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THE ESTIMATION OF TRACES OF OXYGEN AND NITROGEN IN HELIUM BY MASS SPECTROMETRY

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Abstract

Mass spectrometer analysis of helium for traces of oxygen and nitrogen may be made using figures for the relative ionization efficiency of the pure gases.

CONTENTS

1. INTRODUCTION

The analysis of multicomponent gas systems is often carried out on a mass spectrometer using relative sensitivities obtained by introducing pure samples of each component in turn (1). Two doubts arise as to the applicability of this method for the determination of traces of nitrogen and oxygen.

First, helium has two triplet energy levels, 19.8 and 21 e.v. above the singlet ground state. Since the ionization potentials of O_2 and N_2 are 12.5 and 15.5 e.v. respectively, there is the possibility of enhanced ionization of O_2 and N_2 by collision with helium atoms in the metastable triplet state.

Secondly, for the determination of N_2 there is the possibility of "interference" to the 28 background peak. This peak is presumably due to CO and/or N_2 adsorbed on the surfaces of the ion source. Admission of the relatively high pressures of helium used for the trace determination may increase the rate of desorption of the CO and/or N_2, thus leading to over-estimation of the nitrogen impurity.

Both points have been investigated; the first by introducing calibrated amounts of oxygen and nitrogen into helium by electrochemical means, and the second by preparing helium which is "oxygen – and nitrogen– free".

2.1 PRODUCTION OF CALIBRATED MIXTURES

Hersch (2) produced nitrogen with known additional concentrations of oxygen by passing a metered stream of nitrogen through an electrolysis cell in which oxygen was being formed by anodic oxidation of hydroxyl–ions at constant current. By varying the current the oxygen concentration was easily altered. This system is ideal for the present purpose, since it is dynamic and the many errors which arise from blending in a static system (e.g. differential solubility of components in stopcock grease) only affect the time required for the emergent stream to attain equilibrium, whilst not altering the equilibrium concentration.

Lingane (3) has shown that nitrogen may be generated with almost 100% current efficiency by the anodic oxidation of acidic solutions of hydrazine hydrochloride, according to the reaction:

$$N_2H_5^+ - 4\epsilon \rightarrow N_2 + 5H^+$$

This reaction was used to prepare N_2/He mixtures.

2.1.1 Apparatus

The electrolyser used (Fig. 1) is similar to the one described by Hersch (2). A simple transistorized constant current source, providing electrolysis currents of 0–300 milliamps, (Fig.3) was designed and built by the Technical Physics Section of the A.A.E.C. Research Establishment.

The helium flowrate was regulated by means of a needle valve on the cylinder and measured by means of a Fischer and Porter size 08 flowrator tube. The gas was dried by passing it through a tube containing activated silica gel. The gas mixtures were collected in a small sampling tube (Fig.2), provided with a connection for attachment to the mass spectrometer, which was a Metropolitan Vickers MS3 equipped with a 250 ml. expansion flask instead of the standard 2 litre flask.

2.1.2 Procedure

The helium was allowed to flow through the apparatus at 100 ml./min. for 2–3 minutes before the sample was collected. This excluded air from the system and allowed the emergent gas to reach constant composition. The direct deflection method was used to measure the 32, 28 and 4 peak heights. When using N_2/He gas mixtures, the background 28 peak of the mass spectrometer was subtracted from the measured 28 peak height. This was not necessary with O_2/He gas mixtures owing to the small 32 background.

2.2 RESULTS AND DISCUSSION

The calibration curve for oxygen–helium gas mixtures is shown in Figure 4. Owing to the presence of oxygen in the helium supply, and possible background interference, the curve does not pass through the origin. The blank correction amounted to 350 p.p.m. of oxygen in helium.

The calibration curve for nitrogen–helium gas mixtures is also shown in Figure 4. The blank correction which is due to the nitrogen in the helium supply and possible background interference was found to be 1000 p.p.m. of nitrogen in helium. The slopes of these calibration curves were determined by the method of least–squares.

These slopes were found to agree with the relative sensitivities determined for the pure gases. It can be concluded that no enhancement of the ionization of the oxygen and nitrogen impurity occurs under the conditions of the experiment.

3.1 INVESTIGATION OF BACKGROUND INTERFERENCE

Several ways of producing pure inert gases have been described. Samples can be sealed off and gettered with alkali or alkaline earth metals or by passing an electric discharge between zirconium electrodes (3). However, the simplest method for this application appeared to be the use of Linde Molecular Sieves (Type 5A) at low temperatures.

3.1.1 Experimental

The equipment used is shown in Figure 5. The sieve material was first outgassed by evacuation (on the mass spectrometer sample inlet) at room temperature. A pressure of a few cm of mercury above atmosphere was maintained inside the vessel by continuously admitting helium through the stopcock, and the sieve material was cooled with liquid nitrogen. After thermal equilibrium was attained, the stopcock was shut. After a suitable period for absorption of the impurities by the sieves, samples were admitted into the mass spectrometer.

3.2 RESULTS

It was found that initially a high interference of the 28 background occurred, but after 3 or 4 samples were admitted, the instrument was so "conditioned" that no significant increase in the 28 background was detected upon the admission of pure helium.

4. CONCLUSION

It has been shown that the mass spectrometer analysis of helium for traces of oxygen and nitrogen can be carried out using figures obtained for the relative ionization efficiencies of the pure gases.

5. ACKNOWLEDGMENTS

We are indebted to Dr. A.W. Pryor for the design and construction of the transistorized constant current source.

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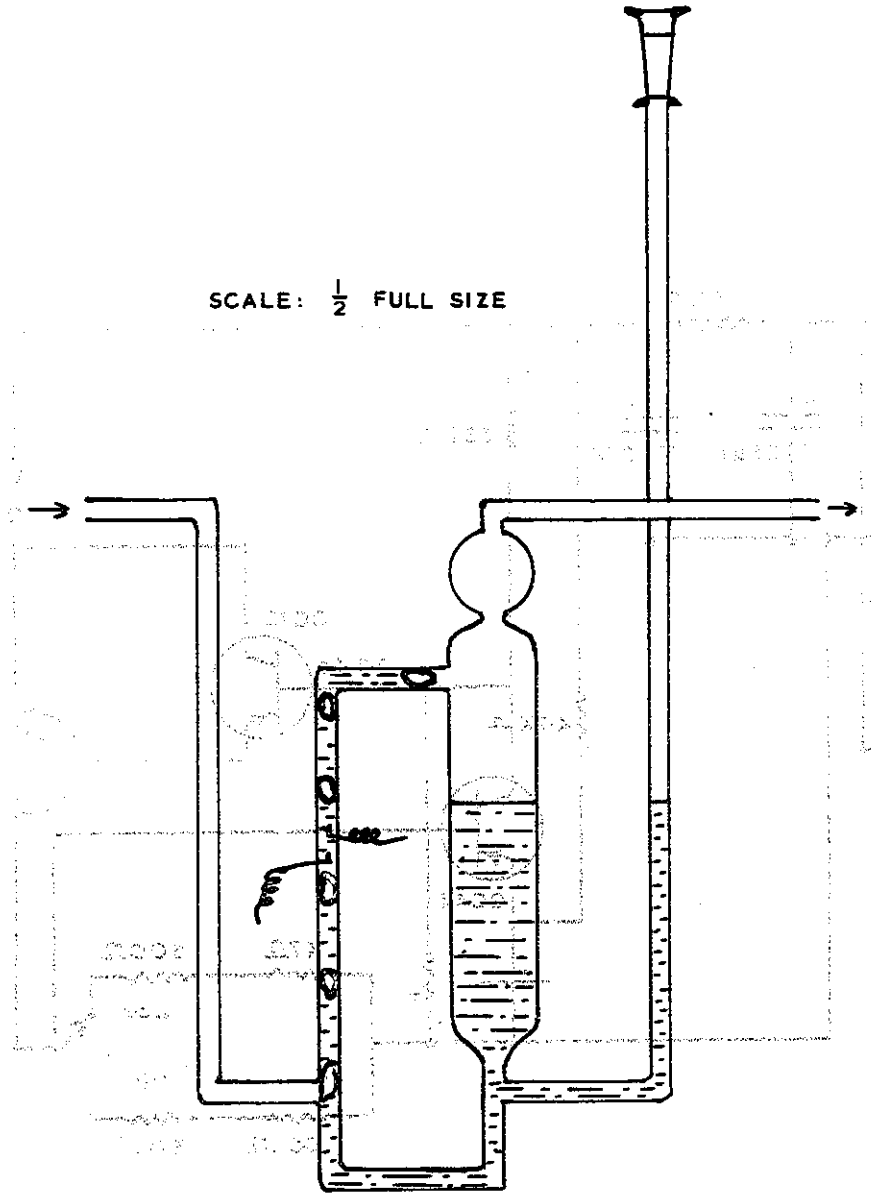

FIG. 1 HERSCH ELECTROLYSER.

SCALE: $\frac{1}{2}$ FULL SIZE.

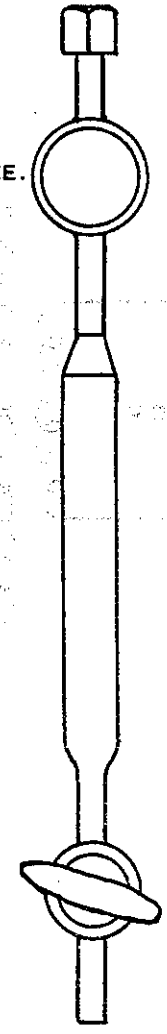

FIG. 2. SAMPLING TUBE.

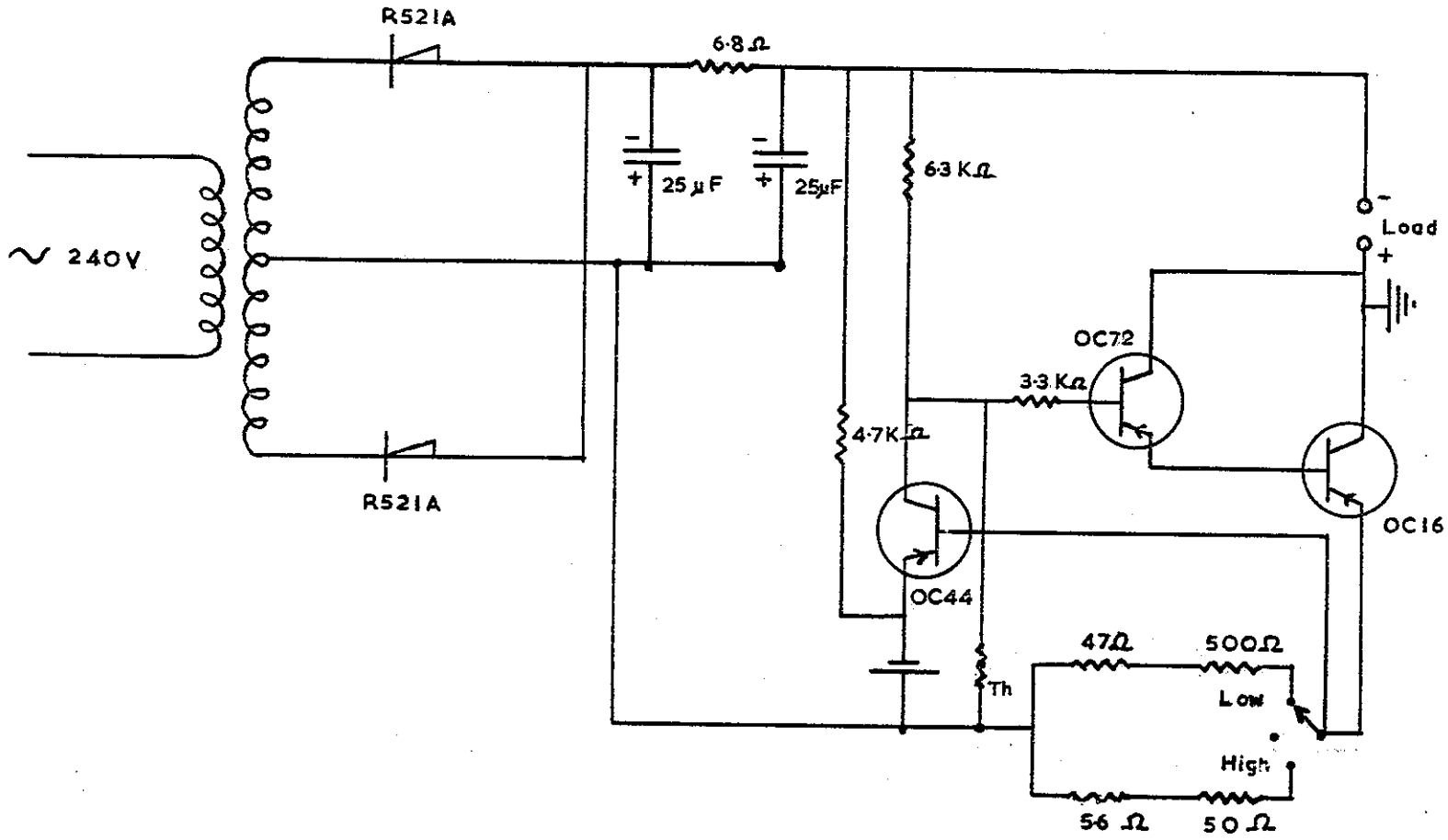

Fig.3 Constant Current Source.

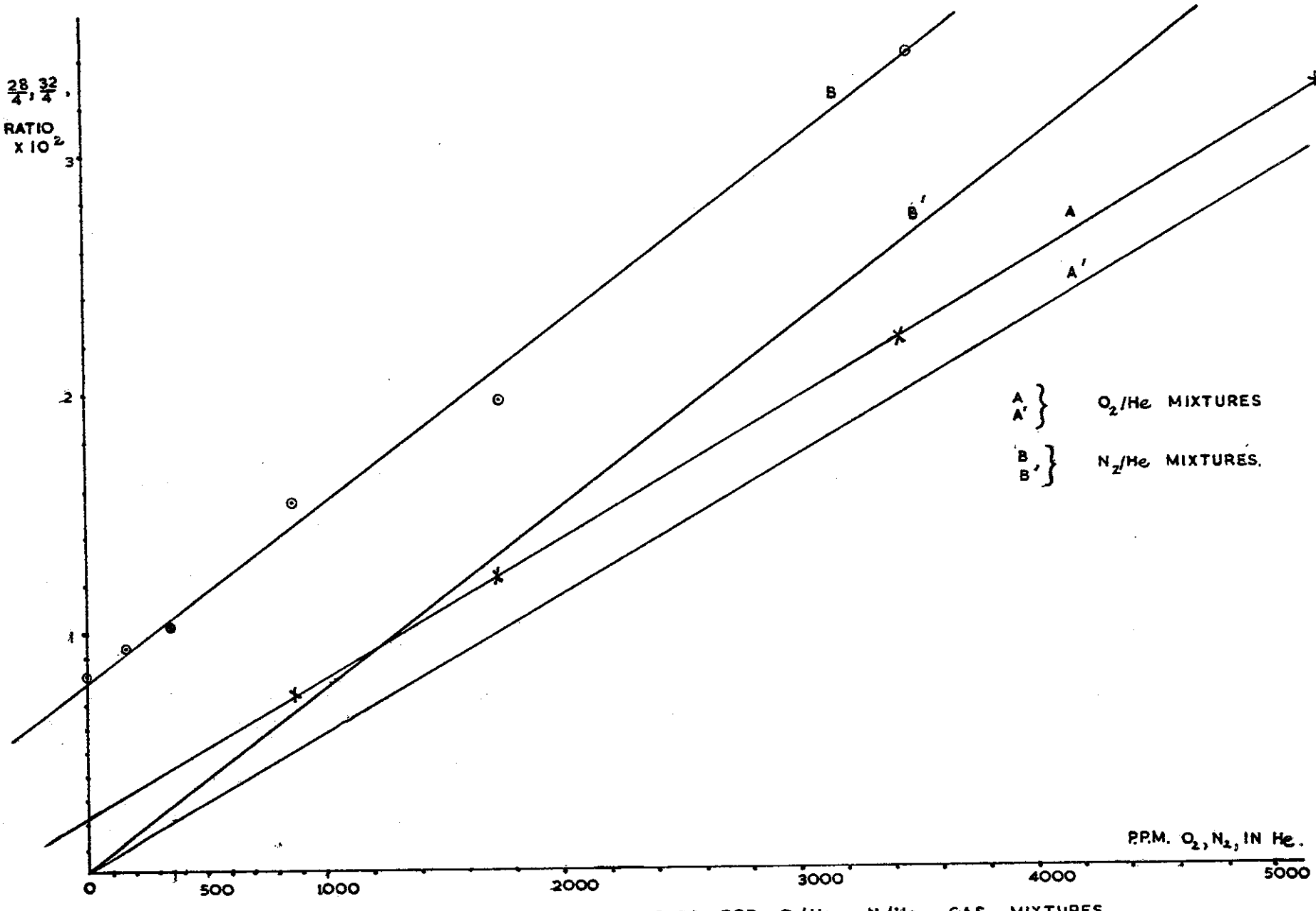

FIG 4 CALIBRATION CURVES FOR O_2/He , N_2/He , GAS MIXTURES.

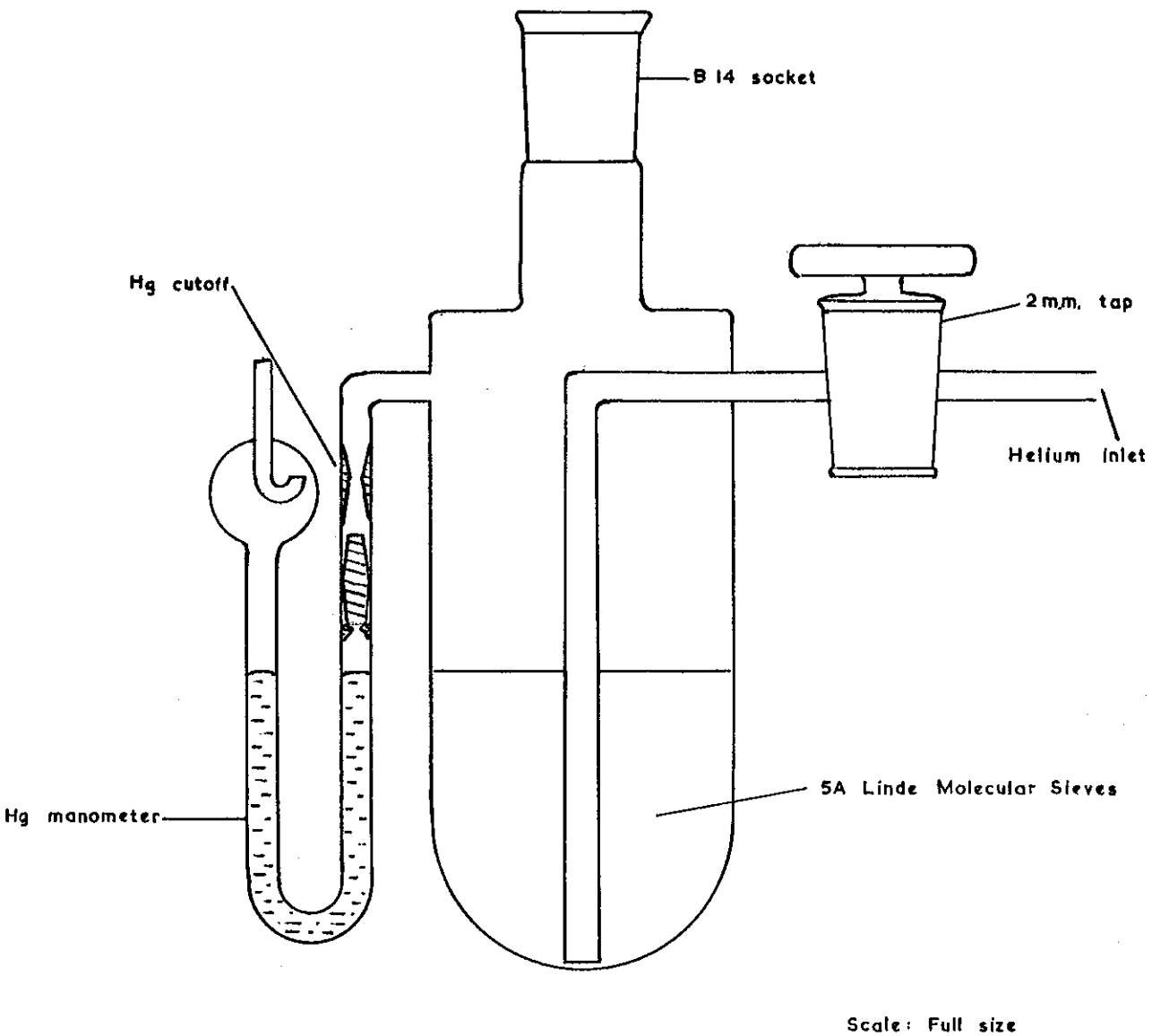

Fig. 5 Helium Purification Apparatus