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## Abstract

An automatic low-temperature system for the neutron four-circle diffractometer is described. The crystal specimen is cooled with a stream of cold nitrogen gas obtained from boiling liquid nitrogen. Cold gas is then warmed to room temperature to facilitate the control of the gas flow without cryogenic components, and recooled by passing it through a heat exchanger immersed in the liquid nitrogen. Techniques for the automatic refilling of the cold gas generator and for preventing ice formation on the crystal are presented. Any desired temperature in the 100-300 K range can be achieved. Performance of the system is discussed.

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# 1. INTRODUCTION

The use of temperature as an experimental variable extends significantly the potentiality of x-ray and neutron diffraction studies. The employment of cryogenic temperatures, particularly, offers some advantages. First, thermal vibrations of the atoms of a crystal are reduced, which results in higher intensities of Bragg reflexions especially at higher reflection angles and in a smaller contribution of cumbersome thermal diffuse scattering, thereby making possible a more accurate determination of crystal structures and electron distribution. Secondly, materials ordinarily liquid or gaseous can, by solidification, be made accessible to the single crystal technique.

Various methods for cooling a crystal specimen and maintaining it at a low temperature during diffraction studies can be categorized according to whether the specimen is cooled by solid, liquid, or gaseous conduction or convection.

In the case of low temperature diffraction work on single crystals with the four circle diffraction technique, very difficult spatial requirements must be met so as to secure the unhampered movement of the crystal and the movable parts of the diffractometer.

The method of cooling applicable in the neutron case of four circle diffractometry must allow homegenous temperature to be achieved in relatively large crystals, ( 5x5x5 $mm^3$) with a minimum of cooling action on the tem - perature sensitive parts of the diffractometer.

The merits of the technique of cooling crystal specimens with a continuous stream of cold gas have been realized in many contexts (see refs. below), and it has become established as the most favoured and succesful technique in this field.

The gas-cooling method was pioneered by Kaufman and Fankuchen (1949), Abrahams et al. (1950), Post et al. (1951), Reed and Lipscomb (1953), and Steinfinketal (1953). The principles of the method have been reviewed by Robertson (1960), and discussed in greater detail by Young (1966).

In recent years several advanced models of the gas cooling apparatus (all of them using nitrogen as the coolant) have been designed. Abowitz and Ladell (1968) have described an automatic low-temperature system tailored for the PAILRED (Philips Automatic Indexing Linear Reciprocal Space Exploring Diffractometer). Its electropneumatic proportional control system maintains temperature by continuously adjusting both the flow rate of the gas stream through a pneumatic valve and the boiling rate of liquid nitrogen. Temperature

is sensed by a thermocouple close to the crystal and is compared with a pre-selected value. Control action is proportional to the deviation signal. Periodic transfer of liquid nitrogen from a large reservoir to the cold gas generator is automatic.

The novel feature of the PAILRED system have been incorporated into ALTA (Automatic Low-Temperature Apparatus), described by Rudman and Godel (1969). A number of modifications have been made, particularly in the method of controlling the production of gaseous nitrogen.

The last two instruments described above necessitate the use of elaborate and expensive vacuum-insulated low-temperature valves and electronic controllers. Silver and Rudman (1971) have recently described a general purpose low-temperature device, which generates a stable gas flow without a sophisticated electronic control system and which can be assembled from readily available, inexpensive components. Its performance compares well with ALTA, whereas its cost is only about 1/10 of that of ALTA.

The low temperature system for the Risø four circle diffractometer described here is based mainly on the device of Silver and Rudman, although certain modifications have been made to improve the performance.

## 2. APPARATUS

### 2.1. General

The collection of complete, three-dimensional, low-temperature, neutron diffraction intensity data requires uninterrupted operation of the gas cooling system for weeks with the study crystal maintained at a constant temperature. Thus the cooling system has to be practically automatic and requiring a minimum of attention. Since the crystal temperature is a function of the mass flow rate, a steady flow of cold gas must be achieved even during the periods of automatic refilling of the cold gas generator. Finally, the condensation of atmospheric gases on the study crystal has to be prevented. The construction to be presented below is designed to accomplish these main objectives.

### 2.2. Cold Gas Generation

The generator of the cold nitrogen gas is a 22-litre stainless steel, vacuum-insulated dewar (1)[x] sealed with an O-ring and a stainless steel cover fixed with bolts on the flange of the dewar. A 5 cm thick polyuretane foam insulation

x) Numbers within brackets in the text refer to fig. 1 which presents a schematic drawing of the low temperature system.

below the cover reduces heat leaks into the system and condensation of ice and water on the outer surface.

During operation the dewar is approximately two thirds full with liquid nitrogen, which is boiled off by a gas heat exchanger (7) immersed on the liquid and by a boil-off heater (15). The relevant boil-off rate required to maintain a constant pressure of 0.5 kp/cm$^2$ in the generator is obtained by an adjustable pressure switch (14). Excess pressure, especially during the refilling periods, is prevented with the aid of an adjustable relief valve (12). In order to prevent the relief valve from freezing closed or open, it is housed in a bulky aluminium cylinder, which is heated and maintained at 70$^{\circ}$C by a thermostatically controlled electrical heater (300 W). The boil-off heater, pressure switch and relief valve, together with a manometer, are mounted on the same 1-inch stainless steel tube to minimize the number of feed holes (heat leaks) through the cover. This tube, as all the other cover connections, is detachable (i.e. fixed in place with a flange) in order to facilitate replacement and maintenance.

The detailed wiring diagram for the pressure switch controlled boil-off heater is shown in fig. 5, and the schematic diagram for all the electrical circuits of the system is shown in fig. 2.

## 2.3. Gas Delivery

Cold nitrogen gas generated in the dewar (1) is released through a gas heater (2), which heats up the gas to room temperature. The heater has an inner-fin construction to facilitate gas flow. The gas temperature at the inner-fin heater outlet can be adjusted to any desired value and kept constant to within $\pm$ 0.5$^{\circ}$K with the aid of a thermocouple sensor (3) connected to the control units "Inner-fin-Heater-Controller" and "Transal Temperature Control". The wiring diagram of this control system is shown in fig. 4.

The warm dry nitrogen gas is then passed through a low-pressure regulator (4), which maintains a constant pressure at the outlet and in this way realizes a constant gas flow rate. It should be noted that the above procedure makes it possible to fulfil the condition of a constant gas flow in a fairly simple way without cryogenic components.

By use of the manual valves (6) the exiting warm gas stream can be divided into three components. The main stream first passes through the dewar cover, is cooled in the copper coil heat exchanger (7), and is directed by a super-insulated, flexible, metal transfer-line (8) and a gas delivery nozzle (9) onto the study crystal (11). The two other streams can be used to mix

warm and cold gas, and to surround the cold gas stream with a stream of dry room -temperature gas, as explained below.

The gas delivery nozzle, attached to the end of the transfer-line by means of cryogenic bayonet couplings, is constructed in the conventional way. It consists of a vacuum-insulated inner tube, which carries the cold nitrogen gas, and an outer jacket, which is used to surround the cold gas stream with a concentric stream of dry room-temperature gas in order to prevent condensation of atmospheric gases on the crystal (see below). The cold stream outlet is made sufficiently large to envelope the crystal totally with a blanket of cold gas of fairly small lateral temperature gradient. The outer jacket is recessed approximately 5 mm into the cold gas tube, and both tubes are covered with stainless steel screens to promote laminar flow of the gas streams. An inlet to the cold gas tube can be used to mix warm and cold gas so as to achieve any desired temperature between ambient and that of the cold gas. A detailed sketch of the gas delivery is shown in fig. 6.

The nozzle is mounted on a rugged support which allows xyz movements of the nozzle as well as rotation around the vertical z-direction and a horizontal axis perpendicular to the axis of the nozzle. In order to maintain the maximum degree of operational freedom of the diffractometer, the cold gas tube of the nozzle is aligned to coincide with the primary beam. Aluminium windows at one end of the nozzle facilitate unhampered passage of neutrons.

## 2.4. Automatic Refilling System

A completely automatic level-sensing and gas generator refilling subsystem is necessary for continuous operation of the apparatus over long periods of time. Numerous methods of sensing and automatically maintaining the level of liquid nitrogen in a dewar can be categorized according to whether the sensing device uses mechanical methods (floats, gas filled bellows, bimetallic sensors), electrical temperature-dependent phenomena (resistance changes, thermocouples), or certain solid state phenomena (ultrasonic-level-control-system, or a device utilizing the difference in dielectric constants of liquid nitrogen and nitrogen gas). In the present case small temperature gradients in the pressurized, nearly isothermal dewar limit the number of methods applicable. The "electromechanical" principle presented by Silver and Rudman was chosen for the construction of the present refilling system.

The liquid level indicator (21) consists of a small magnet fixed on the top of an aluminium rod, which is mounted on a styrofoam float (see fig. 5). The system is free to move in a glass tube sealed onto the dewar cover. Four mag-

netic Reed switches R1, R2, R3, and R4 are placed on steel rods so that their vertical positions can be adjusted. Reed switches R2 and R3 correspond to the maximum and minimum working levels of the liquid during normal operation: When the magnet falls to Reed switch R3, this will be closed and the solenoid valve (18) activated. Liquid nitrogen from a pressurized 160-litre supply dewar will flow into the generator (1) until the magnet has risen to switch R2, which will then open and the solenoid valve will close. Reed switches R1 and R4 act as fail-safe switches. If the magnet falls as far as switch R4, which indicates an empty supply dewar or some fail in the operation of the refilling system, R4 will open and the boil-off-heater will be disconnected, regardless of it will be called on by the pressure switch. If the liquid level, on the other hand, rises as far as switch R1, the solenoid valve (20) is activated and the pressure in the supply dewar is reduced.

A 160-litre supply dewar (19) is pressurized at 1.2 $kg/cm^2$ by a gas bomb (22) through a pressure regulator (23). It is equipped with a liquid level indicator, a manometer, and a relief valve to prevent excess pressure, and is connected to the cold gas generator through a vacuum-insulated, flexible, metal transfer-line. Disturbance within the generator during the refilling periods is reduced by a sintered bronze phase separator (17) placed at the end of the transfer-line. The phase separator reduces the pressure of any gaseous nitrogen generated in the transfer-line, thus making liquid transfer more efficient. Manual valves (24) on the supply dewar meet the needs involved in replacing an empty supply dewar by a full one.

## 2.5. Dry Box

One of the major problems to be overcome in cooling with a cold gas stream method is the condensation of atmospheric water vapour on the study crystal. Ice formation depends on numerous factors: the flow rate and temperature of the cold gas stream, distance of the crystal from the end of the nozzle, dimensions of the cold stream, air currents and humidity conditions in the vicinity of the diffractometer, etc. (Rudman and Godel, 1969). Frost on the study crystal, even to a relatively small extent, may severely distort the diffracted intensity pattern through anomalous background scattering and an absorption factor. This is especially true in the x-ray case, but great caution has to be observed also in neutron diffraction measurements.

A way to reduce the rate of ice formation is to construct the gas delivery nozzle so that it is possible to surround the cold gas stream with a concentric stream of dry warm gas. This method has been found to be only moderately

succesful in test runs; experiments can be run for periods of hours, or at best tens of hours, but not the hundreds of hours required in the present case. This agrees with the findings of Abowitz and Ladell (1968).

In the present case it was found to be preferable to seal the entire diffraction apparatus with a Plexiglass enclosure (Allen, Jeffrey and McMullan, 1963; Abowitz and Ladell, 1968). This is equipped with removable panels for easy maintenance of the instrument at room temperature, with glove ports for making adjustments in the sealed condition, with a hygrometer and a manometer, and with sealed inlets and outlets for electric and gas lines.

A completely automatic drying system required for continuous long term operation was constructed as outlined by Abowitz and Ladell (1968). A molecular-sieve dryer has dual chambers of desiccant which are automatically switched and regenerated with the aid of a timer every 5-10 hours. A compressor is used to circulate gas in the closed system consisting of the enclosure and the dryer. A vacuum-pump is used for regeneration of the molecular-sieve chambers.

The entire low temperature system is dried thoroughly with the aid of the above drying system during start-up operations. A typical drying period lasts 48 hours. Filling of the cold gas generator is initiated only when the dryness of the overall system has reached its steady state. Dryness in the enclosure during runs is maintained by continuous operation of the drying system.

## 3. PERFORMANCE

### 3.1. General

The gas stream method is soundly based on well known heat transfer principles. The relevance of such principles, operating experience under a variety of conditions, succesful equipment configurations, and the performance that may be expected have been recently discussed by Young (1966). In this section the main features of the performance of the Risø system are described.

### 3.2. Temperature of The Cold Gas Stream

Cold gas stream temperatures were measured with copper-constantan thermocouples. The coldest point was 90°K and was achieved at the nozzle orifice. The temperature distribution of the stream was studied and it was found that around a distance of 8 mm from the end of the gas delivery nozzle there existed a region of about 400 $mm^3$, over which the temperature was

uniform to within $3^{\circ}K$ at $100^{\circ}K$. Temperatures at any particular point in this region were found to be constant to better than $\pm 1^{\circ}K$ for several hundreds of hours. At distances greater than 15 mm from the nozzle orifice the temperature showed considerable fluctuations due to mixing of the cold gas stream and dry warm stream. Physical limitations (e. g. crystal support pin), on the other hand, prohibit approach closer than 3-4 mm from the nozzle end. The situation characterized by the above figures can be considered entirely adequate for normal diffraction experiments. Thermocouples were calibrated using some well known temperatures. Heat conduction along the lead wires was eliminated by locating the leads inside the nozzle along the cold stream.

From a room temperature start, the entire low temperature system stabilized under automatic control at the final temperature within half an hour.

## 3.3. Temperature of the Crystal Specimen

A crystal specimen has two means of heat exchange with its surroundings, which might raise its temperature above that of the gas stream: conduction through its support pin, and radiation. The commonly used Quartz glass support can be considered quite satisfactory. If it is assumed that its length and diameter are 10 mm and 0.5 mm, respectively, the rate of heat conduction to the crystal at $100^{\circ}K$ is of the order of 0.2 mcal/s. Heat gain by radiation can be more serious. A crystal of 500 $mm^3$ dimensions can receive approximately a maximum of 5 mcal/s from its room temperature surroundings. Radiation shields (e. g. aluminium foil) around the crystal will improve the situation decisively.

The cold gas stream must counteract these two sources of heat transmission. The "cooling power" of the cold gas stream can be expressed in terms of the heat capacity per unit volume, viz., millicalories of heat taken up per cubic centimetre of gas when the gas temperature is altered by one degree (cf. Robertson, 1960). In the case of nitrogen gas at a temperature of $100^{\circ}K$, the amount of heat which could be absorbed by a stream flow of 1 $cm^3/s$, and rising only $1^{\circ}K$ in temperature, would be about 1 mcal/s. The flow of the present system, being about 250 $cm^3/s$, is thus entirely adequate to counteract the above heat leaks into the crystal, even if heat exchange between the crystal and the gas stream cannot be considered complete or instantaneous.

## 3.4. Consumption of Liquid Nitrogen

Liquid nitrogen consumption is dependent on the flow rate of the cold gas stream, and on the amount of extra gas leaking through a relief valve.

The flow rate has to be held at about 250 $cm^3/s$ because of the moderately bulky crystal specimen used in neutron diffraction experiments. This requirement can be accomplished by proper sizing of the lines carrying the cold gas and by proper choise of pressure in the cold gas generator. The above flow rate corresponds to a liquid nitrogen consumption of approximately 3.5 l/h.

A primary factor causing extra losses of liquid is the heat leak into the liquid line and the solenoid valve, which get warmed up between refilling periods. Another loss factor stems from the heat leak introduced into the cold gas generator by various control and measurement components. In the present system these factors give rise to a loss of about 2 l/h. Any attempts to reduce liquid consumption by improving the heat insulation are therefore highly recommendable.

## ACKNOWLEDGEMENTS

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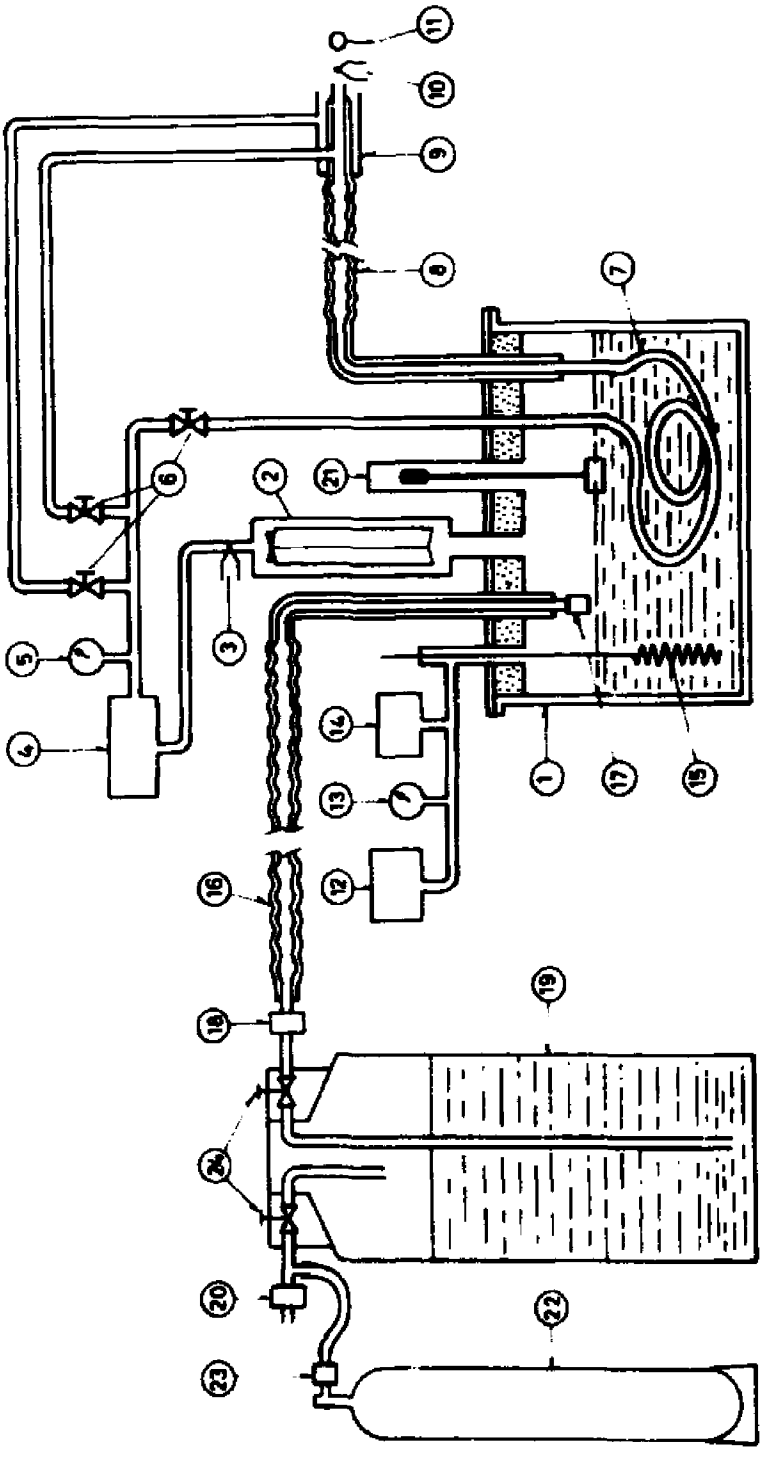



Fig 1 Schematic Drawing of the Low Temperature System

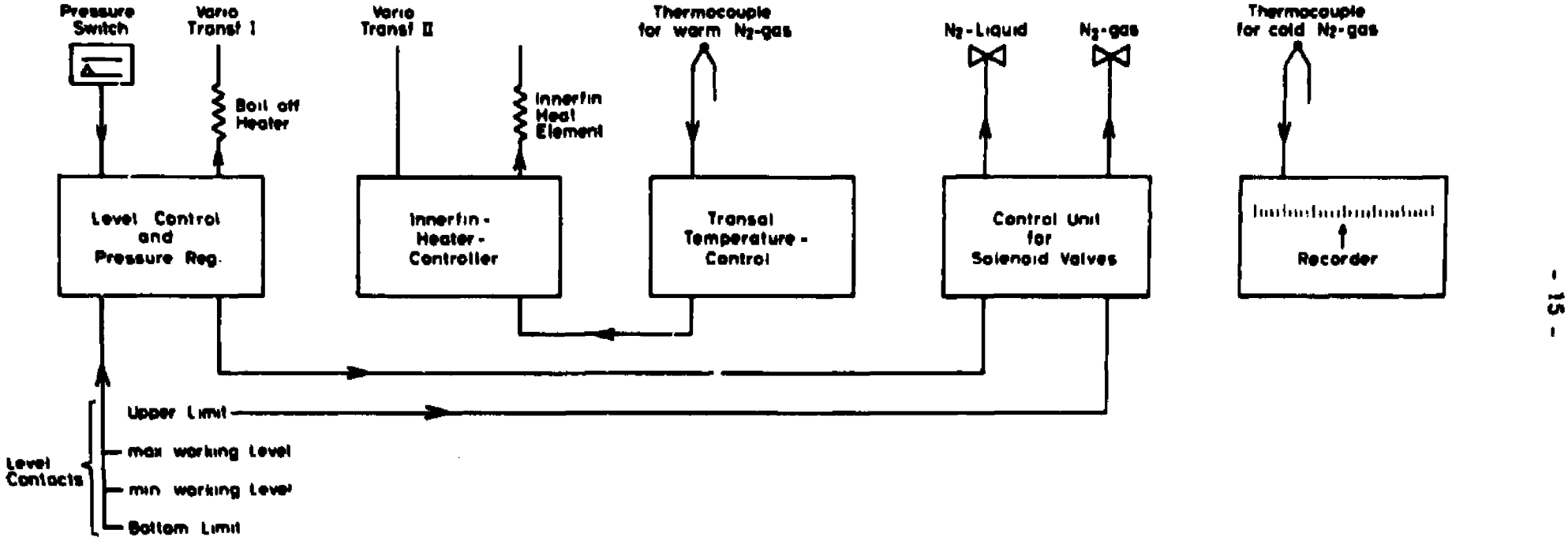



Fig 2 Schematic Diagram of the Electrical Circuits.

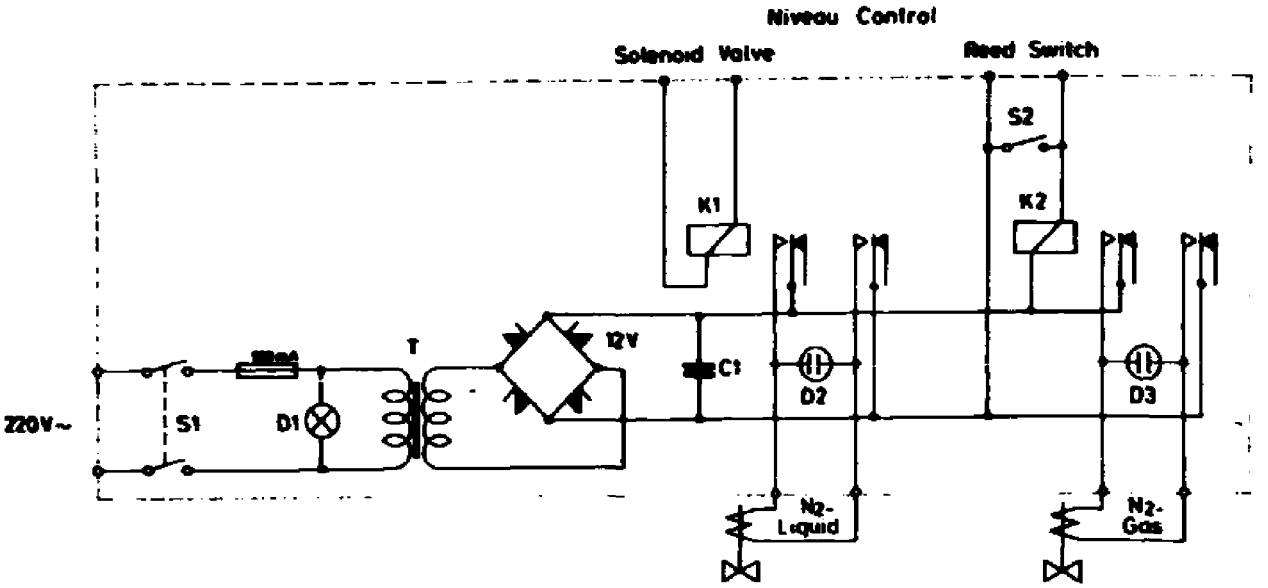



Fig. 3. Control Unit for Solenoid Valves.

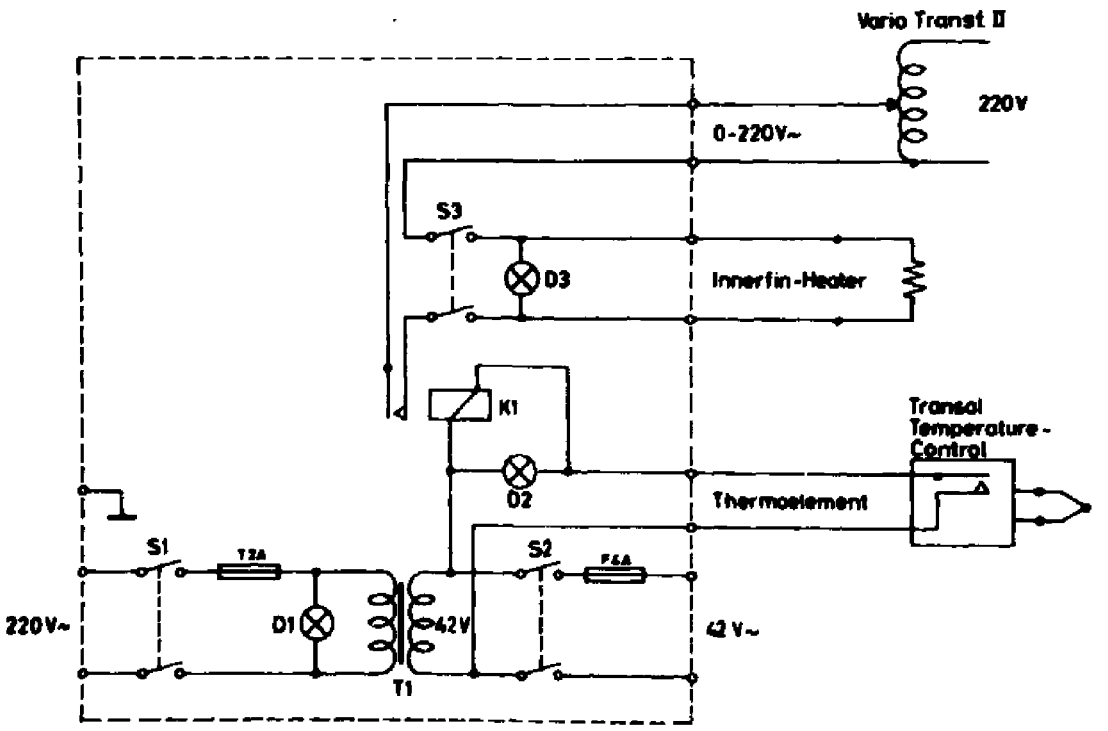



Fig. 4 Innerfin - Heater - Controller

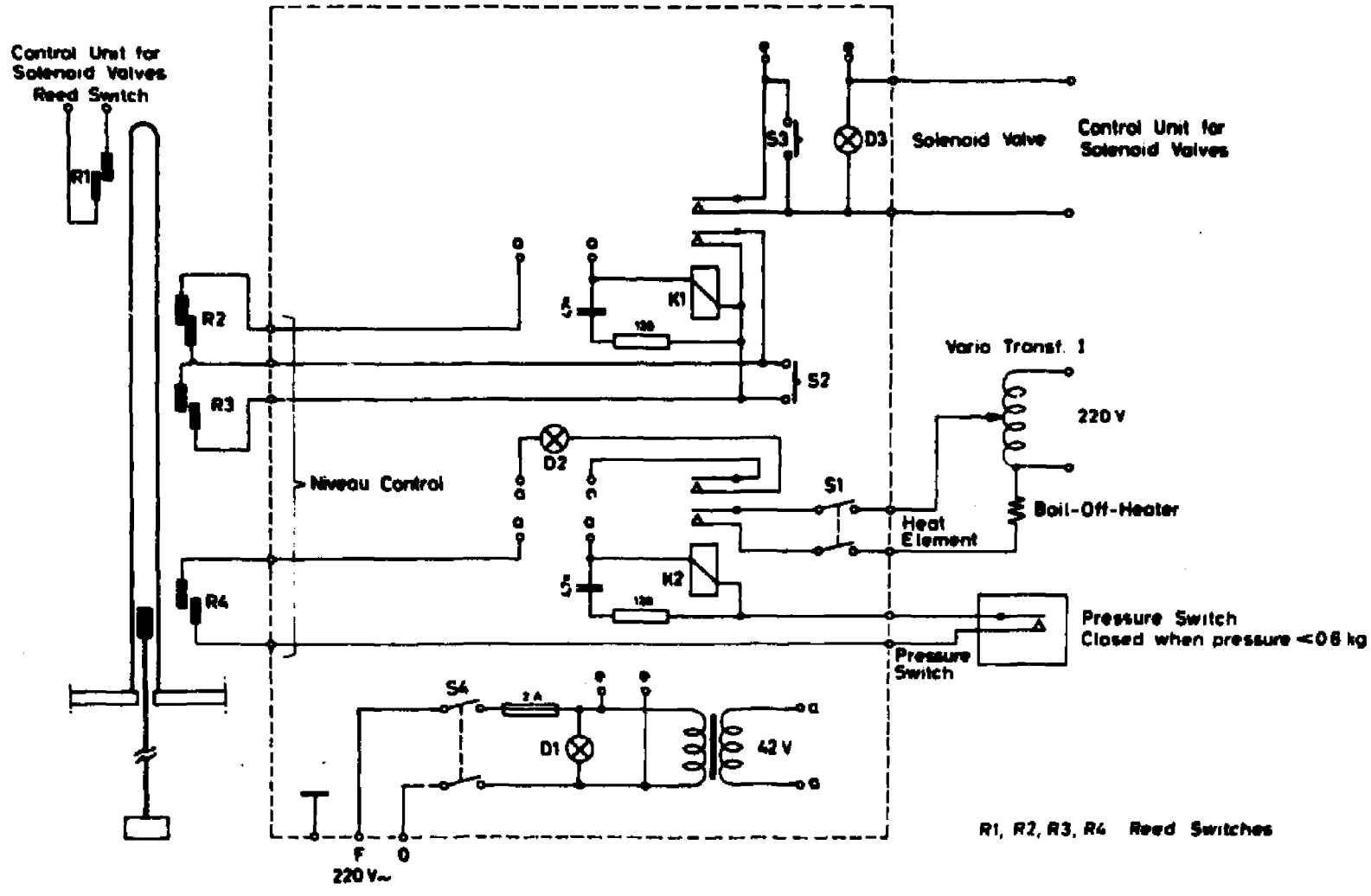
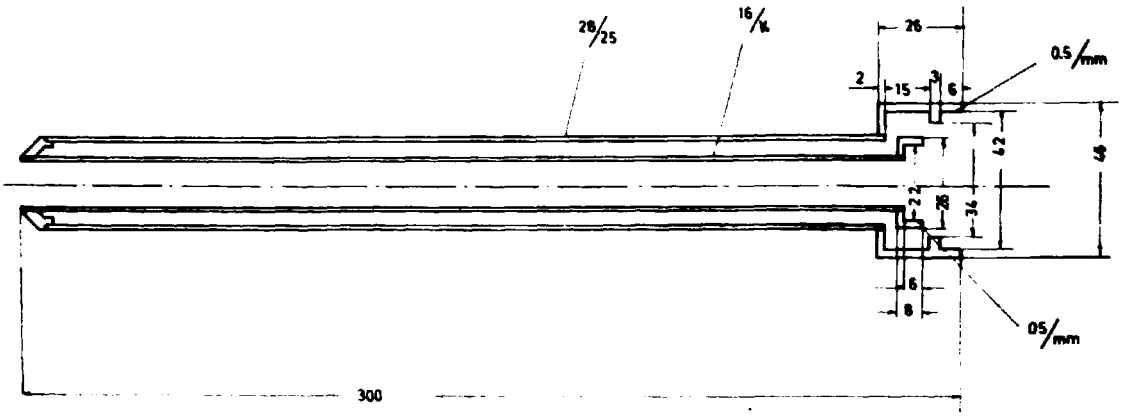



Fig 5. Level Control and Pressure Regulation



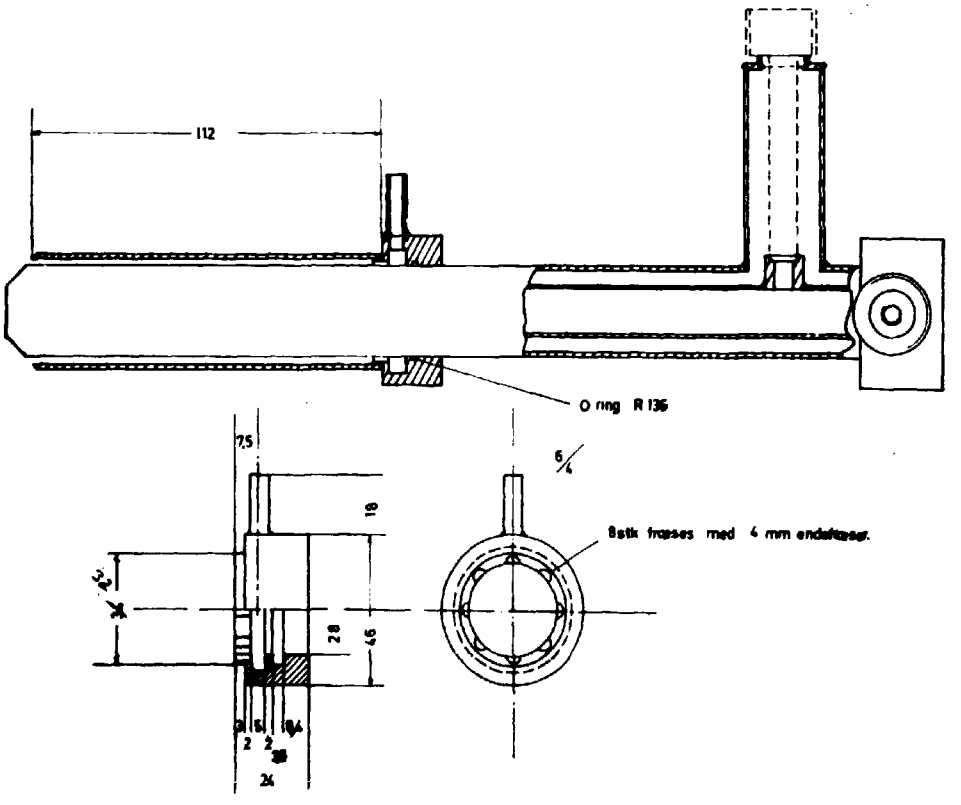




Fig.6 Gas Delivery Nozzle

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