[CONTRIBUTION FROM THE LINCOLN LABORATORY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Rapid, Precise Measurements of Krypton Adsorption and the Surface Area of Coarse Particles[1]

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A thermistor can be adapted by simple circuitry into a precise manometer operable from 50 to 2000 μ. This device has made possible the construction of an apparatus in which the low temperature adsorption isotherms of krypton on small areas of adsorbent (as little as 50 cm.^{2}) can be determined rapidly (<3 hours) and precisely (S.D. <1%). The method is applicable to adsorbents exposing as little as 5 cm.^{2} per cubic centimeter of bulk. Krypton isotherms were obtained on 290 cm.^{2} of a coarse germanium powder—prepared *in situ* by crushing a wafer under vacuum—both before and after approximately one monolayer of oxygen had been chemisorbed on the freshly created surfaces. While this chemisorbed oxygen changes the chemical nature of the metal surfaces, producing marked changes in the krypton isotherm, it cannot, nevertheless, perceptibly affect the surface area. Values of this area, derived from the two isotherms by applying the method of Brunauer, Emmett and Teller differ by 2.1%. This difference, while significant, is remarkably small, demonstrating the consistency of the B.E.T. area calculation. The design, circuitry and calibration of the apparatus, a general correction for thermal transpiration, and a comparison with nitrogen adsorption are discussed.

Introduction

Studies on the chemistry of freshly created surfaces of germanium and silicon are proceeding in these laboratories. In the technique developed by Kafalas and Green,[2] which is used in these studies, a wafer of the metal is transferred to a glass tube with a thickened base. A glass-jacketed iron rod is slipped into the tube, which is then sealed to a vacuum system and outgassed. The sample is crushed by manipulating the hammer with a solenoid, a gas is admitted to the sample chamber, and chemical changes are followed directly by pressure changes or, indirectly, by analysis.

In order to provide a frame of reference for experiments of this kind, and to relate chemical changes to the atomic properties of the crystal surface, it has been necessary to measure the surface area created in a given run.

It was estimated by sieving that about 200 cm.^{2} is created in the usual experiment.[2] The particle size of the crushed sample varies from a few microns to more than a millimeter, and the particle shape, although restricted by the crystal cleavage planes, is almost random. The heat-of-immersion technique of Harkins and Jura,[3] perhaps the only absolute measure of surface in a polydisperse system of this kind, is inapplicable to such a small sample.

A less direct method lies in the application of the Brunauer–Emmett–Teller (B.E.T.) theory of multimolecular physical adsorption to isotherms of chemically inert vapors.[4] In its simplest form this theory predicts that

$$\frac{P}{(P_0 - P)N} = \frac{1}{N_m C} + \frac{C - 1}{N_m C} \times \frac{P}{P_0} \qquad (1)$$

where N is the number of molecules adsorbed at a given pressure, P; N_m is the number of molecules required to form a monolayer of adsorbate; P_0 is the vapor pressure of the adsorbate at the temperature of the experiment; and C is a constant which depends on the particular adsorbate–adsorbent system. While the basic assumptions of the theory have been seriously questioned,[5] there is considerable evidence—both direct[3] and indirect[6]—that acceptable values of N_m are obtained with weakly cohesive adsorbate molecules upon moderately heterogeneous surfaces.[7,8] Knowing the area occupied by an adsorbate molecule, one can then calculate the surface area of a sample.

One to two monolayers of a vapor are generally adsorbed on a surface when the relative pressure, P/P_0, exceeds 0.2.[9] This corresponds very roughly to 10^{17} molecules or 3000 μcc. of the vapor for 200 cm.^{2} of surface. In a gas adsorption apparatus with a 20-cc. dead-space volume, the pressure drop due to adsorption will be 150 μ. If P_0 is an atmosphere, as in the case of nitrogen at its boiling temperature, this pressure drop must be measured at a total pressure of about 150 mm. To determine the change with an uncertainty of less than 1%, one must measure the pressures, know the volumes and control the temperature, all to 1 part in 10^5. It is difficult to control the temperature and volumes, and impossible to measure the absolute pressure in this range, with such precision.

With krypton, originally used in this connection by Beebe, Beckwith, and Honig,[10] P_0 at the temperature of boiling nitrogen is 2800 μ, and the required precision of pressure measurement, etc., is 2 parts in 1000. It is applicable, therefore, providing one employs a precise manometer operable—for reasons seen below—from 50 to $\sim$1200 μ. In this range the thermal conductivity of krypton depends strongly upon pressure.[11] The thermistor[12]—a tiny bead of semi-conducting oxides with a large negative temperature coefficient of resistance—can be adapted to measure thermal conductivity, hence

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[1] The research reported in this document was supported jointly by the Army, Navy and Air Force under contract with the Massachusetts Institute of Technology.

[2] J. A. Kafalas and M. Green, Abstracts, Electronics Division, The Electrochemical Society, Spring Meeting, 1955.

[3] W. D. Harkins and G. Jura, THIS JOURNAL, **66**, 1362 (1944).

[4] S. Brunauer, P. H. Emmett and E. Teller, *ibid.*, **60**, 309 (1938). For a review of surface area measurements by the B.E.T. and other methods, see chapter by P. H. Emmett in "Catalysis," Vol. I, edited by P. H. Emmett, Reinhold Publishing Corp., N. Y., N. Y., 1954.

[5] See review by T. L. Hill, *Advances in Catalysis*, **4**, 211 (1952).

[6] T. L. Hill, P. H. Emmett and L. G. Joyner, THIS JOURNAL, **73**, 5102 (1951).

[7] G. D. Halsey, *Advances in Catalysis*, **4**, 259 (1952).

[8] J. M. Honig, *Ann. N. Y. Acad. Sci.*, **58**, 6, 741 (1954).

[9] S. Brunauer, "The Absorption of Gases and Vapors," University Press, Princeton, N. J., 1945.

[10] R. A. Beebe, J. B. Beckwith and J. M. Honig, THIS JOURNAL, **67**, 1554 (1945).

[11] S. Dushman, "Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y., 1949.

[12] J. A. Becker, C. B. Green and G. L. Pearson, *Trans. A.I.E.E.*, **65**, 711 (1946); *Bell System Tech. J.*, **26**, 170 (1947).

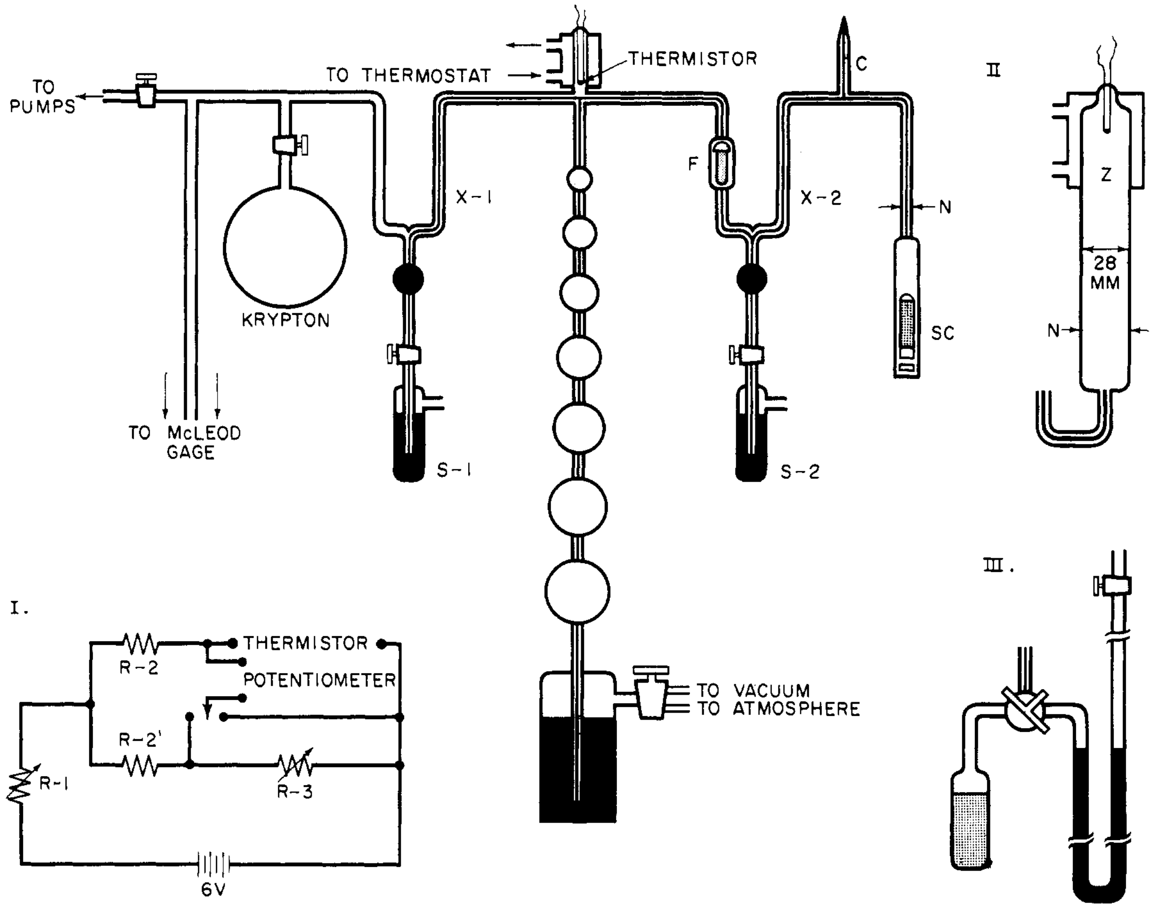

Fig. 1.—Adsorption apparatus.

pressure,[12] with, we have found, great precision. Using such a device, we have constructed a simple apparatus in which the adsorption isotherms of krypton on as little as 50 cm.^{2} of adsorbent can be measured rapidly and precisely. Since the permissible sample chamber of the apparatus is relatively large, the method is applicable to materials with as little as 5 cm.^{2} of surface per cubic centimeter of bulk.

Experimental

a. Design and Calibration of the Adsorption Apparatus.—Current passing through a thermistor raises its temperature, and its resistance falls off exponentially. The device equilibrates to a temperature which depends upon the rate at which heat is dissipated. The type of thermistor employed in our work[13] was supplied with two 0.001″ platinum leads which were spot-welded $^1/_4$″ from the bead junctures to 0.025″ platinum wires sealed in an uranium glass press. This was sealed into an 8 mm. i.d. Pyrex side-arm which is thermostated at 26 ± 0.03° and blackened to prevent photoeffects.

The control circuit, shown in Fig. 1-I, is powered by a partially discharged lead storage battery. R-2 and R-2′ are 1000 ohm wire-wound resistors, while decade resistance boxes, variable in steps of 0.1 ohm, are most suitable for R-1 and R-3. The potentiometer is provided with a switching arrangement whereby either the potential across the thermistor, V_{th}, or that across the bridge, V_{off}, may be measured. The circuit is set by evacuating the system to below 10^{-5} mm., setting R-1 to 40 ohms, and adjusting V_{off} to zero by matching R-3 to the dynamic resistance of the thermistor. This will generally lie between 120 and 190 ohms depending upon the particular thermistor bead and the structure of its support and enclosure. V_{th} is then determined, and its value, which lies between 700 and 950 mv., is taken as a reference point for vacuum ($<10^{-5}$ mm.). It is maintained by small daily adjustments in R-1 which are necessitated by minor drifts in the battery voltage.

Admission of a gas to the system enhances heat dissipation, hence lowers the temperature and raises the resistance of the thermistor, and a bridge imbalance results. (The effect of mercury vapor, always present at its vapor pressure within the thermistor enclosure of this apparatus, is included in the "zero.") The response of the circuit to changes in krypton pressure was found to range from 2 mv./μ below 200 μ to 0.1 mv./μ at 2000 μ. The response at still higher pressures becomes very small. The range of the calibration is 0–1300 mv.; since the off-balance voltage, V_{off}, can be read easily to 0.1 mv., one can determine the pressure to 0.1% over the entire range, 50 to 2000 μ.

The adsorption apparatus is shown schematically in Fig. 1. The buret is the conventional series of bulbs, calibrated with mercury, whose volumes vary from 1.5 to 50 cc. The bore of all capillary tubing, excepting side-arm (C), is 1.4 mm. Mercury cut-offs are used to isolate the buret from the gas reservoir and the sample chamber from the buret. A mercury float-valve was installed between the buret and sample chamber so that samples can be changed without exposing the buret to air. Mercury was introduced to the apparatus by vacuum distillation into the buret reservoir. The cut-offs were filled from the top by forcing mercury over the buret; the bulbs under the cut-offs serve as traps for grease which might rise from the stopcocks below. Needle-valves in the air and vacuum lines facilitate adjustment of the mercury level in the buret.

The thermistor was calibrated, and the dead space volume in the buret (thermistor enclosure, capillaries, etc.)

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[13] Glass-coated bead, diameter ≈0.014″, R_0 at 25° ≈40,000 ohm, R_0 at 0°/R_0 at 50° ≈9, dissipation constant P ≈ 0.1 mw.°C. (Type L 252-A, Thermistor Corporation of America, Metuchen, N. J., or its equivalent.) Beads suitably mounted for the present application are also commercially available.

was determined as follows. A rough calibration of V_{off} *vs.* krypton[14] pressure—measured with a McLeod gage—was made up for the range, 100–400 μ. A charge of krypton was admitted to the buret, and V_{off} was recorded for each bulb setting. From the bulb volumes and the approximate calibration, the dead space volume was calculated to be 4.58 ± 0.02 cc. Since the bulb volumes were known to 0.0002 cc., the uncertainty in the buret volume at each setting was virtually that of the dead space volume alone, *i.e.*, 0.02 cc.; hence, at the four lowest settings, where the buret volume exceeded 16 cc., the uncertainty in each case was less than ~0.1%. These four settings alone were used to obtain a precise internal calibration of V_{off} *vs.* krypton pressure over the entire range, 5 to 2000 μ, by admitting overlapping charges of krypton to the buret. The approximate McLeod calibration was discarded, only a single point being retained to normalize the internal calibration, which was used for an accurate determination of the dead space volume, *viz.*, 4.586 ± 0.003 cc.

The internal calibration appears to hold indefinitely at pressures less than 1000 μ, but may drift slightly at higher pressures, requiring simple periodic checks. Very slow, small fluctuations in the resistance of the thermistor may occur, causing slight imbalances of the bridge; the calibration of *net* V_{off} *vs.* pressure is not perceptibly affected, however.[15]

An adsorption isotherm is determined as follows. The float-valve (F) is seated by raising the mercury from S-2, and the 0.05 mm. capillary (C) is snapped off at the end. A glass enclosure (SC) containing the sample is sealed to the system, which is then evacuated through C and sealed off. F is lowered, SC is opened at X-2 and outgassed. For crystalline samples of less than 1000 cm.^{2}, about 15 minutes outgassing with a Bunsen flame suffices for a static pressure of *ca.* 10^{-5} mm., which is adequate for most experiments. SC is closed and immersed in a beaker of water at room temperature. A charge of krypton is admitted to the buret which is then closed at X-1. By measuring the pressures at different volume settings of the buret, one obtains a precise average for the quantity of krypton, expressed in μcc. at the temperature of the buret. SC is opened and the volume settings are varied again. A precise average for V_{SC}, the dead-space volume in the sample chamber, is thus obtained.

The system is then evacuated, SC is closed, and immersed to level (N) in a Dewar flask containing liquid nitrogen, which is agitated by a slow stream of tank nitrogen. The temperature of the bath is measured to ±0.01° with a simple nitrogen vapor pressure thermometer.[16] Knowing it, one can calculate P_0 for krypton from the data of Meihuizen and Crommelin.[17] A charge of krypton is admitted to the buret and measured as above. The mercury in the buret is brought to its lowest setting, and SC is opened. When the latter has cooled to the temperature of the bath, adsorption equilibrium occurs within a few minutes. The mercury level is then raised to successively higher settings, and the equilibrium pressures are recorded. SC is closed and the gas remaining in the buret is measured, giving by difference the quantity remaining in SC. More krypton is admitted to the buret, and the operation is repeated until the desired pressure range is covered.

The entire procedure, from introducing the sample to completion of the isotherm, takes approximately three hours.

b. **Corrections for Thermal Transpiration.**—Since the buret and SC are maintained at widely different temperatures and are connected by a capillary whose 1.41 mm. diameter is of the same order as the mean free path of the enclosed gas, thermal transpiration[18,19] will, if neglected, lead to erroneously high values of P_{SC}, *i.e.*, P_{SC} at equilibrium is actually less than P_{B}, the pressure in the buret where the manometer is situated. It is essential, therefore, to obtain a transpiration factor, $P_{\text{SC}}/P_{\text{B}}$, as a function of P_{B}. In order to obtain such data directly one must place a manometer directly in the sample chamber; thermistors are, however, inoperable at 78°K. An indirect method was, therefore, used instead.

The arrangement of Fig. I-II, due in its essentials to Liang,[19a] was employed. Varying charges of krypton were admitted and simultaneous equilibrium measurements were made of P_{B} and P_{Z}, the pressure in a second thermistor enclosure, Z, also thermostated at 26°, which was connected to the cold region by 28 mm. tubing. The results, obtained for the pressure range 8 to 1750 μ, are given in Table I.

TABLE I

THERMAL TRANSPIRATION OF KRYPTON

$T_{\text{B}} = T_{\text{Z}} = 299°\text{K.}, T_{\text{SC}} = 78°\text{K.}$

P_{B} (mm.)	P_{Z} (mm.)	$r_0 = P_{\text{Z}}/P_{\text{B}}$	r_1 (eq. 5a)	$R = \frac{P_{\text{SC}}}{P_{\text{B}}} = r_0r_1$	$R_{\text{calcd.}}$ (eq. 6)[a]	$R - R_{\text{calcd.}}$
1.351_2	1.350_7	0.999_6	(1.000)	0.999_6	0.997_5	+0.002
1.049_6	1.045_0	$.995_6$	(1.000)	$.995_6$	$.995_5$	.000
0.880_2	0.871_9	$.990_6$	(1.000)	$.990_6$	$.993_5$	− .003
.4834	.4761	$.984_9$	(1.000)	$.984_9$	$.982_5$	+ .002
.3604	.3494	$.969_2$	(1.000)	$.969_2$	$.973_2$	− .004
.2170	.2051	$.945_1$	(1.000)	$.945_1$	$.945_0$	.000
.1542	.1405	$.911_2$	(1.000)	$.911_2$	$.916_5$	− .005
.0831	.0706	$.849_6$	0.999	$.848_9$	$.847_0$	+ .002
.0641	.0522	$.814_4$	.996	$.811_1$	$.812_0$	− .001
.0634	.0516	$.813_9$	.996	$.810_6$	$.811_0$	.000
.0539	.0428	$.794_0$	.993	$.788_4$	$.788_2$	.000
.0455	.0355	$.780_2$	.990	$.772_2$	$.764_5$	+ .008
$.0268_1$	$.0193_8$	$.722_9$	.976	$.705_6$	$.694_5$	+ .011
$.0087_1$	$.0061_3$	$.703_8$	.895	.630	$.586_0$	+ .044

[a] $R_{\text{calcd.}} = 1 - [0.490/(74.0P^2_{\text{B}} + 20.4P_{\text{B}} + 1)]$.

By this device one measures the combined (opposing) effects of thermal transpiration through the capillary and the wide tube. The individual effects can, however, be separated by the following considerations.

Liang has established[19a] that the effect of thermal transpiration across a single connection can be described by the general empirical equation

$$\frac{P_1}{P_2} = R\{P_2D\} = \frac{(T_1/T_2)^{1/2} - 1}{\alpha_{\text{He}}\phi_{\text{g}}^2(P_2D)^2 + \beta_{\text{He}}\phi_{\text{g}}(P_2D) + 1} + 1 \qquad (2)$$

where P_1 and P_2, and T_1 and T_2, are the pressures and temperatures in the cold and warm sides, respectively, and D is the diameter of the connection between them. α_{He} and β_{He} are constants characteristic of helium, Liang's reference gas, and ϕ_{g} is a constant characteristic of the gas under study.

In the present case, the true transpiration factor, $R = P_{\text{SC}}/P_{\text{B}}$, is related to the measured "apparent" transpiration factor, $r = P_{\text{Z}}/P_{\text{B}}$, by

$$P_{\text{SC}}/P_{\text{B}} = (P_{\text{Z}}/P_{\text{B}})\,(P_{\text{SC}}/P_{\text{Z}}), \text{ or} \qquad (3)$$
$$R\{P_{\text{B}}D_{\text{B}}\} = r \times R\,\{P_{\text{Z}}D_{\text{Z}}\}$$

where D_{B} and D_{Z} are the diameters of the connections to the buret and region Z, respectively, and, in keeping with the earlier designation, SC refers to the cold region between them. But, noting that R is a function only of the product, PD (*cf.* Eq. 2), we have

$$R\{P_{\text{Z}}D_{\text{Z}}\} = R\{P_{\text{B}1}D_{\text{B}}\} \qquad (4)$$

when $P_{\text{B}1} = (D_{\text{Z}}/D_{\text{B}})P_{\text{Z}}$. Repeated substitutions between equations 3 and 4 lead to the generalized expression of equation 5, whereby one can calculate the pressure in the cold region, P_{SC}, corresponding to any pressure, $P_{\text{B}} = P_{\text{B}_0}$, in the warm region, from a knowledge of the apparent transpiration factors alone.

$$\frac{P_{\text{SC}}}{P_{\text{B}_0}} = r_0r_1r_2r_3\ldots r_m\ldots r_nR\{P_{\text{B}n}D_{\text{B}}\} \qquad (5)$$

where

$$r_0 = \left[\frac{P_{\text{Z}}}{P_{\text{B}}}\right]_{P_{\text{B}} = P_{\text{B}_0}}$$

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[14] Spectroscopically pure krypton, supplied by Air Reduction Co. in one-liter flasks equipped with break-off seals. A single flask suffices for several months of routine work.

[15] Aging the thermistor by passing 10 to 11 ma. (a.c. or d.c.) through it for two to three days before the calibration is made will minimize the subsequent tendency to drift.

[16] L. G. Joyner, "Scientific and Industrial Glass Blowing and Laboratory Techniques," edited by W. E. Barr and V. J. Anhorn, Instruments Publishing Co., Pittsburgh, 1949.

[17] J. J. Meihuizen and C. A. Crommelin, *Physica*, **4**, 1 (1937).

[18] M. Knudsen, *Ann. Physik*, **31**, 205, 633 (1910).

[19] (a) S. C. Liang, *J. App. Phys.*, **22**, 148 (1951); (b) *J. Phys. Chem.*, **57**, 910 (1953).

and

$$r_{\mathrm{i}} = \left[\frac{P_{\mathrm{Z}}}{P_{\mathrm{B}}}\right]_{P_{\mathrm{B}} = P_{\mathrm{Bi}}}$$

and

$$P_{\mathrm{Bi}} = r_0 P_{\mathrm{B}_0}\left[\frac{D_{\mathrm{Z}}}{D_{\mathrm{B}}}\right]^{\mathrm{i}}$$

Provided that $(D_{\mathrm{Z}}/D_{\mathrm{B}}) > 1$, each succeeding term on the right of equation 5 more closely approaches unity. For any value of P_{B_0}, it is thus possible to find a value of $i = m$ for which r_m and all the terms following it will be indistinguishable from unity. The smaller is P_{B_0}, the larger is m, so that the value of m which applies to the lowest P_{B_0} in a set of thermal transpiration measurements will necessarily be acceptable for the remainder of the set.

In the present study, $D_{\mathrm{Z}}/D_{\mathrm{B}} = 30.0/1.41 = 19.9$, and the lowest value of P_{B_0} was 8.7 μ. One can ascertain from a rough plot of the data in Table I that $m = 2$ will apply to this value, hence to the entire set. Equation 5 thus reduces to

$$\frac{P_{\mathrm{SC}}}{P_{\mathrm{B}_0}} = r_0 r_1 = \left[\frac{P_{\mathrm{Z}}}{P_{\mathrm{B}}}\right]_{P_{\mathrm{B}} = P_{\mathrm{B}_0}} \times \left[\frac{P_{\mathrm{Z}}}{P_{\mathrm{B}}}\right]_{P_{\mathrm{B}} = 19.9 P_{\mathrm{B}_0}} \times \left[\frac{P_{\mathrm{Z}}}{P_{\mathrm{B}}}\right]_{P_{\mathrm{B}} = P_{\mathrm{B}_0}} \qquad (5a)$$

whereby the true thermal transpiration factors may be calculated (Table I).

At krypton pressures exceeding 50 μ, Liang's equation (equation 2) describes our results with remarkable accuracy (Table I) justifying its use as a precise interpolation formula. Using his values of α_{He} and β_{He} (2.52 mm.$^{-2}$-mm.$^{-2}$Hg and 7.68 $\{1 - (T_1/T_2)^{1/2}]$ mm.$^{-1}$-mm.$^{-1}{}_{\mathrm{Hg}}$, respectively)[19a] the optimum value of ϕ_{Kr} was found to be 3.84 compared to Liang's reported value of 3.90 ± 0.2.[19b] At krypton pressures less than 50 μ ($P_{\mathrm{B}}D \leqslant 0.07$ mm.$_{\mathrm{Hg}}$-mm.) which are not in any event of concern in the present paper, the equation apparently fails.

In studies of krypton adsorption at liquid nitrogen temperatures, one can, therefore, calculate the pressure in the sample chamber from a knowledge of the buret pressure and capillary diameter alone according to the general equation

$$P_{\mathrm{SC}} = P_{\mathrm{B}}\left[1 - \frac{0.490}{37.2D^2(P_{\mathrm{B}})^2 + 14.45D(P_{\mathrm{B}}) + 1}\right] \qquad (6)$$

where P_{B} and D are expressed in mm.$_{\mathrm{Hg}}$ and mm., respectively. The equation is subject only to the restriction that $P_{\mathrm{B}}D \gg 0.07$ mm.$_{\mathrm{Hg}}$mm.

c. **Preparation and Treatment of the Sample.**—To illustrate the nature of the results obtainable with the apparatus, reference will be made to an experiment in which a wafer of germanium was crushed *in situ* (see Introduction and Fig. 1). The wafer—approximately 8 mm. × 8 mm. × 0.8 mm.—was cut from a p-type crystal of zone-purified germanium with a specific resistivity of 5 ohm-cm. Krypton isotherms were determined before and, again, after the sample was crushed. Oxygen was then admitted to the system, and, after approximately a monolayer had been chemisorbed on the fresh germanium surfaces, the excess oxygen was pumped off, and a third krypton isotherm determined.

Prior to crushing the sample, the entire system was outgassed to a point where less than 10 μcc. of gas would be subsequently evolved from the walls and mercury surfaces during the four hours required to crush the sample and complete the second isotherm. Even had the gas consisted entirely of oxygen, gettered by the fresh surfaces, less than 0.005 monolayer of "oxide" would have formed during this part of the experiment.

As a precaution against distillation of mercury onto the metal surfaces, the connection between X-2 and SC was chilled with liquid nitrogen while the wafer was crushed and was not warmed until the capillary above SC had been submerged in liquid nitrogen by raising the Dewar flask into position for the adsorption run.

The dead-space volume of the sample chamber was 7.700 ± 0.009 cc. at 26°. On the assumption that the average cubical expansion coefficient of Pyrex glass is 3.6×10^{-6},[20] it was calculated that the volume was reduced by only 0.07% as the chamber was cooled to 77.8°K. The apparent sample chamber volume, $V_{\mathrm{SC}}(T_{\mathrm{B}}/T_{\mathrm{SC}})$, universally employed for ease of calculation was, therefore, 29.58 ± 0.03 cc. The geometric area of the glass surface within the chamber was 70 cm.^{2}; that of the uncrushed wafer was 1.5 cm.^{2}.

Results

The results are presented in the form of B.E.T. isotherms (*cf.* equation 1) in Figs. 2 and 3. Figure 2 is the isotherm for the system blank, *i.e.*, the glass and uncrushed wafer. The curve is experimentally linear from $P/P_0 = 0.02$ to about 0.30. At higher values of P/P_0 the observed adsorption becomes progressively *less* than that predicted by extrapolation of the data at lower pressures until, at $P/P_0 = 0.66$, the adsorption almost discontinuously *increases*. As more krypton is added, the pressure eventually reaches a limiting value of $P/P_0 = 0.69$, the vapor pressure of solid krypton at 77.8°K. (The value of P_0 used in the calculations is the vapor pressure of supercooled liquid krypton.[10]) The occurrence of desorption hysteresis[9] (not shown in the figure) when $P/P_0 \gtrsim 0.60$ suggests that the apparent onset of condensation at $P/P_0 = 0.66$ is due to capillary condensation within pores of the glass.[21]

Figure 3 is a plot derived from the *net* adsorption upon the freshly created germanium surfaces, both before and after the chemisorption of oxygen. The curves are linear from $P/P_0 = 0.02$ to about 0.23 (better shown in the enlargement in Fig. 3a). Above $P/P_0 = 0.23$ the curves diverge; the untreated sample shows more, the surface-oxidized sample, less, adsorption than anticipated from the data at lower pressures. These deviations will be discussed in another paper. Our present concern is a measure of surface area; this is given by the product of σ_{Kr}, the area subtended by an adsorbed krypton atom, and N_{m}, the number of molecules required to form a monolayer. According to the B.E.T. theory, N_{m} is given by

$$N_{\mathrm{m}} = (\text{slope} + \text{intercept})^{-1} \qquad (7)$$

where the slope and intercept refer to the linear segments of the B.E.T. isotherms (equation 1).

Table II summarizes the slopes and intercepts of the three isotherms. The values were obtained by a least squares treatment, and the assigned errors are

TABLE II

B. E. T. ANALYSIS OF KRYPTON ADSORPTION DATA, 77.78°K.

	Slope, mol.$^{-1}$ × 10^{20}	Intercept, mol.$^{-1}$ × 10^{20}	N_{m}, mol. × 10^{-15}	Cm.^{2} = 19.41 × 10^{-16} N_{m}	C
Glass enclosure	1643 ±12	28.5 ±0.25	60.9 ±0.5	118.3 ±1.1	48
Germanium					
Freshly created surfaces	674.3 ±1.5	3.30 ±0.18	147.6 ±0.3	286.5 ±0.6	204
After chemisorption of *ca.* monolayer of oxygen	685.6 ±3.4	5.92 ±0.37	144.6 ±0.6	280.6 ±1.1	116

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(20) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1953.

(21) The presence of such pores is further indicated by the fact that the B.E.T. surface area of the glass exceeds the geometric area by a factor of 1.8 (see Table II). It has been observed in other experiments that the less porous the glass surface, the higher the subsaturation pressure at which the apparent condensation commences.

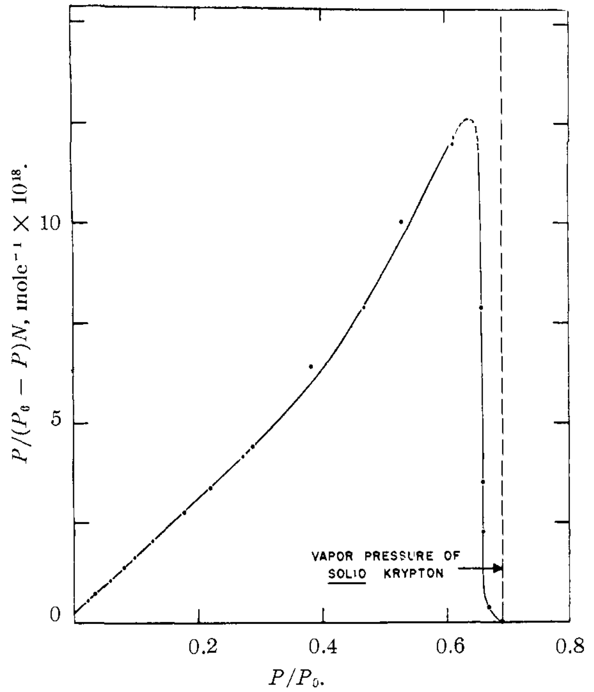

Fig. 2.—B.E.T. adsorption isotherm; krypton on glass 77.78°K.

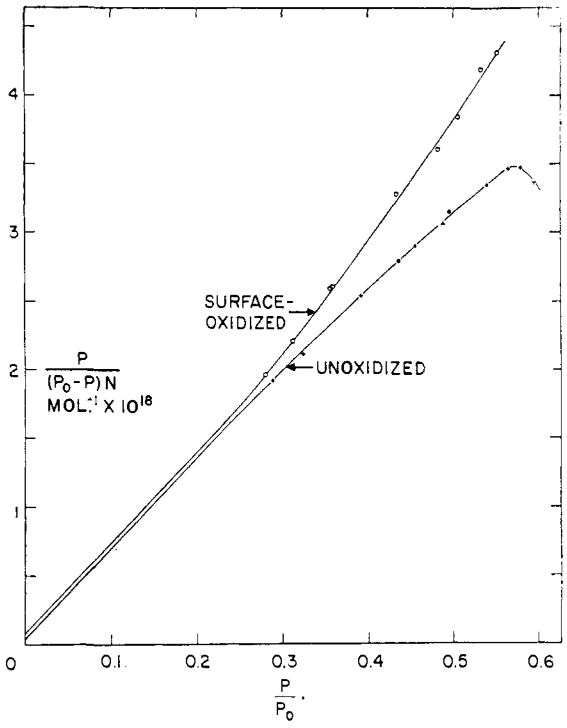

Fig. 3.—B.E.T. adsorption isotherms; krypton on germanium and on surface-oxidized germanium; 77.78°K.

standard deviations.[22] The third column of the table gives values of N_m calculated by equation 7. The next column gives the product, $N_m\sigma_{Kr}$, where 19.4 Å. is taken as σ_{Kr} (see below). The last column gives the B.E.T. constant, C.

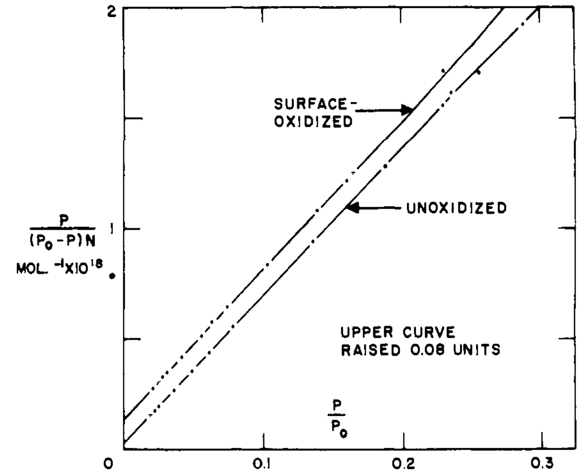

Fig. 3a.—B.E.T. adsorption isotherms; krypton on germanium and on surface-oxidized germanium; 77.78°K.

Discussion

The first objective of this work—high precision—has been achieved. In the illustration, the standard deviation of N_m on a 290 cm.^{2} sample was less than 0.4%, even though the dead-space volume of the sample enclosure was relatively large and the raw data also had to be corrected for adsorption on the walls of the enclosure (120 cm.^{2}). With the present apparatus, the limit to the sensitivity—calculated for zero dead-space volume in the sample chamber— is 0.15 cm.^{2}. In principle it is possible, therefore, to measure 15 cm.^{2} to 1%. In practice, however, a reasonable dead-space volume, coupled with the necessary correction for adsorption on the walls of the sample chamber impose further limitations on precision. It is, nevertheless, quite practicable to measure 50 cm.^{2} to 1%, and precise measurements can be made on samples exposing less than 5 cm.^{2} per cubic centimeter of bulk. Measurements are conveniently made upon 50 to 2000 cm.^{2}. Larger samples become more difficult to handle because of the limited gas-handling capacity of the buret, and the increased time required for adsorption equilibrium at each pressure. Three or four adsorption measurements in the range $P/P_0 = 0.07$ to 0.20 ($P = 190$ to 550 μ) will generally suffice for a precise area determination.

Our second consideration—the *accuracy* of the calculated area— depends first upon the validity of the B.E.T. derivation of N_m and secondly upon the assumed value of σ_{Kr}. It will be observed from Table I that chemisorption of a monolayer of oxygen upon a germanium surface—a process which involves no perceptible change in the surface area—caused a 2.1% decrease in the value of N_m, which, while significant, is certainly very small.[23] Thus, while the isotherms themselves reflect the chemical transformation of the surfaces (Fig. 3), the values of N_m derived therefrom are almost identical. This is a striking confirmation of the consistency of the B.E.T. derivation of N_m. That this value of N_m does indeed correspond to *exactly* a monolayer is, however, less certain.[6]

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[22] W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951.

[23] It has been assumed implicitly that σ_{Kr} is unaffected by the surface transformation. It is possible, however, that the apparent discrepancy in N_m is really attributable to a change in σ_{Kr}.

What is likely a more serious uncertainty in the calculation of surface area arises from the assumptions regarding σ_{Kr}. The conventional device for assigning a cross-section to an adsorbed molecule, X, is to compare the value of N_m obtained with X to the value obtained with nitrogen on the sample, obtaining the ratio σ_X/σ_{N_2}.[24] It is then assumed that σ_{N_2} is approximately the same on all adsorbents, the best value—based on both experimental and theoretical grounds—being 15.4 Å.^{2} at 78°K.[24] σ_{Kr}/σ_{N_2} on a variety of adsorbents have been measured by Beebe, Beckwith and Honig[10] and by Davis, DeWitt and Emmett,[25] the values obtained varying from 1.09 to 1.33 depending on the adsorbent. To obtain a more definitive value for our work, an experiment was performed in which germanium was ground with mortar and pestle to give a specific area of 14,000 cm.^{2} per gram. Both krypton and nitrogen isotherms were derived for a 30-gram sample by employing the adaptor illustrated in Fig. 1-III. The mercury manometer, constructed of 4 mm. tubing and backed with a mirrored meter stick, was employed for metering the gases in both cases, and for measuring equilibrium nitrogen pressures; the thermistor was used for equilibrium krypton pressures.

TABLE III

COMPARISON OF KRYPTON AND NITROGEN ADSORPTION ON AIR-OXIDIZED GERMANIUM SURFACES; 43.2 m.^{2}, 77.8°K.

A.	Slope (mol.$^{-1}$ × 10^{23})	Intercept (mol.$^{-1}$ × 10^{23})	Nm (mol. × 10^{-18})	C
Nitrogen	348.8 ± 1.2	8.03 ± 0.19	280.5 ± 1.2	44.4 ± 1.5
Krypton	438.9 ± 3.3	10.67 ± 0.45	222.5 ± 1.7	41.1 ± 2.0

$$\frac{\sigma_{Kr}}{\sigma_{N_2}} = \frac{(N_m)_{N_2}}{(N_m)_{Kr}} = 1.261 \pm 0.009$$

B. Source	Sample	σ_{Kr}/σ_{N_2}
This work	Surface-oxidized germanium	1.261 ± 0.009
Beebe, Beckwith and Honig[10]	$CaCO_3$	1.09–1.20
	TiO_2	1.20
	Porous glass	1.33
Davis, DeWitt and Emmett[25]	6 Metals and oxides	1.28

The results are given in Table III. It will be noted first that the value of the B.E.T. constant, C, obtained on the air-treated surfaces is less than half the value observed in the previous experiment when oxygen was sorbed from an atmosphere containing low pressures of pure oxygen, the sorption being deliberately limited to a monolayer. There is evidence however, that not much more than a monolayer of oxygen is chemisorbed from air in the 8 hours required to prepare the sample.[2] The change in C is apparently due to a more subtle transformation of the surfaces which will be studied further. It will be assumed here, as above, that σ_{Kr} is unaffected.

Using our value of σ_{Kr}/σ_{N_2}, one obtains σ_{Kr} = 19.4 ± 0.2 Å.^{2} This value is subject to an uncertainty—probably less than a few per cent.—in the value used for σ_{N_2}. It is hoped that a yet more significant value of σ_{Kr} will be obtained by an absolute method on which work is now in progress.

Acknowledgments.—The technical assistance of Miss Alice L. Carney and the many helpful suggestions of Mr. James A. Kafalas are gratefully acknowledged.

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[24] H. K. Livingston, *J. Colloid Sci.*, **4**, 447 (1949).

[25] R. T. Davis, J. W. DeWitt and P. H. Emmett, *J. Phys. Colloid Chem.*, **51**, 1232 (1947).

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

Effects of γ-Radiation on Ice[1]

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The γ-ray induced formation and disappearance of hydrogen peroxide in ice was investigated as a function of total dose, temperature, dissolved gas and thermal cycling with intermittent irradiation. When oxygen saturated water was frozen rapidly and irradiated with cobalt-60 γ-rays, analysis of the melted samples gave the following results. The initial 100 e.v. yield of hydrogen peroxide increased from 0.2 below $-200°$ to 0.7 at $-15°$. The hydrogen yield increased from 0.1 below $-100°$ to 0.25 at $-15°$. Long irradiations at $-196°$ resulted in continued build up of hydrogen peroxide and hydrogen to at least 10^{-3} M while at higher temperatures steady states were reached at much lower concentrations of products. The initial presence of oxygen or hydrogen had little effect on hydrogen peroxide observed after irradiations at $-196°$ but had considerable effect on hydrogen peroxide production at higher temperatures. When samples prepared by freezing hydrogen-saturated 50 μM hydrogen peroxide solution were irradiated for short times at temperatures from -220 to $-5°$, the hydrogen peroxide concentration was observed to decrease at all irradiation temperatures. The initial 100 e.v. yield for peroxide disappearance increased from 0.6 at $-100°$ to 4.0 at $-60°$. When a sample initially containing hydrogen and hydrogen peroxide was subjected to two short irradiations at $-196°$ and was allowed to warm to $-180°$ or above between irradiations, the observed final concentration of hydrogen peroxide was less than that for an equivalent irradiation with the sample held at $-196°$. The greater disappearance of hydrogen peroxide with intermittent warming is attributed to reaction induced by release of some reactive species trapped during irradiation at the low temperature. Ice irradiated at $-196°$ exhibited an absorption peak at 2800 Å. which on warming at a rate of 10° per min. disappeared below $-143°$.

Introduction

Chemical effects of ionizing radiation on ice reported in the literature are difficult to interpret. Gunther and Holzapfel[1] were unable to detect hydrogen in ice irradiated with X-rays at $-180°$. On the other hand Ghormley and Allen[2] found gas yields up to 0.27 molecules per 100 e.v. produced by self irradiation of tritium ice at $-196°$. Bonet-Maury and Lefort[3] irradiated ice containing titanium sulfate and sulfuric acid[4] and observed hydrogen peroxide production with a yield of 0.3 molecules per 100 e.v. in the frozen solution sub-

[1] P. Gunther and L. Holzapfel, *Z. physik. Chem.*, **B44**, 374 (1939).

[2] J. A. Ghormley and A. O. Allen, A. E. C. Document ORNL-128, paper presented at 115th American Chemical Society Meeting, San Francisco, California, March, 1949.

[3] P. Bonet-Maury and M. Lefort, *Compt. rend.*, **226**, 1445 (1948); *Nature*, **162**, 381 (1948).

[4] P. Bonet-Maury and M. Frilley, *Compt. rend.*, **218**, 400 (1944) and Bonet-Maury and Lefort, *J. chim. phys.*, **47**, 179 (1950).