THE
AUSTRALIAN
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THERMOCHEMICAL ENERGY TRANSFER (CHEMICAL HEAT PIPE) DEMONSTRATION BASED ON THE SYSTEM $2NH_3 \rightleftharpoons N_2 + 3H_2$

Progress Report
June 1982

P O Carden

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Department of Engineering Physics
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INSTITUTE OF ADVANCED STUDIES

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PARTICIPANTS IN PROJECT 1982

Dr P O Carden

Mr R Gresham

Mr A Perry

Mr J Butt (resigned February 1982)

ACKNOWLEDGEMENTS: Dr O M Williams who left the project early in the year has given every assistance in the transfer of information.

Mr R E Whelan has given approximately two weeks of valuable assistance.

Mr J Blamey has ably assisted in corroborating thermal stress calculations.

CONTENTS

1. MANAGEMENT OF PROJECT AND STAFFING

Towards the end of 1981 the project entered a critical period as it became more and more evident that it would be very difficult indeed to meet the completion schedule expected by NERDDC. At the beginning of 1982 Dr Williams was obliged to retire from the project following medical advice and his two students Messrs A Perry and J Butt were temporarily (until August 1982) reclassified as part-time research assistants in order to give them time to reassess their positions. In February Mr Butt resigned.

Mr R Gresham has remained as the sole technical staff member of the group. Mr R Whelan was able to give valuable assistance during this year for about two weeks.

Management of the group has now reverted to Dr P O Carden.

2. REVIEW OF PROJECT

2.1 Objectives

The primary objective is to demonstrate thermochemical energy transfer using the ammonia system. This may be divided into several secondary or sub objectives: (1) the construction of major components; (2) the separate testing of major components; (3) the integration of all components into a system for energy transfer; (4) operation and the collection of data that demonstrates quantitatively the transfer of energy under steady state and transient conditions.

2.2 Status

Referring to these secondary objectives it can be said that (1) and (2) have been paramount throughout 1981 in both effort and the formulation of schedules. It is now evident from reviewing the project that secondary objectives (3) and (4) entail a great deal of extra effort not previously allowed for. The most serious short-coming is the lack of accurate methods of measuring flows of liquid ammonia and gas mixtures and this has reflected back to the group's ability to carry out secondary objectives (2) as well as (3) and (4). Another short-coming has been the lack of a system design to enable (4).

On the positive side it can be stated that (1) has been achieved, at least until such time that (2) may expose inherent problems.

2.3 The measurement of fluid flow

Prior to the review it had been intended to measure flow using the following instruments and methods.

(1) A turbine instrument designed by R Whelan to measure liquid flows.

(2) Two differential pressure gauges to measure both gas and liquid flows.

(3) Fixed displacement reciprocating pumps assuming flow to be equal to the product of stroking rate and displacement volume.

(4) Observations of rate of rise of pressure as gas is pumped into constant volume vessels.

Of these methods, we believe liquid flow using (1) is the most reliable. This is because studies have shown (1) to provide a linear output proportional to volumetric flow and practically independent of density and viscosity (Reference 1). This has enabled the instrument calibration to be generalised and confirmed with easily manageable liquids such as water and alcohol.

However, it is known that the calibration is sensitive to wear and now needs checking after a long period of serivce.

Attempts to measure flow with (1) and also to calibrate (2) are inhibited by the fact that the reciprocating pumps do not deliver a constant flow. A gas backed accumulator has been used to try to smooth the flow but this was not entirely satisfactory because the pneumatically driven pump stroked at a varying rate and required constant adjustment. Alternatively the flow can be controlled to be constant by an automatic flow control valve and one of these has been built and tried with limited success. It is hoped that this can be further developed for effective use in the liquid line. The flows are of course quite small (about 0.5 gm/s) and this adds to the difficulty.

With respect to the calibration of the instruments (2) the prerequisite of a constant flow of fluid has added importance because they are known to be non-linear devices.

An alternative method of flow measurement not requiring the above prerequisite might be provided by (3), the pumps, and this has been tried. However, because of the pneumatic drives, the stroking rates are uneven: often the 'out' stroke is ten times faster than the 'in' stroke. Consequently, pressure drops across the valves in the pumps play an important part and sometimes there are substantial delays in valve operation particularly in the gas pump. The result is that we are not able to have any confidence in this method of flow measurement.

The method (4) suffers from the fact that one needs to know whether the gas is undergoing adiabatic or isothermal changes in the vessel or following some law in between. Therefore good temperature data is required and also sensitive pressure measurements free from hysterisis.

2.4 Gas analysis

In the context of this report, gas analysis means primarily the determination of the nitrogen hydrogen ratio so as to ascertain whether hydrogen is being preferentially leaked from the system. At one time it had been intended to do this with the mass analyser but the setting up of this instrument and its calibration were subsequently abandoned because of the considerable effort involved relative to its usefulness to the project.

A system of rotameters operating at low pressure is available but these measure the ammonia-to-gas ratio not the nitrogen-to-hydrogen ratio in the gas.

2.5 Demonstration of energy transfer

Prior to this review it had been intended to explore the possibility of operating the dissociator and synthesiser independently, coupled only through a common gas storage vessel whose pressure was observed visually. It was thought that the dissociator and synthesiser might be operated as batch processors and that subsequent energy accounting would demonstrate the fact of energy transfer.

However, such a system would only demonstrate energy transfer with energy storage as a necessary adjunct. It is now felt that the nub of the problem is to demonstrate energy transfer without thermochemical energy storage since the comparative economics of high pressure gas storage is not favourable (unless underground storage is used - a concept somewhat reserved for the more distant future perhaps). This entails a system in which the rate of synthesis is made equal to the rate of dissociation through all realistic temporal changes. With this as a basis we are now able to firm up on the energy transfer aspects of the system.

3. PROPOSED SOLUTIONS TO MAJOR CURRENT PROBLEMS

3.1 Balancing separator

A common solution has been found to all the problems raised so far. The key is a new device dubbed a balancing separator. A separator is a vessel in which the liquid entrained in a stream of liquid ammonia and gas may settle out. We propose a small separator (0.36 litres) attached to a balance arm so that the contents may be continuously weighed. A full description of this device and design study is given in a separate report (Reference 2).

A separator with continuous level indication would have provided solutions to all our problems except that of gas analysis. Other short comings of this alternative that finally caused us to decide in favour of the balancing separator were: (1) it would have made us completely dependent on rather scarce published data on the densities of two and three component mixtures; (2) despite a great deal of effort the group has not yet come up with a reliable and leak-tight electrical lead-through for the walls of high pressure vessels as would be required for most types of continuous level indicator; (3) similarly the provision of leak-tight frictionless seals for rotating or reciprocating rods connected to mechanical level indicators present a problem at the small scale of our system.

By itself the balancing separator should enable the demonstration of energy transfer in a system in which both dissociator and synthesiser discharge into the balancing separator and in which a decrease in the measured weight is made to increase the rate of synthesis (Figure 1).

By coupling the balancing separator to either the dissociator or synthesiser, the rate of dissociation or synthesis should be determinable absolutely and directly in terms of gm/s of ammonia and hence in terms of energy absorbed or released (Figure 2).

The balancing separator should also enable determination of the nitrogen-hydrogen molar ratio to within 1.5% by direct weighing of gas samples (Figure 3).

When allied with a method for smoothing fluid flow the balancing separator should enable the absolute calibration of turbine and differential pressure flow meters for both liquid and gas (described in the next section).

3.2 Methods for smoothing gas flow and for pressure regulation

In a system where the temperature of some components may vary widely and where gas is generated and consumed, pressure regulation is obviously an important aspect. It is proposed that the gas pump be used to effect pressure regulation at 15 MPa by pumping residual gas into a 20 litre vessel at pressures up to 18 MPa. A similar 20 litre reservoir will be coupled at the 15 MPa level. These vessels should provide adequate attenuation to the pressure pulses caused by the pulsations of the reciprocating pump. In order to alleviate some of the problems with the gas pump and make it more controllable an electric motor drive is to replace the pneumatic drive.

Gas to be passed through the synthesiser will be taken from the higher pressure vessel through a motor controlled valve and thence through a restriction across which is mounted a differential pressure gauge (Figure 4). The electronic output of the gauge will be made to regulate the valve motor so as to maintain uniform flow at any desired level.

For calibrating both liquid and gas flows a variation on this circuit will be used (Figure 5). Here gas will flow from a 15 MPa reservoir to the balancing separator where an equal flow of liquid will be displaced. Liquid flow will be regulated by a flow regulating valve (or possibly a motor controlled valve, differential pressure gauge and restriction in the liquid line). Finally the liquid will be collected in a 20 litre vessel partially filled with gas at less than 15 MPa. Pressure regulation of the 15 MPa reservoir will be achieved by the gas pump operating in a similar manner to that described previously.

4. OTHER PROBLEMS AND SOLUTIONS

4.1 Thermal stresses

At the beginning of this year considerable attention was directed towards thermally induced stresses in the synthesiser vessel. This vessel has been designed as a hot wall pressure vessel with cold flanged ends. The parts of the walls adjacent to the flanges which experience the transition from hot to cold were the areas of concern.

Experiments revealed the nature of the temperature gradients in the transition zones and theoretical studies showed the relationship between the temperature profile and both longitudinal and circumferential stresses. (Refer to the separate report on this subject, Reference 3.) The experiments extended to examining methods of tailoring the temperatures to an optimum profile.

The conclusion reached was that significant thermal stresses could be induced but they were of a self healing nature ie. any yielding would relieve them. This opinion was upheld by an independent assessor Mr J Blamey. It was also concluded that the original allowable stresses used in design were too low by an amount that would adequately cover the thermal stresses.

Nevertheless, it is intended to monitor and record the situation during each operation of the synthesiser so that reassessments may be made from time to time.

4.2 Low system pressure

System pressure is now limited to 15 MPa instead of the originally intended 30 MPa. The reasons for this are: (1) the pressure was limited by the alloy and wall thickness of the hot wall synthesiser vessel which were in turn dictated by cost and availability; (2) two twenty litre pressure vessels used as reservoirs in the system previously rated at 30 MPa have been derated to 15 MPa as a result of more stringent requirements following an accident during September 1981. Steps are being taken to improve the pressure rating of these vessels to a figure close to the original rating. The alternative to a hot wall vessel for the synthesiser, and one which has several advantages despite its greater mass and cost, is to employ a conventional cold wall vessel, the thermal insulation being inside.

The consequences of the lower pressure are unfavourable to synthesis but favourable to dissociation. To some extent a low system pressure can be compensated for by refrigerating the separator and the small balancing separator has been designed with this in mind.

4.3 Calorimetry

A great deal of attention was given early in the year to the problem of measuring heat flows in order to determine the energy balance of the system. Since in both dissociator and synthesiser, a substantial proportion of the energy involved will be lost through the thermal insulation, it seems that one should consider enveloping each of these components in a cool vessel designed to receive and measure all the lost heat. It is to be noted that this would be a natural outcome for the synthesiser if a cold wall pressure vessel were used since the wall would be necessarily water cooled and therefore ideal for calorimetry.

For the time being the effort and delay involved in providing calorimetry vessels is too great to contemplate. It seems more prudent to concentrate on good measurements of the quantities of ammonia synthesised and dissociated for these will give us the total heats involved.

In the case of the synthesiser a separate calorimetric problem is the measurement of the net heat output or dumped. It is analagous to the gross electrical input to the dissociator which of course presents no problem in measurement. There is in existence an air cooled dump but there is some doubt about its ability to handle the required heat flux and, to perform calorimetry with it, we will need a method of measuring rather large volumetric air flows.

A water cooled dump would be more suitable for calorimetry and may have to be built for this reason and for the other reason outlined below.

4.4 Thermostatic control of synthesiser

The synthesiser presents a very interesting control problem in that it may operate in either a stable or unstable regime (Reference 4). In the latter case, without a sophisticated control system to counter the effect, one would expect the reaction to rather suddenly cease after operating at near maximum power.

The stable regime, where practical operation is possible, requires however higher catalyst temperatures and we should therefore take precautions that the sintering temperature is not inadvertently exceeded.

We propose therefore to provide a basic safety loop comprising a measurement of catalyst temperature and control of the flow of coolant, either air or water, through the heat dump.

Experiments have been underway for some time this year aimed at determining the adequacy of heat transfer within the synthesiser for this type of operation. This matter is still to be resolved.

4.5 Safety

Following the accident in September 1981 in which an ammonia storage tank was inadvertently overheated leading to its explosion, there was a review of the project with regard to the safety of components and procedures. Although the repercussions of this accident were largely behind us at the commencement of 1982, the resolution of the thermal stress problem with the synthesiser eat deeply into 1982.

4.6 Fluid flow regimes

The demonstration of energy transfer under transient conditions may be impaired by varying amounts of liquid and gas stored in the connecting pipes of the system. There are many places where the pipework forms a U trap for liquid. At low flow rates these will be almost completely full of liquid with only a small space for the gas passing in stratified or plug flow. As the total flow rate increases the traps will tend to be swept free of excess liquid giving rise to a transient increase in the liquid content of the fluid leaving the trap. If this fluid originated from the synthesiser for example, the proposed control system would get a false measurement of the rate of synthesis. It is unclear at this stage how this might affect stability of the control system.

Studies to date show that, in order to avoid this problem, the transferred energy that would be commensurate with the 1/4" OD piping of the system is of the order of 15 kW instead of the design maximum of 3 kW. Therefore critical parts of the piping may have to be refabricated in a smaller size.

5. WORK SCHEDULE

The major tasks that have to be accomplished before we achieve the primary goal of demonstrating energy transfer are set out in the diagram of Figure 6.

The first stage of this schedule, leading to further operation of the dissociator and a quantitative study of its performance, depends on the availability of the balancing separator (design complete) and the successful operation of some existing components viz the liquid flow control valve and back pressure regulator. This study can be carried out in conjunction with the calibration of liquid flow meters.

Ideally the liquid flow control valve should force the pneumatically powered liquid reciprocating pump to stroke evenly. If this in fact happens the pump displacement and stroking rate will provide a good measurement of flow. There might then be some merit in going straight on to the dissociator study before the balancing separator is ready. In this case the existing rotameters (for measuring low pressure gas only) could be used to measure the nitrogen-hydrogen production from the dissociator. This procedure is not as clean-cut or as reliable as the one using the balancing separator but would probably give meaningful data earlier.

Pressure at this stage will be regulated by an existing back pressure regulator, with the gas flow, other than the samples which pass through the rotameters, being stored in the two 20 litre reservoirs. Once these are full, additional gas will be vented to waste.

The next stage of the schedule will require the electric motor drive for the gas pump to be complete (now being built). This, in conjunction with an existing pressure transducer, should provide accurate system pressure regulation with gas conservation. Once this is established nitrogen-to-hydrogen ratio measurements can be taken routinely to check for hydrogen leakage and then the calibration of gas flow meters may proceed.

The third stage of the schedule requires the additional availability of the motor operated gas flow control valve (yet to be designed and built). This will enable us to proceed with the reduction of the synthesis catalyst (a continuous procedure lasting about 5 days).

Following the reduction of the catalyst the thermostatically controlled heat dump needs to be completed (not yet designed) to enable the synthesis study to begin.

Finally the installation of a relatively minor control link between the balancing separator and motor operated gas flow control valve should enable the demonstration of energy transfer under a variety of conditions.

The balancing separator will probably be completed in September or October by which time the components for system pressure regulation (particularly the gas pump) should also be available. Thus by the end of 1982, if all goes well, we should be at about the stage of reducing the synthesis catalyst or performing the synthesis study. Initial demonstration of energy transfer is possible in early 1983.

At that time, with the system operational, we should be in a position to embark on a very interesting, valuable and unique set of experiments related to the operation of thermochemical energy transfer loops. Hopefully, this period will be all the more fruitful as a result of the firm foundation we are now attempting to build particularly in the areas of measurement and clean operating techniques.

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3. P O Carden, 'Thermal Stresses in the Hot Wall Reaction Vesel for the Synthesis of Ammonia', Energy Conversion Technical Report No 25, Department of Engineering Physics, ANU, March 1982.

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SYMBOLS USED IN FIGURES

Components

D	Dissociator and heat exchanger
F	Flow meter: subscripts t - turbo, p - differential pressure
M	Motor: subscripts e - electric, p - pneumatic
P	Pressure transducer; gauge or switch : subscripts; s - switch, t - transducer, v - visual
R	Reservoir or pressure vessel: subscripts; numerals - capacity in litres, s - separator, bs - balancing separator
S	Synthesiser and heat exchanger
T	Temperature sensor: subscripts; s - switch, t - thermocouple or transducer, v - visual gauge or thermometer
U	Pump: subscripts; g - gas, l - liquid
V	Valves: subscripts; b - backpressure regulating, c - automatic flow control, d - sample discharge, f - manual or motor driven flow control, g - ganged, r - relief, s - sampling valve
————	Fluid lines
- - - - -	Control lines
....	Data lines
⟹	Energy flow

Quantities are ringed eg. $\textcircled{P_s}$

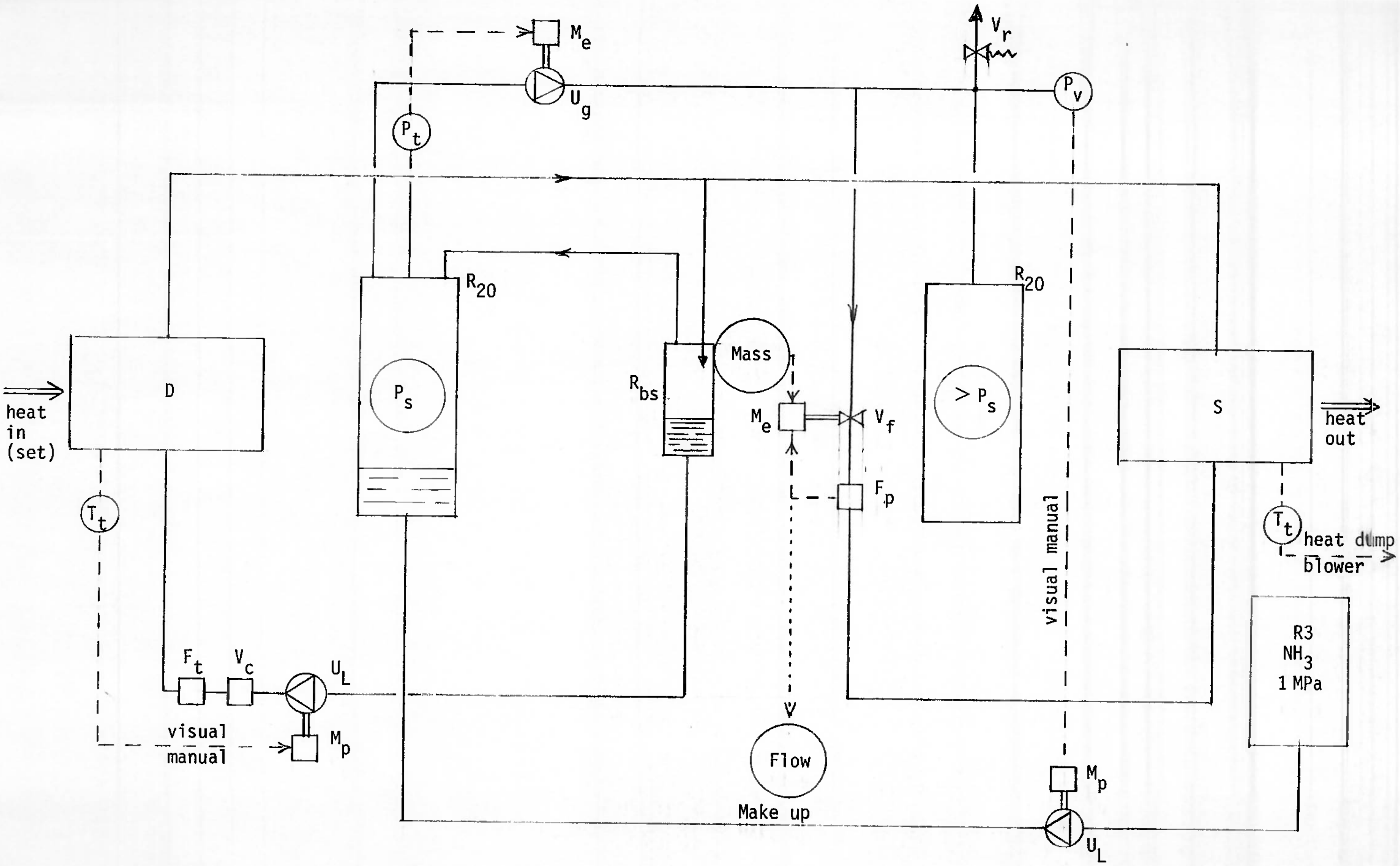


FIGURE 1: Energy transfer demonstration

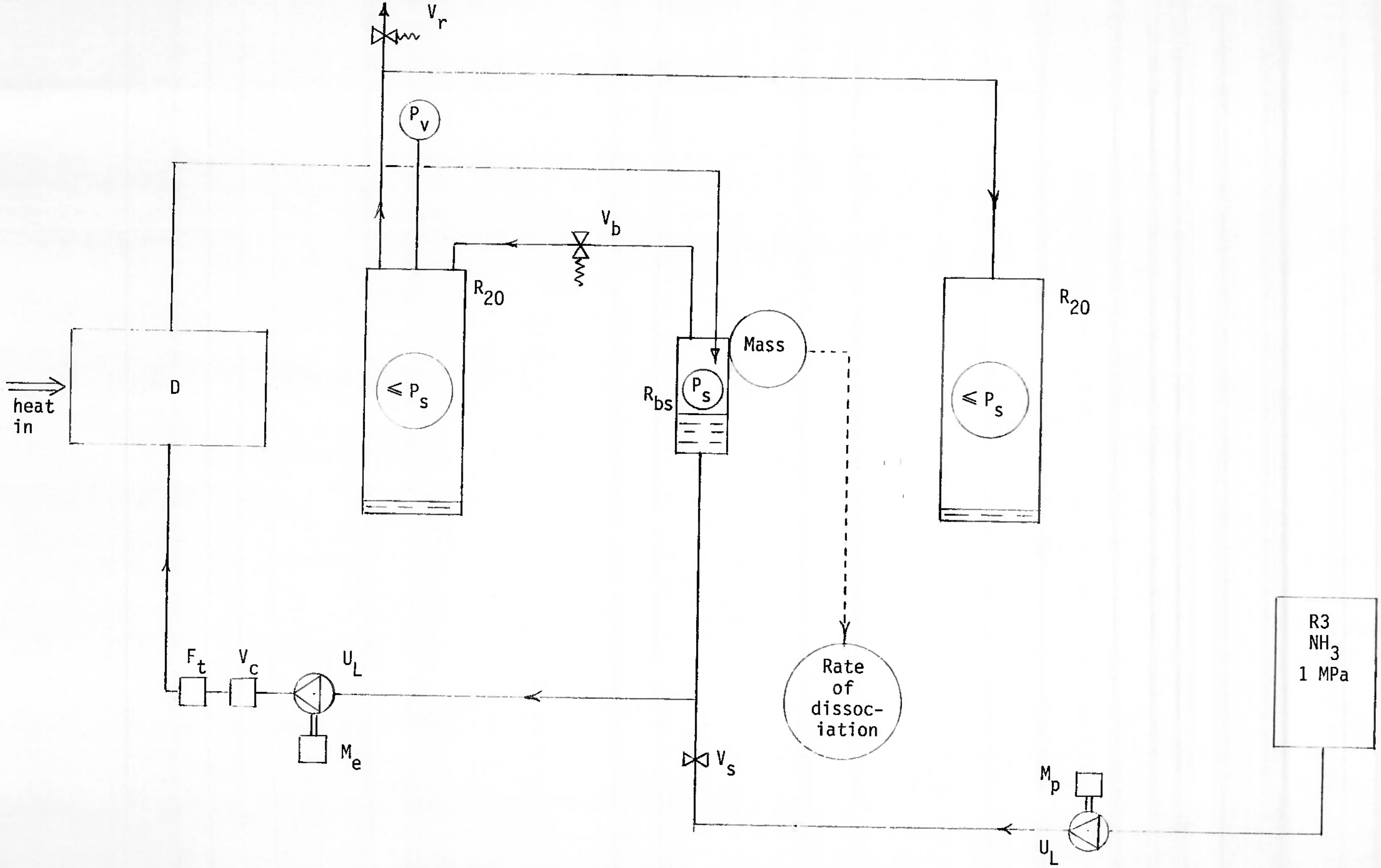


FIGURE 2a: Dissociation study

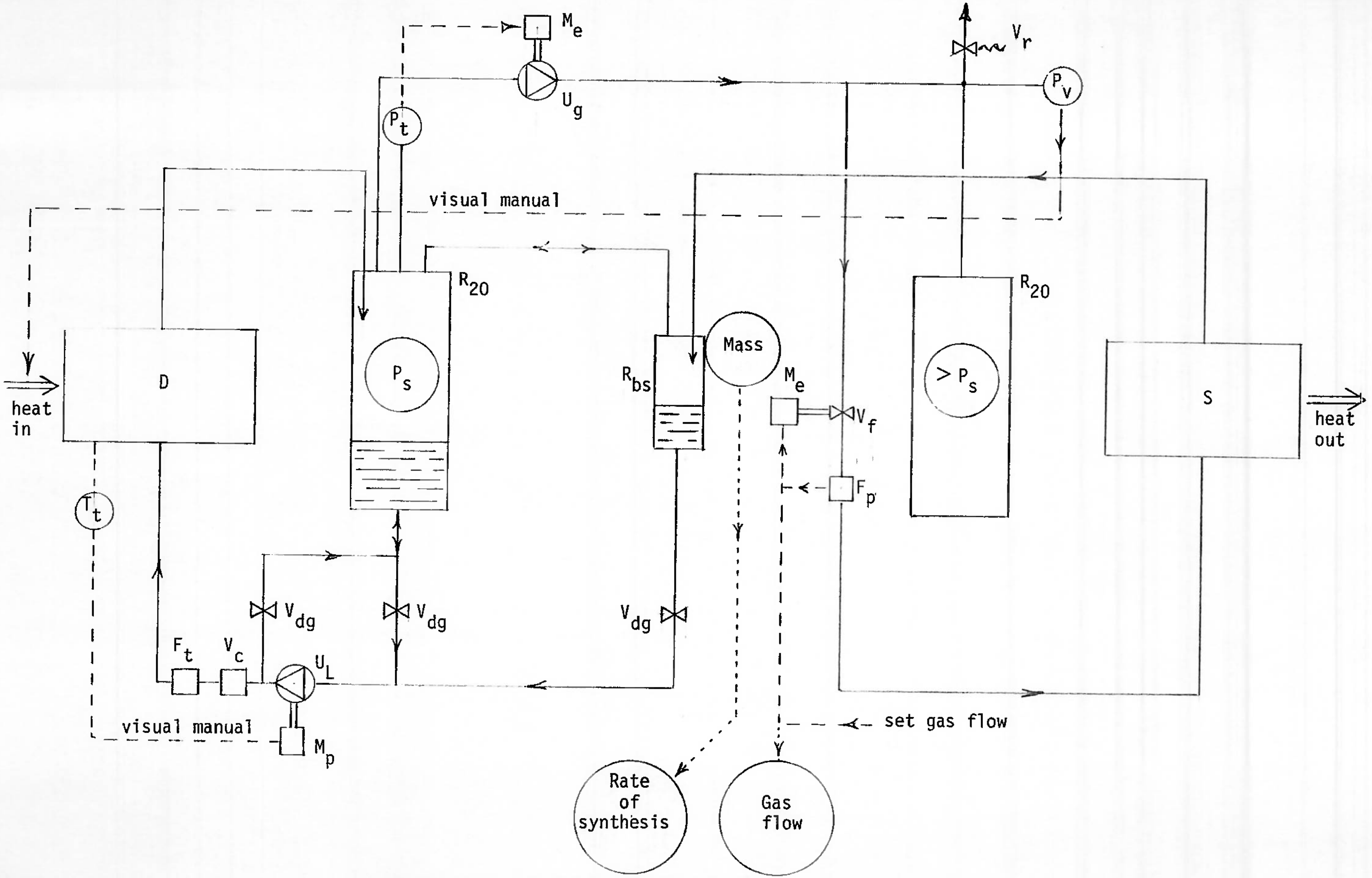


FIGURE 2b: Synthesiser study

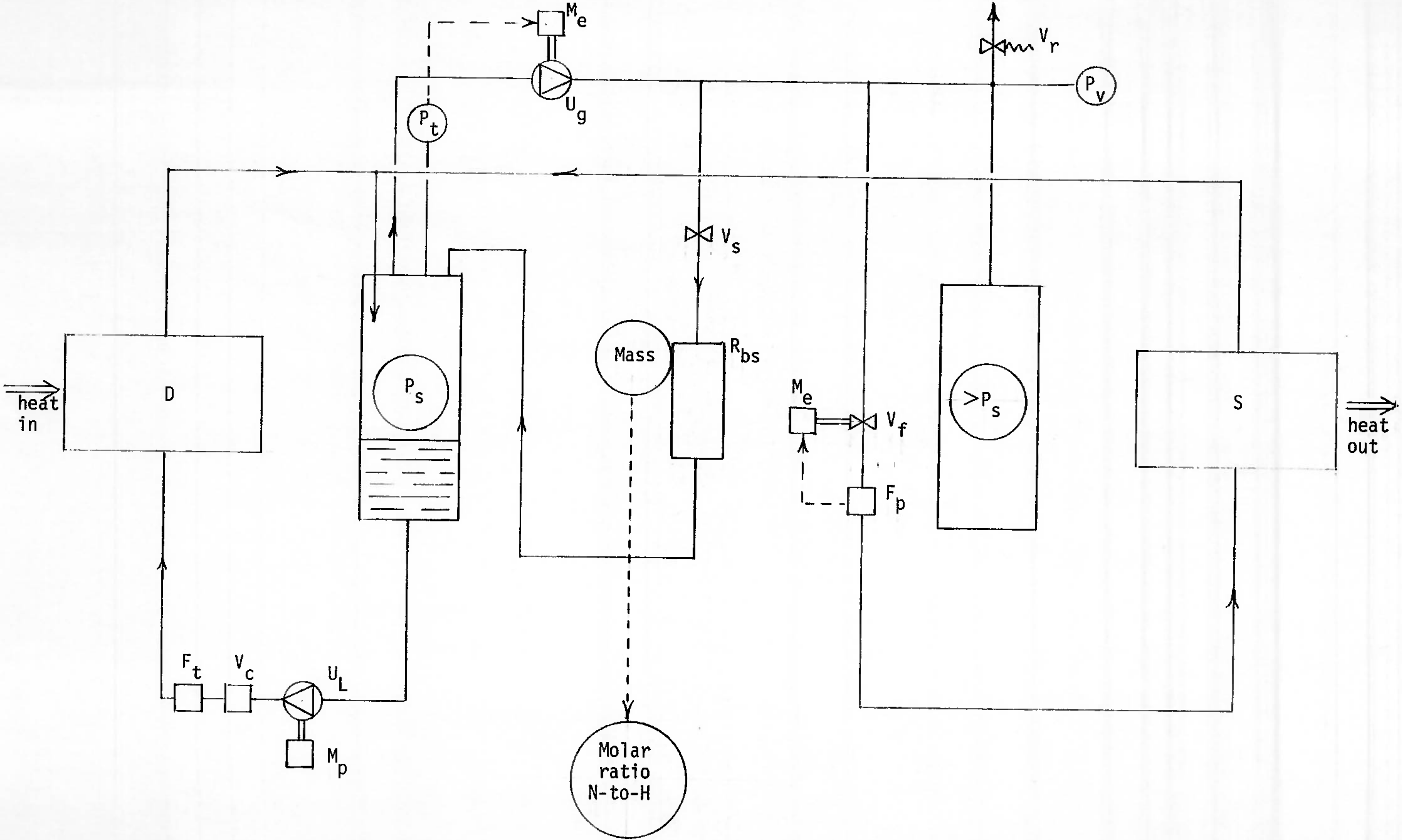


FIGURE 3: Determination of N-to-H ratio

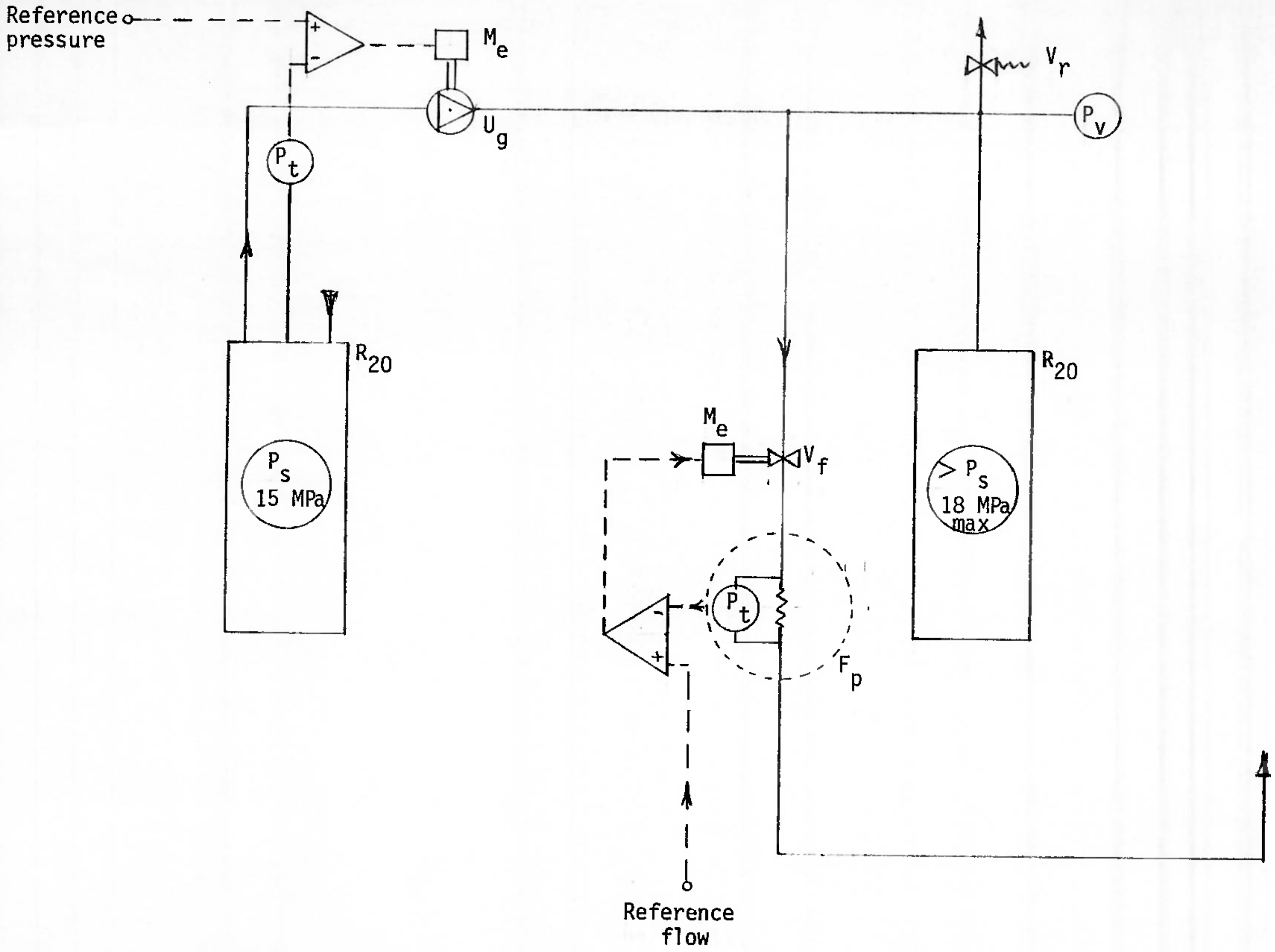
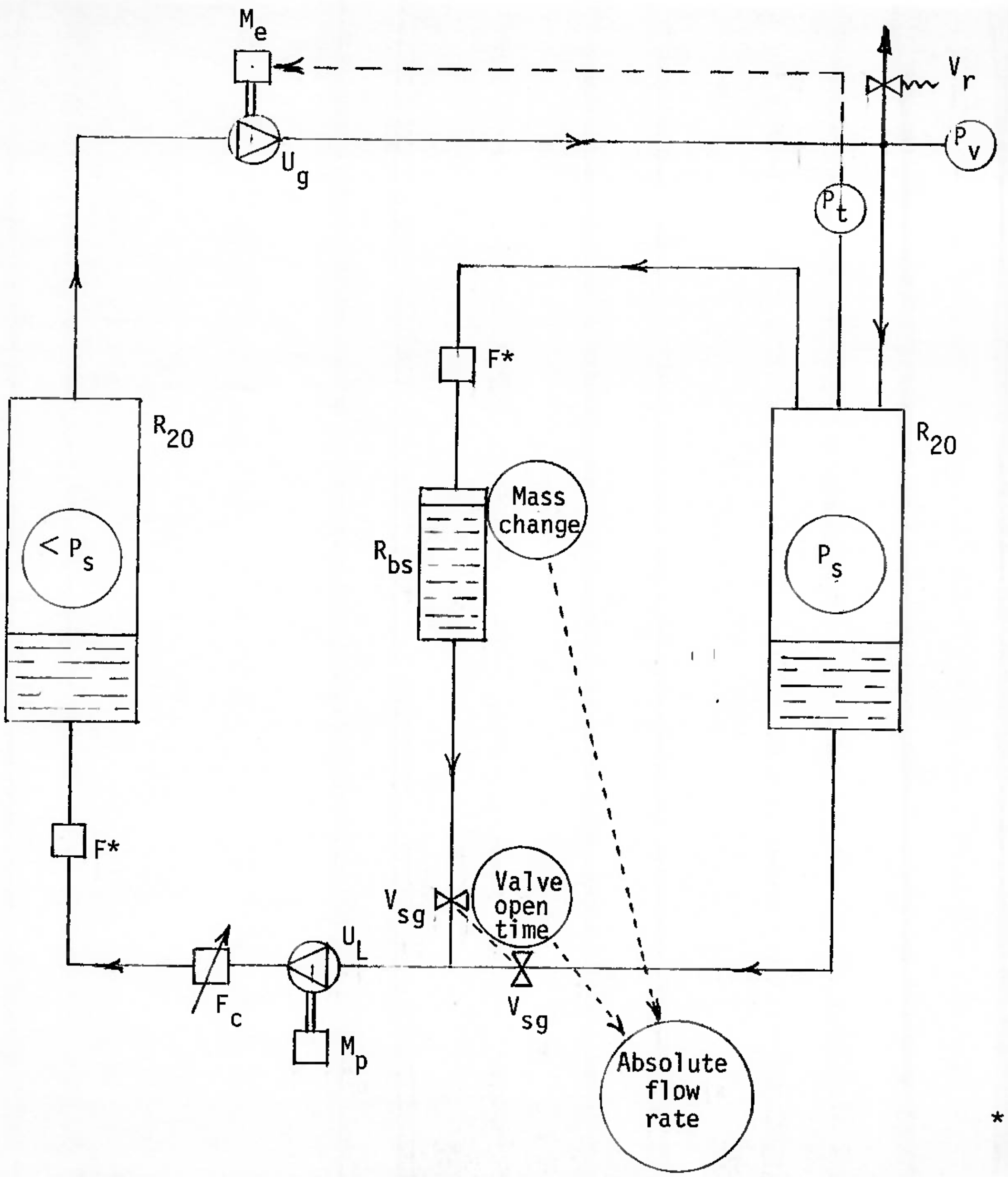


FIGURE 4: Pressure regulation and generation of smooth gas flow



* Flow meters to be calibrated

FIGURE 5: Method of calibrating gas and liquid flow meters