cylinder pick up.

3.6 Procedure to Connect a New Gas Cylinder to an Operative MPS-10 Purge Panel Installation:

1. Verify that the **isolation valve** is closed.

2. Verify that the air operated **main shut off valve** is open.

3. Connect the 316SS connection to the cylinder valve and tighten the CGA fitting.

4. Apply steps outlined in sections 3.3 and 3.4.

5. Open slowly the gas cylinder valve.

6. Close the by-pass of the flow limiting valve.

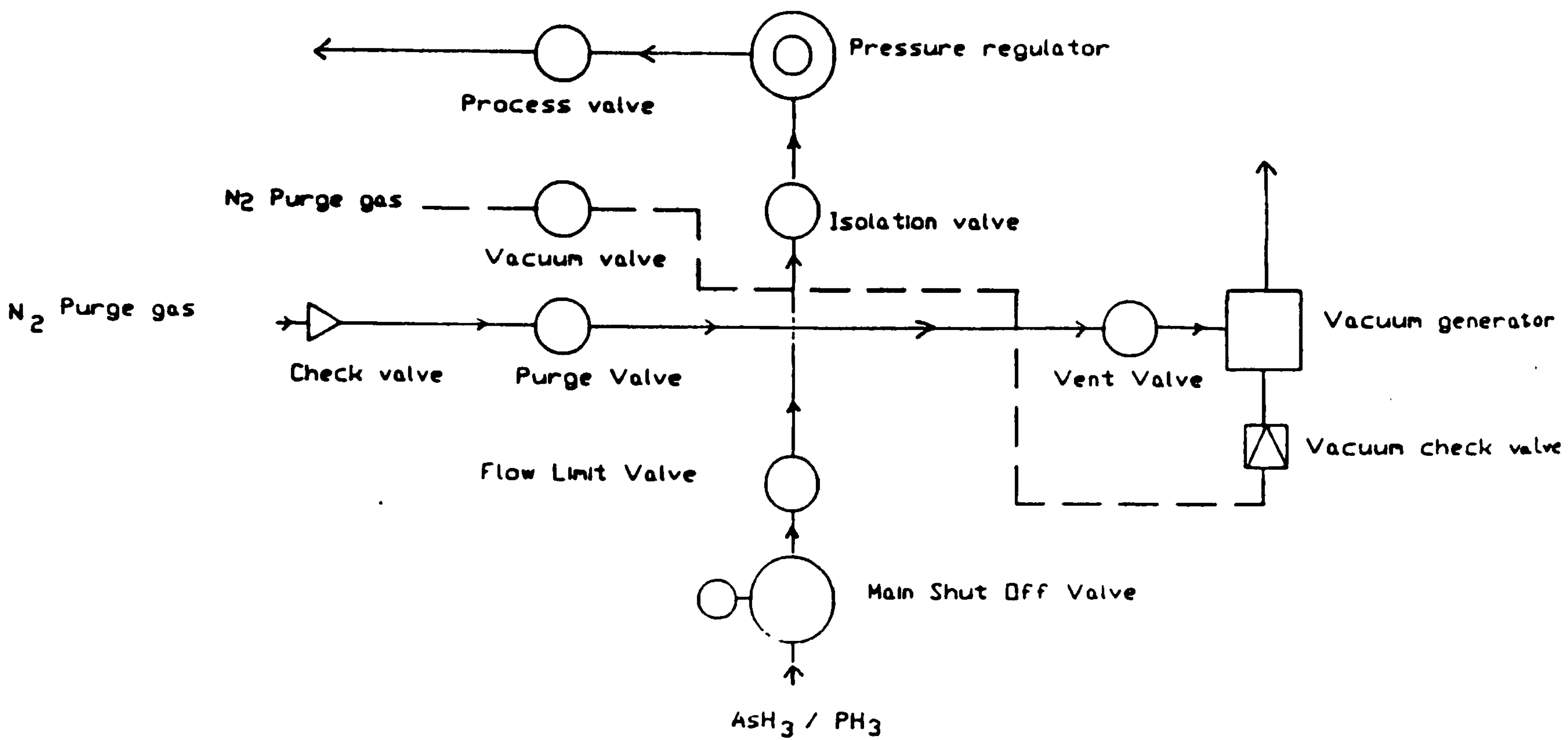


Figure 6.1 -

CHAPTER 7

A STUDY OF DYNAMIC FLUID FLOW IN A VERTICAL MOCVD REACTOR

INTRODUCTION

To obtain a good quality reproducible epitaxial layer of III-V compounds by MOCVD technique, the knowledge of gas flow dynamics and the parameters that affect the growth of these epi-layers is absolutely essential. Past one year's experience with RADC's MOCVD system has indicated that the vertical reactor supplied by CVD Equipment Corporation has a severe turbulant fluid flow problems which has an adverse effect on III-V compound epitaxial growth. To optimize the fluid flow in this reactor as well as to design a new reactor for the growth of InP, GaInAs, GaInP and GaAs epitaxial layers by Metal Organic Chemical Vapor Deposition (MOCVD) technique at low pressure a "smoke" test experiment was performed. The "smoke" which is visible to the naked eye as well as a video camera is generated by reacting NH_3OH + HCl vapors at room temperature and atmospheric pressure. At low pressure and 580° C the "smoke" is generated by reacting $TiCl_4$ + H_2O vapors together.

EXPERIMENTAL

Experimental arrangement of fluid flow visualization apparatus

The schematic of the apparatus used to study the dynamic fluid flow in the vertical MOCVD reactor is shown in Figure 7.1. Ultra pure dehydrated Helium gas is passed through the bubblers which contain NH_3OH & HCl at room temperature and atmospheric pressure. To study the flow pattern at high temperature (580°C) and low pressure the He gas is passed through $TiCl_4$ & H_2O bubblers. The He-gas flowing through the bubblers and as pusher gas is metered by Metheson's ROTOMETERS. The pressure balance between the rotometers and the

reactor is maintained by using a combination of Pressure Gauges Ball, and Throttle valve because the rotometers work only at atmospheric pressure.

The "smoke" created is given by the following reactions:

(a) Room temperature and atmospheric pressure: NH_3OH and HCl vapors react to give a white smoke of NH_4Cl.

(b) High temperature and low pressure:
$TiCl_4$ & H_2O vapors react to give a white smoke of TiO_2.

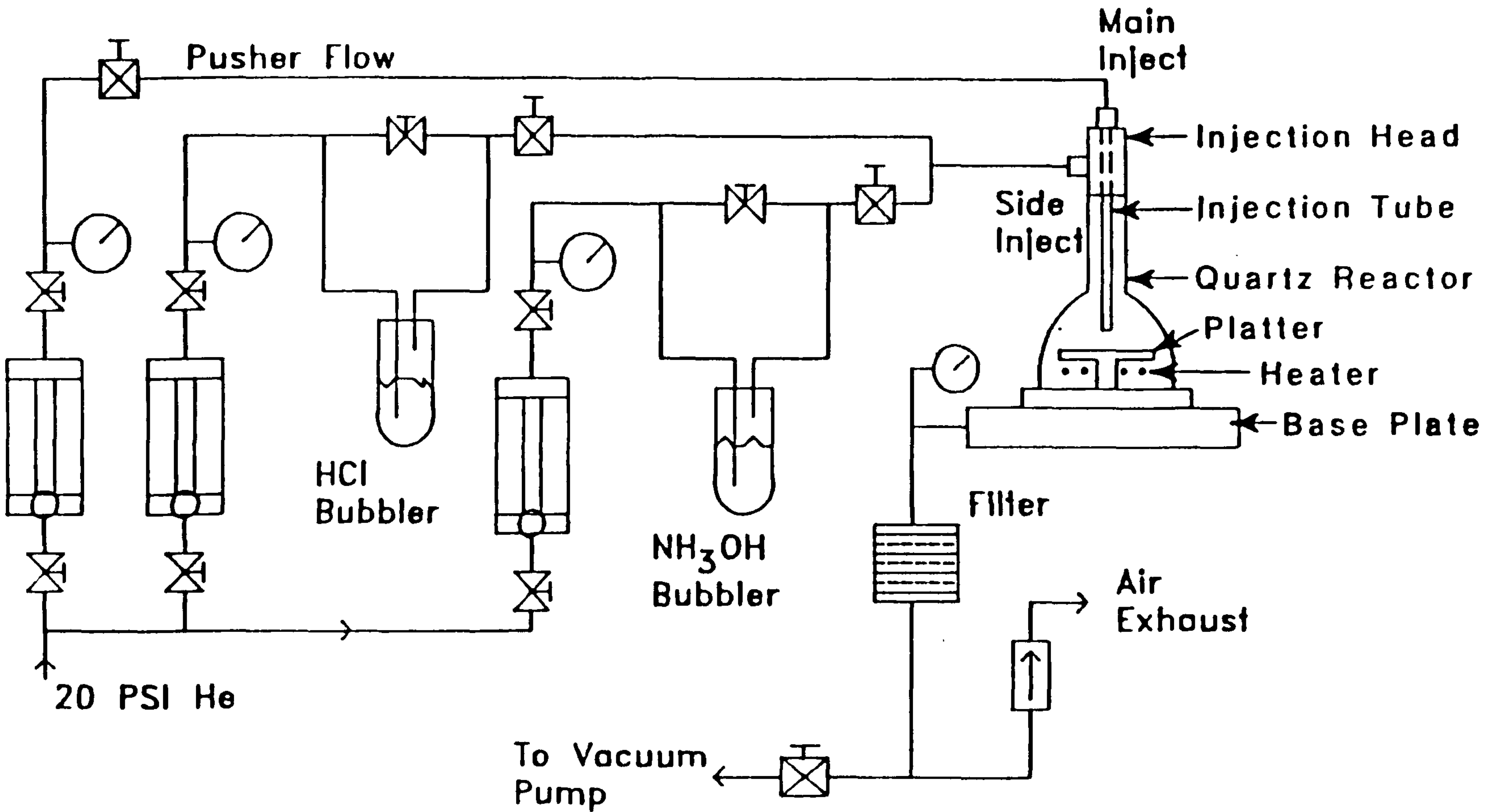


FIGURE 7.1 SCHEMATIC OF THE APPARTUS USED TO STUDY DYNAMIC FLUID FLOW.

Reactor

The vertical reactor used in RADC's MOCVD system is shown in Figure 7.2. This reactor is made of quartz and its shape resembles an inverted funnel. The critical dimensions of the reactor is also shown in Figure 7.2. In an actual MOCVD epitaxial growth system this reactor is water cooled but while performing the "smoke" test experiment it was not cooled so that video film can be taken of the fluid flow patterns under different conditions. Therefore the one major difference between the actual MOCVD flow and the "smoke" test is that in an actual MOCVD growth the reactor wall is cold whereas in the smoke test the wall is hot.

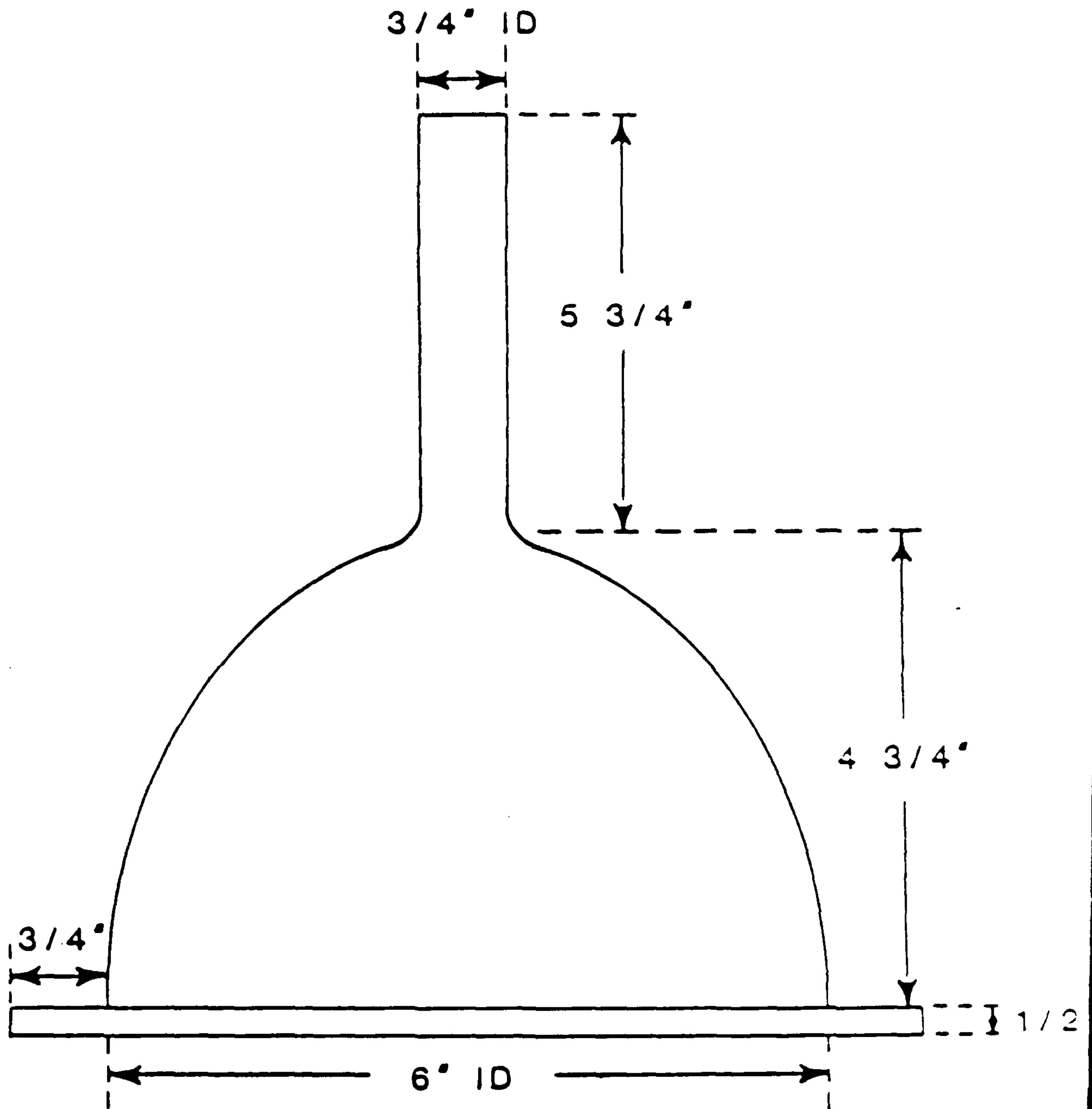


FIGURE 7.2 VERTICAL MOCVD REACTOR.

Injection Head

The figure 7.3 gives a self explanatory detailed diagram of the injection head used with the reactor. The main body of the injection head is made of stainless steel. It has VCR connection for gas coming from the gas handling system. This injection head is very much similar to the actual injection head used in MOCVD system with only very little difference. The O-rings as shown in figure 7.3 go around the injection tube and the reactor stem to make sure that the system is leak tight.

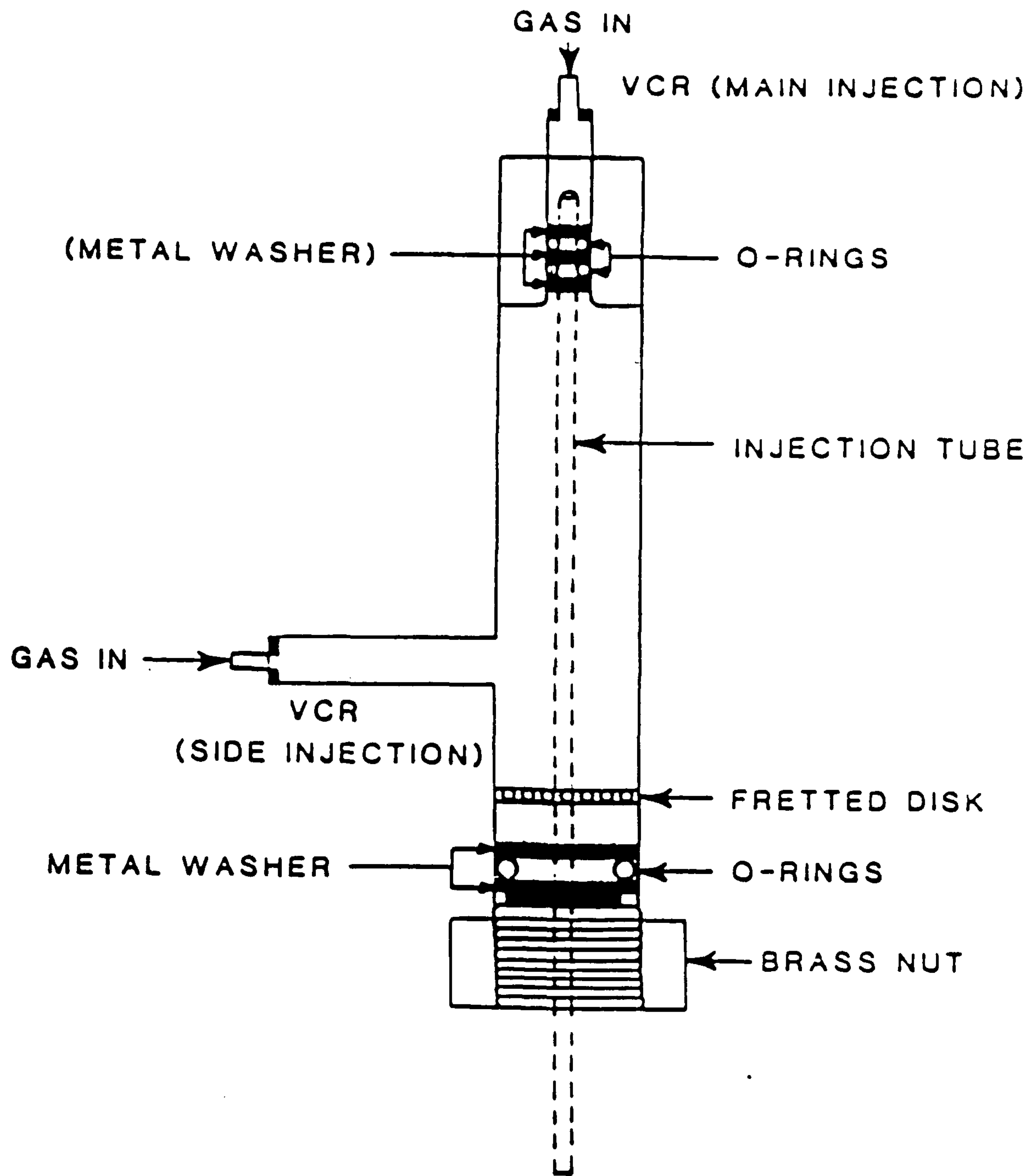
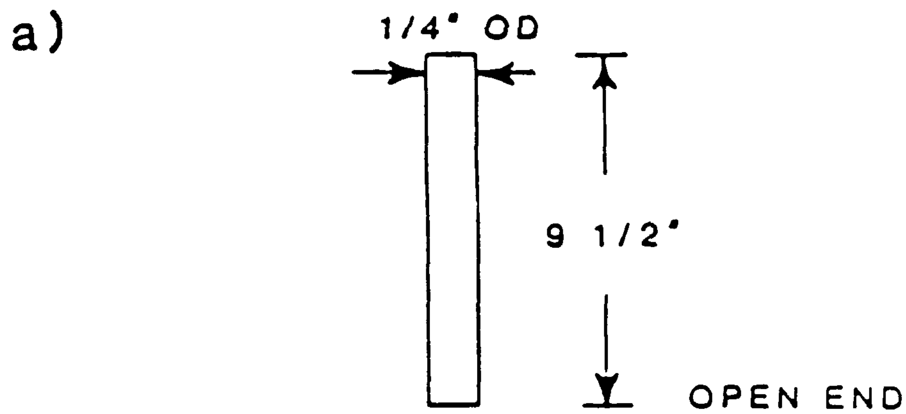


FIGURE 7.3 INJECTION HEAD

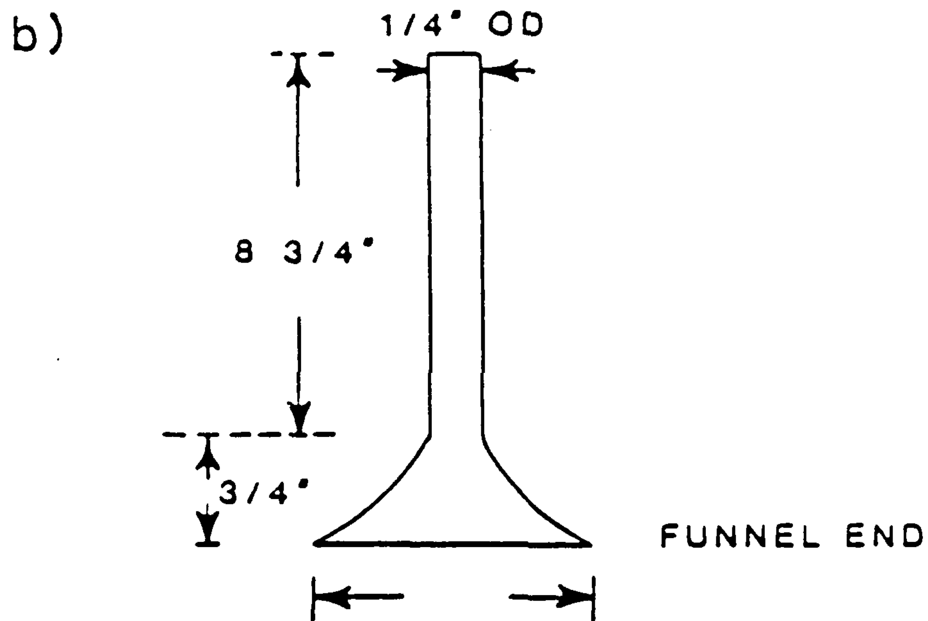
Injection Tubes

Three different injection tubes used in actual MOCVD growth were used for smoke test to see their effect on the fluid flow dynamics. Figure 7.4 gives a detailed schematic of it. After initial experiments, it was decided to use the injection tube shown in Figure 7.4(a) because other two injection tubes created very turbulent flow patterns. All above injection tubes are made of quartz and they end 1" above the platter.

a)



b)



c)

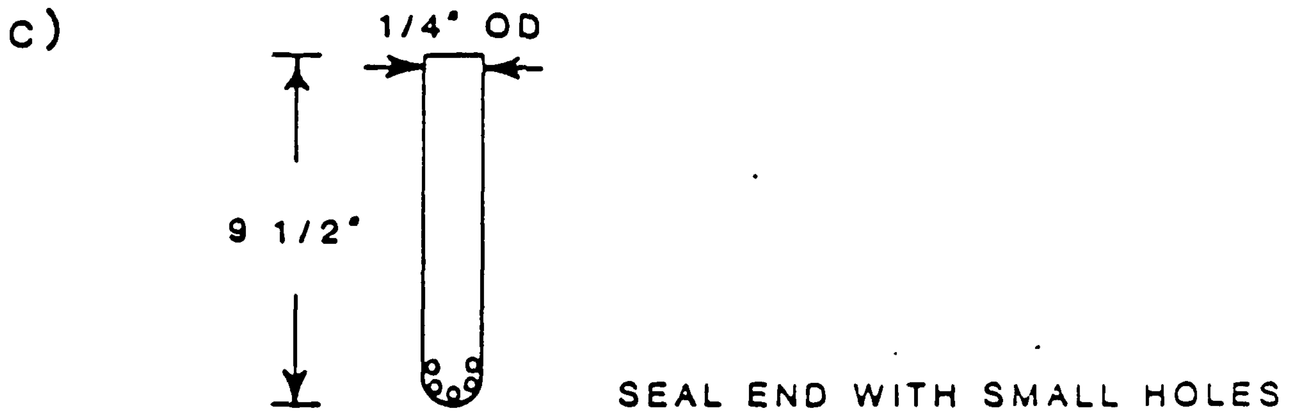
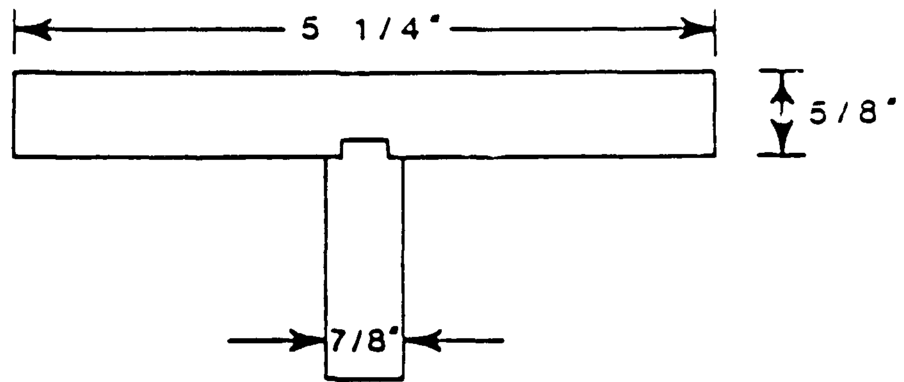


FIGURE 7.4 INJECTION TUBES.

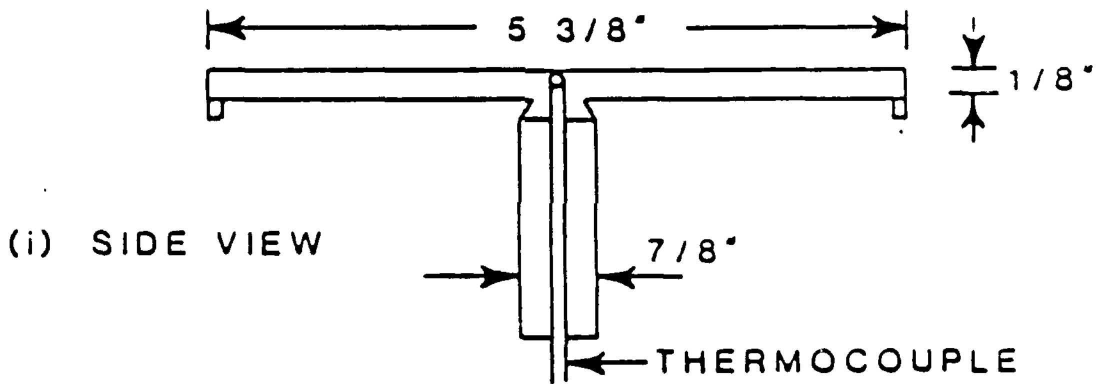
Platter (Substrate holder)

Figure 7.5(a) shows the platter used in smoke test and figure 7.5(b) shows the platter used in actual MOCVD system. The platters used in MOCVD is made of Mollybdenum while one used in smoke test is made of Graphite. The critical dimensions are given in Figure 7.5. In actual MOCVD system the temperature is measured by using Pt-Rh thermocouple as shown in Figure 7.5(b) while in smoke test it is measured using IR-thermometer (Camera).

a) GRAPHITE PLATTER USED FOR DYNAMIC FLUID FLOW VISUALIZATION STUDY.



b) MOLLY PLATTER USED IN MOCVD SYSTEM



(ii) TOP VIEW

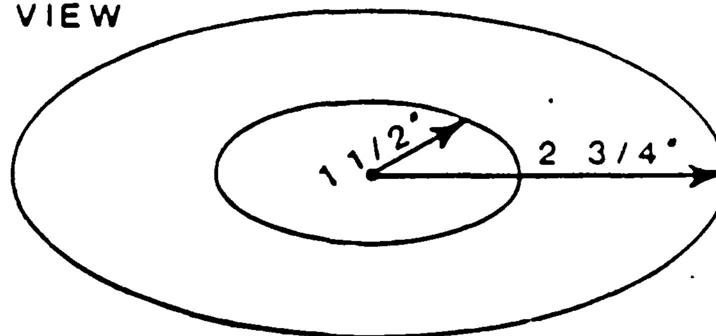
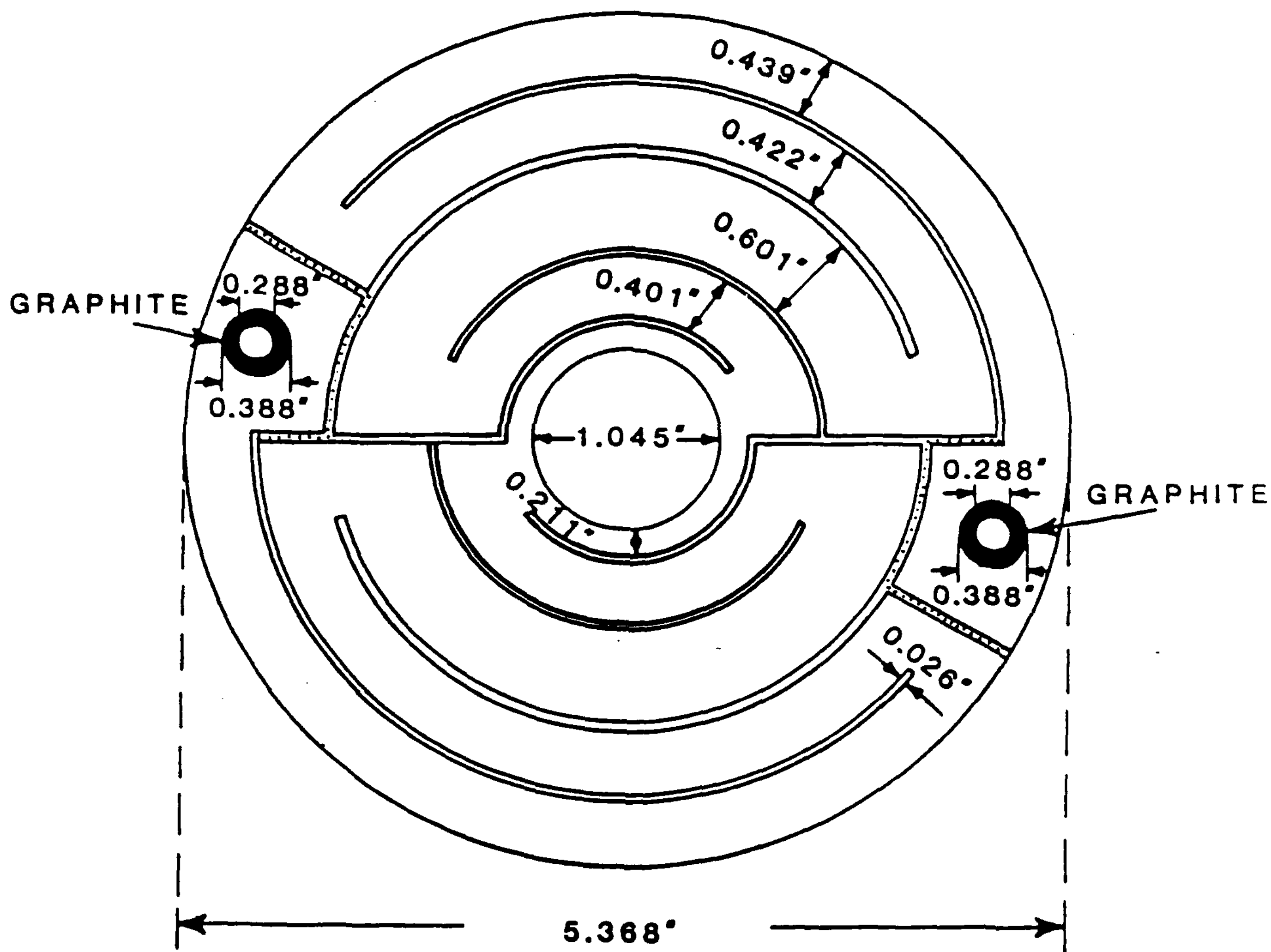


FIGURE 7.5 SUBSTRATE HOLDER (OR PLATTER)

Heater

Figure 7.6 shows the schematic of the heater used in actual MOCVD system. This is a resistance heating element which utilizes Boron nitride thin film (Boralloy(R)) as an insulating substrate and pyrolytic graphite as a resistor. The critical dimensions of this heater are given in the figure 7.6. Figure 7.7 shows the schematic of the coil resistance heater used in the "smoke" test. It is a standard heating element used in cooking stove. The material of the element is call chemtholl.

parks mathematical laboratories, inc
carlisle, massachusetts · 01741



TOTAL THICKNESS = 0.072

ROOM TEMP. RESISTANCE = 11-12

MAX. TEMP. = 1200 °C

SCALE: 1:1

FIGURE 7.6 HEATER USED IN ACTUAL MOCVD SYSTEM.

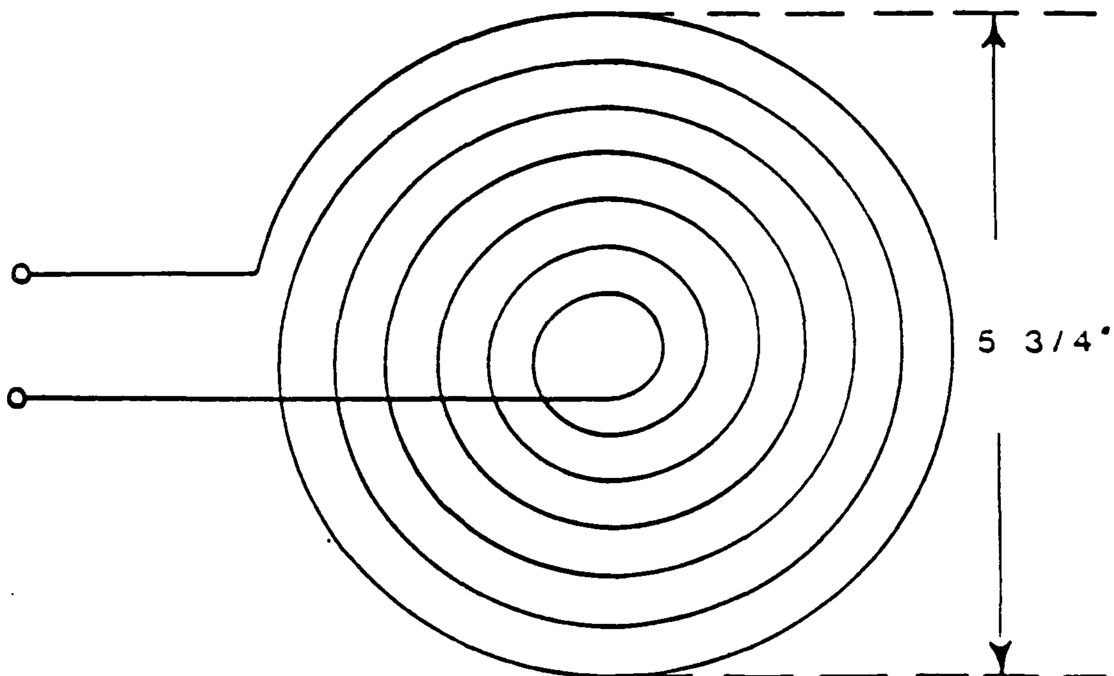


FIGURE 7.7 CHEMTHoLL RESISTANT COIL HEATER.

Major difference between actual MOCVD & smoke test apparatus

The gas handling system used for actual MOCVD and smoke test apparatus is different. Ultrapure hydrogen gas further purified by palladium diffuser is used as carrier gas in the MOCVD system whereas He-gas is used for smoke test. The gases used in MOCVD are metered by Mass flow controllers whereas the rotometers are used for this purpose in smoke test apparatus. The bubblers are made of stainless steel and are cooled at 30°C to -10°C in actual MOCVD system. The bubblers for smoke test are made of pyrex and they are kept at room temperature.

In actual MOCVD system the temperature of platter ranges from 580°C to 700°C while in smoke test apparatus it is kept at 580°C for all conditions.

The low pressure in MOCVD system ranges from 70 torr to 25 torr whereas it is about 200 torr for smoke test. The reason for this is that the smoke is not visible below this pressure.

CHAPTER 8

A STUDY OF DYNAMIC FLUID FLOW IN A VERTICAL MOCVD REACTOR

Experiment 1

This experiment is performed to study the effect of the various gas flow rates through the **side inject** on the flow dynamics in the vertical reactor while keeping the rate of gas flowing through the **main inject** constant.

(A) PARAMETRIC CONDITIONS IN THE REACTOR:

(i) Room temperature (30°C)
(ii) Atmospheric pressure, and
(iii) 1/4" open end injection tube which ends 1" above the platter.

(B) CONSTANTS:

(i) The rate of gas flowing through the main inject is kept constant at 750 cc/min.
(ii) The rate of gases flowing through the main inject are HCl and He (which acts as pusher gas) 375 cc/min each, respectively.

(C) VARIABLES:

(i) The rate of gas flowing through the side inject is varied from 375 cc/min to 10 lit/min.
(ii) The gas flowing through the side inject is NH_4OH.

The table 8.1 summarizes all the flow condition and results.

TABLE 8.1

Figure 1	Constant flow through main inject cc/min		Variable flow through side inject NH_4OH
	HCl	He	
a	375	375	375 cc/min
b	375	375	750 cc/min
c	375	375	1.5 lit/min
d	375	375	4.0 lit/min
e	375	375	10.0 lit/min

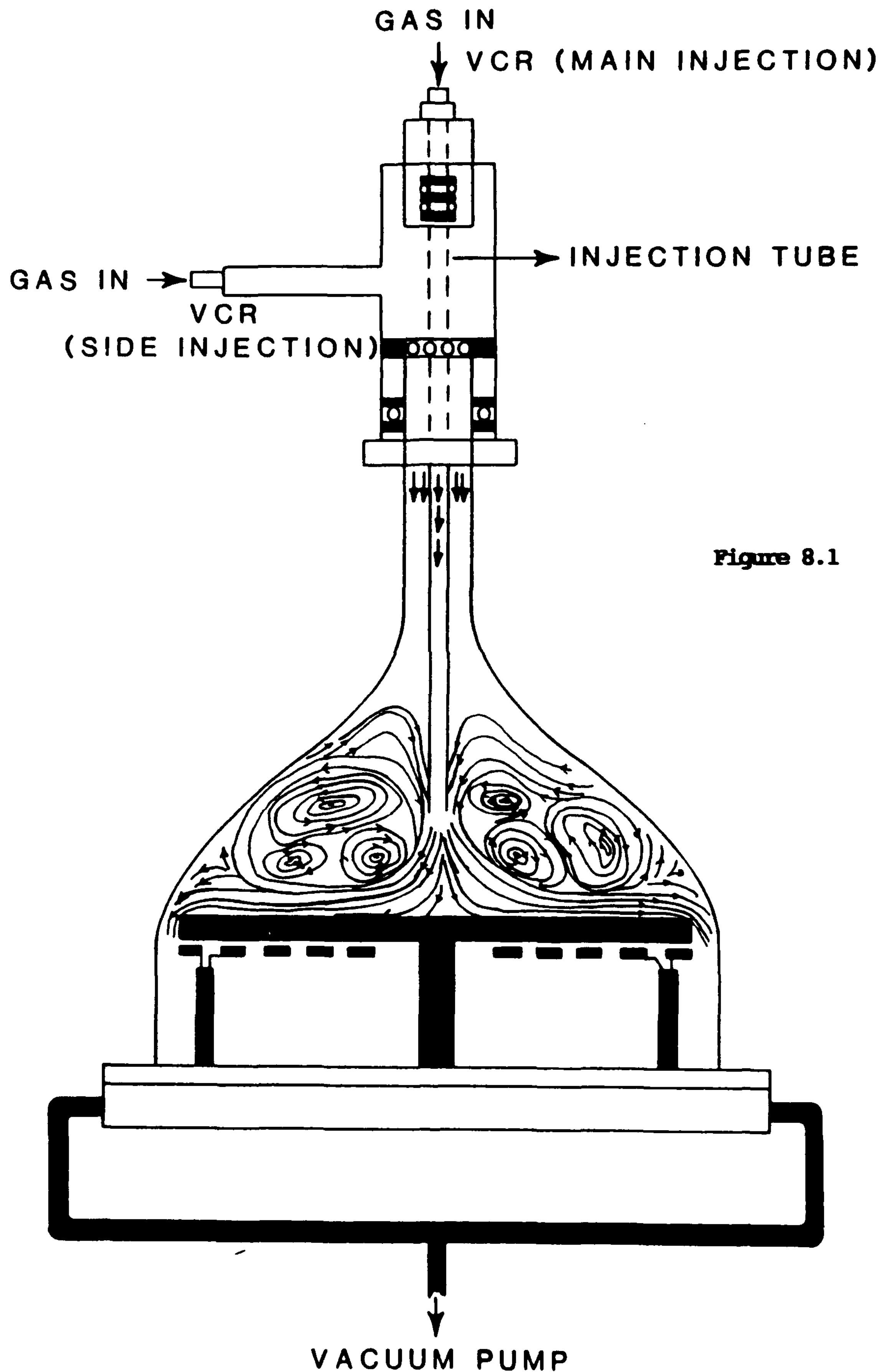
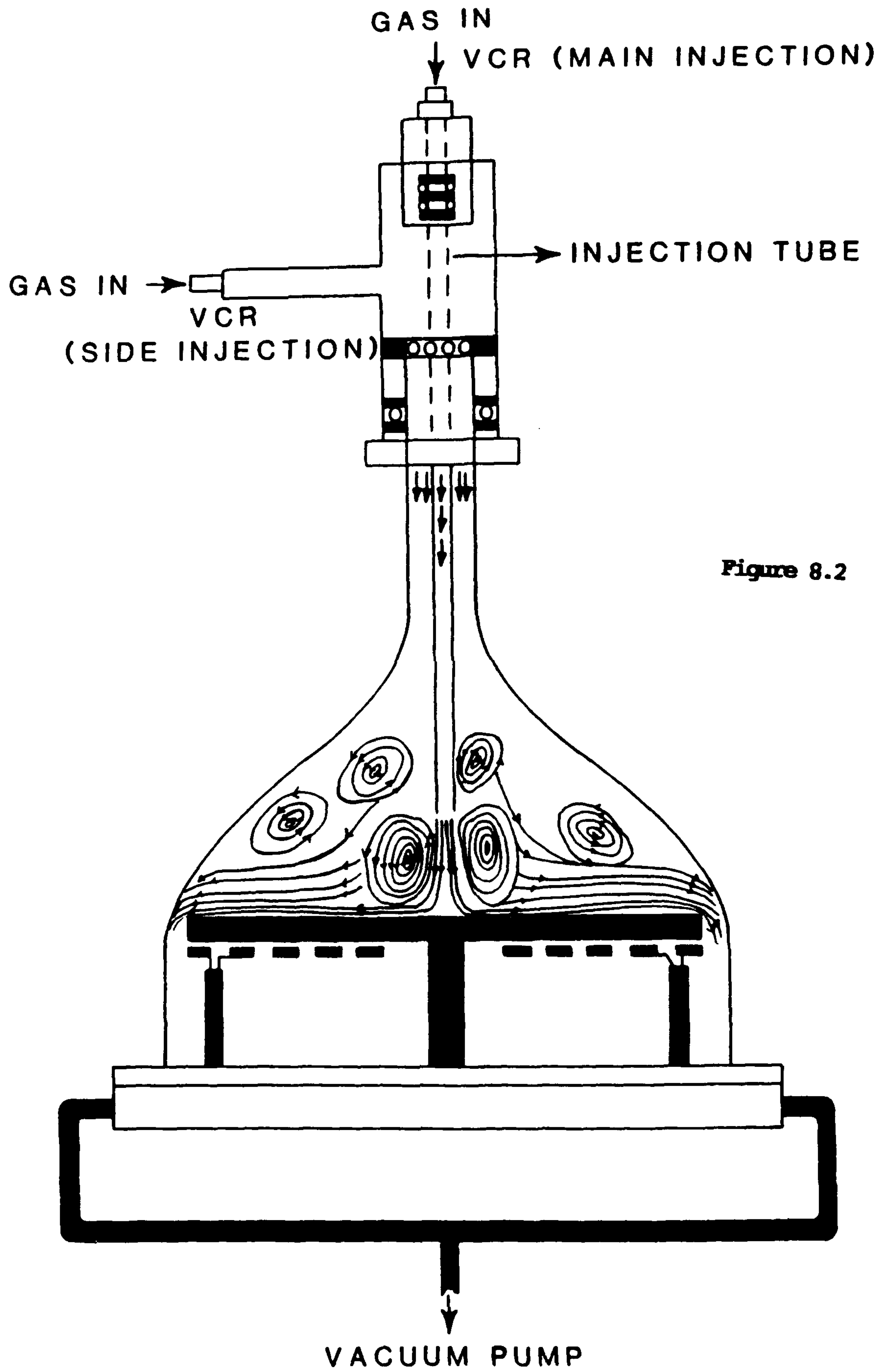


Figure 8.1



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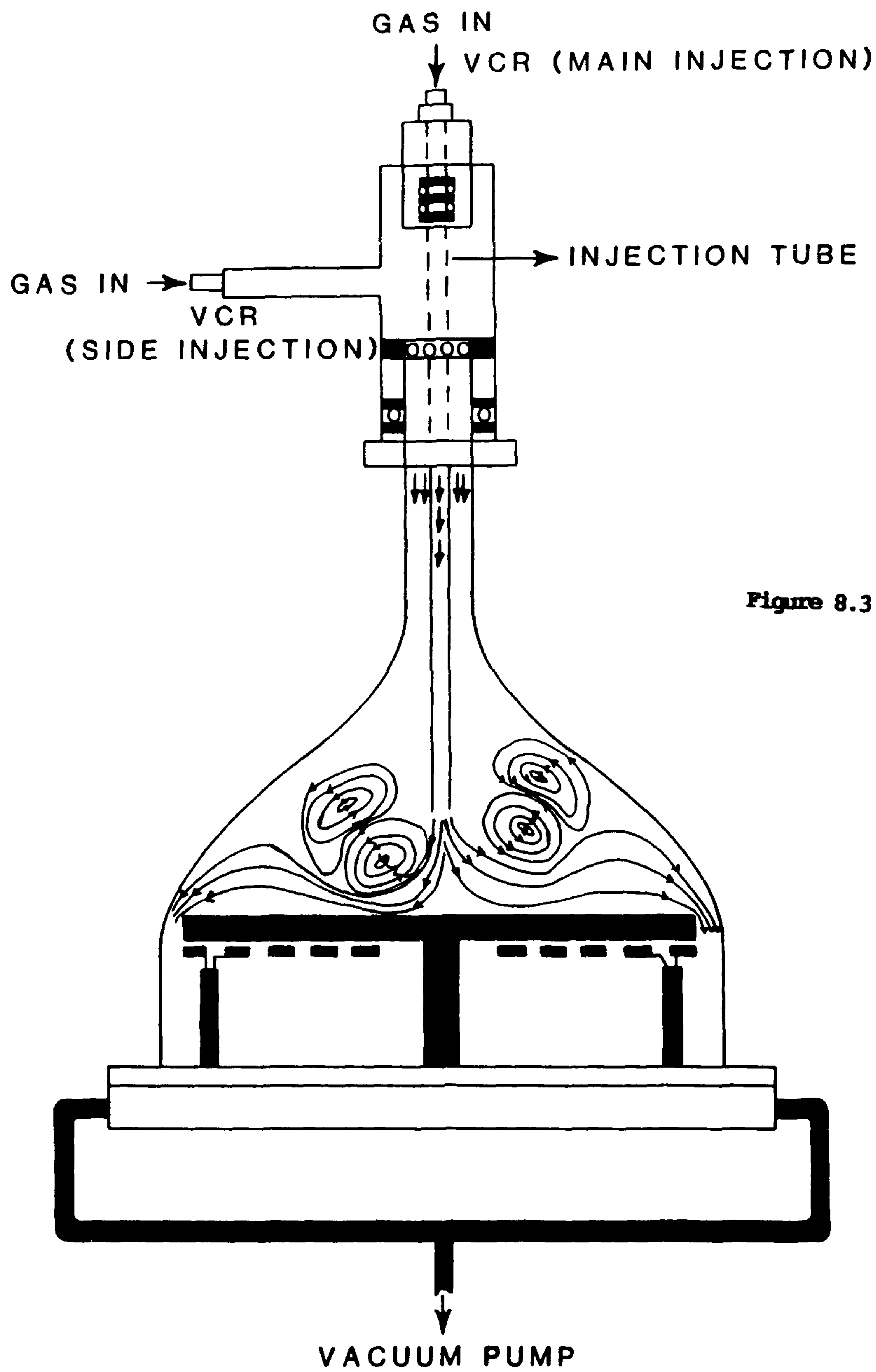

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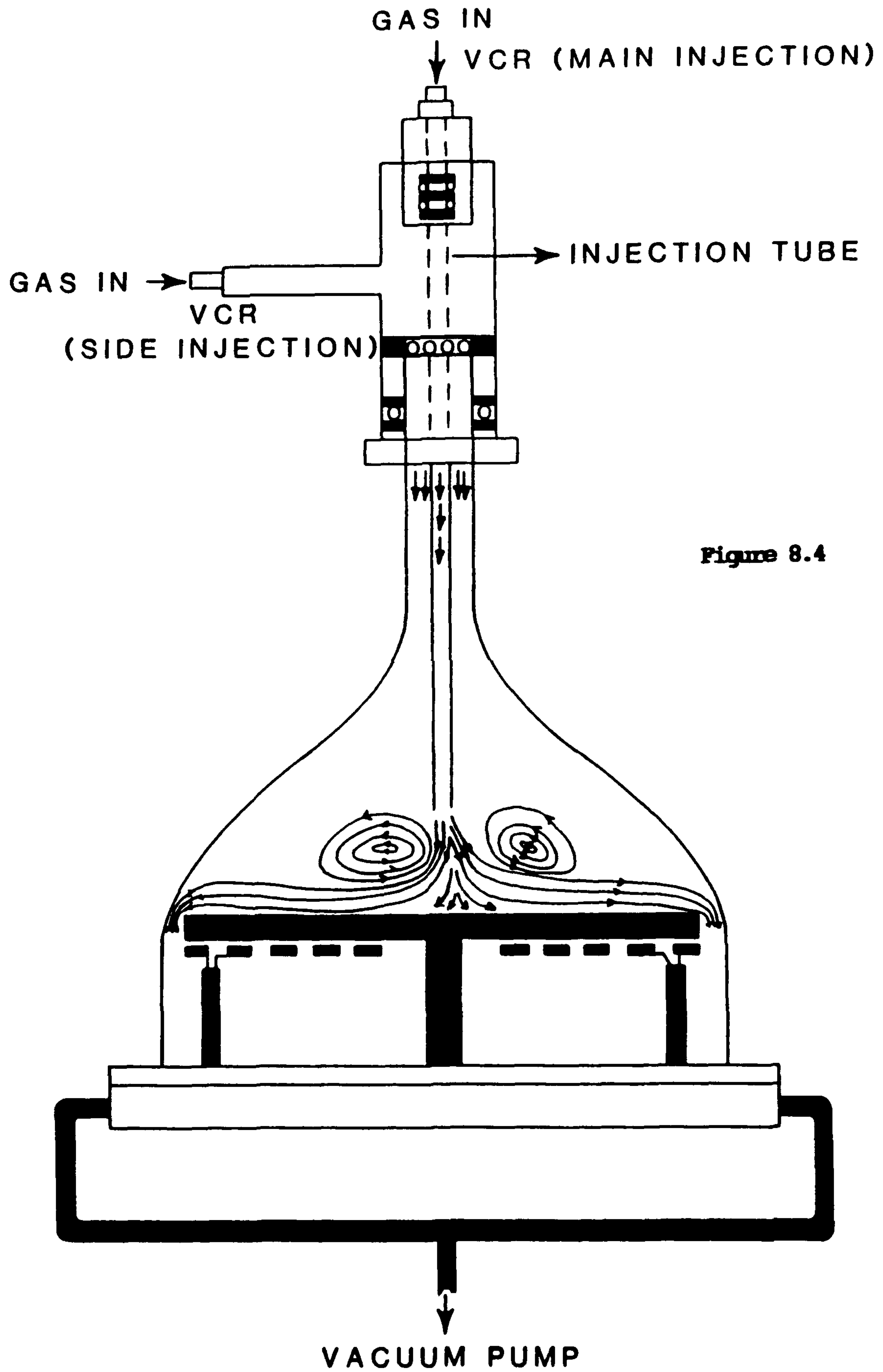

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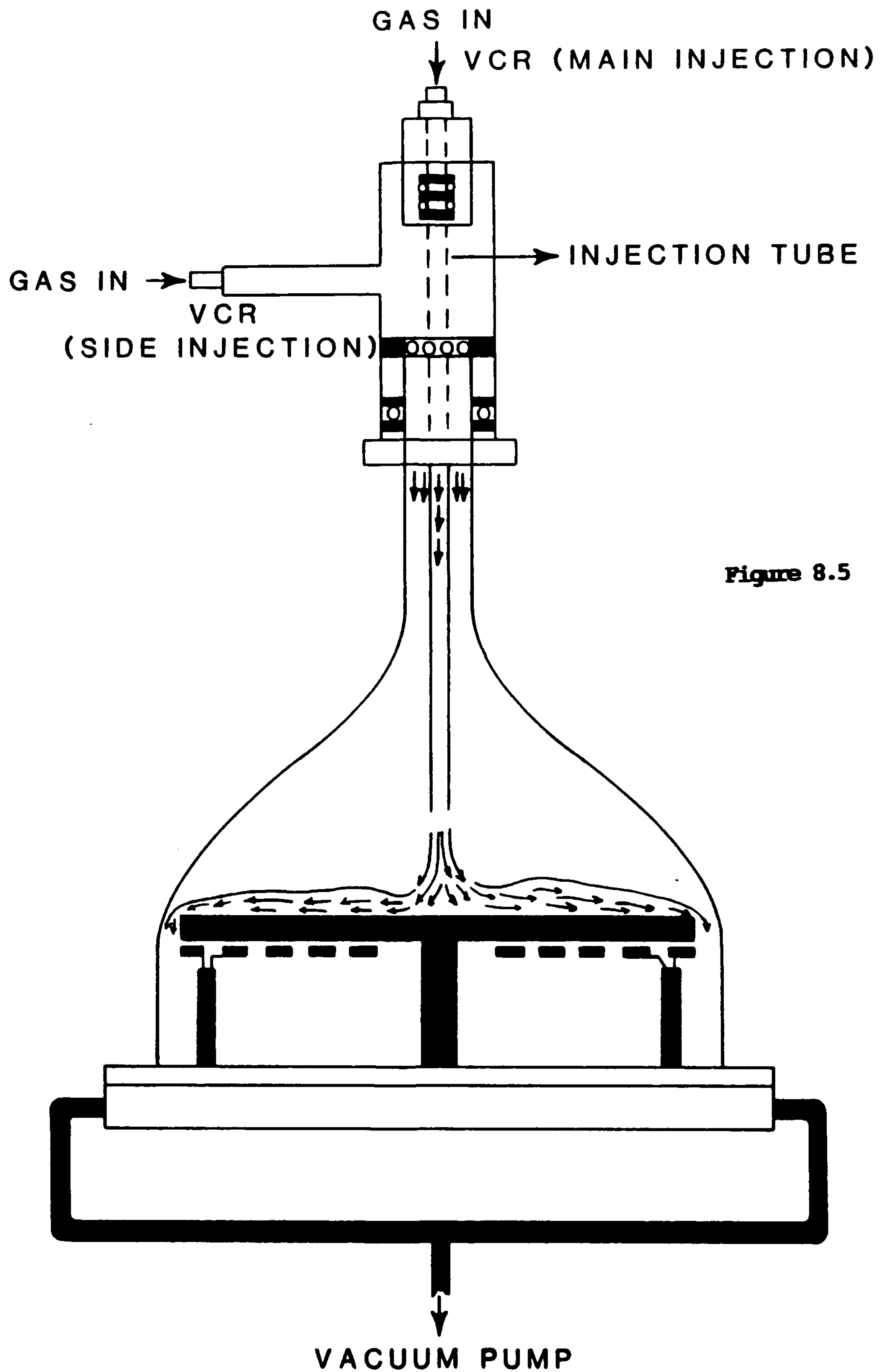

Figure 8.5

Conclusion

(i) Keeping the gas flow rate through the main inject constant, as the gas flow rate through the side inject is increased the turbulance in the gas flow in this particular reactor decreases.

(ii) Best results are obtained when the total gas flow through the main inject is 750 cc/min and the gas flow through the side inject is 4.0 lt/min or above.

(iii) Therefore it can be concluded that by controlling the gas flow through the main inject and the side inject, the turbulance in the gas flow dynamics can be controlled.

CHAPTER 9

EXPERIMENT 2

This experiment is performed to study the effect of various gas flow rates through the main inject on the flow dynamics in the vertical reactor while keeping the rate of the gas flowing through the side inject constant. The flow through the side inject is kept at 5 lit/min because the best results were obtained at this flow rate.

(A) PARAMETRIC CONDITIONS IN THE REACTOR:

(i) Room temperature (30°C)
(ii) Atmospheric pressure, and
(iii) 1/4" open end injection tube which ends 1" above the platter.

(B) CONSTANTS:

(i) The rate of gas flowing through the side inject is kept constant at 5.0 lit/min.
(ii) The rate of gas flowing through the side inject is NH_4OH.

(C) VARIABLES:

(i) The rate of gas flowing through the main inject is varied from 375 cc/min to 4.0 lit/min.
(ii) The gas flowing through the main inject is HCl.

The table 9.1 summarizes all the flow conditions and results.

TABLE 9.1

Figure 2	Constant flow through side inject lit/min		Variable flow through main inject HCl
	HCl	He	
a	5.0	0	375 cc/min
b	5.0	0	750 cc/min
c	5.0	0	4.0 lit/min
*d	10.0	0	4.0 lit/min

* Note: for figure 9.1.d result the side inject flow rate is increased to 10 lit/min to see the effect of it on the flow dynamics in the reactor

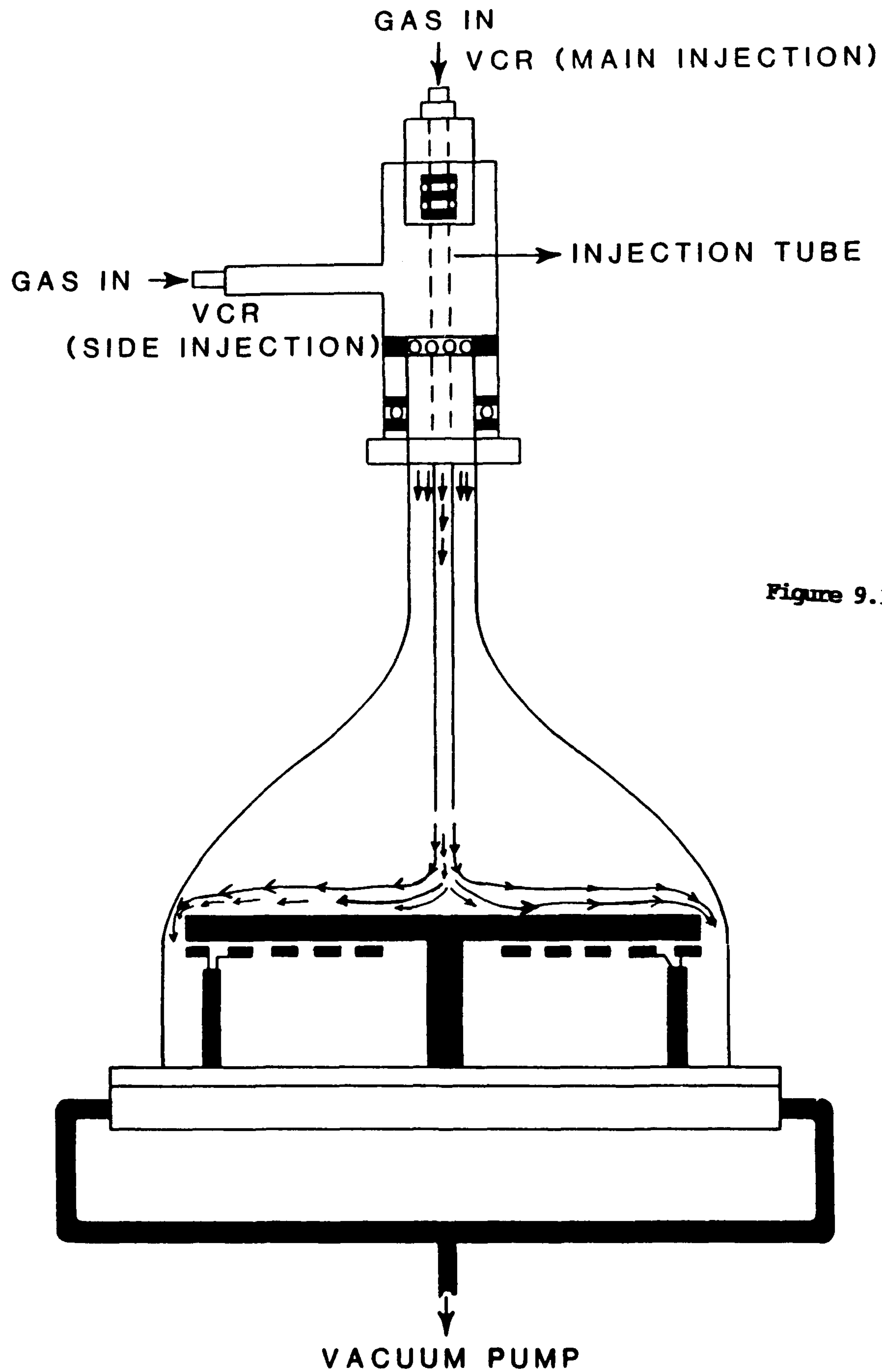

Figure 9.1

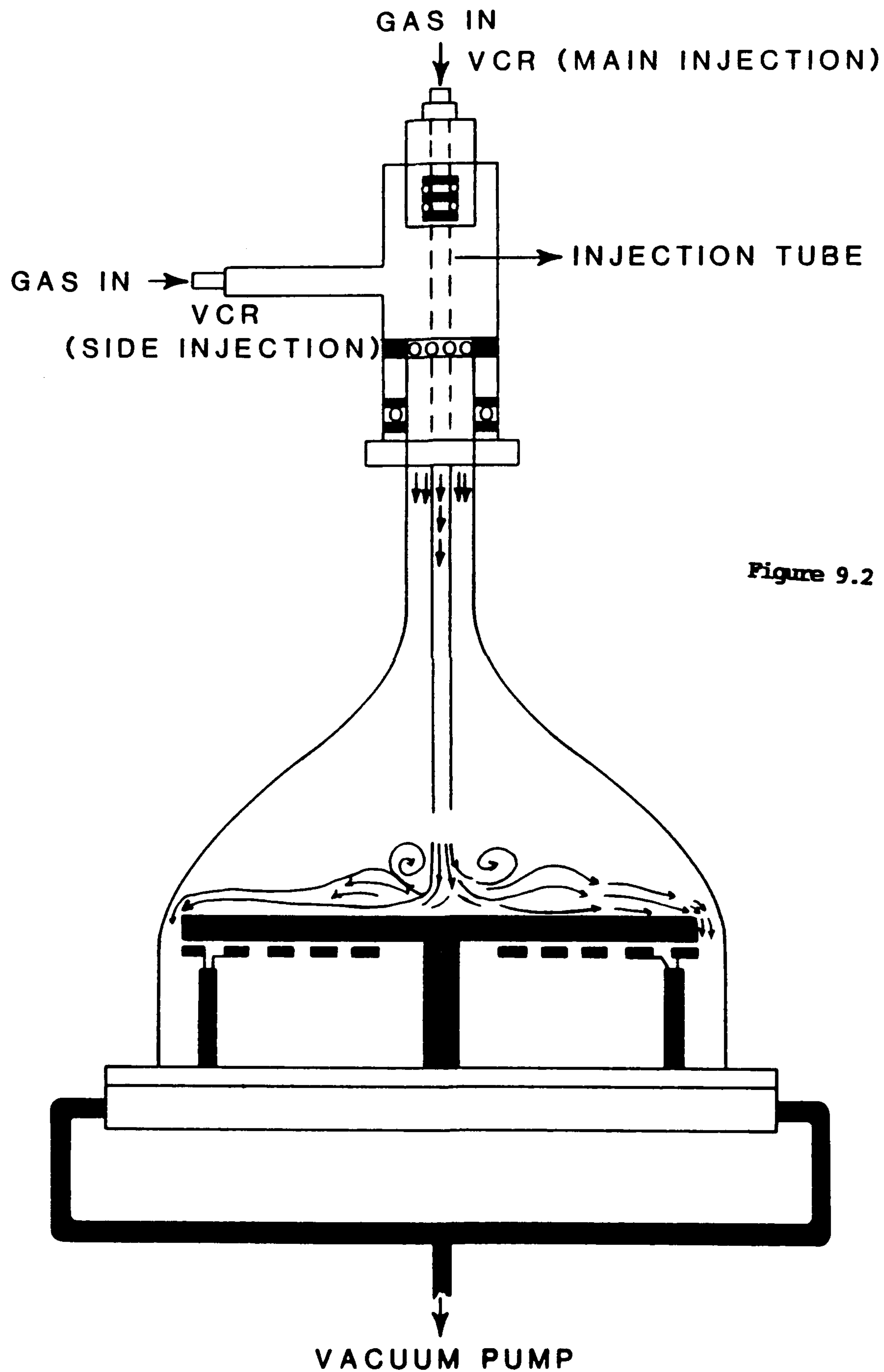

Figure 9.2

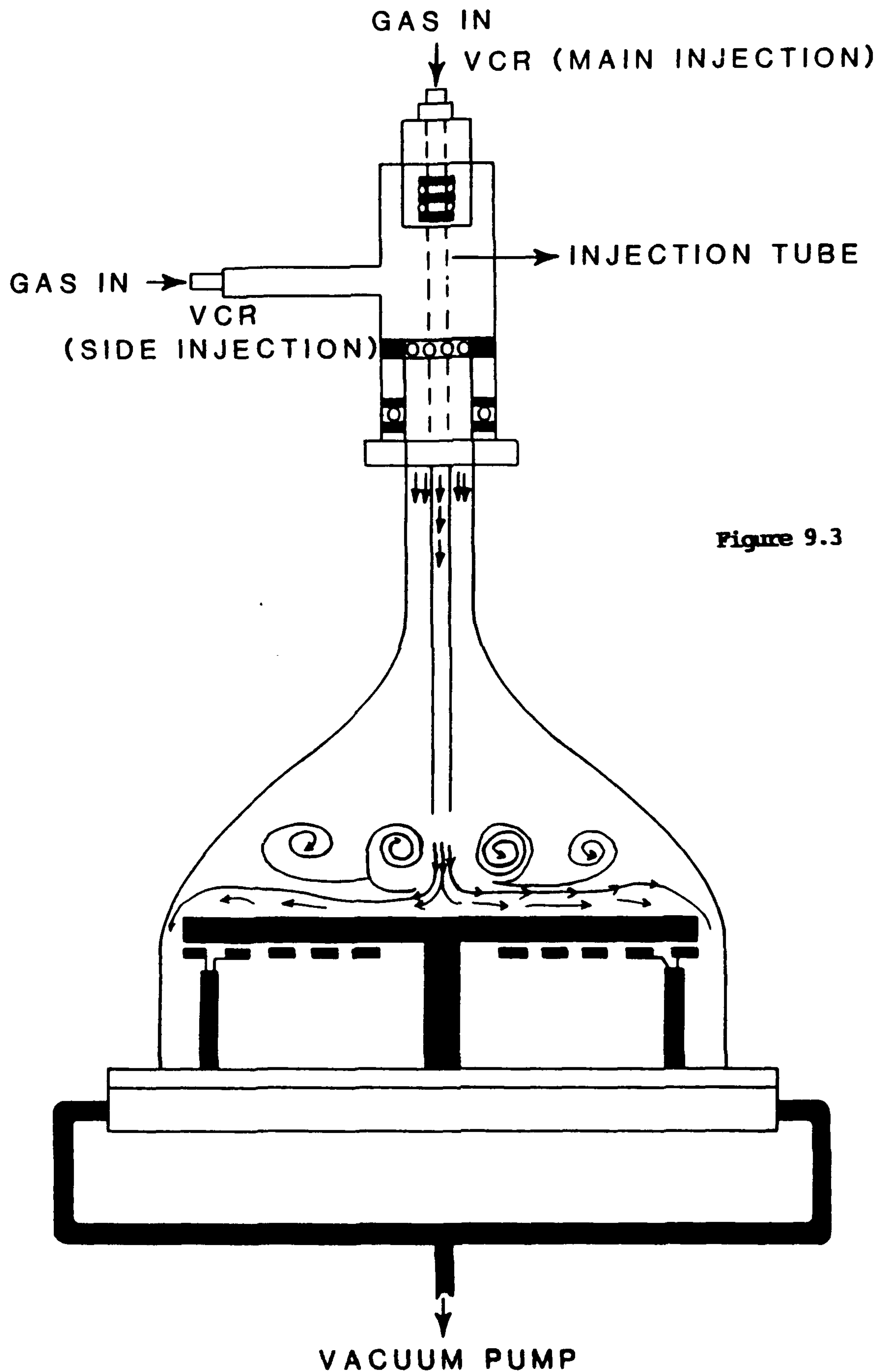

Figure 9.3

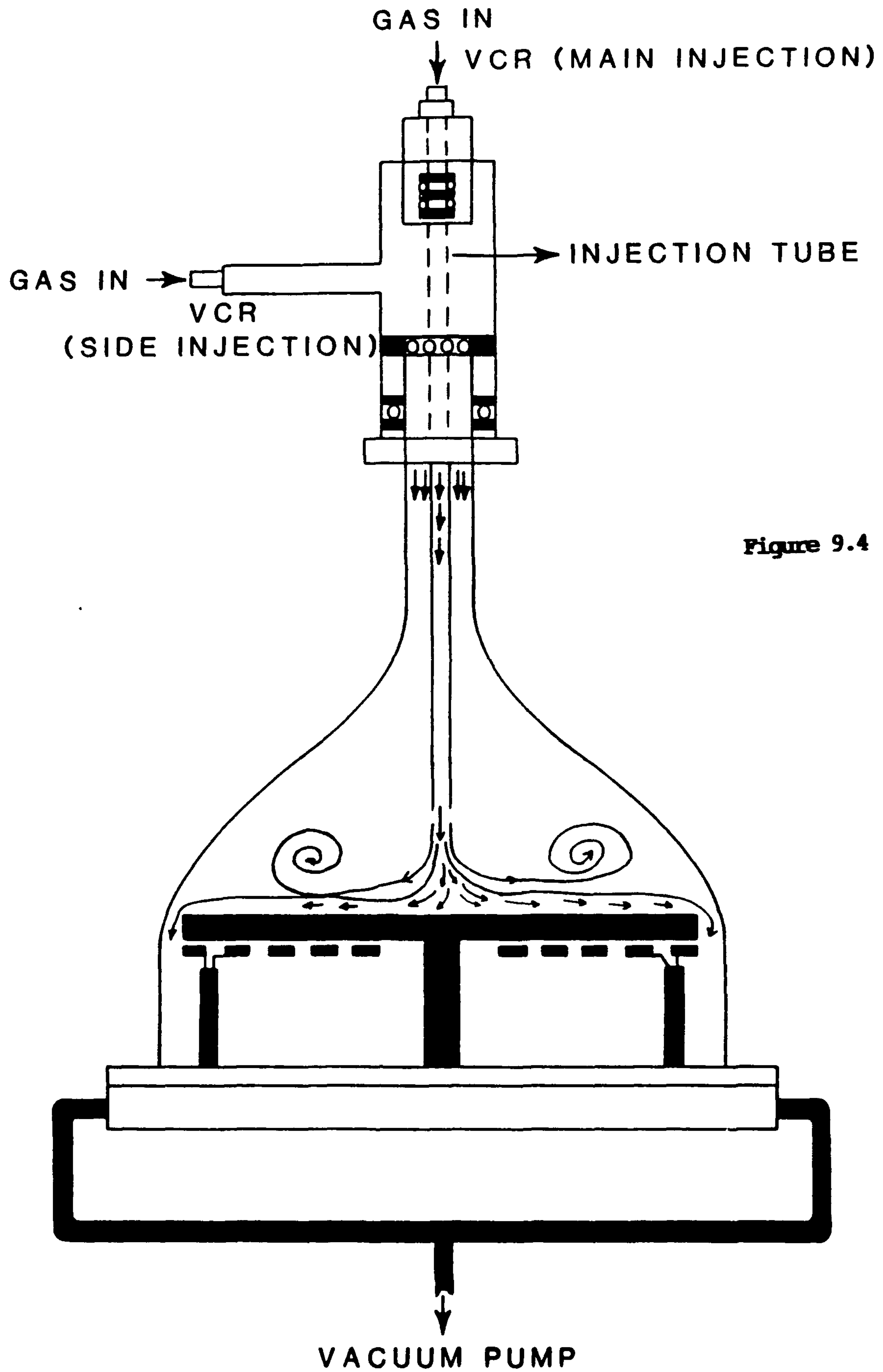

Figure 9.4

Conclusion

(i) Keeping the gas flow rate through the side inject constant as the gas flow rate through the main inject is increased the turbulence in the gas flow in this particular reactor increases.

(ii) Best results are obtained when the total gas flow through the main inject is 375 cc/min and the gas flow through the side inject is 5.0 lt/min.

CHAPTER 10

EXPERIMENT 3

In order to verify that mixing the reactant gases does not affect the flow dynamics in the reactor, the gas plumbing was changed so that the NH_4OH and HCl gases were mixed and injected through the main inject. Pusher gas (He) was injected through the side inject

PARAMETRIC CONDITIONS IN THE REACTOR:

(i) Room temperature (30°C)
(ii) Atmospheric pressure, and
(iii) 1/4" open end injection tube which ends 1" above the platter.

The table 10.1 summarizes all the flow conditions and results.

TABLE 10.1

Figure 3	Flow through the main inject cc/min		Constant flow through side inject pusher gas (He)lt/min
	HCl	NH_4OH	
a	375	375	4.0
b	750	750	5.0

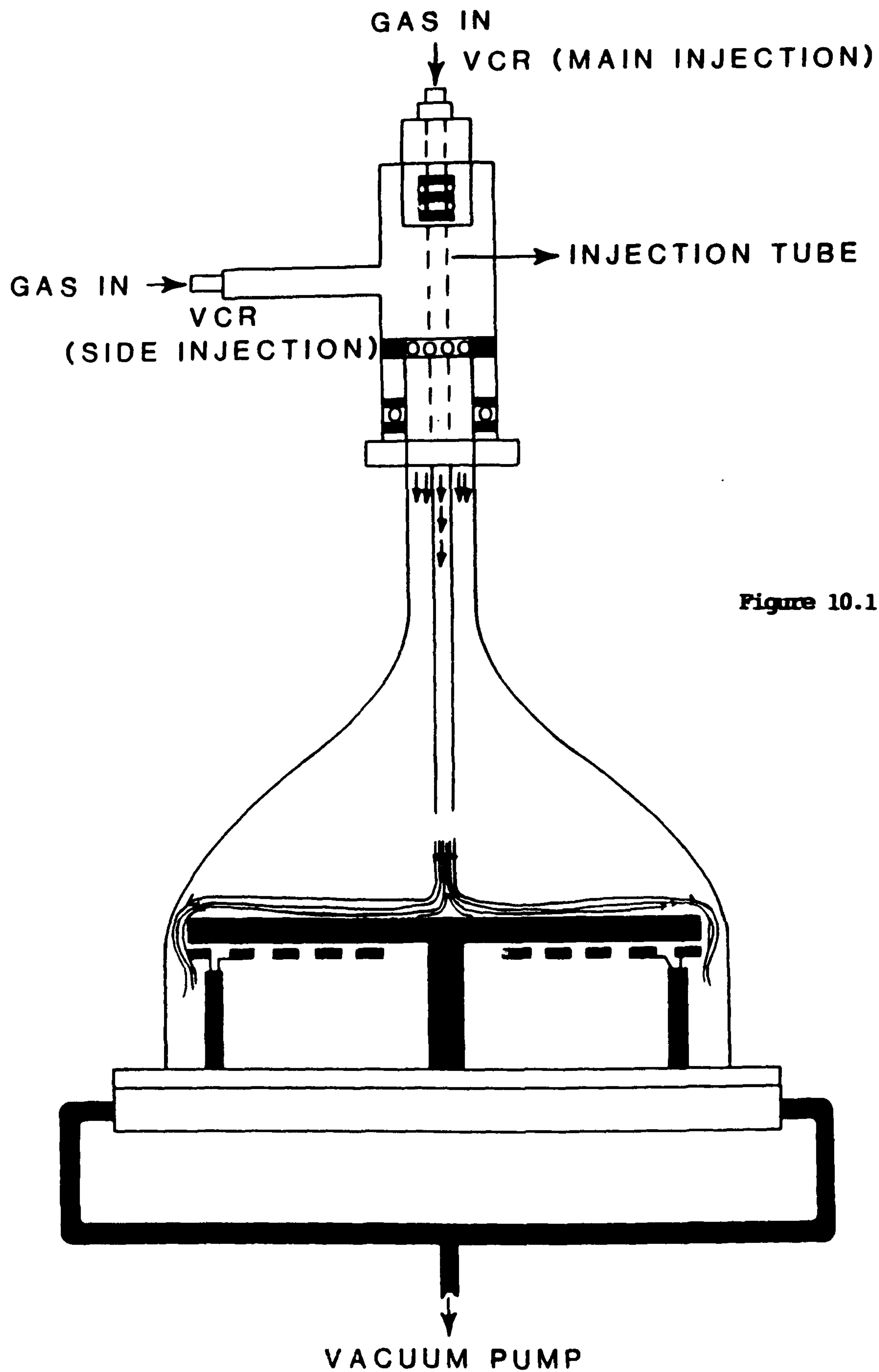

Figure 10.1

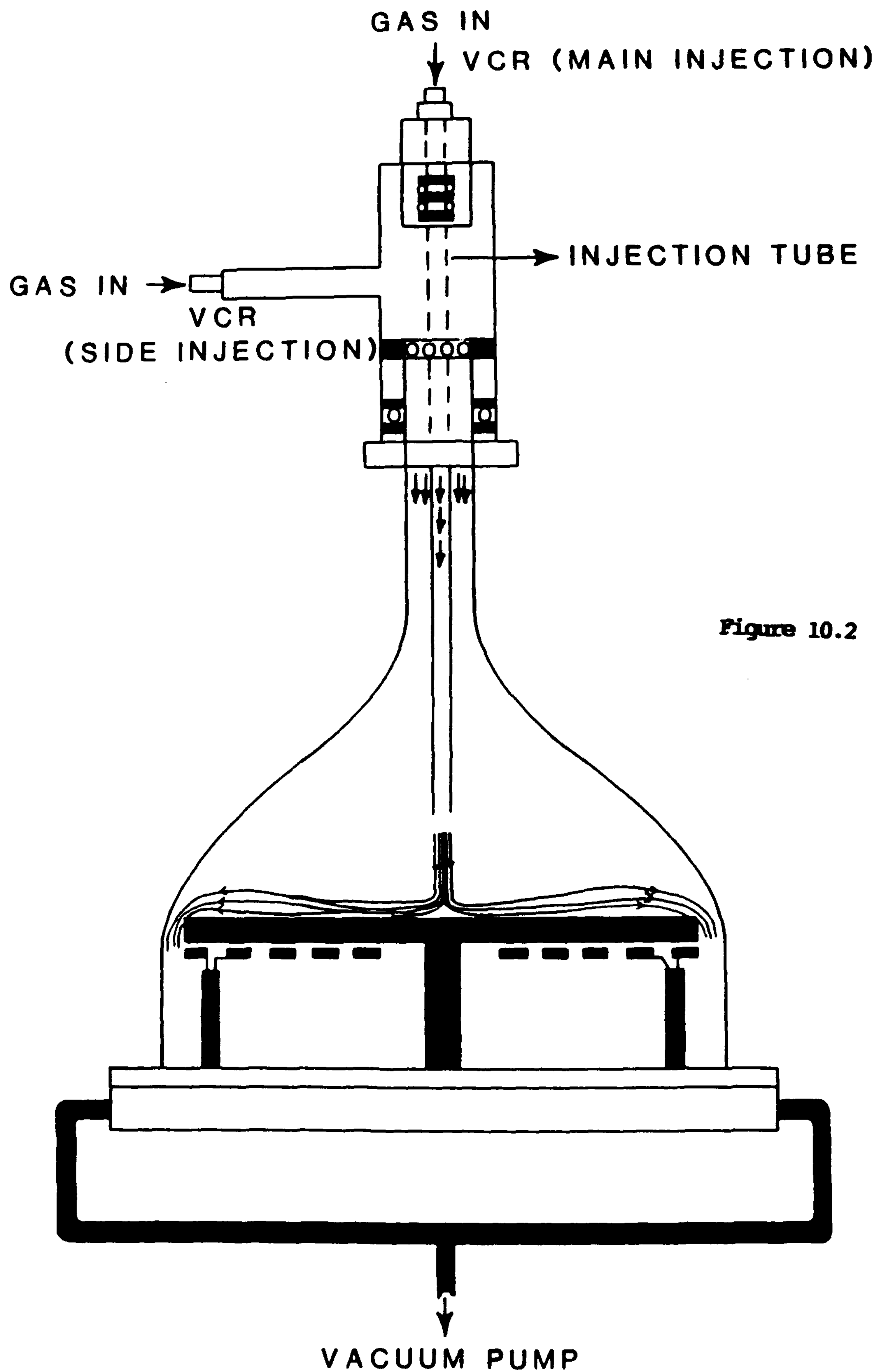

Figure 10.2

Conclusion

It can be seen from the results that as long as the gas flow rates through side inject is 4 lt./min or above and the gas flow rates through the main inject is at least 2 times less than the side inject, the mixing of gases in any manner does not affect the gas flow dynamics in the reactor.

CHAPTER 11

EXPERIMENT 4

In order to see what the pusher gas looks like at high gas flow rate, we changed the configuration. NH_4OH and HCl were mixed and injected through the side inject tube whereas the pusher gas (He) was injected through the main inject.

PARAMETRIC CONDITIONS IN THE REACTOR:

(i) Room temperature (30^oC)

(ii) Atmospheric pressure, and

(iii) 1/4" open end injection tube which ends 1" above the platter.

A summary of the flow condition and result is given in table 11.1.

TABLE 11.1

Figure 4	Flow through side inject lt/min		Flow through the main inject pusher gas (He) lt/min
	HCl	NH_4OH	
	2.5	2.5	1.5

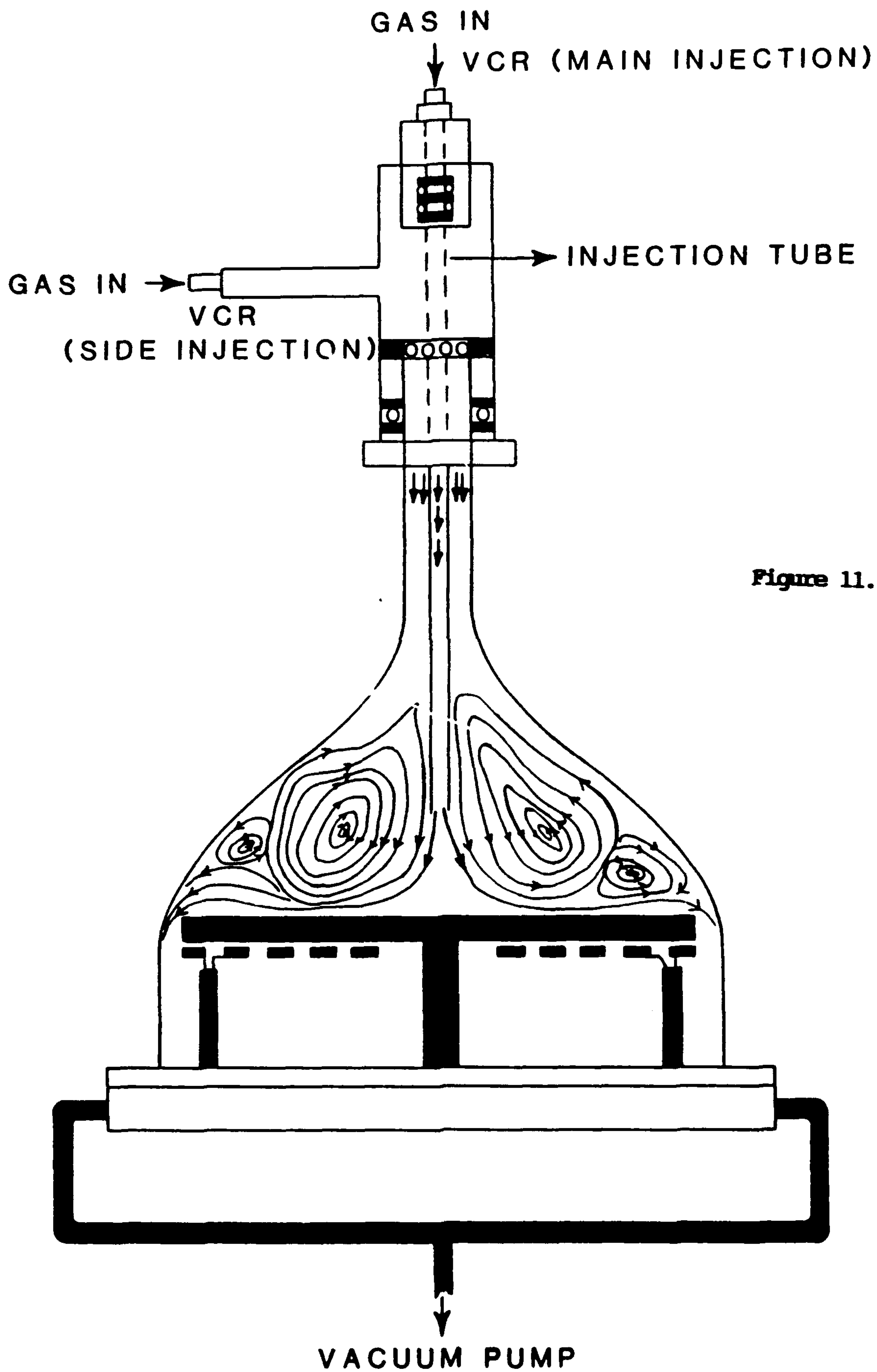

Figure 11.1

Conclusion

It is obvious from the result that if the reactants are premixed in side inject then regardless of the gas flow rate a turbulance gas flow dynamics in the reactor is created. Therefore, the reactant gases should always be premixed in the main inject or they should be injected in the reactor separately.

CHAPTER 12

EXPERIMENT 5

This experiment was performed to study the affect of low pressure on the fluid flow dynamics in the vertical reactor. All other conditions are same as experiment 4.

PARAMETRIC CONDITIONS IN THE REACTOR:

(i) Room temperature (30°C)

(ii) Low pressure (= 200 torr), and

(iii) 1/4" open end injection tube which ends 1" above the platter.

A summary of the flow condition and result is given in table 12.1.

TABLE 12.1

Figure 5	Flow through the side inject lt/min		Flow through the main inject pusher gas (He)lt/min
	HCl	NH_4OH	
	2.5	2.5	1.5

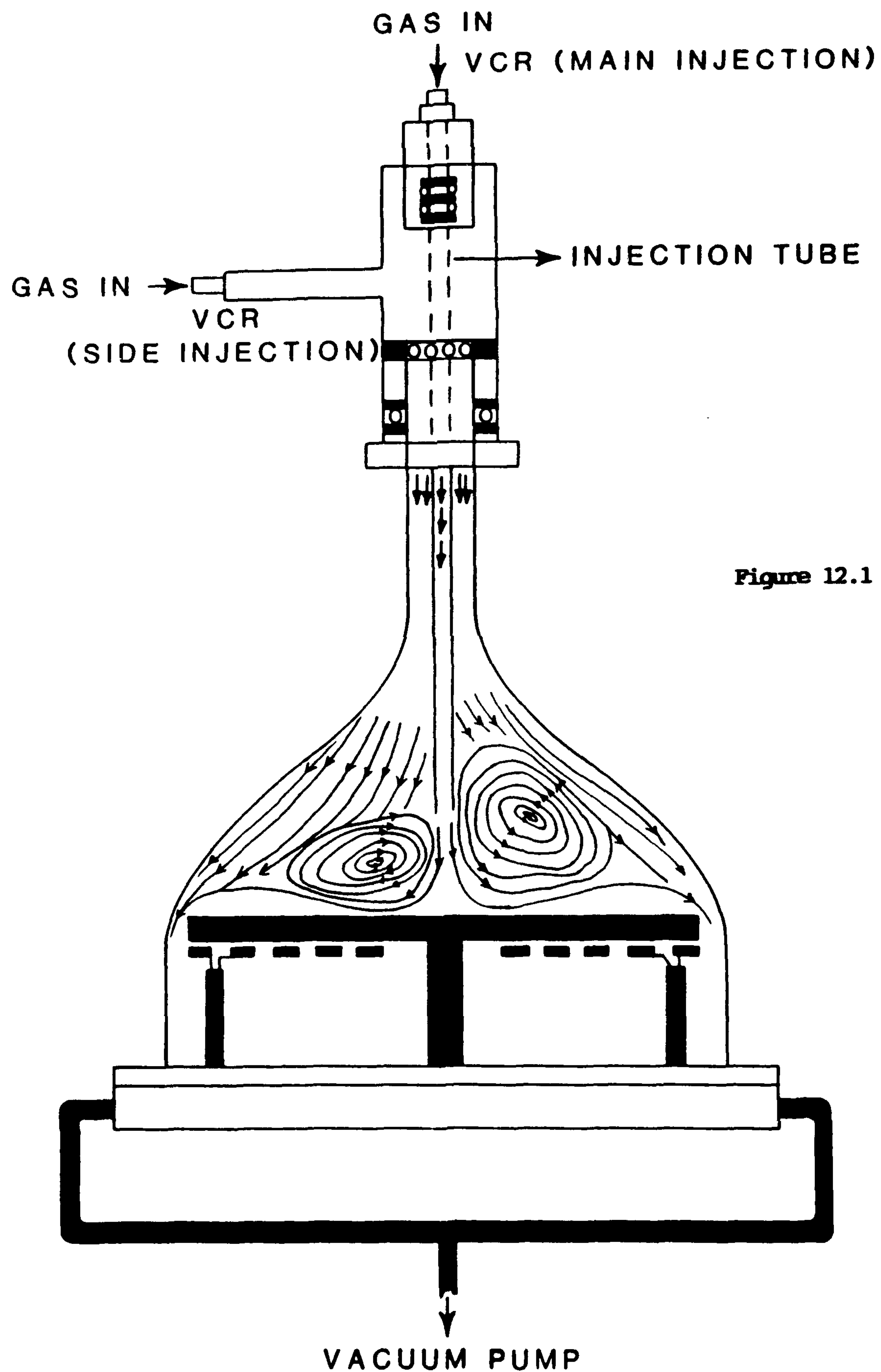

Figure 12.1

Conclusion

Comparing the results of experiments 4 and 5 it can be concluded that the pressure in the reactor does not affect the gas flow dynamics in the reactor very much if the reactant gases are premixed in side inject.

CHAPTER 13

Experiment 6

This experiment is performed to study the effect of the injection tube on the flow dynamics in the vertical MOCVD reactor. The injection tube used is a 1/4" open end injection tube which ends 3" above the platter. The experiments were performed at various parametric conditions in the reactor. The details are given below:

(A) PARAMETRIC CONDITIONS IN THE REACTOR FOR EXPERIMENT 6.1 TO 6.4:

(i) Room temperature ($30^{o}C$)
(ii) Atmospheric pressure

TABLE 13.1

Figure 1	Side Inject 1/m	Main Inject cc/m		
		NH_4OH	HCl	He
	0	375	375	375

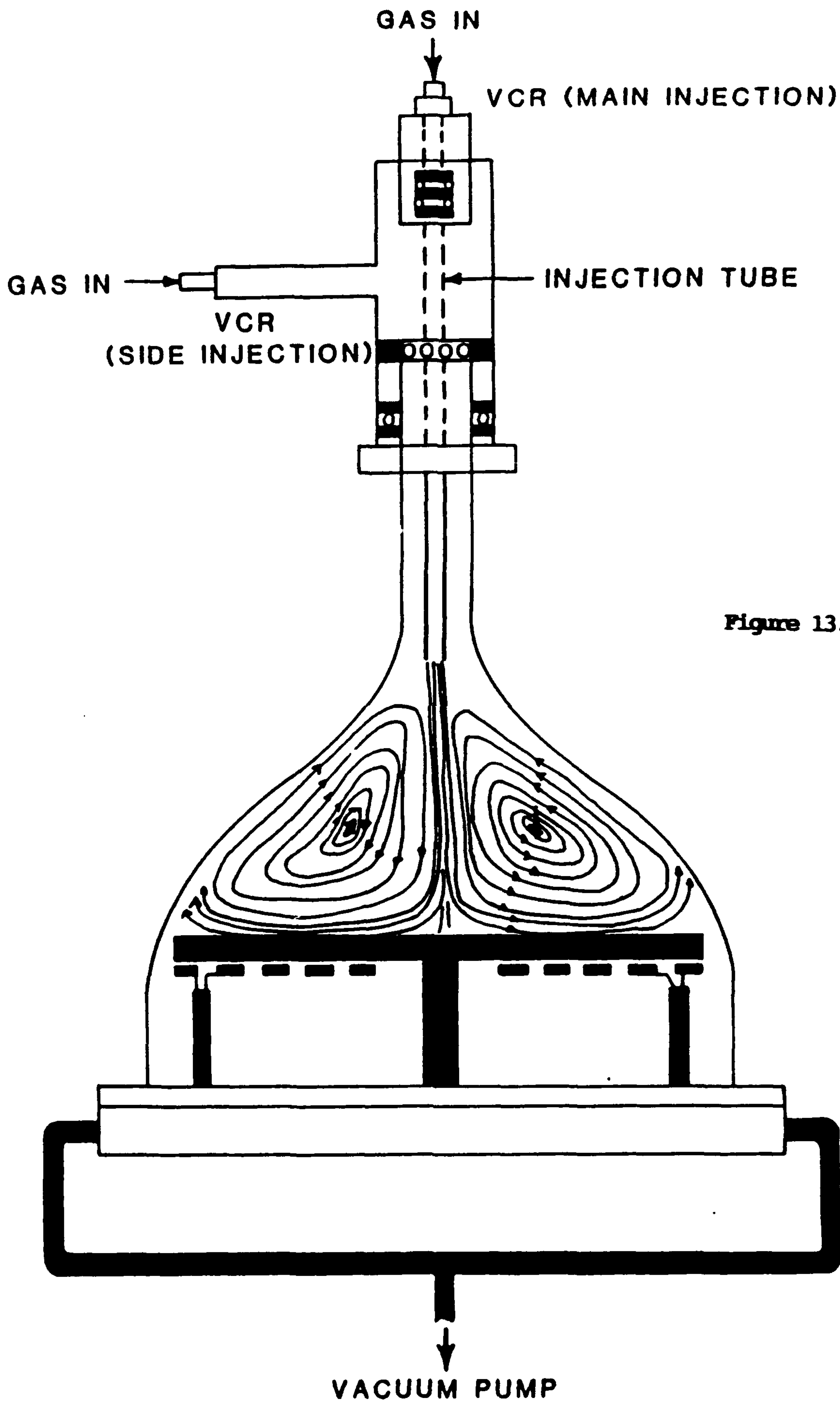

Figure 13.1

Experiment 6.2

TABLE 13.2

Figure 2	Side Inject (lt/min)		Main Inject (lt/min) HCl
	He (Pusher)	NH_4OH	
	3.5	1.5	1.5

Experiment 6.3

TABLE 13.3

Figure 3	Side Inject (lt/min)		Main Inject (lt/min) He(Pusher)
	NH_4OH	HCl	
	2.5	2.5	1.5

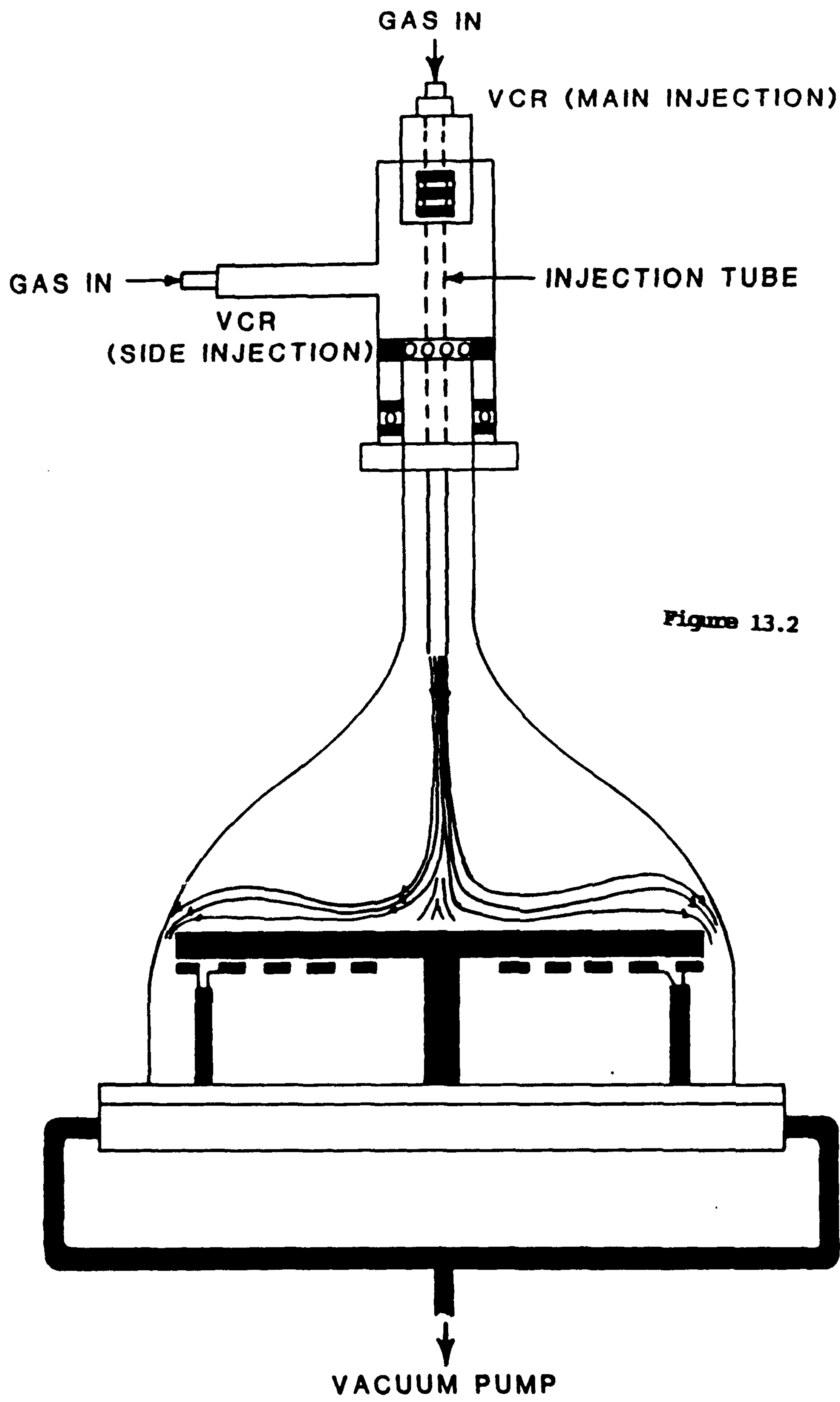

Figure 13.2

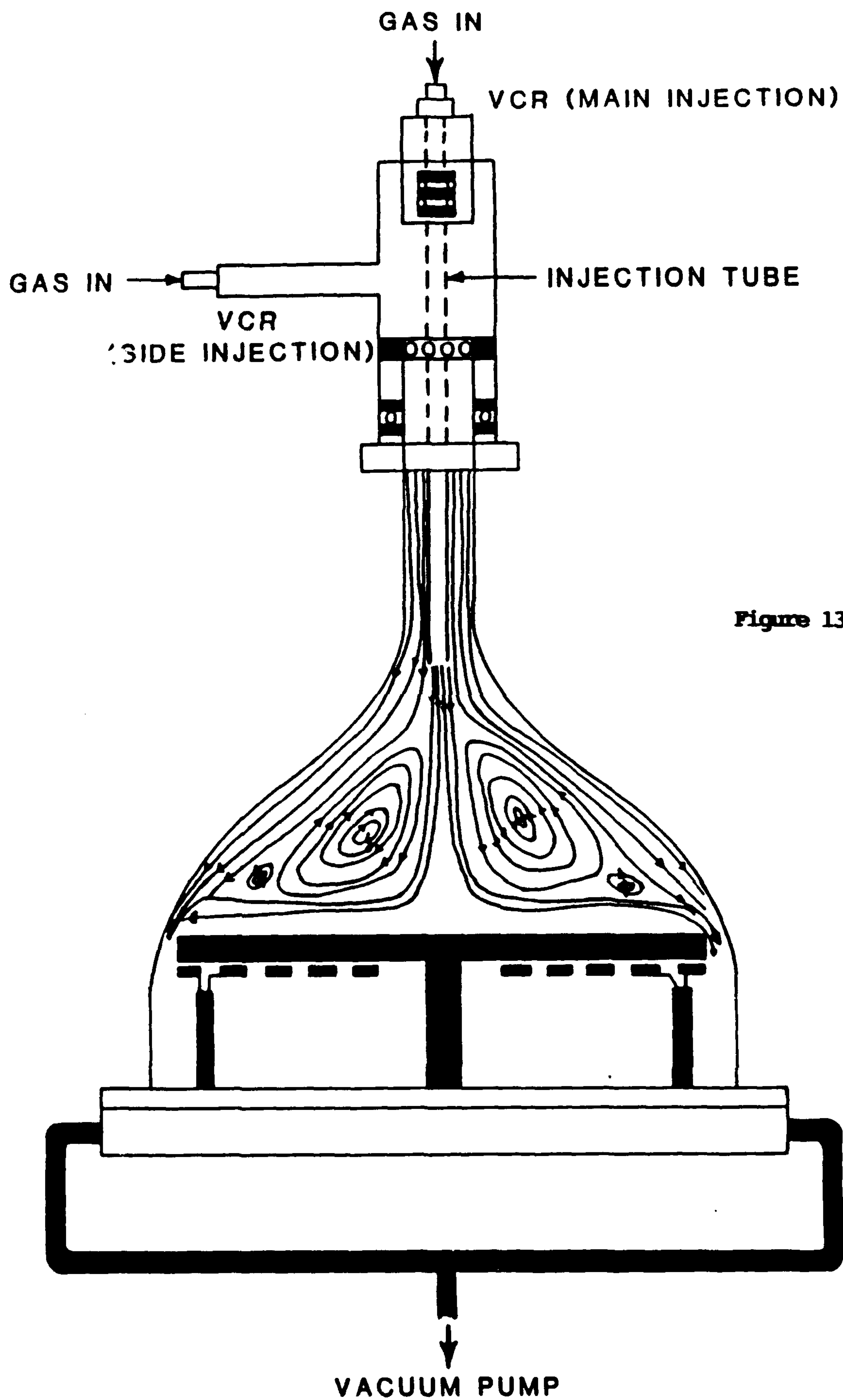

Figure 13.3

Experiment 6.4

TABLE 13.4

Figure 4	Side Inject (lt/min) He(Pusher)	Main Inject (cc/min)	
		NH_4OH	HCl
	5	750	750

(B) PARAMETRIC CONDITIONS IN THE REACTOR FOR EXPERIMENT 6.5 TO 6.7:

(i) Room temperature (30^oC)

(ii) Atmospheric pressure (200 Torr)

TABLE 13.5

Figure 5	Side Inject (lt/min) He(Pusher)	Main Inject (cc/min)	
		NH_4OH	HCl
	5	750	750

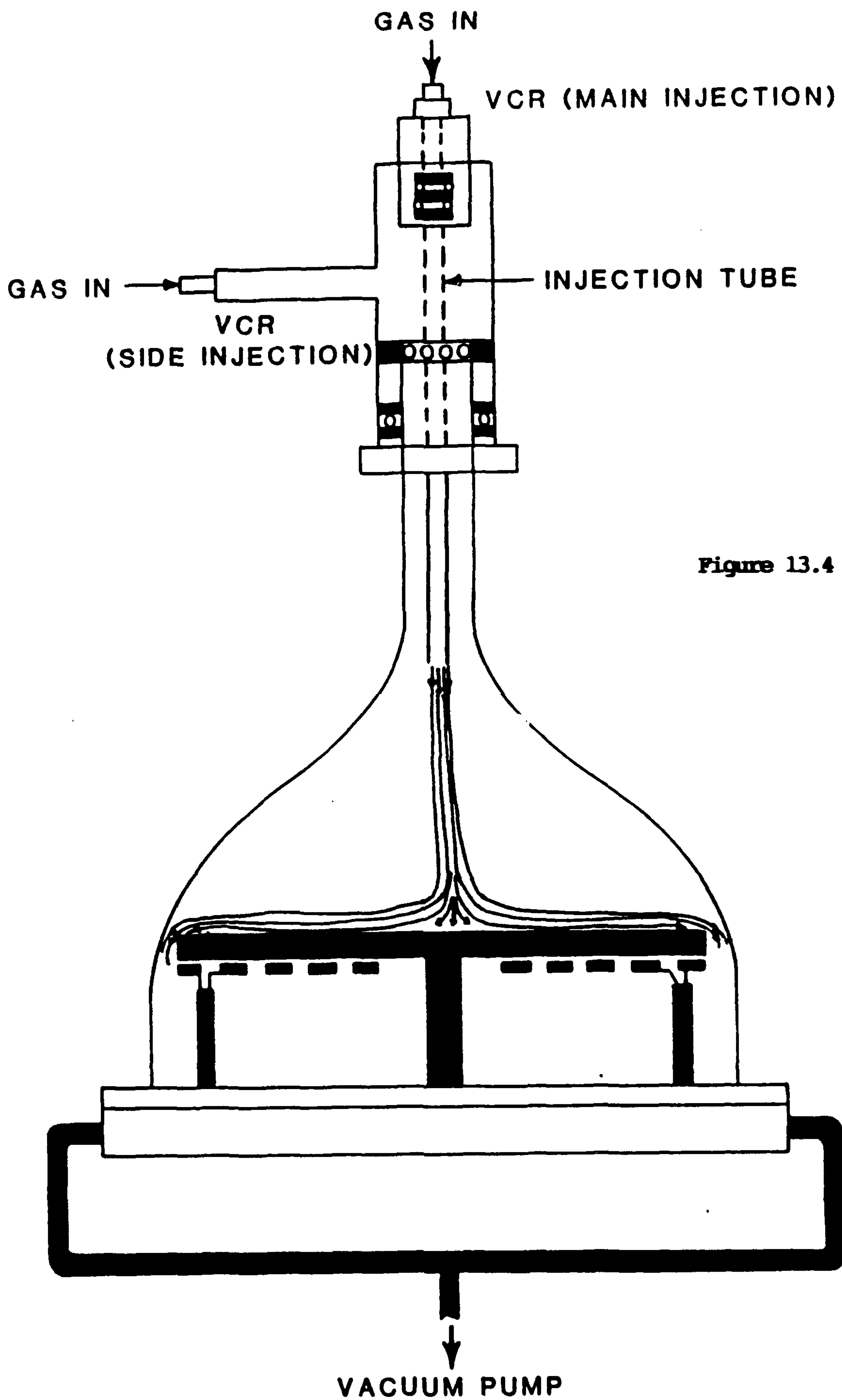

Figure 13.4

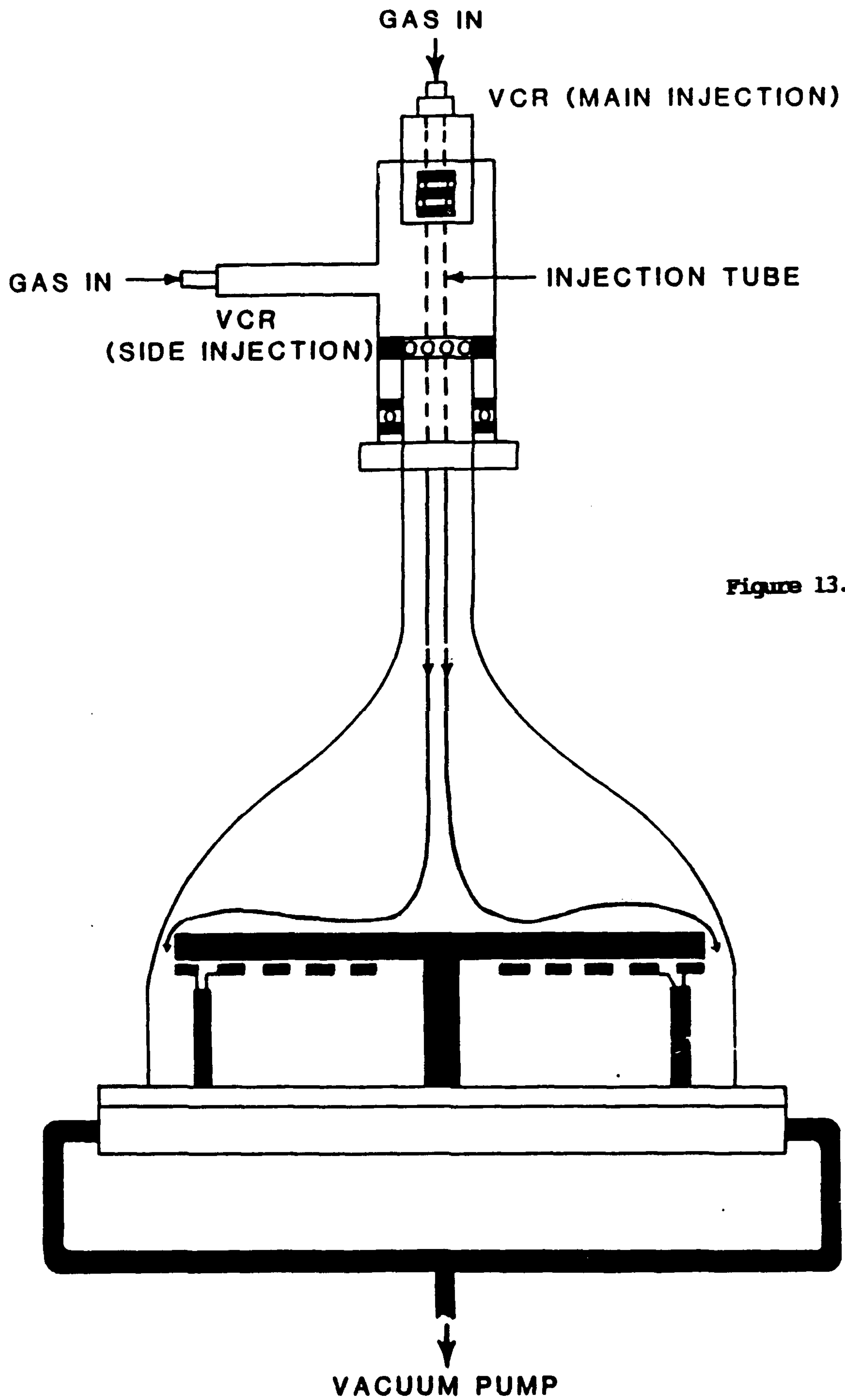

Figure 13.5

TABLE 13.6

Figure 6	Side Inject (lt/min)	Main Inject (cc/min)	
		NH_4OH	HCl
	0	750	750

TABLE 13.7

Figure 7	Side Inject (lt/min)		Main Inject (lt/min) He(Pusher)
	NH_4OH	HCl	
	2.5	2.5	1.5

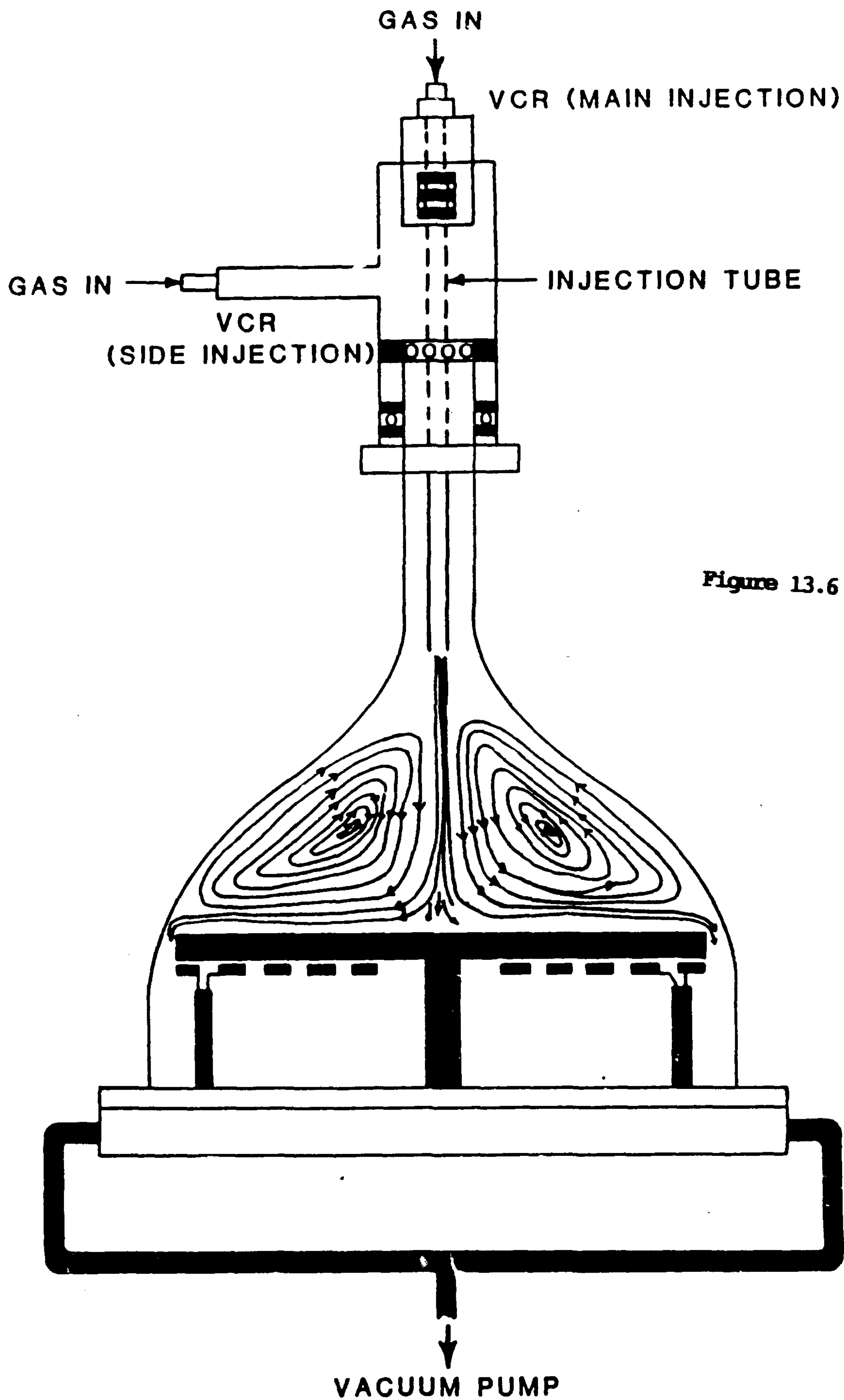

Figure 13.6

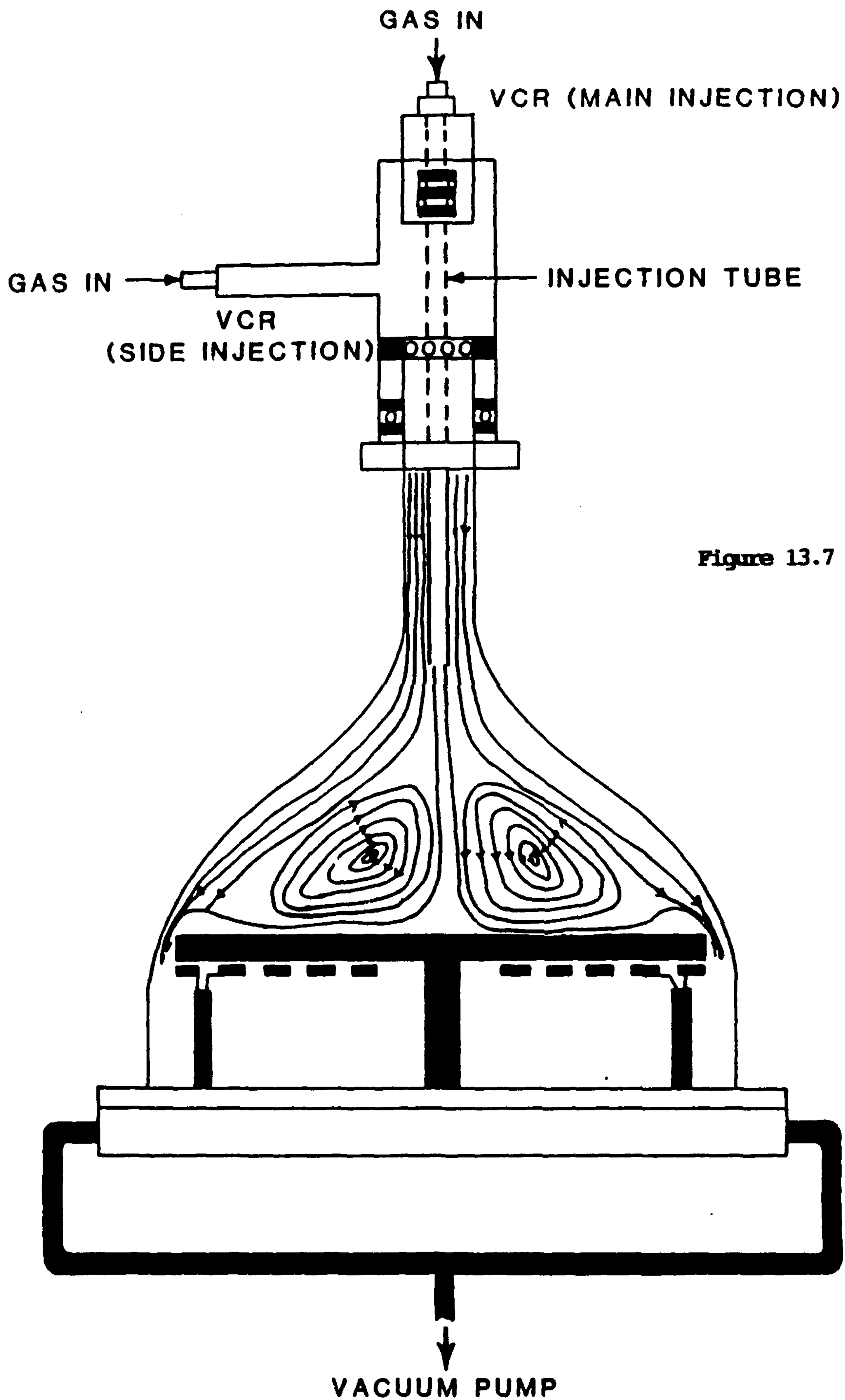

Figure 13.7

Conclusion

(i) Using an 1/4" open end injection tube which ends 3" above the platter does not affect the gas flow dynamics in the reactor very much. The gas flow dynamics in this particular reactor is still dependent on the gas flow rates through the side inject port and main inject port separately.

(ii) As long as the gas flow rate through the side inject port is 4lt/min or above and gas flow rate through the main inject is 1.5 lt/min or below the gas flow dynamics in the reactor is turbulance free.

(iii) The gas flow dynamics in this case also depends on the manner in which reactants are mixed. To avoid turbulant flow dynamics the reactants should never be mixed in the side inject port.

(iv) The low pressure in the reactor does not affect the gas flow dynamics in the reactor at all.

CHAPTER 14

Experiment 7:

In this experiment the injection tube used is a 1/4" funnel shaped end tube which ends 1" above the platter.

Experiment 7.1

PARAMETRIC CONDITIONS IN THE REACTOR:

(i) Room temperature (30°C)
(ii) Atmospheric pressure

TABLE 14.1

Figure 1	Side Inject (lt/min) He(Pusher)	Main Inject (cc/min)	
		NH_4OH	HCl
	5	750	750

Experiment 7.2

PARAMETRIC CONDITIONS IN THE REACTOR:

(i) Room temperature (30°C)
(ii) Low pressure (200 Torr)

TABLE 14.2

Figure 2	Side Inject (lt/min) He(Pusher)	Main Inject (cc/min)	
		NH_4OH	HCl
	5	750	750

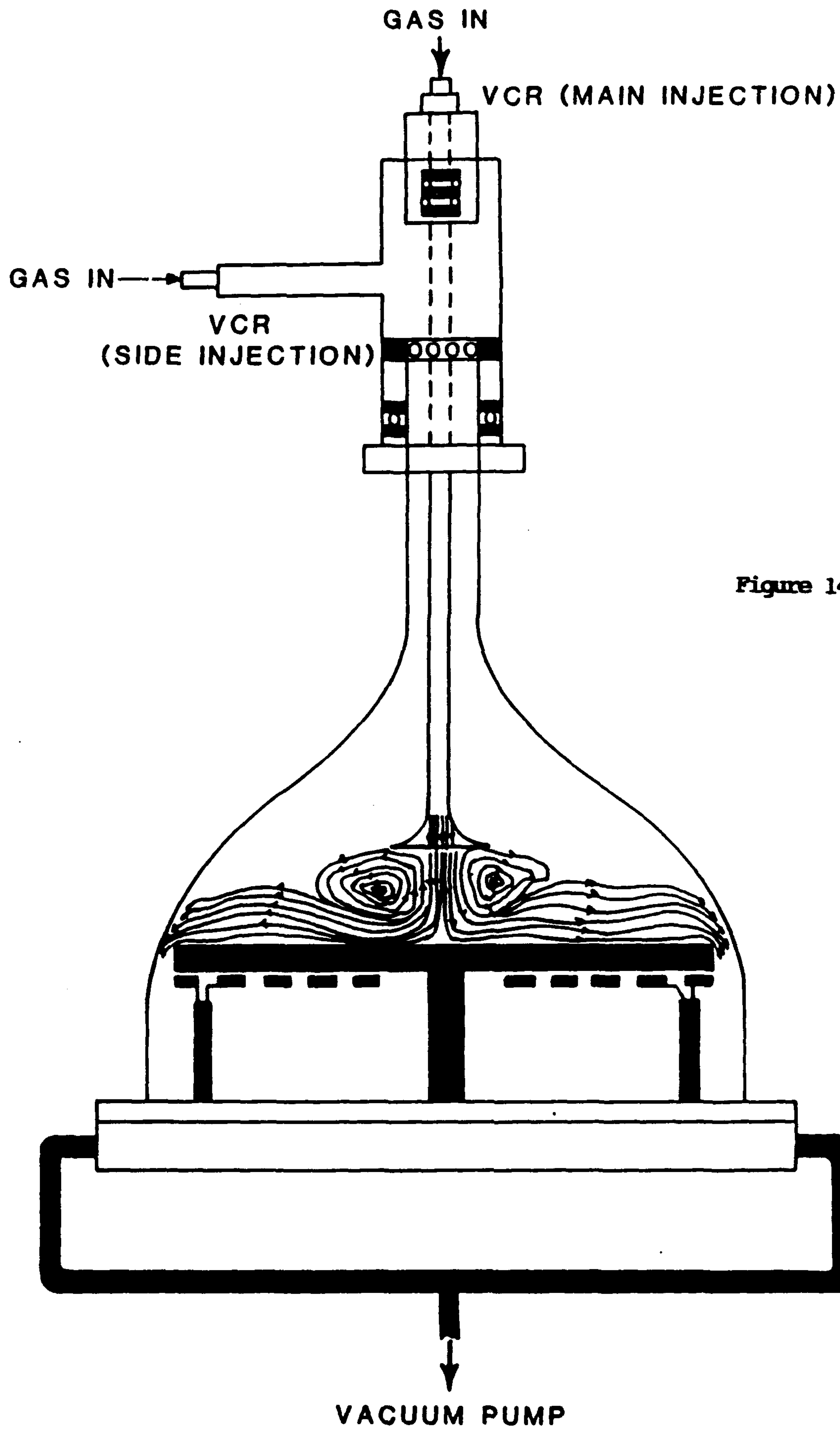

Figure 14.1

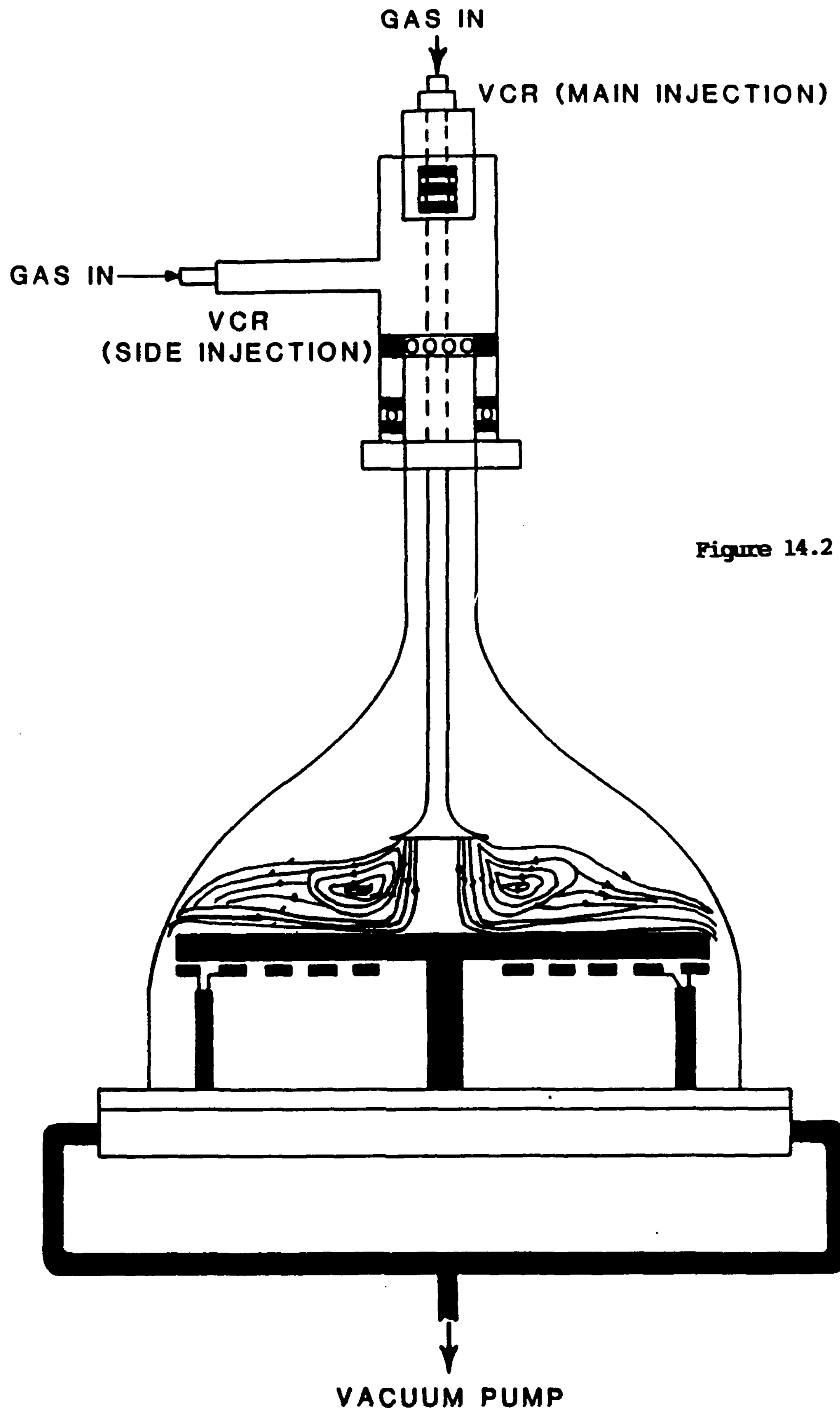

Figure 14.2

Conclusion

(i) The use of 1/4" funnel shaped end injection tube does affect the gas flow dynamics in the reactor for worst.

(ii) Even with a gas flow rates of 5 lit/min and 1.5 lit/min (at atmospheric pressure) through side inject port and main inject port respectively, the gas flow in the reactor is not laminar in the reactor.

(iii) The low pressure in the reactor does not help the gas flow in the reactor to be free of turbulence.

CHAPTER 15

Experiment 8

This experiment is performed to study the effect of the injection tube on the flow dynamics in the vertical MOCVD reactor. The injection tube used is 1/4" in OD with the holes at the bottom and this but ends 1" above the platter. The experiments were performed at various parametric conditions in the reactor. The details are given below:

Experiment 8.1

PARAMETRIC CONDITIONS IN THE REACTOR:

(i) Room temperature (30^oC)
(ii) Atmospheric pressure, and

TABLE 15.1

Figure	Side Inject (lt/m) He (Pushergas)	Main Inject (cc/m) NH_4OH	HCl
1	5	750	750

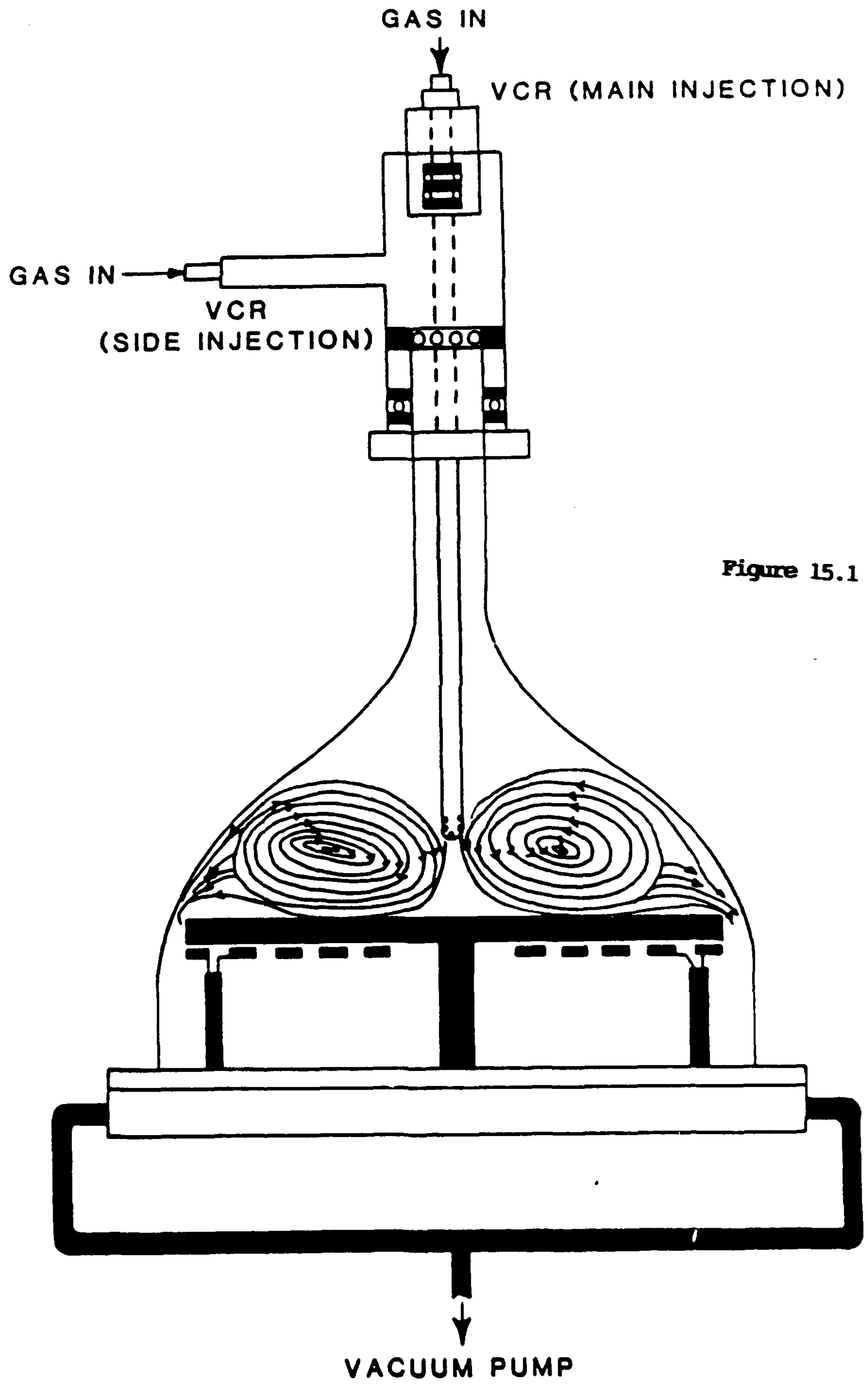

Figure 15.1

Experiment 8.2

PARAMETRIC CONDITIONS IN THE REACTOR:

(i) Room temperature (30°C)
(ii) Low pressure = 200 Torr

TABLE 15.2

Figure	Side Inject (lt/m) He (Pushergas)	Main Inject (cc/m) NH_4OH	HCl
2	5	750	750

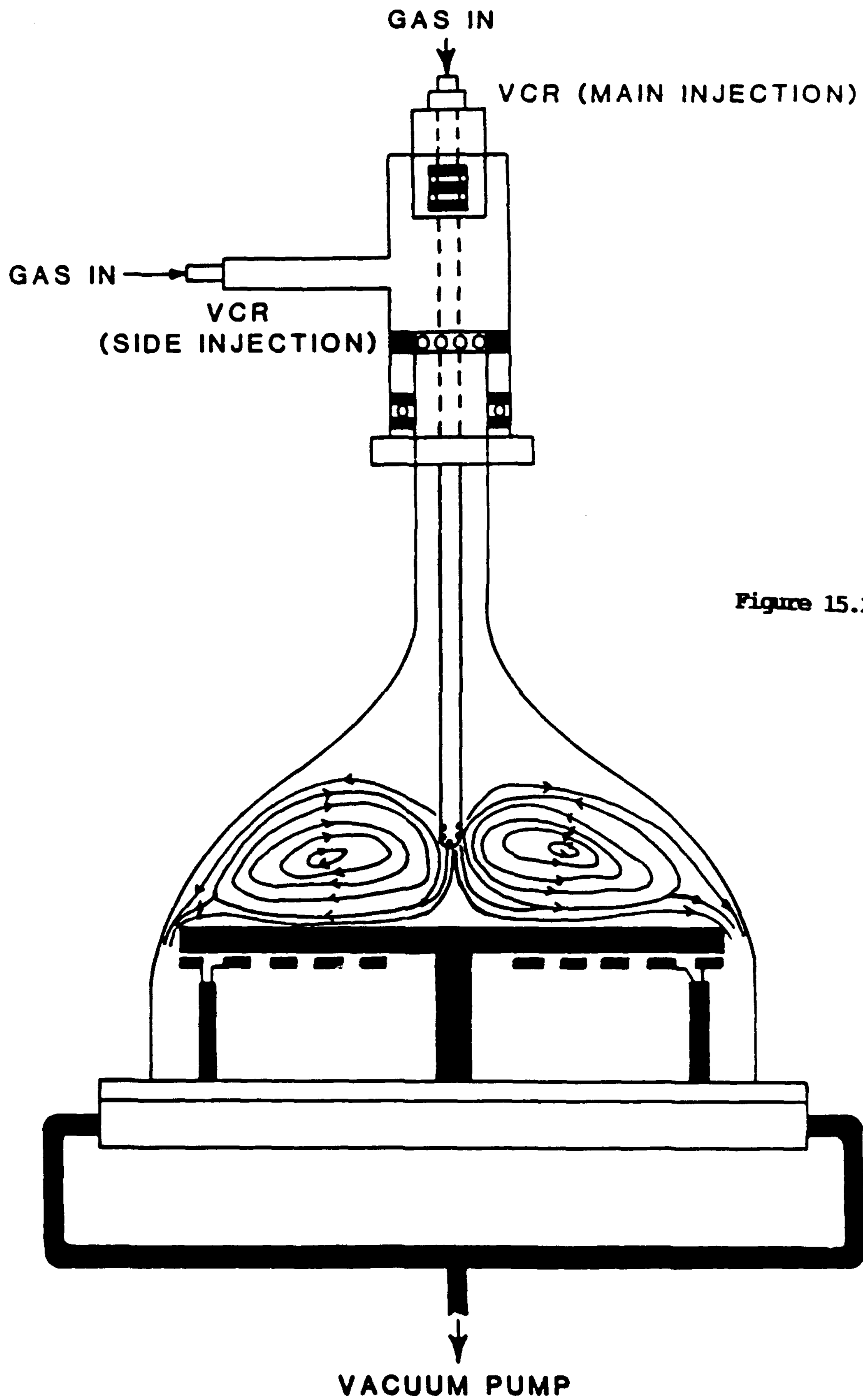

Figure 15.2

Conclusion

(i) The use of 1/4" injection tube with holes at the bottom end which ends 1" above the platter does affect the gas flow dynamics in the reactor for worse.

(ii) Even with a gas flow rates of 5 lit/min and 1.5 lit/min (at atmospheric pressure) through side inject port and main inject port respectively, the gas flow in the reactor is not laminar in the reactor.

(iii) The low pressure in the reactor does not help the gas flow in the reactor to be free of turbulence.

CHAPTER 16

Experiment 9

This experiment is performed to study the effect of a Fretted disk without any Injection tube on the flow dynamics in the vertical MOCVD reactor. The experiments were performed at various parametric conditions in the reactor. The details are given below:

Experiment 9.1

PARAMETRIC CONDITIONS IN THE REACTOR:

(i) Room temperature (30°C)
(ii) Atmospheric pressure, and

TABLE 16.1

Figure	Main Inject (lt/m) He (Pushergas)	Side Inject (lt/m) NH_4OH	HCl
1	0	2.5	2.5

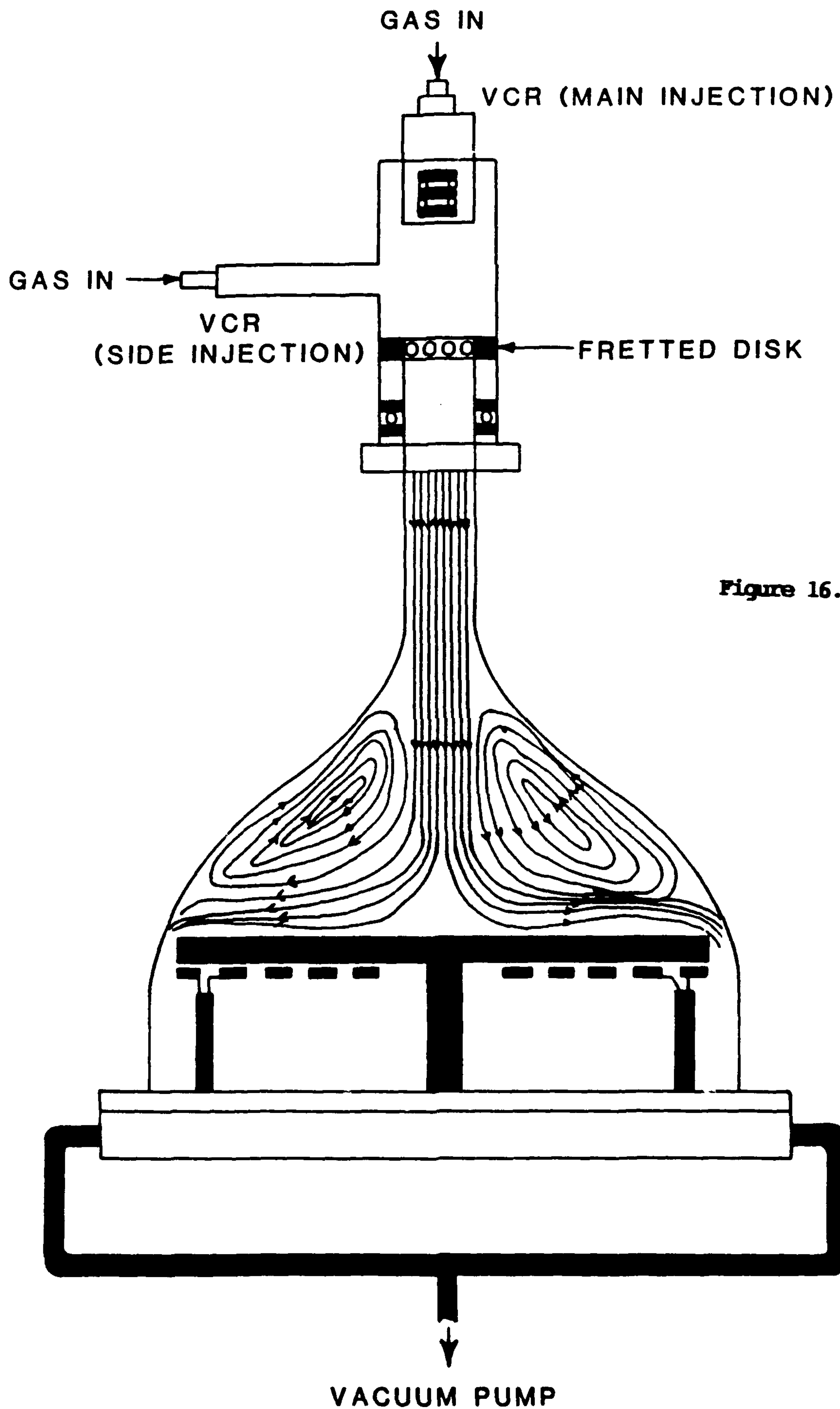

Figure 16.1

Experiment 9.2

PARAMETRIC CONDITIONS IN THE REACTOR:

(i) Room temperature (30°C)
(ii) Low pressure = 200 Torr

TABLE 16.2

Figure	Main Inject (lt/m) He (Pushergas)	Side Inject (lt/m) NH_4OH	HCl
2	0	2.5	2.5

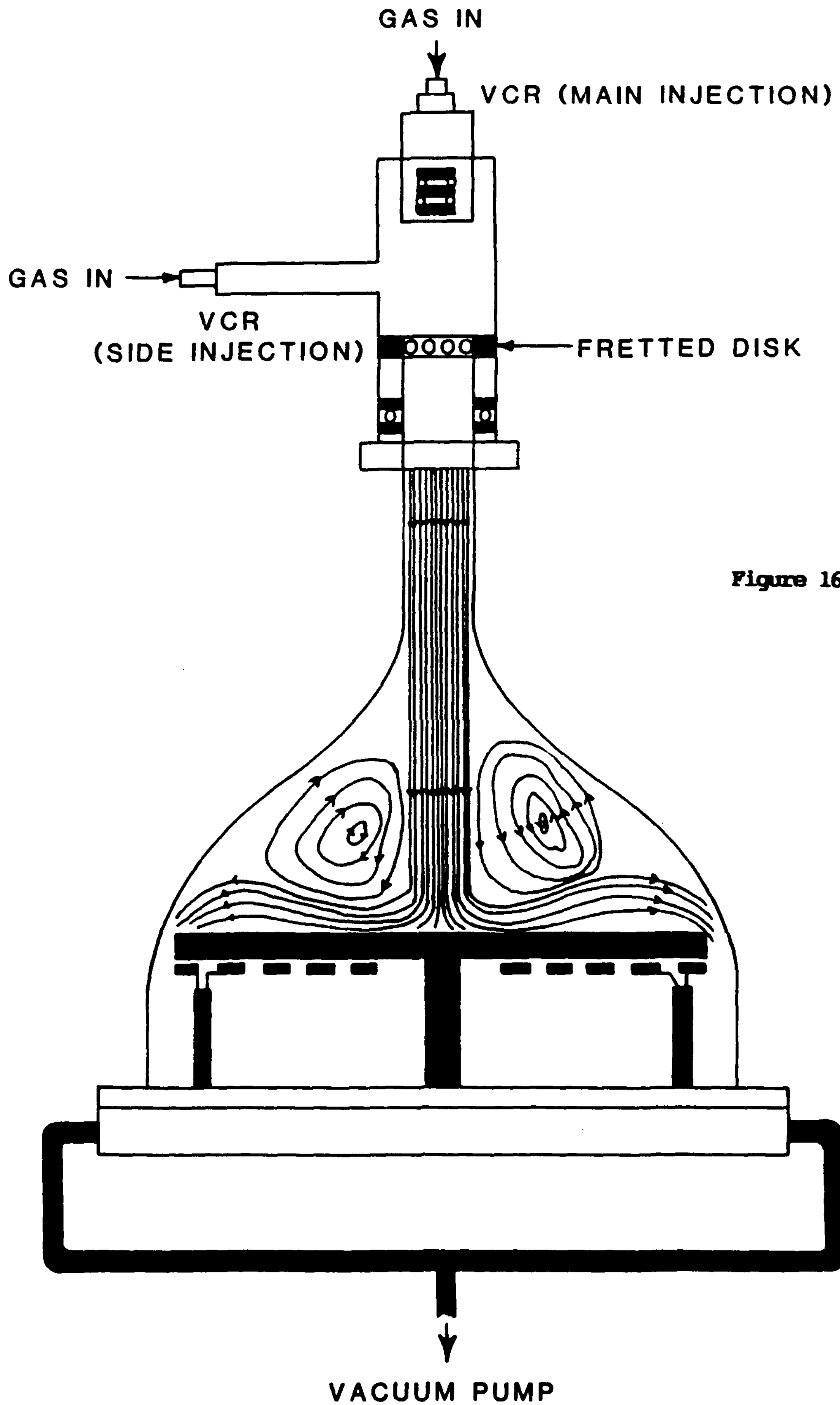

Figure 16.2

Experiment 9.3

PARAMETRIC CONDITIONS IN THE REACTOR:

(i) Platter temperature is 580°C

(ii) Atmospheric pressure, and

TABLE 16.3

Figure	Main Inject (lt/m) He (Pushergas)	Side Inject (lt/m) $TiCl_4$	H_2O
3	0	2.5	2.5

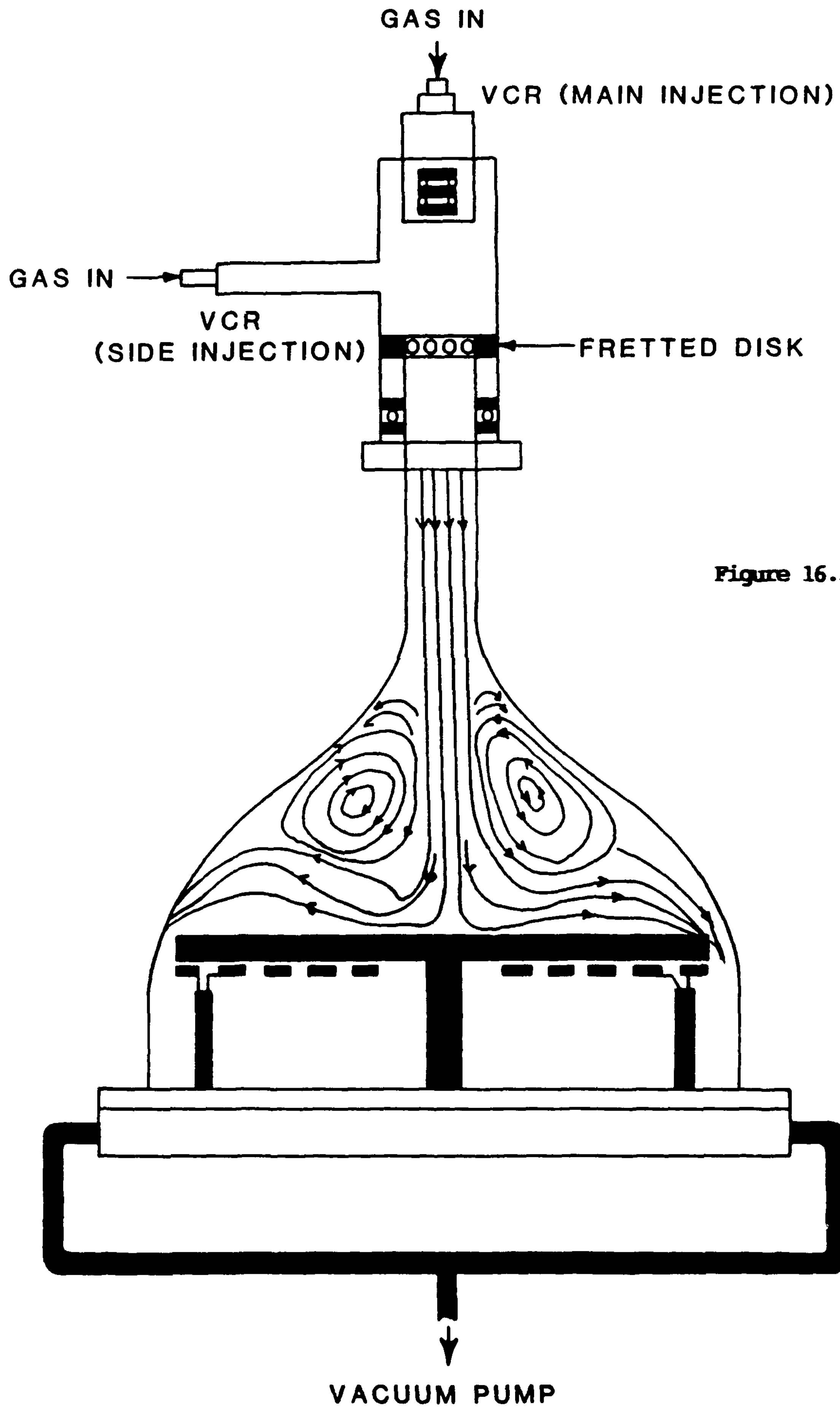

Figure 16.3

Experiment 9.4

PARAMETRIC CONDITIONS IN THE REACTOR:

(i) Platter temperature is 580°C

(ii) Low pressure = 200 Torr

TABLE 16.4

Figure	Main Inject (lt/m) He (Pushergas)	Side Inject (lt/m) $TiCl_4$	H_2O
4	0	2.5	2.5

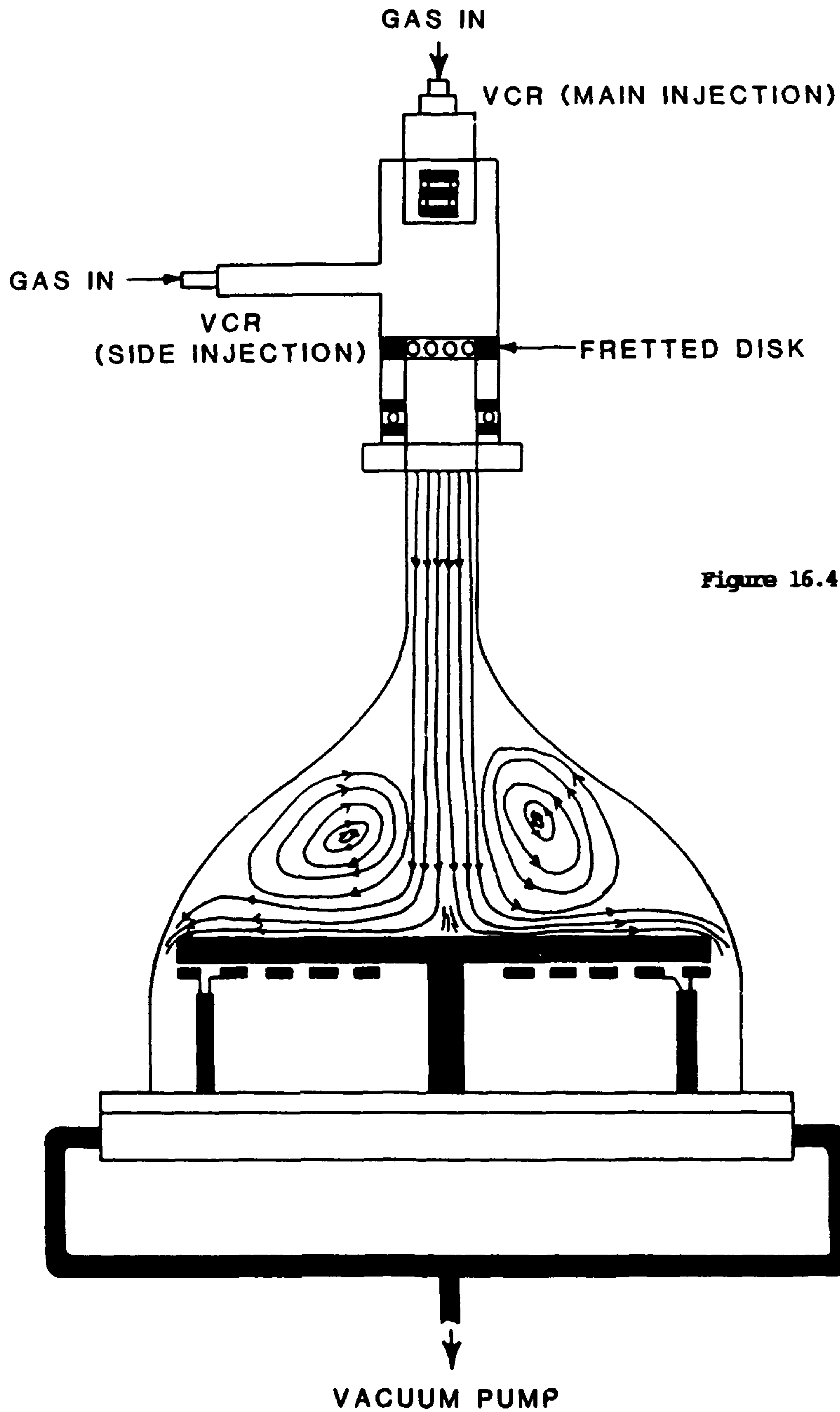

Figure 16.4

Experiment 10

This experiment is performed to study the effect of high temperature, with Injection tube, on the flow dynamics in the vertical MOCVD reactor. The injection tube used is 1/4" in OD which ends 1" above the platter. The experiments were performed at various parametric conditions in the reactor. The details are given below:

Experiment 10.1

PARAMETRIC CONDITIONS IN THE REACTOR:

(i) Platter temperature is 580°C

(ii) Atmospheric pressure, and

TABLE 16.5

Figure	Main Inject (cc/m) $TiCl_4$	Side Inject (lt/m) He	H_2O
1	750	2.5	2.5

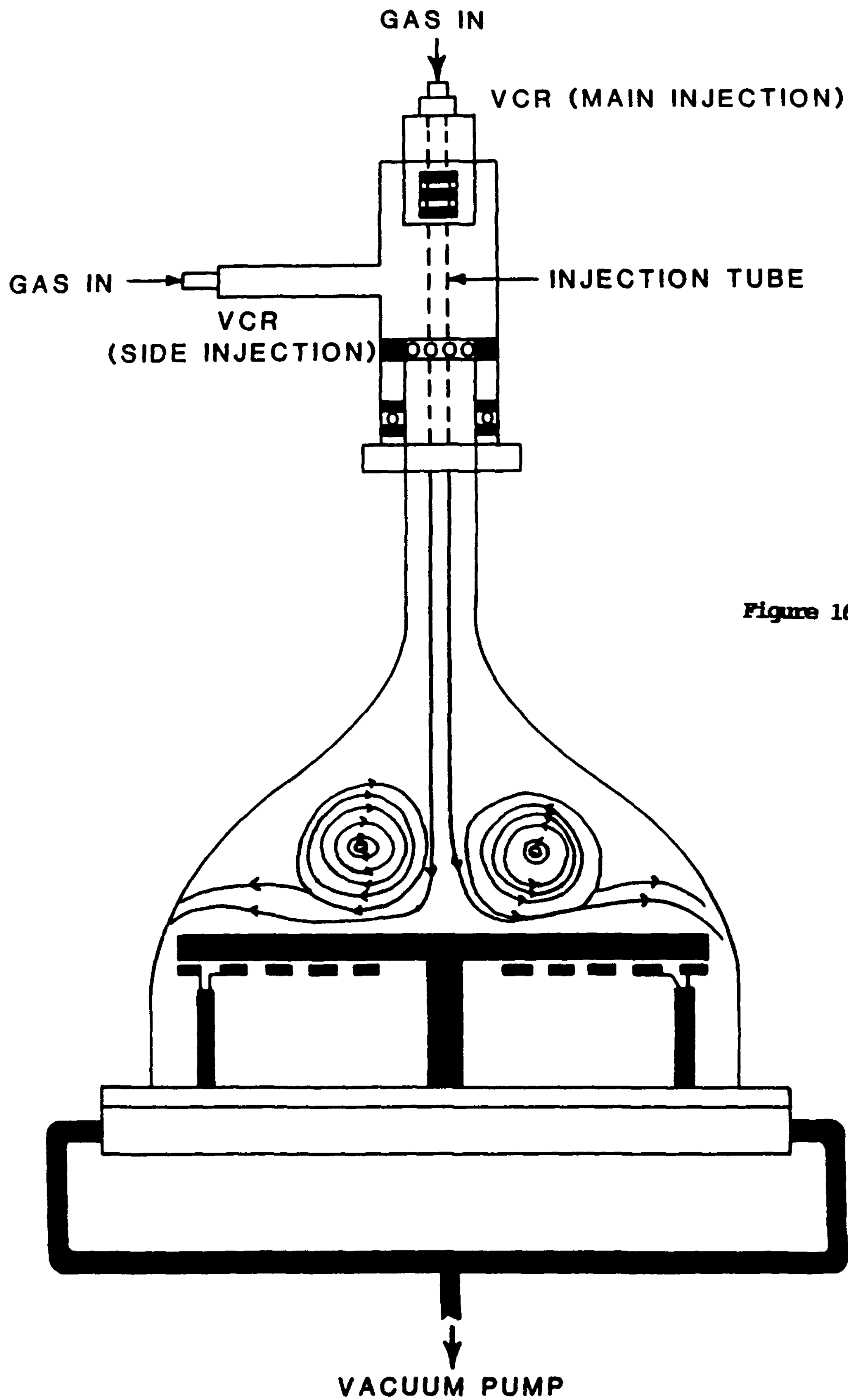

Figure 16.5

Experiment 10.2

PARAMETRIC CONDITIONS IN THE REACTOR:

(i) Platter temperature is 580°C)

(ii) Low pressure = 200 Torr

TABLE 16.6

Figure	Side Inject (lt/m) He (Pushergas)	Main Inject (cc/m) $TiCl_4$	H_2O
2	5	325	325

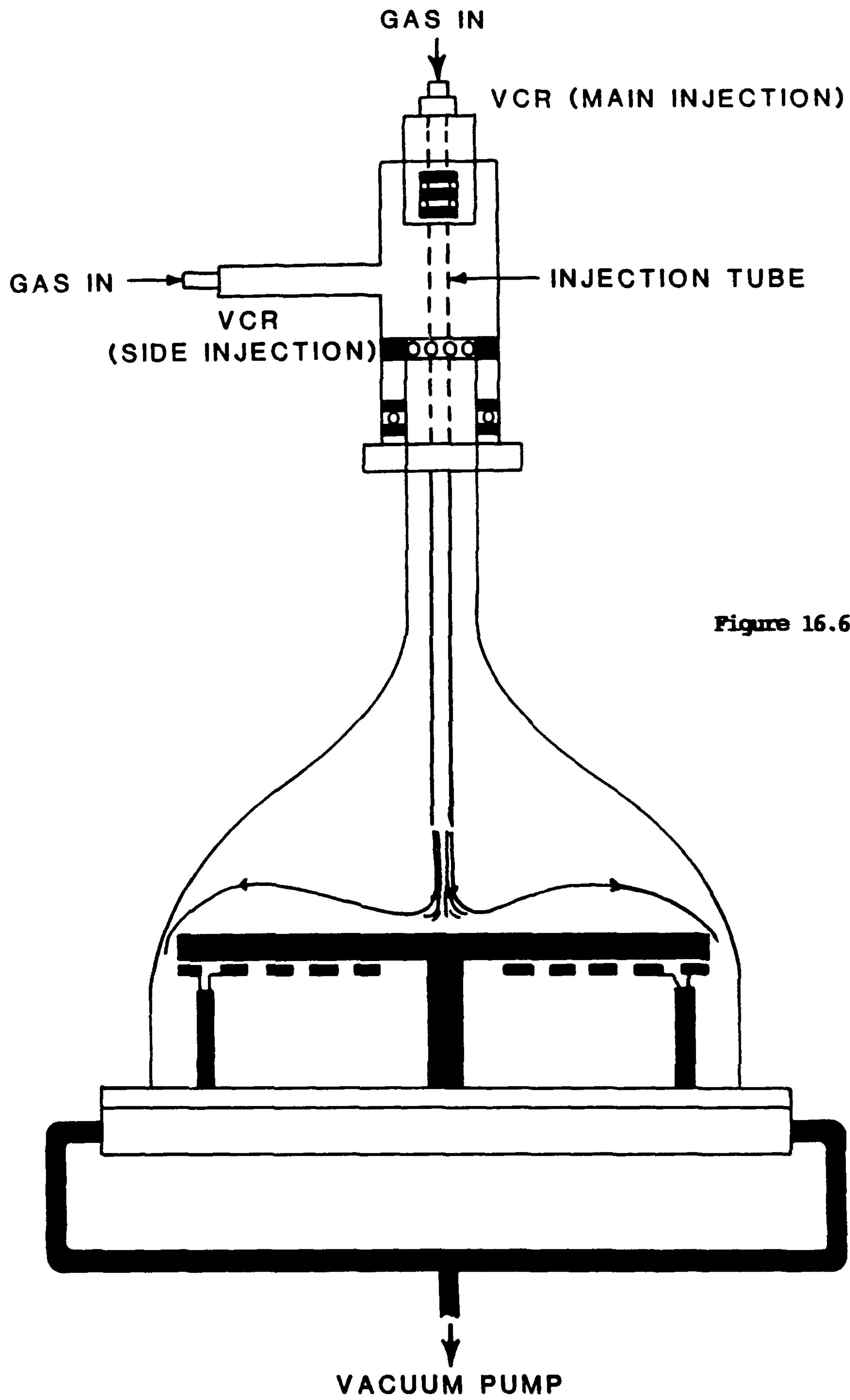

Figure 16.6

REFERENCE

(1) D. H. Reep, Organometallic Chemical Vapor Deposition of Gallium Arsenide : Growth Mechanisms, Ph.D. Dissertation, Rensselaer Polytechnic Institute, Troy, NY 1982.