

TABLE V  
THE MOLAL ENTROPIES OF THE PENTENES, CAL./DEGREE  
 $0^{\circ}\text{C.} = 273.16^{\circ}\text{K.}$

Compound	°Free- dom	Debye		$\Delta S_{120} - T_{T.P.}^{\circ}$ crystals	$\Delta ST_{T.P.}$ fusion	$\Delta ST_{T.P.} - 298.16$ sat. liq.	$S_{298.16}$ sat. liq.	$T_{T.P.}$ °K.
		$\theta$	$S_{120}$					
1-Pentene	5	123.0	0.238	16.93	12.86	32.72	$62.75 \pm 0.20$	107.9 <sup>a</sup>
<i>cis</i> -2-Pentene	5	132.4	.242 <sup>b</sup>	18.592 <sup>c</sup>	13.955	29.019	$61.81 \pm .12$	121.80
<i>trans</i> -2-Pentene	6	146.2	.171	19.657	15.013	26.466	$61.31 \pm .12$	132.95
2-Methyl-1-butene	5	122.5	.241	20.243	13.941	26.272	$60.70 \pm .12$	135.62
3-Methyl-1-butene	5	123.1	.300 <sup>b</sup>	15.209 <sup>c</sup>	12.232	32.796	$60.54^d \pm .12$	104.72
2-Methyl-2-butene	5	129.1	.206	21.808	13.024	24.966	$60.00 \pm .12$	139.42

<sup>a</sup> This value from reference 5. <sup>b</sup> Debye entropy at  $13^{\circ}\text{K.}$  <sup>c</sup>  $\Delta S_{120} - T_{T.P.}$ . <sup>d</sup> Above normal boiling point. <sup>e</sup>  $T_{T.P.}$  = triple point temp.

nificant effect on the experimentally determined entropy. The effect of impurity on the measurement of the heat of fusion has been discussed above. The calculated heats of fusion for these compounds are given in Table IV. The uncertainties listed are precision uncertainties.

The experimental data have been utilized to calculate the entropies of these compounds. These calculations are summarized in Table V.

### Discussion

It should be noted that under the conditions of the measurements the quantity actually measured is the heat capacity of the saturated liquid ( $C_{\text{sat.}}$ ). All of these compounds boil in the neighborhood of room temperature, and at the higher temperatures the difference between  $C_{\text{sat.}}$  and  $C_p$  may be barely significant. The calculated entropies for the liquid state are also for the saturated liquid.

In some of the measurements at low temperatures the temperature rise is rather large. An estimate of the error produced by not allowing for the curvature showed that it was less than the experimental error so no correction has been

applied for curvature. At the higher temperatures a small correction, less than 0.1%, has been applied for vaporization into the gas space. In the case of 2-methyl-2-butene the measurements of Parks and Huffman<sup>3</sup> agree with those of this research within the 1% limit of error of the former workers.

**Acknowledgment.**—The authors wish to express their thanks to Mr. D. R. Douslin who assisted with the measurements and calculations. Grateful acknowledgment is also made to the American Petroleum Institute and to the National Bureau of Standards for the loan of the samples measured.

### Summary

Heat-capacity data on the six pentenes have been given over the temperature range 12 to  $300^{\circ}\text{K.}$

Values of the triple points and heats of fusion have been given.

Entropy values for the liquid state at  $298.16^{\circ}\text{K.}$  were calculated.

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[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY, OFFICE OF NAVAL RESEARCH, WASHINGTON 20, D. C.]

## Ethylene Adsorption Isotherms at $-183^{\circ}$

BY ROBERT L. BURWELL, JR.,<sup>1</sup> P. ALLEN SMUDSKI<sup>2</sup> AND THOMAS P. MAY

In connection with corrosion problems, it was desired to measure surface areas of sheet metal. The specific surface of smooth metal foil is too low to permit application of the Brunauer, Emmett and Teller equation<sup>3</sup> to nitrogen adsorption isotherms. The use of much lower pressures would permit the measurement of smaller quantities of gas and reduce the effect of dead space. The method of Wooten and Brown,<sup>4</sup> adsorption of ethylene at the temperature of liquid oxygen, was

adapted to this purpose. Some unusual features of the adsorption isotherms have been found which are apparently occasioned by the temperature of the adsorption isotherms lying  $14^{\circ}$  below that of the freezing point of ethylene.

### Experimental

**Adsorbents.**—Aluminum foil from the J. T. Baker Chemical Co. was  $28 \mu$  thick and about 99.5% pure. Spectroscopically there was about 0.25% silicon, an equal quantity of iron, and a little copper. Before use the foil was carefully solvent cleaned.

Foil was subjected to one or more of the following treatments: fifteen seconds in a 5% solution of sodium carbonate at  $86^{\circ}$  (I); two minutes in a solution of 30 g. of chromic anhydride and 100 cc. of concentrated sulfuric acid in 900 cc. of water at  $90^{\circ}$  (II); anodizing in 15%

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(3) Brunauer, Emmett and Teller. *THIS JOURNAL*, **60**, 309 (1938).

(4) Wooten and Brown. *ibid.*, **65**, 113 (1943).

sulfuric acid (by weight) at 21°, 15 milliamperes per sq. cm. (III)<sup>5</sup>; anodizing in 10% by weight solution of chromic anhydride in water at 40 volts and 40° (IV).<sup>6</sup> The only variable in III and IV was time of anodizing. Times and thicknesses of the resulting anodic film were: IIIa, thirty minutes, 12.5  $\mu$ ; IIIb, fifteen, 6.3; IVa, forty-two, 5.5; IVb, twenty-two, 2.9; IVc, eleven, 1.4. Thicknesses of IIIa and IVa were measured on a dial micrometer before and after stripping.<sup>7</sup> The thickness of other films was taken as proportional to time of anodizing. Successive application of II and IIIa yielded V; II followed by IVa yielded VI.

One- to two-hundred mesh porous glass was employed as a reference substance. It was obtained from Dr. P. H. Emmett who had reported<sup>8</sup> its nitrogen isotherm. Beebe<sup>9</sup> has also determined the krypton isotherm.

**Apparatus.**—The apparatus of Wooten and Brown<sup>4</sup> was modified. The tube containing gold foil to prevent access of mercury to the adsorbent was replaced by a short U-tube cooled with Dry Ice. Application of Dry Ice resulted in no change in pressure.

Ethylene was kept in a storage bulb connected with the mercury valve controlling admission to the system by a tube fitted with two stopcocks to act as a gas lock.

Owing to thermal transpiration,<sup>10</sup> the pressure in the adsorption vessel of Wooten and Brown was not determinable when the total pressure rose beyond that at which the square root law,

$$P/P' = \sqrt{T/T'} \quad (1)$$

is obeyed. Therefore the magnetically operated plunger shown in Fig. 1 was inserted just above the adsorption bulb

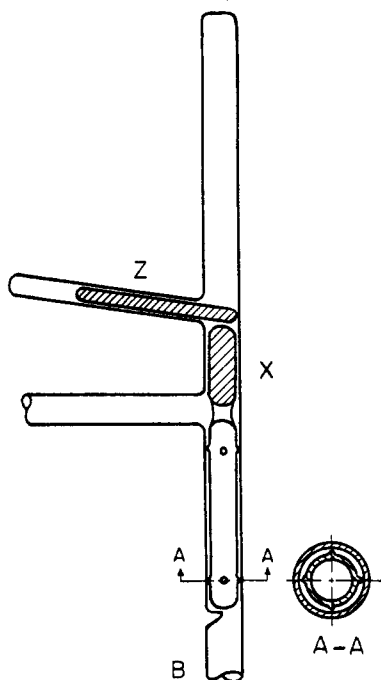


Fig. 1.—Magnetically operated plunger.

(5) This is in the range of commercial procedure. The voltage is about 17. See Edwards and Keller, *Trans. Electrochem. Soc.*, **79**, 135 (1941).

(6) This is in the range of commercial procedure. The current density is about 6.5 milliamperes per sq. cm. See Tarr, Durrin and Tubbs, *Ind. Eng. Chem.*, **33**, 1575 (1941).

(7) Edwards, *Proc. Am. Soc. Testing Materials*, **40**, 959 (1940).

(8) Emmett and DeWitt, *This Journal*, **65**, 1253 (1943).

(9) Beebe, Beckwith and Honig, *ibid.*, **67**, 1554 (1944).

(10) Loeb, "The Kinetic Theory of Gases," 2nd ed., McGraw-Hill, New York, N. Y., 1934.

attached at point B. The distance between the outer tube and the plunger was 0.4 mm. Upon raising the plunger above the magnetically operated stop Z by means of the iron filling at X, rapid pumping and equilibrium at low pressures were possible. The plunger was lowered at pressures above 2.5  $\mu$ . Experimentally, lowering the plunger first increases pressure readings at about 5  $\mu$ . Since the outer tube is 9 mm., one might expect lowering the plunger to extend the range of equation (1) upward by a factor of 10.

An adsorption tube of about 18 mm. inside diameter was sealed to one of 9 and that sealed below the plunger. Liquid oxygen was placed about the bulb and its upper level kept at slightly above A-A in Fig. 1. Increasing quantities of ethylene were admitted and resulting pressures measured on the McLeod gage. The bulb was then cracked open at the upper end of the larger section, the foil inserted and the bulb resealed. To prevent oxidation at somewhat elevated temperatures produced during sealing, a stream of nitrogen was delivered by a quartz tube centered within the outlet tube of the adsorption bulb. This operation did not produce measurable changes in the glass area. Pressures resulting from increasing quantities of ethylene were again determined, subtracting interpolated quantities of ethylene in the first series from those of the second corrected for gas in dead space and adsorbed on container.

Nitrogen isotherms at -195° were determined by standard methods.<sup>8</sup>

### Experimental Results

Nitrogen isotherms were determined on a collection of foil specimens treated according to V with apparent area of 471 sq. cm. Ethylene isotherms were determined on sections from the centers of the same foils with apparent area of 5.68 sq. cm. The nitrogen isotherm was Type IV.<sup>11</sup> The saturation adsorption was  $2.38 \times 10^{-3}$  mole. Areas were determined by the Point B method<sup>3</sup> and by the equation of Brunauer, Emmett and Teller<sup>3</sup> (BET)

$$\frac{P}{n(P_0 - P)} = \frac{1}{n_{mc}} + \frac{c-1}{n_{mc}} \frac{P}{P_0} \quad (2)$$

where  $n$  is the number of moles adsorbed and  $n_m$  that number which corresponds to a unimolecular layer. The factor,  $F$ , was computed as the ratio of measured surface to apparent geometric surface. The area per molecule of nitrogen is taken as 16.2 sq. Å., that per molecule of ethylene, 17.55<sup>4</sup>. A similar procedure was followed for 0.281 and 0.00575 g. of porous glass, respectively. Results are shown in Table I. Those for nitrogen

TABLE I  
COMPARISON OF AREAS COMPUTED BY ADSORPTION OF NITROGEN AND ETHYLENE ON THE SAME MATERIAL

Adsorbent	Area sq. cm.	Gas	Method	F
V	471	N <sub>2</sub>	Point B	653
			BET	651
			Harkins and Jura	607
	5.68	C <sub>2</sub> H <sub>4</sub>	Point B	619
			BET	556
Porous glass	0.00575 <sup>a</sup>	C <sub>2</sub> H <sub>4</sub>	Point B	113 <sup>b</sup>
			BET	106 <sup>b</sup>

<sup>a</sup> Weight in g. <sup>b</sup> Area in sq. meters per g.

(11) Brunauer, Deming, Deming and Teller, *This Journal*, **62**, 1723 (1940).

on porous glass checked previous reports,<sup>8,9</sup> 121 sq. meters per g.

The equation of Harkins and Jura<sup>12</sup> was tested against these isotherms. Ethylene on porous glass gave excellent straight lines in plotting  $\log P$  against  $1/n^2$ . From these, the value of  $k$  in the equation

$$S = kA^{1/2} \quad (3)$$

is  $5.16 \text{ cm.}^{-1}$  assuming that the surface area of the porous glass is 120 sq. m. per g. Other values of area have been computed by the Harkins and Jura (HJ) method using this value. The ethylene adsorption isotherm on V did not obey the HJ equation; the plot was convex upwards.

General results for ethylene adsorption are shown in Table II. All sulfuric acid anodized foils gave convex plots in the HJ method; but other adsorbents gave reasonably good straight lines. Typical plots are shown in Fig. 4. Values of area computed by equation (2) are presented with two assignments of  $P_0$ ,  $33 \mu$  and the experimentally measured saturation pressure, about  $21 \mu$ . All reported values of pressure are corrected by equation (1) for thermal transpiration. It did not appear necessary to perform the  $P_0 = 33 \mu$  or the HJ computation on all treatment III adsorbents.

Several adsorption isotherms were determined on pieces of solvent-cleaned aluminum foil intended for further treatment and area determination. The relative surface,  $F$ , about 1.5, was not determined with precision as, owing to subsequent treatment, sections had been chosen with unfavorable ratios of total adsorption to correction terms

TABLE II

RELATIVE SURFACE,  $F$ , FROM ADSORPTION OF ETHYLENE AT  $-183^{\circ}$  FOR SEVERAL ADSORBENTS BY SEVERAL METHODS OF COMPUTATION

Treatment	Appar-ent area, sq. cm.	Relative area, $F$			
		BET <sup>c</sup> $P_0 = 21\mu$	BET $P_0 = 33\mu$	Point B	HJ
I	12.5	10.2	12.8	11.0	12.2
I	17.4	7.4	7.9	$7.9 \pm 0.6$	9.8
II	95.5	80	98	$87 \pm 3$	87
II	96.2		84	$70 \pm 4$	84
IVa	25.4	79	89	$86 \pm 5$	102
IVa <sup>a</sup>	25.4	6.1	7.0	$5.6 \pm 0.5$	6.4
IVa <sup>b</sup>	10.2	76	84	89	93
VI	14.2	75	85	78	85
VI	11.4	74		79	
IVb	11.0	40		40	
IVb <sup>b</sup>	10.3	36		36	
IVc	25.3	21		19	
IIIa	3.30	406	490	450	<sup>d</sup>
IIIb	10.8	226	265	246	<sup>d</sup>
V	5.68	556	606	619	<sup>d</sup>

<sup>a</sup> Previous foil "sealed" for fifteen minutes in steam at  $100^{\circ}$ . <sup>b</sup> After this determination, sample was "sealed," but resulting adsorption was too small to give reliable area determinations. <sup>c</sup> The experimental value of the saturation pressure was used. <sup>d</sup> Does not obey the Harkins and Jura equation.

(12) Harkins and Jura, *ibid.*, **66**, 1366 (1944).

(dead space plus adsorption on the bulb). The error could reach  $\pm 0.3$  unit. Electron microscopic examination of lacquer replicas, gold-shadowed by the method of Williams and Wyckoff,<sup>13</sup> shows the surface of the foil to be quite smooth save for rolling lines having a separation of less than  $0.1 \mu$ .<sup>14</sup> The very large surface areas produced by treatment II are confirmed by an electron micrograph made as above. Very heavily convoluted surface is found with the structure of the order of  $0.1 \mu$  to less than  $0.01$ . No structure is visible in the light microscope.

Experimental values of the saturation pressure, *i. e.*, the vapor pressure of solid ethylene at  $90^{\circ} \text{K.}$ , were not very reproducible. The mean of several experiments with no adsorbent in the bulb gave  $21.6 \mu$ . Measured values during the runs with adsorbent in the bulb varied between 20 and  $22 \mu$  with one value at  $19.3$ .

**Types of Adsorption Isotherms.**—Typical ethylene adsorption isotherms are shown in Fig. 2. That for treatment IIIb resembles curve E. So would, presumably, that for the other sulfuric acid anodized foil, V, but this is not assured since it was run only to  $10 \mu$ . Isotherms for the other adsorbents shown in Table II resemble curves C and D as do those for the walls of the Pyrex containing bulbs and for solvent-cleaned aluminum. The nearly straight line regions of such isotherms intersect the saturation pressure at values of ethylene adsorption corresponding to 2 to 3 molecular layers in reference to Point B.

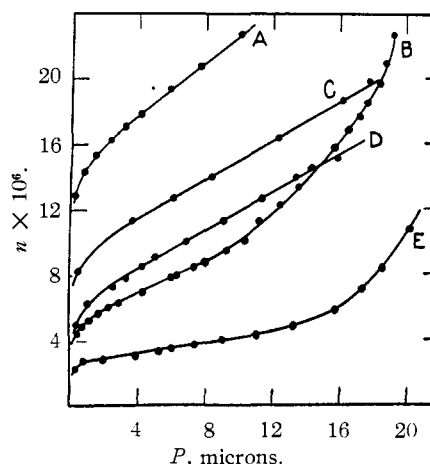


Fig. 2.—Adsorption of ethylene on several adsorbents at  $-183^{\circ}$ : B, porous glass, 0.00575 g.; D, treatment II, 95.5 sq. cm. apparent area; C, treatment IVa, 25.4 sq. cm. apparent area, moles adsorbed multiplied by 5 in plotting; E, treatment IIIa, 3.30 sq. cm. apparent area, moles adsorbed multiplied by 2 in plotting; A, treatment V, 5.68 sq. cm. apparent area, moles adsorbed multiplied by 5 in plotting.

(13) Williams and Wyckoff, *Science*, **101**, 594 (1945).

(14) The authors are indebted to Mr. LaVerne S. Birks and Dr. Herbert Friedman of the Naval Research Laboratory for supplying the electron micrographs.

### Discussion

Isotherms in which an approximately linear portion extends to the saturation pressure are not unknown. Those of a number of alcohols on silica gel are of this type<sup>15</sup>, also that of ethylene<sup>4</sup> on mixed barium-strontium carbonates at  $-183^{\circ}$ , those of krypton<sup>16</sup> at  $-195^{\circ}$  and some of carbon dioxide<sup>17</sup> at  $-78^{\circ}$ . The stable condensed form of the gas at these temperatures is the solid save for the alcohols.

Beebe's use<sup>9</sup> of the extrapolated saturation pressure of the liquid appears a reasonable procedure here. By the Clapeyron-Clausius equation

$$\ln \frac{P_0(\text{sub.})}{P_0(\text{evap.})} = \frac{-\Delta H(\text{fusion})}{RT} + A$$

According to Egan and Kemp,<sup>18</sup>  $\Delta H(\text{fusion}) = 800$  cal. per mole at the m. p.,  $-169.2^{\circ}$ , whence, at  $-183^{\circ}$ , the b. p. of oxygen

$$P_0(\text{sub.})/P_0(\text{evap.}) = 0.55$$

and if  $P_0(\text{sub.})$  is  $21.6 \mu$ ,  $P_0(\text{evap.})$  would be  $39 \mu$ .

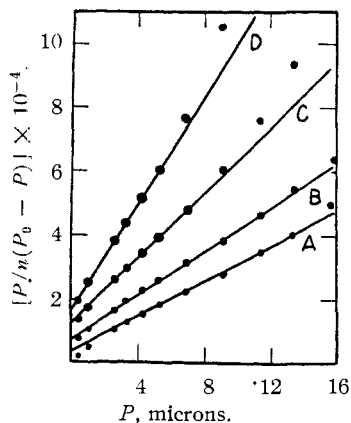


Fig. 3.—BET plot of ethylene adsorption on aluminum foil dipped in chromic acid-sulfuric acid solution (II, 95.5 sq. cm.): A,  $P_0 = 37 \mu$ ; B,  $P_0 = 33 \mu$ ,  $0.5 \times 10^4$  added to ordinate; C,  $P_0 = 25 \mu$ ,  $1 \times 10^4$  added to ordinate; D,  $P_0 = 18 \mu$ ,  $1.5 \times 10^4$  added to ordinate.

A number of values for  $P_0$  were tried for ethylene adsorption on II (95.5 sq. cm.) for which many points were available. The BET plots are shown in Fig. 3. The function

$$\frac{P}{n(P_0 - P)} \times 10^{-4}$$

is plotted against pressure rather than relative pressure to permit comparison of the relative extents of the straight line portions. In agreement with Anderson,<sup>19</sup> use of larger values of  $P_0$  extends the straight line region to higher pressures but displaces its beginning to higher pressures. The

(15) Foster, *J. Chem. Soc.*, 769, 773 (1945).

(16) These isotherms were reported<sup>9</sup> only to one-half the saturation pressure of solid krypton but similarity seems likely in view of footnote (11).

(17) Brunauer and Emmett, *THIS JOURNAL*, **59**, 2682 (1937).

(18) Egan and Kemp, *ibid.*, **59**, 1264 (1937).

(19) Anderson, *THIS JOURNAL*, **68**, 686 (1946).

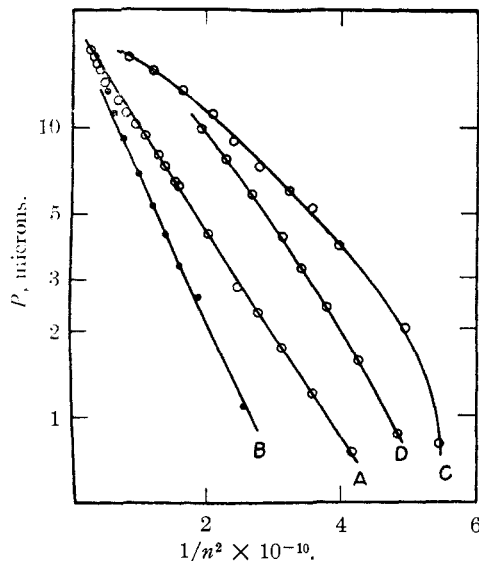


Fig. 4.—Application of Harkins and Jura equation to ethylene adsorption data: A, porous glass, 0.00575 g.; B, treatment II, 95.5 sq. cm.; C, treatment IIIa, 3.30 sq. cm.; D, treatment V, 5.68 sq. cm.,  $1/n^2$  multiplied by 0.4 in plotting.

longest linear region results from  $P_0 = 33 \mu$ . Relative areas deriving from  $P_0 = 18, 25, 33$  and  $37 \mu$  are 74, 87, 98 and 104. Similar results were obtained on other foils. BET plots for several other adsorbents are shown in Fig. 5. Considerable error in assigning  $P_0$  results in small change in area. The use of  $P_0 = 33 \mu$  seems to give somewhat better agreement with the HJ and the Point B methods.

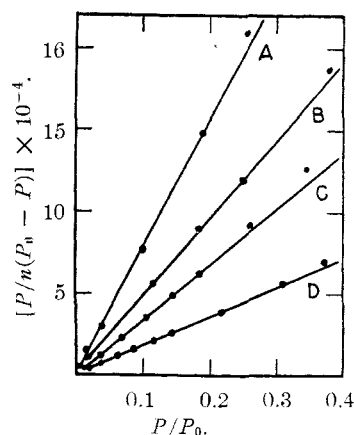


Fig. 5.—BET plots of ethylene adsorption: A, IIIa,  $P_0 = 20.4 \mu$ ; B, IVa, 25.4 sq. cm.,  $P_0 = 33 \mu$ ; C, V,  $P_0 = 21.6 \mu$ ; D, porous glass,  $P_0 = 20 \mu$ .

The BET equation which results from restriction of adsorption to a limited number of layers can give linear sections extending to the saturation pressure though it is difficult to see why such restriction should prevail on so many of our adsorbents. Our experimental isotherms are fairly well

reproduced by  $n = 3$  and  $c = 100$  applied in equation (B).<sup>3</sup> Areas so computed differ but little from those found by equation (2).

The occurrence of S-shaped isotherms (ethylene on porous glass and on III) would seem to imply adsorbed gas in a different state, possibly one corresponding to the solid rather than the liquid. The nature of an adsorbent might well influence the structure of an adsorbed film near the melting point of the vapor being adsorbed. These adsorbents appear to have the finest pores of any of the adsorbents, 50–60 Å. in diameter for porous glass and about 107 Å. for sulfuric acid anodic film.

Use of a larger value of  $P_0$  extends the range of the BET equation for these two adsorbents but like the results of Anderson<sup>19</sup> the start of the linear region is displaced to higher pressures. In contrast to the case with the other isotherms, beyond the higher pressure limit of the linear range, points fall below the extrapolated straight line.

**Surface Areas of the Adsorbents.**—The large relative surface of the anodized aluminum agrees with the hypothesis of porous structure which has been recently supported by electron microscopic examination.<sup>20</sup> From the relative surface, 652, of  $V$ , the quantity of nitrogen required to fill the pores,  $2.38 \times 10^{-3}$  mole, and the thickness of the anodic film, 0.00125 cm., and assuming liquid

(20a) Fischer and Kurz, *Korrosion u. Metallschutz*, **18**, 42 (1942). Upon electrolytically polished 99.99% aluminum anodized in 28% sulfuric acid at 12 volts, the average pore diameter is 150 Å., the average number per sq. cm.,  $0.8 \times 10^{11}$ .

(20b) Edwards and Keller, *Trans. Am. Inst. Mining Met. Engrs., Inst. Metals Div.*, Tech. Pub. No. 1710 (1944). Upon 99.75% aluminum anodized in 7.5% sulfuric acid at 7.5 volts, the average pore number per sq. cm. is reported as  $2.7 \times 10^{11}$ , the average diameter appears to be slightly greater than 100 Å. The pore diameter in chromic acid anodic film is about 160 Å. but this is for anodization at but 5 volts in 1% solution.

packing, the average pore diameter is 107 Å. and the number of pores per sq. cm.,  $1.55 \times 10^{11}$ . This agrees well with electron microscopic results.

The relative surface is roughly proportional to time of anodization. This also accords with a porous structure. For equal thicknesses the coatings formed in sulfuric acid have about three times the area of those formed in chromic acid. "Sealing" an anodic film forms boehmite,  $\alpha$ - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ,<sup>5</sup> the growth of the crystals of which has been believed to seal the pores. Our surface area measurements support this view.

Anodic coating is amorphous to X-rays. That by chromic acid is substantially pure alumina<sup>21</sup> while that formed in sulfuric acid contains a little water<sup>5,21</sup> plus 13% sulfate.<sup>21</sup> Surfaces of the aluminum foil undoubtedly are covered by a layer of oxide a few molecules deep. The only surely crystalline surface studied in this investigation was the boehmite one.

### Summary

The adsorption of ethylene at  $-183^\circ$  has been applied to the determination of surface areas on aluminum foil subjected to various etching and anodic treatments.

The results accord with the hypothesis of porous structure of anodic coatings.

Two kinds of isotherms have been found, S-shaped ones and ones whose linear portions continue to the experimental saturation pressure. It is surmised that the nature of the adsorbent surface may influence the type of adsorption which occurs at temperatures for which the stable condensed phase is the solid.

(21) Pullen, *Metal Ind. (London)*, **54**, 327 (1939).

WASHINGTON, D. C.

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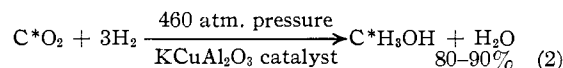
[CONTRIBUTION FROM THE RADIATION LABORATORY AND CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA]

## Synthesis of Carbon Radioactive Methyl Iodide and Methanol from Carbon Dioxide<sup>1</sup>

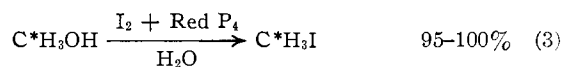
BY B. M. TOLBERT

Carbon radioactive methyl iodide and methanol are of considerable importance in the synthetic chemistry of radioactive compounds for the introduction of labeled carbon. In this paper, a small scale (25 millimoles) and high yield (81–86% based on  $\text{C}^{14}\text{O}_2$  taken) synthesis of these two compounds from carbon dioxide is presented.

The following reactions were used for the several steps



(1) This paper is based on work performed under Contract #W-7405-Eng-48 with the Manhattan Project in connection with the Radiation Laboratory, University of California.



Special techniques are necessary for the handling of small amounts of volatile organic compounds. Thus all reactions, washings and transfers were done in a closed system that had been evacuated to 10 microns or less pressure. Purification methods were chosen that could be adapted to vacuum line work. Liquid nitrogen was used to freeze contents of reaction vessels and traps during evacuation. Quantitative transfers were effected by distilling compounds from one vessel to another using liquid nitrogen. The vacuum line used for this work (see Fig. 1) was developed for general organic synthesis. Reaction tubes and vessels may be closed off, removed from the line, and as