These results point to a methylene ether and not a dithiazane derivative or a methylene dithio ether, $CH_2(SC{=}NC_6H_5NHC_6H_5)_2$, which has nearly the same percentage composition but a molar weight of 468.

1,5 - Diphenyl - 2 - thiolmethyl - 4 - thiolmethylenedipseudodithiobiuret Hydroiodide and Base.—A corresponding methylene ether was obtained from 1,5-diphenyl-2-thiolmethylpseudodithiobiuret ($C_6H_5N{=}C(SCH_3)NHCSNHC_6H_5$) when heated with methylene iodide alone at 120° or in alcoholic solution. This was obtained as the difficultly soluble hydroiodide salt (m. p. 275°) together with phenyl mustard oil.

Anal. Calcd. for $C_{16}H_{16}IN_3S_2$: N, 9.52. Found: N, 9.53, 9.58.

The light yellow base melted at 125°.

Anal. Calcd. for $C_{16}H_{15}N_3S_2$: N, 13.48. Found: N, 13.44.

Benzal chloride failed to give ethers of this type. Heated with thiocarbanilide or di-*p*-tolyl thiourea at 160° it gave only the triphenyl or tritolyl guanidine.

2 - Phenylimino - 3 - thioformanil - tetrahydrothiazole.—While 1,5-diphenyldithiobiuret with methylene iodide gave a dithiazane ring, with ethylene dibromide, a thiazole is formed. An alcoholic solution of the thiobiuret and ethylene dibromide with an excess of ammonium hydroxide was allowed to stand for several days, when light yellow crystals of the thiazole separated (m. p. 165°).

Anal. Calcd. for $C_{16}H_{15}N_3S_2$: N, 13.41. Found: N, 13.39.

Hydrolysis with alcoholic potassium hydroxide gave phenyl mustard oil and 2-phenylaminothiazolidine.

Thiazolidone Synthesis.—The action of chloroethyl acetate on 1,5-diphenyl-2-thiolmethylpseudodithiobiuret was studied in order to note the influence of the two groups upon the constitution of the possible thiazolidone. Heating the two components in alcoholic solution gave a thiazolidone $\underline{SC(NCSCH_3NC_6H_5)NC_6H_5COCH_2}$, melting at 127° with the structure phenyl-4-thiazolidone-thiolmethylpseudothiourea. This was shown by the fact that the 5-benzal derivative melting at 157° (N, calcd. 9.79; found, 9.86) on hydrolysis yielded the known 5-benzal-3-phenyl thiazoledione identified by melting point and analysis.

Anal. Calcd. for $C_{17}H_{15}N_3OS_2$: N, 12.26. Found: N, 12.17.

α,α-Phenylmethyl-β-thiazolidone Thiourea.—This compound was readily formed by heating the phenylmethyldithiobiuret with chloroethyl acetate or chloroacetyl chloride with one mol of pyridine in acetone solution for four hours (m. p. 222°).

Anal. Calcd. for $C_{11}H_{11}N_3OS_2$: N, 15.85. Found: N, 15.92, 15.95.

Hydrolysis of the 5-benzal derivative (m. p. 274°) with 50% sulfuric acid gave 5-benzal-2,4-thiazoledione, thus proving that the thiourea grouping was at position 2.

Anal. Calcd. for $C_{18}H_{16}N_3OS_2$: N, 11.86. Found: N, 11.37, 11.38.

Summary

Methylene dihalides reacted with thiourea, monoaryl thioureas and 1,5-diaryldithiobiurets to form dithiazanes while α,β-diaryl thioureas formed methylene ethers or products of hydrolysis.

LAWRENCE, KANSAS RECEIVED JULY 1, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Densities of Adsorbed Gases. I. Carbon Dioxide on Charcoal[1]

BY THOS. DE VRIES

It is possible, by the use of Polanyi's theory,[2] to calculate from an adsorption isotherm, the isotherms for other temperatures. It is also possible to calculate the average density of the adsorbed layer. An experimental method was developed to determine the density of adsorbed carbon dioxide, and the agreement between observed and calculated densities lends confirmation to the reasonableness of the underlying assumptions. The density of water on silica gel at 25° has been determined by Ewing and Spurway.[3] No other densities of adsorbed vapors have been recorded in the literature. In this paper an apparatus and technique are described which gave results with a precision of 3 to 5% for the density of carbon dioxide adsorbed on activated coconut charcoal. In brief the method consisted in using helium as the displaced fluid to determine, before and after carbon dioxide adsorption, the unoccupied volume in a tube containing charcoal. A temperature of 30.00° was chosen which is just under the critical temperature of carbon dioxide.

Experimental

Carbon dioxide was prepared according to the method of Lowe and Guthmann,[4] and thoroughly dried by passing over anhydrous magnesium perchlorate. Helium was

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[1] Presented before the Division of Physical and Inorganic Chemistry at the New York Meeting of the American Chemical Society, April 22–26, 1935.

[2] Polanyi, *Verh. d. Deutsch. Phys. Ges.*, **18**, 55 (1916); Berényi, *Z. physik. Chem.*, **94**, 628 (1920).

[3] Ewing and Spurway, THIS JOURNAL, **52**, 4635 (1930).

[4] Lowe and Guthmann, *Ind. Eng. Chem.*, *Anal. Ed.*, **4**, 440 (1932).

purified by passing over hot copper oxide and over activated charcoal cooled with liquid air. It was stored in glass flasks sealed to the apparatus. When used the helium was again passed over charcoal cooled with liquid air. No rubber connections were used, and all possible precautions were taken to prevent contamination of the gases with stopcock grease, moisture or traces of air. For the experiments, ash-free coconut charcoal was used.

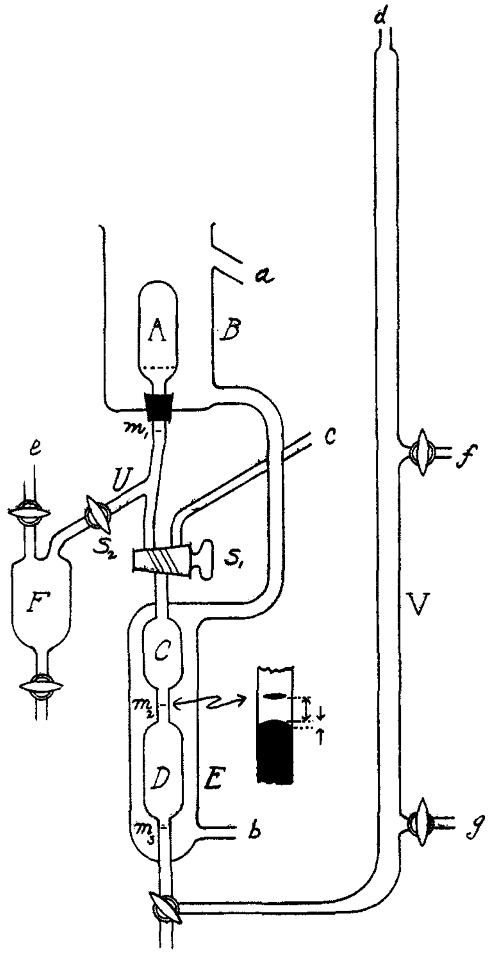

Fig. 1.—a, Return to thermostat; b, from thermostat via pump; c, to carbon dioxide and helium supply, and vacuum; d, e, to vacuum; f, g, to leveling bulbs; other symbols described in the text.

A diagrammatic sketch of the apparatus is given in Fig. 1. Water from a thermostat was circulated by pump around bulbs C and D (55.158 and 78.024 ml., respectively) in which the gases were measured and into the can surrounding the charcoal bulb, A. The temperature was read at this point and was kept constant to within 0.01°. The charcoal was supported by an iron washer covered with iron gauze. This made it possible to fill the tube with charcoal and move the washer in position with a magnet before inverting the tube and sealing it on to the apparatus.

The successive steps for a typical determination were as follows. The charcoal was degassed at 375° by slipping an electric heater over the charcoal tube. The time varied from twelve to forty-eight hours. A high-capacity double-stage mercury vapor pump of special design was used, backed by a Cenco Hyvac. There was a slow change in the volume of the bulb when a higher temperature was used for degassing. Bore 1 of stopcock S_1 was filled with mercury before the volume of carbon dioxide was measured in bulb C. The pressure on the gas was measured with a Gaertner cathetometer reading to 0.005 cm. By the use of an auxiliary lens the cathetometer could be brought close to the menisci and thus a more precise setting was obtainable. A thermometer, reading to 0.1°, was used to determine the temperature of the mercury columns and the appropriate corrections were made to 30° as standard. Corrections were also made for capillary depression in the tubes m_1, m_2, m_3 and V. These corrections were taken from "International Critical Tables,"[5] for mercury menisci of different heights and were checked experimentally to eliminate any error arising from the refraction of light as it passed through the outer glass wall and the intervening water. The optimum size for tubes m and V was 6 and 12 mm., respectively. A third important factor which added materially to the precision of the results was to bring the mercury meniscus up to but not opposite the reference mark (see Fig. 1), and then from the cathetometer readings and with the aid of an alignment chart, the volume was determined of the space between the mark and the curved mercury surface. The variability in the curvature of the mercury surface introduced errors of sufficient magnitude to make this correction necessary when volumes of gas must be measured with precision. The pressure on the gas was given directly from the difference in height of the two mercury menisci since the tube F was evacuated.

When the carbon dioxide was admitted into the charcoal bulb, mercury floating over into tube U would completely prevent leakage of air into the apparatus or loss of helium when it was used. When the pressure of the carbon dioxide in equilibrium with the charcoal became steady or changed very slowly at a constant rate, a known amount of helium was admitted to the charcoal bulb. The mercury between the mark m_1 and stopcock S_2 was first drawn down into the reservoir F, and the helium was admitted slowly so that the mercury might not be carried up into the bulb above the mark m_1. After about an hour, when the helium had diffused through the carbon dioxide, the pressure was constant and was measured. The same kind of corrections were applied as when the gases were measured in bulb C. After subtracting the partial pressure of the carbon dioxide from the total pressure, the volume of space occupied by the helium was easily calculated by using the gas law (*V* in Table II). Several determinations at different times with the carbon dioxide omitted gave values for the volume when no carbon dioxide was adsorbed. These values are recorded in Table I as V_0. The difference was the volume of the adsorbed layer into which the helium could not penetrate. The calculations with Polanyi's theory showed that the helium did not penetrate very far into the adsorbed layer. The weight of adsorbed gas was calculated from the amount measured in the bulb C, allowing for the amount left unadsorbed in the charcoal

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(5) "International Critical Tables," Vol. I, p. 72.

bulb. In the calculations PV values were used with the pressure in cm. of mercury and the volume in ml. The acceptable results of the experiments are tabulated in Tables I and II.

TABLE I

VOLUME OF BULBS CONTAINING CHARCOAL

PV of helium used	2817	2857	2719
Volume of bulb, cc.	36.214	36.213	36.214

PV of helium used	1900	2014	1974	1918
Volume of bulb, cc.	33.219	33.200	33.200	33.200

TABLE II

DENSITY OF ADSORBED CARBON DIOXIDE

PV of CO_2(p. in cm.; V in ml.)	PV of helium	Eq. press. CO_2, cm.	Obsd. vol. change	Density adsorbed CO_2
2925	2329	1.856	0.073	0.91
2983	2741	1.945	.075	.90
4884	1913	2.230	.124	.90
10003	1852	5.119	.263	.860
10572	1918	5.584	.278	.866
9887	1907	5.956	.263	.854
14612	1914	8.367	.377	.882
15434	1765	8.628	.407	.865
30666	1545	21.100	.822	.845
30532	1520	21.252	.814	.850

Lowry and Olmstead's[6] method of calculation was followed in applying Polanyi's condensed film theory to the experimental data. Their notation is also used in this paper. These authors showed that the work of compressing carbon dioxide at 303.1°K. from a molal volume,[7] $V = 1$ to a molal volume V_{δ_i}, is given by

$$\epsilon_i = 4.5767T\left[\frac{0.4343(b_g)_T}{V_{\delta_i} - (b_0)_T} - \frac{237.213\ a_T}{TV_{\delta_i}} - \log V_{\delta_i} - \frac{(b_g)_T}{(b_0)_T}\log\left(1 - \frac{(b_0)T}{V_{\delta_i}}\right)\right]$$

If the original pressure is such that V is not equal to 1, then a $\Delta\epsilon$ is calculated by $\Delta\epsilon = 4.5767\ T \log V_{\delta_x}$. The values given by this equation (see Table III) are needed to calculate the curve. The values given in Table IV and calculated from the experimental results are also needed. The resulting ϵ–φ curve (see Table V and Fig. 2) was used to calculate the milligrams of carbon dioxide adsorbed per gram of charcoal (see last column in Table IV). The calculations for one of the experimental values are given in Table VI, which shows how the average density can vary with the adsorption volume, φ.

It is also possible to calculate how far the helium penetrated into the layer of adsorbed carbon dioxide by using the ϵ–φ curve. The experiments gave the volume of the adsorbed layer (see Table II). The boundary of this layer is characterized by an "adsorption potential" which corresponds to the work required to compress the gas from the density at the equilibrium pressure to the density at the boundary of the adsorbed layer. Hence when $\Delta\epsilon$ is subtracted from ϵ, values of ϵ_i are obtained from which densities of carbon dioxide can be determined with the use of the data in Table III. The results of the calculation are given in

TABLE III

VALUES OF ϵ_i FOR DIFFERENT DENSITIES δ_i

δ_i	$V_{\delta_i} \times 10^3$	ϵ_i (calc.)	ϵ_i (used)
0.01	195.23	958	958
.05	39.05	1825	1825
.10	19.52	2113	2113
.20	9.762	2300	2300
.30	6.507	2325	2325
.334	5.857	2321	2321
.4	4.881	2303	
.5	3.905	2269	
.6	3.254	2246	2321
.7	2.789	2251	2326
.8	2.440	2302	2377
.9	2.169	2424	2499
1.0	1.952	2652	2727
1.1	1.775	3039	3114
1.2	1.627	3693	3768
1.3	1.502	4818	4893
1.4	1.394	6945	7020
1.5	1.302	11669	11744

$a = 0.007312 \quad b_g = 0.002381 \quad b_0 = 0.001171$

Density of vapor (30°) 0.334.

Density of liquid[a] 0.598.

[a] Lowry and Erickson, THIS JOURNAL, **49**, 2729 (1927).

TABLE IV

MILLIGRAMS OF CARBON DIOXIDE ADSORBED PER GRAM OF CHARCOAL

CO_2 pressure	x (obsd.)	$\Delta\epsilon$	x (calcd.)
1.856	3.78	2299	3.77
1.945	3.87	2271	3.87
2.230	4.30	2189	4.45
5.119	8.80	1688	8.89
5.584	9.70	1636	9.57
5.956	8.68	1597	10.11
8.367	12.83	1392	12.92
8.628	13.56	1374	13.19
21.100	26.84	835	26.69
21.252	26.72	830	26.83

$V_{\delta_i} = 84.337/P$(cm. of Hg): $\epsilon_s = \Delta\epsilon + 2321$.

TABLE V

ADSORPTION POTENTIAL, ϵ, AND VOLUME OF ADSORPTION, φ

ϵ, cal.	7250	6000	5000	4606	3982	3702
φ, cu. mm.	0	0.50	1.80	2.84	7.50	10.90
ϵ, cal.	3153	2500	2000	1500	1000	500
φ, cu. mm.	22.90	50.0	85.0	120	139	149

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[6] Lowry and Olmstead, *J. Phys. Chem.*, **31**, 1601 (1927).

[7] In Lowry and Olmstead's notation, $V = 1$ represents a volume of 22,416 ml. and V_{δ_i} a molal volume corresponding to the density δ_i g. per ml.

Table VII. It is evident that the helium did not penetrate appreciably into the layer of adsorbed carbon dioxide when the density was larger than 0.09 g. per ml.

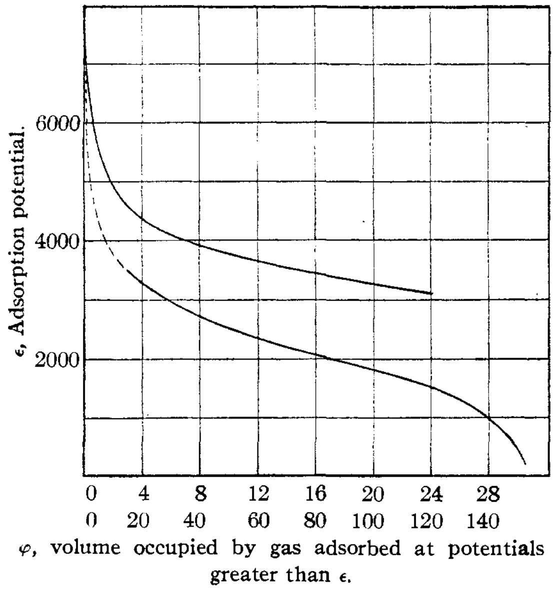

Fig. 2.—Upper curve is a five-fold extension of the dotted section. See Table V for values of the complete lower graph.

TABLE VI

CALCULATION OF AMOUNT OF CARBON DIOXIDE ADSORBED

δ_i	ϵ_i	ϵ	φ	$\Delta\varphi$	$\bar{\delta}$	x
	0	830	143			
0.01	958	1788	100	43	0.005	0.215
.05	1825	2655	43	57	.03	1.710
.10	2113	2943	30.5	12.5	.075	0.937
.334	2321	3151	23.0	7.5	.067	.488
.6	2321	3151	23.0			
.9	2499	3329	18.8	4.2	.750	3.150
1.0	2727	3557	13.5	5.3	.950	5.040
1.1	3114	3944	7.3	6.2	1.050	6.510
1.2	3768	4598	2.9	4.4	1.150	5.070
1.3	4893	5723	0.7	2.2	1.250	2.750
1.372		7250	0.0	0.7	1.336	0.960
1.4	7020	7850				

x (calcd.) = 26.83. x (obsd.) = 26.72. x_s = 23.48

TABLE VII

LIMIT OF PENETRATION OF HELIUM INTO CARBON DIOXIDE

x, mg.	φ (obsd.)	ϵ	$\Delta\epsilon$	ϵ_i	δ_i
3.78	4.20	4360	2299	2061	0.087
3.87	4.30	4340	2271	2069	.089
4.30	4.80	4270	2189	2081	.091
8.80	10.23	3760	1688	2072	.090
9.70	11.20	3690	1636	2054	.086
8.68	10.16	3770	1597	2173	(.115)
12.83	14.54	3520	1392	2128	.105
13.53	15.68	3460	1374	2086	.092
26.84	31.76	2900	835	2065	.088
26.72	31.44	2910	830	2080	.091
				Average	0.091

When the application of Polanyi's theory to the experimental data is considered from the viewpoint of how much of the adsorption volume, φ, must be included to obtain an average density equal to that observed experimentally, then it is evident, as can be seen from one of the calculations given in Table VI, that the experimental values agree well with the densities which can be calculated with the aid of Polanyi's theory, and that less than 10% of the carbon dioxide, which can still be considered as under the attractive influence of the charcoal, mixes with the helium.

The author acknowledges with gratitude a Grant-in-Aid from the National Research Council for this research project which is being continued.

Summary

1. By using helium as an inert gas the density of adsorbed carbon dioxide on charcoal was determined at 30°.

2. By using Lowry and Olmstead's modification of Polanyi's theory, an ϵ–φ curve was calculated. From the experimental results and this curve, it was shown that helium did not penetrate the carbon dioxide layer when its density was more than 0.09 g. per ml.

3. Polanyi's theory gives densities for the adsorbed layer equal to those observed if the assumption is made that the helium penetrates the outer portion of the adsorbed layer.

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