

Summary

1. Methyl glucoside can be oxidized cathodically to methyl glucuronide. This electrolytic oxidation proceeds best at higher pressures.

2. At pressures of 11 atm., with agitation and at room temperature, over 20% conversion of methyl glucoside into glucuronic acid could be obtained.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Densities of Vapors Adsorbed on Charcoal

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Only two direct measurements of the density of adsorbed gases or vapors are available in literature. Ewing and Spurway² determined the density of water on silica gel at 25°. De Vries³ determined the density of carbon dioxide on charcoal at 30° and showed that the density of the adsorbed layer could be calculated from an adsorption isotherm, using the Lowry and Olmstead⁴ modification of the Polanyi theory. In neither of these two cases were the densities determined over the entire isotherm of the adsorbed substance. Emmett and Brunauer⁵ calculated, from an adsorption isotherm, the volume of gas needed to form a monomolecular layer and from that the surface area of the adsorbent, assuming that the adsorbed layer had a density comparable to that of the normal liquid. In our work the densities of carbon tetrachloride and acetone, adsorbed on charcoal, were determined at 30° over the entire isotherm up to near saturation pressures. The results verify the choice of density made by Emmett and Brunauer.

Experimental and Results

Procedure.—A commercially available steam-carbon dioxide activated coconut charcoal was used. For the carbon tetrachloride and the acetone experiments, 11.88 and 10.23 g. of charcoal were used, respectively.

Dow Chemical Co. carbon tetrachloride of 99.9% purity and Mallinckrodt analytical grade of acetone were used.

The apparatus and experimental method was essentially similar to that described by De Vries.³ The charcoal was degassed under high vacuum at 375° for ten to fifteen hours. All pressure measurements were made in triplicate by slightly changing the height of the mercury column and then making the corrections described in the above-

mentioned paper. The final data are good to about 3% for the low pressure values and to about 1% for the higher pressures. The volume of the free space in the tubes containing the adsorbent was determined with carefully purified helium. For the carbon tetrachloride experiments the mean value of nine determinations scattered amongst the density measurements was 21.840 ± 0.008 ml. For the acetone experiments the volume of the free space in the bulb was similarly found to be 23.077 ± 0.035 ml.

A known amount of the organic liquid, previously made air-free, was allowed to vaporize into the charcoal bulb, and after five to eight hours, when the pressure became steady or changed very slowly at a known rate, a measured amount of helium was introduced. The total pressure was measured after one to three hours, a correction being made for the partial pressure of the organic vapor. When larger amounts of material were adsorbed, the pressure did not approach a steady value so quickly. The partial pressure of the vapor was then calculated, using the three constant equation, $p = a + bt^n$, for the extrapolation.

In this work the assumption has been made that helium is not adsorbed on the charcoal at 30°, and that it does not influence the amount of vapor adsorbed after it is added to the vapor already in equilibrium with the adsorbent. Homfray⁶ has reported that helium was not measurably adsorbed on an active charcoal at room temperature under a pressure of 70 cm. One of us determined on a previous occasion³ the rate at which helium was absorbed by 17.5 g. of coconut charcoal. The unpublished result of numerous experiments, some extending over as much as sixty hours with helium at a pressure of 55 cm., was that helium was "dissolving" in the charcoal at a uniform rate of 0.00082 ml. per hour. We therefore believe that in our experiments when measurements were taken after one to three hours, and when no appreciable change in total pressure was observed after that time, no more than what could be accounted for by the slow change in the equilibrium pressure of the organic vapor on the charcoal, the volume of the free space could be calculated after subtracting the partial pressure of the vapor from the total pressure of the helium plus the vapor. Furthermore, Lambert and Heaven⁷ have reported that helium is not adsorbed on silica gel at 0°, and that oxygen is adsorbed from an O₂-He mixture in the same amount that it would be in the ab-

(1) Present address: Universal Oil Products Co., Riverside, Ill. This paper is an abstract of the thesis submitted by J. D. Danforth in partial fulfillment of the requirements for the degree of Doctor of Philosophy in chemistry.

(2) Ewing and Spurway, *THIS JOURNAL*, **52**, 4635 (1930).

(3) De Vries, *ibid.*, **57**, 1771 (1935).

(4) Lowry and Olmstead, *J. Phys. Chem.*, **31**, 1601 (1927).

(5) Emmett and Brunauer, *THIS JOURNAL*, **59**, 1553 (1937); Brunauer, Emmett and Teller, *ibid.*, **60**, 309 (1938).

(6) Homfray, *Z. physik. Chem.*, **74**, 129 (1910).

(7) Lambert and Heaven, *Proc. Roy. Soc. (London)*, **A153**, 584 (1936).

sence of helium provided the gel had been "washed out" with oxygen before the runs.

Carbon Tetrachloride.—The results of the work with carbon tetrachloride are given in Table I and Fig. 1. The large value which was obtained for the density of small amounts of material adsorbed verifies a viewpoint that a small portion of the charcoal surface possesses very large forces of attraction for the adsorbed molecules. As more material is adsorbed the average density

decreases rapidly to a minimum value, but increases again as the equilibrium pressure is increased. The final density values approached the value for the normal liquid.

Several explanations of the data seem probable but more results are needed to indicate the best answer. Work is now in progress with charcoals of different activities and with organic molecules of different sizes. One of the less probable explanations for the increase in density after a minimum was reached is that capillary condensation is taking place, but there is practically no evidence in the literature that such condensation can take place until nearly saturation pressures have been reached. Furthermore, McBain⁸ has found an expansion of charcoal which excludes the possibility of capillary condensation at pressures less than saturation pressure. If the assumption is made that there is no migration of the molecules on the surface of the charcoal, then it is possible to calculate the density of each successive portion of the adsorbed layer from points taken off the curve shown in Fig. 1, by the equation $1/\rho_0 = 1/\rho - (W/\rho^2)d\rho/dW$, where ρ_0 is the density of each increment of volume, and ρ and W are the average density and the weight of the adsorbed layer which occupies a volume, V , on the adsorbent. The above equation is derived from the obvious relations that $\rho_0 = dW/dV$ and that $V = W/\rho$. In Table II are given the results of such a calculation. Note that after about 1.5 g. of carbon tetrachloride had been adsorbed, the density of further portions of the adsorbed layer was about 90% of the density of the normal liquid. This might suggest that part of the adsorbed layer was similar to a liquid, perhaps being adsorbed in crevices or capillaries.

The assumption can also be made that migration of the molecules can take place on the surface of the charcoal. There is evidence in the literature that such lateral movement of molecules may account for the large area of active adsorbents.⁹ The active centers on the charcoal are first covered, giving a large value for the density of the adsorbed gas. As the equilibrium pressure is increased the less active centers are covered with a layer having a density less than that of the normal liquid. With further rise of pressure the molecules are forced to move laterally to make room for further adsorbed molecules, pro-

TABLE I
DENSITIES OF ADSORBED CARBON TETRACHLORIDE

G. CCl ₄ adsorbed	Eq. press., cm.	PV of He units, cm.-ml.	ΔV	Density ads. layer
0.736	0.07	510.0	0.383	1.92
.743	(.15)	549.6	.370	2.00
.854	(.24)	522.2	.590	1.45
.990	.10	509.4	.610	1.60
1.050	(.06)	553.6	.765	1.37
1.394	.15	539.2	.990	1.39
1.508	.22	527.3	1.106	1.36
2.287	.34	525.0	1.66	1.37
4.330	.35	526.6	3.09	1.40
4.965	1.48	520.5	3.48	1.42
7.161	1.53	540.2	4.83	1.48
7.405	2.81	525.7	4.86	1.52
7.718	5.40	415.7	4.86	1.58
8.304	9.86

Density of normal liquid, 30° 1.576
 Vapor pressure, 30° 14.30 cm.
 Volume of free space in bulb 21.840 ml.
 Weight of charcoal sample 11.88 g.

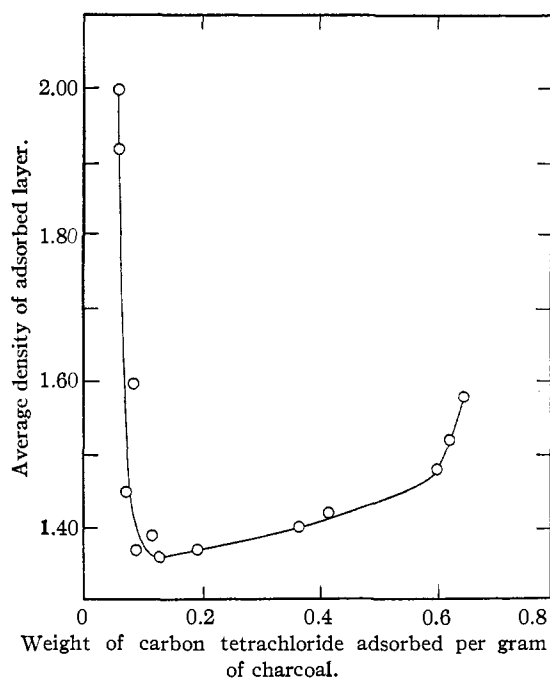


Fig. 1.

(8) McBain, *THIS JOURNAL*, **55**, 2294 (1933).

(9) Smithells, "Gases and Metals," John Wiley and Sons, Inc., New York, 1937, p. 58.

ducing an *increase* in the average density at a practically uniform rate. When the surface is covered, capillary condensation probably takes place, for there is then a rapid increase to a density nearly equal to that of the normal liquid.

TABLE II
DENSITY OF SUCCESSIVE PORTIONS OF ADSORBED CARBON TETRACHLORIDE

Total wt. adsorbed	Average density	$\frac{d\rho}{dW}$	ρ_0
0.75	1.90	-6	0.56
.75	(1.80)	-6	(.52)
1.00	1.37	-0.067	1.31
1.50	1.36	.000	1.36
2.0	1.37	.016	1.41
3.0	1.38	.016	1.43
4.0	1.40	.016	1.47
5.0	1.42	.016	1.50
6.0	1.43	.018	1.55
7.0	1.47	.067	2.16
7.5	1.54	.188	(10)

Acetone.—The results of the work with acetone are presented in Table III and in Fig. 2. There is at first a decrease of the density to a minimum and then an increase to a value approximately equal to that of the normal liquid. The general trend of the average density suggests that much the same type of adsorption mechanism takes place as with carbon tetrachloride, and that probably there is a lateral movement of the molecules as the equilibrium pressure is increased.

Surface Area of Charcoal.—Some assumption must be made as to the packing arrangement of molecules when calculations are based on the density of a liquid to find the volume of the domain of a single molecule and from that the area covered per molecule. In an immobile arrangement of molecules, the hexagonal type of arrangement seems reasonable. Hence in a monomolecular layer the area per molecule will be $2\sqrt{3}r^2$ and the radius, r , can be calculated from the density, d , with the equation $r = (m/4\sqrt{3}d)^{1/2}$, where m is the mass of one molecule. The surface area, A , of adsorbent covered by w grams of condensed vapor will be given by

$$A = 2\sqrt{3}\left(\frac{m}{4\sqrt{3}d}\right)^{1/2}\left(\frac{w}{m}\right)$$

Recently Brunauer, Emmett and Teller⁵ have demonstrated that it is possible to calculate the amount of gas that is needed to form a monomolecular layer on the surface of an adsorbent. Their equation, using weight of gas instead of the

volume, is $p/W = p_s/cW_m + p/W_m$, where p_s is the saturation pressure and W_m is the weight of gas that is needed to form a monomolecular layer. By plotting values of p/W against the corresponding values of p , straight lines were obtained from both the carbon tetrachloride and the acetone data. From the slope of these lines it was calculated that 0.68 g. of carbon tetrachloride and 0.39 g. of acetone were needed per gram of charcoal to form a monomolecular layer. These values correspond to the experimentally observed weight of substance for which densities were found that were equal to the densities of the liquids. This confirms the assumption of Brunauer, Emmett and Teller that the density of the adsorbed layer is equal to that of the normal liquid at the point chosen for the completion of the monomolecular layer.

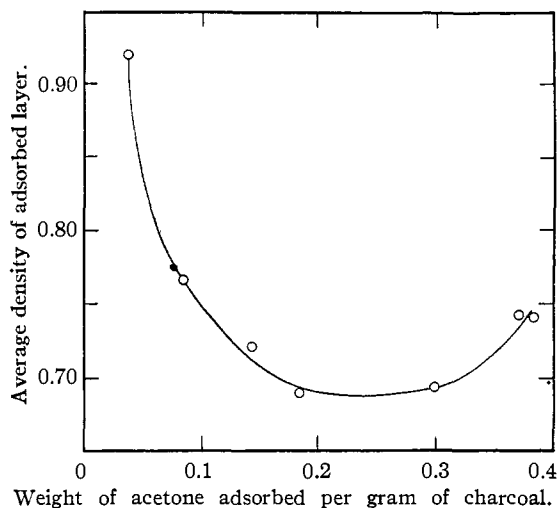


Fig. 2.

Using the above equation, the surface area of the charcoal which was used for the carbon tetrachloride experiments was calculated to be 760 sq. meters per gram, and for the carbon used for the acetone experiments to be 950 sq. meters per gram. The discrepancy in the surface areas may be due to the fact that the first sample had been used longer before reportable results were obtained. These values compare favorably with those reported in the literature.⁵ On the basis of the above surface areas, it was calculated that about 15% of the surface was covered in the case of the carbon tetrachloride adsorption when the increase in density occurred and about 21% of the surface was covered in the case of the acetone experiments.

TABLE III

DENSITIES OF ADSORBED ACETONE				
G. acetone adsorbed	Eq. press., cm.	PV of He units:cm.-ml.	ΔV	Density ads. layer
0.391	0.10	521.7	0.425	0.920
.878	.25	751.4	1.144	.767
1.466	.36	632.3	2.035	.721
1.878	(.34)	549.2	2.700	.690
3.060	1.54	613.2	4.403	.694
3.791	11.48	592.9	5.100	.743
3.919	20.83	376.2	5.290	.741
1.171	0.27			
2.38	.63			
2.78	1.02			
Density of normal liquid, 30°			0.779	
Vapor pressure, 30°			28.27 cm.	
Volume of free space in bulb			23.077 ml.	
Weight of charcoal sample			10.23 g.	

The authors are indebted to the National Research Council for the Grant-in-Aid with which a Gaertner cathetometer was purchased.

Summary

1. The average densities of adsorbed carbon tetrachloride and acetone on a steam-carbon dioxide activated coconut charcoal were determined at 30°.

2. The average densities show a sharp decline after which a rise occurs.

3. About 15 to 20% of the surface is covered with condensed vapor held by active center forces. The remainder of the surface seems to be covered by a different process.

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The Determination of the Vapor Pressure of Thorium Acetylacetonate by Radioactivity Measurements

BY RALPH C. YOUNG, CLARK GOODMAN AND JULIUS KOVITZ

Minute quantities of the radioactive elements can be measured accurately from the ionization produced by their radiations. Because of these electrical effects, properties of compounds of such elements can be determined which are outside the sensitivity of ordinary methods of measurement. In these particular investigations, consideration is given to those elements occurring in the thorium and uranium series which emit alpha particles. The subjects under immediate study are those of

Radioactively inert nitrogen was passed through tubes (Fig. 1) of calcium chloride, potassium hydroxide, and phosphorus pentoxide into a 5 mm. X 600 cm. saturator tube A containing finely powdered thorium acetylacetonate. The saturator was constructed to fit into an insulated glass jacket, E. The temperature was maintained between 99.6 and 100.4° by steam. Mercury manometers, B, were joined to each side of the saturator. It was found by experiment that equilibrium conditions could be attained readily if the nitrogen flow was maintained at a slow rate (see Table I). The length of the column and the fineness of subdivision of the compound were contributory factors. The nitrogen from the saturator was passed through tube C, which was cooled in ice, and then into an absorber D, containing acidified alcohol (3% hydrogen chloride). The volume of the nitrogen was measured by displacement of water.

After two to four liters of the gas had passed through the apparatus, the tubes beyond the saturator were washed out with acidified alcohol, the total volume of which, including that of the absorber, amounted to about 150 cc. After standing for at least thirty days, a small portion, usually 10 cc. of this solution, was evaporated on a clean platinum foil 5 cm. X 5 cm. The alpha activity of this basic thorium chloride deposit was then measured by means of an alpha counter similar to that described by Finney and Evans.¹ From these data the saturation concentration of thorium acetylacetonate in nitrogen at 100° can be calculated.

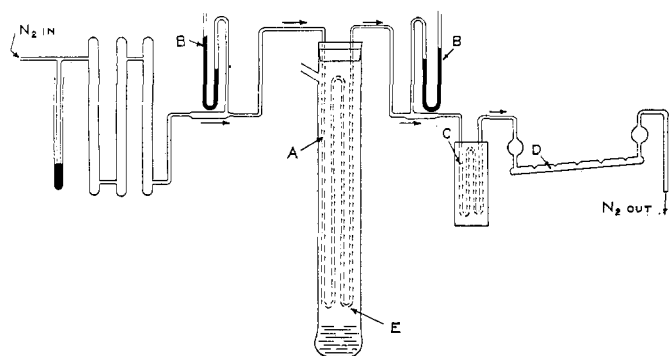


Fig. 1.—Apparatus for saturating nitrogen gas with thorium acetylacetonate.

vapor pressure and solubility, and the first report to be presented is that of the vapor pressure of thorium acetylacetonate at 100°.

(1) Finney and Evans, *Phys. Rev.*, **48**, 509 (1935).