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ON THE UTILIZATION OF A NEW TYPE MERCURY MANOMETER IN THE DETERMINATION OF SURFACE AREA BY THE B. E. T. METHOD

By

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I. Introduction

Present authors have come upon a problem of determining the surface area of the electrode; but since the surface areas of the electrodes are generally of the order of several hundred sq. cm or less, it was necessitated to increase the accuracy of the measurement of pressure difference caused by adsorption for the application of the B. E. T. method. It is also preferable to cover the whole pressure range of measurement with one and the same apparatus without combining as usally done, for instance, the MACLEOD gauge (10^{-6}–10^{-2} mm Hg) or the PIRANI gauge (10^{-5}-10^{-1} mm Hg) with an ordinary mercury manometer with or without catheto meters (0.05–10^{+3} mm Hg).

The present authors deviced a new type of mercury pressure gauge, which covers the range from 1×10^{-2} mm Hg to 10^{2} mm Hg or more. This device can be used for absolute as well as differential measurements with a sensitivity of 1×10^{-2} mm Hg. The apparatus used and the method of measurements are described and the results of the surface area determination of some nickel oxides by the B. E. T. method are given demonstratively in the followig sections.

II. Apparatus and Method of Measuring Pressures

Figs. 1–1 and 1–2 show a part of the whole apparatus used, in which A is the reaction vessel and m_1 is the manometer. The main parts of manometer m_1 are a wide U-tube filled with pure mercury and a steel-made micrometer screw gauge –M.S.– having a sensitivity

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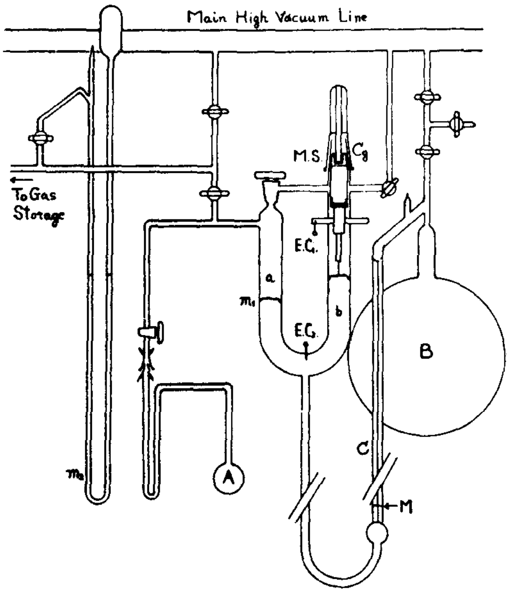

Fig. 1·1.

A part of the apparatus showing the micrometer manometer.

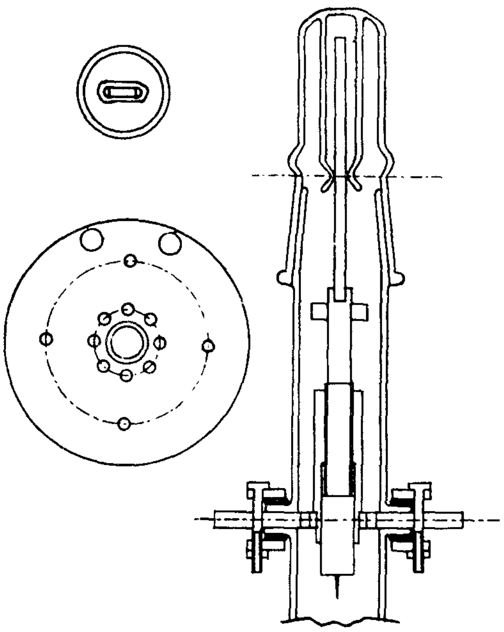

Fig. 1·2.

A diagram of the micrometer manometer in detail.

of $\frac{1}{2}\times10^{-2}$ mm with a sharp platinum needle electric contact fitted to the spindle; EC_2 connects mercury in the U-tube with outside. The two branches *a* and *b* of the U-tube were carefully selected to have a uniform diameter of 20.0 mm. At the bottom of the U-tube another U-tube –*c*–, having a capillary branch with a neniscus pointer, M, is connected; and the other end of this U-tube is attached to a large bulb –B– as shown in Fig. 1. The capillary tube was carefully selected to have a uniform diameter of 2.0 mm and the volume per unit length is calibrated along its full length. By means of a greased cap-joint, Cg, at the top of the M.S., the platinum needle can be moved upward and downward by turing Cg from out side of the apparatus. By the use of both electric contacts, EC, and EC_2, the mercury level in branch *b* is accurately determined.

For a pressure measurement below 10^2 mm Hg, the mercury level in the U-tube *c* is set at M, and branch *b* is kept under high vacuum, while the pressure *P* is admitted to branch *a*. Then the mercury level in branch *b* will rise simultaneously as the level in branch *a* falls. The difference in height of the two mercury levels in *a* and *b* shows the absolute value of the pressure *P* admitted, as the mercury level in *c* is maintained at rest at M. The setting of the mercury level at M is easily established by the fine pressure adjustment of the air pressure in B. Since the diameter of *a* and *b* has been carefully chosen to have a uniform value (20.0 mm), the absolute change in height of the mercury level in *b* may be taken $\frac{1}{2}P$. Using the M.S. of 50 mm stroke pressure could be measured from 1×10^{-2} up to 10^2 mm Hg.

The same apparatus is used for observing the pressure change in *a* as below in the case when the latter is greater than 100 mm Hg. The pressure is first admitted to the branches *a*, *b*, and *c* to render the three mercury levels to almost the same position. The same levels in *a* and *b* are marked by M.S., and the level in *c* is also marked as M_1 on a scale. Thereafter only *a* is opened to the pressure in A, resulting in a drop in the levels in *b* and *c*. Now finely adjusting the pressure in *b*, the mercury level in *b* is restored exactly to the former value by means of M.S. The volume of the mercury transferred from *c* to *a* is now determined by the change of mercury levels in *c* from M_1 to M_2. As the diameter of *c* is chosen to have one tenth of *a*, and the volume of bulb B is large compared with that of *c*—that is, the pressure in *c* remains constant—the pressure change in *a* can be expressed $1.01\times(M_1-M_2)$ mm Hg.

This magnification method was found less accurate than the direct M.S. indicator method described above, although the latter is very sensitive to the volume change of the mercury, so that the temperature of *a*, *b*, *c*, and B have to be kept constant by a thermostat. The magnification method could be replaced by the direct method throughout, if we could have a micrometer screw gauge of a stroke of 100 mm and a sensitivity of $\frac{1}{2} \times 10^{2}$ mm ; in our case the gauge was hand-made.

III. Demonstrative Determination of the Surface Area of Some Nickel Oxides by the B.E.T. Method.

(1) Preparation of nickel oxides.

Sample 1.——Aqueous 1N-sodium carbonate solution was added to an aqueous solution of 1N-nickel nitrate. The nickel carbonate precipitate was thoroughly washed with redistilled water, separated, and then dried at 110°C. The dried precipitate was transferred to the reaction vessel A in Fig. 1, decomposed at 300°C in vacuo for 48 hrs, washed with distilled 0.1 N-HCl solution and then with redistilled water, dried at 270°C for 15 hrs. in vacuo and then cooled.

Sample 2.——Sample 2 differs from Sample 1 only in the preparation of the nickel carbonate precipitate, i.e. that both nickel nitrate and sodium carbonate solutions were of 0.1N concentration.

Sample 3.——A part of the nickel carbonate dried at 110°C for Sample 1, was taken, and decomposed at 400°C under atmospheric pressure. The other steps of the preparation were the same as those of Sample 1 and 2.

The composition of the above three samples are concluded NiO, from the weights of $NiCO_3$ and oxides.

(2) Determination of the surface areas of three samples by the B.E.T. method, using M.S. manometer.

Using purified carbon tetrachloride and 0.03 gm. of the above samples as the adsorbent, the present authors determined the surface area per gram of the three samples by the B.E.T. method at 25°C. The results are shown in Figs. 2 and 3, and Table I-1, 2, 3, from which the areas and other constants in B.E.T. isotherm were obtained as shown in Table II. It is evident that the difference in decomposition-procedure of the nickel carbonate causes the difference in the surface areas of the samples. Sample 3, decomposed at 400°C under atmospheric pressure, has an area only about one third of Sample 1 and 2.

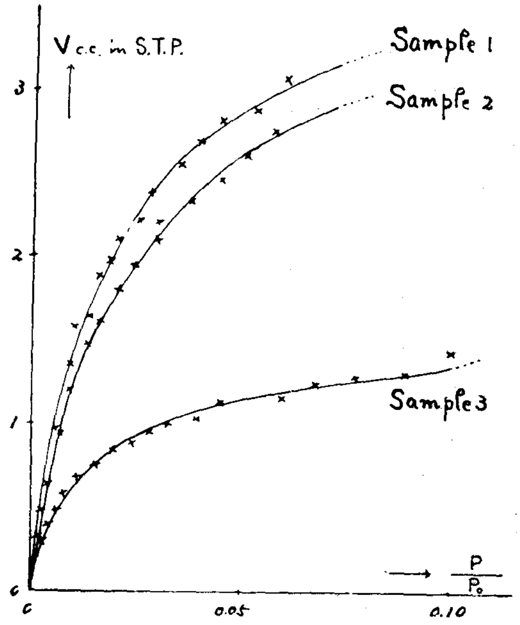

Fig. 2.

B. E. T. Isotherms of Carbontetrachloride on Nickel Oxides at 25°C.

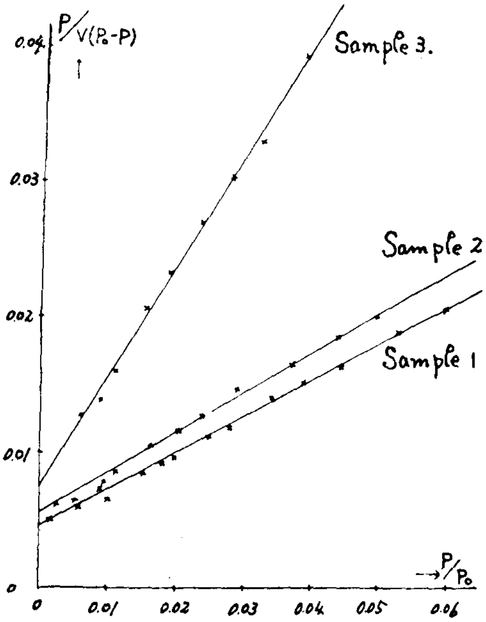

Fig. 3.

Analysis of the B. E. T. Isotherms of Carbontetrachloride on Nickel Oxides.

TABLE I. $P-V$ Data and Calculated Values of Variables in B.E.T. Equation.

(P…equilibrium pressure in mm Hg;
V…amount adsorped in c.c. S.T.P.
per 1 g of samples.)

I-1. For Sample 1

No.	P	V	$P/V(P_0-P)$	P/P_0
1	0.04	0.166	0.0020	0.003
2	0.20	0.327	0.0051	0.0017
3	0.30	0.493	0.0051	0.0025
4	0.48	0.650	0.0062	0.0040
5	0.62	0.800	0.0065	0.0052
6	0.70	0.975	0.0060	0.0058
7	0.80	1.12	0.0060	0.0067
8	1.10	1.35	0.0068	0.0092
9	1.24	1.60	0.0065	0.0103
10	1.58	1.65	0.0041	0.0132
11	1.80	1.80	0.0085	0.0150
12	2.18	1.97	0.0094	0.0180
13	2.42	2.11	0.0097	0.0202
14	3.00	2.26	0.0113	0.0250
15	3.36	2.38	0.0119	0.0280
16	4.14	2.54	0.0140	0.0345
17	4.70	2.69	0.0151	0.0392
18	5.34	2.83	0.0164	0.0445
19	6.36	2.87	0.0188	0.0530
20	7.16	3.09	0.0206	0.0598

I-2. For Sample 2.

No.	P	V	$P/V(P_0-P)$	P/P_0
1	0.14	0.108	0.0108	0.0012
2	0.18	0.273	0.0055	0.0015
3	0.30	0.407	0.0062	0.0025
4	0.40	0.545	0.0062	0.0033
5	0.50	0.673	0.0070	0.0047
6	0.62	0.805	0.0065	0.0052
7	0.86	0.951	0.0076	0.0072
8	0.94	1.06	0.0075	0.0078
9	1.14	1.21	0.0078	0.0095
10	1.34	1.34	0.0085	0.0112
11	1.60	1.48	0.0092	0.0133
12	1.94	1.62	0.0102	0.0162
13	2.46	1.80	0.0116	0.0205
14	2.90	1.96	0.0126	0.0242
15	3.50	2.09	0.0143	0.0291
16	3.54	2.23	0.0137	0.0295
17	4.48	2.35	0.0165	0.0373
18	5.28	2.47	0.0186	0.0440
19	6.00	2.62	0.0201	0.0500
20	6.84	2.76	0.0219	0.0570

I-3. For Sample 3.

No.	P	V	$P/V(P_0-P)$	P/P_0
1	0.20	0.093	0.0180	0.0017
2	0.32	0.184	0.0146	0.0027
3	0.40	0.296	0.0113	0.0033
4	0.56	0.392	0.0120	0.0043

I-3 (continued).

No.	P	V	$P/V(P_0-P)$	P/P_0
5	0.74	0.486	0.0127	0.0062
6	0.98	0.596	0.0138	0.0082
7	1.36	0.685	0.0160	0.0113
8	1.86	0.765	0.0206	0.0155
9	2.32	0.843	0.0232	0.0193
10	2.84	0.895	0.0270	0.0236
11	3.38	0.955	0.0304	0.0282
12	3.88	1.01	0.0331	0.0324
13	4.66	1.03	0.0394	0.0389
14	5.20	1.13	0.0400	0.0452
15	5.96	1.14	0.0460	0.0522
16	6.76	1.17	0.0511	0.0596
17	7.62	1.24	0.0548	0.0674
18	8.62	1.31	0.0574	0.0775
19	9.74	1.32	0.0650	0.0885
20	10.84	1.45	0.0685	0.0993

TABLE II. Calculated Values of V_m, C and the Area of the Samples.

No. of Sample	$1/V_m \cdot C$	$C-1/V_m \cdot C$	C	V_m	A (m^2)
1	0.0045	0.269	58.8	3.78	33.0
2	0.0055	0.294	52.5	3.46	30.2
3	0.0072	0.820	114.0	1.22	10.7

IV. Summary

A. A new device of measureing a small pressure change over a wide range was described.

B. The device was exemplified by the B.E.T. surface area determination of nickel oxide of different preparations. The surface area of nickel oxide prepared by decomposing $NiCO_3$ at 400°C under atmospheric pressure was found only one third of that prepared by the decomposition at 300°C in vacuum.