refluxing the substance melting at 141.5° contained 0.276% solids, while that of the substance melting at 161.5° contained 0.115% total solids. Two hundred mg. of the substance melting at 141.5° dissolved completely in 15 cc. of $N/60$ hydrochloric acid solution. In contrast 180 mg. of the substance melting at 161.5° did not dissolve in the same solvent after prolonged stirring. Warming at 56° for thirty minutes caused the solution of the latter mixture, but neutralization with sodium bicarbonate and cooling caused it to flocculate. Sodium bicarbonate did not show this effect on the solution of the substance melting at 141.5°.

Summary

p-Hydroxylaminobenzenesulfonamide melting sharply at 141.5° and a related substance melting sharply at 161.5° have been studied.

The higher melting substance is a crystalline trimolecular complex composed of two molecules of *p*-hydroxylaminobenzenesulfonamide and one molecule of *p*-aminobenzenesulfonamide. This has been shown by chemical analyses, oxidation and quantitative determination of sulfanilamide in the presence of *p*-hydroxylaminobenzenesulfonamide.

PHILADELPHIA, PA. RECEIVED MAY 29, 1942

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INC.]

Surface Area of Oxide Coated Cathodes by Adsorption of Gas at Low Pressures[1]

BY L. A. WOOTEN AND CALLAWAY BROWN

Introduction

The high thermionic emission obtainable with the oxide-coated cathode has been generally attributed to a film of free barium adsorbed on the surface of the alkaline earth oxide coating.[1a,2,3,4] The influence of surface area on the electron emission, however, has not been determined and no direct measurements of the surface area of oxide-coated cathodes have been reported. The present paper describes a new method for the measurement of relatively small surface areas and its application to oxide coated cathodes, activated and aged under conditions closely appproximating those obtaining in commercial vacuum tubes.

The method developed represents an extension of the method of Emmett and Brunauer,[5] which depends on physical adsorption of gases at temperatures near their boiling points. A comprehensive theory of adsorption in multimolecular layers has been developed[6,7] which makes it possible to deduce the quantity of gas in a monomolecular adsorbed layer from adsorption isotherms covering a range of pressures from 0.05–0.30 p_0, where p_0 is the vapor pressure of the gas at the temperature of the isotherm. Previous applications of the method have used temperatures near the boiling point of the gas so that adsorption measurements at pressures up to several hundred mm. were necessary. Thus butane at 0° ($p_0 = 770$ mm.) has been used as an adsorption reagent to measure the surface area of silica gel.[6] The theory[6,7] indicates that butane at $-116°$ ($p_0 = 0.17$ mm.) should be equally suitable with adsorption measurements necessary only at pressures less than 0.05 mm. Since it is possible to measure much smaller quantities of adsorbed gas at low pressures, use of the relatively low temperature greatly increases the sensitivity of the surface area measurements. In the present work, adsorption isotherms obtained for butane at $-116°$ and ethylene at -183 and $-196°$, at pressures less than 0.01 mm. in the case of ethylene, are found to resemble closely isotherms of gases near their boiling points and to allow measurement of the surfaces of oxide coated cathodes with areas of the order of 100 square centimeters. The ethylene isotherms on alkaline earth oxides are of interest from an adsorption standpoint in that they exhibit a very abrupt reversible rise in adsorption in the pressure region 0.25–0.30 p_0.

Experimental

Experimental Cathode.—The cathode, of the indirectly heated type, consisted of a nickel tube coated with a mixture of barium and strontium oxides—38 mole per cent. of barium. A thick suspension of the carbonate mixture in amyl acetate containing 2% pyroxylin was ball milled with flint pebbles for forty-eight hours. The suspension was

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(1) Original manuscript received March 10, 1942.

(1a) J. A. Becker, *Phys. Rev.*, **34**, 1323 (1929); *Trans. Electrochem. Soc.*, **59**, 207 (1931).

(2) J. A. Becker and R. W. Sears, *Phys. Rev.*, **38**, 2193 (1931).

(3) A. L. Reimann, "Thermionic Emission," John Wiley and Sons, Inc., New York, N. Y., 1934, pp. 194–199.

(4) J. H. DeBoer, "Electron Emission and Adsorption Phenomena," Cambridge University Press, Cambridge, England, 1935.

(5) P. H. Emmett and S. Brunauer, THIS JOURNAL, **59**, 1553 (1937).

(6) S. Brunauer, P. H. Emmett and E. Teller, *ibid.*, **60**, 309 (1938).

(7) S. Brunauer, L. S. Deming, W. E. Deming and E. Teller, *ibid.*, **62**, 1723 (1940).

then sprayed uniformly over the cathode surface, the cathode mounted in the experimental vacuum tube and heated *in vacuo* for two minutes at 1000° to convert carbonates to oxides. Dimensions of the cathode are given in Table I.

TABLE I

DIMENSIONS OF EXPERIMENTAL CATHODE

Length, cm.	4.4
Diameter, cm.	0.35
Wall thickness, cm.	0.0125
Coated area, sq. cm.	4.25
Coating weight, 4 mg. of carbonates/sq. cm.	
Coating thickness (approx.), cm.	0.003

Adsorption Reagents.—Gas from a Matheson Co. lecture bottle of butane was passed through concentrated sulfuric acid, thence over soda lime and Dehydrite into an evacuated apparatus where it was fractionally distilled. The middle fraction was allowed to evaporate into an evacuated storage bottle of the type described by Prescott and Morrison.[8] The storage bottle, sealed off before the gas pressure reached 1 atmosphere, was equipped with a mercury-sealed porous plug to allow gas to escape into the evacuated adsorption apparatus on contact with a similar porous plug sealed to the apparatus. Each time a charge of gas was admitted to the apparatus, it was again fractionated with the middle fraction used for adsorption.

Purification and storage of ethylene was identical with that for butane except that the sulfuric acid wash was omitted.

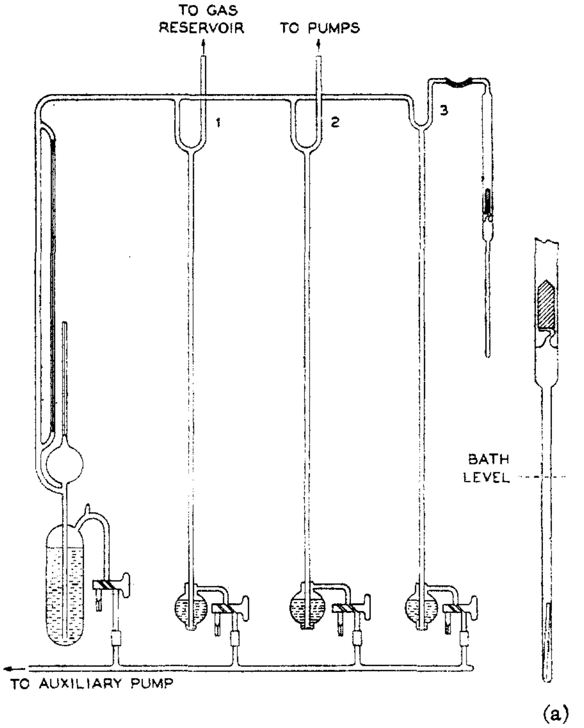

Fig. 1.—Adsorption apparatus; (1a) adsorption chamber containing cathode demounted from experimental vacuum tube.

Temperature Control.—The following constant temperature baths were used: −183°—liquid oxygen, agitated by a stream of oxygen; −196°—liquid nitrogen, agitated by a stream of nitrogen; −116°—melting ethyl ether, stirred frequently.

Apparatus and Procedure.—The essential features of the apparatus are shown in Fig. 1. The pumping system consisted of a single stage mercury diffusion pump backed by a high capacity mechanical oil pump. The McLeod gage volume was 198.0 cc. and the capillaries were of 0.6 mm. diameter so that the gage was sensitive to a pressure of 1×10^{-5} mm. The interior surface of the capillaries was ground to diminish sticking of mercury.[9] Gas law corrections for ethylene and butane amount to 0.2 and 1.0%, respectively, at the highest pressures used in the gage and consequently were not applied.

The cathode was protected from mercury vapor by a plug of thin gold foil just beyond cut-off 3. The foil was rolled to fit snugly in the glass tubing and was normally surrounded by a small furnace capable of heating it to 400° for frequent removal of sorbed mercury and for outgassing. The remainder of the system was outgassed by torching with a Bunsen flame for thirty minutes.

The adsorption chamber, shown enlarged in Fig. 1a, was originally part of the experimental vacuum tube. After tests, the cathode was demounted,[10] transferred *in vacuo* to the adsorption chamber, and the chamber was sealed off close to the vacuum tube. The section of large tubing above the break-off tip, open to the atmosphere, was sealed to the apparatus as shown. The break-off slug consisted of permalloy powder completely enclosed by Pyrex glass. After the apparatus was evacuated and outgassed, the break-off slug was lifted magnetically, allowed to fall and break the tip.

Adsorption of gas was measured by the usual difference method by use of the McLeod gage capillary as a gas buret. The volume calibration was carried out with the cathode at room temperature (adsorption negligible) and it was reproducible to about 1 cc. The volume of the gage and connecting tubing up to cut-off 3, V_c, was 245 cc., and the total volume, V_t, was usually about 275 cc. including V_c and the cathode chamber beyond cut-off 3. After the adsorption chamber was surrounded by the low-temperature bath, adsorption of gas was calculated from the difference between the total gas charge and the quantity of gas in the gas phase. At pressure, p, the amount of gas in the gas phase is V_tp cc. mm.[11] at room temperature plus a small correction for the cold spot (the volume of free space surrounded by the cooling bath was only about 1 cc.). With cut-off 3 closed, gas was added or removed to change the total gas charge by $V_c\Delta p$ cc. mm. When cut-off 3 was again lowered, adsorption equilibrium was reached at a new pressure, so that adsorption at a series of pressures could be measured. The total gas charge was checked at the end of a run by measurement of the pressure with the cathode at room temperature. Adsorption values were

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[8] C. H. Prescott, Jr., and J. Morrison, *Ind. Eng. Chem., Anal. Ed.*, **11**, 230 (1939).

[9] P. Rosenberg, *Rev. Sci. Instruments*, **10**, 131 (1939).

[10] Details of the vacuum tube and of the demountable cathode technique, will be described in a forthcoming paper by L. A. Wooten and G. E. Moore.

[11] The unit of gas quantity used throughout this paper is cc. of gas at 1 mm. pressure at 25°. 1 cc. mm. at 25° = 1.205×10^{-3} cc. at S. T. P. or 5.38×10^{-8} mole.

then calculated back from this final gas charge with the small amount of "lost" or "excess" gas, assumed to be due to the cumulative errors, divided equally among the several adsorption points.

Typical Low Pressure Adsorption Isotherm. Results for a typical isotherm are given in Table II. The cathode was coated with 17.6 mg. of an equimolar mixture of barium and strontium carbonates. It was found convenient to start at the higher pressures and remove gas successively for the lower pressure points since the adsorption was found to be completely reversible. Adsorption equilibrium was reached within ten minutes at the lowest pressures and within five minutes at the higher pressures.

TABLE II

ADSORPTION OF ETHYLENE AT −183° ON CARBONATE COATED CATHODE

V_t = 295 cc., V_c = 245 cc.

Total gas, cc.-mm.	p mm. × 10^{-3}	p/p_0	v_{ads}, cc.-mm.	Cor. v_{ads}, cc.-mm.	$\frac{p}{v(p_0 - p)}$
31.55	30.60	1.000	22.50	22.50	..
24.20	30.35	0.992	15.20	15.22	..
16.90	22.30	.729	10.30	10.34	0.260
11.55	12.70	.415	7.79	7.85	.0904
8.50	7.30	.239	6.34	6.42	.0488
6.75	4.48	.1464	5.42	5.52	.0311
5.67	2.74	.0896	4.86	4.98	.0197
5.02	1.85	.0605	4.47	4.60	.0140
4.57	1.32	.0431	4.18	4.33	.0104
liquid oxygen bath removed					
4.72	16.00		−0.15	0.00	

The column under $p/v(p_0 - p)$ is computed for comparison with the theoretical equation[6]

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} p/p_0$$

where v is the quantity of gas adsorbed at pressure p, v_m the quantity of gas which forms a monomolecular adsorbed layer on the underlying surface, p_0 the vapor pressure of the condensed phase of the gas at the adsorption temperature, and c is a constant usually much greater than 1. The adsorption isotherm of Table II is shown in Fig. 2 along with an isotherm for nitrogen adsorption at −196° on an iron synthetic ammonia catalyst, taken from the data of Emmett and Brunauer.[4] Although the saturation pressures for the two gases at the temperature of the isotherms is 0.0306 mm. and 760 mm., respectively, the curves are quite similar. In the inset is plotted $p/v(p_0 - p)$ *vs.* p/p_0 for ethylene at −183°. The points fall on a straight line almost up to $p/p_0 = 0.40$ and curve upward at higher pressures in further agreement with the high pressure data. The value of v_m computed from the slope of this line is 5.10 cc.-mm. as compared with 5.30 cc.-mm. at the point B, the beginning of the linear portion of the isotherm.

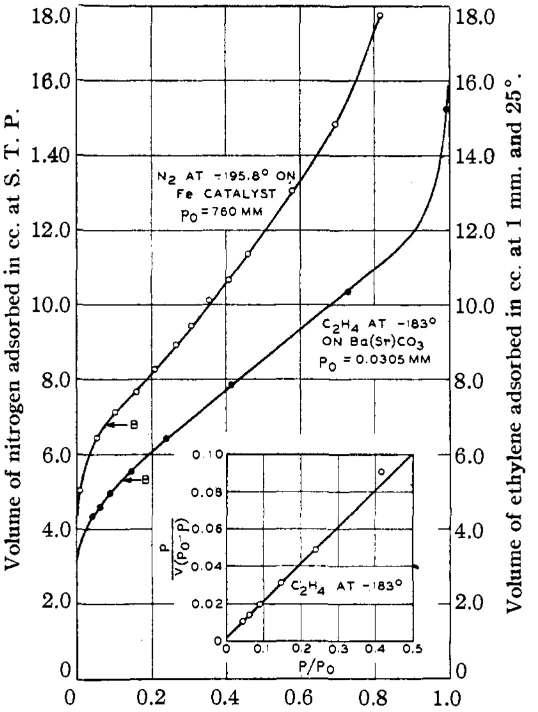

Fig. 2.—High and low pressure adsorption isotherms: nitrogen isotherm from data of Emmett and Brunauer.[5]

Further application of the adsorption theory to these data is probably not justified at the present time because the pressure measurements are uncorrected for the effect of thermal diffusion. Over most of the pressure range the mean free path of the gas molecules is smaller than the diameter of the tubing (4 mm.) which carries the temperature gradient, so the correction factor is best determined empirically. Since the free space at the temperature of the adsorption isotherm is so small (*circa* 1 cc.), thermal diffusion has a negligible effect on the calculation of the amount of gas adsorbed by any apparent pressure. Although the true pressure is uncertain, it seems unlikely that the point B will be much affected. Consequently, thermal diffusion is ignored and v_m is taken as the quantity of gas adsorbed at the point B. Comparison of surfaces is unaffected by any error involved in this procedure.

The absolute value of the surface area is obtained from an estimate of the density of packing in the adsorbed layer. Consistent results are obtained if the average cross section of an adsorbed molecule is assumed to be the same as that corresponding to the plane of closest packing in the solidified gas.[5] From the density of solid ethylene at −175° as determined by X-ray analysis,[12] an average cross section of 17.55×10^{-16} sq. cm. is calculated. This leads to a conversion factor of 57.2 sq. cm. per cc.-mm. of adsorbed ethylene. For butane, Emmett and Brunauer[5] obtained 32.0×10^{-16} sq. cm. as the average cross section on the assumption that the adsorbed molecules lie flat on the surface and cover an average rectangle of 4.3 × 7.45 Å., based on X-ray analysis of long chain hydrocarbons.[13] The conversion factor calculated from this cross section is 104.4 sq. cm. per cc.-mm. of adsorbed butane.

Results on Oxide Coated Cathodes.—An application of the method described is shown in Fig. 3. The upper curve shows butane adsorption at −116° on an oxide coated cathode, demounted from an experimental vacuum tube after conversion of carbonates to oxides. The two lower curves show the adsorption on an uncoated cathode sleeve similarly treated and on the glass tubing alone, respectively. Most of the adsorption is due to the oxide coating. Several blanks were obtained on cathode sleeves after removal of the oxide coating with similarly low adsorption values, but care is necessary in outgassing the nickel sleeves to avoid oxidation and increase in area of the nickel surface.

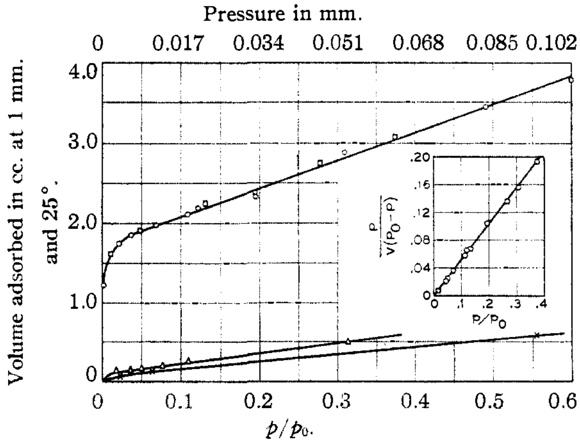

Fig. 3.—Adsorption of butane at −116° on an oxide-coated cathode, on uncoated cathode sleeve, and on glass tubing only.

The volume of gas adsorbed at the beginning of the linear portion of the isotherm is 1.90 cc.-mm. The slope of the straight line $p/v(p_0 - p)$ *vs.* p/p_0, shown in the inset, gives a value of 1.92 cc.-mm. if the best straight line is drawn through the circles and 2.01 cc.-mm. if the best straight line is drawn through the squares. The two sets of points for the isotherm on the coated cathode fit a single curve within experimental error. The points represented by circles were obtained on the cathode initially. Carbon dioxide[14] was then admitted at room temperature and a total of 8.90 cc.-mm. was sorbed irreversibly by the oxide over a period of several days. The points represented by squares were then obtained, showing that any change in surface area was small.

The isotherms of Fig. 4 show the similarity of adsorption of ethylene at −183 and −195.8° on cathode no. 4 (curves 1 and 2) and compare ethylene at −183° with butane at −116° on cathode no. 7 (curves 3 and 4). The butane isotherm is similar to that of Fig. 3 but the ethylene isotherms show a striking rise in adsorption at a pressure less than half the saturation pressure. Curves 1 and 2 are desorption isotherms but the points of curve 3 were obtained by successive increases in pressure. The reversibility of the adsorption is seen in Fig. 5. Points of curve A were obtained in the order indicated by the numbers. The comparatively large volume of adsorbed gas of curve A is due to the use of a larger sample of the mixed oxides.

Table III summarizes results obtained on seven typical oxide-coated cathodes. These cathodes were demounted from experimental tubes, after being activated, aged and tested for thermionic

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[12] W. K. Keesom and K. W. Taconis, *Physica*, **2**, 463 (1935).

[13] S. B. Hendricks, *Chem. Rev.*, **7**, 431 (1930).

[14] The carbon dioxide treatment was made in an unsuccessful attempt to determine the surface area of the oxide coating from the rate of chemisorption of carbon dioxide at room temperature. It is of interest that the rate of sorption of carbon dioxide was so rapid that it was limited by the rate of flow of gas through the gold foil and connecting tubing at about 5×10^{-3} mm. pressure until 4.0 cc.-mm. were sorbed. The rate of sorption then fell off rapidly until at 7.0 cc.-mm. sorbed the rate was 1/100 the initial diffusion limited rate and at 8.5 cc.-mm. sorption, 1/1000 the initial rate, although over 1500 cc.-mm. would be required to convert the entire oxide coating to carbonate. When the cathode was allowed to stand overnight *in vacuo*, however, rate of sorption of carbon dioxide the next day was found to have increased enormously for the first increments of sorbed gas but the rate rapidly fell below that of the preceding day, indicating that sorbed carbon dioxide is in a dynamic state, presumably slowly undergoing some form of recrystallization which brings fresh oxide to the surface. Rate of carbon dioxide sorption by a cathode with one-fourth normal coating thickness, at 0° instead of room temperature, with the gold foil removed, and with larger connecting tubing showed similar behavior. The point at which rate of carbon dioxide sorption became measurable in our apparatus, 4.0 cc.-mm. sorbed, is not greatly in excess of a monomolecular adsorbed layer as indicated by Fig. 3 (1.90 cc.-mm. butane), but the possibility of a dynamic adsorbed layer makes carbon dioxide chemisorption too complex to be a reliable tool for surface area determination. However, the result suggests interesting possibilities for the study of the mechanism of carbonate formation.

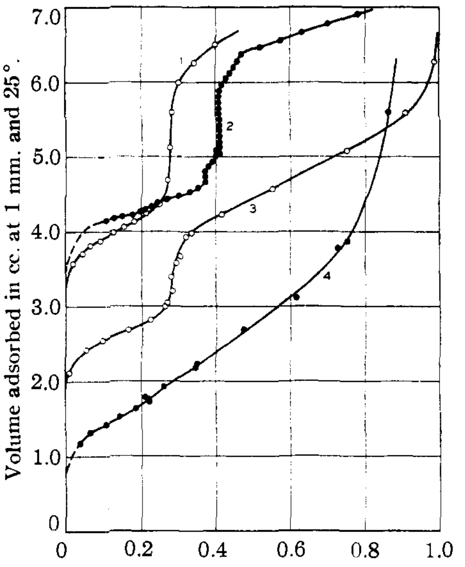

Fig. 4.—Adsorption isotherms on oxide-coated cathodes: Curve 1, ethylene at −183° on cathode 7, p_0 = 0.0305 mm.; 2, ethylene at −195.8° on cathode 7, p_0 = 0.00073 mm.; 3, ethylene at −183° on cathode 4, p_0 = 0.0305 mm.; 4, butane at −116° on cathode 4, p_0 = 0.169 mm.

emission by conventional methods. In the preparation of the cathode the carbonate coating was decomposed in vacuum by heating at approximately 1000° for two minutes. The operating or aging temperature was 730° for all cathodes except cathode no. 7, aged at 800°. The level of thermionic emission obtained on all the cathodes measured was equivalent to that of acceptable commercial tubes.

TABLE III

SURFACE AREA OF OXIDE COATED CATHODES

No. of cathode	Age, hr.	v_m, cc.-mm. C_4H_{10} (−116°)	v_m, cc.-mm. C_2H_4 (−183°)	Area, sq. cm. C_4H_{10}	Area, sq. cm. C_2H_4	Ads. rise, cc.-mm.
1	0.25	1.92	..	175	..	..
2	0.25	1.10	..	90	..	..
3	0.25	..	2.86	..	139	0.60
4	0.25	..	3.95	..	201	1.60
5	23	1.12	..	92	..	..
6	23	0.85	1.72	64	73	0.15
7	1904	1.30	2.44	110	115	1.00

The adsorption on several uncoated cathode sleeves indicated an average surface for the sleeve and glass tubing of the adsorption chamber of 25 sq. cm. This "blank" was subtracted from each value of the area obtained on multiplying v_m by the suitable conversion factor to obtain the area of the oxide coating alone. The column under "Ads. rise" is the height of the abrupt rise in ethylene adsorption at −183°, in the region 8 to 9 × 10^{-3} mm. pressure.

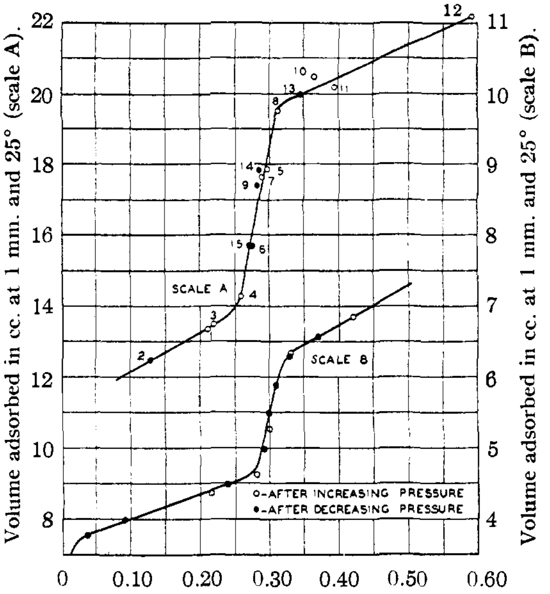

Fig. 5.—Reversibility of ethylene adsorption at −183° on oxide coated cathodes.

Discussion

The results in Table III show considerable variation in surface area of similarly prepared and treated cathodes. A study of these and other results obtained on similar cathodes indicates that control of variables affecting surface area was inadequate to allow any correlation of surface area with thermionic activity. Factors probably important in determining surface area of the oxides are particle size of the applied carbonates, impurity content with respect to compounds such as silica, and the temperature of decomposition of the carbonates. The most likely cause of the wide range in surface area obtained on the oxide coatings is temperature variations during conversion of the carbonates to oxides. The thermal emissivity of the coating changes rapidly during the conversion process and cathode coatings are quite variable from one to another with respect to this behavior. Although the emissivity of the oxide coating is fairly uniform[15] the uncontrolled variations during the carbonate decomposition are probably sufficient to prevent reproducible temperatures obtaining during the process.

The difficulties appearing in the preparation of cathode coatings with reproducible surface areas

(15) G. E. Moore and H. W. Allison, *J. Applied Phys.*, **12**, 431 (1941).

indicate that the present method can be most effectively used to study changes in areas of a given cathode after various treatments. Measurements of the surface area of a cathode before and after conversion of carbonates to oxide and after various heat treatments are being made. By thus concentrating several surface area measurements on a given cathode it is believed that more complete knowledge of the factors affecting cathode coating surface will be obtained with the consequent possibility of greater reproducibility of cathode surfaces.

A rough average for the surface area of the cathodes shown in Table III is 130 sq. cm. This is equivalent to a ratio of the true surface to the geometrical surface of approximately 30, and to an area of 10 sq. cm. per milligram of alkaline earth oxide in the coating.

The abrupt rise in ethylene adsorption at p/p_0 = 0.26–0.32 at −183° and p/p_0 = 0.37–0.43 at −196° (Figs. 4 and 5) is definitely associated with the alkaline earth oxides since it does not appear on the carbonates (Fig. 2). The usual explanation of such curves is capillary condensation.[7] Capillary condensation is usually, but not always,[16,17] accompanied by adsorption hysteresis. Heat treatment of the adsorbent tends to make hysteresis disappear.[17] The low relative pressures at which the adsorption rise occurs and the sharpness of the rise would indicate very fine capillaries of uniform size. Furthermore the pressure range of the rise is nearly the same for different samples given different heat treatments (Fig. 4 and Table III). These considerations make it difficult to accept capillary condensation as a satisfactory explanation for the abrupt rise obtained on oxide coatings.

An interesting alternative explanation is that the second adsorbed layer on the oxide has a definite vapor pressure. Thus at relatively low pressure a monolayer is formed, adsorption increases gradually with increase in pressure until a critical concentration in the second layer is reached, then the second layer is almost completed with little further increase in pressure. If the entire second layer had a definite vapor pressure, the height of the rise would equal v_m. That this is not the case is shown by the data in Table III.

Acknowledgment.—The assistance of Mr. G. E. Moore in pumping, activating and making thermionic measurements on the cathodes used in this study is gratefully acknowledged.

Summary

1. Adsorption isotherms for ethylene at −183 and −196° and butane at −116° on oxide coated cathodes have been used to deduce the surface area of the oxide coating. Areas of approximately 10 sq. cm./mg. of oxide were obtained. The method is capable of determining surface areas as small as 10 sq. cm.

2. Adsorption isotherms closely resembled those of gases near the boiling point although condensation pressures were less than 0.1 mm.

3. Ethylene adsorption at −183° on alkaline earth oxides showed an abrupt adsorption rise in the pressure region 0.25 to 0.30 p_0. Adsorption curves for the carbonates did not exhibit this rise.

NEW YORK, N. Y. RECEIVED OCTOBER 15, 1942

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[16] K. S. Rao, *J. Phys. Chem.*, **45**, 531 (1941).

[17] Harry B. Weiser, W. O. Milligan and James Holmes, *ibid.*, **46**, 586 (1942).