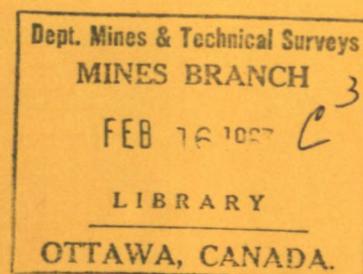




DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

*MEASUREMENT OF THE SURFACE AREAS
OF POWDERS BY KRYPTON GAS
ADSORPTION METHOD. CONSTRUCTION
AND OPERATION OF THE APPARATUS*



SYED M. AHMED

MINERAL SCIENCES DIVISION

JULY 1966

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MEASUREMENT OF THE SURFACE AREAS OF POWDERS BY
KRYPTON GAS ADSORPTION METHOD.
CONSTRUCTION AND OPERATION OF THE APPARATUS

by

S. M. Ahmed*

ABSTRACT

An apparatus has been constructed for studying the adsorption of Kr on finely divided materials of low as well as high specific surface areas, in the low pressure range, $< 1 \text{ mm}_{\text{Hg}}$, at -196°C . The apparatus is designed to handle four samples at a time. The use of a thermistor in measuring the low pressures to a high accuracy is found to offer several advantages over the conventional methods of measuring pressures. The adsorption isotherms have been used to calculate the specific surface areas of powders by the B.E.T. method. The applicability of the Harkins-Jura equation for the determination of the surface areas has also been investigated.

*Research Scientist, Mineral Physics Section, Mineral Sciences Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

Direction des mines - Bulletin technique TB 84
MESURE DES AIRES DE SURFACE DES POUDRES PAR
LA MÉTHODE D'ADSORPTION DU GAZ KRYPTON.
DESCRIPTION ET FONCTIONNEMENT DE L'APPAREIL

par

S. M. Ahmed*

RÉSUMÉ

On a mis au point un appareil qui permet de mesurer l'adsorption du Kr sur les matériaux finement pulvérisés d'aires de surface spécifiques, aussi bien petites que grandes, dans le champ des basses pressions, $< 1 \text{ mm}_{\text{Hg}}$ à -196°C . L'appareil a été conçu de façon à pouvoir traiter quatre échantillons à la fois. La mesure des basses pressions à l'aide d'un thermistor, permettant d'atteindre un haut degré de précision, offre plusieurs avantages sur les méthodes classiques de mesure des pressions. On a utilisé les isothermes d'adsorption pour calculer les aires de surface spécifiques des poudres, par la méthode B. E. T. On a également étudié l'application possible de l'équation Harkins-Jura pour déterminer les aires de surface.

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- - -

INTRODUCTION

The specific surface area S (area/g) of materials in the finely divided state may represent several important characteristics of the materials, e.g., the degree of fineness, the porosity and surface roughness, the exposed area, or the number of active centres available for numerous interfacial reactions such as adsorption and catalysis. A knowledge of S is, therefore, an essential requirement in research and industry when dealing with powdered materials. Of the several physical and chemical methods available for the determination of S , the most reliable and widely used is that based on the physical adsorption, at low temperatures, of the chemically non-reactive gases at their saturation pressure. The well known B.E.T. (Brunauer, Emmet and Teller) equation, which has been derived from the theory of multimolecular adsorption of gases on solids, can be used to calculate S from the adsorption data; the theoretical details

may be found elsewhere (1, 2, 3). In spite of certain unrealistic assumptions in the theory, as discussed by Brunauer (3), reliable values of S can be obtained from the B.E.T. method that are also in good agreement with the S-values obtained from independent methods such as electron microscopy and that of Harkins and Jura (4).

The B.E.T. equation for non-porous solids may be written as :

$$\frac{P}{v(P_0 - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \cdot \frac{P}{P_0}, \quad \text{-----(1)}$$

where v is the volume (in cc ST.P/g material) of the gas adsorbed at the equilibrium pressure P, V_m is the volume (cc ST.P/g material) of the gas required to cover the entire surface with a monolayer of adsorbed gas (usually at liquid nitrogen temp., -195.8°C), P_0 is the saturation pressure of the gas, and C is a constant related to the net heat of adsorption. Most of the gas-solid systems give an S-shape isotherm on plotting P against V. For such systems, a plot of $\frac{P}{v(P_0 - P)}$ against P/P_0 , according to the B.E.T. equation, is linear within certain ranges of the relative pressure P/P_0 of 0.05-0.35 for nitrogen and 0.07-0.20 for Krypton as adsorbates. A monolayer adsorption usually occurs in this range of the relative pressure. From the slope ($= \frac{C - 1}{V_m C}$) and the intercept ($= \frac{1}{V_m C}$) of the linear portion of the B.E.T. plot, it can be shown that

$$V_m = \frac{1}{\text{Slope} + \text{Intercept}} \quad \text{-----(2)}$$

and hence,

$$S = \frac{V_m \times N \times 10^{-16} \times \sigma_{Kr}}{22400}, \quad \text{-----(3)}$$

where N is the Avogadro number and σ_{Kr} is the cross-sectional area of Kr molecule in the condensed phase (19.5 \AA^2 used). A modified B.E.T. equation has to be used for porous materials with extremely fine pores.

According to the theory of Harkins and Jura (4), a plot of $\log P/P_0$ against $1/v^2$ is linear in the region of monolayer adsorption, and if A is the slope of this plot, then

$$S = K A^{\frac{1}{2}}, \quad \text{-----(4)}$$

where K is a constant related to the compressibility of the adsorbate. The value of K is independent of the solid and is equal to 4.06 for nitrogen as adsorbate, when S is in units of square metres/g material. The value of K for Kr may be different from 4.06. Beebe, Beckwith and Honig (5) have arrived at a value of 4.2 for K_{Kr} by indirect methods at $-194 \pm 1^\circ\text{C}$, and it appears this value may have to be further verified.

The gas most widely used as adsorbate, until recently, was nitrogen at liquid nitrogen temperature. Nitrogen cannot be used, however, for the determination of low surface areas ($S < 1000 \text{ cm}^2$) of coarse and crystalline materials, because its P_0 value is so high (~ 1 atmosphere) that small changes in P (due to low S) in a dead space of about $10\text{-}15 \text{ cm}^3$ cannot be measured with any accuracy. This difficulty was overcome by Beebe, Beckwith and Honig (5), using Kr which has a P_0 value of only 2-3 mm_{Hg} at liquid nitrogen temperature. This method is applicable for the determination of low ($\sim 100 \text{ cm}^2/\text{g}$ adsorbate) as well as high surface areas. Rosenberg (6) made a significant improvement in the method of measuring pressures, by the use of a thermistor.

The following section describes an apparatus, developed by the author, which uses a thermistor in measuring pressures and is designed to handle four samples at a time.

APPARATUS

The apparatus is designed as shown in Figure 1 and constructed of pyrex glass. A mercury diffusion pump and an oil pump, separated from the manifold by a liquid nitrogen trap (N), are used to evacuate the apparatus to a pressure $<10^{-5}$ mm_{Hg}. Attached to the manifold are a thermocouple gauge (T_2) and two gas storage bulbs for He and Kr, which in turn are provided with manometers to indicate the gas pressure during use and refilling. It is important that, after the assembly, the mercury in the manometers be boiled in vacuum to remove the traces of trapped air and moisture. There are also two main storage and supply tanks for He and Kr, connected to the manifold through another liquid nitrogen trap (N'). High-vacuum stopcocks with evacuable hollow plugs have been used throughout.

The main adsorption unit comprises a low-sensitivity McLeod gauge (M), a gas burette (G), a thermistor assembly (T_1), and a set of four adsorption bulbs (B_{1-4}). This unit is finally connected to the manifold through a doser (D). The doser, consisting of a small 2-mm capillary tube, is used for admission or removal of gas to or from the adsorption unit. The low-sensitivity McLeod gauge (M) was constructed and calibrated linearly to measure pressures in the range 100-3000 μ . A cathetometer

was used to read the mercury levels. In gauge M, the gas cutoff and the lower part, as shown in Figure 1, were designed to give better accuracy in calibration and pressure measurements than the usual designs in use. In between the cutoff and the grease trap there is a precision bore capillary tube bearing a reference mark for precise determination of the Hg level. The gas burette (G) is provided with a jacket through which water at constant temperature ($26 \pm 0.01^\circ\text{C}$) is circulated. The bulbs I-IV in G are separated from each other by a 1.6-mm (i.d) capillary tube which also bears reference marks for the purpose of calibration. The McLeod gauge and the gas burette were calibrated before assembly, using pure and freshly distilled Hg. The calibrated constants of M and G are given in Appendix I.

A thermistor, L252-A, which had the characteristics recommended by Rosenberg (6), was originally supplied by Gulton Industries Inc.*. This was assembled as shown in Figure 2B and used as one arm of a Wheatstone bridge (Figure 2A). The bridge was used to measure the off-balance potential (V_{off}) as the pressure is increased in the adsorption unit. Further details for the operation of the thermistor gauge are found elsewhere (6) and will be further elaborated upon in the next section.

MATERIALS AND METHOD

Research-grade Kr and He ($\sim 99.99\%$ pure) were supplied by Matheson of Canada Ltd., in steel cylinders. Helium was passed, for further

* 212 Durham Ave., Metuchen, N.J., U.S.A.

purification, through a liquid nitrogen trap before filling the storage bulb. Krypton was solidified in a liquid nitrogen trap and the middle fraction of it was evaporated to fill its storage bulb, rejecting the first and the last fractions. In order to obtain better and more reliable vacua in a much shorter period, the stopcock grease, Apiezon N, had to be degassed in vacuum at about 100°C (water bath used) in an apparatus as shown in Figure 2C. The resultant grease was stored in vacuum before use.

Calibration Procedure

The manifold and the adsorption unit were freshly evacuated before use. If the thermocouple gauge (T_1) showed a pressure $< 1 \mu$ when the apparatus was left closed for several hours after evacuation, the apparatus was assumed to be leak-proof and well evacuated. The thermistor, before calibration, was first seasoned in vacuum for stable performance by passing current through the circuit for prolonged periods lasting for several days. Water at constant temperature ($26.0 \pm 0.01^\circ\text{C}$ just after the water leaves T_1) was circulated through the water jackets of T_1 and G during pressure measurements. A calibration of the gas pressure against the off-balance potential V_{off} was obtained for He and Kr separately, the absolute gas pressure being measured by the use of the McLeod gauge. A pressure range of 100-500 μ for He and 100-2500 μ for Kr was covered. Calibration charts were drawn so that pressures can be read within the prescribed range, to a third digit, knowing any value of V_{off} . The gauge was subsequently closed at S_5 and was not included in any of the adsorption measurements.

The volume V_c , enclosed in between T_1 , $S_{2,5,10-13}$ and the reference mark above bulb I, was then calibrated by compressing He in G by means of mercury and reading the corresponding values of Voff (hence the pressure). V_c was calculated using the ideal gas laws. The calibrated volumes, along with the electrical constants of the thermistor and specimen calculations for V_c , are shown in Appendix II.

Adsorption Measurements

An adsorption bulb B ($\sim \frac{3}{4}$ in. x $\frac{1}{4}$ in.) with a side arm, as shown in Figure 1, was made and fused to the capillary tube on the apparatus. A suitable amount of the material under investigation (total area $\sim 1000-2000$ cm²) was transferred to the bulb through the side arm, which was subsequently sealed, taking care not to heat the material. The bulb was gradually evacuated so that the material was not blown out. The bulb was heated in a small electric oven at precalibrated settings such that the temperature of the material was $\sim 100^\circ\text{C}$. The bulb was simultaneously evacuated overnight to remove all traces of moisture and any condensable matter. The bulb, along with about 5 in. length of the capillary tubing, was immersed in liquid nitrogen (whose level should be kept constant, particularly at the time of reading Voff). The average dead space (adsorption bulb with the material + capillary) in cm³ at S.T.P./mm_{Hg}, (V_{ds}), was determined by taking a known volume of He in G and/or V_c and expanding it into the dead space. Helium is not adsorbed noticeably at liquid nitrogen temperatures. The room temperature corresponding to each pressure reading was noted to the

second decimal place, using a calibrated Beckman thermometer. The tabulated data and specimen calculations for Vds are shown in Appendix III. The apparatus was subsequently evacuated free of He, and adsorption measurements with Kr were carried out similarly. It takes about 1-1½ hours to reach the adsorption equilibrium after the first addition of Kr, depending on the amount of the adsorbent present. In subsequent additions of Kr, the equilibrium was attained rapidly. About 3 or 4 points obtained in the P/P_0 range of 0.07-0.2 (or $P = 190$ to 550μ), where a monolayer adsorption usually occurs, are enough to obtain a B.E.T. plot.

The saturation pressure of solid Kr ($\sim 1800 \mu$) was finally obtained by admitting a sufficiently large quantity of the gas in the adsorption bulb, so that the gas was visibly solidified. It is, however, the saturation pressure of liquid Kr (P_0) that is used in the B.E.T. equation, and this parameter was obtained as follows. Knowing the vapour pressure of solid Kr from experiment, the temperature in the adsorption bulb immersed in liquid nitrogen was obtained from the vapour pressure data of Keesom, Mazur and Meihuizen (7). The corresponding value of P_0^* was then obtained, using the vapour pressure data of liquid Kr from the work of Meihuizen and Crommelin (8).

The equilibrium pressures inside the adsorption bulb may be somewhat less than the measured pressures outside the bulb, as a result of thermal transpiration effect* (6). Corrections for this effect were made

* Computer analysed data from which P_0 is obtained are kept in this laboratory for rapid conversion.

using the equation given by Rosenberg (Eqn. 6, Ref. 6). It is important to note, however, that this correction is applicable only to equilibrium pressures that are used in the calculation of V_{ds} and in the B.E.T. equation. No such correction is applicable in calculating the amount of gas taken or left over in G and/or V_c .

RESULTS AND CONCLUSIONS

Specimen data for the adsorption of Kr on a sample of magnetite (I) are given in Appendix IV A, and the corresponding calculations for the volume of Kr adsorbed are shown in Appendix IV B. The adsorption data have been tabulated for the B.E.T. and Harkins and Jura plots, in Appendix V A. The B.E.T. plot has been shown in Figure 3, and the specimen calculations of S ($= 789 \text{ cm}^2$) are shown in Appendix V B. Similar B.E.T. plots for other samples of magnetite (II) and Hematite (I and II) are also shown in Figure 3.

In Figure 4 the Harkins and Jura plots for the two samples of magnetite studied are also shown to be linear. From these and numerous other results obtained, the following conclusions are drawn:

1. Both the B.E.T. and the Harkins and Jura methods are applicable for the determination of low surface areas of solids by the Kr gas absorption method. The value of K for Kr, however, has to be indirectly evaluated to use the Harkins and Jura method.

2. The use of thermistors in measuring pressures, which is presently a matter of a few seconds for each reading, has eliminated the cumbersome and time-consuming process of using the McLeod gauge throughout the experiment. This has also helped for fast checking of the equilibrium conditions and in reducing the volume V_c to a great extent.

3. In Appendix III it is seen that the value of V_{ds} is known within $\pm 2\%$, which error most probably originates from the McLeod gauge calibration ($\pm 1\%$). In the present determination of V_{ds} , only V_c ($\sim 20 \text{ cm}^3$) was used. If a larger volume, $G + V_c$ (about 10 times V_{ds}), is used, the total error in V_{ds} may be as high as $\pm 20\%$. It is, however, seen in Appendix IV B that the volume of Kr remaining unadsorbed in V_{ds} is only about 5-6% of the total volume of Kr adsorbed (V_{ads}) on the solid. Hence, the error in V_{ads} when only V_c is used for dead space calibration is still negligible ($< 1\%$). However, if using $V_c + G$ for the dead space calibration, the error could be considerable. It should also be noted that using still larger surface areas, the error arising from the dead space calibration is accordingly reduced, whereas it may be much more enhanced for much lower surface areas. This should be taken into account when using the apparatus.

4. The error in the calibration of pressures against V_{off} , using the McLeod gauge, usually arises at low ($P \sim 0.1 \text{ mm}$) and high values of P ($> 0.5 \text{ mm}$). This error can be considerably reduced by making only one or two accurate measurements with the McLeod gauge at a moderate

pressure. With reference to this pressure, the gas burette (whose calibration is precisely known) can then be used for the rest of the calibration of P against Voff. This will be done in the near future.

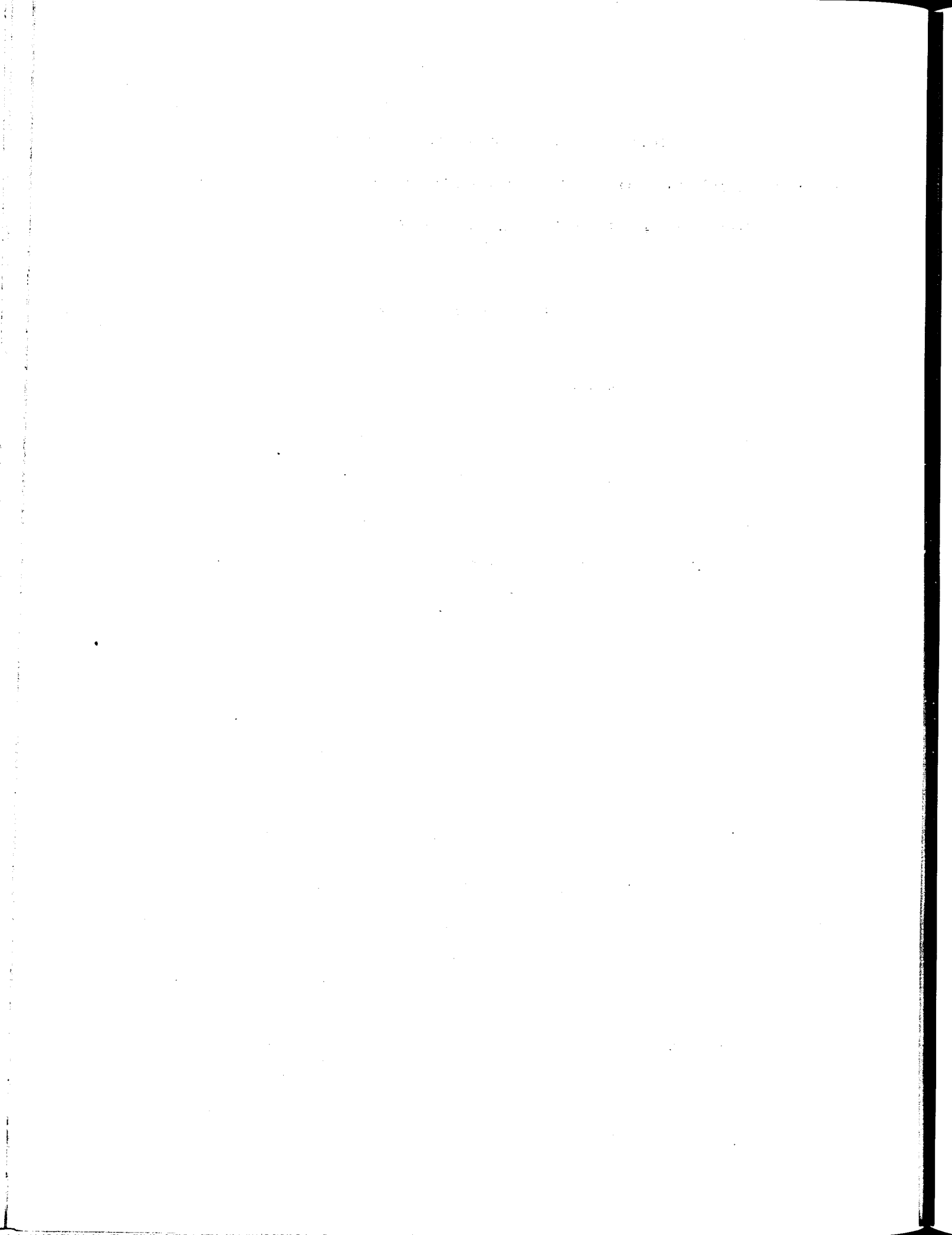
ACKNOWLEDGEMENTS

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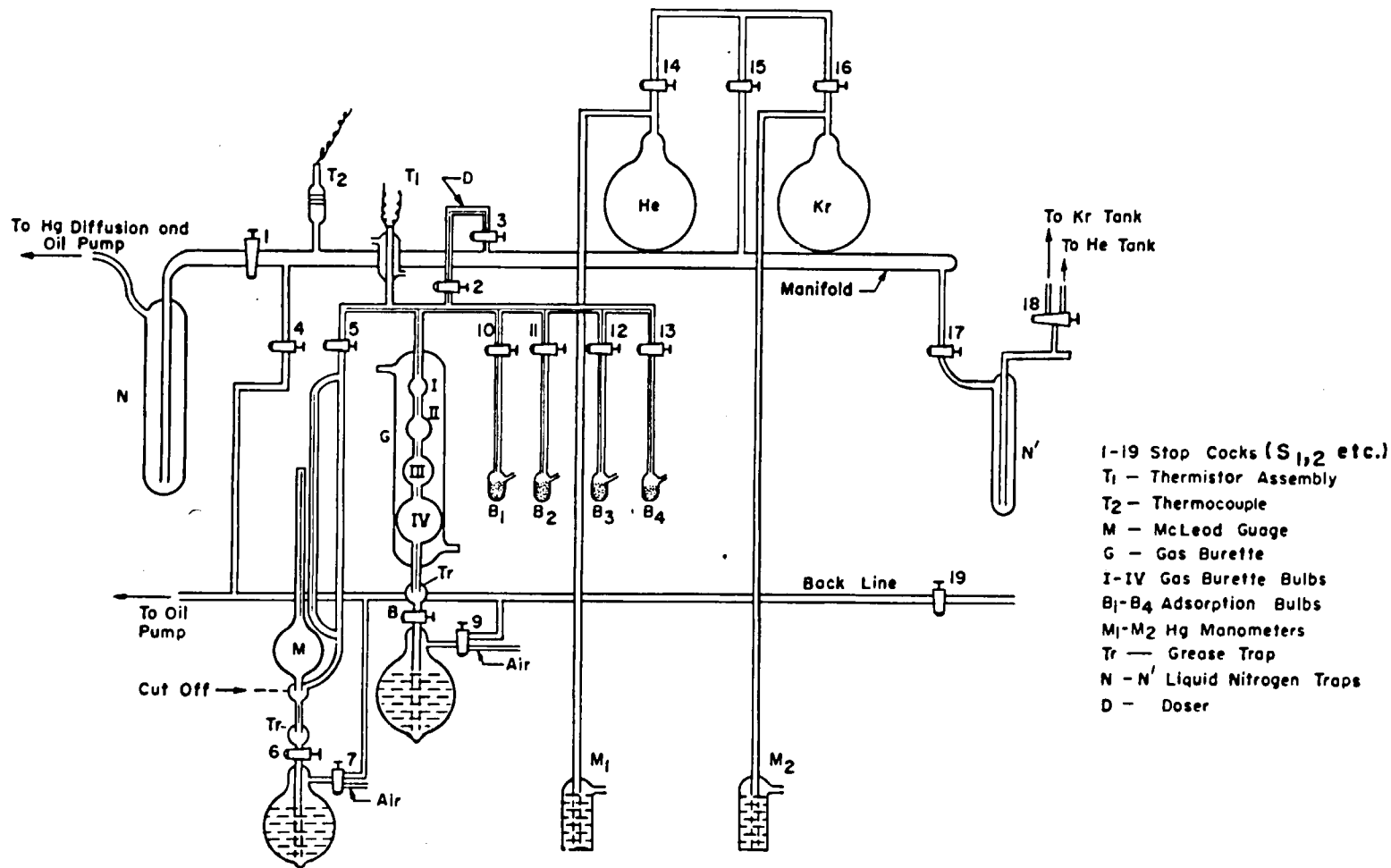


Figure 1. Apparatus for the determination of surface areas of powders by Kr gas adsorption.

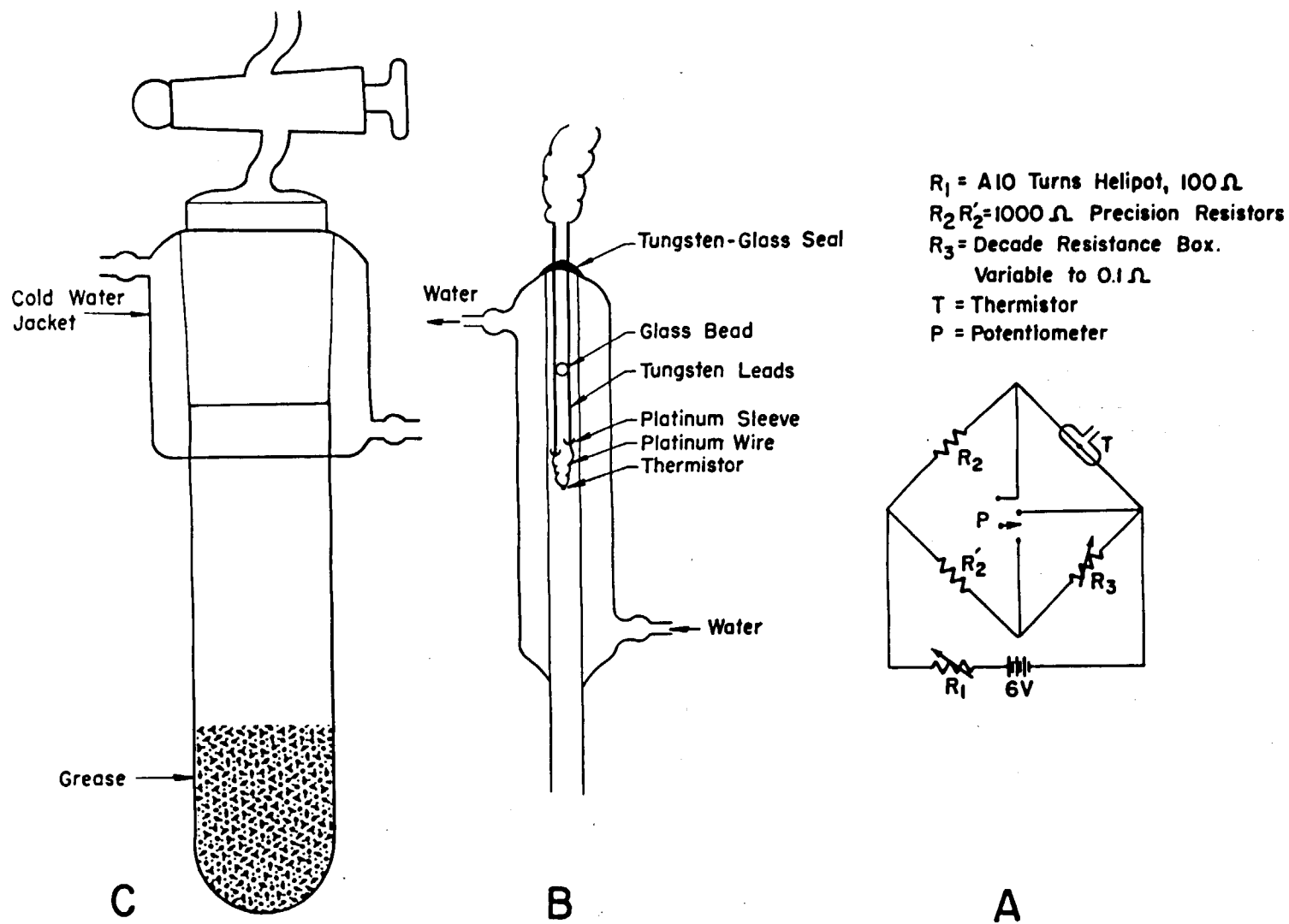


Figure 2. (A) Diagram of the electrical circuit for the thermistor assembly.
 (B) The thermistor assembly.
 (C) Apparatus for degassing grease.

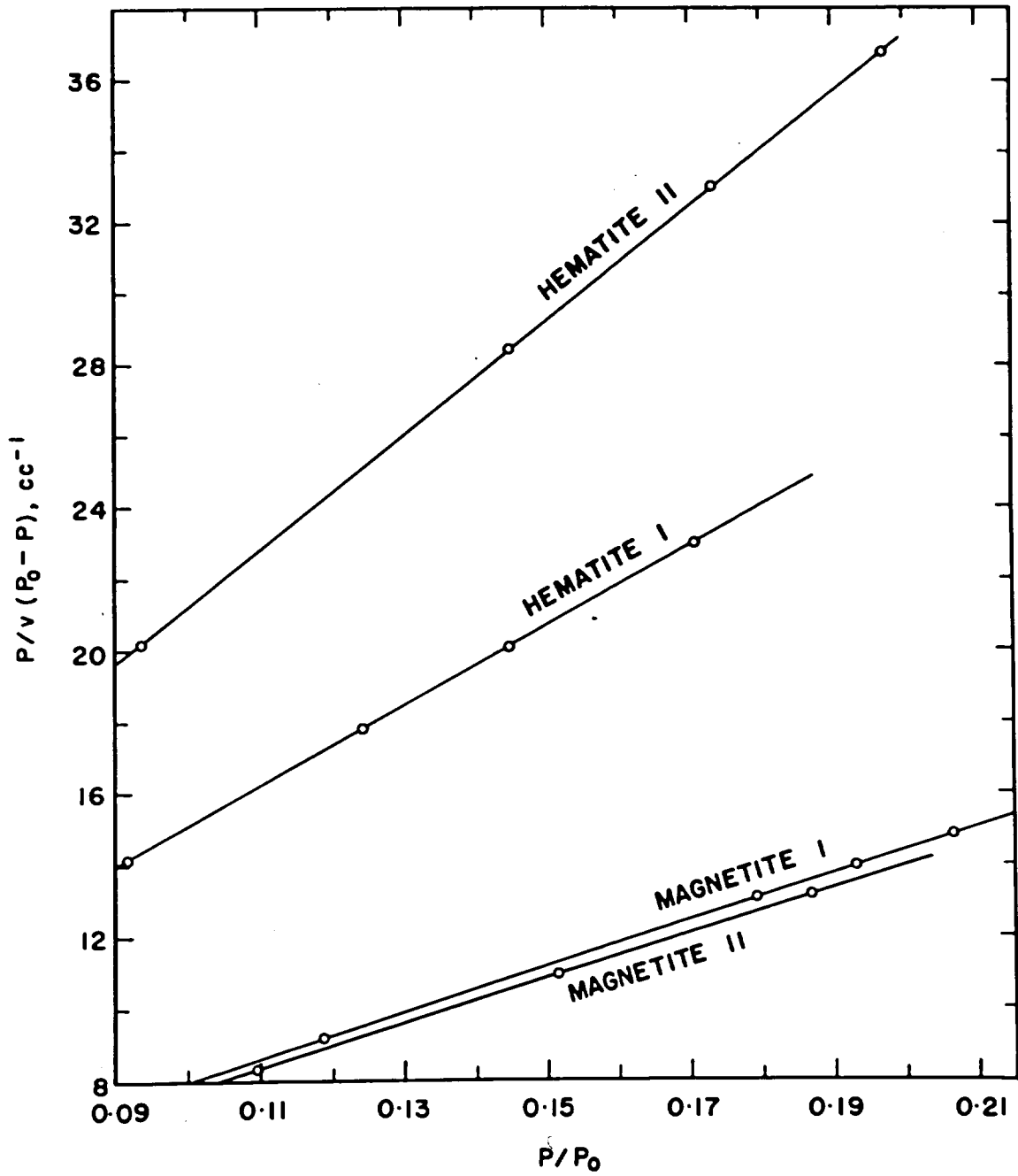


Figure 3. The B.E.T. plots for Kr gas adsorption on magnetite and hematite samples.

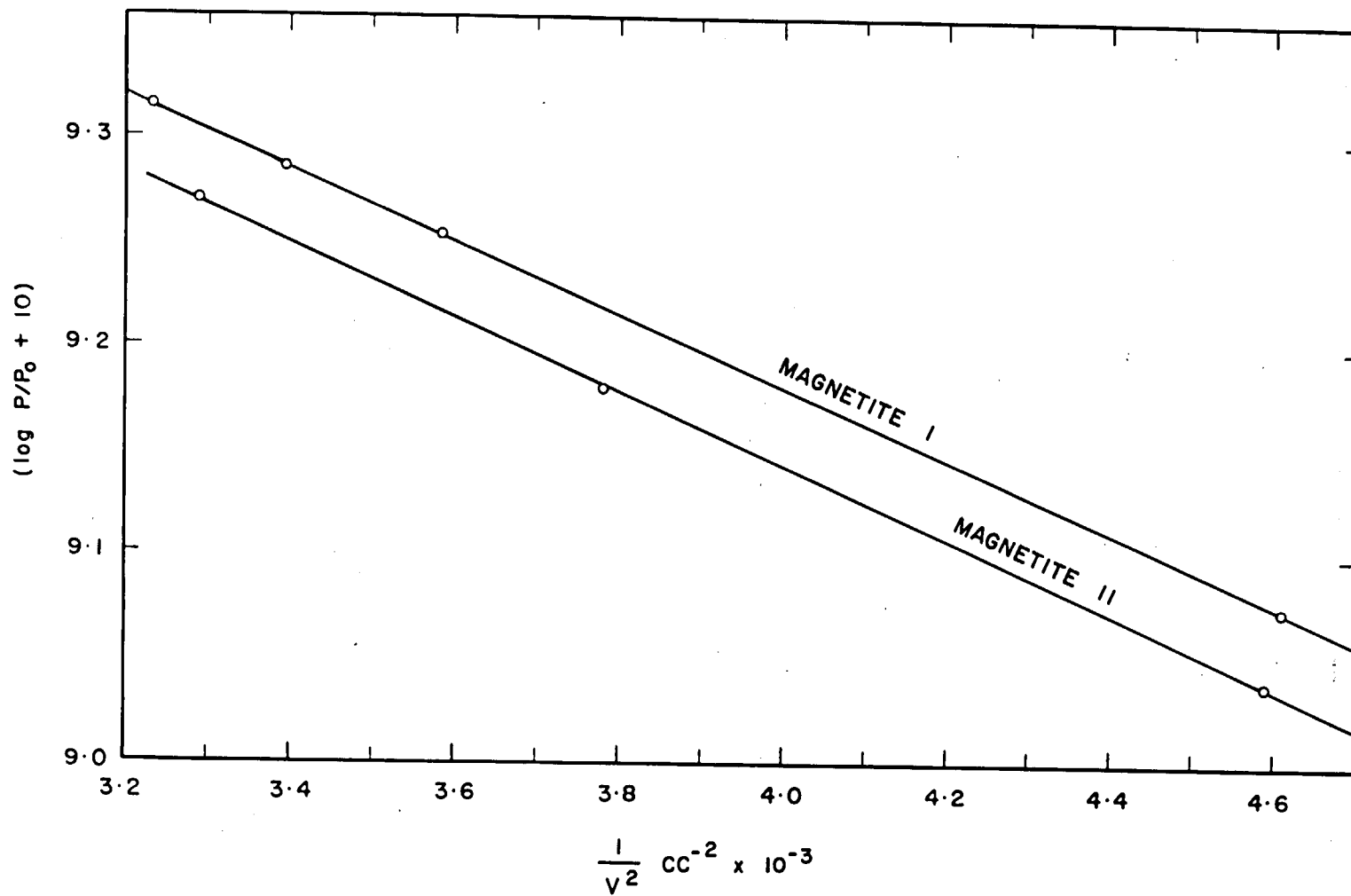


Figure 4. The Harkins and Jura plots for Kr gas adsorption on Magnetites I and II.

APPENDIX I

A. McLeod Gauge Constants

1. Diameter of the capillary = 2.00 mm
2. Volume of the bulb up to a reference mark
at the bottom of the capillary } = 41.3470 cm³
3. Volume of the (bulb + capillary) = 41.8015 cm³
4. Volume of the entire McLeod gauge = 68.3470 cm³

Pressures may be calculated (in mm_{Hg}) from the McLeod gauge measurements, using the formula

$$P = \frac{a}{V} (h + h') \Delta H$$

$$P = 7.5185 \times 10^{-5} (h + h') \Delta H, \quad \text{where}$$

a/V is the ratio, $\frac{\text{cross sectional area of the capillary (mm}^2\text{)}}{\text{Volume of the (capillary + bulb) (mm}^3\text{)}}$

$$= 7.5185 \times 10^{-5} \text{ mm}^{-1},$$

h = height of the gas column (mm) in the closed capillary above the Hg-meniscus,

h' = correction for the gas in the Hg-meniscus (= effective height of the gas around the meniscus), and

ΔH = difference in the heights of the Hg columns in mm. (= pressure difference).

Corrections are applied for linear expansion of the cathetometer scale and for the cubical expansion of Hg. Tables have been made for the rapid conversion of the gauge readings to pressures, and also for corrections.

APPENDIX I (cont'd)

B. The Calibrated Constants of the Gas Burette

Volume of the Bulb	I	=	1.99980 cm ³
Volume of the Bulb	II	=	4.62783 cm ³
Volume of the Bulb	III	=	19.85632 cm ³
Volume of the Bulb	IV	=	50.21575 cm ³
Volume of the Bulb	I + II + III + IV	=	76.6997 cm ³
Volume of the Bulb	I + II + III	=	26.4839 cm ³
Volume of the Bulb	I + II	=	6.6276 cm ³

==

APPENDIX II

A. Operating Conditions of the Thermistor Gauge T₁

Voltage = 6V from a partially discharged lead storage cell.

Temperature of the circulating water just after it leaves T₁ =
26.00 ± 0.01°C when V_{off} = 0, Resistance R₃ = 180.3Ω

and $V_{th} = 941.5 \pm 0.5$ mV where

V_{off} and V_{th} are the potential difference across the bridge and the thermistor respectively, when the apparatus is being evacuated.

R₁ should be adjusted to obtain the above conditions, as the battery is slowly discharged. The battery should be recharged when the

APPENDIX II (cont'd)

adjustment of R_1 is not enough to get the above balancing conditions. The room temperature should be between 25° to 26°C; otherwise the gas may not attain the temperature of T_1 .

B. Calibration of the Volume V_c

V_c is the volume bound by T_1 , $S_{2,5,10-13}$ and the reference mark above bulb 1 in G. Part of the V_c is enclosed in the water jacket (26.0°C) (= 0.0535 cm³), and the rest of it (say V_c') is at room temperature. This is taken into account in the following calculations:

TABLE 1
Calibration of V_c

Step No.	Operation	V _{off} , mV	P, mmHg	Room Temp. (t + 273.18)° Abs.
1.	He in Bulbs I + II + III + IV + V_c	597.6	0.1885	298.96
2.	He compressed to II, III, IV + V_c	1227.5	0.3904	299.08
3.	He in I + II + III + IV + V_c	580.2	0.1830	298.77
4.	He compressed to II + III + IV + V_c	1192.5	0.3793	298.83
5.	He in Bulb IV + V_c	1125.8	0.3578	299.01
6.	He compressed to V_c	1238.5	0.3938	299.10

APPENDIX II B (cont'd)

Calculation of Volume V_c'

Step 1. From Appendix IB, $V_I + V_{II} + V_{III} + V_{IV} = 76.6997 \text{ cm}^3$

Part of V_c in water jacket at 26°C = 0.0535

Total vol. at 26°C = 76.7532 cm^3

Step 2. $V_{II} + V_{III} + V_{IV} + \text{part of } V_c \text{ at } 26^\circ\text{C} = 26.5374 \text{ cm}^3$

Applying ideal gas laws to Steps 1 and 2,

$$0.1885 \left(\frac{76.7532}{299.18} + \frac{V_c'}{298.96} \right) = 0.3905 \left(\frac{26.5374}{299.18} + \frac{V_c'}{299.08} \right).$$

Solving, $V_c' = 20.32 \text{ cm}^3$.

Similarly for Steps 3 and 4, $V_c' = 20.50 \text{ cm}^3$

and for Steps 5 and 6, $V_c' = 20.46 \text{ cm}^3$.

Average volume of $V_c' = 20.43 \pm 0.07 \text{ cm}^3$.

==

APPENDIX III

Determination of the Dead Space Volume (Vds) for Magnetite I

TABLE 2

Data Used in Determination of Dead Space Volume (Vds) for Magnetite I

Step No.	Operation	V _{off} , mV	P, mm _{Hg}	Room Temp. (t + 273.18)° Abs.
1.	He in V _c only	1269.0	0.4037	298.91
2.	He in V _c + V _{ds}	869.6	0.2755	298.91
3.	He in V _c only	1413.1	0.4500	299.03
4.	He in V _c + V _{ds}	1227.1	0.3903	298.33

$$\left(\frac{P \times V}{T}\right)_{S.T.P} = \frac{P_1 V_1}{T_1} \quad \text{or}$$

$$\text{Step 1. } V_{S.T.P} = 0.4037 \left(\frac{0.0535}{299.18} + \frac{20.43}{298.91} \right) \frac{273.18}{760}$$

$$V_{S.T.P} = 0.4037 (0.00018 + 0.06853) 0.35945$$

$$V_{S.T.P} = 9.944 \mu\text{l.}$$

$$\begin{aligned} \text{Step 2. } V_{S.T.P} &= 0.2755 \left(0.00018 + \frac{20.43}{298.91} \right) 0.35945 \\ &= 6.783 \mu\text{l} \end{aligned}$$

$$\text{Vol. of Kr in Vds at S.T.P} = (9.944 - 6.783) = 3.161 \mu\text{l.}$$

$$\text{Vds at S.T.P/mm}_{\text{Hg}} = \frac{3.161}{0.2755} = 11.47 \mu\text{l.}$$

Similarly, from Steps 3 and 4,

$$\text{Vol. of Kr in Vds at S.T.P} = 4.63 \mu\text{l.}$$

$$\text{Vds at S.T.P/mm}_{\text{Hg}} = \frac{4.63}{0.3903} = 11.86 \mu\text{l.}$$

$$\text{Hence the average Vds at S.T.P/mm}_{\text{Hg}} = 11.7 \pm 0.2 \mu\text{l.}$$

APPENDIX IV

A. The Adsorption Data of Kr on Magnetite I.

Total weight of the sample = 4.6194 g.

TABLE 3

Data Used in Calculation of Kr Adsorption on Magnetite I

Step No.	Operation	V _{off} , mV	P, mmHg	Room Temp. (t + 273.18)° Abs.
1.	Kr in I + II + III + IV + V _c	779.5	0.923	298.84
2.	Volumes in Step 1 were opened to ads. bulb	410.0	0.3075 0.3012*	298.81
3.	Kr in I + II + III + V _c	653.5	0.6513	298.85
4.	Volumes in Step 3 opened to ads. bulb	530.0	0.4583 0.4534*	299.01
5.	Kr in I + II + V _c	606.4	0.5715	299.02
6.	Volumes in Step 5 opened to ads. bulb	554.9	0.4934 0.4887*	299.03
7.	Kr in I + II + V _c	624.9	0.6020	298.95
8.	Volumes in Step 7 opened to ads. bulb	578.0	0.5275 0.5230*	298.86
9.	Solid Kr in ads. bulb	1002.1	1.780 1.778*	

* Pressures corrected for thermal transpiration effect.

APPENDIX IV (cont'd)

B. Calculation of the Volume of Kr Adsorbed, V at S.T.P

$$\text{Step 1. } V_{S.T.P} = 0.923 \left(\frac{76.7532}{299.18} + \frac{20.43}{298.84} \right) \frac{273.18}{760}$$

$$V_{S.T.P} = 0.923 (0.25655 + 0.06836) \quad 0.35945$$

$$V_{S.T.P} = 107.476 \mu\text{l.}$$

$$\text{Step 2. } V_{S.T.P} = 0.3075 \left(0.2565 + \frac{20.43}{298.81} \right) \times 0.35945$$

$$V_{S.T.P} = 35.914 \mu\text{l.}$$

Volume of the Kr remaining unadsorbed at P equilibrium

$$\text{in Vds} = (V_{\text{ds at S.T.P}} / \text{mm}_{\text{Hg}}) \times P \text{ equilibrium.}$$

Amount of Kr transferred to the adsorption bulb,

$$\text{in Step 2} = (107.476 - 35.914) \quad = 71.562 \mu\text{l at S.T.P}$$

$$\text{The dead space volume available} = 11.7 \times 0.3012^* \quad = \underline{3.524 \mu\text{l at S.T.P}}$$

$$V \text{ Kr adsorbed at P} = 0.3012 \text{ mm}_{\text{Hg}} \quad = 68.038 \mu\text{l at S.T.P}$$

$$\text{Similarly in Step 3, } V_{S.T.P} = 36.770 \mu\text{l,}$$

$$\text{in Step 4, } V_{S.T.P} = \underline{25.868 \mu\text{l.}}$$

Extra volume of Kr transferred

$$\text{to Ads. bulb in Step 4} \quad = 10.902 \mu\text{l at S.T.P}$$

Volume of Kr already present

$$\text{in Step 2} \quad = \underline{71.562 \mu\text{l at S.T.P}}$$

Total vol. of Kr in ads.

$$\text{bulb in Step 4} \quad = 82.464 \mu\text{l at S.T.P}$$

* Pressures corrected for thermal transpiration effect.

APPENDIX IV (cont'd)

Volume available in Vds

$$= 0.4534^* \times 11.7 = \underline{5.305} \text{ } \mu\text{l at S.T.P}$$

Kr adsorbed at P

$$= 0.4534 \text{ mm}_{\text{Hg}} = 77.159 \text{ } \mu\text{l at S.T.P}$$

Similarly, extra volume of Kr transferred

$$\text{to the ads. bulb in Steps 5 and 6} = 2.545 \text{ } \mu\text{l at S.T.P}$$

$$\text{Kr already present from Step 4} = \underline{82.464} \text{ } \mu\text{l at S.T.P}$$

$$\text{Total Kr in ads. bulb in Step 4} = 85.009 \text{ } \mu\text{l at S.T.P}$$

$$\text{Vol. of Kr in Vds} = 0.4887^* \times 11.7 = \underline{5.718} \text{ } \mu\text{l at S.T.P}$$

$$\text{Kr adsorbed at P} = 0.4887 \text{ mm}_{\text{Hg}} = 79.291 \text{ } \mu\text{l at S.T.P}$$

It can be similarly shown that in the 7th

and 8th steps, Kr adsorbed at

$$P = 0.5230 \text{ mm}_{\text{Hg}} = 81.235 \text{ } \mu\text{l at S.T.P}$$

The vapour pressure of solid Kr (= 1.778*) when converted into that of liquid Kr (P_o) = 2.532 mm_{Hg}.

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* Pressures corrected for thermal transpiration effect.

APPENDIX V

TABLE 4

A. Data for the B.E.T. and Harkins and Jura Plots

Step No.	P_{eqbm} , mm_{Hg}	V ads. at S.T.P, cc	$v = V/g$ at S.T.P, cc	$(P_o - P)$ $P_o = 2.532$ mm_{Hg}	$\frac{P}{v(P_o - P)}$	$\frac{P}{P_o}$	$\log \frac{P}{P_o} + 10$	$\frac{1}{v^2} cc^{-2}$
1-2	0.3012	68.038×10^{-3}	14.729×10^{-3}	2.2309	9.169	0.1189	9.075	4.6096×10^3
3-4	0.4534	77.16×10^{-3}	16.703×10^{-3}	2.0787	13.059	0.1791	9.253	3.5844×10^3
5-6	0.4887	79.292×10^{-3}	17.165×10^{-3}	2.0434	13.935	0.1930	9.286	3.3940×10^3
7-8	0.523	81.235×10^{-3}	17.586×10^{-3}	2.0091	14.803	0.2065	9.3150	3.2334×10^3

APPENDIX V (cont'd)

B. Calculation of S

The slope of the straight line for Magnetite I in Figures 3 = 64.4 cc⁻¹.

The intercept C was calculated from the straight line equation $C = y - mx$ (where the slope $m = 64.4$) to be 1.504.

$$\text{Hence } V_m = \frac{1}{64.4 + 1.504} = 0.01517 \text{ cc at S.T.P.}$$

$$\text{Hence } S = \frac{0.01517 \times 6.023 \times 10^{23} \times 10^{-16} \times 19.5}{22400}$$

$$S = 795.5 \text{ cm}^2.$$

The surface area of the adsorption bulb and column was estimated to be 30 cm² or 6.5 cm²/g material.

$$\text{Hence } S = 795.5 - 6.5 = 789 \text{ cm}^2.$$

SMA:(PES):vb