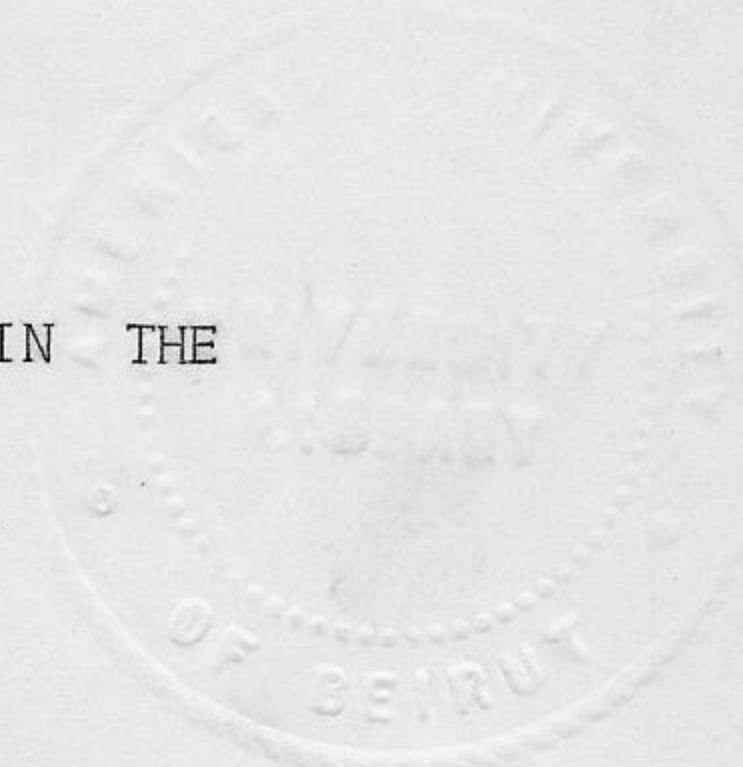


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FLUID-SOLID EQUILIBRIUM OF He^3 - He^4 MIXTURES IN THE
LOW He^3 CONCENTRATION REGION



By

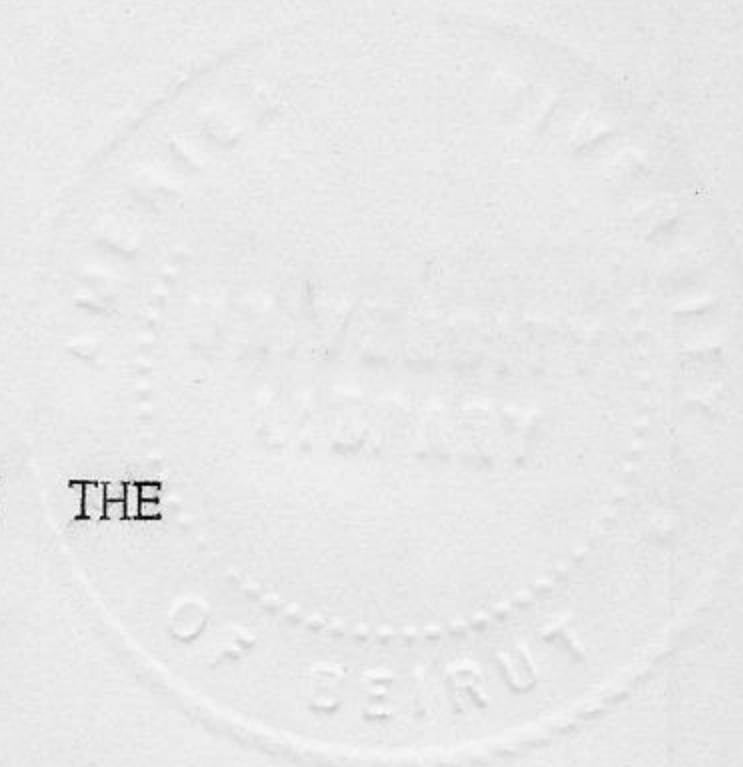
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A B S T R A C T

Major experimental work on $\text{He}^3\text{-He}^4$ mixtures is reviewed. Some of the theoretical work on dilute $\text{He}^3\text{-He}^4$ mixtures is discussed. Finally, an experimental technique which will facilitate the pressurizing of dilute $\text{He}^3\text{-He}^4$ mixtures and the accurate measurement of their freezing and melting lines down to 0.35°K is reported.

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I. INTRODUCTION

Helium, in the liquid state, is a unique substance. Its two isotopes, He^3 and He^4 and their mixtures remain liquid down to the absolute zero of temperature under their own vapor pressures, although classical statistics predict that all substances should be in the solid state at absolute zero. This behaviour is ascribed to the small interatomic Van der Waals attractive forces and to the comparatively large zero-point energy which not only reduces the absolute magnitude of the internal energy but also "blows out" the liquid to a large volume. In this respect, the zero-point energy is equivalent to an extra repulsive force between the atoms. At equal distances, the interatomic potentials are almost the same for the two isotopes, but the zero-point energy varies inversely with the atomic mass which gives He^3 a larger molar volume, a larger saturated vapor pressure, and a smaller absolute magnitude for its internal energy.

He^4 at about 2.17°K shows a transition to a superfluid. Below 2.17°K the liquid is referred to as helium II to distinguish it from the normal fluid helium I above the transition temperature. While pumping the vapours above the surface of the liquid it continues to boil. However, when the transition temperature is reached, the liquid suddenly stops boiling and

liquid helium II appears as a transparent liquid. He II has many peculiar properties, one of which is a very high thermal conductivity which explains the absence of boiling. Another remarkable property of liquid helium II is its "superfluidity." Liquid helium II flows through very narrow capillaries with almost no signs of viscosity and almost independently of the pressure head. However, if the viscosity is estimated by observing the damping of a torsional disk immersed in the liquid, then, as long as the peripheral velocity of the disk is not too great, the behavior is that of a normal liquid and the viscosity has a comparatively large value. The solution of this dilemma is provided by the two-fluid theory which considers the liquid to be a mixture of two components, a normal component and a superfluid component. The normal component is assumed to have a normal viscosity and is therefore responsible for damping the oscillating disk. The superfluid component is the part capable of flowing through very narrow channels with high velocity and with no viscous retardation. The theory was originated by Tisza, developed later by Landau¹ and expanded by Feynman.^{2,3} The two-fluid model of Tisza was empirical. Landau's theory, however, described the normal part as being made up of quasiparticles carrying the energy (and entropy). Feynman introduced macroscopic quantization in the form of vortices.

The specific heat of liquid He⁴ shows a sharp peak at 2.17°K which corresponds to a transition from the superfluid state He II to the normal state He I. On account of the shape of the specific heat-versus-temperature curve, this transition was called the λ -transition by Keesom. Moreover,

very accurate specific heat values close to the lambda line which were measured by Fairbank et al⁴ show that at a temperature close to the lambda point (T_λ), the specific heat is equal to $C \log |T - T_\lambda|$, where the constant C is different on both sides of the λ -transition. The specific heat, therefore, tends logarithmically towards infinity. The superfluid properties of He^4 are attributed to the peculiarities of Bose-Einstein statistics, since the He^4 atom contains an even number of fundamental particles, and Bose-Einstein condensation in momentum space to zero momentum occurs together with a scarcity in low energy excitations. He^3 , which contains an odd number of fundamental particles and obeys Fermi-Dirac statistics, shows no indication of superfluidity or λ -transition down to 0.0035°K as shown by Abel et al.⁵

Liquids can be solidified by exerting external pressure on them. Both isotopes He^3 and He^4 have minima in their melting curves. For He^3 , Pomeranchuk predicted a minimum in the melting curve in 1950.⁶ In 1959, this minimum was measured to be at 0.33°K by Baum et al.⁷ The reasoning given by Pomeranchuk in 1950 is as follows: the nucleus of He^3 has a spin of $\frac{1}{2}h$, with an accompanying magnetic moment. In each He^3 nucleus in the liquid were free to orient its spin in two directions with equal probability, the entropy would be at least $R \ln 2$, or $5.75 \text{ joule/mole}^\circ\text{K}$. Since the nuclear spins exhibit some ordering, and thus the entropy of the liquid falls below $R \ln 2$, at a temperature where the entropy of solid He^3 is still about $R \ln 2$, the minimum should appear. The nuclear spins in the solid do not exhibit some ordering until very low temperatures (about 0.01°K)

are reached, because the nuclei are then localized very close to the lattice sites and their amplitude of oscillation is smaller than the interatomic distance which means that the wave functions do not overlap sufficiently to give the strong exchange effect needed to align the nuclear spins. Hence, below 0.33°K $\Delta S = S_L - S_S$, where S_L and S_S refer to the entropy in the liquid and the entropy in the solid respectively, is negative. If $\Delta V = V_L - V_S$, where V_L and V_S refer to the volumes of the liquid and the solid respectively, remains positive, it follows from the Clausius-Clapeyron equation $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$ that the slope of the melting curve will be negative and thus a minimum will be observed.

A minimum in the He^4 melting curve was predicted by Goldstein in 1960^{8,9} and then estimated more accurately by him in 1967.¹⁰ The basis for the He^4 minimum as given by Goldstein is that solid He^4 contains transverse as well as longitudinal phonons, while the liquid can support longitudinal phonons only. At low enough temperatures where only phonons contribute to the entropy, the entropy of the solid will be larger than that of the liquid for pertaining values of the sound velocities. According to the Clausius-Clapeyron equation, the slope of the melting line will become negative if ΔV remains positive. The melting line anomaly in He^4 was first encountered experimentally by Wiebes and Kramers¹¹ who observed that below a certain temperature the melting of solid He^4 was accompanied by a release of heat while above that temperature the melting process was normal. Shortly thereafter, le Pair et al¹² measured the melting pressure directly and confirmed its slow rise with decreasing temperatures. More

recently, Straty and Adams¹³ performed measurements, with better resolution than those of le Pair, of the He⁴ melting-pressure line between about 0.35 and 0.95°K. They found the minimum to be placed at 0.775 ± 0.005°K with a subsequent rise in pressure of 7.5 x 10⁻³ atmospheres upon cooling to 0.35°K.

Helium, in the solid state, has been of interest to many experimentalists and theorists and many review articles have been written about it (e.g. reference 14). Solid He⁴ at pressures greater than 25 atmospheres assumes a "hexagonal-close-packed" atomic structure. Over a very small region of pressures and temperatures (between 1.3 and 1.8°K; 26 and 31 atmospheres), He⁴ has a "body-centered-cubic" structure. At very high pressures (higher than 1100 atmospheres), the solid has a "face-centered-cubic" structure. The solid region in the He³ phase diagram is different from that of He⁴ in that the temperature pressure region over which He³ exists in the "body-centered-cubic" phase is considerably greater than the corresponding range for He⁴ and probably extends to 0°K.

Fig. 1.--The phase diagram of He⁴ (schematic)

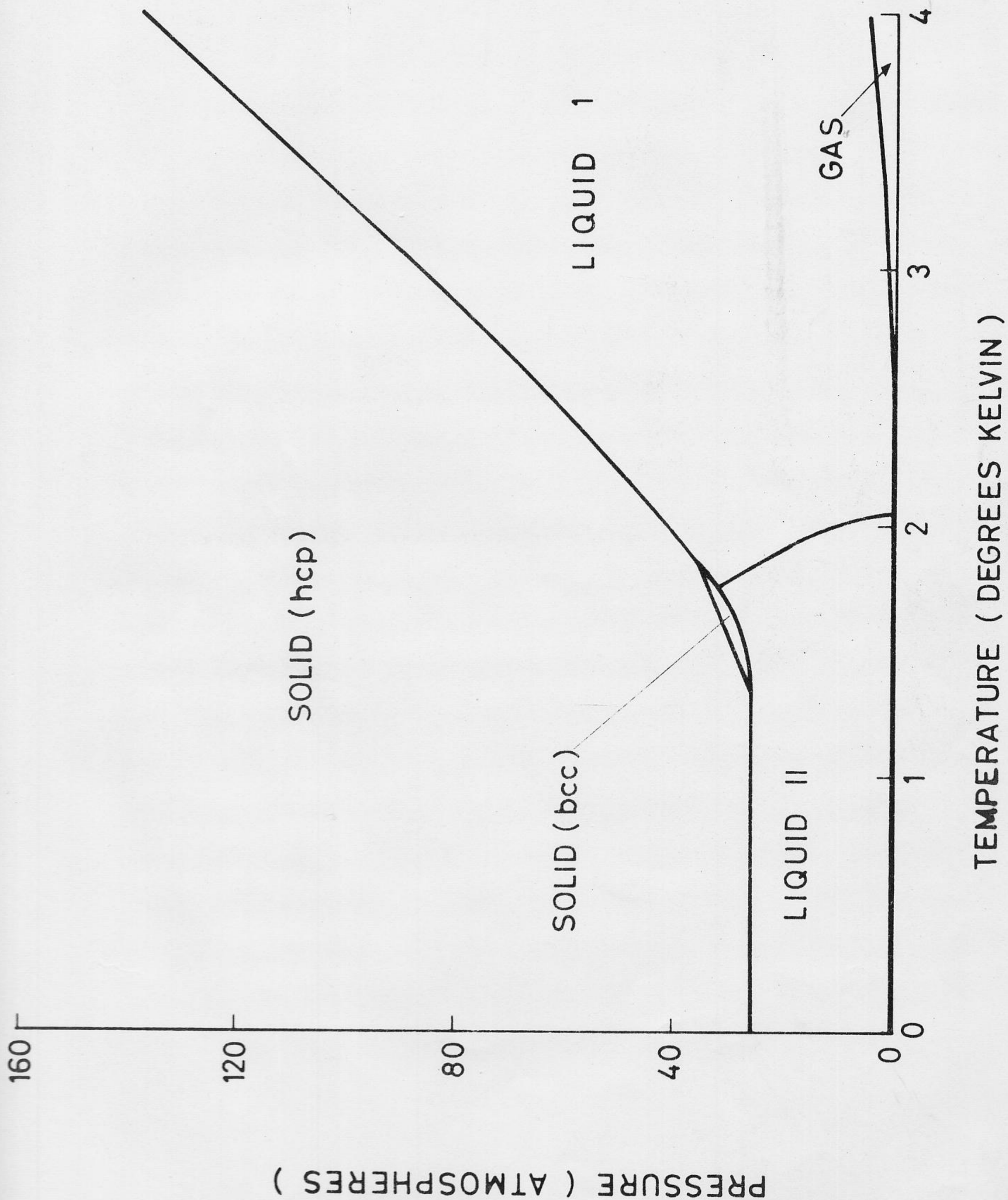
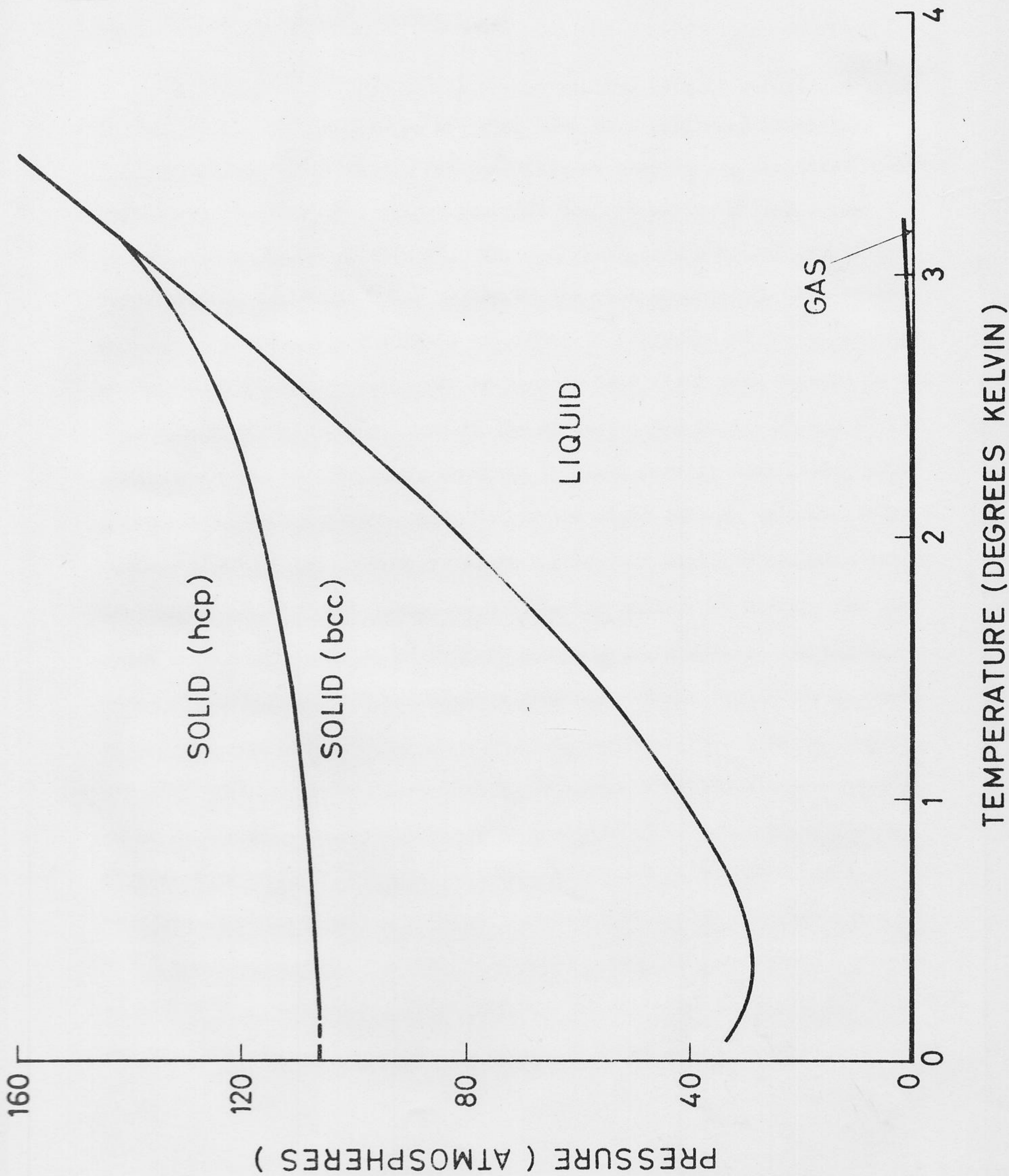


Fig. 2.--The phase diagram of He³ (schematic)



II. HELIUM³ - HELIUM⁴ MIXTURES

Mixtures of He³ and He⁴ have been studied by many experimentalists and theorists and many review articles have been published about them (e.g. reference 15). Liquid He³-He⁴ mixtures show strong positive deviations from ideality like a positive heat of mixing H^E and a positive excess Gibbs function G^E . These deviations are mainly due to the large difference in the molar volume of the pure components. Neglecting entropy effects, one may expect, according to Prigogine et al¹⁶, that the mixing becomes ideal if the pure components have first been brought to the same molar volumes as they have in the mixture. The excess G^E and H^E is then, according to Prigogine, equal to the work done by compressing pure liquid He³ and by expanding pure He⁴ to the right mixture volume. Below a certain critical temperature T_C where the heat of mixing H^E becomes larger than the product of the temperature T and the entropy of mixing, the tendency to find a situation of minimum energy overcompensates for the tendency of maximum entropy, or maximum disorder. Hence, the mixture becomes unstable below the critical temperature T_C and separates into two phases, one rich in He³ and the other rich in He⁴. The stratification of liquid mixtures was discovered by Walters and Fairbank.¹⁷ Recent measurements by D.O. Edwards et al¹⁸ show that mixtures of small He³ concentrations do exist at 0°K. De Bruyn Ouboter¹⁹ showed that in the neighborhood of 0.9°K the liquid mixture exhibits a regular behavior with a positive heat of mixing $H^E = X(1 - X)W$, where X is the He³ concentration, and $W/R \approx 1.54^\circ\text{K}$. His results were in reasonable agreement with the predictions of Prigogine

et al. Also, Edwards et al²⁰ who measured the specific heat of isotopic mixtures of solid helium, found evidence for phase separations at very low temperatures and concluded that the isotopes formed a regular mixture with a heat of mixing $H^E = X(1 - X)E_M$, where $E_M/R = 0.76^\circ\text{K}$. Klemens et al²¹ explained the existence of the positive heat of mixing in solid mixtures using a phenomenological theory. They supposed that the energy of solid helium was composed additively of the energies of individual atomic cells, and that the latter consists of a zero-point energy, a lattice potential and a pressure term. The distortions of the lattices around isotopic impurities were expressed, according to the assumption of Klemens and Maradudin²², in terms of the difference in atomic volume of the two pure components and of their elastic constants assuming that the zero-point energy varies inversely with the atomic mass. The heat of mixing was calculated by them and E_M/R was found to be 0.75°K in agreement with the experimental data.

Measurements of the specific heat of solid mixtures²⁰ reveal that solid mixtures are unstable below a critical temperature $T_C = G_S^E/1/2R = E_M/2R = 0.38^\circ\text{K}$. The heat of mixing is temperature independent and equal to $H_S^E = G_S^E = X_S(1 - X_S) E_M$, and there is no excess entropy down to 0.05°K . This means that above this temperature, the entropy of mixing of the solid is given by the classical expression $-R[X_S \ln X_S + (1 - X_S) \ln (1 - X_S)]$. On the other hand, quantum degeneracy of the entropy of mixing in the liquid starts below 1°K which means that below 1°K the entropy of the liquid becomes lower than the "constant" entropy of the solid. Consequently the freezing and melting curves of the $\text{He}^3\text{-He}^4$

mixtures have a minimum at a certain temperature and a negative slope below that temperature.

At this point, we define the difference between the freezing and melting points of a mixture. The freezing point of a mixture of known concentration at a certain temperature is determined by measuring the pressure at which a relatively large quantity of liquid mixture is in equilibrium with a negligible quantity of solid so that the concentration of the liquid is still known and not changed by the existence of crystals of different composition. The melting point of a mixture is similarly defined at some temperature by measuring the pressure at which the almost completely solid mixture is in equilibrium with a negligible quantity of liquid so that the different concentration of the latter does not disturb the solid composition.

Le Pair et al²³ measured the freezing as well as the melting pressure for mixtures over the whole concentration region in the temperature range 0.5 - 2.17°K. They found a dependence between the freezing pressure $P(T,X)$ and the He³ molar fraction X defined by the equation:

$$P(T,X) = XP_3^0(T) + (1 - X) P_4^0(T) + P^E(T,X)$$

where $P_3^0(T)$ and $P_4^0(T)$ are the freezing pressures of the pure components and $P^E(T,X)$ is the "excess pressure of freezing." Le Pair and coworkers found $P^E(T,X)$ to be negative and as large as -9 atmospheres at lower pressures and temperatures. Recently Pandorf et al²⁴ made measurements on He³-He⁴ mixtures over the whole concentration range between 1.5°K and 4.5°K and at pressures between 50 and 150 atmospheres. They also found a dependence between the freezing pressure and the He³ molar fraction

similar to that found by le Pair et al. At their higher temperatures they found $P^E(T,X)$ to be within ± 1 atmosphere. Their P - V results show that the excess volume, that is:

$$V^E(P,T,X) = V(P,T,X) - XV_3^0(P,T) - (1 - X) V_4^0(P,T)$$

is less than ± 0.04 cm³/mole. They also find that the heat capacity of a mixture at constant volume is approximately a linear function of X :

$$C_V(T,X,V) = XC_{V3}^0(T,V) + (1 - X) C_{V4}^0(T,V)$$

Their measurements show that He³-He⁴ mixtures are almost ideal at pressures higher than 50 atmospheres.

The λ -transition plays an important role in the thermodynamic properties of liquid He³-He⁴ mixtures. Addition of He³ to liquid He⁴ lowers its λ -transition temperature and the height of the peak in the specific heat at the λ -temperature falls rapidly with increasing concentration.²⁵ Also, they found a singularity in the specific heat at the point where the λ -curve meets the stratification curve. A discontinuity in the slope of the freezing curves was also found by le Pair et al.²⁶

Dilute mixtures of He³ in He⁴ (X is below 6%) which are the main topic of this thesis are of special interest because they provide a new class of strongly interacting low-density fermion systems. This situation arises when the temperature is below 1°K and He⁴ has few excitations so that it is mainly a medium which maintains the He³ atoms at a distance from one another and modifies their Hamiltonian.

III. THEORY

Measurements on the specific heat of He³-He⁴ mixtures⁸ at concentrations 4.66, 9.40 and 15% of He³ in He⁴ show between 0.4°K and 1°K an almost constant contribution of the He³ to the specific heat which is close to 3/2 RX. This behavior can be explained by means of the theory of Pomeranchuk^{27,28,29} in which he considers dilute solutions only and assumes that the He³ atoms do not interact with one another and that the assembly of the He³ atoms is non-degenerate. The He³ atoms can be treated as free particles which move through the liquid with an effective mass m_3^* . Hence, the specific heat will be that of an ideal monatomic gas. A small concentration of He³ modifies the Landau (phonon + roton) excitation spectrum by adding to the liquid a branch of Fermi particles equal in number to the number of the He³ atoms and with an energy spectrum:

$$E = E_{03} + \frac{P^2}{2m_3^*}$$

where E_{03} is the effective potential of a He³ atom in the He⁴ surrounding and the second term on the right-hand side of the above equation is the kinetic energy associated with the translational motion through the superfluid of the He³ atom which has an effective mass m_3^* . The statistical mechanics of the He³ atoms is almost the same as for an ideal gas. The internal energy U , the entropy S , the specific heat C and the partial chemical potentials μ_i can be expressed according to the following equations:

$$U = (1 - X)U_4^0 + X(NE_{03} + 3/2 RT)$$

$$S = (1 - X)S_4^0 + XR \left[\ln \left\{ \frac{g_3 V_4^0}{XN} \left(\frac{m_3^* kT}{2\pi h^2} \right)^{3/2} \right\} + 5/2 \right]$$

$$C = (1 - X)C_4^0 + \frac{3}{2}RX$$

$$\pi_4 = \pi_4^0 + RT \ln(1 - X)$$

$$\pi_3 = NE_{03} + RT \ln \left[\frac{XN}{g_3 V_4^0} \left(\frac{2\pi h^2}{m_3^* kT} \right)^{3/2} \right]$$

All these quantities are expressed per mole; g is the statistical weight (degree of degeneracy, which is two for He^3).

Later, it was suggested^{30,31} that there should be an attractive interaction between two He^3 atoms in solution which arises from the exchange of a He^4 phonon, and that this interaction might lead to a superfluid transition. Calculating this effective interaction between two He^3 atoms in a dilute solution of He^3 in He^4 might lead to a better agreement with the experiment. Many theorists worked on the calculation of the above mentioned effective interaction between two He^3 atoms in a He^4 environment^{32,33,34,35}. The interaction potential V_0 was found to be attractive. This explains why, at low He^3 concentrations, it becomes energetically favorable for the mixture not to decompose into two liquid phases. V_0 was found to be $-\alpha^2 m_4 S^2/n_4$ where α is the relative increase in the mixture volume when a He^3 atom is substituted for a He^4 atom, m_4 is the He^4 atomic mass, n_4 is the He^4 density and S is

the velocity of sound in pure He⁴. If, according to Kerr's measurements³⁶, α is taken to be 0.28, one gets a value for V_0 which is in striking agreement with the value determined empirically from the experimental data on spin diffusion and phase separation in dilute mixtures of He³ in He⁴.

The Hamiltonian of a He³ - He⁴ mixture is of the form:

$$H = \sum_{n_4} \frac{p_i^2}{2m_4} + \frac{1}{2} \sum_{i,j} U(r_i - r_j) + \sum_{n_3} \frac{p_j^2}{2m_3} \quad (1)$$

where the first term represents the kinetic energy of the He⁴ atoms, the second term represents the bare interatomic potential and the third term represents the kinetic energy of the He³ atoms. Since $m_3 = 3/4 m_4$, the Hamiltonian of the mixture can be written in the form:

$$H = \sum_{n_4+n_3} \frac{p_i^2}{2m_4} + \frac{1}{2} \sum_{\bar{i},j} U(r_i - r_j) + \sum_{n_3} \frac{p_i^2}{6m_4} \quad (2)$$

where the sum in the first term is over both the He³ and He⁴ atoms. The first two terms in equation (2) represent the Hamiltonian of $n = n_3 + n_4$ He⁴ atoms, while the last term represents the additional kinetic energy of the He³ atoms due to their lighter mass.

Bardeen et al³⁵ estimate the energy of the mixture E by taking as a trial wave function the true ground state wave function of pure He⁴ at the same particle density n as in the mixture. With this trial function, a

solution is found:

$$E(n) = E_0(n) + n_3 E_1(n) \quad (3)$$

where $E_0(n)$, the expectation value of the first two terms in equation (2), is the ground state energy per unit volume of pure He^4 at density n , and $E_1(n)$, the expectation value of the third term in (2), is one-third the average kinetic energy per particle in pure He^4 at density n and $T = 0$. Equation (3) states that the energy of the mixture is equal to the energy of pure He^4 at the same density, plus a correction term, representing the additional ground state energy of the He^3 .

The chemical potentials of the two isotopes in the liquid mixture, μ_{4L} and μ_{3L} can be calculated directly from equation (3):

$$\mu_{4L} = \left(\frac{\partial E}{\partial n_4} \right)_{n_3} = \frac{\partial E_0}{\partial n} + n_3 \frac{\partial E_1}{\partial n} \quad (4)$$

$$\mu_{3L} = \left(\frac{\partial E}{\partial n_3} \right)_{n_4} = \frac{\partial E_0}{\partial n} + n_3 \frac{\partial E_1}{\partial n} + E_1(n) \quad (5)$$

Subtracting equation (4) from equation (5), one gets the following relationship:

$$\mu_{3L} - \mu_{4L} = E_1(n) \quad (6)$$

which states that the difference between the chemical potentials of He^3 and He^4 in a liquid mixture is just the additional ground state energy $E_1(n)$ of a He^3 atom, and that this quantity depends only on the system density.

The chemical potential of the He⁴ component in a liquid mixture can be expressed by the following equation:

$$\mu_{4L}(P,T,X) = \mu_{4L}^{\circ}(P,T) + RT \ln(1 - X) + \mu_{4L}^E(P,T,X) \quad (7)$$

where μ_{4L}^E can be neglected in a regular mixture approximation, since it is a function of X^2 which is very small for a dilute mixture. Substituting the right hand side of equation (7) into equation (6), one obtains the following result:

$$\mu_{3L} = \mu_{4L}^{\circ} + E_1 + RT \ln(1 - X) \quad (8)$$

which enables one to calculate the chemical potential of the He³ component in a dilute mixture.

Similarly, the chemical potential of the He⁴ component in a solid mixture can be expressed by the following equation:

$$\mu_{4S}(P,T,X) = \mu_{4S}^{\circ}(P,T) + RT \ln(1 - X) + \mu_{4S}^E(P,T,X) \quad (9)$$

Since the measurements of Edwards et al²⁰ and the theoretical considerations of Klemens et al²¹ show that solid helium mixtures are regular, μ_{4S}^E can be neglected by the same reasoning as that given for μ_{4L}^E .

Following the argument of Klemens et al²¹, one can consider the difference between μ_{3S} and μ_{4S} to be the sum of E_2 , the energy associated with the change in the volume of the atomic cell, and E_3 , the energy required to distort the host lattice when a He³ atom is substituted for a He⁴ atom in a solid mixture.

$$\mu_{3S} - \mu_{4S} = E_2 + E_3 = E_M \quad (10)$$

E_M/R was calculated by Klemens et al to be 0.75°K . Substituting the right hand side of equation (9) into equation (10) gives the result:

$$\mu_{3S} = \mu_{4S}^0 + RT \ln(1 - X) + E_M \quad (11)$$

which enables one to calculate the chemical potential of the He^3 component in a dilute solid mixture.

In order to calculate μ_{4L} or μ_{4S} we start from the PT equilibrium values of pure He^4 and express μ_{4L} , by the following relation, keeping in mind that $(\frac{\partial \mu_{4L}}{\partial P})_T = V_{4L}$

$$\mu_{4L}(P, T, X) = \mu_{4L}^0(P^0, T) + (P - P^0)V_{4L}^0 + RT \ln(1 - X) + \mu_{4L}^E \quad (12)$$

where μ_{4L}^E may be neglected for small He^3 concentrations. Absolute knowledge of $\mu_{4L}^0(P^0, T)$ is not necessary, since it is cancelled by $\mu_{4S}^0(P^0, T)$ when the equilibrium condition $\mu_{4L}(P, T) = \mu_{4S}(P, T)$ is applied. A similar expression can be obtained for μ_{4S} . The equations (8) and (11) enable us to calculate $\mu_{3L}(P, T, X)$ and $\mu_{3S}(P, T, X)$ from μ_{4L} and μ_{4S} .

Applying the following two equilibrium conditions:

$$\mu_{3S}(P, T) = \mu_{3L}(P, T) \quad (13)$$

$$\mu_{4S}(P, T) = \mu_{4L}(P, T) \quad (14)$$

enables us to calculate the equilibrium pressure and X_S at a certain temperature for a known X_L . This equilibrium pressure should be consistent with our measurements.

IV. EXPERIMENTAL

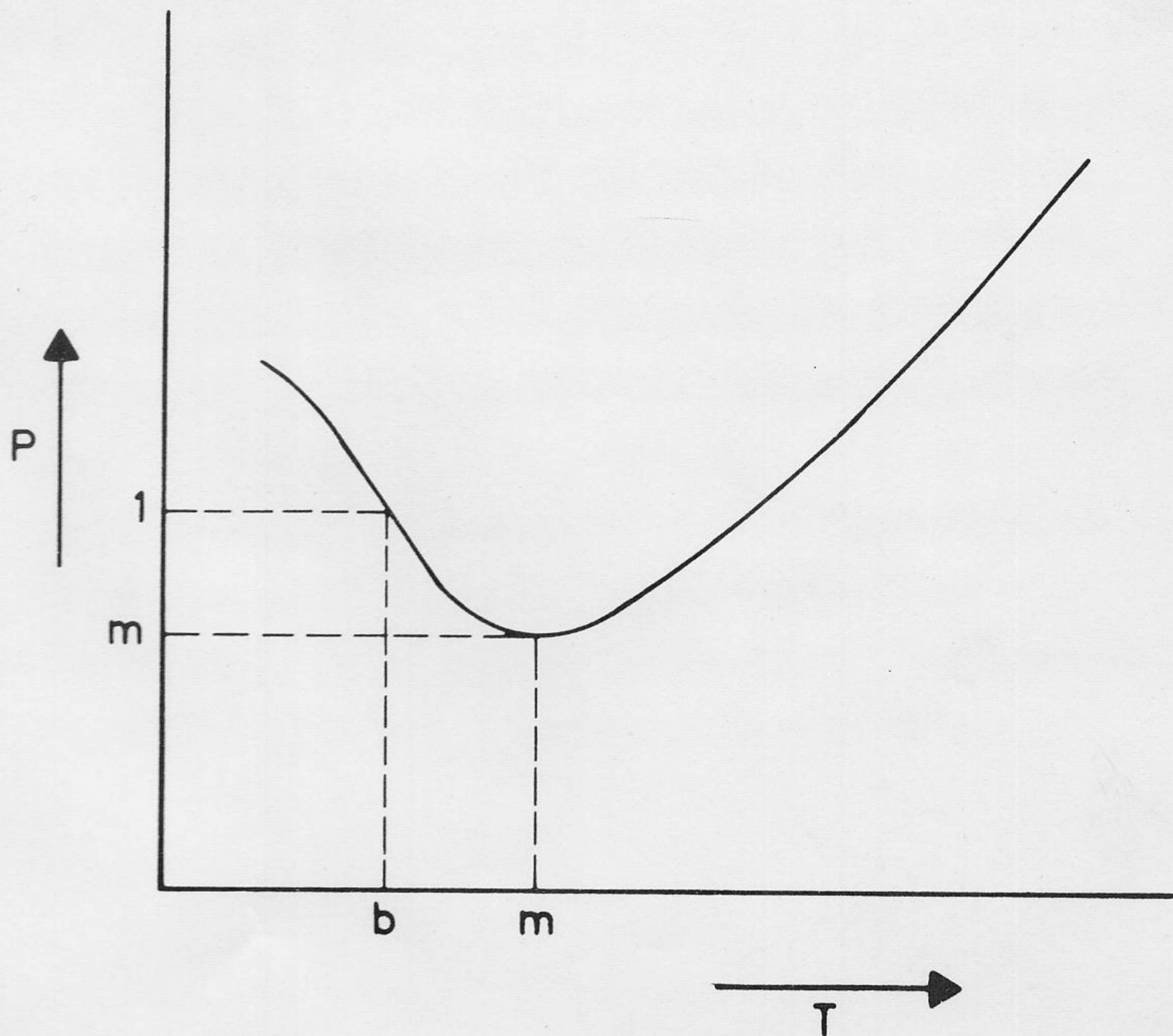
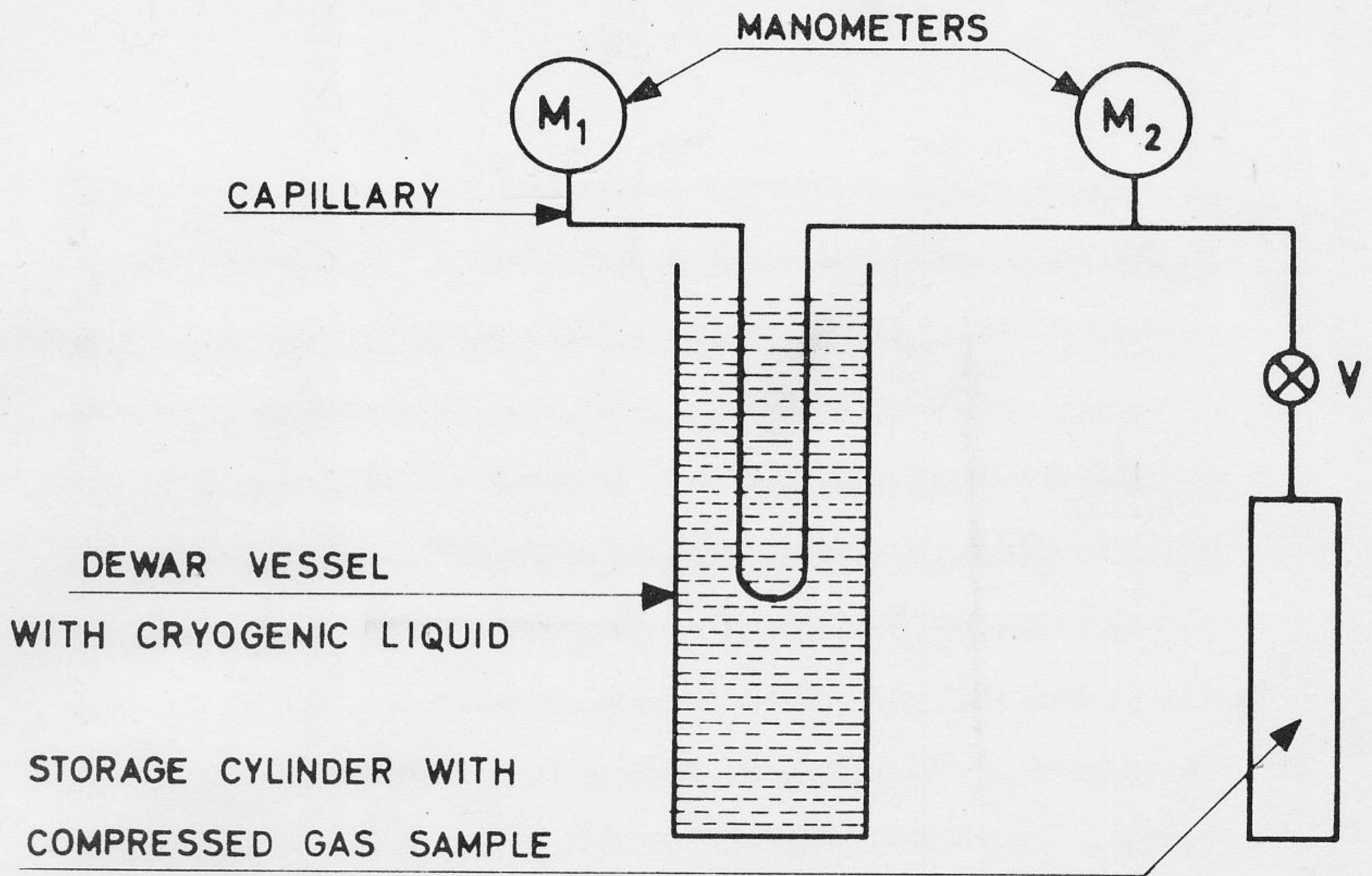
Measurements on the PT values for the phase equilibria provide the experimental data for the calculation of the chemical potential μ . In order to measure the freezing and melting lines of He^3 - He^4 mixtures in the required region, a differential manometer was constructed to facilitate pressure measurements on the spot, i.e. in the low temperature region. The necessary low temperatures are obtained by means of a He^3 -cryostat. Special care had to be taken about the precision of the absolute pressure measurement. Also, a special apparatus had to be constructed to pressurize the mixture samples. The subsequent pieces of equipment are discussed below.

1. Differential Manometer

The easiest method for the measurement of freezing pressures is the so-called "blocked capillary method" of Kamerlingh Onnes and Van Gulik.³⁷ In this method, two manometers M_1 and M_2 are connected by means of a narrow capillary C as shown in figure (3). The lower part of the capillary is immersed in a dewar vessel containing a cryogenic liquid. Through a needle valve V, the gas is slowly admitted into the capillary and the two manometers indicate the same increasing pressure. When the freezing pressure is reached, a solid block forms in the capillary and M_1 stops, indicating the freezing pressure, while M_2 continues to indicate a steadily inc-

Fig. 3.--Principle of the "blocked capillary method"

Fig. 4.--A freezing curve which has a minimum



reasing pressure. This method was applied by Keesom when he performed the first experiments on the solidification of helium. This is why many experimentalists refer to the "blocked capillary method" as Keesom's method.

If the freezing curve of a certain substance shows a minimum in the PT graph, the "blocked capillary technique" will not yield good results below the temperature T_M at which the minimum occurs. In order to understand why the "blocked capillary method" ceases to give good results below T_M , let us imagine a freezing curve as drawn in figure (4). The capillary is kept at a constant temperature T_b somewhere below room temperature. As the capillary itself has a finite heat conductivity, its temperature changes continuously from room temperature to T_b . Somewhere, the temperature of the capillary will be T_M . If one carries out the blocked capillary process, the capillary will block at $P = P_M$. This will not take place down in the capillary, but somewhere above the level of the cooling liquid. For the observer, the outcome is the same and at any temperature $T < T_M$, he will measure P_M instead of P_1 .

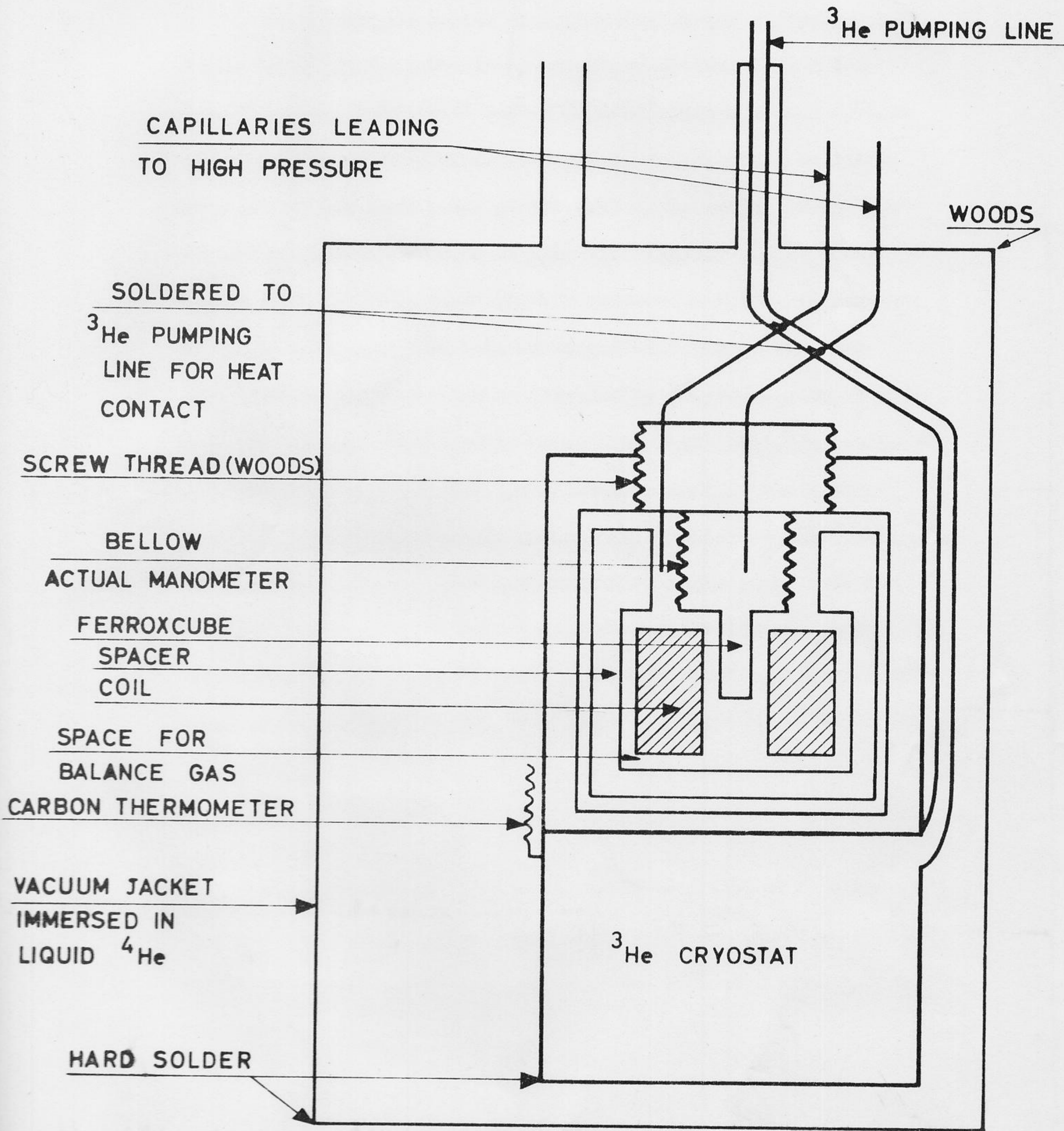
Since He^3 - He^4 mixtures have a minimum in their freezing curve, and since we are interested in measuring their freezing pressures below T_M , the "blocked capillary method" could not be used and a differential manometer as shown in figure (5) had to be constructed.

The most important part in the differential manometer is the bellow which is a flexible vessel in which the pressure can be measured at low temperatures (lower than T_M). The bellow is a Servometer Corporation electro-deposited type nickel bellow, which has a length of 12.5 mm, an outer diameter of 12.5 mm, and an inner diameter of 8 mm. Among the properties which make this nickel bellow a very good manometer are its retained toughness at low temperatures, its negligible hysteresis, and its absolute leak tightness. Moreover, the bellow can stand a net pressure of one atmosphere. The bellow is connected via a very narrow capillary to the pot containing the pressurized sample. Glued to the free end of the bellow, is a piece of ferroxcube 7.5 mm wide and 16 mm long. The ferroxcube is surrounded by a coil whose inductance can be measured by an AC Anderson bridge. The temperature dependence of the ferroxcube has to be accounted for by measuring the inductance of the coil as a function of temperature only. The coil is separated from the walls of the copper cell to which the bellow is soldered by a teflon spacer. This minimizes the effect of the eddy currents that might form in the copper walls. The bellow is surrounded by a small space for balance gas. The copper pot containing the bellow contains also a He^3 -cryostat which will enable us to perform measurements down to about 0.35^0K . The differential manometer is surrounded by a brass vacuum jacket which is immersed in a He^4 bath.

The most important part in the differential manometer is the bellows which is a flexible vessel in which the pressure can be measured at low temperatures (lower than 20°). The bellows is a horizontal cylindrical elastic bellows type elastic bellows which has a length of 12.5 cm, an outer diameter of 12.5 mm, and an inner diameter of 8 mm. Along the horizontal axis there is a small bellows a very good manometer and the constant length at low temperatures, its negligible hysteresis, and the constant length. Moreover, the bellows can stand a very pressure of 100 mm Hg. The bellows is connected via a very narrow capillary to the gas containing the pressurized sample. Glass to the tube and at the bellows.

Fig. 5.--Differential manometer

The instrument is surrounded by a cell whose temperature can be measured by an Pt resistance thermometer. The temperature dependence of the resistance can be determined by measuring the resistance of the cell at a function of temperature only. The cell is separated from the walls of the outer cell in which the bellows is enclosed by a thin layer of air. This material, the effect of the only material that might have in the outer cell. The bellows is surrounded by a wall of the outer cell. The outer cell containing the bellows contains also a thin layer of air. The outer cell contains the bellows and also a thin layer of air. The differential manometer is surrounded by a glass vacuum jacket which is lowered in a cell.



The principle behind the operation of the differential manometer is as follows: the pressurized mixture is led into the bellow which is first cooled by a He⁴ bath and then by contact with the He³-cryostat. The pressure inside the bellow is detected by the inductance of the coil surrounding the ferroxcube. The inductance depends upon the position of the ferroxcube inside the coil which in turn depends upon the net pressure inside the bellow. The total pressure on the sample is the pressure inside the bellow as measured by the inductance of the coil plus the pressure in the space around the bellow which is measured by a very precise Texas Instruments Quartz Manometer. A kink indicates onset of freezing, i.e. a point of the freezing curve of the mixture. The temperature is measured by a carbon resistor whose resistance is measured by a Wheatstone bridge. The thermometer is calibrated before every "run" against the He³ vapor pressure (1962 scale).

2. Gashandling

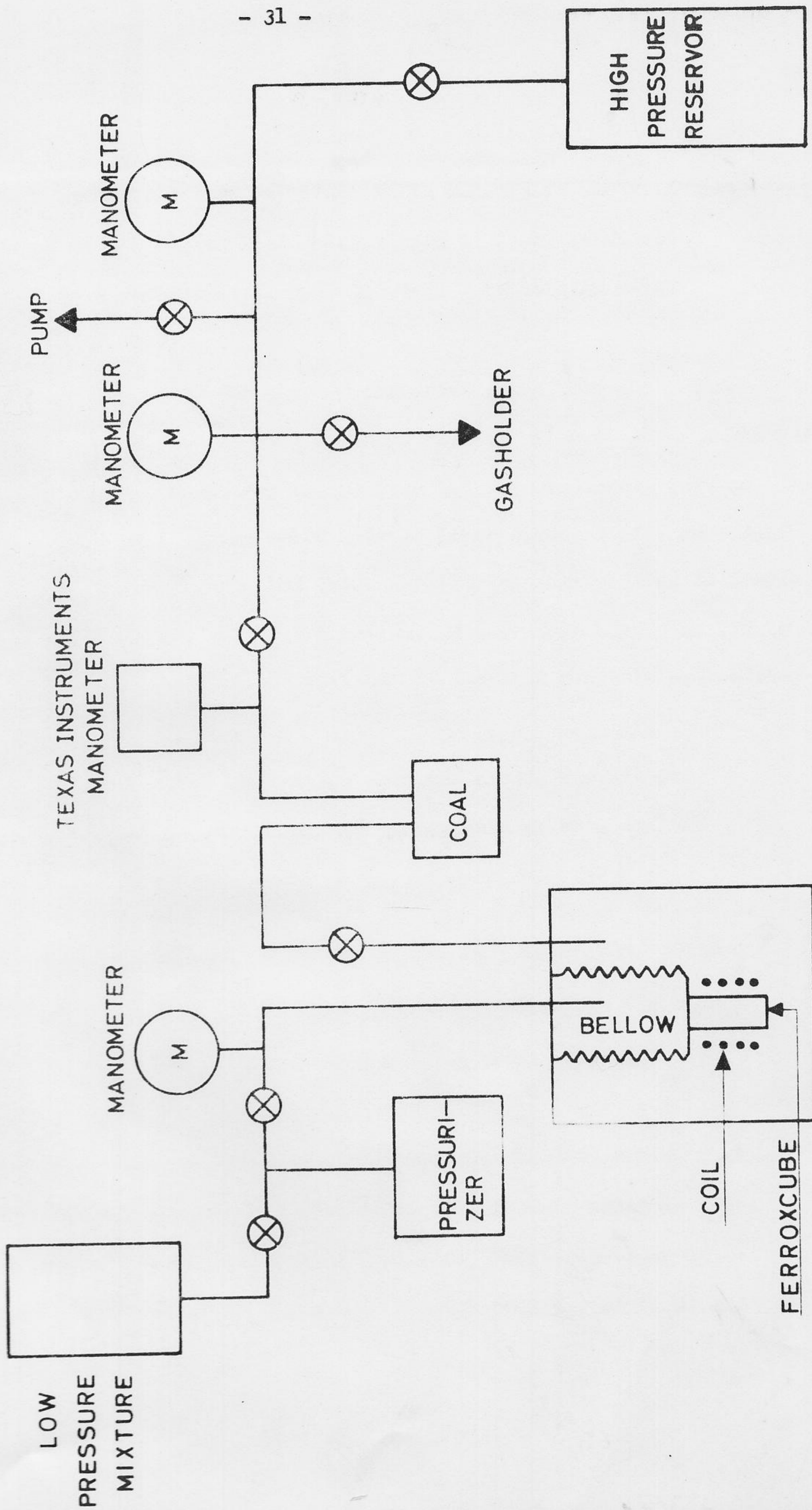
An all metal vacuum system was constructed. The use of an oil vapor diffusion pump (Edwards, model E02) backed by a rotary pump (Welch, duo-seal model 1400) can reduce the pressure in the system to about 3×10^{-5} mm mercury which is good enough for our purpose.

A three-inch central punping line makes it possible to reduce the temperature of a He^4 bath with a moderate heat leak to about 1.2°K which is a low enough temperature to start condensing He^3 in the He^3 -cryostat which is constructed to cool down the bellow of the differential manometer to about 0.35°K .

The He^3 is punped by a rotary pump (Welch, duo-seal model 1402B), which is especially equipped with an oil seal which prevents air from leaking in or He^3 from leaking out. The He^3 cylinder is mounted on the pump which can be connected to the He^3 -cryostat using a flexible stainless steel tube and an O-ring in about two minutes. This makes it possible to use the He^3 cylinder and pump in other experiments.

A high pressure helium gashandling system, as shown in figure (6), was also constructed. It involves the use of a Texas Instruments Quartz Manometer which is accurate up to 0.002 atmospheres over a range of thirty atmospheres. Such an instrument provides the necessary reference point for precise pressure measurements from one day to another. A new mixture sample of different composition is used during every "run" and the results of one day have to be compared with those of another. The manometer is basically a quartz spiral connected to a mirror in such a way that the slightest pressure in the spiral will turn the mirror sideways. This eliminates any mechanical hysteresis. The only remaining hysteresis will be that of the quartz which has a

Fig. 6.--High pressure helium gashandling system



smaller hysteresis than any other known material. The slightest movement of the mirror upon which a beam of light is directed will cause a photoelectric cell to steer a calibrated meter which can be read.

The two stainless steel capillaries going into the bellow and the space around it have an inner diameter of 0.18 mm to avoid big heat leaks. When they emerge from the vacuum jacket, they go into thicker capillaries which have an inner diameter of 1 mm. Just above the vacuum jacket, the thick capillaries are spiraled to freeze the last impurities out of the helium. A coal trap cooled by liquid air serves as a first stage purifier in the high pressure gas handling system.

Also, a glass Toepler low pressure closed circuit gas-handling system was built for the preparation of well defined mixtures.

3. Pressurizer

He^3 - He^4 mixtures are prepared at low pressures. In order to pressurize them we constructed a pressurizing apparatus, a sketch of which is shown in figure (7). The pressurizer consists of a "superfluid pump" which "pumps" superfluid helium into a glass vessel which surrounds a stainless steel cylinder, which we shall call pot (1), where our mixture condenses. Pot (1), shown in figure (8), is 43 mm long and has an outer diameter of 21 mm and

Fig. 7.--Pressurizer

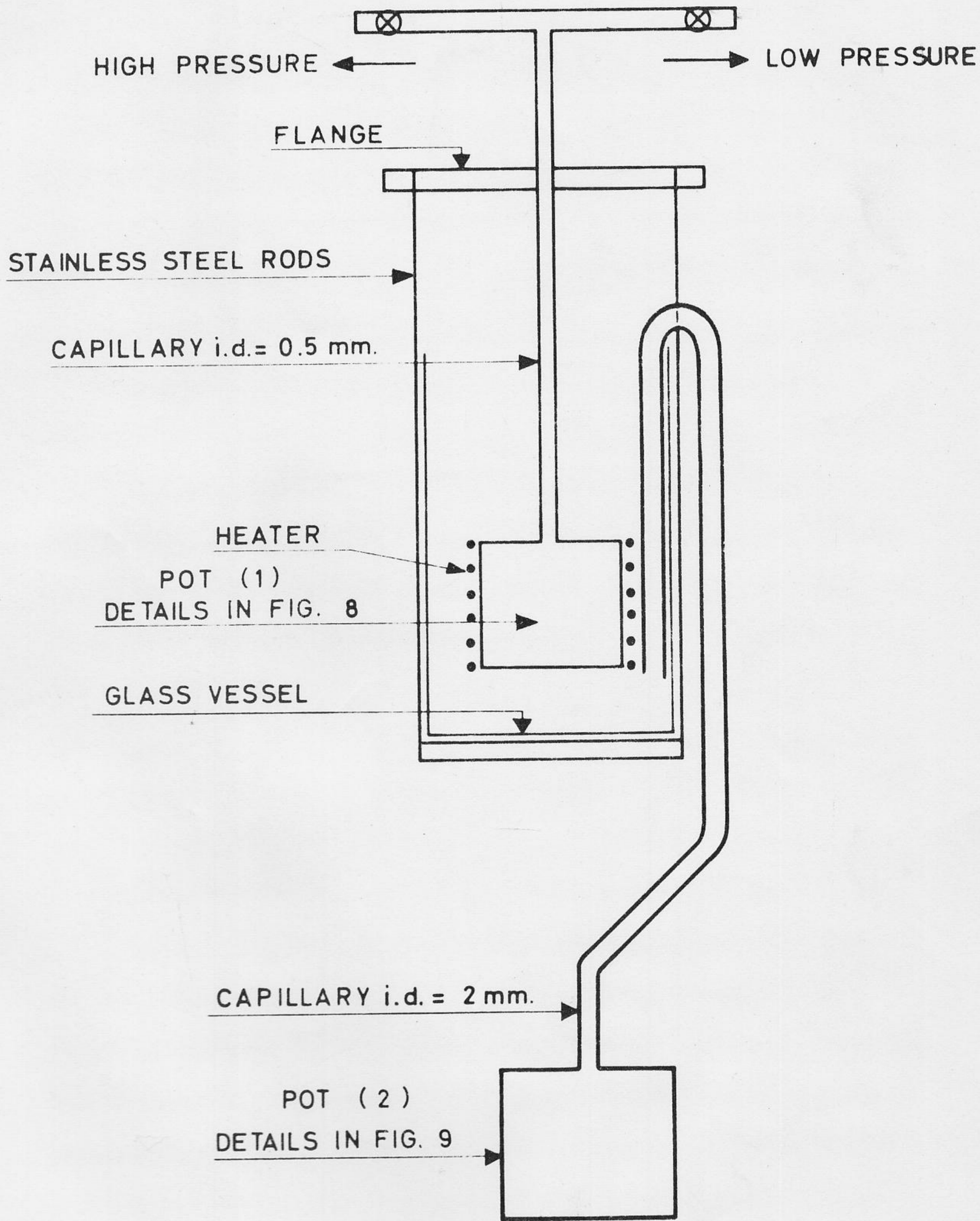


Fig. 8.--Details of pot (1) in the pressurizer

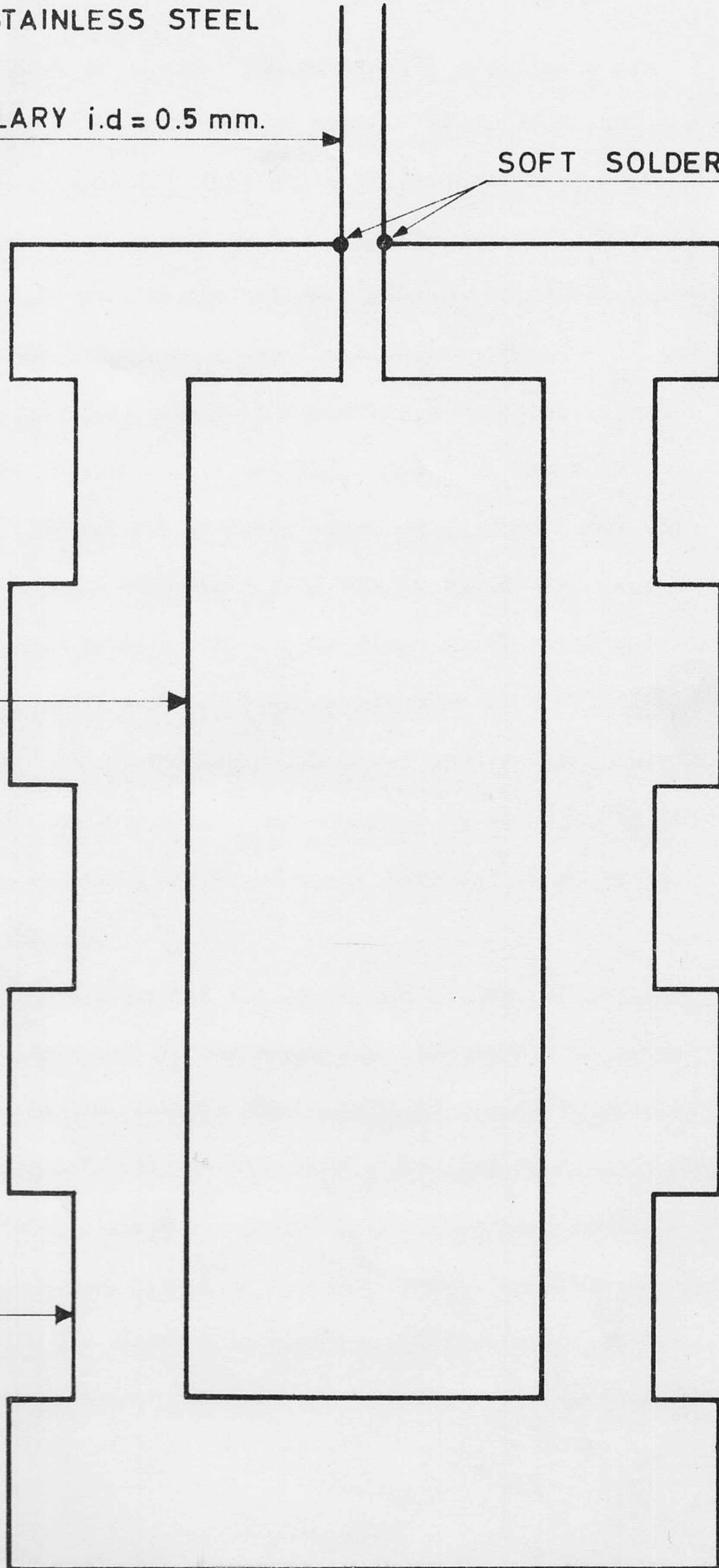
MATERIAL : STAINLESS STEEL

CAPILLARY i.d = 0.5 mm.

SOFT SOLDER

INNER WALL

OUTER WALL

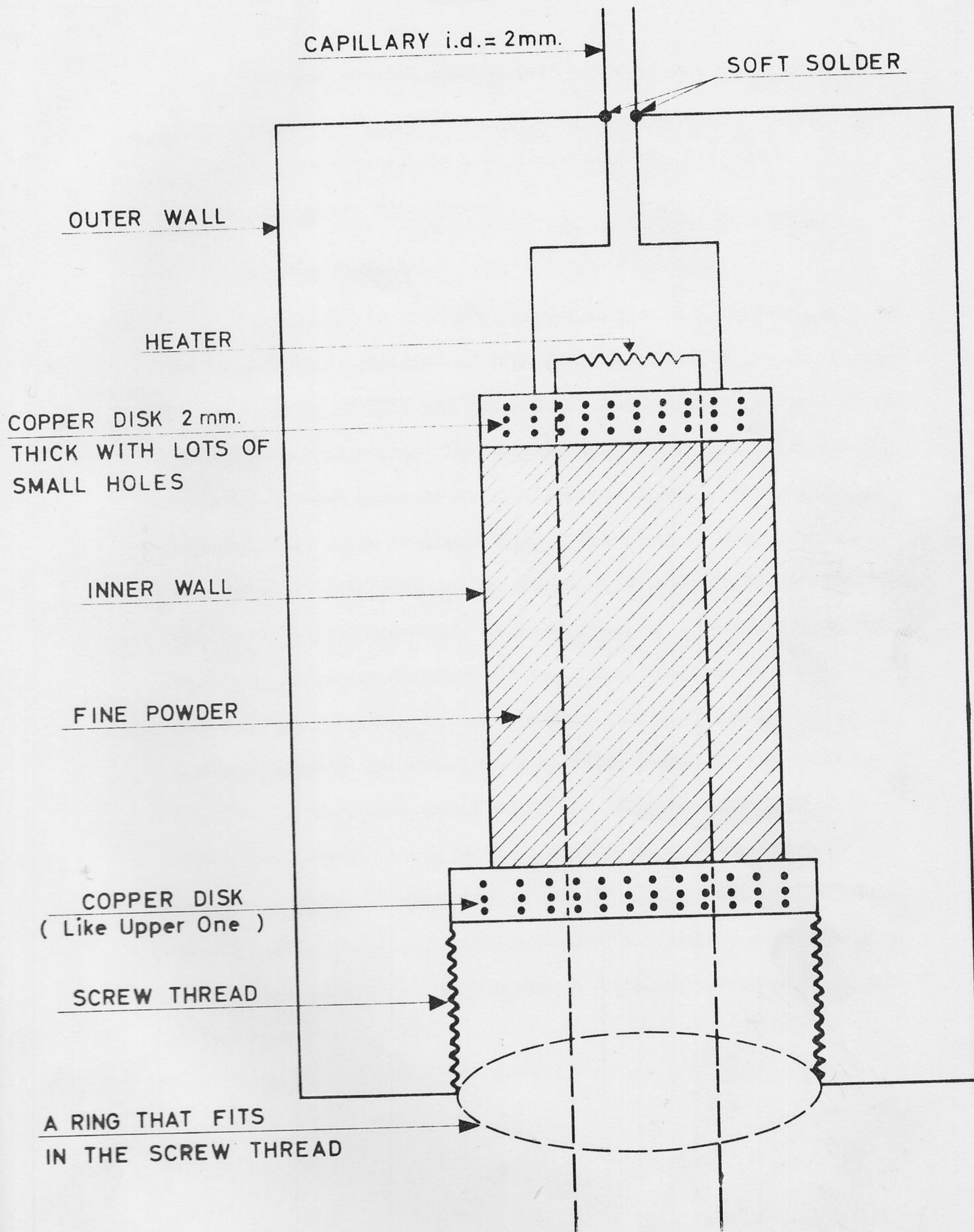


an inner diameter of 11 mm. The outer wall contains a few grooves where a 240-ohm heater is wound. Soldered to the top of pot (1) is a capillary with an inner diameter of 0.5 mm. This capillary is connected by means of two valves to both the low pressure mixture and the bellow of the differential manometer, where the actual measurements are performed.

The "superfluid pump" is basically a stainless steel cylinder which we shall call pot (2). Pot (2), shown in figure (9), is 70 mm and an inner diameter of 6 mm. Pot (2) is completely packed with very fine powder (jewelers' rouge) which is enclosed between two copper disks which contain a large number of very small holes. Each copper disk is 2 mm thick. A 35-ohm resistor is placed above the upper copper disk. A stainless steel capillary with a 2-mm inner diameter is soldered to the upper end of the "superfluid pump" and pours into the glass vessel surrounding pot (1).

The principle behind the operation of the pressurizer is as follows: the upper end of the superleak (the jewelers' rouge) is heated by the 35-ohm heater, thus creating a fountain pressure above the superleak. Superfluid helium is then "pumped" through the capillary into the glass vessel which surrounds pot (1) which will cool down to about 1.3°K . At this time, the mixture is admitted to pot (1) where it condenses. When enough gas has condensed, the fountain pressure is switched off, the admitting

Fig. 9.--Details of pot (2) in the pressurizer

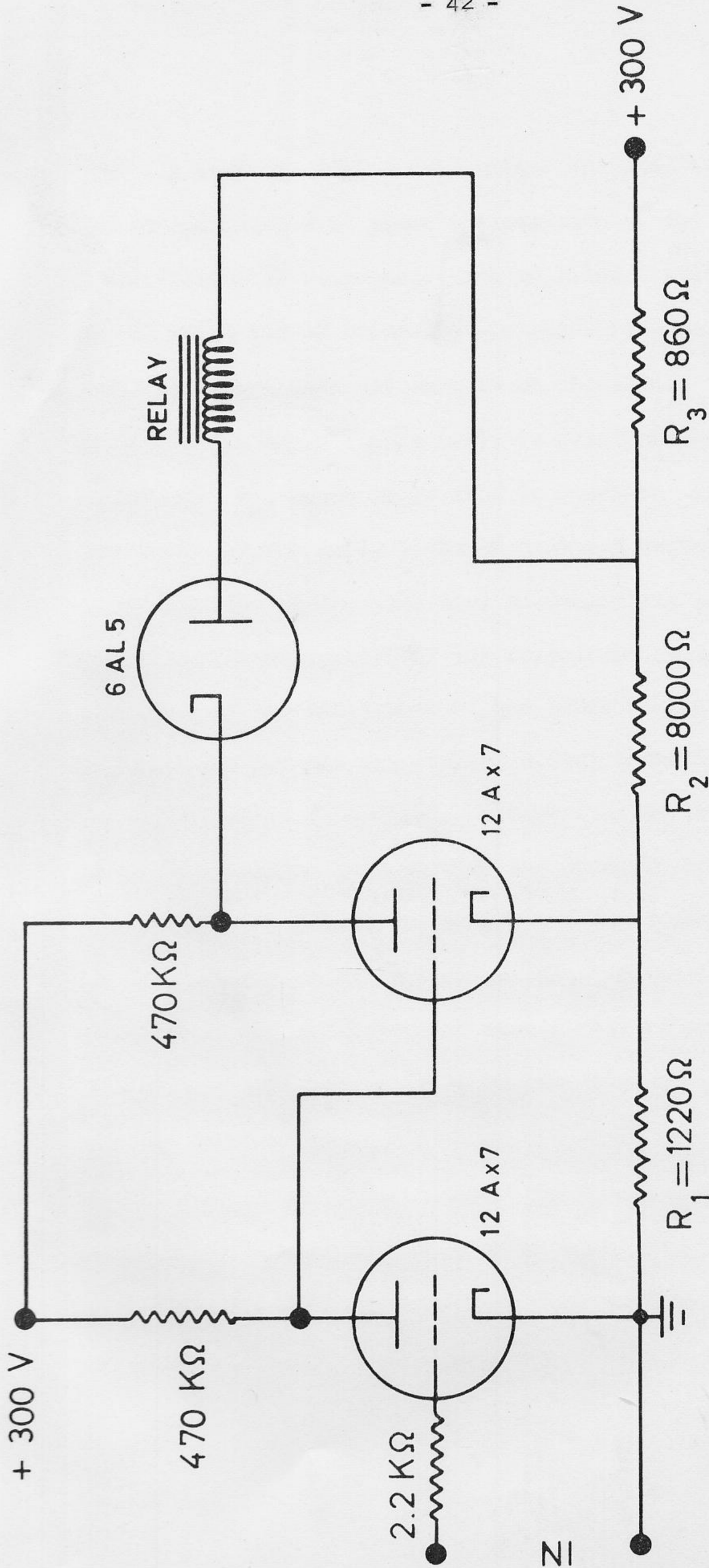


valve is closed and the 240-ohm heater around pot (1) is switched on to evaporate the mixture. The heater warms up the mixture until the pressure exceeds 100 atmospheres which is quite sufficient for our measurements.

4. Electronics

If the He^3 in the He^3 -cryostat is pumped on continuously, the temperature continues to fall and a temperature control mechanism is needed so that one can measure the freezing pressure at one particular temperature. For this purpose a non-commercial switch was designed and built by Mrs. L. Ghuneim Jammal. The circuit of the switch is shown in figure (10). The input of the circuit of the switch is connected to the output of a Keithley 150 AR Microvolt-Ammeter which is connected, as a detector, to a Wheatstone bridge where one of the resistances is the carbon thermometer in the differential manometer. When the temperature of the carbon thermometer changes, the detector detects the change in the voltage. This voltage is first amplified by the microvolt-ammeter and amplified further in the switch circuit. When the voltage on the relay, which is connected to the amplifying part of the switch circuit, is 41 volts, the switch closes the heating circuit. When the voltage across the relay drops to 24 volts the heating circuit is opened.

Fig. 10.--Thermal control switch



Voltage Across R₁ = 39 Volts

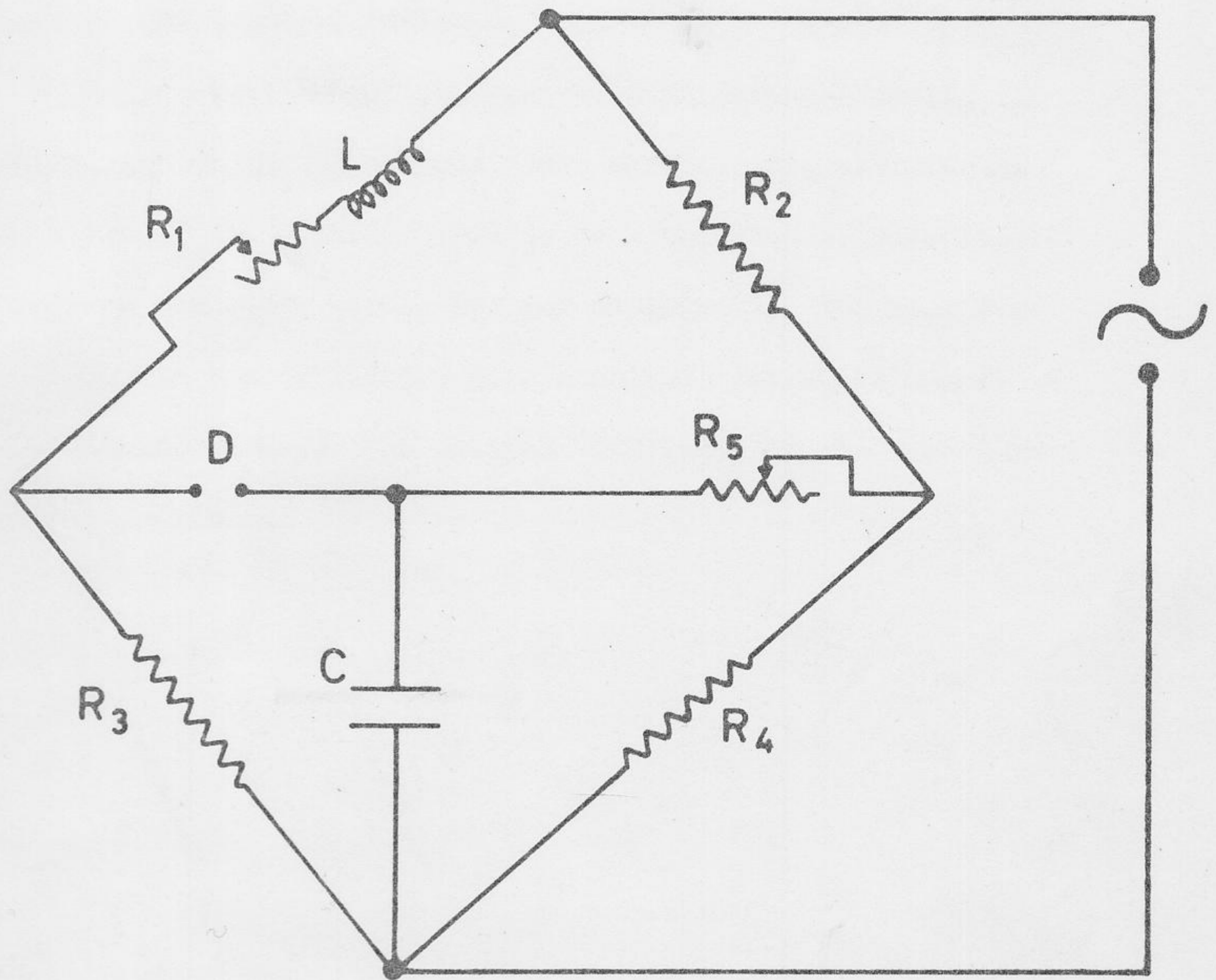
Voltage Across R₂ = 236 Volts

Voltage Across R₃ = 25 Volts

A standard AC Anderson bridge operated at 10 kilocycles per second is used to sense the position of the ferroxcube of the differential manometer. The 10 kilocycle per second frequency, at which the AC bridge is operated, is comparatively low so that the bridge does not have to be shielded. The Anderson bridge, as shown in figure (11), is practical because only one resistance, R_5 , needs to be read in order to calculate the inductance of the coil, although a second resistance, R_1 , has to be adjusted at the same time to compensate for the small effect caused by the hysteresis of the ferroxcube core, for the small variation of the resistance of the leads to the coil in the cryostat and for the transformer effect between the coil L and the copper walls of the pot. The coil L, surrounding the ferroxcube, is connected as a part of the Anderson bridge. The detector D consists of a General Radio Company tuned amplifier type 1232-A and a type 503 Tektronix oscilloscope. On the horizontal declination of the oscilloscope, the same signal is put as that on the AC bridge. This way, a quick registration of the pressure inside the bellow is possible.

Each of the carbon thermometers in the differential manometer and in the glass vessel around pot (1) in the pressurizer is a part of a Wheatstone bridge. The voltage on the Wheatstone bridge is 0.1 volts. The heaters above the superleak and around

Fig. 11.--AC Anderson bridge



pot (1) in the pressurizer are operated by means of a 6-volt battery. However, the heater in the differential manometer, which is used to stabilize the temperature at which the freezing pressure is being measured, is operated by means of two 6-volt batteries connected in series.

A lot of technical problems were encountered during the construction of the apparatus; leaks were our biggest problem. Many parts of the apparatus had to be resoldered or even rebuilt to get the necessary vacuum for our experiment. The apparatus is finally in a sufficiently good condition for measurements to be performed. However, no data was available at the time this thesis was written.

REFERENCES

1. L. LANDAU, J. Physics (USSR) 5, 71 (1941).
2. R.P. FEYNMAN, Phys. Rev. 91, 1291 (1953).
3. R.P. FEYNMAN, Phys. Rev. 91, 1301 (1953).
4. W.M. FAIRBANK, M.J. BUCKINGHAM and C.F. KELLERS, Proceedings of the 5th International Conference on Low Temperature Physics and Chemistry, Madison, Wisconsin, edited by J.R. Dillinger, University of Wisconsin Press, Madison, 50 (1958).
5. W.R. ABEL, A.C. ANDERSON, W.C. BLACK and J.C. WHEATLEY, Phys. Rev. Letters, 14, 129 (1965).
6. I. POMERANCHUK, Zh. eksper. teor. Fiz. (USSR) 20, 919 (1950).
7. J.L. BAUM, D.F. BREWER, J.G. DAUNT AND D.O. EDWARDS, Phys. Rev. Letters 3, 127 (1959).
8. L. GOLDSTEIN, Phys. Rev. 122, 726 (1961).
9. L. GOLDSTEIN, Phys. Rev. 128, 1520 (1962).
10. L. GOLDSTEIN and R.L. MILLS, Phys. Rev. 159, 136 (1967).
11. J. WIEBES AND H.C. KRAMERS, Phys. Letters 4, 298 (1963).
12. C. LE PAIR, K.W. TACONIC⁵, R. DE BRUYN OUBOTER and P. DAS, Physica 29, 755 (1963).
13. G.C. STRATY and E.D. ADAMS, Phys. Rev. Letters 17, 290 (1966).
14. C. DOMB and J.S. DUGDALE, Progress in Low Temp. Phys. 2, Chapter XI, edited by C.J. Gorter, North Holland Publishing Company, Amsterdam (1957).

15. K.W. TACONIS and R. DE BRUYN OUBOTER, Progress in Low Temp. Phys. 4, Chapter II, edited by C.J. Gorter, North Holland Publishing Company, Amsterdam (1964).
16. I. PRIGOGINE, R. BINGEN and A. BELLEMANS, Physica 20, 633 (1954).
17. K.G. WALTERS and W.M. FAIRBANK, Phys. Rev. 103, 262 (1956).
18. D.O. EDWARDS, D.F. BREWER, P. SELIGNAM, M. SKERTIC and M. YAGUB, Phys. Rev. Letters 15, 773 (1965).
19. R. DE BRUYN OUBOTER, Thesis, Leiden (1961).
20. D.O. EDWARDS, A.S. McWILLIAMS AND J.G. DAUNT, Phys. Letters 1, 218 (1962).
21. P.G. KLEMENS, R. DE BRUYN OUBOTER and C. LE PAIR, Physica 30, 1863 (1964).
22. P.G. KLEMENS and A.A. MARADUDIN, Phys. Rev. 123, 804 (1961).
23. C. LE PAIR, K.W. TACONIS, R. DE BRUYN OUBOTER, P. DAS and E. DE JONG, Physica 31, 764 (1965).
24. R.C. PANDORF, E.M. IFFT and D.O. EDWARDS, Phys. Rev. 163, 175 (1967).
25. R. DE BRUYN OUBOTER, K.W. TACONIS, C. LE PAIR and J.J.M. BEENAKKER, Physica 26, 853 (1960).
26. C. LE PAIR, K.W. TACONIS, R. DE BRUYN OUBOTER and P. DAS, Physica 28, 305 (1962).
27. I. POMERANCHUK, Zh. eksper. teor. Fiz. 19, 42 (1949).
28. R.P. FEYNMAN, Phys. Rev. 94, 262 (1954).

29. P.B. LINHART and P.J. PRICE, Physica 22, 57 (1956).
30. D. PINES, "Liquid Helium," Proceedings of the 1961 Varenna School of Physics, Academic Press (1963).
31. J.M.J. VAN LEEUWEN and E.G.D. COHEN, "Proceedings of the Eighth Conference on Low Temp. Phys.," Butterworths, London (1963).
32. J. BARDEEN, G. BAYM and D. PINES, Phys. Rev. Letters 17, 372 (1966).
33. G. BAYM, Phys. Rev. Letters 17, 952 (1966).
34. V.J. EMERY, Phys. Rev. 161, 194 (1967).
35. J. BARDEEN, G. BAYM AND D. PINES, Phys. Rev. 156, 207 (1967).
36. E.C. KERR, Proceedings of the 5th International Conference on Low Temperature Physics and Chemistry, Madison, Wisconsin, edited by J.R. DILLINGER, University of Wisconsin Press, Madison, 158 (1958).
37. H. KAMERLINGH ONNES and W. VAN GULIK, Proc. Roy. Acad. Amsterdam 29, 1184 (1926).